

Energy Band Diagram Modeling and Experiments to Explore the Effects of Piezoelectric Materials in Electrochemical Heterostructures

By

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Abstract

Modern technology for information processing, energy harvesting and energy storage work by shuttling mobile electric charges through specialized devices that are often composed of multiple materials. Directing the flow of mobile charging in these devices is key to their functionality and is often achieved by the creation of depletion regions and built-in electric fields which form at the interface between two dissimilar materials (a heterojunction). These built-in electric fields bias the flow of mobile charges through the device, without them solid-state diodes wouldn't exist and photovoltaic and photoelectrochemical devices would be unable to put photoexcited charges to work on an outside load. The origin of these built-in fields is entropy. Conventionally techniques to engineer the magnitude of the built-in field relied heavily on manipulating the free charge concentration in two dissimilar materials, as well as their dielectric constants. Because the built-in fields are so fundamental to the functionality of modern electronic devices, it is desirable to have additional means of influencing their magnitude and direction within these devices and thus engineering their properties and performance.

Piezoelectrics are a class of materials capable of generating electric dipole fields within themselves in response to mechanical strain. Pyroelectrics and ferroelectrics are classes of piezoelectric materials capable of sustaining electric dipole fields within themselves even the absence of strain. By integrating piezoelectric materials into the heterostructures of electronic devices, strain becomes a parameter for influencing built-in electric fields and thus mobile charge flow. Research is under way to explore the integration of piezoelectrics into memory devices, transistors, photovoltaics, photoelectrochemical cells and light emitting devices.

Traditionally, in the design of such heterojunction devices, energy band diagrams would be used for the conceptually planning, engineering and understanding of the electronic devices. This practice has been carried over in the design and understanding of piezoelectric heterojunction devices. Unfortunately, the energetic effects of introducing surface charge densities (equivalent to the uniform electric dipole fields the piezoelectric generates) are not as easy to intuit as the other variables (e.g., Fermi level offset and electrical permittivity) when conceiving energy band diagrams. Consequently, many of the (schematic) energy band diagrams currently found in the literature to explain the results of piezoelectric-embedded heterostructures are inaccurate. The inaccuracy doesn't only effect the conclusions proposed in the literature, the inaccuracies also effect the general research direction the investigators initially take because today energy band diagrams are often used as a mental tool for designing the devices and devising the experiments.

In our work, we acted to remove the errors of intuition by creating and making freely available to everyone a Mathematica computer code which utilizes Anderson rules and bulk material approximations to generate heterojunction band diagrams. Unlike other tools freely available for auto-generating energy band diagrams, this code includes the effects of piezoelectric and ferroelectric electric dipole fields and can be modified to incorporate whichever material(s) is being studied at that moment. The code is capable of accommodating perfect metals and insulators, as well as piezoelectric and ferroelectric insulators and semiconductors. The code is also capable of generating energy band diagrams for heterojunctions that include liquid solutions and interfaces.

We applied our code to various experimental conditions, including: 1) self-assembled surfactant/solution interfaces used to grow 2D single-crystalline nanosheets; 2) a semiconductor/ferroelectric-insulator/solution and a piezoelectric/insulator/solution heterojunction used to create photoelectrochemical cells; and 3) piezoelectric/monolayer-

conductor/semiconducting-quantum-dots used for create a quantum dot solar cell. The ability of piezoelectric dipoles to effect the energetic landscape could depend significantly on the material properties, and insulator thicknesses, within heterojunction stack. There is still significant room for improvement, for example utilizing more accurate approximations (beyond Anderson's rule) of conduction and valence band offsets in heterojunctions of dissimilar materials, as well as integrating experimentally verified values of band offsets where available.

During my study, I took a particular interest in electrochemical phenomenal and photoelectrochemical structures. I explored the use of piezoelectric potential as a direct means of driving electrochemical reactions on the surface of metal-coated piezoelectric beams. Through calculation I explored the possibility of bare (non-metal coated) piezoelectric beams to drive electrochemical reactions by pushing and pulling charges out of their valence bands and into their conduction bands, respectively. This eventually led me to learn about catalysis and challenged me to find a way for piezoelectric dipoles to improve a materials catalytic property directly: to use piezoelectric dipoles to change the rate constant of a particular electrochemical reaction.

By combining Marcus theory for inner-sphere single electron transfer reactions with basic piezoelectric and solid state physics I theorize that piezoelectric surface charge can affect reaction kinetics. In Marcus theory, the rate of electron transfer between an electron donor and acceptor is dependent on the Gibbs free energy difference between the donor and acceptor state. If the electron donor is said to be a semiconducting piezoelectric, and the acceptor species in a molecule in solution that is in contact with the semiconductor, than the rate of electron transfer between the semiconductor and molecule is dependent on the energy difference between the semiconductors conduction band edge and the electron acceptor's unoccupied orbital's energy level. I propose that straining the piezoelectric semiconductor will affect the semiconductor/solution interface in such

a way as to shift the relative energy difference between the semiconductor's conduction band and the acceptor's unoccupied state, thus changing the free energy difference between the two and in turn effect the electron transfer rate between them. It is predicted that is possible to increase or decrease the electron transfer rate by putting the piezoelectric in either tension or compression, the details of which depend on the particulars of the specific semiconductor/solution system. I call this process "piezocatalysis".

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No one ever said that graduate school was easy, but don't let anyone tell you hard things can't be fun. Far and away, my time in graduate school has been the most enjoyable period of my life. Before graduate school I had never before been so empowered and had such freedom to explore topics and questions big and small, to sit back and enjoy purely intellectual pursuits in the welcoming and safe space that graduate school provides. I am fortunate to have had experienced the thrill of scientific discovery, been humbled by the unending sifting and winnowing of learning new truths and unlearning old ones, and felt pride in delivering an effective teaching experience to a room full of undergraduate engineers. These treasured experiences, and many, many more would not have been possible without the patients, leniency, humor and support of my research advisor Prof. Xudong Wang. Through my time in graduate school my respect for Xudong has only grown as I've seen his patients persevere through times of funding challenges, manuscript and grant deadlines, and the productivity delays characteristic of a procrastinating graduate student. I will always appreciate the way Xudong was forthcoming when he didn't understand something and the many hours-long conversations we had in his office about exciting tangential research topics.

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Chapter 1: Prospects for Flexible Electronics

1.1 Introduction to flexible electronics

Traditional electronics are bulky, hard and brittle. Over the past decade, the explosive adoption of digital technology in the consumer products space (e.g., “smart” phones, watches), as well its use extensive use in mobile military applications, has driven the research and development of electronic materials and device designs that are smaller and more flexible. When it comes to computing power and convenience, the needs of the soldier on the battlefield are similar to those of the pedestrian on the street: batteries, transistors, antennas and displays combined in compact and light weight packages that resist impact and abrasion. The pursuit of durable, portable electronics has driven device and materials design to develop flexible alternatives to do the work of constituent components in today’s consumer electronics.

Other market forces are also at play, advances in medical diagnostic technology and the quantified-self movement have pushed electronics into domains where they hadn’t been before: within and in symbiosis with our bodies.[1-7] For medical devices and diagnostic sensors to be implanted within the body, or attached to the skin, requires that they possess a degree of mechanical compatibility with biological tissues that is unprecedented.[8-11]

Progress in the development of flexible electronics has run the gamut. Research has produced an array of flexible solar [12-50], thermal [51-64], and mechanical energy converters [65-96] for energy collecting and transmitting purposes. Flexible energy storage in the form of flexible batteries [97-116] and capacitors [101, 117-154] have been produced, as well as flexible transistors [131, 155-198] and memory components.[139, 197, 199-227] The principle concern the researchers face when developing flexible electronic component is how to deal with the strain that inevitably develops when a material is deformed. Whereas traditional devices could be assumed

to be mechanically static, and thus differentials in device performance with bending could for the most part be neglected, work in flexible electronics has brought strain to the forefront as a parameter in device design.

In the pursuit of realizing flexible electronics, three main approaches have been pursued:

- 1) Use of traditional ‘hard’ and ‘bulk’ components, separated by flexible interconnects (“flexible printed circuits”) (Figure 1)
- 2) Extensive use of “soft” (polymer) materials (Figure 2)
- 3) Use low-dimensional (e.g., thin films, nanowires) inorganic materials (Figure 3)

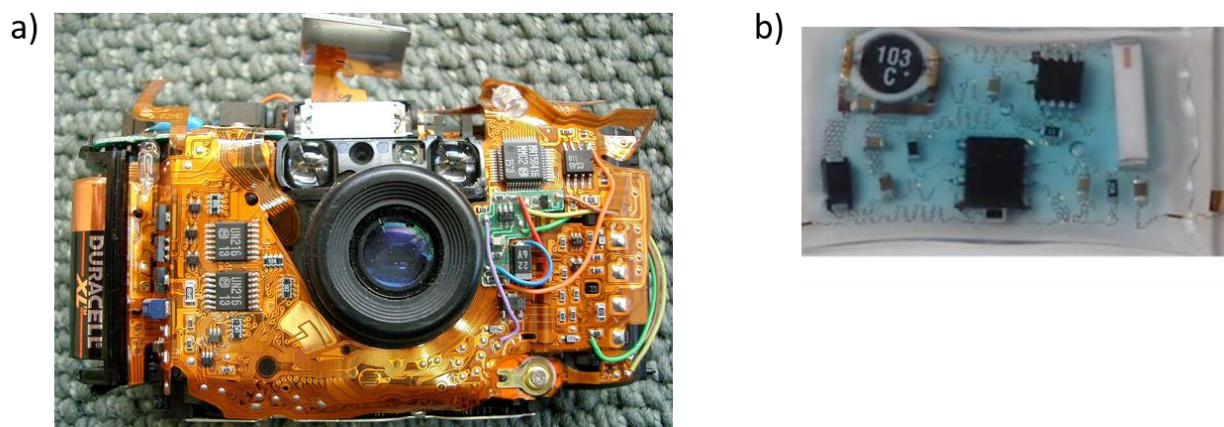


Figure 1. Combining traditional bulk electronic components with flexible substrates and interconnects to achieve a degree of electronic malleability. a) An Olympus Stylus camera without the case, showing the flex circuit assembly. b) a stretchable and skin mountable physiological measurement device.[228]

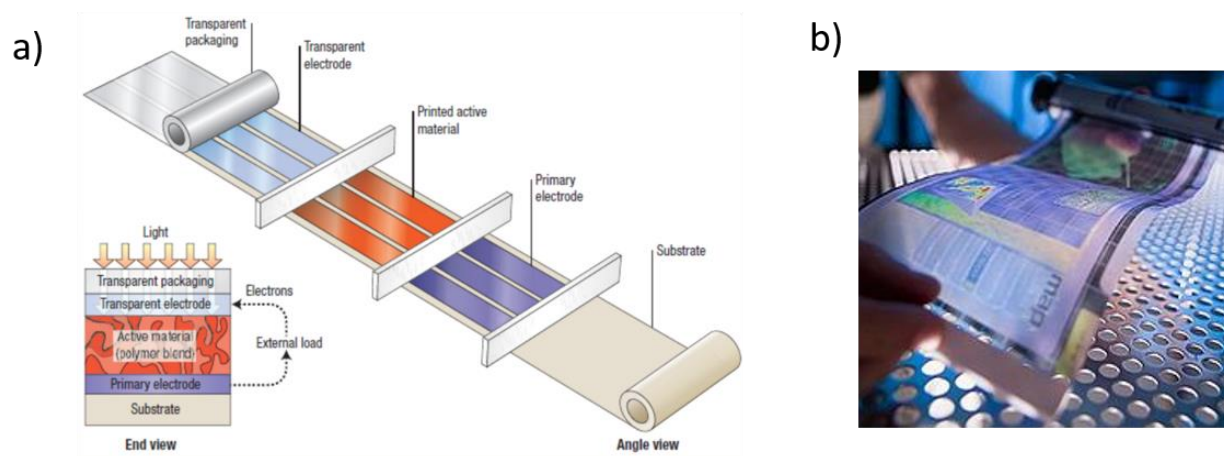


Figure 2. Organic electronics as an approach to achieving flexible devices. A) Organics-based flexible display. B) Roll-to-roll processing of organic electronics.

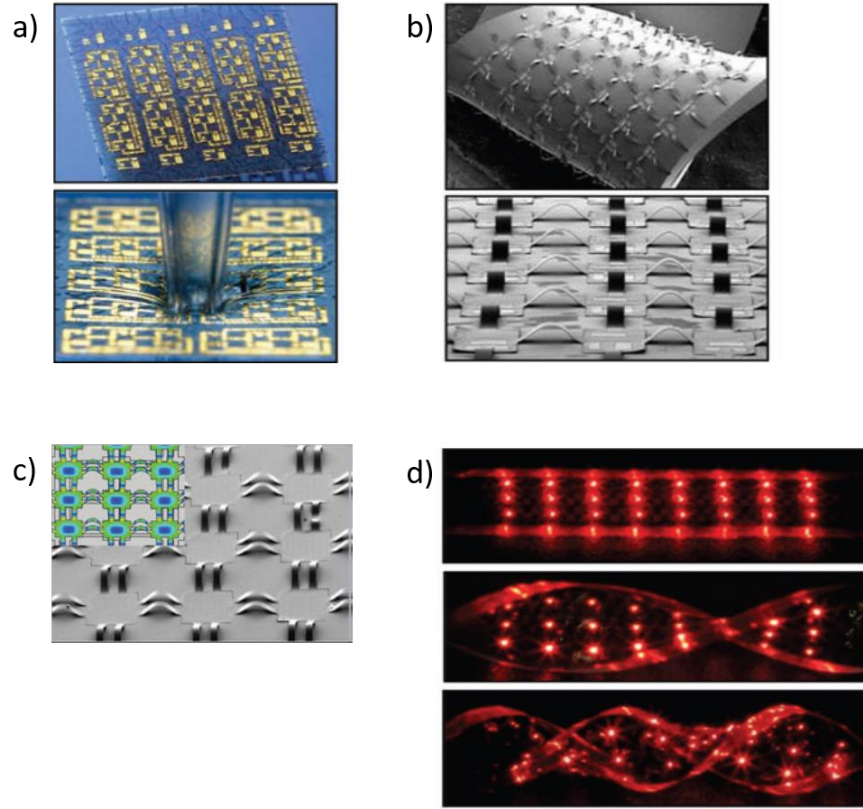


Figure 3. a) Stretchable CMOS circuit that uses a “wavy” layout on an elastomeric substrate shown (*top*) before and (*bottom*) during application of normal force with a glass rod.[229] b) and c) non-coplanar bridge structures with connecting inorganic semiconductor materials. SEM image of an array of stretchable, 3-stage CMOS ring oscillators in a twisted configuration.[230]. d) Stretchable array of GaAs microscale inorganic light-emitting diodes with serpentine interconnects in flat, 360° twisted, and 720° twisted states.[231])

While researchers and engineers explored strategies for both increasing the flexibility of their devices and enhance their robustness under strain, they were exploring the use of strain as a parameter in the performance of their devices.[232-300] In addition to enhancing device performance with strain, researchers set out creating devices that had properties which were exquisitely sensitive to their strain state. A class of materials which have a particularly strong mechanical –electrical coupling, called piezoelectrics, attracted significant attention for their use in these devices. In piezoelectric materials, strain results in an electric dipole field permeating the

material. These strain-induced dipole fields effect the movement of free charges within the material and thus effect mobile charge carrier conduction and device performance.

Research into the embedding of active piezoelectric materials into miniature electronic devices has already yielded a variety of results with potential applications, including piezotronic transistors, memory, solar cells and photodetectors[238, 246, 253, 254, 261, 274, 277, 301-349], light emitting diodes[246, 303, 310, 312, 315, 318, 324, 326, 330, 336, 339, 343-345, 347, 348, 350], and photoelectrochemical cells.[257, 351-353]

1.1.1 Piezotronic Transistors

A transistor is a device that is able to amplify a small stimulus (electrical or mechanical) into a large electrical signal. These devices typically require current to flow through a region of material whose electrical properties can be significantly varied via the application of a small stimulus. In semiconducting materials, careful engineering of device structure and properties can produce regions where charge carriers are relatively rare and thus the resistivity of the material is relatively high. In a piezotronic transistor, strain is used to either change the free carrier concentration in this region or to reduce some other electronic barrier impeding charge flow.[241, 256, 267, 272, 273, 289-295, 297, 354, 355] Figure 4 schematically demonstrates how a piezotronic transistor may work.

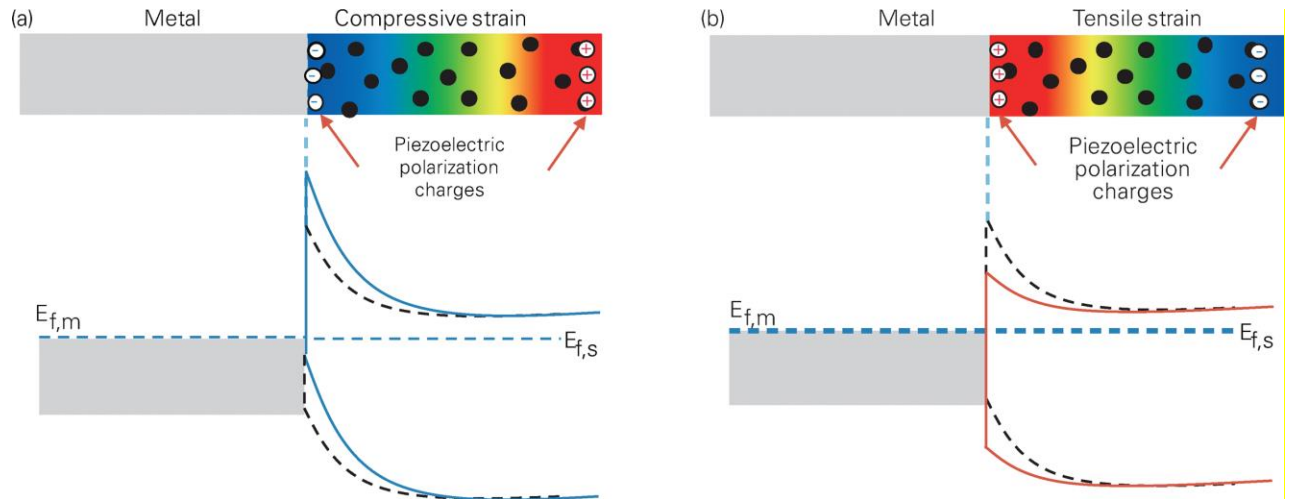


Figure 4. Schematic of energy diagram illustrating the effect of piezopotential on modulating the metal–semiconductor characteristics. (a) With compressive strain applied, the negative piezoelectric polarization ionic charges induced near the interface (symbols with ‘–’) increases the local SBH. (b) With tensile strain applied, the positive piezoelectric polarization ionic charges induced near the interface (symbols with ‘+’) decreases the local SBH. The color gradients indicate the distribution of piezopotential, with red representing positive piezopotential and blue representing negative piezopotential. The band diagrams for the M–S contact with and without the presence of piezotronic effect are shown using the solid and black dashed curves, respectively. The black dots represent the free-charge carriers in the bulk semiconductor. Adapted from [356].[351]

By applying strain to the piezoelectric element, surface charge at the heterointerface causes a charge rearrangement which in turn reduces the built in potential at the metal/semiconductor Schottky junction. With a reduced barrier impeding charge flow, current is able to flow more readily through the junction (Figure 5). The current conduction characteristics through the piezoelectric semiconductor depend on the degree of strain applied to the piezoelectric element. Piezotronic transistors research is naturally focusing on tactile sensor applications, where ‘skins’ of piezotronic transistors may one day produce prosthetic skins for humans and robots alike.

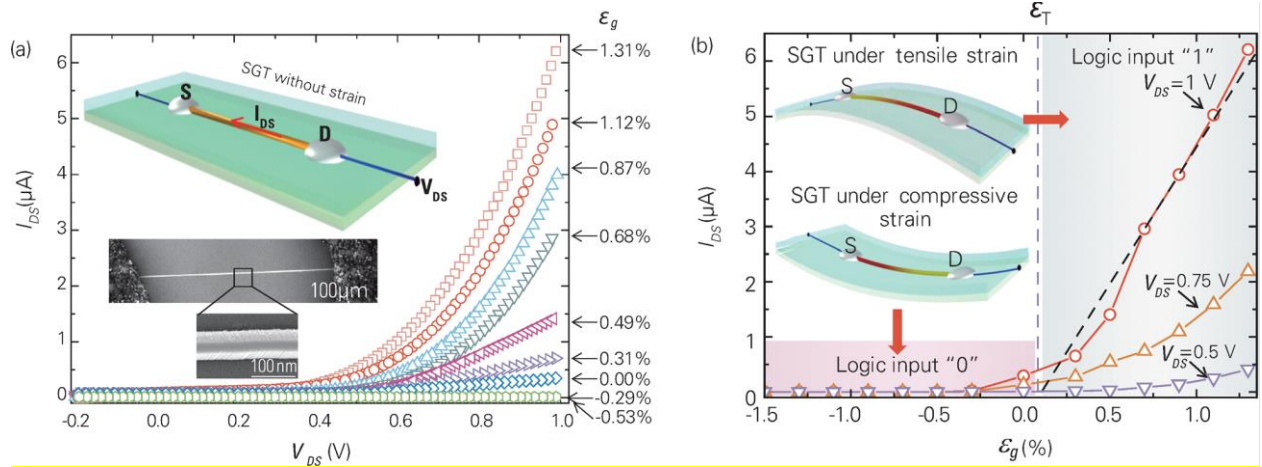


Figure 5. Single ZnO NW SGT. (a) I_{DS} - V_{DS} output characteristic for a ZnO SGT device. (b) I_{DS} - ϵ_g transfer characteristic for the same ZnO SGT device under three different V_{DS} bias values: 1, 0.75, and 0.5 V [[357]] (Copyright 2010 WILEY-VCH, Weinheim). [351]

1.1.2 Piezotronic photovoltaics, photodetectors, photoelectrochemical cells

Photovoltaics, photodetectors [238, 246, 253, 254, 261, 274, 277, 303-349] and photoelectrochemical cells [257, 352, 353] work by converting the electromagnetic energy of photons into electrical potential energy of electrons or electrochemical energy of molecules. To achieve this, a material must absorb photons in such a way that causes mobile charges in the photo-sensitive material to flow predominantly in one direction. This feat is typically accomplished by creating a depletion region in the material, a region where there is an electric field present and there are few mobile charges. Since a piezoelectric material is capable of generating electric fields which permeate the material, it is expected that strain is capable of effecting the performance of these photo-responsive devices. Figure 6 shows how a nanowire solar cell composed of piezoelectric cadmium sulfide and copper sulfide are capable of wielding the piezoelectric response to change the depletion region within the heterojunction.

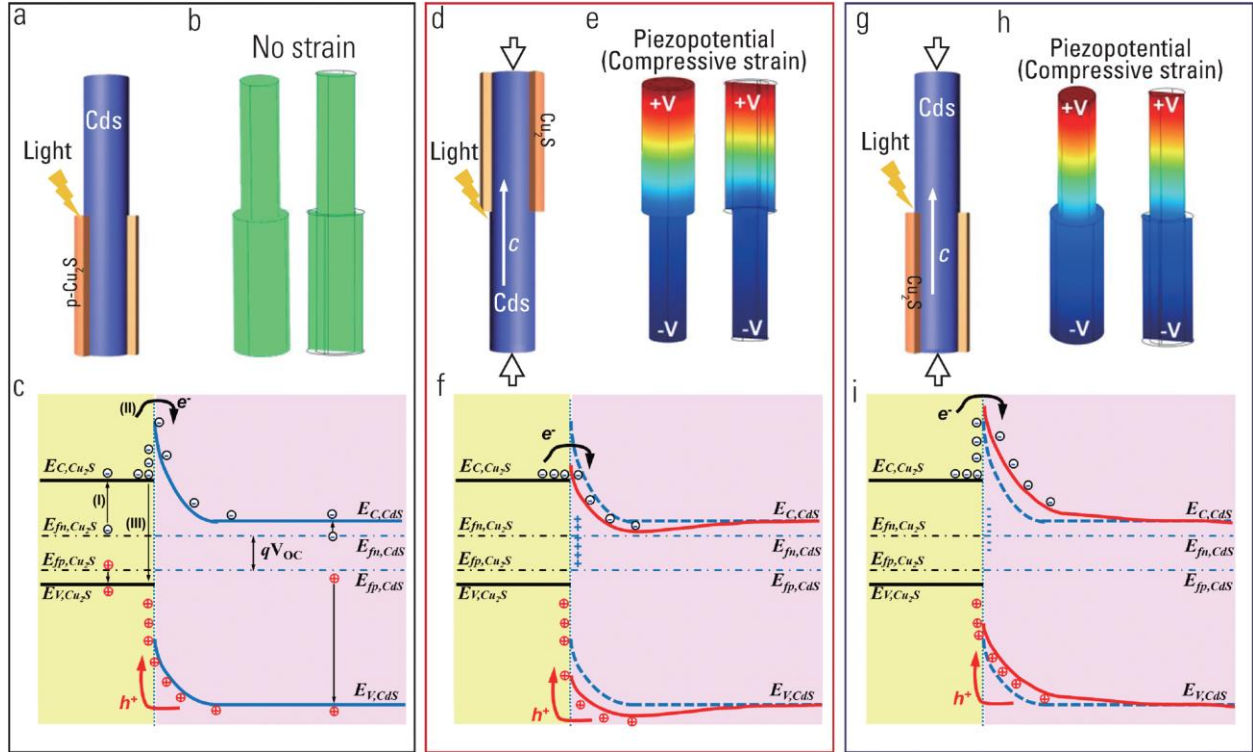


Figure 6. Schematics and energy-band diagrams demonstrate the piezo-phototronic effect on coaxial piezoelectric NW solar cells. (a–c) Numerically calculated piezopotential distribution and the corresponding energy-band diagram of a strain-free coaxial piezoelectric NW solar cell. (d,e) Numerically calculated piezopotential distribution and the corresponding energy band diagram of a coaxial piezoelectric NW solar cell under compressive strain for a PV device with configuration. The upper part of the CdS NW is positively charged, while the lower part is negatively charged due to the piezoelectric potential under compressive strain. The positive charges at the CdS side lower the conduction and valence bands of CdS at the interface of the p–n junction that decreases the barrier height at the interface of the heterojunction, resulting in an enhancement of the PV performance. (g–i) Numerically calculated piezopotential distribution and the corresponding energy-band diagram of a coaxial piezoelectric NW solar cell under compressive strain for a PV device with configuration II. The negative charges at the CdS/Cu₂S interface lift up the conduction and valence band of CdS at the interface of the p–n junction, thus resulting in a drop of the PV device [302](Copyright 2012 American Chemical Society).[246]

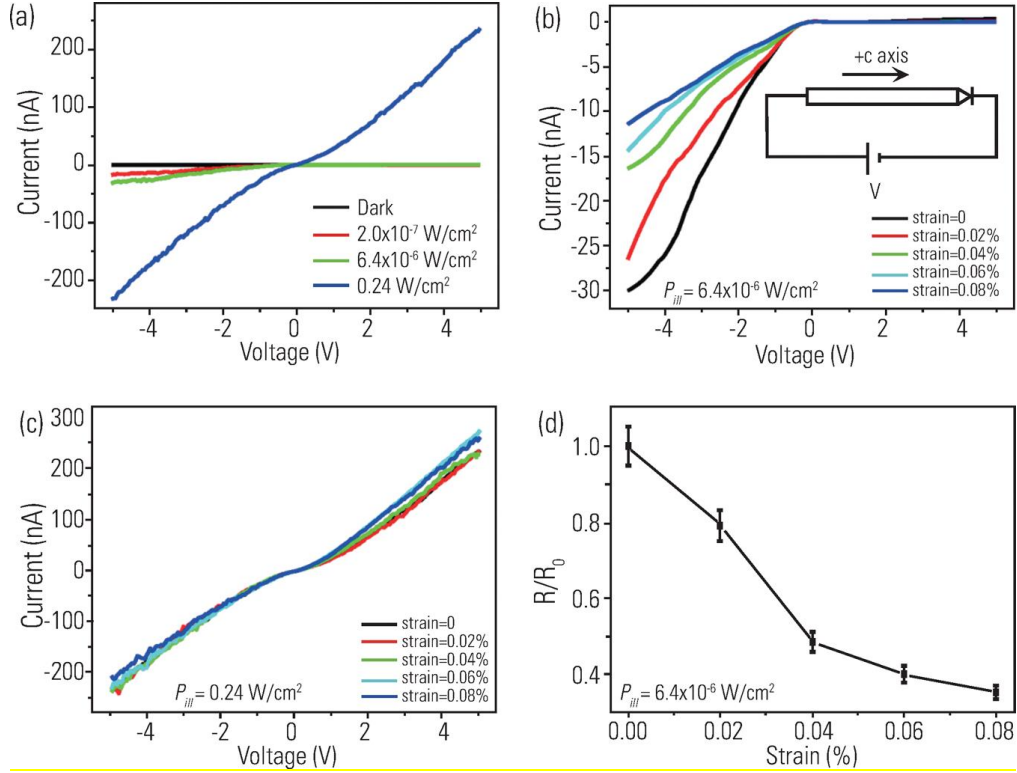


Figure 7. Experimental results for a CdS NW MSM photodetector with a single Schottky contact. Light illumination with monochromatic blue light centered at 486 nm. (a) Current–voltage characteristic under different illumination power. The inset shows the dark current without strain. (b) Current–voltage characteristic under different strain when the illumination power is $6.4 \times 10^{-6} \text{ Wcm}^{-2}$. Inset is the configuration of the device and the direction of the forward bias. (c) Current–voltage characteristic under different strains when the illumination power is 0.24 Wcm^{-2} . (d) Calculated relative responsivity under various applied strain when the illumination power is $6.4 \times 10^{-6} \text{ Wcm}^{-2}$ [301] (Copyright 2012 WILEY-VCH, Weinheim).[246]

Figure 7 and 8 demonstrates the performance of the device under varying luminosities and strain states. The ability of piezoelectric materials to modulate the photo response is thwarted when the carrier concentration inside the piezoelectric element is too high. High carrier concentration can arise from doping, thermal excitation or photoexcitation, as in the case of Figure 7c. When the luminosity falling on the piezoelectric element approached 0.24 Wcm^{-2} , the concentration of mobile charges within the material was sufficient to effectively screen the piezoelectric's electric field without significantly changing device performance.

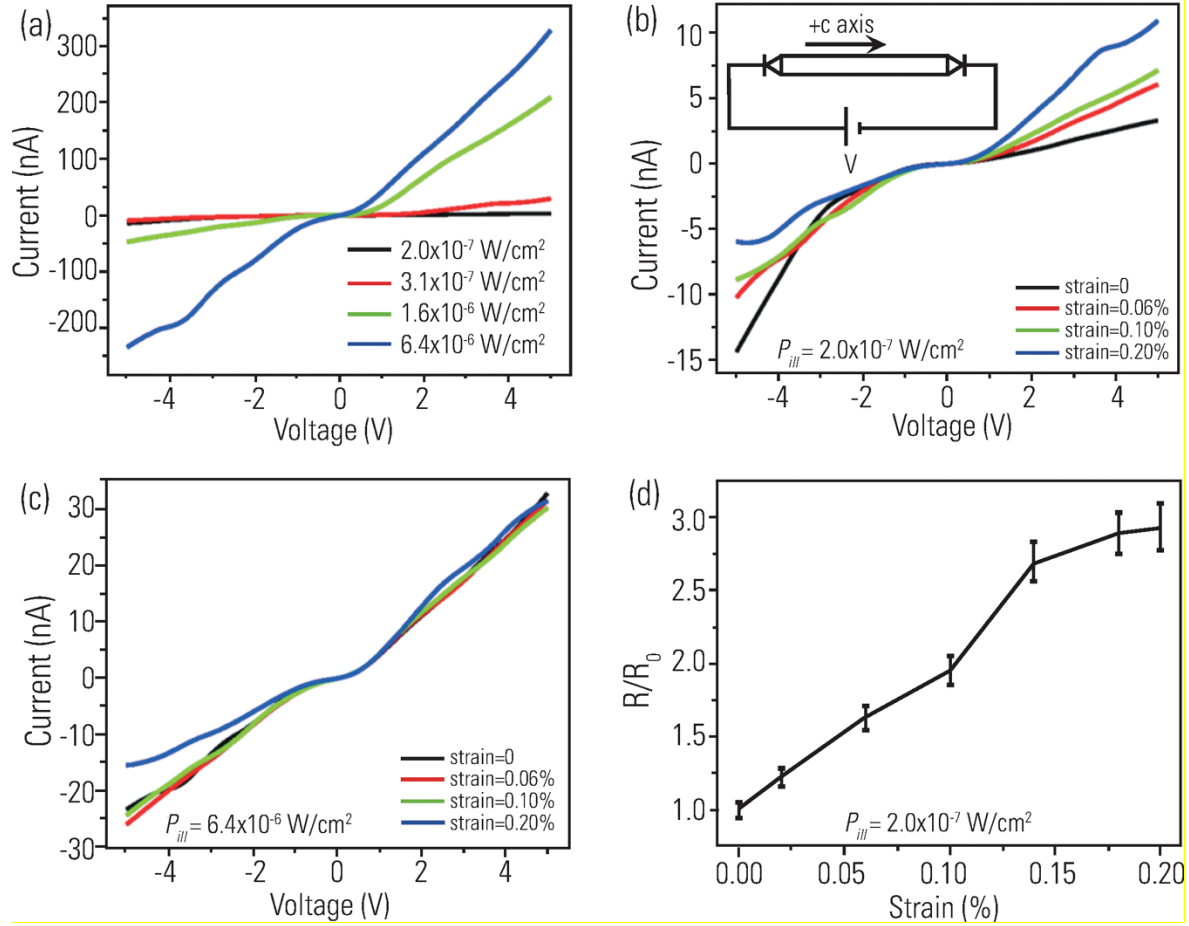


Figure 8. Experimental results for a CdS nanowire MSM photodetector with double Schottky contacts. Light illumination with monochromatic blue light centered at 486 nm. (a) Current–voltage characteristic under different illumination power. (b) Current–voltage characteristic under different strain when the illumination power is $2.0 \times 10^{-7} \text{ Wcm}^{-2}$. Inset is the configuration of the device and the direction of the forward bias. Inset is the configuration of the device and the direction of the forward bias. (c) Current–voltage characteristic under different strains when the illumination power is $6.4 \times 10^{-6} \text{ Wcm}^{-2}$. (d) Calculated relative responsivity under various applied strain when the illumination power is $2.0 \times 10^{-7} \text{ Wcm}^{-2}$. R_0 is set as responsivity under zero strain for this illumination power [301] (Copyright 2012 WILEY-VCH, Weinheim).[246]

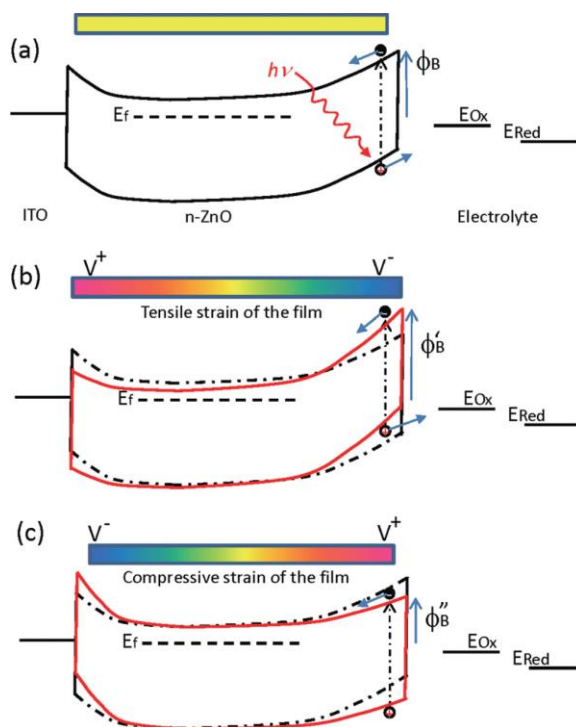


Figure 9. Effect of piezopotential in the semiconductor on the PEC process. (a) Band structure of the PEC with the absence of piezopotential. (b) Band structure of the PEC when the film is under tensile strain, so that the side directly interfacing with the electrolyte has a lower piezopotential. (c) Band structure of the PEC when the film is under compressive strain, so that the side directly interfacing with the electrolyte has a higher piezopotential [351] (Copyright 2013 Springer).[246]

Piezoelectric fields, which act on the depletion width in the material, can also effect the materials ability to photo-react with chemical species in its surroundings (Figure 9). In a photoelectrochemical cell, photoexcited electrons (or holes) move to the semiconductor/solution interface and reduce/oxidize chemical species in solution. The chemical species in solution possess electrons in occupied states, and lack electrons in unoccupied states, which exist at some electrical potential relative to the valence band and conduction band of the photo-active material. If electrons in the material's conduction band, at the interface, possess an energy greater than the energy of an unoccupied orbital of a molecule in solution then it is energetically favorable for the electron to transfer from the material to the molecule. Conversely, if there is an electron in an occupied state

in a molecule in solution which possesses an energy greater than an unoccupied surface state in the semiconductors valence band, it is energetically favorable for the electron transfer from the occupied molecular state to the semiconductor's valence band.

Applying strain to a piezoelectric material that is in contact with solution causes a dipole to form at the material/solution interface. The dipole is formed between the piezoelectric's surface charge and a charged molecular layer in solution. Some of the effect of the piezoelectric charge may also be shared within the semiconductor. The effect of the solution dipole is to shift the valence and conduction band energies relative to reduction and oxidation potentials in solution. Thus, straining piezoelectrics can influence the ability of electrochemical cells to undergo photoelectrochemical reactions with the solution environment.

1.1.3 Piezotronic light emitting diodes

Light emitting diodes (LEDs) work by creating a region in a material where mobile electrons in the conduction band and mobile holes (vacancies of electrons) in the valence band are able to combine without requiring a significant amount of momentum transfer between the electrons and the lattice. In this case, most of the energy difference between the electron and hole is able to be transferred into a photon which then can then be emitted from the device. In these devices, energy difference between the electron and hole is important because it determines the wavelength of photon emitted, the number of electrons and holes matter because they are the source of the photons, and how closely the electrons and holes can be brought together matters because that increases the rate of recombination and thus emission. Electrons and holes are both mobile charges and thus they respond to the influence of an electric field, which includes one that is created by straining a piezoelectric material. Thus, piezoelectric materials can be used to influence the movement and location of charged species, and thus their emissivity. Numerous

studies have been conducted to verify that piezoelectric fields can influence the emissivity of a piezoelectric LED. [246, 303, 310, 312, 315, 318, 324, 326, 330, 336, 339, 343-345, 347, 348]

Figure 10 demonstrates the effect of straining a piezoelectric LED.

Both the LED's intensity and efficiency increased as a function of strain. The observed behavior of the LED is attributed to an effect on the band structure of the heterojunction which occurs with strain, namely a quantum well-like feature. As the piezoelectric material is strained, a surface charge develops at the heterointerface. The effect of this surface charge is to isolate and concentrate mobile electrons at the interface. The increase in electron concentration is thought to increase the rate of electron/hole recombination, increasing the rate of emission and thus the intensity of illumination.

Besides directly using the piezoelectric effect in devices as a way of enhancing performance, piezotronics plays to a future where electronic devices have become so small, powerful, and ubiquitous, that they are in everything (Figure 11).

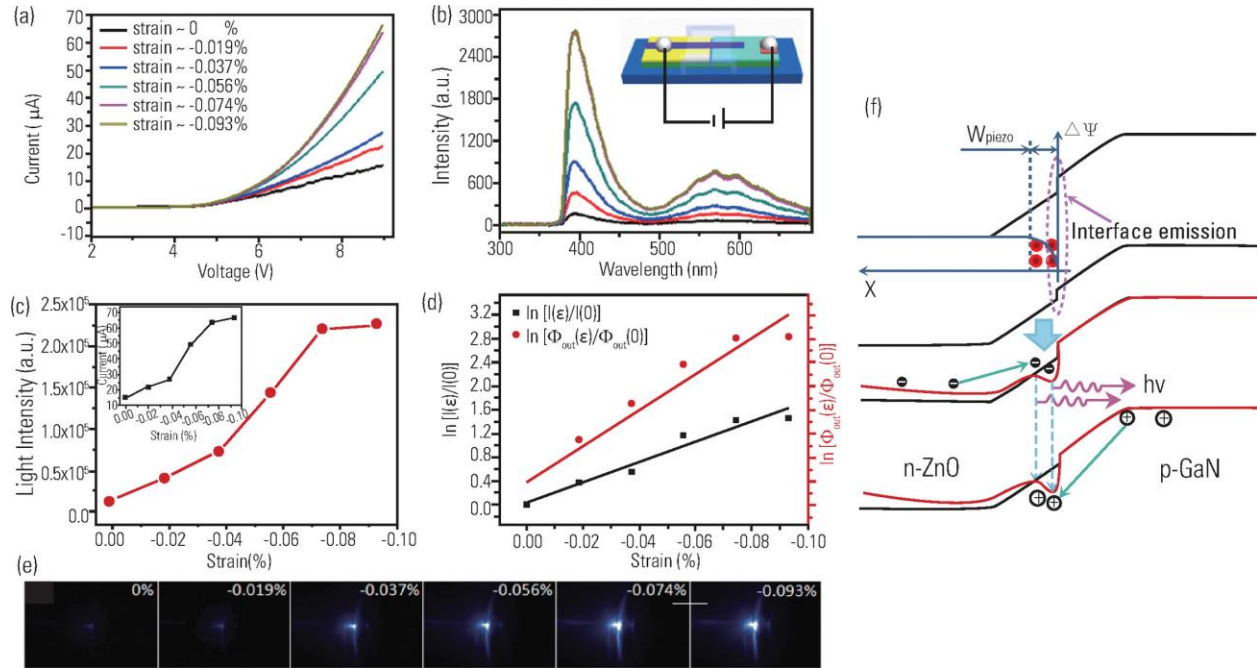


Figure 10. Enhancement of light emission intensity and conversion efficiency of an (n-ZnO wire)–(p-GaN film) LED under the applied strain. A schematic diagram of the fabricated device. (a) I - V characteristics of the device at the forward bias with the variation of the applied strain; and (b) the corresponding optical spectra of the emitted light at a bias of 9 V. (c) Integrated light emission intensities from the data shown in (b), showing a huge increase in the emission intensity with the increase of the applied compressive strain. The inset is the injection current of the LED at 9 V biasing voltage with the increase of the strain. (d) Change in relative injection current and relative light emission intensity under different strain. The LED efficiency has been increased by a factor of 4.25 at the maximum applied strain in comparison to the zero strain case. (e) CCD images recorded from the emitting end of a packaged single wire LED under different applied strain. (f) Schematic energy-band diagram of the p-n junction without (upper) and with (lower, red line) applied compressive strain, where the channel created at the interface inside ZnO is due to the piezopotential created by strain [350] (Copyright 2011 American Chemical Society).[246]

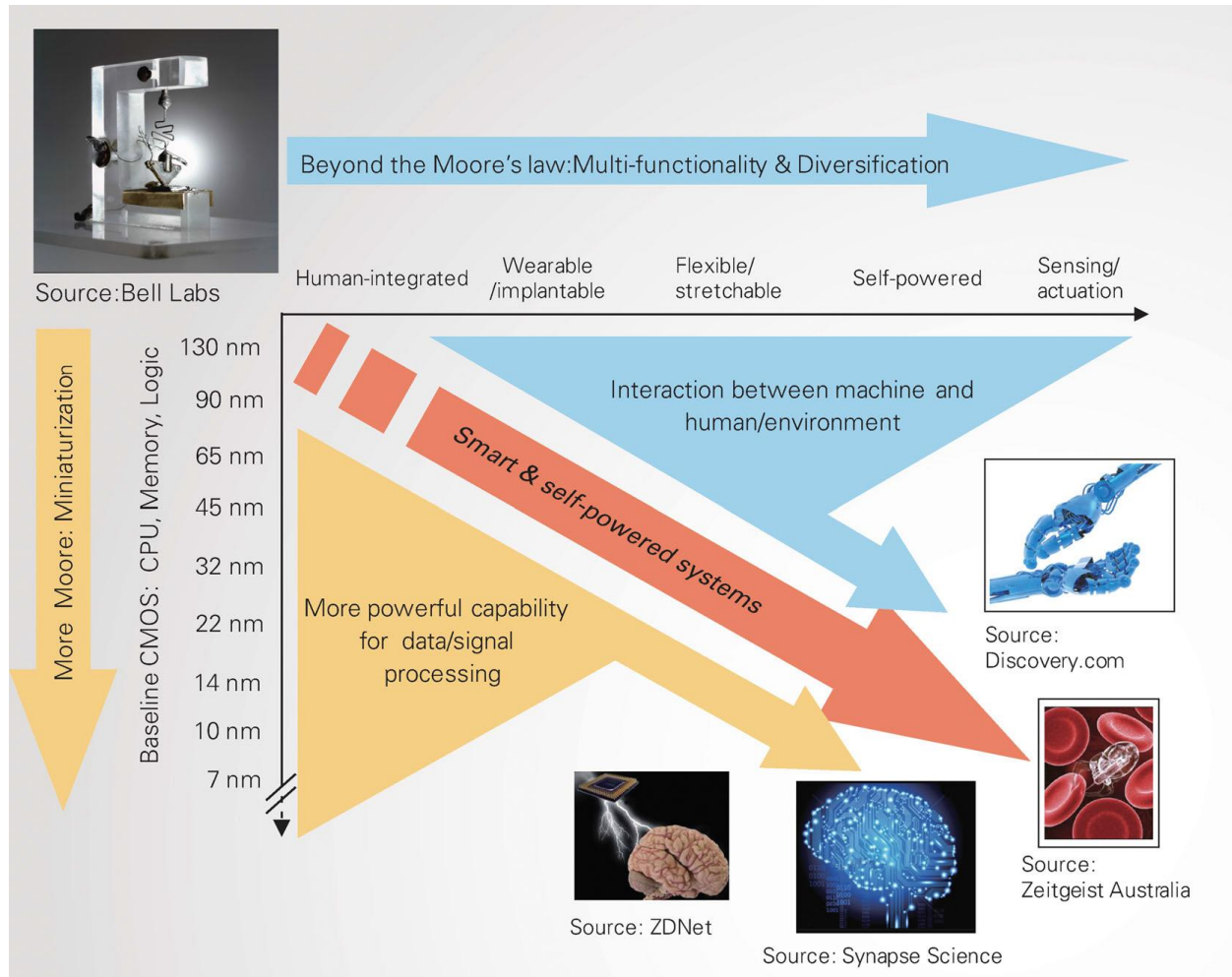


Figure 11. Future perspective of electronics beyond the Moore's law. The vertical axis represents a miniaturization and increase of device density, CPU speed and memory. The horizontal axis represents the diversity and functionality for personal and portable electronics. The future of electronics is an integration of CPU speed and functionality. It is anticipated that an integration of mechanical action through piezotronics in electronic systems is an important aspect of interfacing human and CMOS technologies. (REF: Adapted from: Progress in Piezotronics and Piezo-Phototronics) [246]

In this future world, the electro-mechanical coupling property of piezoelectrics put them at the nexus between the 'natural' and the machine worlds that we interact with every day. With the potential to offer a seamless transduction between the digital and physical world, further research into the potential of imbedding active piezoelectric components into miniature electronic devices is a warranted activity. To engineer these piezotronic devices, and heterojunction electronic

devices in general, electric potential band diagrams are often used as a means of quickly predicting and explaining device behavior. While this is clearly the case seen the literature, it is also evident that few researchers have access to ways of generating band diagrams that are qualitatively and quantitatively accurate. This is especially problematic in the case of piezotronics, where a piezoelectric material introduces surface charge densities at interfaces, because the means in which heterojunctions redistribute charge in response to an introduced piezo-driven surface charge is not typically intuitive. Several basic rules exist for thinking about how heterojunction band diagrams come together, but none of them easily account for the addition of surface charge. In order to better understand how to engineering piezotronic devices, Mathematica code was generated to quantify heterojunctions between metals, insulators, semiconductors, and solutions. The code made use of Anderson rules, bulk approximations for materials, and incorporated ferroelectric and piezoelectric effects into the semiconducting and insulating materials.

Chapter 2. Quantifying and Automating Heterojunction Band Diagrams

2.1 Introduction to Band Diagrams.

In the 1920's, scientists focused their attention to applying the rules of quantum mechanics to understand the electrical properties of materials. It was observed that for varying materials, the electrical conductivity could vary over 27 orders of magnitude[358], and no theory prior to the application of quantum mechanics yielded fruitful results. An attempt at explaining these electrical properties, which ultimately proved extremely productive, was formulated by Felix Bloch, Alan Herries Wilson and Rudolf Peierls and focused on the concept of propagating electron waves in periodic mediums. The results of their work came to be known as band theory and described an energetic landscape within the material composed of energy bands, ranges of energies that an electron within the solid may and may not have. This theory went a long way to explaining a mystery that had existed since the 1970's, when it was discovered that by combining materials with different charge densities and electrical permittivities, the flow of electrical current could be impeded, made exquisitely sensitive to mechanical, electrical, or chemical stimuluses, and even used to drive chemical transformations. [359-361] It was discovered that the alignment of energy bands in one material relative to another was extremely significant in determining the ability of electrons to flow across the interface from one material to the next.

The flow of electrical charges to, through and from multi-junction material architectures (i.e. heterojunctions) has since become the working principle governing computer logic and transistors, volatile and nonvolatile computer memories, electrical and chemical energy storage

devices, and many other energy harvesting and transduction technologies. A key process that occurs at the junction between dissimilar materials, which gives rise to this plurality of conductivity properties and behaviors, is that of: 1) free-charge flow, and 2) the formation of a ‘depletion region’ and its associated built-in field. In many cases, the useful properties that emerge from these heterojunctions depend strongly (e.g., exponentially) on the magnitude of the built-in field, length scale of the depletion region and other associated factors such as electrical permittivities and band gaps.

Band structure diagrams originated from band theory as a quick and intuitive way to describe the range of energies in a material that electrons may or may not occupy. The use of band structure diagrams in educating a generation of engineers and physicists has resulted in an evolution of their role from that of a simple descriptive graphic to that of a predictive and explicative tool. As evidenced by their massive presence in the scientific literature, band structure diagrams are now often the default tool that scientists around the world over turn to not only to explain, but also predict heterojunction material properties and engineer stacks of heterojunction materials for devices. The discussion and conclusion section of many publications base their content on a band structure diagram depicted in the paper. Today, many of these diagrams are formed in an iterative process combining intuition and data-fitting. The problems with this strategy are twofold: 1) it is difficult for human intuition to fully grasp the many-body interactions that take place at active heterojunctions, and 2) fitting diagrams to the data is a self-fulfilling act, resulting in internally self-consistent logic which may not be objectively true. Because of their increasingly important role in the engineering and discovery process, it is necessary that scientists have access to tools for accurately predicting, plotting, and manipulating band structure diagrams.

2.2 Resources for Automatically Generating Heterojunction Energy Band Diagrams.

A number of paid and free efforts current exist on the web to assist with the general construction of band diagrams, for example: Pymatgen from the materials genome project; siLENSe; efforts by the Snide Lab at the University of Notre Dame; the Mindlab at the University of California Davis; efforts at Boise State University; and Silvaco. These efforts suffer from a number of shortcomings which inhibit their wide-spread use in the scientific community. Of the few programs available, the most polished applications are behind paywalls. For a service to be utilized by the majority of the scientific community, it must be free to access. Additionally, most of the available programs are only capable of using a few materials which are already predetermined (e.g., Nitrides, GaAs, etc.) and don't let the user manipulate fundamental properties that would change the identity of the material. If users are unable to enter their own material properties then there is no way for researchers to tailor the programs to the needs of their specific labs, or for the program to evolve as new materials become the focus of scientific research. And finally, except in the case of some nitride-containing programs, it is no possible to incorporate piezoelectric dipoles into the heterostructures. We set about to create free, augmentable code that, crucially, allows for the addition of piezoelectric charge to the energetics of the heterojunctions band energy diagram.

2.3 Calculating Heterojunction Energy Band Diagrams.

Mathematica is used to auto generate the energy band diagrams. To calculate heterojunction energy band diagrams we employ the Anderson's rule (electron affinity rule) whereby the vacuum levels of two adjacent materials are aligned at the same energy. Metals are perfect conductors and insulators are perfect insulators. All materials are given bulk properties unless otherwise stated

(e.g. in the case of PbS quantum dots). The length scales of the materials are sufficient large such that adjacent semiconducting interfaces can be calculated independently, i.e. the depletion region of one interface does not influence the depletion region of the other. If no piezoelectric material is present, the Fermi level difference between two adjacent materials is assumed to be the only driving force for charge exchange across the heterojunction interface. Strained piezoelectric materials introduce bound surface charges to the interface. Ferroelectric materials contribute bound surface charges to the interface even in the absence of strain.

There are four types of materials that are commonly used to build junctions: 1) metals, 2) insulators, 3) semiconductors, and 4) liquid solutions.

- Metals have extremely high free-carrier concentrations ($> 10^{23}$) and no band gaps (a continuum of states exist about its fermi energy), these properties tends to dominate their behavior at the junction.
- Insulators are assumed to have zero mobile charges so their electrical permittivity and thickness determine the effect they have on the junction.
 - If the insulator is piezoelectric or ferroelectric then the insulator also brings with it an immobile surface charge density.
- Semiconductors have intermediate free charge densities (10^{14} - 10^{18}) composed of mobile positive (holes, p) and negative (electrons, n) charges which often follow a mass-action relationship ($n_b p_b = n_i^2$, where n_i is the intrinsic carrier concentration). Semiconductors also often have immobile dopant charge centers with a fixed concentration (N_D or N_A for donor (positive) or acceptor (negative) ions, respectively).
- Liquid solutions can have a wide range of mobile charge carrier concentrations (10^{13} - 10^{20}). The mobile positive and negative charge carriers may be asymmetric in charge (e.g., Mg^{2+}

and Cl^{1-}) and unequal in concentration (e.g., 2:1). Attention must be paid to the physical dimensions of the mobile ions to ensure that the charge-density does not exceed a physically reasonable limit (i.e. in general the charge density of hydrated ions should not exceed the atomic density of solids).

Semiconductors and liquid solutions are sometimes approximated to be equivalent when their energetics (Fermi energies) are similar, but as we will see, this approximation breaks down at moderate potentials.

2.3.1 Metal/Semiconductor Junctions

It is appropriate to begin the analysis of single junction systems with those that consist of metals and semiconductors in intimate contact. These are by far the most common systems employed in material heterojunction engineering and their description will be familiar. In metal/semiconductor junctions, the semiconductor have a work function that is greater or less than the metals, as is demonstrated in Figure 12a and Figure 12b with n-type and p-type semiconductors, respectively. As a general rule, It isn't necessary that the semiconductor be n-type in order for its work function to be less than the metal's, nor is a p-type semiconductor necessary for the work function to be larger than the metals. Figure 12c and Figure 12d shows a typical cartoon for both systems at equilibrium.

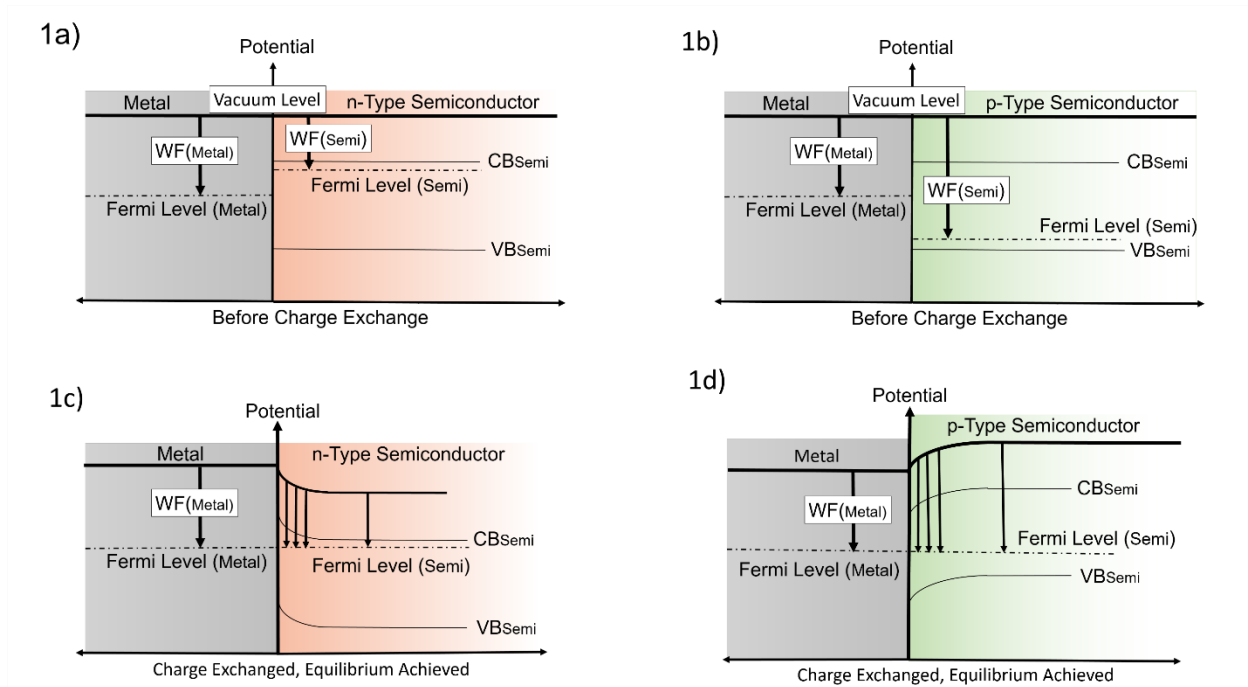


Figure 12. Representations of metal/semiconductor junctions. A) A metal n-type semiconductor junction. WF (Metal) is the work function of the metal and WF (Semi) is the work function of the semiconductor. CB_{semi} and VB_{semi} are the conduction and valence bands of the semiconductor, respectively. B) A metal p-type semiconductor junction. C) A schematic of the electrical potential profile across the metal/n-type semiconductor junction after equilibrium is established between the two materials. D) A schematic of the electrical potential profile across the metal/p-type semiconductor junction after equilibrium is established between the two materials.

In the case where the semiconductor's work function was less than that of the metals (Figure 12a), it is energetically favorable for electrons to flow from the semiconductor to the metal, resulting in an electric field between the two (pointing from the semiconductor to the metal). At equilibrium the Fermi energy across the entire diagram is constant but that the vacuum energy with respect to the Fermi energy will vary and thus the work function across the heterojunction is not constant. To achieve equilibrium when the work function of the semiconductor is greater than that of the metal (Figure 12b), electrons will flow from the semiconductor to the metal. As before, the charge flow creates an electric field but points from the metal to the semiconductor.

A metal/semiconductor junction is often used to build Schottky solar cells, in which case it is appropriate to ask: To what depth does the band bending (or ‘depletion region’) extend within the semiconductor? It is only within this depletion length that photons absorbed by the semiconductor will contribute to a photocurrent. If one is building a scintillator or photomultiplier device out of a metal/semiconductor junction, an appropriate question might be: What is the magnitude of the electric field within the semiconductor as a function of distance? The electric field within this region will impart an acceleration to photoexcited charges and influence the impact ionization rate. How can an externally applied influence the depletion width? Applying a potential to the metal electrode will surely change the depletion width and electric field present within the depletion region, but by how much? Are there diminishing returns for applying a greater and greater potential to the electrode?

To quantitatively address these questions, we built a model of this single junction system (See Code Section). Before any charge flows between the metal and semiconductor, as depicted in Figure 12a and Figure 12b, no electric field exists between the two. Under ordinary conditions, as time passes, electrical charges in both materials will explore all of the electronic states available to them. If an electron goes from a high energy state to a low energy state, energy will be dissipated (i.e. spread out in space) and this will hinder the ability of the electron to return to its previous high-energy state.

Before metal/semiconductor contact, if the electrons in the semiconductor tend to be in higher energy states than those of the metal (Figure 12a) then after metal/semiconductor contact electrons that flow from the semiconductor to the metal will have difficulty returning to the semiconductor. If the electrons in the metal tend to be in higher energy states than those of the semiconductor (Figure 12b) then electrons that flow from the metal into the semiconductor will

have difficulty returning to the metal. The average energy state of a mobile electron in the metal or the semiconductor is defined by their bulk Fermi level or work function (denoted as dotted lines in Figure 12).

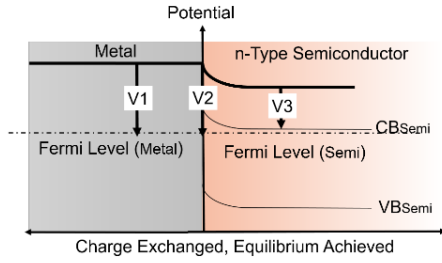
The net flow of charge from one material to the other is not unending: for every net charge that flows across the material interface, an electric field is created at the interface which tugs charge back. As more charges flow across the interface, a stronger electric field accumulates there, hindering further charge flow. The electric field present at the interface is an energetic barrier to additional charge flow which counterbalances the original driving force for net charge flow (i.e. the mismatch between materials' work functions). This electric field—through which all mobile charges must pass—eventually accumulates an electrostatic barrier equal to the magnitude difference between the two materials' work functions. This equilibrates the driving forces for electric currents in either direction, thus resulting in zero net charge flow across the interface (Figure 12c and Figure 12d). Thus, the total potential difference (band bending) that occurs between the metal and semiconductor is equal to the work function difference between the materials.

Potential difference is a function of the charge, electrical permittivity, and distance over which the charge is distributed. The electrical permittivities of the system can be deduced from the materials chosen, but how does one determine how much charge has been transferred from one material to the next? Over what distance is that charge distributed?

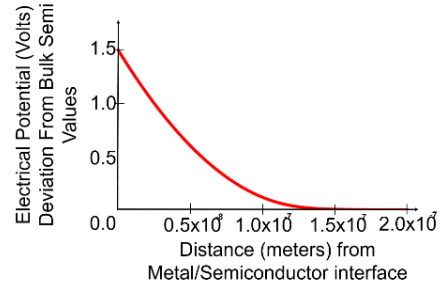
Using a metal as one side of the heterojunction simplifies the matter significantly. Bulk metals have extremely high concentrations of free charges and the spacing in energy between any two occupiable electronic states is miniscule. As such, there will always be an abundance of charge ready to accumulate or deplete at the surface of a metal incident to an electric field. Here, 'surface'

means a length scale on the order of an angstrom. Regardless of charge magnitude, any potential drop within the metal over this distance is going to be relatively small—indeed negligible—when compared to the very poor electrical field screening capacity associated with semiconducting materials. Thus, the entirety of the potential drop in the metal/semiconductor junction (which is equal to the work function difference between the two materials) will occur within the semiconducting material. This is graphically demonstrated in Figure 13a, where V_1 is the potential within the bulk of the metal, V_2 is the potential at the interface between the metal and semiconductor, and V_3 is the potential within the bulk of the semiconductor. In this case, the potential energy change within the metal is $V_{MetalDrop} = V_1 - V_2 = 0$, and the potential energy within the semiconductor is $V_{SemiDrop} = V_2 - V_3 = V_1 - V_3$.

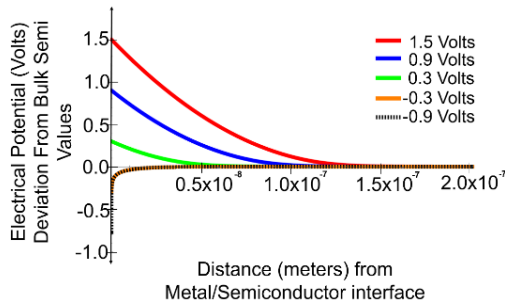
2a)



2b)



2c)



2d)

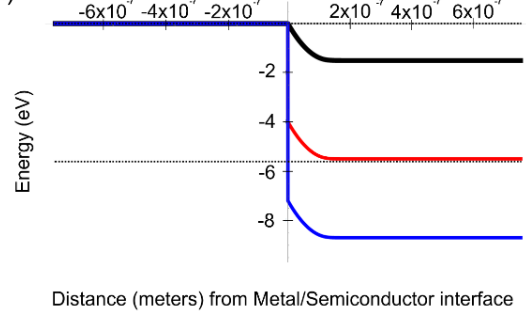


Figure 13. Calculating the electrical potential profile that results from establishing equilibrium at a meta/n-type semiconductor junction. A) A metal/n-type semiconductor junction. V1, V2 and V3 represent the work function in the bulk of the metal, at the metal/semiconductor interface, and in the bulk of the semiconductor, respectively. B) Result of the electrical potential profile calculated in code at the metal/semiconductor interface. C) Multiple electrical potential profiles at the metal/semiconductor interface that result from varying the work function difference between the metal and semiconductor. The spatial extent of the potential profile is greater when there is a positive voltage difference between the two work functions than when there is a negative potential difference because the n-type semiconductor is more easily able to accumulate electrons (negative charges) than holes (pseud-positive charges). D) An equilibrium energy band diagram of the metal/n-type semiconductor interface generated by the code for a work function difference of 1.5V.

To calculate the potential profile in the heterojunctions, the potential energy change $V_{SemiDrop}$ must now be related to the length scale of the depletion region. Knowing that we must relate the potential at the semiconductor junction to the amount of net charge in the semiconductor over some distance x , we begin with the one-dimension Poisson equation:

$$\rho(x) = -\epsilon_r \epsilon_0 \frac{d^2 \phi(x)}{dx^2} \quad (2.1)$$

Where $\rho(x)$ is the charge density at position x , ϵ_r is the relative electrical permittivity of the medium, ϵ_0 is the permittivity of vacuum, and $\varphi(x)$ is the potential at distance x from the interface.

There are four possible sources of charge inside the semiconductor: 1) mobile electrons (n) due to thermal excitation and dopant atoms, 2) mobile holes (p) due to thermal excitation and dopant atoms, 3) negatively charged ionized dopant atoms (N_A), 4) positive charged ionized dopant atoms (N_D).

$$\rho(x) = n + p + N_A + N_D = -\epsilon_{semi}\epsilon_0 \frac{d^2\varphi(x)}{dx^2} \quad (2.2)$$

Or, after rearrangement:

$$\frac{d^2\varphi(x)}{dx^2} = \frac{n+p+N_A+N_D}{-\epsilon_{semi}\epsilon_0} \quad (2.3)$$

The concentration of ionized dopant atoms, N_A and N_D , in Equation (2.3) can have a spatial and thermal dependence but pragmatically they can be taken as constant. Here, the relative permittivity of the medium ϵ_r has been further specified as the relative permittivity of the semiconductor, ϵ_{semi} . The concentration of mobile electrons (n) and holes (p) within in the semiconductor depend sensitively on the local potential in the following way[362]:

$$n = n_b \exp\left[\frac{-z_n e \varphi(x)}{kT}\right] \quad (2.4)$$

And

$$p = p_b \exp\left[\frac{-z_p e \varphi(x)}{kT}\right] \quad (2.5)$$

Where n_b and p_b are the concentration of electrons and holes in the bulk of the semiconductor, respectively, where the location potential ($\varphi(x)$) is constant,. z_n and z_p are the charge of the electron and hole, respectively [units]. e is the magnitude of elementary charge [units], k is the Boltzmann constant [units] and T is the absolute temperature [Kelvin]. Combining equation (2.3), (2.4), and (2.5), yields the following expression:

$$\frac{d^2 \varphi(x)}{dx^2} = \frac{n_b \exp\left[\frac{-z_n e \varphi(x)}{kT}\right] + p_b \exp\left[\frac{-z_p e \varphi(x)}{kT}\right] + N_A + N_D}{-\varepsilon_{semi} \varepsilon_0} \quad (2.6)$$

Where ε_{semi} is the relative permittivity of the semiconductor.

The bulk concentrations of electrons (n_b) and holes (p_b) depend both on the carrier density that is thermally excited over the bandgap of the semiconductor and those contributed by the dopant species. In a semiconductor with a moderate bandgap (e.g., 1.2 eV or higher) and dopant density ($1 * 10^{16} \text{ cm}^{-3}$), the charge carriers contributed by the dopant atoms will be several orders of magnitude greater than those contributed by thermal excitation across the bandgap. For the case of an n-type semiconductor (e.g., Figure 12a), that would mean that $n_b = N_D$, and for a p-type semiconductor (e.g., Figure 12b), $p_b = N_A$.

If the semiconductor is not degenerately doped, the concentration of electrons and holes will obey the mass-action law:

$$n_b p_b = n_i^2 \quad (2.7)$$

Where the bulk mobile electron and hole concentration sum to the square of the intrinsic, thermally excited charge concentration n_i . n_i is expressed as follows:

$$n_i = N_C \exp\left[\frac{E_g}{kT}\right] \quad (2.8)$$

Where N_C is the density of states in the conduction band of the semiconductor [cm^{-3}] and E_g is the bandgap of the semiconductor [eV]. Thus, in the case of a n-type semiconductor with no p-type doping:

$$n_b = N_D, N_A = 0 \quad (2.9)$$

And

$$p_b = \frac{n_i^2}{n_b} = \frac{n_i^2}{N_D} = \frac{(N_C \exp\left[\frac{E_g}{kT}\right])^2}{N_D} \quad (2.10)$$

If we were looking at the case of an p-type semiconductor with no n-type doping, then:

$$p = N_A \quad , \quad N_D = 0 \quad (2.11)$$

And

$$n_b = \frac{n_i^2}{p_b} = \frac{n_i^2}{N_A} = \frac{(N_V \exp[\frac{E_g}{kT}])^2}{N_A} \quad (2.12)$$

Where N_V is the density of states in the valence band.

To express the relationship between electrical potential and charge density within the n-type semiconductor featured in Figure 12a, we combine equation (2.6), (2.9) and (2.10):

$$\frac{d^2 \varphi(x)}{dx^2} = \frac{N_D \exp[-\frac{z_n e \varphi(x)}{kT}] + \frac{(N_C \exp[\frac{E_g}{kT}])^2}{N_D} \exp[-\frac{z_p e \varphi(x)}{kT}] + N_A + N_D}{-\varepsilon_{semi} \varepsilon_0} \quad (2.13)$$

If equation (2.13) can be integrated twice then it would be an expression for the entire potential profile $\varphi(x)$, and thus band bending, throughout the semiconductor. The first integration is achieved by recognizing that far from the metal/semiconductor interface the potential is the bulk potential of the semiconductor ($\varphi(\infty) = 0$) and the gradient in potential (i.e. the electrical field) is zero ($\frac{d\varphi(x)}{dx} = 0$). Integrating equation (2.13) with these boundary conditions gives us:

$$\frac{d\varphi(x)}{dx} = - \left(\frac{2kT}{\varepsilon_{semi} \varepsilon_0} \left[N_D \exp \left[\frac{-z_n e \varphi(x)}{kT} \right] + \frac{(N_C \exp[\frac{E_g}{kT}])^2}{N_D} \exp \left[\frac{-z_p e \varphi(x)}{kT} \right] - \frac{e N_D z_N \varphi(x)}{kT} - \left(N_D + \frac{(N_C \exp[\frac{E_g}{kT}])^2}{N_D} \right) \right] \right)^{\frac{1}{2}} \quad (2.14)$$

Equation (2.14) can be integrated again if a boundary condition is known, though the result may not always be analytic and thus a numerical solver must be used to visually represent the result. The boundary condition used in equation (2.14) is the fact that at the interface between the metal and semiconductor, where $x = 0$, the potential $\varphi(x)$ is maximum and takes the value of the full potential difference between semiconductor and metal, as seen in Figure 13a:

$$\varphi(0) = V_{SemiDrop} = V_2 - V_3 = V_1 - V_3 \quad (2.15)$$

The full code used to solve and plot equation (2.14) can be found in the supplementary materials under the code Section.

The general form of the output function `PotentialProfileCurve1[x]`, within the bounds that is interpolated, will be that of Figure 13b. To automatically convert these potential curves into band diagrams is relatively straight forward: define the regions of interest and plot the work functions of each region together. For the single metal/semiconductor heterojunction example:

- when $x \leq 0$: the potential (φ) = V_1 ,
- when x is within the depletion region: $\varphi = V_1 - (\text{PotentialProfileCurve1}[x] - V_{SemiDrop})$,
- when $x \geq \text{depletion layer thickness}$: $\varphi = V_3$.

To determine how far along x the depletion region extends, find the root of `PotentialProfileCurve1[x]`. Mathematica code for both determining the root of `PotentialProfileCurve1[x]`, which defines the depletion region, and creating the band diagram for the metal/depletion region/semiconductor interface is contained within the code section. These band diagrams also contain the vacuum level's energy landscape.

It is important to note that the calculated length over which the depletion region extends (i.e. 'EndofDepletionWidth' within the code) can be much larger than is physically relevant. This length scale is calculated by determining when the electrical potential gradient (i.e. electric field) is equal to zero within the vicinity of the interface. The function describing the electrical potential gradient is exponential and thus may maintain a value that is extremely small over a long distance before it becomes zero. The process described above is necessary to compute and generate an accurate band diagram but a more pragmatic length scale is the region over which the potential

within the vicinity of the metal/semiconductor junction deviates significantly ($> kT$) from equilibrium (bulk semiconductor) potential values (V_3).

With the code able to integrate and plot equation (2.14), we can now easily plot the electrical potential profile within the vicinity of the metal/semiconductor heterojunction as a function of metal work function V_1 (or alternatively, *applied* potential), and semiconductor dopant density N_D , work function V_3 , and electrical permittivity ϵ_{semi} . Figure 13c depicts the electrical potential profiles of a metal/semiconductor junction under various values of metal work functions (V_3), which is also equivalent to varying the potentials applied to the metal electrode. Figure 13d is the output from the code for a work function difference between the metal and semiconductor of 1.5eV.

2.3.2 Metal/Piezoelectric Semiconductor

Of considerable interest to the field to piezotronics is what effect, if any, will using a piezoelectric semiconductor have on the energetics of the heterojunction, and thus its electronic properties? Piezoelectrics are a class of materials that have a particular property: when they are mechanically deformed they generate a non-zero dipole density within themselves (Figure 14a). In general, just as strain fields can act in three dimensions, so too can the induced dipole fields. For simplification, we examine the effect of piezoelectric semiconductors on metal/piezoelectric semiconductor heterojunction energetics in one dimension, normal to the interface.

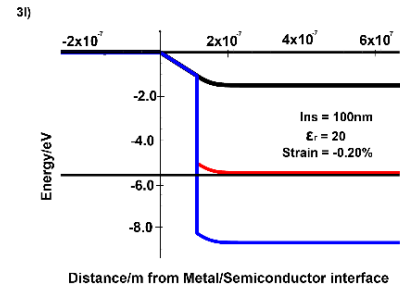
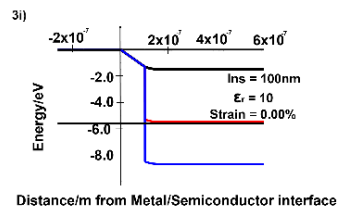
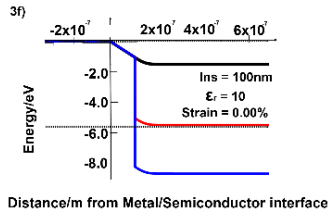
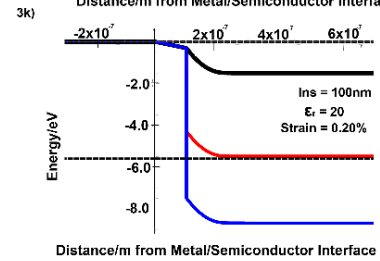
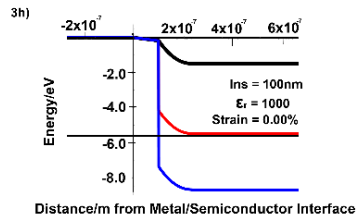
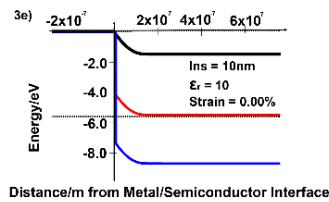
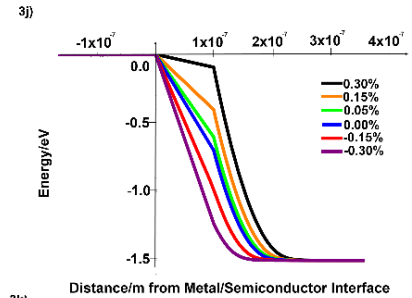
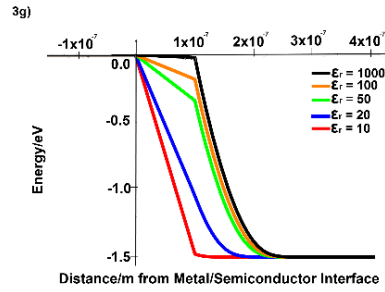
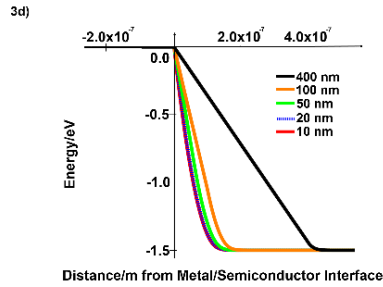
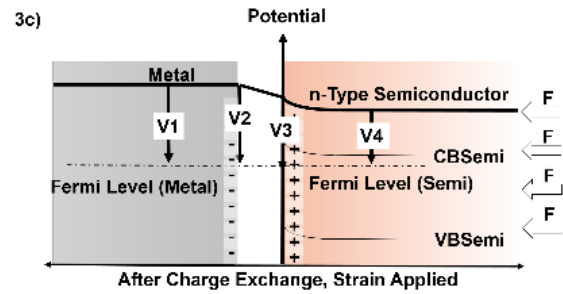
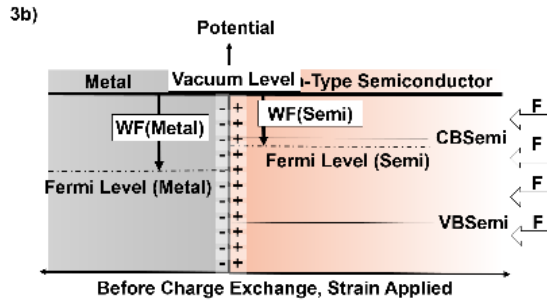
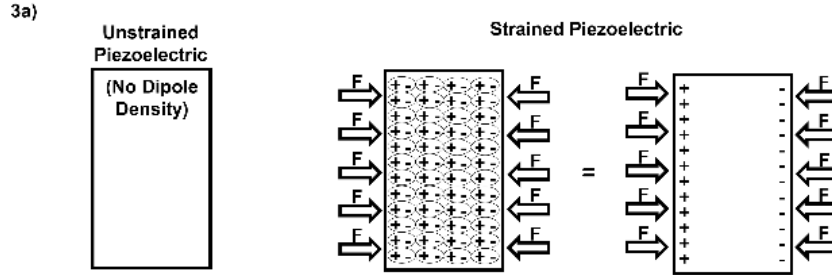


Figure 14. The effect of introducing surface charge to the semiconductor material in a metal/insulator/n-type piezoelectric semiconductor heterojunction. A) A piezoelectric material generates a change in its electric dipole density in response to strain. If the material as a uniform electric dipole density, it is equivalent to a surface charge density. B) A schematic of a metal/piezoelectric-semiconductor junction. If there is no space between the metal and piezoelectric, and the metal is perfect, all of the piezoelectric's surface charge will be perfectly screened by the metal and result in no potential shift between the two. C) If there is an insulating layer between the metal/piezoelectric-semiconductor then perfect charge screening by the metal is no longer possible and a potential shift across the insulator will result. D) The electrical potential profile in a metal/insulator/semiconductor junction with varying insulator thicknesses. E) and F) show calculated energy band diagrams for metal/semiconductor and metal/insulator/semiconductor junctions. G) Calculated electrical potential profiles in the metal/insulator/semiconductor junction for a fixed insulator thickness with varying electrical permittivity. H) and I) are calculated energy band diagrams for metal/insulator/semiconductor heterojunctions with insulator electrical permittivities of 1000 and 10, respectively. J) Calculated electrical potential profiles for a metal/insulator/piezoelectric semiconductor heterojunction that demonstrates the effect of strain on the potential profile. K) and L) are calculated energy band diagrams for the metal/insulator/piezoelectric semiconductor heterojunction for piezoelectric materials strained to 0.20% and -0.20%, respectively.

In a piezoelectric, a uniform dipole field ($D_{Piezo} \left(\frac{m \cdot \text{Coulomb}}{m^3} \right)$) that results from straining (E) the piezoelectric perpendicular to the interface is equivalent to a surface charge density ($Q_{Piezo} \left(\frac{\text{Coulomb}}{m^2} \right)$) of the surface of the piezoelectric given by:

$$Q_{Piezo} = (d_{31})(E)(Y) \quad (2.16)$$

Where d_{31} is the direct piezoelectric coefficient $\left(\frac{\text{Coulomb}}{N} \right)$ and Y is Young's modulus (Pa). What remains is to describe how this surface charge density Q_{Piezo} affects the potential landscape of the metal/piezo-semiconductor heterojunction (Figure 14b).

In a typical material junction, both materials start off as charge neutral and it is exclusively the work function difference between the two dissimilar materials that drives a net exchange of charge between them (Figure 14a and Figure 14b). In contrast, a metal/piezo-semiconductor system introduces with an additional driving force for charge flow. In a metal/piezo-semiconductor heterojunction, straining the piezo-semiconductor *introduces* charge (Q_{Piezo}) to the heterojunction

interface. In-fact, straining the piezoelectric introduces two surface charge layers (Q_{Piezo} and $-Q_{Piezo}$) to opposite ends of the material (Figure 14a). Given a sufficiently thick specimen of semiconducting piezoelectric material (i.e., bulk) both surfaces will have independent screening mechanisms and so can be treated separately. When Q_{Piezo} is introduced to the metal/piezoelectric-semiconductor interface, charges opposite in sign to Q_{Piezo} will accumulate in the vicinity until:

- 1) Charge neutrality is achieved,
- 2) The lowest energy configuration of charge distribution is achieved.

While charge neutrality is a straightforward concept, the distribution of charge which achieves the lowest energy configuration for the system is often non-intuitive. The energy of the system is the sum of all the charges and the potentials between them. Only in cases where the two materials that compose the junctions have vastly different electrical properties, such as in the case of a perfect metal/semiconductor junction, is the distribution trivial. When the system contains of a strained piezoelectric semiconductor, the surface charge (Q_{Piezo}) introduced into the system is fixed by the material's piezoelectric coefficient, d_{31} , strain state, E , and Young's modulus Y (equation (2.16)). Thus, the lowest energy configuration of the system is when the counter ions, which accumulate within the vicinity of the interface to achieve charge neutrality, are in the closest proximity possible to the surface charges.

In order to properly address the physical system in the mathematics we must consider the assumptions we make about specific interfaces. In the case of an ideal metal/piezoelectric-semiconductor junction, both the metal and semiconductor are in intimate, atomic level contact with the piezoelectric surface charge. The metal--treated as an 'ideal conductor' within this manuscript--always contains a mobile charge density orders of magnitude greater than the semiconductor, and thus will accumulate whatever charge is required to achieve charge neutrality

at the interface and be able to do so at effectively the same position as the piezoelectric's surface charge. A finite, atomic or sub-atomic distance may remain between the accumulated counterions in the metal and the piezoelectric's surface charge, and within that distance there will be a small potential change (Figure 14b), but it will be negligible assuming the metal is perfect and has atomic contact at the junction. Thus, in an ideal system, piezoelectric charge is expected to have no effect on the metal/piezoelectric semiconductor interface because it will be perfectly screened by the adjacent metal.

2.3.3 Metal/ Insulator/Piezoelectric-Semiconductor Junctions

In many experimental systems, i.e. non-ideal systems, the material interface is not perfect and there will be a contaminant or insulating oxide material between the metal and semiconductor. Additionally, in many device designs it is desired to place thin oxide layers between the metal and semiconductor for reasons pertaining to charge flow and chemical stability. An insulating layer between the metal and piezoelectric negates the metal's ability to complete cancel the piezoelectric's surface charge. We now explore the effect of strain on the piezoelectric's potential profile within the vicinity of the metal/piezoelectric semiconductor's interface where there is a finite distance between the two (see code).

We again invoke the ideal metal approximation, where no potential drop occurs within the metal and thus $V_1 = V_2$. The total potential drop across the system is no longer confined solely to the piezoelectric semiconductor; the (perfectly) insulating interface layer of thickness d_{Ins} and relative electrical permittivity ϵ_{Ins} will also sustain a potential drop (Figure 14c). V_1 , V_2 , V_3 , and V_4 are the work function of the metal, the potential at the metal-insulator interface, the potential at the insulator-semiconductor interface, and the bulk work function of the semiconductor,

respectively. The values of V_1 , V_2 , and V_4 are known. With knowledge of V_3 the potential profile across the entire interface can be generated, assuming one knows the electrical properties of the insulating and semiconducting material. To solve for V_3 we turn our attention to the constraint of charge neutrality.

The charge contained within the metal, piezoelectric surface, and within the semiconductor must sum to zero. In addition, as seen from Figure 3b and Figure 3c, the sum of the piezoelectric surface charge and the charge contained within the semiconductor must be equal and opposite to the charge contained within the metal. This condition follows from the reasoning that any electric field lines that exit the surface of the semiconductor (which includes both the semiconductor and piezoelectric charge) must terminate at opposite charges in the metal. If the metal is to have no potential drop within its bulk, then all electric field lines entering the metal must be canceled by an equal number of charges at the metals' surface. Thus, the electric field is key: the electric field magnitude exiting the semiconductor must be equal to the electric field entering the metal.

By definition, the electric field ($E(x)$) is the gradient in the potential with distance $\left(\frac{d\phi(x)}{dx}\right)$, which for the semiconductor is given by equation (2.14). The electric field going into the semiconductor is thus equal to:

$$E(interface) = - \left(\frac{2kT}{\epsilon_{semi}\epsilon_0} \left[N_D \exp \left[\frac{-z_n e(V_4 - V_3)}{kT} \right] + \frac{\left(N_C \exp \left[\frac{E_g}{kT} \right] \right)^2}{N_D} \exp \left[\frac{-z_p e(V_4 - V_3)}{kT} \right] \right. \right. \\ \left. \left. - \frac{eN_D z_{N_D} (V_4 - V_3)}{kT} - \left(N_D + \frac{\left(N_C \exp \left[\frac{E_g}{kT} \right] \right)^2}{N_D} \right) \right] \right)^{\frac{1}{2}}$$

(2.17)

Where the potential, $\varphi(x)$, has been replaced by the potential difference $V_4 - V_3$ located at the insulator/semiconductor interface. If the surface of the semiconductor is planer then it follows from Gauss's Law that the charge density in the semiconductor, Q_{Semi} ($\frac{Coulomb}{m^2}$), is given by the following expression:

$$Q_{Semi} = \epsilon_{Semi} \epsilon_0 E(interface) \quad (2.18)$$

And thus,

$$Q_{Semi} = -\epsilon_{Semi} \epsilon_0 \left(\frac{2kT}{\epsilon_{Semi} \epsilon_0} \left[N_D \exp \left[\frac{-z_n e (V_4 - V_3)}{kT} \right] + \frac{(N_C \exp \left[\frac{E_g}{kT} \right])^2}{N_D} \exp \left[\frac{-z_p e (V_4 - V_3)}{kT} \right] - \frac{e N_D z N_D (V_4 - V_3)}{kT} - N_D - \frac{(N_C \exp \left[\frac{E_g}{kT} \right])^2}{N_D} \right] \right)^{\frac{1}{2}} \quad (2.19)$$

Q_{Semi} is the charge density that resides in the semiconductor, which now is a function of V_3 . V_3 is still an unknown, so our objective is to get V_3 in terms of our known variables (i.e., V_1 and V_2 , or in this particular case $V_1 = V_2$). The difference in potential between V_3 and V_2 is the potential change across the insulating interface layer. Calculating the potential change across an insulating layer is straight forward, and is given by the linear expression:

$$\Delta V_{Ins} = Q_{Ins} d_{Ins} \epsilon_{Ins} \quad (2.20)$$

where Q_{Ins} is the charge density on either side of the insulator.

In the case of the metal/insulator/piezoelectric semiconductor interface, the charge density is given by:

$$Q_{Ins} = Q_{Semi} + Q_{Piezo} \quad (2.21)$$

Combining equation (2.20) and (2.21) gives us:

$$\Delta V_{Ins} = V_3 - V_2 = (Q_{Semi} + Q_{Piezo}) d_{Ins} \epsilon_{Ins} \quad (2.22)$$

Which, combining equations (2.22) and (2.19) gives:

$$V_2 = V_3 - (Q_{Semi} + Q_{Piezo})d_{Ins}\epsilon_{Ins} \quad (2.23a)$$

Or

$$V_2 = V_3 - \left((-\epsilon_{Semi}\epsilon_0 \left(\left(\frac{2kT}{\epsilon_{Semi}\epsilon_0} \left[N_D \exp\left[\frac{-z_n(V_4-V_3)}{kT}\right] + \frac{(N_C \exp[\frac{E_g}{kT}])^2}{N_D} \exp\left[\frac{-z_p(V_4-V_3)}{kT}\right] - \frac{eN_D z N_D (V_4-V_3)}{kT} - \left(N_D + \frac{(N_C \exp[\frac{E_g}{kT}])^2}{N_D} \right) \right]^{\frac{1}{2}} \right) + (d_{31})(E)(Y) \right) d_{Ins}\epsilon_{Ins} \right. \\ \left. \right) \quad (2.23b)$$

Mathematically, equation (2.23) will often need to be solved numerically and not analytically. In the code section, we show Mathematica code that can be used to solve for V_2 using the FindRoot command. After V_3 is determined, generating a potential profile of the metal/insulator/piezoelectric semiconductor heterojunction is again straight forward and the entirety of the code necessary for generating the potential profile of the heterojunction is present in code section.

The potential profile within the metal is constant and held at potential $V_1 = V_2$. The potential within the insulator takes a linear form because it possesses no charge density, by definition. Thus, the potential in this region is a line between V_2 and V_3 . The potential profile within the semiconductor is an exponential function determined by integrating equation (2.14) such that the potential at the insulator/semiconductor interface is V_3 and the potential in the bulk of the semiconductor is V_4 . Throughout the calculation described in the code, the material properties of zinc oxide are used for the piezoelectric semiconductor and at times for the insulator, though any

material values can be used in the code. The code now allows for the calculation of the potential profile through the metal/insulator/piezoelectric semiconductor junction as a function of metal work function, insulating thickness (Figure 14d-f), insulating electrical permittivity (Figure 14g-i), and piezoelectric strain and charge density (Figure 14j-l). Varying the metal's work function by an amount ΔV is equivalent to applying a potential to the metal of an amount ΔV . *Note that it is possible to create approximately identical band profiles in the semiconductor by varying completely different properties, as is shown in Figures 14e, 14h and 14k with respect to each other, as well as Figures 14f, 14i and 14l. Depending on the constraints of the system, e.g., space, material choice or allowed strain, the code allows the researcher to choose the heterojunction parameters necessary to achieve a desired band potential profile.*

2.3.4 Metal/piezoelectric (Ferroelectric) Insulator/Piezoelectric

Semiconductor Junctions The insulator used in the above scenario was a classical dielectric, but a functional dielectric such as a piezoelectric or ferroelectric insulating layer can also be used. All ferroelectric materials are piezoelectric, meaning that they too respond to a strain field by manifesting a corresponding electric dipole field. Ferroelectric materials have an additional property: they can maintain an electric dipole field, and thus surface charge density ($\frac{\text{Coulomb}}{\text{m}^2}$), in the absence of a strain field (Figure 15a). In a ferroelectric, the magnitude and direction of polarization depends on the history of the material, what magnitude and direction of electric field the material has been exposed to in the past. If a ferroelectric material is exposed to a large electric field, E , polarized 'domains' within the material will align with the field, increasing the material's aligned dipole density and overall polarization, P ($\frac{\text{Coulomb}}{\text{m}^2}$). This increase in polarization with applied field will continue to increase until all polarizable domains within the

material are aligned with the external field.). Note: polarization points in the opposite direction of the electric field. When all polarization domains throughout the material are aligned, the material is said to be saturated and the polarization takes on the value P_s (Figure 15a). If the incident electric field is then removed, many of the domains within the ferroelectric may remain aligned with each other and result in a non-zero remnant polarization in the ferroelectric, P_r . To reduce the bulk polarization below its remnant value, P_r , an electric field in the opposite direction to that of the polarization field must be applied. When the applied electric field reaches the *coercive* value, E_c , the overall polarization within the ferroelectric is reduced to zero. Applying a field stronger than E_c to the ferroelectric will cause the polarizable domains within the ferroelectric to align again but this time in the opposite direction. To simplify matters, if the ferroelectric has a relatively flat hysteresis curve about the remnant polarization P_r then a small electric field applied to the material will result in a relatively small excursion of the ferroelectric polarization away from the remnant polarization. Ferroelectrics with this type of hysteresis curve are called ‘hard’, and are exemplified in Figure 15b. A small field applied in either direction to a hard ferroelectric will not significantly change the magnitude of its polarization (P). Only when the field strength approaches E_c will a significant change in P result.

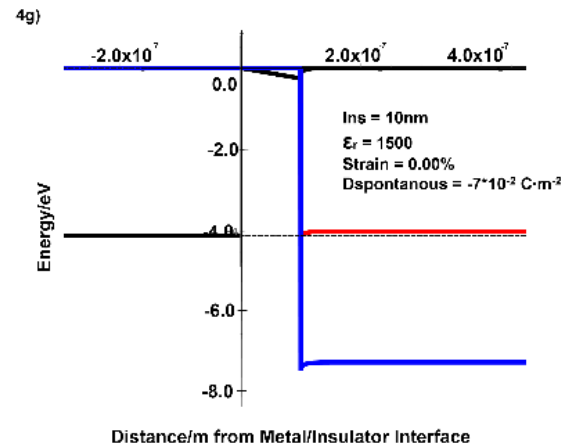
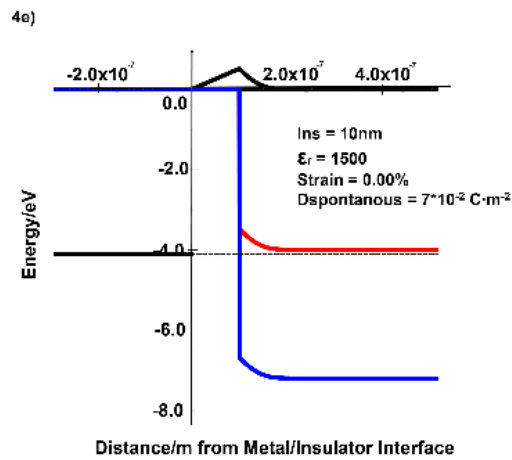
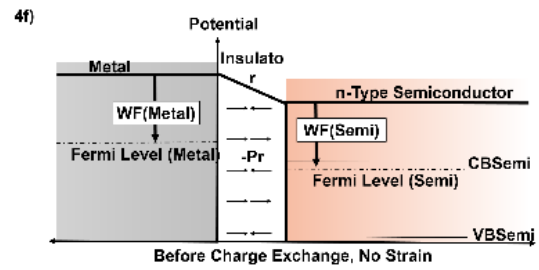
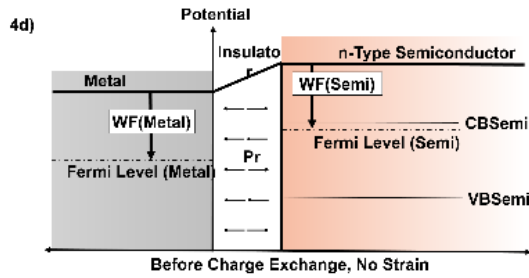
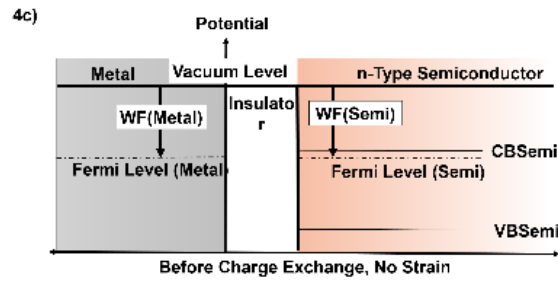
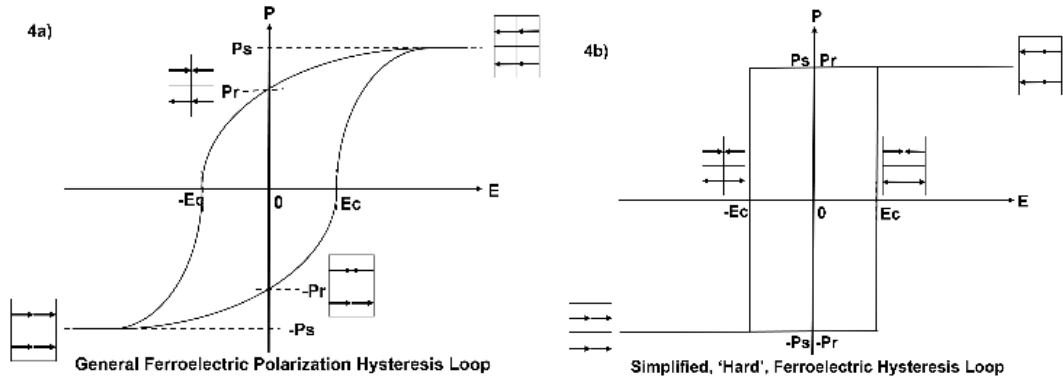


Figure 15. The effect of Ferroelectric polarization on energy band diagrams. A) The electrical polarization hysteresis curve for a ferroelectric material. B) An idealized “hard” ferroelectric hysteresis curve. C) Schematic of a metal/ferroelectric insulator/n-type semiconductor heterojunction. D) Schematic of the energetics of a metal/ferroelectric insulator/n-type semiconductor heterojunction before equilibrium is established. E) Calculated energy band diagram of the metal/ferroelectric insulator/n-type semiconductor heterojunction after equilibrium is established. F) Schematic of a metal/ferroelectric insulator/n-type semiconductor heterojunction before equilibrium is established, with an electrical polarization opposite in direction to that depicted in D). G) Calculated energy band diagram of the metal/ferroelectric insulator/n-type semiconductor heterojunction in F after equilibrium is established.

A ferroelectric insulator between the metal and semiconductor can have a profound effect on the resultant electrical potential profile in the metal/ferroelectric-insulator/piezoelectric-semiconductor heterojunction. In Figure 15c the result of using a ferroelectric insulator with remnant potential P_r as the insulating layer is shown *before* the metal and semiconductor exchanged charge and equilibrium is established. As can be seen in the figure, the ferroelectric polarization affects the driving force for charge exchange between the metal and semiconductor ($V_1 - V_4$).

These systems can become quite complex. While the heterojunctions are tending toward equilibrium, the charge that is exchanged between the metal and semiconductor creates an electric field between them, and this electric field passes through the ferroelectric. From the perspective of the ferroelectric, this new field is an applied field which will cause a change in its remnant polarization. This change in ferroelectric polarization then influences the net driving force for charge exchange (i.e. $(V_1 - V_4)$), Figure 15d and Figure 15e. Because all ferroelectrics are also piezoelectric, the magnitude of ferroelectric polarization will also be a function of material strain. Together, the sum of ferroelectric and piezoelectric polarizations give a resultant polarization density, $D_{FerroIns}$, within the insulator given by:

$$D_{Ferro} = D_{Remnant} + (d_{31})(E_{Ferro})(Y_{Ferro}) \quad (2.24)$$

Where $D_{Remnant}$ is the polarization density due to the remnant polarization, P_r , and the second term is the same as that used in a typical piezoelectric (equation (2.16)). To calculate the effect of hard ferroelectric polarization, one must prepare for 2 circumstances:

- 1) After charge exchange between the metal and semiconductor, the electric field present in the ferroelectric is $< E_c$,
- 2) After charge exchange between the metal and semiconductor, the electric field present in the ferroelectric is $> E_c$.

In the first case, the calculation is straight forward. The heterojunction is treated as a typical metal/insulator/piezoelectric semiconductor junction with the exception that an electric field is introduced to the insulating layer. This electric field acts to shift the relative positions of the metal's and semiconductor's work functions (Figure 15d and Figure 15e) prior to any charge exchange between the two. Functionally, the remnant polarization acts to change the total potential drop that is going to occur due to charge exchange, meaning that it changes $V_1 - V_4$ by an amount $\frac{D_{Ferro}d_{Ins}}{\epsilon_{Ins}\epsilon_0}$. Since the polarization within the ferroelectric is restricted to the insulating region, $\frac{D_{Ferro}d_{Ins}}{\epsilon_{Ins}\epsilon_0}$ specifically modifies the potential change between V_2 and V_3 . In the code, terms have been added that recognize it is possible for the insulating layer to have a ferroelectric and piezoelectric contribution to the charge density and thus resultant potential profile. T

The following changes to the code make the majority of changes necessary to accommodate this charge density:

ElectricFieldInInsulator = $-(q_{semiconductorperarea} + SemiDFromStrainPiezo)/\epsilon_{psIns}$;
 Becomes
 ElectricFieldInInsulator

= $-(q_{semiconductorperarea} + SemiDFromStrainPiezo + InsulatorDFromRemnantAndStrainPiezo)/\epsilon_{psIns}$

Where the third term accounts of the electric field contributed by the ferroelectric's remnant polarization.

Propagating this change through the calculation,

$$V2 = V3 + ((-(q_{\text{semiconductorperarea}} + \text{SemiDFromStrainPiezo}) * d_{\text{Ins}})/\epsilon_{\text{Ins}}) \quad (2.24)$$

Becomes

$$V2 = V3 + ((-(q_{\text{semiconductorperarea}} + \text{SemiDFromStrainPiezo}) * d_{\text{Ins}})/\epsilon_{\text{Ins}}) + (\text{InsulatorDFromRemnantAndStrainPiezo} * d_{\text{Ins}}/\epsilon_{\text{Ins}}) \quad (2.25)$$

2.3.5 Metal/Ferroelectric Insulator/ Ferroelectric Semiconductor Junctions

In addition to the insulating ferroelectric's charge density being added to these functions, there is no reason why the semiconducting piezoelectric material cannot itself also be ferroelectric. Adding an additional term, $D_{\text{SpontaneousSemi}}$, to both of these functions (equation (2.24) and equation (2.25)) now gives the code the capability of calculating the potential profile of a metal/ferroelectric-insulator/ferroelectric-semiconductor junction. With both the insulator and semiconductor also being piezoelectric, both have piezoelectric charge densities that are sensitive to strain.

The effect of an insulating ferroelectric is highlighted when the metal and semiconductor have similar work functions ($V_1 = V_4$). Without a ferroelectric or piezoelectric component in the system, the situation where $V_1 = V_4$ means that no charge would be exchanged between the metal and semiconductor and thus no depletion region would exist (Figure 15c). When a ferroelectric

insulator is introduced, there is instantaneously a driving force for charge exchange between the metal and semiconductor (Figure 15d-e, and Figure 15f-g).

It is important to draw attention to the fact that the polarization of the hard ferroelectric will change magnitude as a function of electric field (in this case the switch is digital, from the value of P_r to $-P_r$, Figure 15a and Figure 15b). Care should be taken to check the magnitude of the electric field, $\text{ElectricFieldInInsulator}$, within the ferroelectric after the calculation is conducted to ensure that the field within the ferroelectric, after charge has been exchanged between the metal and semiconductor, does not exceed E_c . If $\text{ElectricFieldInInsulator} > E_c$ then regardless of which direction the remnant polarization was believed to be before the experiment, the polarization has now been switching, or ‘poled’, in accordance with the applied electric field. The magnitude of effect that polarization switching will have on the system will depend on the details of the electronic properties of the entire heterojunction stack and so polarization switching should be accounted for whenever possible.

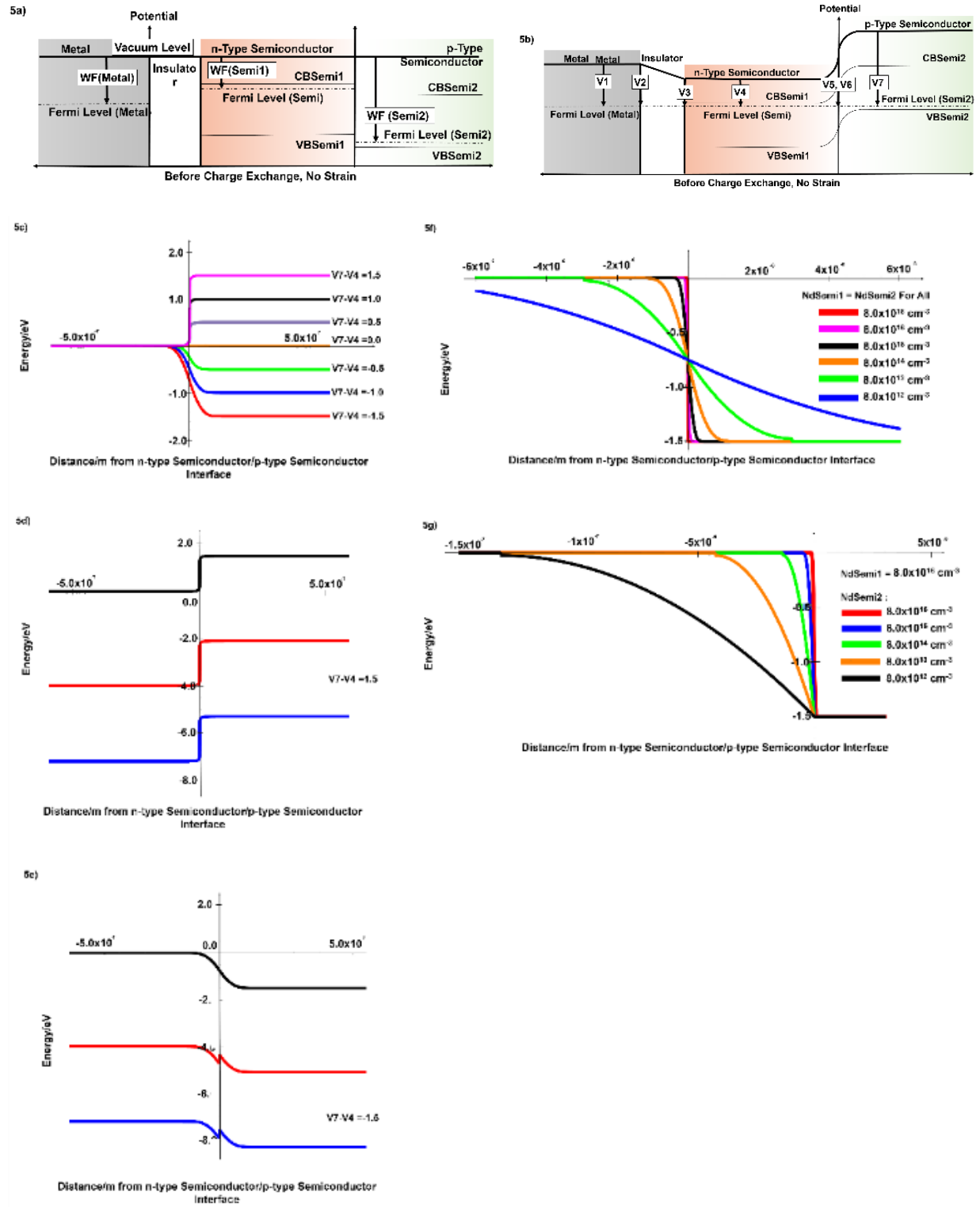
2.3.6 Ferroelectric Semiconductor / Piezoelectric-Insulator/ Ferroelectric Semiconductor Junctions

Until now, all calculations have been performed using a perfect metal as a material composing one side of the heterojunction. This heterojunction is the most common seen in literature and so was natural with which to begin. Another commonly encountered heterojunction is the semiconductor/semiconductor heterojunction. Heterojunctions of this nature can be far more complicated and unintuitive than their metallic counterparts because when two semiconductors compose the junction; the difference in work functions between them is compensated for on *both sides* of the interface. How much of the work function difference is compensated for by one side versus relative to the other, and what the effect of ferroelectric and piezoelectric charge densities

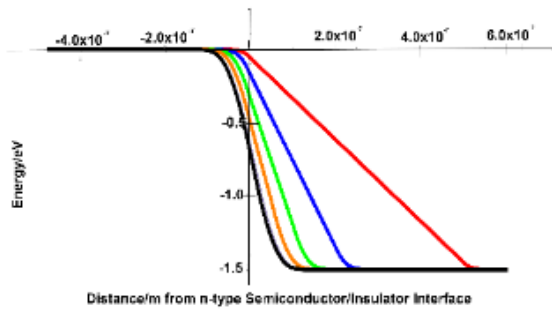
are on this potential profile is often the topic of significant interest when engineering devices. We will now detail how to calculate the potential profile through one of these junctions. We will continue to use the code generated previously, adding to it a semiconductor/semiconductor junction on the right side of the previously existing semiconductor material.

In the following section, as with the previous section, the materials are given bulk properties. In the case of a semiconductor/insulator/semiconductor junction, this means that *potential gradients (i.e. band bending) on either side of the junction goes to zero within the semiconducting material*. If the semiconductor/semiconductor heterojunction is one of multiple junctions in the materials stack (as will be the case here) then this means that the band bending from one heterojunction does not influence the band bending from the other. Depending on the details of the materials' properties, these criteria might necessitate that the heterojunction be several nanometers thick or several microns thick.

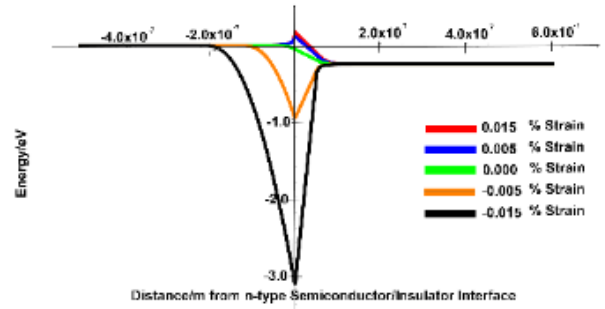
Figure 16a shows a metal/insulator/n-semiconductor/insulator/p-semiconductor junction both before and after charge is exchanged between the layers and equilibrium is established across the heterojunction. V_4 through V_7 have been added to denote the potential within and across the semiconductor/insulator/semiconductor junction. We have neglected piezoelectric and ferroelectric components from this diagram but they may also be added. The diagram shown in Figure 16b, which depicts the energy landscape of the heterojunction after equilibrium is established, *is of a typical form seen in publications and it is often the result of little more than an intuitive guess as to the potential profile across the heterojunction*. We now analyze this junction and generate a quantitative depiction of the potential profile.



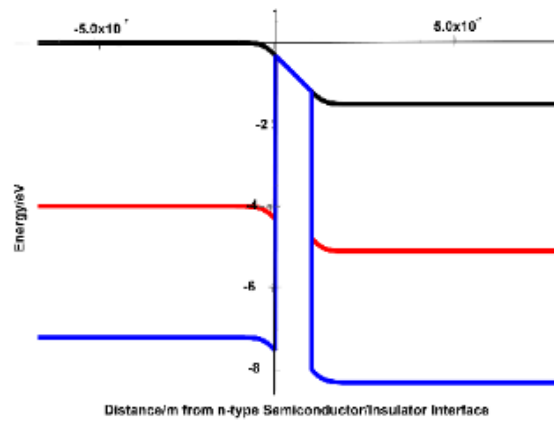
5h)



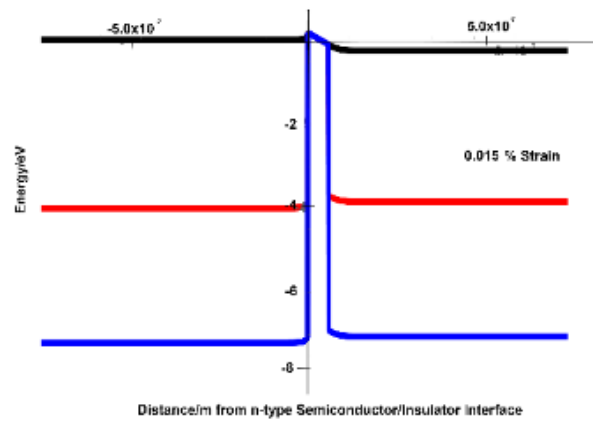
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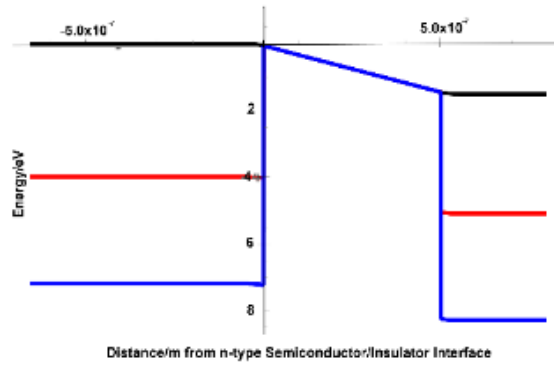
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5l)



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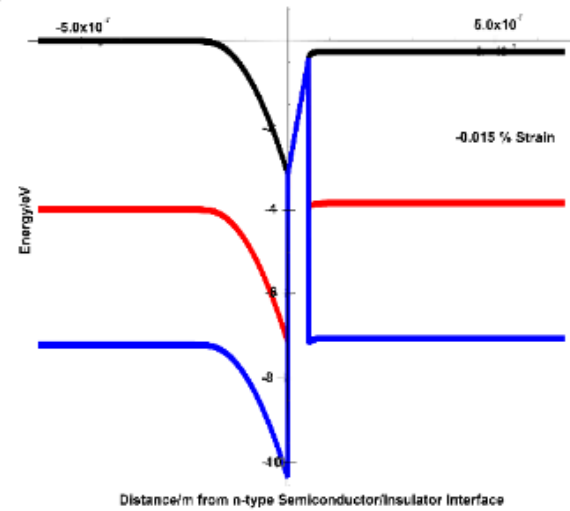


Figure 16. Electrical Potential profile across an n-type semiconductor/insulator/p-type semiconductor junction. a) Schematic of the energy levels across the heterojunction before equilibrium is established. B) Schematic of the energy band diagram across the heterojunction after charge is allowed to flow and equilibrium is established. C) Electrical calculated potential across the n-type semiconductor/p-type semiconductor as a function of fermi level difference between the two materials. D) and E) are calculated energy band diagrams for Fermi level difference of 1.5 and -1.5 Volts, respectively. F) The effect of varying (equally for both semiconductors) the dopant density of the materials. G) Effect of varying the dopant density of just one of the semiconducting materials composing the heterojunction on the electrical potential distribution at the interface. H) The effect an insulating layer between the two semiconductors has on the electrical potential distribution in the interface. I) and J) show calculated energy band diagrams for an insulator that is 10 microns and 50 microns thick, respectively. The effect strain has on electrical potential in the piezoelectric n-type semiconductor/insulator/p-type semiconductor junction. L) and M) are calculated band diagrams for the piezoelectric n-type semiconductor/insulator/p-type semiconductor heterojunction for strain levels of 0.015% and -0.015%, respectively.

Unlike the metal/semiconductor junction analyzed previously, the total potential drop $V_7 - V_4$ will not happen within a single side of the junction. Instead, the potential change on both sides of the heterojunction will sum to the work function difference between the two semiconductors:

$$V_7 - V_4 = (V_7 - V_6) + (V_6 - V_5) + (V_5 - V_4) \quad (2.26)$$

V_4 and V_7 are known quantities, V_5 and V_6 are unknown but linearly related to each other via the thickness and electrical permittivity of the second insulating layer:

$$V_5 = V_6 - \text{ElectricFieldInInsulator2} * d_{\text{Ins2}} \quad (2.27)$$

Where d_{Ins2} is thickness of the insulating layer between the two semiconductors and $\text{ElectricFieldInInsulator2}$ is the electric field in this insulating layer, given by:

$$\text{ElectricFieldInInsulator2} = \frac{q_{\text{semiconductor1Rightperarea}}}{\epsilon_{\text{psIns2}}} = - \frac{q_{\text{semiconductor2Leftperarea}}}{\epsilon_{\text{psIns2}}} \quad (2.28)$$

Where $q_{\text{semiconductor1Rightperarea}}$ and $q_{\text{semiconductor2Leftperarea}}$ are the charge densities in the two semiconductors at the semiconductor/insulator/semiconductor junction.

Without any piezoelectric or ferroelectric charge density in the interface, all charge at the interface of semiconductor2 must have come from semiconductor1 during the equilibration process. The charge density in semiconductor1 at the interface, $q_{\text{semiconductor1Rightperarea}}$, is given by:

$$q_{\text{semiconductor1Rightperarea}} = \epsilon_{\text{Semi1}} * \text{ElectricFieldInRightSemi1} \quad (2.29)$$

Where ϵ_{Semi1} is the permittivity of semiconductor 1, and $\text{ElectricFieldInRightSemi1}$ is the electric field at the interface within semiconductor1 and thus is given by:

$$\begin{aligned} E(\text{ElectricFieldInRightSemi1}) = & -\left(\frac{2kT}{\epsilon_{\text{Semi1}}\epsilon_0}\right) [N_{D\text{Semi1}} \exp\left[\frac{-z_n(V_5-V_4)}{kT}\right] + \\ & \frac{(N_{C\text{Semi1}} \exp\left[\frac{E_{g\text{Semi1}}}{kT}\right])^2}{N_{D\text{Semi1}}} \exp\left[\frac{-z_p(V_5-V_4)}{kT}\right] - \frac{eN_{D\text{Semi1}}zN_{D\text{Semi1}}(V_5-V_4)}{kT} - (N_{D\text{Semi1}} + \\ & \left.\left(\frac{(N_{C\text{Semi1}} \exp\left[\frac{E_{g\text{Semi1}}}{kT}\right])^2}{N_{D\text{Semi1}}}\right))^{\frac{1}{2}} \right] \end{aligned} \quad (2.30)$$

The electric field in semiconductor2 at the interface is due to the same charge density but as a function of its own material parameters:

$$\begin{aligned} E(\text{ElectricFieldInLeftSemi2}) = & -\left(\frac{2kT}{\epsilon_{\text{Semi2}}\epsilon_0}\right) [N_{D\text{Semi2}} \exp\left[\frac{-z_n(V_7-V_6)}{kT}\right] + \\ & \frac{(N_{C\text{Semi2}} \exp\left[\frac{E_{g\text{Semi2}}}{kT}\right])^2}{N_{D\text{Semi2}}} \exp\left[\frac{-z_p(V_7-V_6)}{kT}\right] - \frac{eN_{D\text{Semi2}}zN_{D\text{Semi2}}(V_7-V_6)}{kT} - (N_{D\text{Semi2}} + \\ & \left.\left(\frac{(N_{C\text{Semi2}} \exp\left[\frac{E_{g\text{Semi2}}}{kT}\right])^2}{N_{D\text{Semi2}}}\right))^{\frac{1}{2}} \right] \end{aligned} \quad (2.31)$$

Recognizing that the charge density in both materials must be equal to each other, equation (2.29), (2.30) and (2.31) can be combined into the following expression:

$$E(\text{ElectricFieldInRightSemi1}) * \epsilon_{\text{Semi1}} = E(\text{ElectricFieldInRightSemi2}) * \epsilon_{\text{Semi2}} \quad (2.32)$$

Or

$$\begin{aligned}
& -\varepsilon_{Semi1}\varepsilon_0 \left(\frac{2kT}{\varepsilon_{Semi1}\varepsilon_0} \left[N_{DSemi1} \exp \left[\frac{-z_n(V_5-V_4)}{kT} \right] + \frac{\left(N_{CSemi1} \exp \left[\frac{E_{gSemi1}}{kT} \right] \right)^2}{N_{DSemi1}} \exp \left[\frac{-z_p e(V_5-V_4)}{kT} \right] - \right. \right. \\
& \quad \left. \left. \frac{eN_{DSemi1}zN_{DSemi1}(V_5-V_4)}{kT} - \left(N_{DSemi1} + \frac{\left(N_{CSemi1} \exp \left[\frac{E_{gSemi1}}{kT} \right] \right)^2}{N_{DSemi1}} \right) \right] \right)^{\frac{1}{2}} = \\
& -\varepsilon_{Semi1}\varepsilon_0 \left(\frac{2kT}{\varepsilon_{Semi2}\varepsilon_0} \left[N_{DSemi2} \exp \left[\frac{-z_n(V_7-V_6)}{kT} \right] + \frac{\left(N_{CSemi2} \exp \left[\frac{E_{gSemi2}}{kT} \right] \right)^2}{N_{DSemi2}} \exp \left[\frac{-z_p e(V_7-V_6)}{kT} \right] - \right. \right. \\
& \quad \left. \left. \frac{eN_{DSemi2}zN_{DSemi2}(V_7-V_6)}{kT} - \left(N_{DSemi2} + \frac{\left(N_{CSemi2} \exp \left[\frac{E_{gSemi2}}{kT} \right] \right)^2}{N_{DSemi2}} \right) \right] \right)^{\frac{1}{2}} =
\end{aligned} \tag{2.33}$$

If material properties in equation (2.33) are known then equation (2.27) gives us the means to relate V_5 to V_6 . All that is left for establishing a potential profile of the semiconductor/insulator/semiconductor junction is to find the value of V_5 in equation (2.33) for which both sides equate. The majority of the expressions like this that one encounters need to be solved numerically. We have created Mathematica code to solve this expression using the FindRoot command, the code in its entirety can be found in the code section.

The semiconductor/insulator/semiconductor junction is a well-utilized heterojunction in the literature and deserves attention. In Figure 16, the potential profiles across multiple semiconductor/insulator/semiconductor junctions are shown as a function of Fermi level difference (Figure 16c-e), dopant density (Figure 16f-g), insulator thickness (Figure. 16h-j), and piezoelectric strain (charge density) on the left semiconductor (Figure 16k-m). Both semiconductors are treated as having mirrored properties (e.g., equal permittivities and bandgaps, equal and opposite dopant densities).

The general trend of varying these materials parameters are as follows:

- All else being equal, increasing the Fermi level difference between the two semiconductors will cause a symmetric sharing of the total voltage difference between them, increasing the band bending (electric field strength) at the interface. As the voltage difference between the two semiconductors increases, minority carriers in the bulk of the semiconductors will eventually go into accumulation at the interface, causing a dramatic increase in the charge carrier density and electric field strength localized there.
 - Both materials have the same electrical permittivity, band gap, and temperature, but equal and opposite dopant density and mobile carrier density. Thus, both semiconductors act identically opposite when equilibrating a voltage change.
- As the dopant density in a semiconductor increases, the percentage of voltage drop occurring within that material will decrease.
 - Both the mobile charge density in bulk and the immobile charged cores of ionized dopant atoms will increase with dopant density. Together, higher dopant densities allow a larger charge density to accumulate in response to an impinging electric field over a smaller length scale than a material with lower dopant density. A smaller charge-accumulation distance means a lower voltage drop inside that material because voltage drops are equal to electric fields multiplied by the distance of that field.
- All else being equal, increasing the electrical permittivity of semiconductor 2 causes the distribution of potential drop in both semiconductors to shift from being

equally distributed to having a greater proportion of the potential change occurring within the semiconductor with lower electrical permittivity (semiconductor 1).

- The two semiconductors are together accommodating a total potential drop equal to the difference in work function between them. To create voltage differences, electric fields must be established over finite distances and electric fields are caused by the accumulation of net charge. Since both semiconductors accumulate equal and opposite charge during equilibration, the most voltage drop is going to occur in the material over which the electric field is strongest and the distance over which the electric field travels is longest. Both semiconductors have identical dopant densities so the depth into the semiconductor needed to accumulate charge may be equal; however, the electrical permittivities and thus electric fields in both materials are different. The semiconductor with smaller electrical permittivity will have a stronger electric field inside (equation (2.18)) and so will accommodate the majority of the potential change.
- As the thickness of an insulating layer between the two semiconductors increase, less band bending will occur within the semiconductors.
 - While this rule is true, the effect becomes less insignificant if the insulator has an extremely high (~ 1500) relative electrical permittivity. High electrical permittivities mean low electric fields, and very low electric fields over long distances still equate to small potential differences. When the insulator has high electrical permittivity, the majority of voltage drop will

take place within the semiconductors where the fields can be several of orders of magnitude stronger.

- When piezoelectric charge is introduced at the interface, it is distinctly different from the previous cases analyzed. When there are no bulk work function differences to drive charge in one direction or the other and a charge density is introduced at an interface, the only driving force for charge rearrangement in these materials is the lowest energy condition for charge neutrality. In this case, the magnitude of voltage drop in these materials is not a constant but the charge neutrality rule remains a constant. The lower the charge densities and electrical permittivities of the materials in contact with the piezoelectric charge, the greater the voltage change across the materials. If there is no insulating layer between the two materials or the insulating layer has a high electrical permittivity then both materials will have equal opportunity to screen the piezoelectric charge. Voltage drops are a measure of the systems energy; in order to minimize the system's energy the voltage drop will be minimized.

2.3.7 Ferroelectric Semiconductor / Ferroelectric-Insulator/Solution Junctions

The final heterojunctions that we will examine are semiconductor/solution and semiconductor/insulator/solution interfaces (Figure 16). These interfaces are studied for use in a wide range of applications, including energy storage (e.g., batteries and capacitors) and energy conversion (e.g., photoelectrochemical cells), and materials synthesis (e.g., electrochemical deposition).

Analyzing the semiconductor/insulator/solution interface is similar to the case of the semiconductor/insulator/semiconductor heterojunction except that the expression for charge density will no longer depend on material bandgaps and the density of immobile, ionized donor atoms as is the case within semiconductors, instead it will depend on the concentration, charge, and size of dissolved charged species in solution. There are three phenomena that one should be vigilant of when preparing a heterojunction with a solution:

- 1) Charged species in solution are not point-particles like electrons or holes in a semiconductor. Hydrated ions in solution occupy physical space and have a maximum packing density, and thus a maximum charge density. If a potential difference at the interface of a solution is different enough from the potential in the bulk of solution so as to cause an accumulated charge density that exceeds the atomic density of solid matter, then measures need to be taken to prevent this unphysical result from happening (i.e. creating a charged stern layer)
- 2) Species in solution (atoms, molecules, etc.) can store or release charge through electrochemical reactions. If a potential difference at the interface of a solution is sufficiently different from the potential in the bulk of solution, it may become energetically favorable for electrons to be added to (e.g. $M^{+2} + e^{-1} \rightarrow M^{+1}$) or removed from (e.g., $M^{+1} \rightarrow M^{+2} + e^{-1}$) atoms or molecules in the vicinity. This process of electrochemical oxidation or reduction can cause significant changes to the material properties within the vicinity. This process is *not* taken into account within our calculation.
- 3) In general, the solution will react with the solid's surface, protonating or deprotonating the surface of the solid (especially metal oxides). This causes the formation of a surface

dipole—the magnitude of which can depend on pH and other conditions—resulting in a band shift between everything on one side of the interface verse the other conditions include the processing history of the material, the material facet exposed to solution, the activity of ions in solution which also comprise the material itself (e.g., the activity of sulfide ions in solution in contact with an iron sulfide material), etc.

2.3.7.1 Establishing Conditions in Solution – Charge Density

The charge density (equation (2.2)) in solution is a function of the solution chemistry. For example:

- Water (H_2O) self disassociates into hydronium (H^+ or H_3O^+) and hydroxide (OH^-) ions:



The concentration of H^+ and OH^- in pure water and given by a mass action law similar to that describing the concentration of electrons and holes in a non-degenerately doped semiconductor (equation (2.12)):

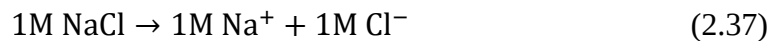
$$[\text{H}^+][\text{OH}^-] = 1 * 10^{-14} @ 25^\circ\text{C} \quad (2.35)$$

Where $[\text{H}^+]$ and $[\text{OH}^-]$ are the molarity of the hydronium and hydroxide ions, respectively.

For a solution of pure water, the charge concentration $\rho(x)$ would be described as follows:

$$\rho_{\text{Solution}}(x) = [\text{H}^+] + [\text{OH}^-] \quad (2.36)$$

In addition to hydronium (H^+ or H_3O^+) and hydroxide (OH^-) ions, mobile charged species in the form of an electrolyte can be introduced to the water system. In an aqueous 1 Molar sodium chloride (NaCl) solution, the sodium and chlorine will disassociate into hydrated sodium and chlorine ions:



In the case of a sodium chloride aqueous solution, the charge density is given by:

$$\rho_{Solution}(x) = [Na^+] + [Cl^-] + [H^+] + [OH^-] \quad (2.38)$$

- If the solution is made basic or acidic by adding something like sodium hydroxide (NaOH) to the water then care should be taken to apply equation (2.35) to the charge density relationship. Increasing the concentration of hydroxide will decrease the concentration of hydronium, and the reverse is also true.

The charge concentration in this case would be given by:

$$\rho_{Solution}(x) = [Na^+] + [H^+] + [OH^-] \quad (2.38)$$

- ‘Nonsymmetrical’ electrolytes (i.e. additives that disassociate into unequally charged parts) may also be added to solution, such as Na_2SO_3 . Here, the additive dissociates as follows:



In every semiconductor/solution junction, an equation for charge density $\rho(x)_{Solution}$ will need to be generated, which means that the first step to calculating a heterojunction’s proper electrical potential profile is to determine the chemical nature (species and concentrations) of solution.

After a general expression for $\rho_{Solution}(x)$ is defined, we next need to know the electrical potential of bulk solution. In electrochemistry, electrical potentials of solutions are defined by the Nernst potential of solution[363]. The Nernst potential is given by the Nernst equation, which relates the electrochemical potential of a medium (E) to temperature and activity of charged chemical species within the medium. The Nernst equation is of the following form:

$$E_{Solution} = E^0 - \frac{RT}{nF} \log_{10} \frac{a_{Ox}}{a_{Red}} \quad (2.40)$$

Where E^0 is the standard reduction potential for redox couple, R is the universal gas constant, T is temperature, F is the Faraday constant, n is the number of electrons transferred per oxidation/reduction reaction, a_{Ox} and a_{Red} are the activity of the oxidized and reduced species in solution, respectively. E is often given with respect to a reference electrode that is submerged in solution and care must be taken to reference E to vacuum when preparing calculations that involve semiconductor or metallic materials whose Fermi levels are already referenced to vacuum energy. When E is referenced to vacuum it can represent a work function of bulk solution.

With the charge density $\rho_{Solution}(x)$ and work function $E_{Solution}$ defined, attention must now be paid to the surface of the semiconducting material to determine if a surface dipole exists, and if so, to determine what magnitude and direction it has. The presence of the surface dipole is a detail often overlooked by a casual analysis and yet it can have a dramatic effect on the resultant heterojunction properties.

2.3.7.2 Establishing the Conditions in Solution – Surface Dipoles

When a solid material is exposed to solution, the surface of the material will exchange atoms with the solution environment until the interface has achieved (chemical) thermodynamic equilibrium. Since the species in solution are charged ions, the exchange of atoms between the solution and the surface will induce a surface charge. This induced surface charge, and its associated counter charge that exists in the vicinity, composes a surface dipole that is situation between the bulk of the material and the bulk of solution.

We take for example the case of a simple oxide (ZnO) in contact with water (Figure 17a). After chemically cleaning (etching) ZnO, the surface is known to be ZnOH terminated (Figure

17b) [364]. When ZnO makes intimate contact with water, OH^- and H^+ from solution will chemically interact with the surface of the ZnO, removing H^+ from the surface under basic conditions (Figure 17c) or removing OH^- from the surface under acidic conditions (Figure 17d). The pH at which the surface has a net neutral charge is called the isoelectric point and it varies between materials, crystallographic facets of a given material, and can depend on the processing history of the material [365]. As the pH of solution differs from the isoelectric point, a dipole forms at the surface of the material. Figure 6e and Figure 6f show the type of band behavior expected after equilibrium has been established at both the semiconductor/solution interface and the entire stack of heterointerfaces discussed thus far, respectively.

For the purposes of our calculation, this dipole is relevant because it acts to change the difference in work function between the semiconductor and solution. Experimentally, this is the cause for the flat-band potential shift that coincides with a change in the pH of solution. It's important to note that the material's surface chemistry can respond to changes in solution chemistry other than pH, especially if the solid is not an oxide. In general, the flat-band potential shift with pH (and thus the work function difference as a function of pH) is approximately 59mV per unit of pH change.

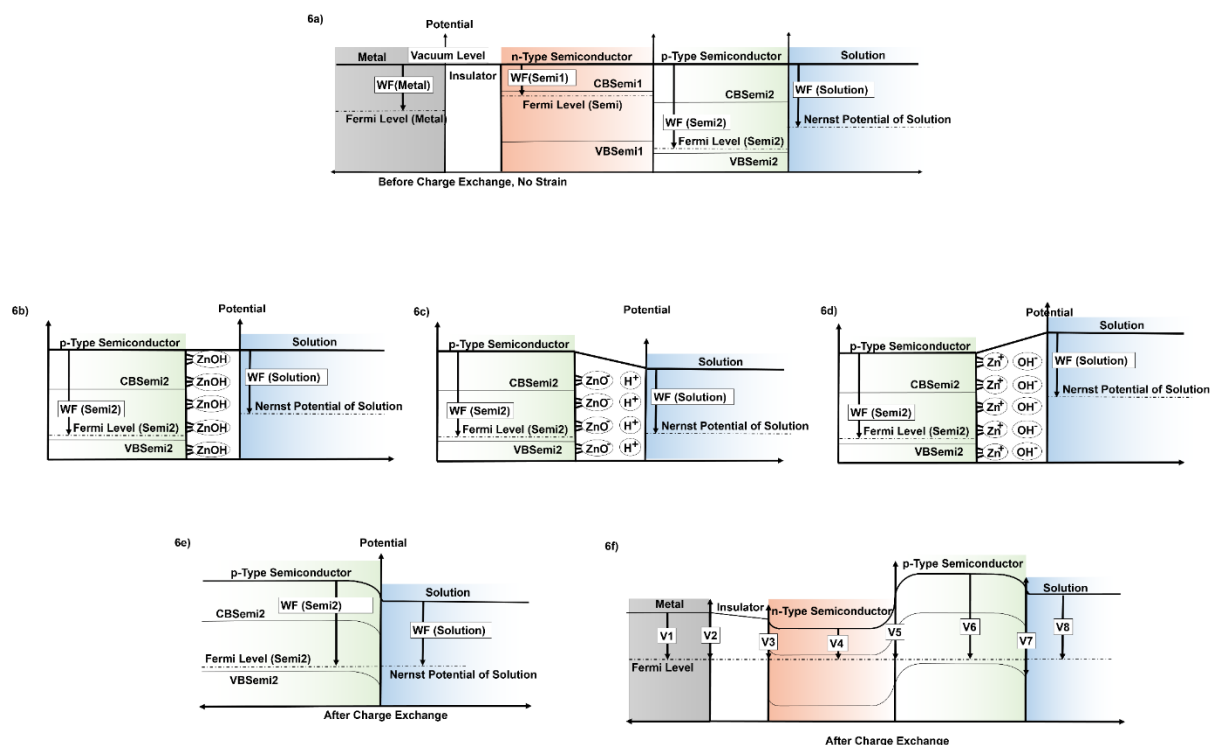


Figure 17. Interface effects at a semiconductor/solution interface. A) Schematic of the material energetics at a metal/insulator/semiconductor/semiconductor/solution heterojunction prior to charge rearrangement and equilibrium. B) Schematic of a semiconductor (p-type zinc oxide)/solution interface. The surface of the semiconductor becomes protonated or deprotonated depending on the chemical composition of the solution and the isoelectric point of the semiconductor. This atomic exchange at the interface introduces an electric dipole when the solution conditions are such that they are not equal to the isoelectric point of the semiconductor (C and D). E) and F) are schematics of the heterojunction after equilibrium has been established.

To calculate the band positions and work functions of the semiconductor with respect to solution, care must be taken to account for the circumstances under which the original data was acquired. If photoelectron measurements are used as the source of band and Fermi level positions, understand that a neutral surface in vacuum is not necessarily equal to a neutral surface submerged in water. If the position data comes from electrochemistry literature then one must account for the solution conditions under which the experiment was conducted so that the surface dipole effect can be properly taken into account. If the Fermi level ($E_{Fermi\ at\ iso}$) of the semiconductor relative to

solution at the isoelectric point (pH_{iso}) is known, then the Fermi level (E_{Fermi}) at any pH can be approximated by:

$$E_{Fermi} = E_{Fermi \text{ at } iso} - (0.059) * (pH - pH_{iso}) \quad (2.41)$$

Taking ZnO as an example, the isoelectric point (pH_{iso}) has been measured to be between 8.7 and 10.3, the exact value depending on substrate, facet, and processing history. In our calculation of the potential profile across the semiconductor/insulator/solution junction, we take $pH_{iso} = 9.5$.

After accounting for the adjustment to work function difference that comes about through the pH-sensitive surface dipole phenomena, the calculation of the heterojunction electrical potential profile can proceed as discussed in previous sections and can be found in the code section

2.3.7.3 Establishing the Conditions in Solution – Stern Layer

Within the mathematics of the code all charges are treated as point particles and this can have important implications for the results when this simplification is applied to ionic solutions. Ions in solution have physical dimensions on the order of spheres with diameters of a few hundred picometers [366]. If we assume the hydrated ions are hard spheres capable of close-packed packing, then this means a maximum ionic density of $\sim 10^{27}$ to $\sim 10^{28}$ is possible (Figure 18). If the charge density calculated at the solution interface is greater than the maximum possible ionic density, then a charged Stern layer (Figure 19) should be introduced to reducing the electric potential in solution and thus reduce the charge density within the vicinity of the solution interface. The charge density of the Stern layer (σ^S) necessary to reduce the potential at the interface to a physically meaningful quantity (V_{max}) is determined by subtracting the surface charge density

determined at the semiconductor interface from the charge density necessary to acquire $V_{\max}$ in solution (see supplemental information on Stern Layer).

If a Stern layer is a necessary addition to the calculation, then depending on the length scales of interest it may be important to include the physical thickness of the Stern layer in the electrical potential diagram. The Stern thickness will be the hydration diameter of ions comprising the Stern layer.

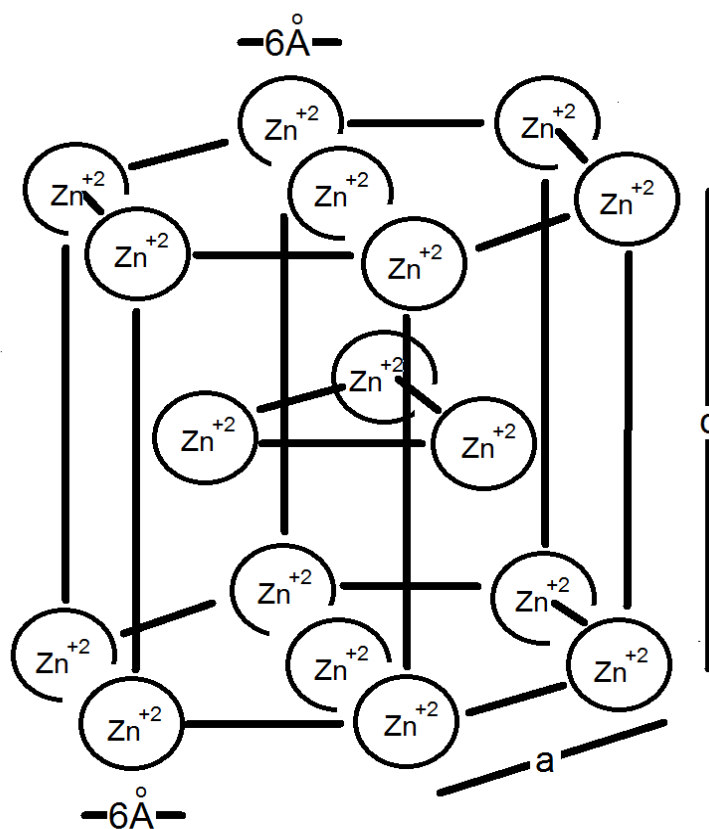


Figure 18. If we model the hydrated ions as hard spheres, then the maximum packing density possible is the close packing structure

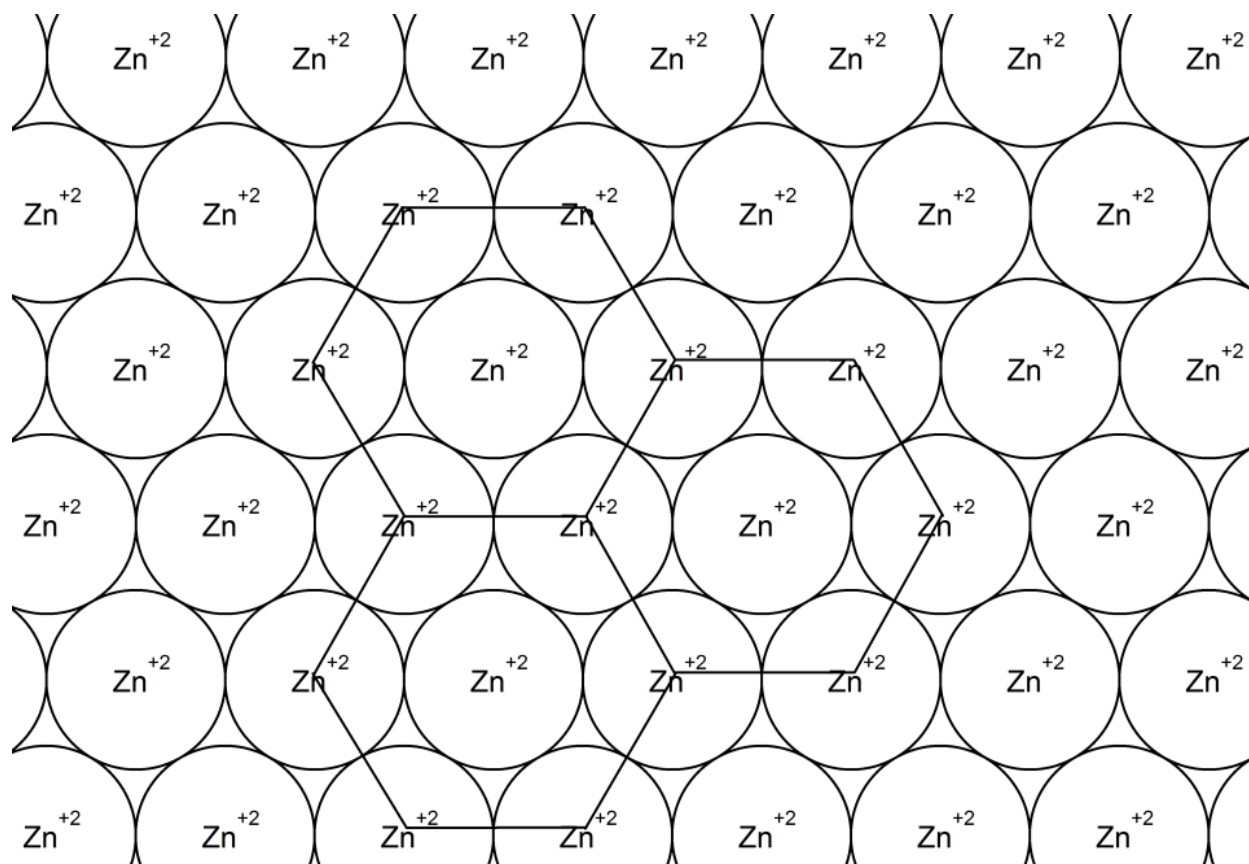


Figure 19. If we model the hydrated ions as hard spheres, then the maximum packing density in a 2D plane is closed packed layer.

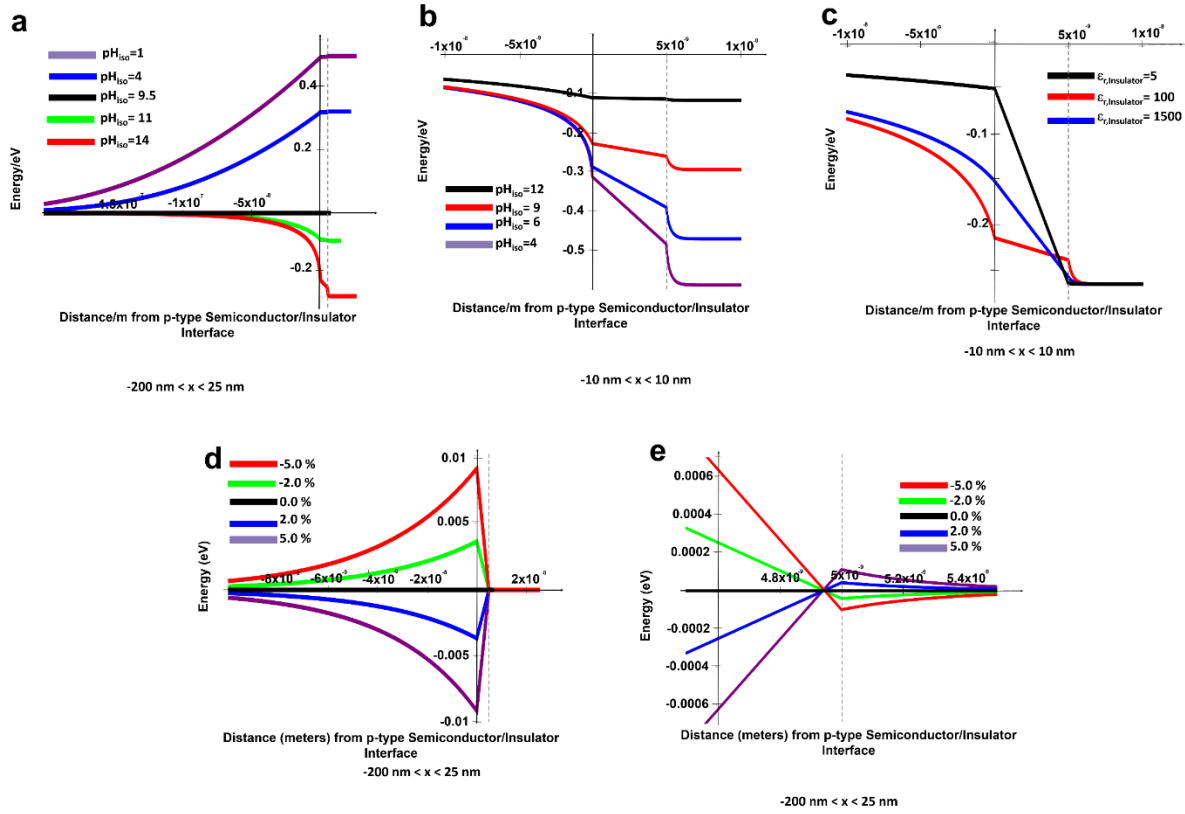


Figure 20. Calculated electrical potential profiles at a piezoelectric p-type semiconductor/insulator/solution heterojunction. A) Calculated electrical potential profile of a semiconductor/insulator/solution interface as a function of solution pH. B) Calculated electrical potential profile of a semiconductor/insulator/solution interface as a function of the isoelectric point of the solution-facing material. C) Calculated electrical potential profile across the heterojunction as a function of the electrical permittivity of the insulating material. D) and E) Calculated electrical potential profile across the heterojunction interface as a function of the piezoelectric-semiconductor's strain.

Utilizing the code, we demonstrate the effect of changing the pH of solution (Figure 20a), the isoelectric point of the solution-facing material (Figure 20b), insulating layer's permittivity (Figure 20c), and strain of the piezoelectric (Figure 20d) on the heterojunction potential profiles. The direction of band bending at the semiconductor/insulator interface in Figure 20a-d depends both on the value of the semiconductor's Fermi level relative to work function of solution, as governed by equation (2.41) (Figure 7a-c), and the ferroelectric and piezoelectric charge density

introduced at the interface (Figure 20d). If no piezoelectric surface charge is introduced to the interface, band bending at the solution/insulator interface is always in the opposite direction to that at the semiconductor/insulator interface due to the charge neutrality constraint. The broadness of the band bending depends on the types of charges—mobile, lattice, and/or dopant ion cores—which constitute the space charge regions in equilibrium.

Figure 20a shows the effect of pH on the potential profile of the semiconductor/insulator/solution junction, where the bands in the semiconductor bend up for $\text{pH} < \text{pH}_{\text{iso}}$ (Figure 21a) and bend down for $\text{pH} > \text{pH}_{\text{iso}}$ (Figure 21b). The relatively sharp band bending in the semiconductor—in this case, p-type—for $\text{pH} > \text{pH}_{\text{iso}}$ is attributed to the accumulation of mobile holes at the semiconductor-insulator interface, whereas the broad band bending for $\text{pH} < \text{pH}_{\text{iso}}$ is attributed to the accumulation of minority carriers and the presence of diffuse, immobile ionized dopant cores. This broad bending is also reflected in the potential profile of the solution for $\text{pH} < \text{pH}_{\text{iso}}$. For constant pH and $\text{pH} > \text{pH}_{\text{iso}}$, decreasing the difference between pH and pH_{iso} (Figure 22a) decreases the extent of band bending in the semiconductor. It is important to note that while pH is a property of *solution* that effects the potential profile, it does so because of its relationship to pH_{iso} , which is a *materials* property. *Thus, by carefully selection of surface-facing materials OR solution conditions, engineering of the heterojunction's potential profile is possible*

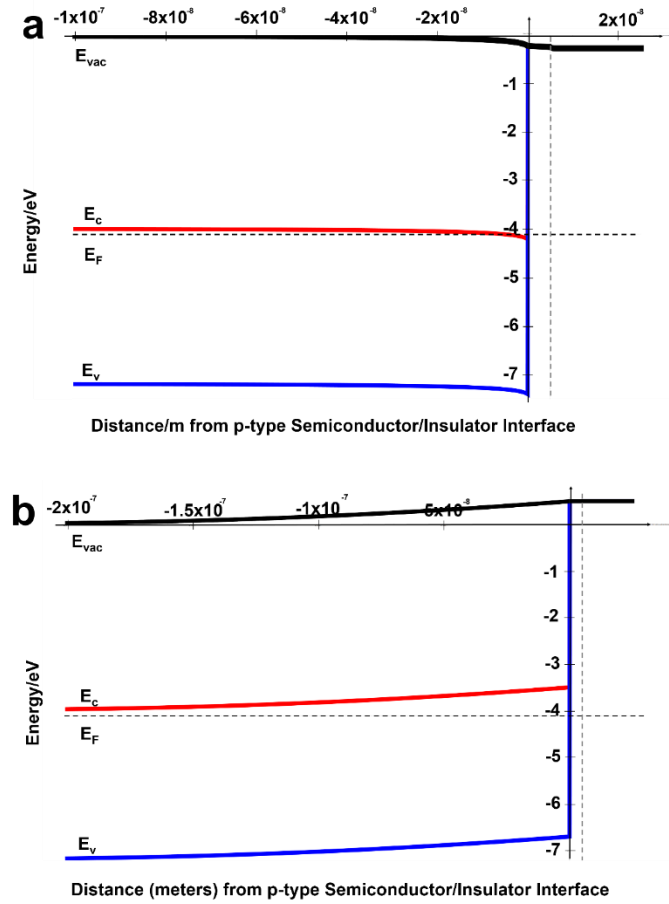


Figure 21. The effect of pH on the potential profile of the semiconductor/insulator/solution junction, where the bands in the semiconductor bend up for $\text{pH} < \text{pH}_{\text{iso}}$.

The amount of band bending in the semiconductor can be tuned by the permittivity of the insulating dielectric layer. Dielectric materials with high permittivities (Figure 23a) are more susceptible to lattice polarization, which increases the amount of charge that must be accumulated on either side of the junction in order to generate a given potential difference. This accumulated charge must come from deeper within the materials, further away from the interface, and thus high permittivity dielectrics increase the amount of band bending at the interface. On the other hand, low permittivity dielectrics decrease the amount of band bending at the interface. On the other hand, low permittivity dielectrics (Figure 23b) do not require as much charge to acquire a given potential difference and thus the band bending is less prominent.

Strain in the piezoelectric semiconductor (Figure 20d) shows comparatively less of an influence, this is due to the fact that mobile charges are relatively abundant in this system and thus can easily screen the piezoelectric surface charge. The effects of pH, pH_{iso} , and permittivity are seen at the scale of 100s of meV whereas the effects of strain-induced charge from the piezoelectric are on the scale 1-10 meV. Note: the upper limit of 10 meV in magnitude, which is the approached value in Figure 20d, corresponds to relatively large strains (i.e., 5% strain in Figure 20d).

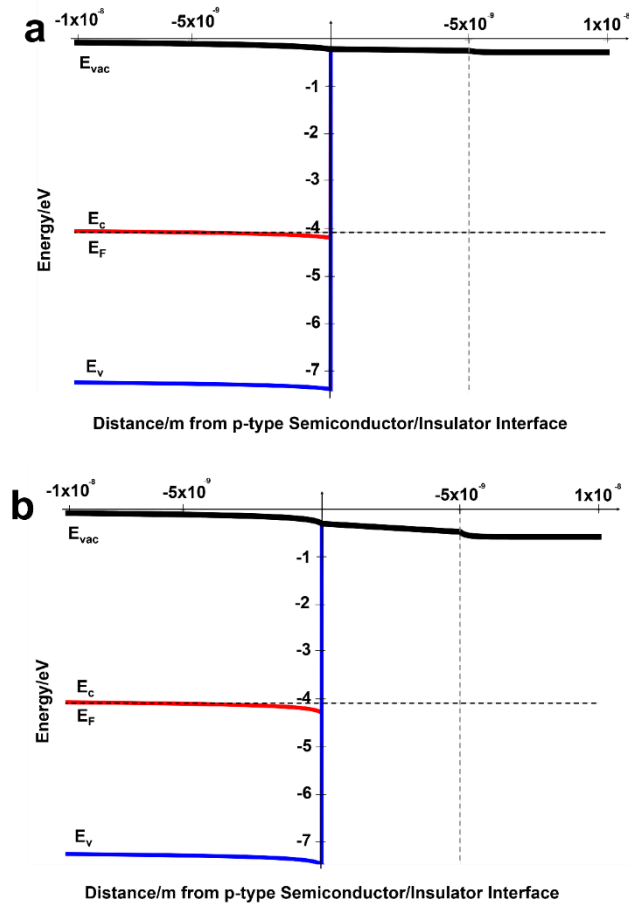


Figure 22. The effect of pH on the potential profile of the semiconductor/insulator/solution junction, where the bands in the semiconductor bend down for $\text{pH} > \text{pH}_{\text{iso}}$.

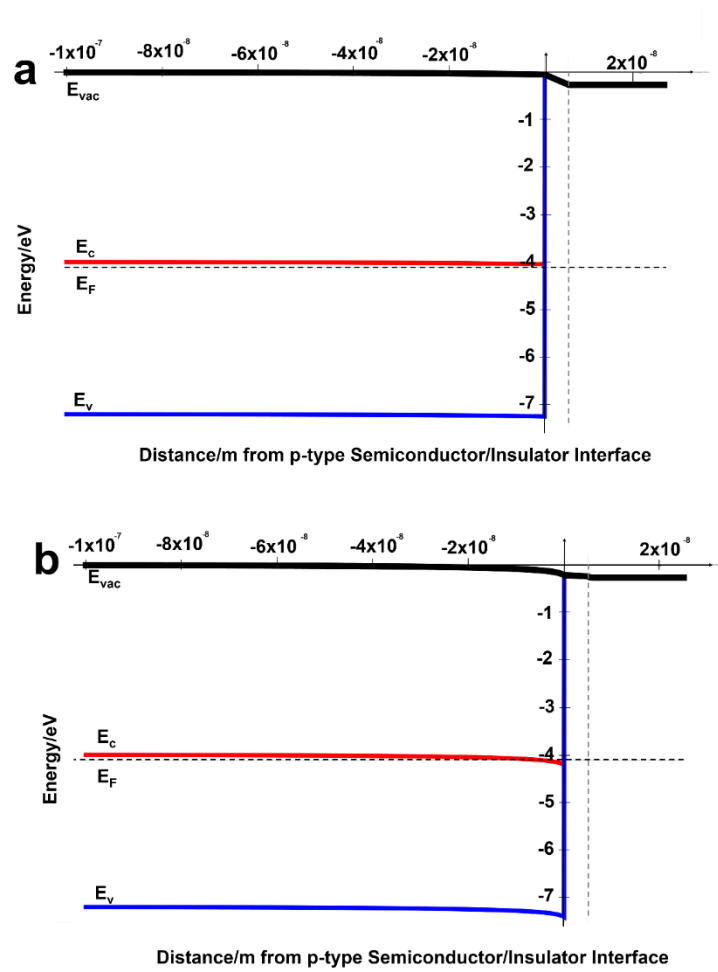


Figure 23. For constant pH and $pH > pH_{iso}$, decreasing the difference between pH and pH_{iso} decreases the extent of band bending in the semiconductor

Chapter 3: Application of Band Diagram Calculator to experiments

3.1 Charged Surfactant/Solution

To date, the preparation of free-standing 2D nanomaterials has been largely limited to the exfoliation of van de Waals solids. The lack of a robust mechanism for the bottom-up synthesis of 2D nanomaterials from non-layered materials has become an obstacle to further explore the physical properties and advanced applications of 2D nanomaterials. We conducted a study to demonstrate that surfactant monolayers can serve as soft templates guiding the nucleation and growth of 2D nanomaterials in large area beyond the limitation of van der Waals solids. 1 to 2 nm thick, single-crystalline free-standing ZnO nanosheets with sizes up to tens of microns are synthesized at the water-air interface. In this process, the packing density of surfactant monolayers adapts to the sub-phase metal ions and guides the epitaxial growth of nanosheets.[367]

Two-dimensional (2D) nanomaterials, particularly when their thickness is just one or a few atomic layers, exhibit physical properties dissimilar to those of their bulk counterparts and other forms of nanostructures. [368-377] Real-world 2D nanostructures so far have been largely limited to naturally layered materials, *i.e.* the van der Waals solids, synthesized either from top-down or bottom-up.[378-380] A much larger and diverse portfolio of 2D materials including non-layered compounds are desirable to meet the specific requirements of individual components in various devices.[381] When seeking a synthesis route to create nanosheets from non-layered materials, it is critical to break the crystal symmetry and foster the anisotropy in crystal growth. Unlike one-dimensional (1D) nanostructures whose growth mechanisms have been well described, syntheses of ultrathin 2D nanomaterials from non-layer materials without an epitaxial substrate have remained a case-by-case practice.[382] In the sporadic literature reports, such as PbS nanosheets

by oriented attachment and Pd nanosheets by a solvothermal method,[383-385] the size of the nanosheets is usually below one micron and much smaller than that of graphene and TMDs, which presents myriad fabrication challenges for real devices. In this regard, a novel and yet robust synthesis strategy dedicated to the growth of general 2D nanostructures of large sizes would enable many novel materials to be grown at a practical dimension for applications.

To control the morphology of nanomaterials in solution synthesis, one of the most common strategies is to employ surfactant molecules or inorganic ions that are preferentially adsorbed on specific crystallographic facets, the growth of which is then retarded and thus the growth of other facets are promoted.[386, 387] One intriguing strategy is to use surfactant monolayer at the water-air interface as a soft template to guide the growth of nanostructures underneath. By using an arachidonic acid monolayer as templates, oriented, sub-100 nm-sized PbS nanoplates and nanorods were obtained when the surface pressure of the monolayers were optimized.[388-390] We hypothesize that once a strong recognition between the surfactant monolayer and the target materials in the aqueous sub-phase was established, epitaxial growth could be realized over a large area. In our prior work, a few hundred nanometer-thick, micron-sized zinc hydroxyl dodecylsulfate nanomembrane laminates were synthesized at the water-air interface by introducing high-concentration sodium dodecylsulfate to the ZnO growth solution,[391, 392] revealing the possibility of using an anionic sulfate monolayer to induce the growth of single-crystalline ZnO nanosheets with large sizes. Here, we report that ~1-2 nanometer thick single-crystalline ZnO nanosheets with sizes up to tens of microns can be synthesized at the water-air interface.

Synthesis method for ZnO nanosheets

In a typical synthesis, 17 mL aqueous solution containing 25 mM $\text{Zn}(\text{NO}_3)_2$ and hexamethylenetetramine (HMT) was prepared in a glass vial. Subsequently, 10 μL chloroform

solution containing 0.1 vol % sodium oleyl sulfate was spread on the water surface. This glass vial was then screw-capped and placed in a 60 °C convection oven. ZnO nanosheets would appear in about 1 hour 40 minutes and could be scooped using an arbitrary substrate for characterization

Results

Morphology and Structural Characterization of ZnO nanosheets

In this synthesis, oleylsulfate anionic monolayers were employed to guide the growth of ~1-2 nanometer thick single-crystalline ZnO nanosheets at the water-air interface. Sodium oleylsulfate was first dissolved in chloroform and subsequently spread over the surface of an aqueous solution containing precursors that would otherwise produce chunky ZnO nanocrystals (see methods section above). While ZnO nanocrystals still form in the bulk part of the solution, there appeared a single layer of ZnO nanosheets that covered the entire water-air interface. As schematically shown in Figure 24a, the oleylsulfate anions forms a close-packed monolayer at the water-air interface, under which Zn^{2+} cations are supersaturated and precipitate into nanosheets. Much like graphene, when the nanosheets were transferred onto oxide-coated Si substrates, they became visible under the optical microscope, and this was very useful for subsequent characterization and device fabrication.[393] Figure 24b is a scanning electron microscopy (SEM) image of ZnO nanosheets on a 100 nm SiO_2 -coated Si substrate. These nanosheets were densely packed and nearly covered the entire. A small number of nanoparticles were found sparsely distributed around the nanosheet layer. We suspect that the formation of these nanoparticles is due to the precursors being dissolved in the residue chloroform that is used to disperse the monolayer. Figure 24c shows a single triangular nanosheet with edges longer than 20 μm . This is the typical morphology of the as-received nanosheets. A topography atomic force microscopy (AFM) scan revealed the nanosheet was 2.28 nm in thickness and nearly uniform across the entire area (Figure

24d). The surface roughness was found to be 0.2 nm. Because of the way we transferred the nanosheets to substrates, an oleylsulfate monolayer was inevitably transferred along with the nanosheets. X-ray photoelectron spectroscopy (XPS) characterization of the nanosheets confirmed the presence of oleylsulfate on the surface of nanosheets and the specific bonding between sulfate groups and Zn^{2+} ions.

Transmission electron microscopy (TEM) was applied to investigate the crystallinity of these nanosheets as well as their formation mechanism. The size of the nanosheet was too large to be fully imaged. Figure 24e shows a corner of a triangular nanosheet, which is slightly darker in contrast compared to the background due to its ultra-small thickness. For a clear presentation, we highlighted the edges with red dashed lines. Several very thin whiskers also were observed, which might be concentrated surfactant residues. Selective area electron diffraction (SAED) pattern revealed a single-crystalline hexagonal lattice with a d -spacing of 0.281 nm, which matches the Wurtzite ZnO (0001) facet (Figure 24f). High-resolution (HR) TEM images were obtained on the area through the holes of the holey-carbon film, as shown in Figure 24g. The HRTEM revealed the single-crystalline nature of the nanosheet; whereas dislocations or small defective areas could also be observed on the nanosheet. Corresponding fast Fourier transfer (FFT) pattern of the HRTEM image clearly matches the SAED pattern, confirming the single crystallinity across the entire nanosheet (Figure 24h). Nanosheets with uneven surfaces were also observed as shown in Figure 24i. There appeared to be a developing overlayer on the nanosheet surface, indicative of a layer-by-layer growth mode.

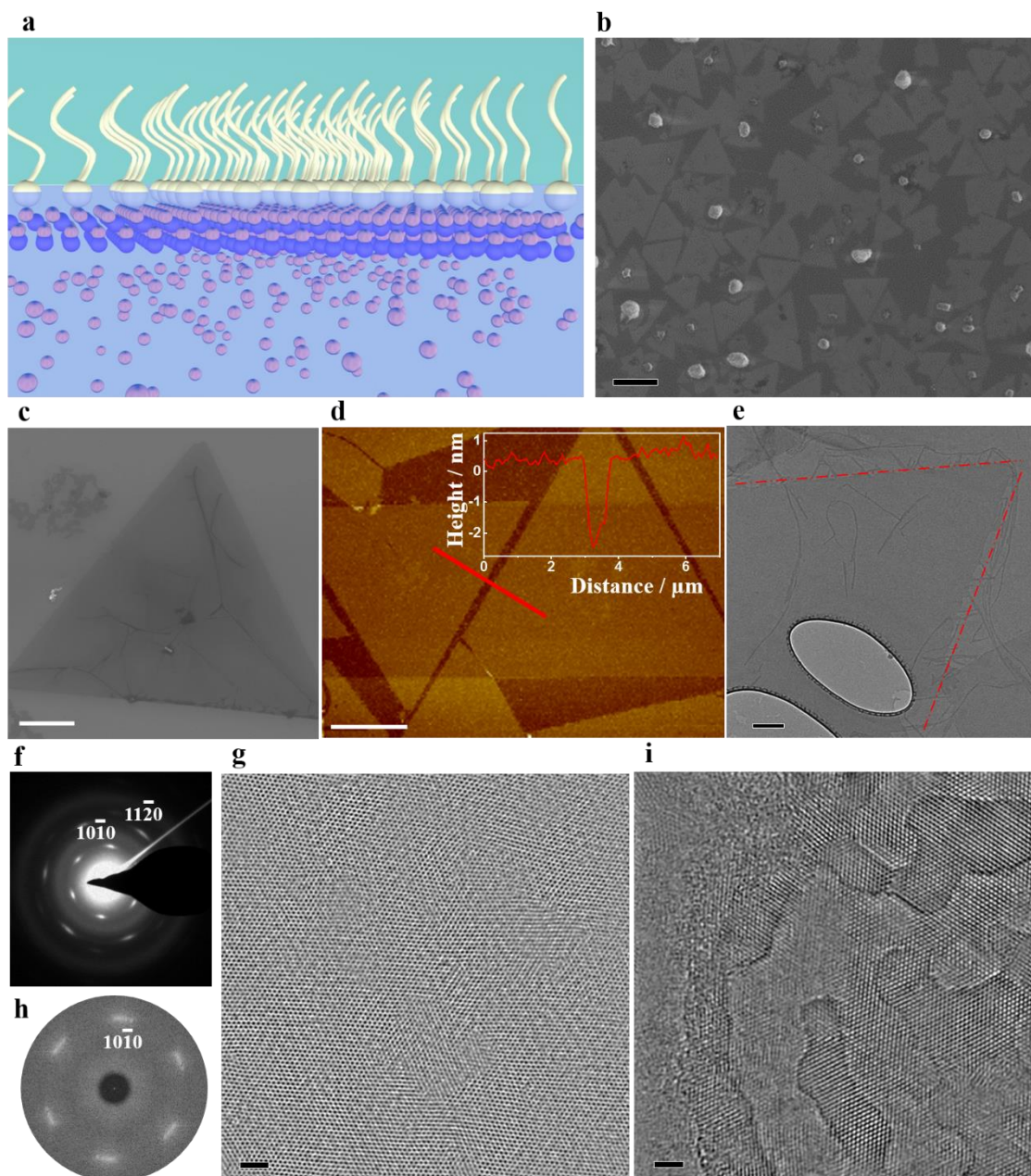


Figure 24. Morphology of ZnO nanosheets. a, Schematic illustration of the formation of ZnO nanosheets directed by surfactant monolayer. b, SEM image of the nanosheets on a silicon substrate coated with 100 nm SiO₂. Scale bar= 10 μm. c, SEM image showing a typical nanosheet with an equiangular triangle shape. Scale bar=5 μm. d, AFM topography scans of typical nanosheets with flat surfaces on a Si substrate. Scale bar=5 μm. e, TEM image of a corner of a 20 μm-sized ZnO nanosheet. Scale bar=200 nm. f, Corresponding SAED pattern of the nanosheet shown in E. g, HRTEM image of the same nanosheet. Scale bar=2 nm. h, Corresponding Fourier transformation that shows a hexagonal symmetry. i, HRTEM image of a nanosheet showing overlayer growth. Scale bar=2 nm.[367]

Time evolution of ZnO nanosheets

The nanosheets at the water-air interface were collected at different reaction times to investigate their formation mechanism. TEM images in Figure 25a-d and the conceptual drawing below them respectively illustrate the crystal structure evolution of the nanosheets. What appeared at the interface first was a continuous amorphous film (Figure 25a), which is supported by the inset FFT pattern. Tiny crystallites are embedded in the largely amorphous film although hardly visible. These crystallites then grew in lateral size, and were all oriented with the same hexagonal crystal plane exposed; however, their in-plane rotation appeared to be stochastic, as shown in Figure 25b. These crystallized grains grew larger and had aligned orientation, as shown in Figure 25c. Finally, a large-area single-crystalline nanosheet formed, as shown in Figure 25d. The insets are fast Fourier transfer patterns of the TEM images, respectively. The four schematic drawings below TEM images conceptually depict the crystal structure of each stage during the evolution of ZnO nanosheets. Regions with lighter gold colored spheres are amorphous and regions with deeper gold colored spheres are crystallized. Scale bars are 5 nm, 2 nm, 2 nm, and 2 nm, respectively.[367]

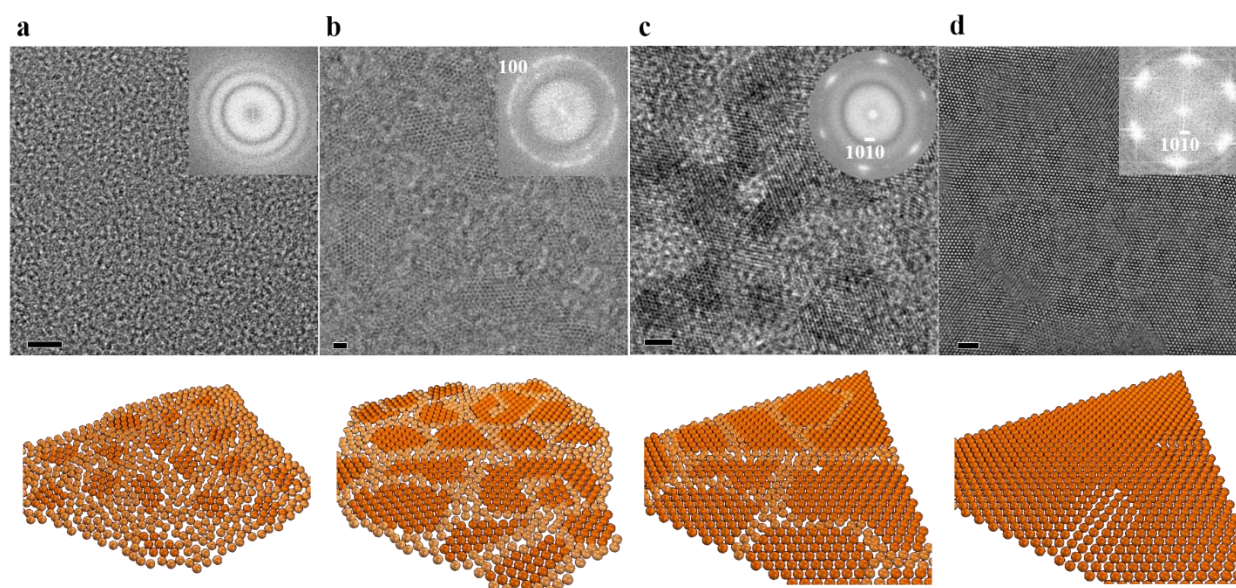


Figure 25. TEM images and schematic drawings showing the time-dependent evolution of ZnO nanosheets. a, Mostly amorphous films with tiny crystalline grains and curved edges. b, More crystallized nanosheets with 2 to 3 nm grains that are randomly oriented. c, These crystallized grains grew larger and had aligned orientation. d, Large-area single-crystalline nanosheet. The insets are fast Fourier transfer patterns of the TEM images, respectively. The four schematic drawings below TEM images conceptually depict the crystal structure of each stage during the evolution of ZnO nanosheets. Regions with lighter gold colored spheres are amorphous and regions with deeper gold colored spheres are crystallized. Scale bars are 5 nm, 2 nm, 2 nm, and 2 nm, respectively.[367]

Calculation of electric potential profile and Zn^{2+} concentration profile from the surfactant-water interface into the bulk solution.

Considering the formation of ZnO from solution was driven by Zn^{2+} concentration, we simulated the effects of a negatively charged surfactant monolayer on the concentration profile of Zn^{2+} near the water-air interface to understand the origin of the nanometer-level thickness.

A charged surface, such as the surfactant monolayer, will push and pull on charged species in solution. The ions in solution will reorganize themselves about the charged surface, screening monolayer's influence on the bulk solution. The ratio of concentrations of species i in bulk solution (n_i^0) at bulk solution potential ($\phi^0=0$) to its concentration (n_i) found at any other potential (ϕ) is taken to depend upon the Boltzmann factor in the following way:

$$n_i = n_i^0 e^{\left(\frac{-z_i e \phi(x)}{kT}\right)} \quad (2.42)$$

where z_i is the charge of ion i , e is the charge of the electron, ϕ is the potential relative to bulk solution, x is a measure of distance into solution and perpendicular to the monolayer surface, k is the Boltzmann constant, and T is absolute temperature. Under meager potentials, e.g. 1 Volt, and reasonable bulk ion concentrations, equation (2.42) will produce large, nonphysical ion concentrations (e.g. $n_i > \frac{1 \text{ Mole}}{\text{cm}^3}$). To determine whether 'large' potentials would be found in the studied system, equation (2.43) and equation (4.44) were used.[394]

$$\sigma^M = \epsilon \epsilon_0 \left(\frac{d\phi}{dx} \right)_{x=0} \quad (2.43)$$

$$\left(\frac{d\phi}{dx} \right)^2 = \frac{2kT}{\epsilon \epsilon_0} \sum_i \left(n_i^0 \left[e^{\left(\frac{-z_i e \phi}{kT} \right)} - 1 \right] \right) \quad (2.44)$$

where σ^M is the charge density of the monolayer, ϵ is the relative permittivity of the material (80 for water), ϵ_0 is the electrical permittivity of free space, $\left(\frac{d\phi}{dx} \right)_{x=0}$ is the potential gradient (electric field strength) at the monolayer's surface, and $\phi_{x=0}$ is the potential at the monolayer's surface.

Taking σ^M as -0.801 C m^{-2} (i.e. $\frac{1 \text{ electron}}{20 \text{ \AA}^2}$) and solving for $\phi_{x=0}$, we indeed encountered large potentials that were capable of inducing large, nonphysical ion concentrations. Table 1 shows the type of ion concentrations expected from applying equation (2.43) directly to the experimental conditions we studied.

Species i	$n_i^0 (\frac{\text{ions}}{\text{m}^3})$	z_i	$\phi_{x=0} \text{ (V)}$	$n_i(\frac{\text{ions}}{\text{m}^3})$
Zn^{2+}	1.12734×10^{25}	2	0.23309	1.27136×10^{32}
H^+	1.51269×10^{21}	1	0.23309	5.07991×10^{24}
OH^-	2.39746×10^{18}	-1	0.23309	7.13914×10^{14}
NO_3^-	2.93399×10^{25}	-1	0.23309	8.73681×10^{21}
NH_4^+	6.02063×10^{24}	1	0.23309	2.02184×10^{28}
ZnNO_3^+	7.70834×10^{23}	1	0.23309	1.27158×10^{27}

Table 1. Parameters used and calculated concentrations of various ions from Supplementary equation (2.43) assuming no physical size of ions.

If we model the hydrated ions as hard spheres, then the maximum packing density possible is the close packing structure (Figure 26). Taking Zn^{2+} ions as an example, each with a hydration diameter (d) of 6 Å,[395] then the maximum 3D packing density possible is given by:

$$\text{Maximum 3D Density} = \frac{\text{Zn}^{+2} \text{ ions}}{\text{Volume}} = \frac{\left(\frac{3}{2}\right)+3+\left(\frac{3}{2}\right)}{\frac{3\sqrt{3}}{2}a^2c} = \frac{6}{\frac{3\sqrt{3}}{2}d^2(2d\sqrt{\frac{2}{3}})} = 6.54729 * 10^{27} \frac{\text{ions}}{\text{m}^3} \quad (2.45)$$

Thus, the total of all ion concentrations at the closest approach to the 2D charged layer must be equal to or less than this atomic density.

$$\sum n_i \leq 6.54729 * 10^{27} \frac{\text{ions}}{\text{m}^3} \quad (2.46)$$

Table 1 shows a clear violation of this condition.

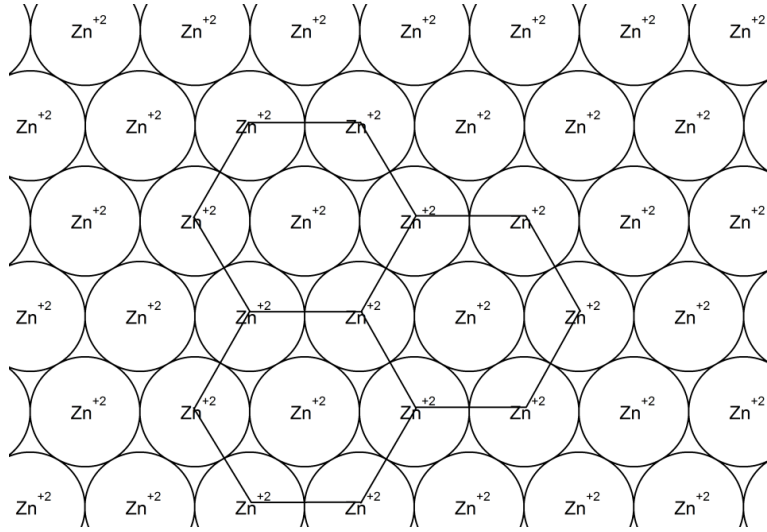


Figure 26. A 2D array of Zn^{2+} ions used to calculate the theoretical maximum 2D charge density, σ_{Max}^S , in order to check the charge density we obtained from equation (2.42) is physically possible.[367]

Iterative numerical calculation was applied to find the limit of ϕ at which equation (2.43) and equation (2.44) obtained the condition required in equation (2.46). This yielding the critical criteria for the surface potential: $\phi_{x=0} \leq 0.090994$ V. In order to achieve this potential, far less than the 0.23309 V previously determined to be present at the charged monolayer, a charged stern layer is assumed to form adjacent to the charged self-assembled surfactant monolayer. Using equation (2.43) and equation (2.44) again, except now fixing $\phi_{x=0} = 0.090994$ V and solving for σ , it is found that a surface charge density of $0.0651358 \frac{C}{m^2}$ is capable of maintaining a $\phi_{x=0} = 0.090994$ V in the required aqueous conditions. Physically, this apparent surface charge density σ^A is the 2D charge density necessary to create an electric field strong enough to condense the charged species in solution into a close packing structure. Because the superposition principle applies in electromagnetism, the 2D charge density (σ^A) that the solution experiences is a sum of the surfactant monolayer's charge density (σ^M) and the Stern layer's charge density (σ^S).

$$\sigma^A = \sigma^M + \sigma^S \quad (2.47)$$

To gain insight into the nature of the charged Stern layer, and determine if it is physical reasonable, rearranging equation (2.48) and solving for σ^S yields:

$$\sigma^S = \sigma^A - \sigma^M = (-0.0651358) - (-0.801) = 0.735952 \frac{C}{m^2} \quad (2.48)$$

This value for σ^S is well within the theoretical maximum 2D charge density (σ_{Max}^S) obtained by modeling the Stern layer as a 2D array of charged Zn^{+2} ions.

The following is used to calculate σ_{Max}^S :

$$\sigma_{Max}^S = \frac{\text{Charge}}{\text{Area}} = \frac{\left(\frac{Zn^{+2} \text{ ions}}{\text{hexagon}}\right) \times \left(\frac{\text{Charge}}{Zn^{+2} \text{ ion}}\right)}{\frac{3\sqrt{3}}{2}d} = \frac{\left(6\left(\frac{1}{3}\right)+1\right) \times (2 \times e)}{\frac{3\sqrt{3}}{2}(d)} = 1.0278 \frac{C}{m^2} \quad (2.49)$$

σ_{Max}^S is greater than the previously determined value of $0.735952 \frac{C}{m^2}$ for σ^S and thus σ^S is deemed a physically reasonable value for the stern layer charge density.

To summarize, we assumed the average area occupied by a single oleylsulfate molecule in the monolayer is 0.2 nm^2 , which corresponded to a charge density of -0.801 C m^{-2} . A positively charged Stern layer with a uniform charge density of 0.736 C m^{-2} was established at a distance of 0.30 nm away from the surfactant layer. The electric field resultant from superimposing both charged surfactants and Stern layers influences the charged species in solution, attracting (concentrating) or repulsing (diluting) positively and negatively charged ions, respectively. The electrical potential profile, ($\phi(x)$), between the Stern layer and bulk solution was solved numerically using equation (2.44). The potential adjacent to the Stern layer at the closest approach by ions in solution, $\phi(6\text{\AA})$, was taken as 0.065 V . As the concentrations of all species are constantly changing during the reaction, we calculated the chemical environment near the interface only at the relevant reaction time point (1.5 hours into the reaction) assuming the concentration of each ion as listed in Table 1. Consistent with equation (2.44), the ratio of concentrations of species i in

bulk solution (n_i^0) at bulk solution potential ($\phi^0=0$) to its concentration (n_i) found at any other potential (ϕ) is given by equation (2.42).

Figure 27a and b are raw outputs from the Mathematica code, plotting the electrical potential and Zn^{+2} ion profile at the surfactant/solution interface. Figure 28 stylizes Figure 27b, presenting a plot of Zn^{2+} concentration as a function of distance from the surfactant monolayer into the bulk solution.

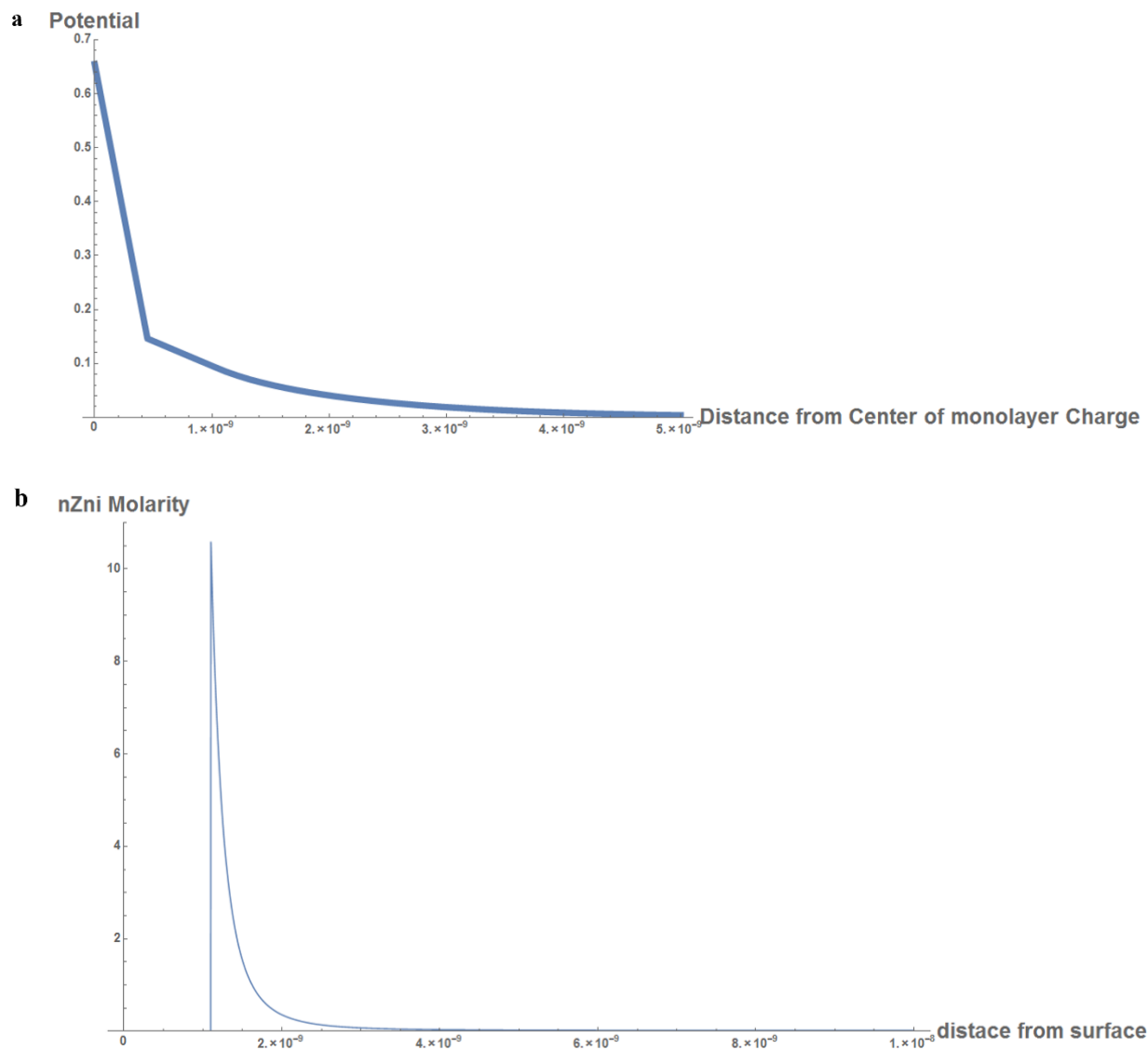


Figure 27. A 2D array of Zn²⁺ ions used to calculate the theoretical maximum 2D charge density, σ_{Max}^S , in order to check the charge density we obtained from equation (2.48) is physically possible. A region directly adjacent to the surfactant is composed primarily of immobile Zn²⁺ ions and makes up a Stern layer. The electrical potential falls linearly within this region, reducing the potential difference between bulk solution and surfactant to that of a critical value. Adjacent to the Stern layer is solution composed of diffuse mobile ions, resulting in an approximately exponentially decaying electrical potential. b) Applying equation (2.42) to potential profile in Figure 3a results in a plot of Zn²⁺ ions within solution.[367]

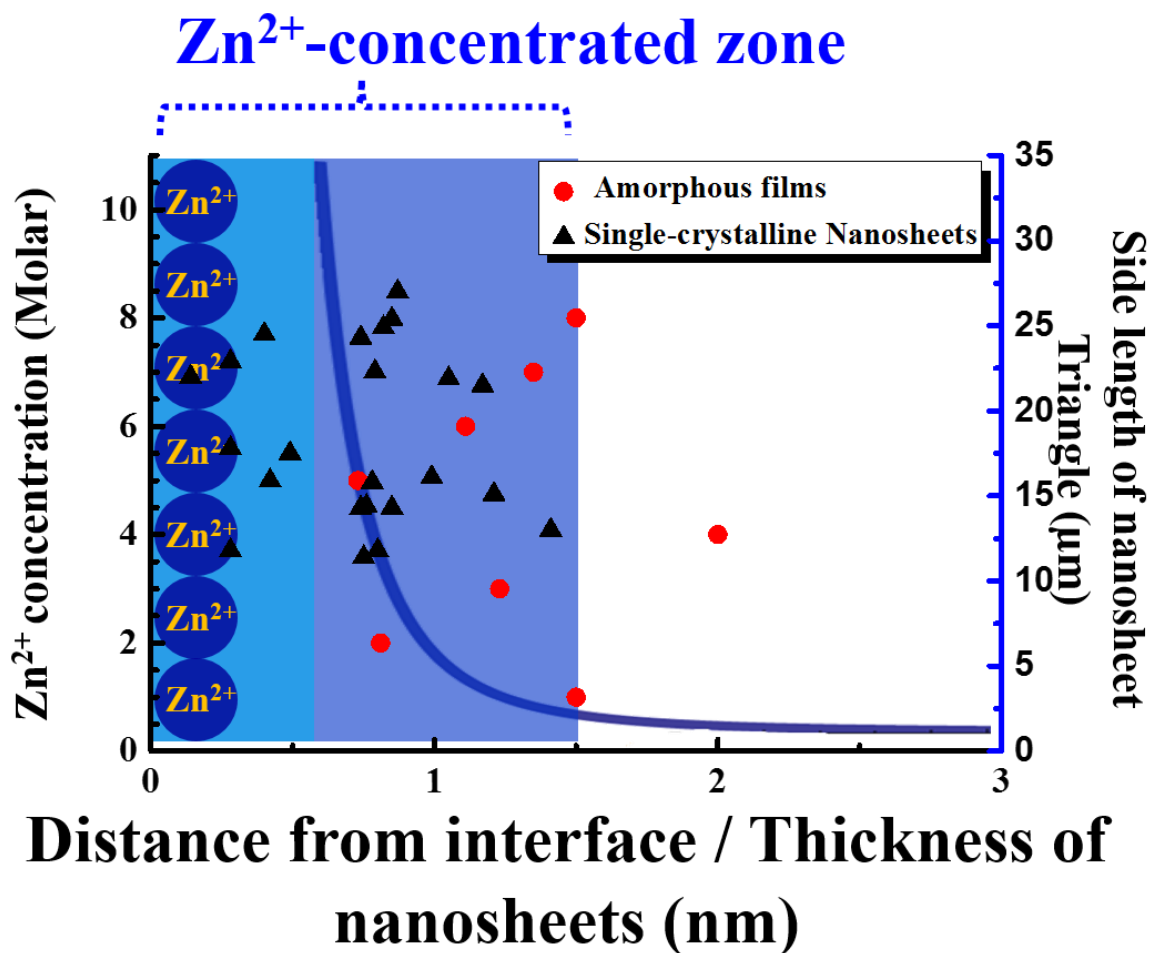


Figure 28. Thickness and size relation to Zn²⁺ concentration distribution. The blue shaded band represents a positively charged stern layer primarily composed of Zn²⁺ ions. The blue curve plots the concentration of Zn²⁺ from the end of the Stern layer (blue shaded area within the first 0.6 nm) into the bulk solution. The black triangles and red round dots marks the thickness of monocrystalline nanosheets and amorphous nanosheets formed prior, respectively, measured by AFM. The right vertical axis is the side length of single-crystalline nanosheet triangles. Note that the size of amorphous nanosheets are hundreds of microns and are not displayed in this plot.[367]

Comparing experimental results to predictions from calculations

It can be observed that the concentration of Zn²⁺ ions dropped drastically within a very short distance from the Stern layer. At distant $x = 1.5$ nm, its concentration became only marginally different from bulk concentration. Therefore, the Stern layer and the diffuse Gouy layer up to 1.5 nm from the interface constituted a Zn²⁺-concentrated zone. In Figure 28 we also marked the

measured thickness of the single-crystalline nanosheets and the amorphous films by black triangles and red round dots, respectively.

The single-crystalline triangular ZnO nanosheets and amorphous films have an average thickness of 2.84 ± 0.26 nm and 3.28 ± 0.41 nm, respectively. The single-crystalline ZnO nanosheets were generally thinner than the amorphous films, possibly due to a volume reduction and removal of non-native ions (*e.g.* nitrate and ammonium ions) during the crystallization. Given the fact that the oleylsulfate adsorbed on the surface of nanosheets may have contributed a thickness of ~ 2 nm,[396] the thickness of the amorphous ZnO nanosheets is about the same as the width of the Zn^{2+} -concentrated zone near the interface (~ 1.5 nm). We therefore propose that this Zn^{2+} -concentrated zone has provided an interfacial chemical environment different from the bulk concentration which drove the growth of ZnO nanosheets and was directly related to the thickness of the initial amorphous ZnO films that subsequently transformed into single-crystalline nanosheets. We also found that the thickness of the nanosheets increased by increasing the density of the oleylsulfate monolayers. With a denser anionic monolayer, there would be more Zn^{2+} cations in the Stern layer to screen the electric field formed by the anionic monolayer, providing more precursors for the growth of nanosheets. Therefore, the nanosheets formed in the Zn^{2+} -concentrated zone were thicker.

Discussion

While phase transformations from amorphous films to single-crystalline nanosheets have been seen in literature,[397, 398] the transformation to ultrathin 2D nanostructures in the scale of tens of microns is unprecedented. We believe that the densely packed anionic monolayer of oleylsulfate at the water-air interface has not only stimulated the growth of large, amorphous ZnO films but has also directed the crystallization process of ZnO nanosheets across a large 2D scale. This multistep process began when the anionic monolayer created a negative surface potential that

raised the concentration of Zn^{2+} near the monolayer, resulting in the initial formation of the amorphous films described in Figure 25a. As the amorphous ZnO film began to crystallize, the individual ZnO crystallites would align themselves and merge into larger crystalline nanosheets. The driving force of such a long-range self-alignment is expected to be the combined effect of the strong association between the oleylsulfate head groups and the Zn^{2+} ions below, and the van der Waals interaction among the hydrocarbon tails. Calculations of the electrical potential and Zn^{2+} ion concentration within the vicinity of the interface agree well with the observed ZnO film thickness.

3.2 Semiconductor/Ferroelectric Insulator/Solution

The performances of heterojunction-based electronic devices are extremely sensitive to the interfacial electronic band structure. Here we report a largely enhanced performance of photoelectrochemical (PEC) photoanodes by ferroelectric polarization-endowed band engineering on the basis of $\text{TiO}_2/\text{BaTiO}_3$ core/shell nanowires (NWs). Through a one-step hydrothermal process, a uniform, epitaxial, and spontaneously poled barium titanate (BTO) layer was created on single crystalline TiO_2 NWs. Compared to pristine TiO_2 NWs, the 5 nm BTO-coated TiO_2 NWs achieved 67% photocurrent density enhancement. By numerically calculating the potential distribution across the $\text{TiO}_2/\text{BTO}/\text{electrolyte}$ heterojunction and systematically investigating the light absorption, charge injection and separation properties of TiO_2 and TiO_2/BTO NWs, the PEC performance gain was proved to be a result of the increased charge separation efficiency induced by the ferroelectric polarization of the BTO shell. The ferroelectric polarization could be switched by external electric field poling and yielded PEC performance gain or loss based on the direction of the polarization. This study evidences that the piezotronic effect (ferroelectric or piezoelectric

potential-induced band structure engineering) holds great promises in improving the performance of PEC photoelectrodes in addition to chemistry and structure optimization.

Hydrogen production from photoelectrochemical (PEC) water splitting is a promising pathway for solar energy conversion.[399] To achieve efficient and durable solar to hydrogen conversion, PEC photoelectrodes desirably need the following characteristics: effective and broad band light absorption, rapid charge separation, and superior stability. Small band gap semiconductors (e.g., silicon and III-IV group of composites) can efficiently absorb light and separate charges.[400, 401] However, they suffer from surface corrosion and passivation during the redox reactions, constraining their life time to hours.[402-404] N-type semiconductor oxides, such as titanium dioxide (TiO_2), hematite (Fe_2O_3), bismuth vanadate (BiVO_4) and tungsten trioxide (WO_3), are popular candidates for constructing robust photoanodes due to their excellent chemical stability.[368, 405-410] The main drawbacks of these oxides are the limited light absorption and poor charge separation efficiency due to their large band gap and high trapping density.[411, 412] There are two predominant strategies to enhance the separation of electron-hole pairs in photoanodes: reducing the crystal size to the scale of the hole diffusion length; and increasing the carrier conductivity by morphology and crystallography control. Nevertheless, both strategies are restricted by the limit of synthesis procedures.[405, 413]

Permanent electrical polarization induced by ionic displacement (e.g., ferroelectric and piezoelectric potential) has shown great promises in engineering the interfacial band structure and manipulating the charge transfer property of heterostructures.[414-418] When a ferroelectric material is involved in a heterojunction, its electrical polarization would induce considerable free carrier redistribution in the adjacent semiconductor. As a consequence, the magnitude and width of depletion region in the semiconductor can be effectively tuned towards favorable direction.[417]

A variety of studies have evidenced the effectiveness of implementing ferroelectric polarization to adjust the performance of semiconductor devices. For example, ferroelectric polymer was employed to facilitate the charge separation in organic photovoltaics, and thus improved the overall cell efficiency.[414] Coupling the ferroelectric materials to field-effect transistors enabled the ferroelectric polarization gating effect.[415] Ferroelectric polarization was also found to be able to tune certain electrochemical reactions (e.g. degradation of rhodamine B, ethylene, congo red, methyl orange and methyl blue) on bulk ferroelectric surfaces (e.g. barium titanate (BTO), lead zirconate titanate (PZT) and bismuth ferrite (BFO)) decorated with photoactive materials.[416, 419-421] PEC water splitting is a similar electrochemical system driven by energy discontinuity at the electrode/electrolyte interface. One can expect positive (maybe significant) performance gain when ferroelectric polarization is appropriately introduced to such a system. However, the high dielectric constant and insulating nature of typical ferroelectric materials exclude them from the applications involving charge transport, such as PEC photoelectrodes. In this paper, we report a development of ferroelectric-enhanced PEC photoanode on the basis of TiO_2 /BTO core/shell nanowire (NW) arrays. Through surface converting reaction, a very thin film of BTO was uniformly and epitaxial created on TiO_2 NW surfaces with its [001] direction parallel to the radius direction. The spontaneous electrical polarization on the BTO film increased the band bending of TiO_2 NWs and enhanced the charge generation and separation efficiency, resulting in improved photocurrent density of both water and sodium sulfite (Na_2SO_3) oxidation reactions. This research provided a successful demonstration of the ferroelectric effect in nanostructured heterojunctions as an effective strategy for improving the PEC performance.

The development of TiO_2 /BTO core/shell NWs included two main steps: hydrothermal growth of TiO_2 NWs array and BTO surface conversion. Four different thicknesses of BTO shell

were produced by converting TiO_2 NWs at various reaction temperatures ranging from 150 to 210 °C. Figures 29a-e show the morphology of TiO_2 NWs array and the four TiO_2 /BTO core/shell NWs heterostructures. The average length and diameter of TiO_2 NWs were $\sim 1.6 \mu\text{m}$ and $\sim 100 \text{ nm}$, respectively (Figure 29a). After converting TiO_2 NWs to BTO at 150 °C for 2 h, the NW morphology was well preserved and no surface roughness could be observed from the SEM image (Figure 29b). When the reaction temperature increased to 170 °C, a number of nanoparticles with diameter of $\sim 250 \text{ nm}$ appeared at the top of TiO_2 NWs, whereas the majority of TiO_2 NW surface remained smooth (Figure 29c). Further raising the reaction temperatures to 190 and 210 °C significantly accelerated the conversion speed and generated numerous BTO nanoparticles, yielding a thick BTO film on TiO_2 NWs (Figure 29d, e). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were performed to characterize the composition and crystallography of TiO_2 NWs before and after BTO conversion (Figure 29f, g). XRD pattern of pristine TiO_2 NWs confirmed the rutile phase of TiO_2 with two diffraction peaks centered at 36.5° and 63.2° , corresponding to the (101) and (002) planes of rutile TiO_2 (JCPDS No. 88-1175). For 150 °C TiO_2 /BTO sample, a small peak of tetragonal BTO (31.6° , JCPDS No. 05-0626) appeared. With the rising of reaction temperatures, the intensity of tetragonal BTO peaks drastically increased; while the rutile TiO_2 peaks gradually diminished, evidencing the evolving of BTO with the consumption of TiO_2 . The BTO evolution trend was further confirmed by XPS spectra shown in Figure 29g, where the signature peaks of Ba emerged at 150 °C TiO_2 /BTO NWs and kept increasing following the increment of reaction temperatures.

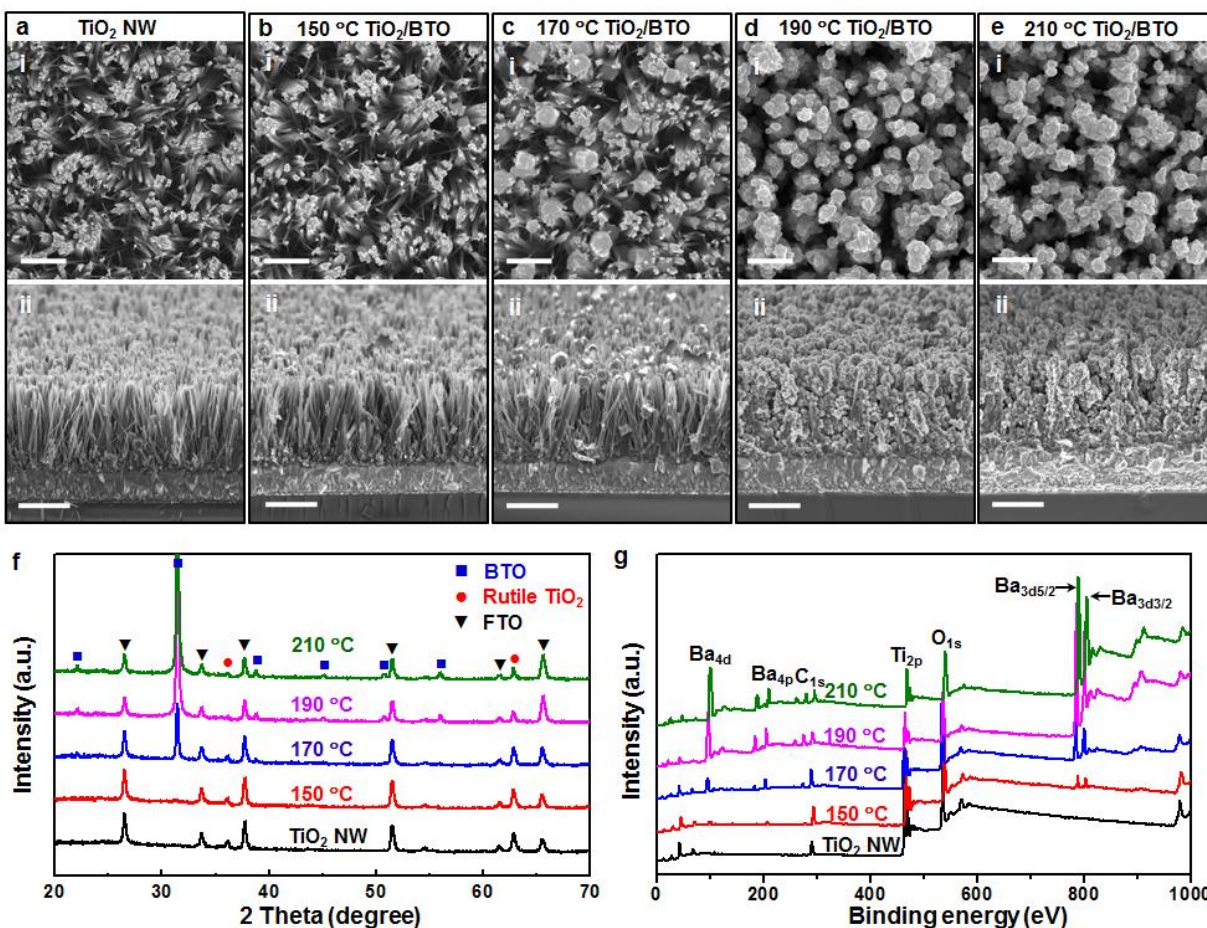


Figure 29. Morphology and composition characterizations of pristine TiO₂ NWs and TiO₂/BTO core/shell NWs. (a-e) Top-view (i) and 15° tilted cross-sectional (ii) SEM images of the TiO₂ NWs (a) and TiO₂/BTO NWs with different conversion temperatures: (b) 150 °C, (c) 170 °C, (d) 190 °C, (e) 210 °C. Scale bars are 500 nm for i and 1 μm for ii. (f) X-ray diffraction patterns and (g) X-ray photoelectron spectra of TiO₂ NWs and TiO₂/BTO core-shell NWs.[352]

TiO₂/BTO core/shell structure was further investigated by transmission electron microscopy (TEM). The 150 °C TiO₂/BTO NW sample was characterized as shown in Figure 30a. Low magnification TEM image illustrates a conformal core/shell NW with a smooth surface (Figure 30b). High resolution TEM (HRTEM) image revealed the good lattice match of the core/shell structure (Figure 30c). The BTO/TiO₂ interface was fairly coherent. The BTO shell thickness was measured to be 5 nm, which was above the critical thickness (~2.4 nm) for BTO to show ferroelectricity.[422] The BTO shell thickness and surface roughness increased at elevated

conversion temperatures. A maximum BTO thickness of approximately 40 nm was obtained at 210 °C (Figure 30). The lattice spacing of core NW was measured to be 0.32 nm and 0.29 nm, matching well with the (110) and (001) plane of rutile TiO_2 , respectively. Based on the HRTEM and fast Fourier transform (FFT) pattern (inset of Figure 30c), the lattice spacing of the shell was measured to be 0.20 nm, corresponding to the (002) plane of tetragonal BTO. This observation evidenced that the c-axis (i.e., ferroelectric polarization direction) of BTO was perpendicular to the TiO_2 surface. Selected area electron diffraction (SAED) pattern (Figure 32) further confirmed that the (220) and (002) planes of the BTO shell were parallel to the (001) and (110) planes of the TiO_2 core, respectively. A reverse filtered FFT image was constructed from the selected (002) and (00-2) diffraction spots of BTO (as circled in the inset of Figure 30d). The bright contrasts in Figure 30d represented the BTO phase. The image revealed that BTO was predominately distributed along the TiO_2 surface and its c-plane oriented single crystal structure was also confirmed. The electron energy loss spectroscopy (EELS) elemental mapping under scanning transmission electron microscopy (STEM) mode (Figure 30e) revealed the spatial element distributions of Ba, Ti, and O along an individual core/shell NW (Figure 30f-h). Ba and O were concentrated at the NW edge; while Ti was uniformly distributed along the entire NW. The element distribution was in good agreement with the TiO_2 /BTO core/shell configuration.

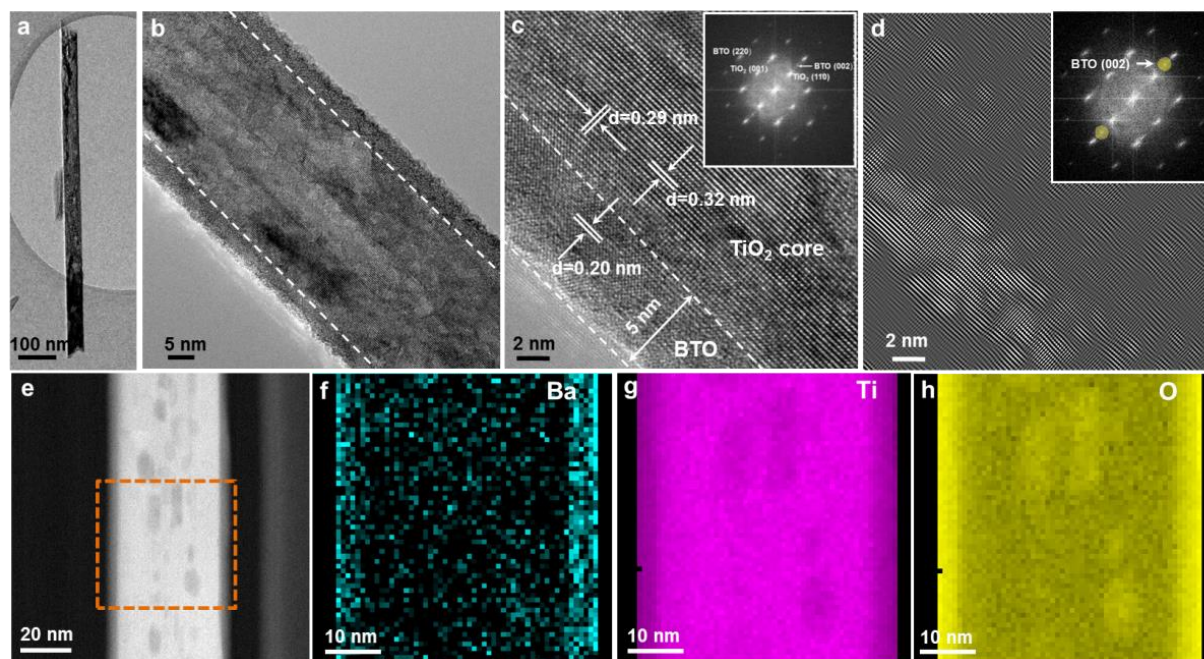


Figure 30. Crystallography and elemental characterizations of TiO_2/BTO core-shell NWs. (a, b) Representative TEM images and (c) High-resolution TEM image of an individual TiO_2/BTO NW synthesized at 150 °C. Inset is the corresponding FFT image. (d) Selected inverse FFT image obtained from the marked FFT spots in the inset, which corresponds to (002) and (00-2) planes of BTO. The bright area represents the BTO composition. (e) STEM image of the TiO_2/BTO NWs. (f-h) EELS elemental mapping of the dashed-square marked region in Figure 2e for (f) Ba, (g) Ti and (h) O. [352]

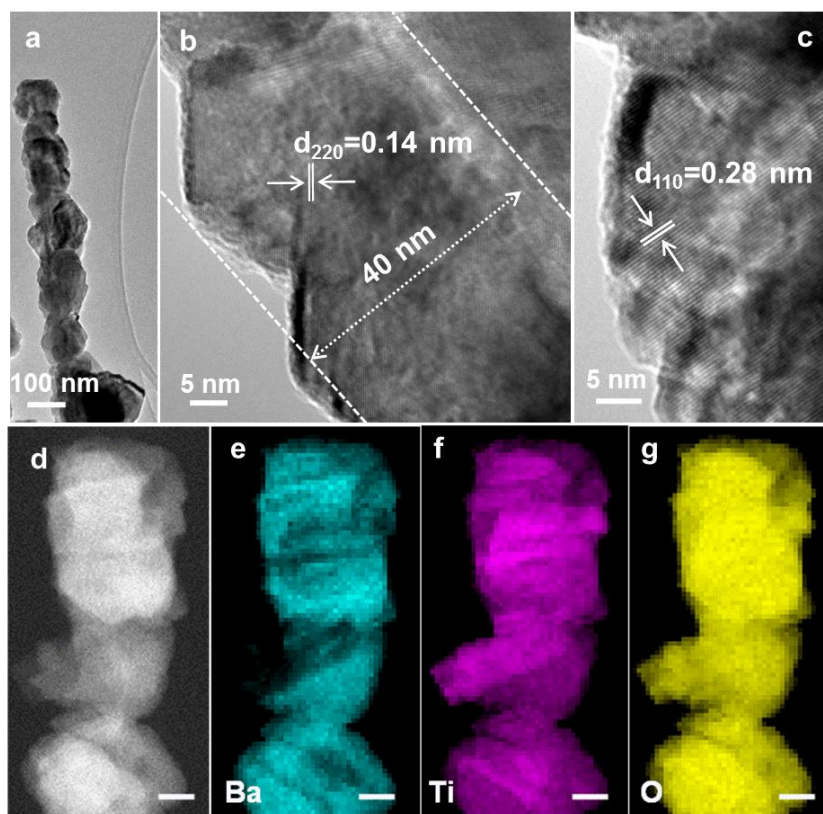


Figure 31. Structure and elemental characterizations of 210 °C TiO₂/BTO core/shell NWs. (a) Representative TEM image and (b, c) high-resolution TEM images of a 210 °C TiO₂/BTO core/shell NWs. The BTO shell thickness was measured to be ~40nm. A lattice spacing of 0.28 nm in the shell corresponds to the (110) plane of tetragonal BTO. (d) STEM image of a 210 °C TiO₂/BTO core/shell NW. (e-g) EELS elemental mapping images for Ba (e), Ti (f) and O (g), respectively. Scale bars are 20 nm.[352]

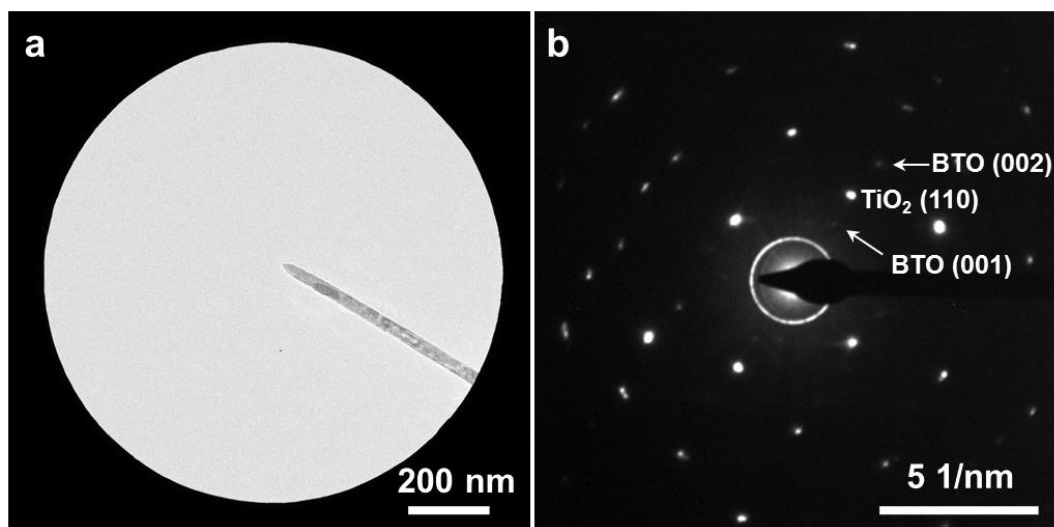


Figure 32. (a) TEM image of an individual 150 °C TiO₂/BTO core/shell NW. (b) Corresponding selected area electron diffraction (SAED) pattern, showing the perpendicular c-axis of TiO₂ and BTO. [352]

PEC performance of TiO₂ NWs and TiO₂/BTO core/shell NWs were first evaluated in 1M sodium hydroxide (NaOH) solution with an exposed photoactive area of 0.1 cm² under one sun illumination. Figure 33a shows the photocurrent density-potential (J_{ph} -V) curve of pristine TiO₂ NWs and TiO₂/BTO NWs. J_{ph} of water oxidation from the TiO₂ NWs was 0.78 mA/cm² at 1.23 V versus the reversible hydrogen electrode (RHE), which was comparable to previous reports.[423, 424] 150 and 170 °C TiO₂/BTO NWs with thin BTO shells yielded markedly higher J_{ph} of 1.30 and 1.14 mA/cm² at 1.23 V versus RHE, corresponding to 67% and 46% improvements over pristine TiO₂ NWs, respectively. When the BTO shell thickness increased by raising the reaction temperatures to 190 and 210 °C, J_{ph} decreased to 0.81 and 0.74 mA/cm² at 1.23 V versus RHE, respectively. Different from J_{ph} , the onset potential exhibited an opposite trend in response to BTO shell thickness variation, *i.e.*, thicker BTO shell offered more negative onset potential. As shown in Figure 33b, the specific onset potentials determined by the chronopotentiometric measurements were 204, 186, 176, 77 and -38 mV versus RHE for TiO₂ NWs and 150-210 °C TiO₂/BTO NWs,

respectively. The onset potential variation revealed that thicker BTO shell yielded more negative flat-band potential (E_{FB}), agreeing with the reported E_{FB} of BTO that was ~ 50 mV more negative than that of rutile TiO_2 . [425]

Theoretically, J_{ph} is governed by the relation (2.50):

$$J_{ph} = J_{abs} \times \eta_{separation} \times \eta_{injection} \quad (2.50)$$

where J_{abs} is the photocurrent density at 100% internal quantum efficiency; $\eta_{separation}$ is the photogenerated electron-hole separation efficiency for producing surface-reaching holes; $\eta_{injection}$ is efficiency of surface-reaching holes participating in desired electrochemical reactions. [405, 426] To understand the J_{ph} improvement, the light absorption property, charge separation and injection efficiencies of TiO_2 NWs and TiO_2/BTO NWs were systemically studied.

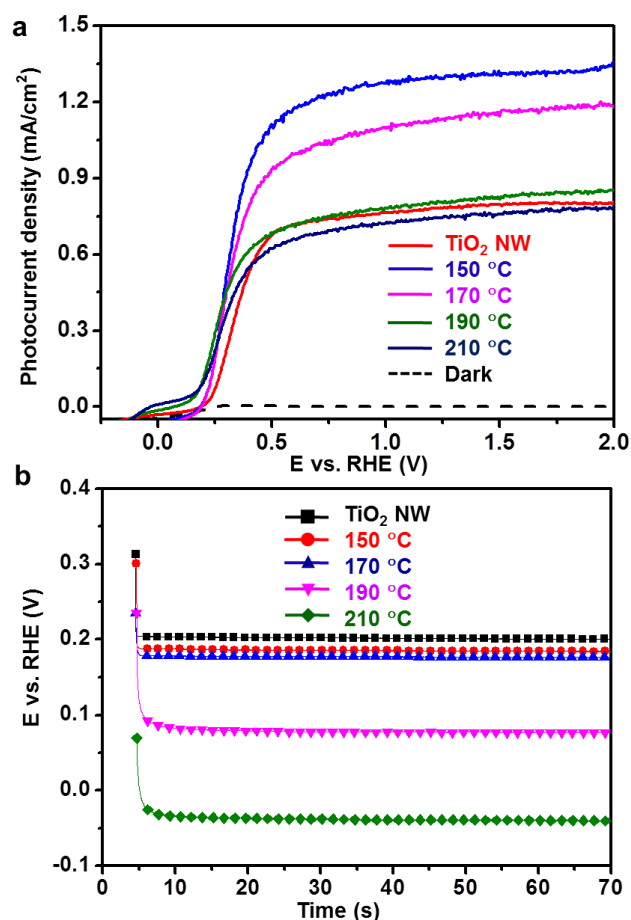


Figure 33. PEC water oxidation performance of TiO₂ NWs and TiO₂/BTO NWs. (a) Photocurrent density-potential (J - V) curves of TiO₂ NWs and 150-210 °C TiO₂/BTO NWs measured in 1 M NaOH electrolyte under AM1.5 G illumination with intensity of 100 mW/cm² (one sun). (b) Chronopotentiometric curves of TiO₂ NWs and 150-210 °C TiO₂/BTO NWs measured in 1 M NaOH electrolyte under AM1.5 G illumination with a constant current of zero, showing their onset potentials were 204, 186, 176, 77 and -38 mV, respectively.[352]

The UV-visible light-absorption spectra for the TiO₂ NWs and TiO₂/BTO NWs were obtained first (Figure 34a). Although these samples exhibited slightly different light absorption spectra, the integrated light absorption values over 300-420 nm did not show appreciable differences, which can be attributed to the similar light absorption coefficients of rutile TiO₂ and BTO.[427] By integrating the absorbance across the AM 1.5G solar spectrum, J_{abs} (i.e. the maximum achievable electron flux at the photoanodes) were calculated to be 1.57, 1.57, 1.63, 1.58

and 1.67 mA/cm^2 for the five TiO_2 and TiO_2/BTO samples (see Figure 34b-d for calculation details). The variation of these values is substantially smaller than the observed J_{ph} variation. Therefore, light absorption should not be the main reason of PEC performance improvements.

PEC sulfite oxidation was thermodynamically and kinetically more favorable than water oxidation, which can be considered as a hole scavenger.[405, 428-430] $\eta_{injection}$ of TiO_2 NWs and TiO_2/BTO NWs can be determined by comparing their PEC performance of water and sulfite oxidation ($\eta_{injection} = J_{PEC}/J_{sulfite}$). The experiments were conducted in a 0.5 M phosphate buffer solution containing 1 M sodium sulfite (pH=7) under one sun illumination. Figures 34a-d compares the J_{ph} -V curves of sulfite oxidation and water oxidation using TiO_2 NWs and TiO_2/BTO NWs photoanodes. In general, the variation of J_{ph} for sulfite oxidation followed the same trend as water oxidation. 150 and 170 °C TiO_2/BTO NWs achieved significantly higher J_{ph} for sulfite oxidation over pristine TiO_2 NWs (Figure 34a, b). With the increase of BTO conversion temperature, J_{ph} for sulfite oxidation of TiO_2/BTO NWs decreased accordingly (Figure 34c, d). The J -V curves of the 190 and 210 °C TiO_2/BTO NW photoanodes showed negligible difference in their sulfite oxidation and water oxidation PEC reactions.

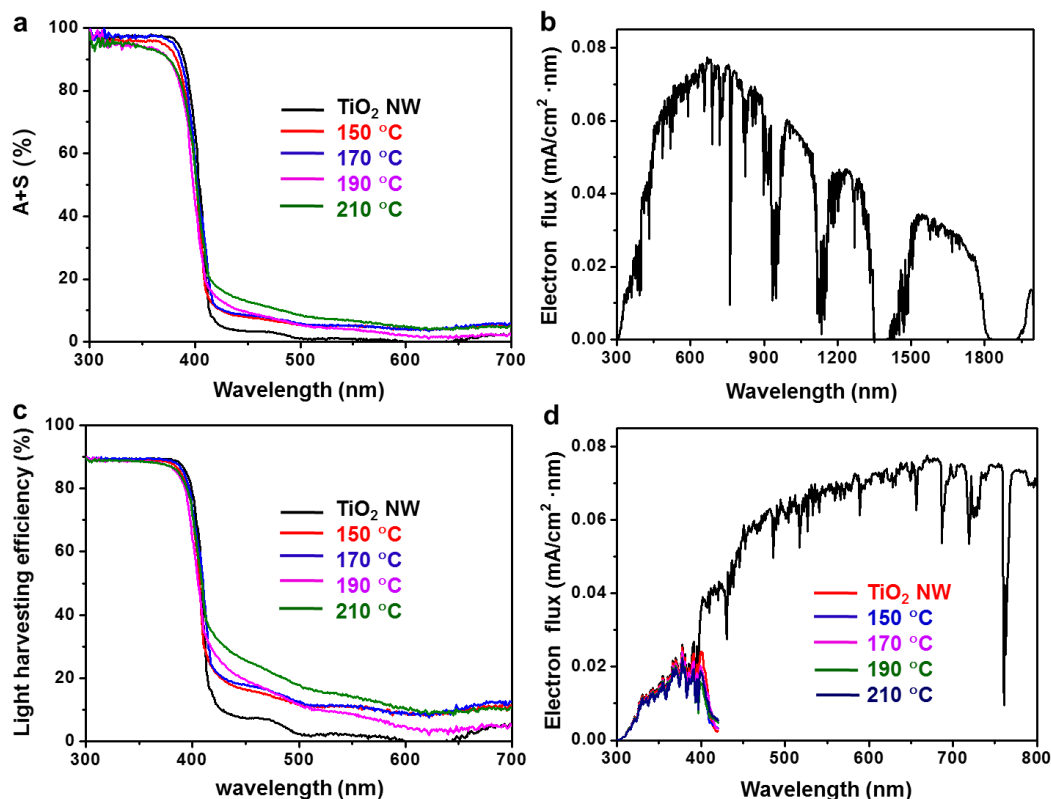


Figure 34. (a) UV-visible absorption of TiO₂ NWs and TiO₂/BTO core/shell NWs with different conversion temperatures (150-210 °C). Absorption (A) + scattering (S) = 100 – transmittance (T) – reflectance (R). The integrated light absorption (plus scattering) values over 300-420 nm were 84.5%, 81.9%, 84.6%, 80.0% and 81.7% for the TiO₂ NWs and TiO₂/BTO core/shell NWs with the conversion temperature of 150-210 °C, respectively. (b) Electron flux of AM 1.5G solar spectrum. (c) The light harvesting efficiencies (η_{LHE}) of TiO₂ NWs and TiO₂/BTO NWs with different conversion temperatures (150-210 °C). η_{LHE} was calculated from the absorbance data (η_{ABS}) shown in Figure S2a: $\eta_{LHE} = (1 - 10^{-\eta_{ABS}}) \times 100\%$. (d) Electron flux of the TiO₂ NWs and four TiO₂/BTO NWs photoanodes. The electron flux of photoanode was the product of the AM 1.5G electron flux and η_{LHE} . Photocurrent density (J_{abs}) under 100% absorbed photon conversion efficiency can be estimated by integrating the electron flux at the photoanodes across 300-420 nm wavelength range.[352]

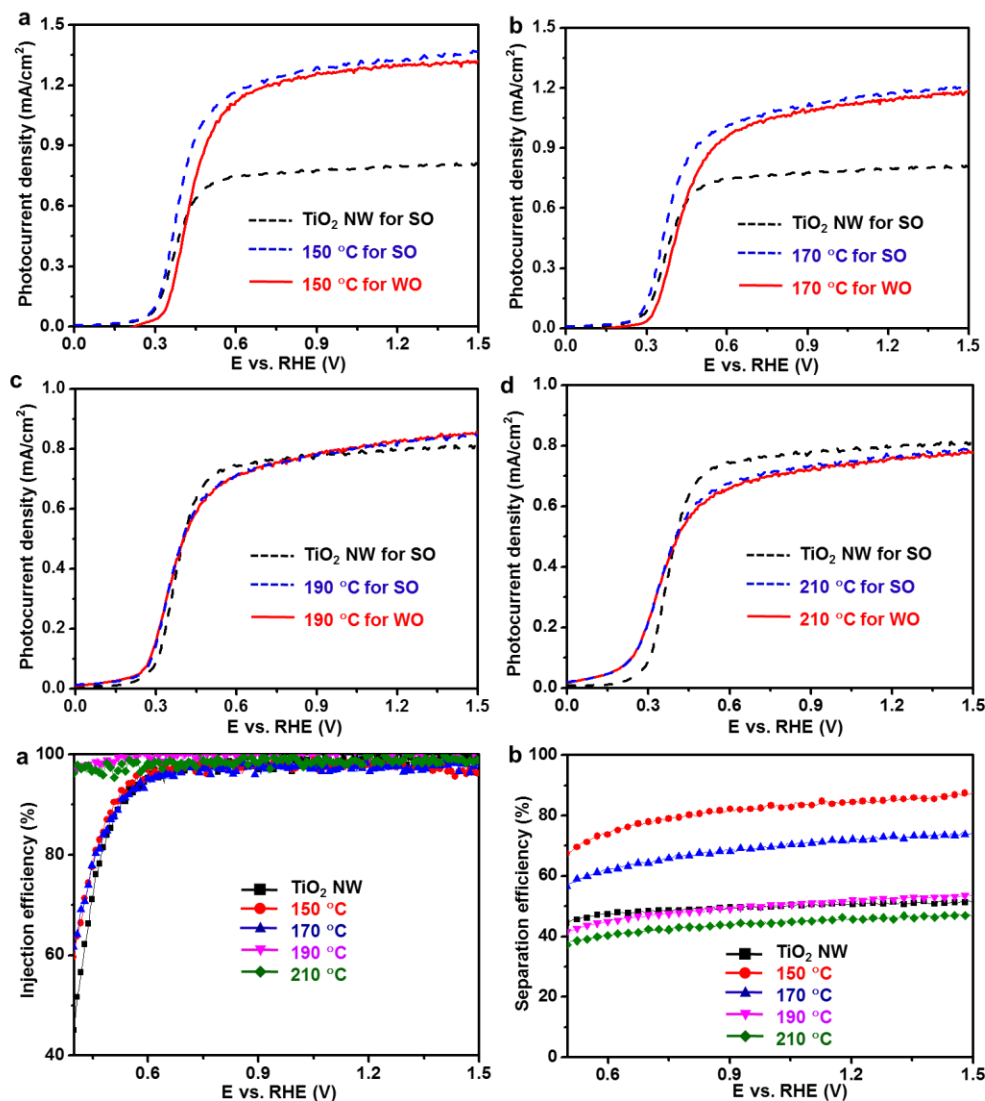


Figure 35. Sulfite oxidation (SO), water oxidation (WO), charge separation and injection properties of TiO₂ NWs and TiO₂/BTO NWs. (a-d) *J-V* curves of the TiO₂/BTO NWs converted at (a)150 °C, (b)170 °C, (c)190 °C and (d) 210 °C for WO (solid line) measured in 0.5 M phosphate buffer (pH=7) and SO (dashed line) measured in 0.5 M phosphate buffer with 1 M Na₂SO₃ (pH=7) as the hole scavenger under one sun illumination. *J-V* curves of TiO₂ NWs for SO (black dashed line) were included as the comparison. (e) Efficiency of charge injection from the photoanodes to the electrolyte for WO. (f) Efficiency of charge separation inside the photoanodes.[352]

Based on the measured photocurrent density, $\eta_{injection}$ was calculated and illustrated in Figure 35e and Figure 36a. The 190 and 210 °C TiO₂/BTO NWs exhibited notably higher $\eta_{injection}$ than the TiO₂ NWs within the low bias region (<0.7 V versus RHE). Approximately 100% of

$\eta_{injection}$ can be obtained with the 190 and 210 °C TiO₂/BTO NWs over the entire potential window. This reflected the beneficial nature of the highly-crystalline BTO shell surface that can facilitate the efficient interfacial charge injection from BTO surface to the electrolyte. At high bias region (>0.7 V versus RHE), $\eta_{injection}$ of both TiO₂ NWs and TiO₂/BTO NWs approached 100%, suggesting $\eta_{injection}$ had little contribution to the J_{ph} enhancement at high bias region.

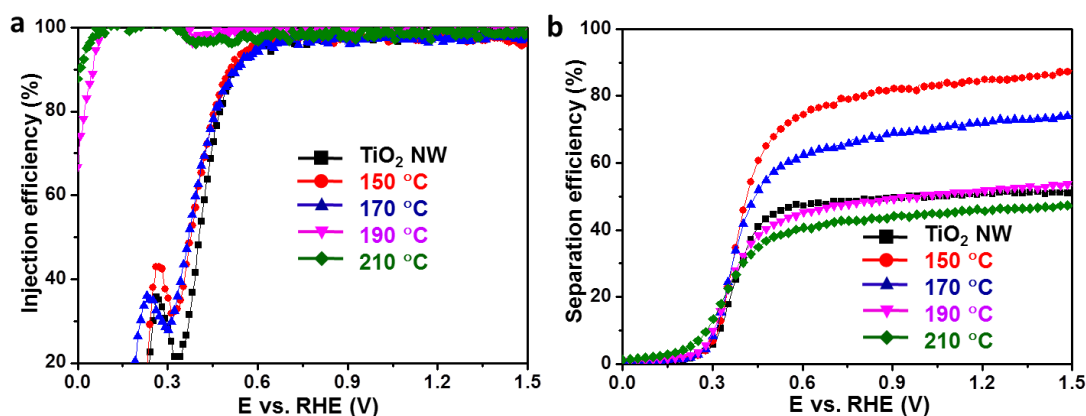


Figure 36. (a) Efficiency of charge injection from the photoanodes to the electrolyte within the full bias window. (b) Efficiency of charge separation inside the photoanodes within the full bias window.[352]

Similarly, $\eta_{separation}$ can be determined by comparing the photocurrent density of sulfite oxidation and maximum electron flux calculated from light absorption ($\eta_{separation} = J_{sulfite}/J_{abs}$). As shown in Figure 35f and Figure 36b, substantially higher $\eta_{separation}$ were identified from the 150 and 170 °C TiO₂/BTO NW photoanodes, which were 84.8% and 72.0% at 1.23 V versus RHE, 1.67 and 1.41 times higher than that of TiO₂ NW (50.9%). As for the two thicker BTO samples (190 and 210 °C conversion), $\eta_{separation}$ dropped to 51.9% and 41.7%, which was 1.02 times higher and 0.82 times lower than that of TiO₂ NW, respectively. All the change ratios of $\eta_{separation}$ matched well to the J_{ph} variation shown in Figure 33a, suggesting $\eta_{separation}$ would be the predominant factor responsible for J_{ph} enhancement.

Considering the magnitude and width of the depletion region is a significant factor that controls $\eta_{separation}$ in semiconductor heterojunction-based systems, the remarkably improved PEC performance was most likely a result of the ferroelectric polarization-induced interfacial electronic band structure shifting by the BTO shell. The potential distributions across the TiO_2/NaOH solution and $\text{TiO}_2/5\text{-nm BTO}/\text{NaOH}$ solution heterojunction were calculated numerically (Figure 37a). When the spontaneous polarization in BTO appears negative at the BTO/ TiO_2 interface (*i.e.* positive polarization), it can induce upward band bending and increase the width of the depletion region in TiO_2 . Such a change of the interfacial band structure facilitates the separation of photo-generated electron-hole pairs, and thus leads to the improved $\eta_{separation}$ and PEC performance. Since the thickness of BTO shell was as thin as 5 nm for 150 °C TiO_2/BTO NWs, the photogenerated holes could tunneling through the shell disregard the opposite electrical field inside BTO.[431, 432] Compared to the 150 °C sample, the relatively lower J_{ph} of the 170 °C TiO_2/BTO NWs might be a result of the slightly increased BTO shell thickness, which impaired the tunneling efficiency of holes. The much thicker BTO shells (~40 nm, Figure S1) in the higher temperature samples and the relatively high resistance of BTO would substantially hinder hole transport from the TiO_2 core and J_{ph} would mostly be contributed by the light absorption from BTO itself. Under this circumstance, the spontaneous ferroelectric polarization inside BTO was expected to impose opposite effect to charge separation. As shown in Figure 37b, positive polarization at the BTO/ TiO_2 interface becomes favorable for driving photo-generated holes towards the electrolyte to complete the PEC reaction. Nevertheless, the poor electronic property of BTO yielded an even lower $\eta_{separation}$ and J_{ph} compared to the pristine TiO_2 NW photoanodes.

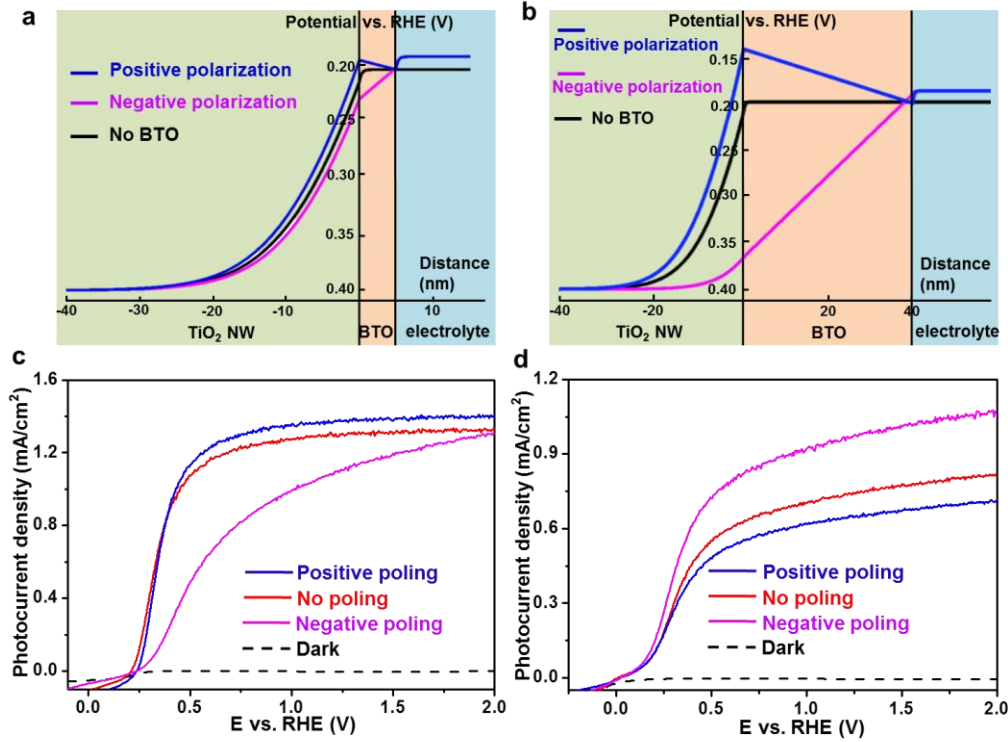


Figure 37. Calculated potential distribution and electric poling test of the ferroelectric enhancement. (a) Potential distribution of 150 °C TiO₂/5-nm BTO/NaOH heterojunction, where the spontaneous polarization in BTO shell induced an upward band bending of TiO₂ core and facilitated the charge separation and transportation inside TiO₂. (b) Potential distribution of the 210 °C TiO₂/40-nm BTO/NaOH heterojunctions, showing a strong electric field inside BTO, which facilitates the hole transport towards solution. (c) *J-V* curves of the as-prepared (red), positively poled (blue) and negatively poled (magenta) 150 °C TiO₂/BTO NWs. (d) *J-V* curves of the as-prepared (red), positively poled (blue) and negatively poled (magenta) 210 °C TiO₂/BTO NWs.[352]

Calculation details:

From electrostatics, the Poisson equation describes how the charge density at location x ($\rho(x)$) is influenced by the potential at location x ($V(x)$):

$$\frac{d^2V(x)}{dx^2} = \frac{-\rho(x)}{\epsilon_0\epsilon_r} \quad (2.51)$$

Where ϵ_0 and ϵ_r are the electrical permittivity of vacuum and the medium inhabited by the charge, respectively. $V(x)$ can be solved for all x by twice integrating $\rho(x)$, but we first must get ρ as a function of $V(x)$.

In the TiO₂ semiconductor, the charge density is comprised of mobile electrons and holes as well as the immobile charged atoms that we attribute to dopant atoms:

$$\rho_{TiO_2}(x) = (z_n)(n(x)) + (z_p)(p(x)) + z_d Nd_{TiO_2} \quad (2.52)$$

Where z_n , z_p and z_d are the charge of an electron (-1), hole (1) and dopant atom (1) in TiO₂, respectively, and $n(x)$, $p(x)$ and Nd_{TiO_2} are the charge density of electrons, holes, and dopant atoms, respectively.

The charge density of electrons and holes varies with position because the electrical potential (relative to bulk potential in TiO₂) varies as x approaches the heterojunction.

In both semiconductors and solutions, the ratio of concentration of charged species i in bulk (n_i^0) at bulk potential ($\phi^0=0$) to its concentration (n_i) found at any other potential (ϕ) is taken to depend upon the Boltzmann factor in the following way (equation (2.53)):

$$n_i = n_i^0 e^{\left(\frac{-z_i e \phi(x)}{kT}\right)} \quad (2.53)$$

where z_i is the charge of ion i , and e is the charge of the electron, ϕ is the potential relative to bulk solution, x is a measure of distance into solution and perpendicular to the monolayer surface, k is the Boltzmann constant, and T is temperature in Kelvin.

Combining equation (2.52) and (2.53) results in the following expression for charge density in the semiconductor:

$$\rho_{TiO_2}(x) = (z_n)(n_b) e^{\frac{(z_n)V(x)e}{kT}} + (z_p)(p_b) e^{\frac{(z_p)V(x)e}{kT}} + z_d Nd_{TiO_2} \quad (2.54)$$

Where n_b and p_b are the bulk concentrations of electrons and holes, respectively.

Applying this same treatment to the liquid solution medium, where H^+ , OH^- and Na^+ ions comprise the charge density, yields the following expression for the charge density in the aqueous medium:

$$\rho_{H_2O}(x) = (z_{H^+})(H^+_b)e^{\frac{(z_{H^+})V(x)e}{kT}} + (z_{OH^-})(OH^-_b)e^{\frac{(z_{OH^-})V(x)e}{kT}} + (z_{Na^+})(Na^+_b)e^{\frac{(z_{Na^+})V(x)e}{kT}} \quad (2.55)$$

Where z_{H^+} , z_{OH^-} and z_{Na^+} are the charge of hydronium (1), hydroxyl (-1) and sodium (1) ions, respectively, and H^+_b , OH^-_b and Na^+_b are the bulk concentrations of hydronium, hydroxyl and sodium ions in solution, respectively.

Equations (2.54) and (2.55) can be combined with equation (2.51) to yield the following expressions that describe how potential and charge density are interrelated in both the H₂O and TiO₂:

$$\text{In the Semiconductor: } \frac{d^2V}{dx^2} = \frac{-((z_n)(n_b)e^{\frac{(z_n)V(x)e}{kT}} + (z_p)(p_b)e^{\frac{(z_p)V(x)e}{kT}} + z_dNd_{TiO_2})}{\epsilon_0\epsilon_r} \quad (2.56)$$

$$\text{In the Solution: } \frac{d^2V}{dx^2} = \frac{-((z_{H^+})(H^+_b)e^{\frac{(z_{H^+})V(x)e}{kT}} + (z_{OH^-})(OH^-_b)e^{\frac{(z_{OH^-})V(x)e}{kT}} + (z_{Na^+})(Na^+_b)e^{\frac{(z_{Na^+})V(x)e}{kT}})}{\epsilon_0\epsilon_r} \quad (2.57)$$

To solve these second order differential equations requires two boundary conditions for each expression.

In the semiconductor, the boundary conditions are as follows:

1. The electric field ($\frac{dV}{dx}$) in the bulk of the TiO₂ is zero.

$$\left(\frac{dV}{dx}\right)_{x=-\infty} = 0 \quad (2.58)$$

2. The electrical potential in the bulk is equal to the Fermi level of TiO₂ ($V_{EF_{TiO_2}}$)

$$V_{x=-\infty} = V_{EF_{TiO_2}} \quad (2.59)$$

In the solution phase, the boundary conditions are similar:

1. The electric field ($\frac{dV}{dx}$) in the bulk of H₂O is zero.

$$\left(\frac{dV}{dx}\right)_{x=\infty} = 0 \quad (2.60)$$

2. The electrical potential in the bulk is equal to the Fermi level of H₂O ($V_{EF_{H_2O}}$).

$$V_{x=\infty} = V_{EF_{H_2O}} \quad (2.61)$$

Applying boundary conditions (2.58) and (2.59) to expression (2.56) during integration yields the following expression for the potential gradient in the TiO₂:

$$\frac{dV_{TiO_2}}{dx} = \sqrt{-\frac{2kT}{\epsilon_0\epsilon_{TiO_2}} \left[\left(n_b \left(e^{\frac{z_n V_e}{kT}} \right) - 1 \right) + \left(p_b \left(e^{\frac{z_p V_e}{kT}} \right) - 1 \right) + \frac{z_{Nd} N_{dTiO_2} V_e}{kT} \right]} \quad (2.62)$$

Applying boundary conditions (2.60) and (2.61) to expression (2.57) during integration yields the following expression for the potential gradient in the H₂O:

$$\frac{dV_{H_2O}}{dx} = \sqrt{-\frac{2kT}{\epsilon_0\epsilon_{H_2O}} \left[\left((H^+_b) \left(e^{\frac{(z_{H^+}) V_e}{kT}} \right) - 1 \right) + \left((OH^-_b) \left(e^{\frac{(z_{OH^-}) V_e}{kT}} \right) - 1 \right) + \left((Na^+_b) \left(e^{\frac{(z_{Na^+}) V_e}{kT}} \right) - 1 \right) \right]} \quad (2.63)$$

Up to this point, the derivation of the potential profile in the ZnO (equation (2.62)) and H₂O (equation (2.63)) have remained independent from one another. To join the two expressions, we make use of two conditions: 1) the potential profile is continuous, and 2) charge is conserved.

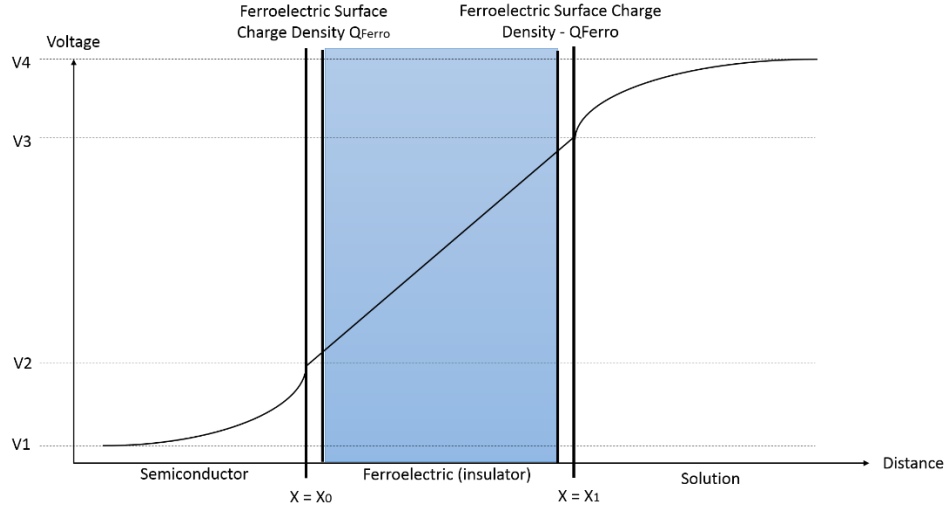


Figure 38: Electrical potential profile through a typical semiconductor/insulator/solution junction.[352]

The electrical potential profile through a typical semiconductor/insulator/solution junction (Figure 38) is nonlinear in the semiconductor and solution within the vicinity of the interfaces because the charge density within these regions are non-uniform. There are no free charges inside the insulator and thus the electric field is constant, resulting in a linear potential profile.

At a heterojunction under no external bias, the net charge density ($\frac{C}{m^2}$) in the semiconductor (equivalent to surface charge density Q_{TiO_2}) is equal and opposite to the charge density ($\frac{C}{m^2}$) in the solution (equivalent to surface charge density Q_{H_2O}). Because the charge densities are equal at the interface, the electric field ($\frac{dV}{dx}$) at the semiconductor and solution interface must be equal:

$$\left(\frac{dV_{TiO_2}}{dx}\right)_{x=X_0} = \left(\frac{dV_{H_2O}}{dx}\right)_{x=X_1} \quad (2.64)$$

This expression stitches together the physical processes described by expression (2.62) and (2.63). In order to combine the potential profiles generated for the semiconductor (equation (2.62)) and solution (equation (2.63)), generated by solving equation (2.64), into a cohesive diagram, it is necessary to account for the electrical potential gradient within the insulating layer.

The potential shift across an insulator (V2-V3) is equal to the electric field within the insulator (a constant) multiplied by the distance over which the electric field travels (the insulator thickness: X1-X0):

Voltage drop in the Insulator

$$= V2 - V3 = \frac{Q_{H2O}(X1-X0)}{\epsilon_0 \epsilon_{Insulator}} = \frac{-Q_{TiO2}(X1-X0)}{\epsilon_0 \epsilon_{Insulator}} \quad (2.65)$$

where $\epsilon_{Insulator}$ is the relative permittivity of the insulating layer. ***When a ferroelectric materials is used for the insulating layer, a remnant electrical polarization within the ferroelectric will alter the electric field present within the insulating layer, deviating the voltage drop from the equation (2.65).*** The remnant polarization contributes equal and opposite surface charge densities (Q_{Ferro}) to both surfaces:

Voltage drop in the Insulator

$$= V2 - V3 = \frac{(Q_{H2O}+Q_{Ferro})(X1-X0)}{\epsilon_0 \epsilon_{Insulator}} = \frac{-(Q_{TiO2}-Q_{Ferro})(X1-X0)}{\epsilon_0 \epsilon_{Insulator}} \quad (2.66)$$

Depending on the sign of the charges in the semiconductor and solution medium, and direction of the remnant polarization within the ferroelectric insulator, Q_{Ferro} may act to increase or decrease the field within the insulator caused by Q_{TiO2} and Q_{H2O} (e.g. Figure 37a and 37b).

Checking for physically reasonable values

At every step of the calculation, the properties of the physical environment were checked to ensure that physically reasonable quantities were being produced. A particularly concerning value is the density of charged species in solution at the insulator/solution interface, care needs to be taken to ensure this density does not exceed atomic density of a condensed phase.

To calculate the maximum charge densities we could physically expect from our model, we modeled the hydrated ions (Na^+ , H^+ , and OH^-) as hard spheres and fit them into the maximum

packing density possible, the close packing structure. Taking OH⁻ ions as an example, each with a hydration diameter (d) of 3.5 Å, the maximum 3D packing density possible is given by:

$$\text{Maximum 3D Density} = \frac{\text{Total ions}}{\text{Volume}} = \frac{\left(\frac{3}{2}\right) + 3 + \left(\frac{3}{2}\right)}{\frac{3\sqrt{3}}{2}a^2c} = \frac{6}{\frac{3\sqrt{3}}{2}(d^2)(2d\sqrt{\frac{2}{3}})} = 3.29846 * 10^{28} \frac{\text{ions}}{\text{m}^3} \quad (2.67)$$

Thus, the total of all ion concentrations at the closest approach to the interface must be approximately equal to or less than this atomic density.

$$n_{\max} \leq 3.29846 * 10^{28} \frac{\text{ions}}{\text{m}^3} \quad (2.68)$$

Summing up the concentration of all hydrated ions in solution at the interface means summing up the value from equation (2.53) for each hydrated ion (Table 2):

$$\sum n_i = \sum n_i^0 e^{\left(\frac{-z_i e \phi (V_3 - V_4)}{kT}\right)} \quad (2.69)$$

Potential Applied to TiO ₂ vs RHE	Thickness of BTO (X ₁ -X ₀)	Polarization of BTO	Potential Drop (V) in Solution (V ₄ -V ₃)	Σ n _i at Solution Interface ($\frac{\text{ions}}{\text{m}^3}$)
0.4V	0	None	-0.0111	1.3205×10^{27}
0.4V	5nm	Positive	-0.0105	1.3094×10^{27}
0.4V	5nm	Negative	-0.0117	1.3345×10^{27}
0.4V	40nm	Positive	-0.0034	1.2154×10^{27}
0.4V	40nm	Negative	-0.0131	1.3684×10^{27}

Table 2: Concentration of solution species as a function of BTO thickness and polarity.[352]

Material Properties Used in our Model:

Potential of bulk TiO₂ vs RHE after potential is applied:

$$((-4.44) + (0.59) * (\text{pH})) + 0.135 - (\text{potential applied vs RHE})$$

Where : $((-4.44) + (0.59) * (\text{pH}))$ accounts for RHE potential shift as a function of pH, 0.135 accounts for the voltage difference between the Fermi level of the TiO₂ we produced in our experiment and those recorded elsewhere from literature[433, 434] and ‘potential applied vs RHE’

is the potential recorded by the potentiostat has having been applied vs RHE (usually chosen as 0.4 for the sake of comparing calculations to experimental data).

Potential of bulk TiO₂ vs RHE before potential is applied:

(Fermi level of TiO₂ with isoelectric surface) + (0.059)*(pH - (pH of Isoelectric point of solution interface))

Where Fermi level of TiO₂ with isoelectric surface is the V vs RHE of the bulk of TiO₂ when it's surface is isoelectric: ((-4.44 - .2444) + (Flat band of TiO₂ at pH vs SCE) + (0.059)*(pH of Isoelectric point of TiO₂)).

Where 'Flat band of TiO₂ at pH vs SCE' is 0.18V[433, 434] and 'pH of Isoelectric point of TiO₂' is 5.2[435] for rutile TiO₂.

The 'Isoelectric point of solution interface' is 5.2 in the case of a TiO₂/Solution interface and 5.0[436] in the case of a TiO₂/BTO/Solution interface.

pH:

Experimental value: 14

Insulator Thickness:

Measured from experiment (Figure 31) 0, 5nm, 40nm.

Temperature:

295.15K

Relative Electrical Permittivity of TiO₂:

160[434]

Relative Electrical Permittivity of BTO:

1500[437]

Relative Electrical Permittivity of H₂O:

80

Bandgap of Rutile TiO₂:

3.02eV[438]

Donor Concentration in TiO₂:

$9 * 10^{18} / \text{cm}^3$ [439]

Bulk Concentration of Electrons in TiO₂:

Donor Concentration in TiO₂

Concentration of Holes in TiO₂:

Mass action with intrinsic electrons

Density of States in the Conduction band of TiO₂:

$1 * 10^{20} / \text{cm}^3$ [440]

Remnant Polarization of BTO:

Measured from experiment (Figure 39): $5 * 10^{-6} \text{ uC}/(\text{cm}^2)$

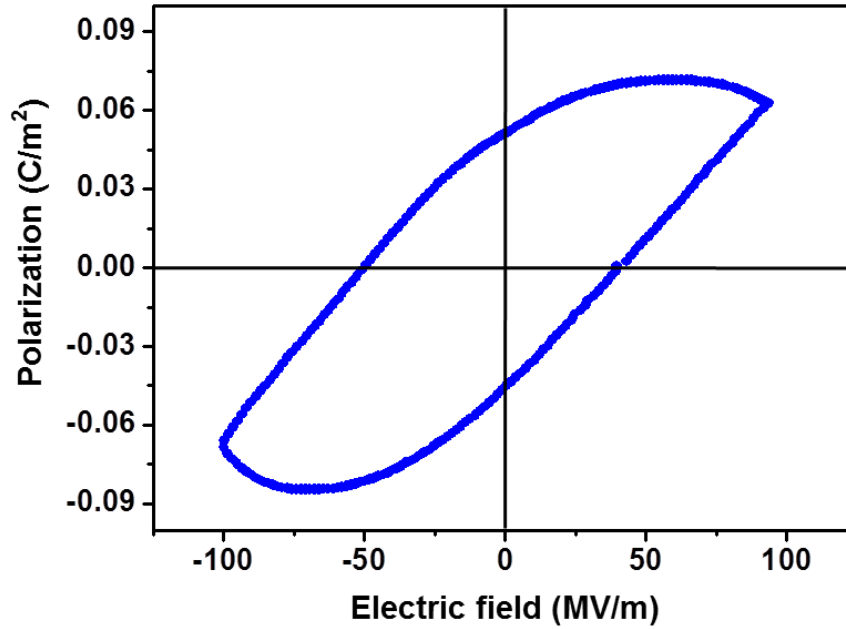


Figure 39. Polarization-electric field hysteresis loop measured on the 150 °C TiO₂/BTO NWs at room temperature.[352]

When the spontaneous polarization in BTO appears negative at the BTO/TiO₂ interface (*i.e.* positive polarization), it can induce upward band bending and increase the width of the depletion region in TiO₂. Such a change of the interfacial band structure facilitates the separation of photo-generated electron-hole pairs, and thus leads to the improved $\eta_{separation}$ and PEC performance. Since the thickness of BTO shell was as thin as 5 nm for 150 °C TiO₂/BTO NWs, the photogenerated holes could tunneling through the shell disregard the opposite electrical field inside BTO.[431, 432] Compared to the 150 °C sample, the relatively lower J_{ph} of the 170 °C TiO₂/BTO NWs might be a result of the slightly increased BTO shell thickness, which impaired the tunneling efficiency of holes. The much thicker BTO shells (~40 nm, Figure 31) in the higher temperature samples and the relatively high resistance of BTO would substantially hinder hole transport from the TiO₂ core and J_{ph} would mostly be contributed by the light absorption from

BTO itself. Under this circumstance, the spontaneous ferroelectric polarization inside BTO was expected to impose opposite effect to charge separation. As shown in Figure 37b, positive polarization at the BTO/TiO₂ interface becomes favorable for driving photo-generated holes towards the electrolyte to complete the PEC reaction. Nevertheless, the poor electronic property of BTO yielded an even lower $\eta_{separation}$ and J_{ph} compared to the pristine TiO₂ NW photoanodes.

To test the proposed mechanism, polarization-electric field (PE) hysteresis loop and dynamic contact-electrostatic force microscopy (DC-EFM) were used to confirm the polarization of BTO. The PE loop of 150 °C TiO₂/BTO NWs presents a remnant polarization (P_r) of ~ 0.051 C/m² and a coercive field (E_c) of ~ 49.8 MV/m at room temperature (Figure 39). These values are comparable to those of bulk BTO,[441] evidencing the strong ferroelectricity of the hydrothermal converted BTO shell. Figure 40 reveals a positively charged surface from the 150 °C TiO₂/BTO NW. This evidenced the spontaneous ferroelectric polarization of as-synthesized BTO shell was primarily aligned along the favorable direction (*i.e.* positive polarization) as shown in Figure 37a, where the PEC performance can be enhanced.

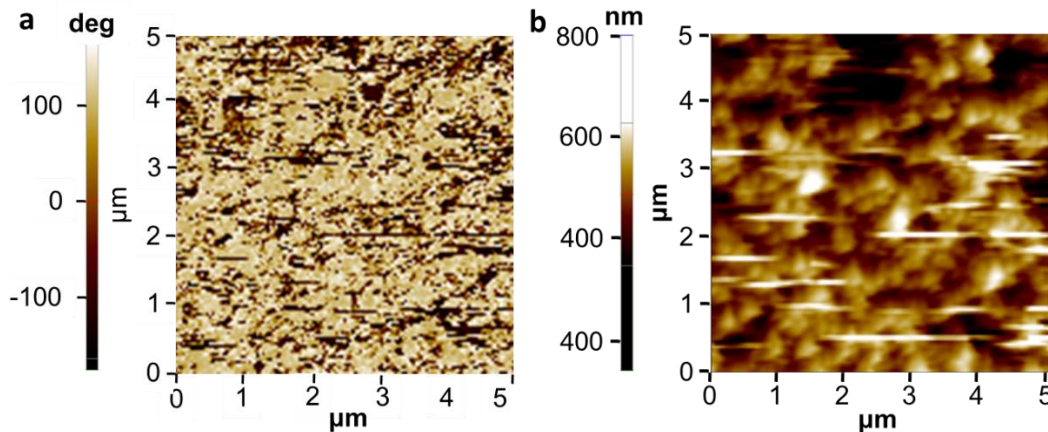


Figure 40. (a) DC-EFM phase images of the TiO₂/BTO core/shell NWs with the conversion temperatures of 150 °C, representing its spontaneous polarization direction. (b) DC-EFM topography images of the TiO₂/BTO core/shell NWs with the conversion temperatures of 150 °C.[352]

To further verify the ferroelectric polarization effect, TiO₂/BTO NW photoanodes were poled to different directions prior to PEC tests. Poling of the 150 °C TiO₂/BTO NW sample was performed in 2 M KCl aqueous solution using Pt wire as counter electrode. As shown in Figure 37c, positive poling (i.e. the same direction as the spontaneous ferroelectric polarization) of the 150 °C TiO₂/BTO NW photoanode further enhanced J_{ph} compared to the un-poled sample. However, the magnitude of improvement was not substantial since the as-synthesized BTO shell was mostly aligned favorably. When negative poling was applied to the NWs, J_{ph} and fill factor was significantly impaired due to the downward band bending at the TiO₂ surface and jeopardized charge separation efficiency. The onset potential variation were individually characterized by chronopotentiometric measurements and were probed to be 246, 197 and 178 mV for positive poling, no poling and negative poling, respectively (Figure 41a). For comparison, same poling conditions were applied to pristine TiO₂ NWs photoanode and the negative poling barely affected its PEC performance (Figure 41b).

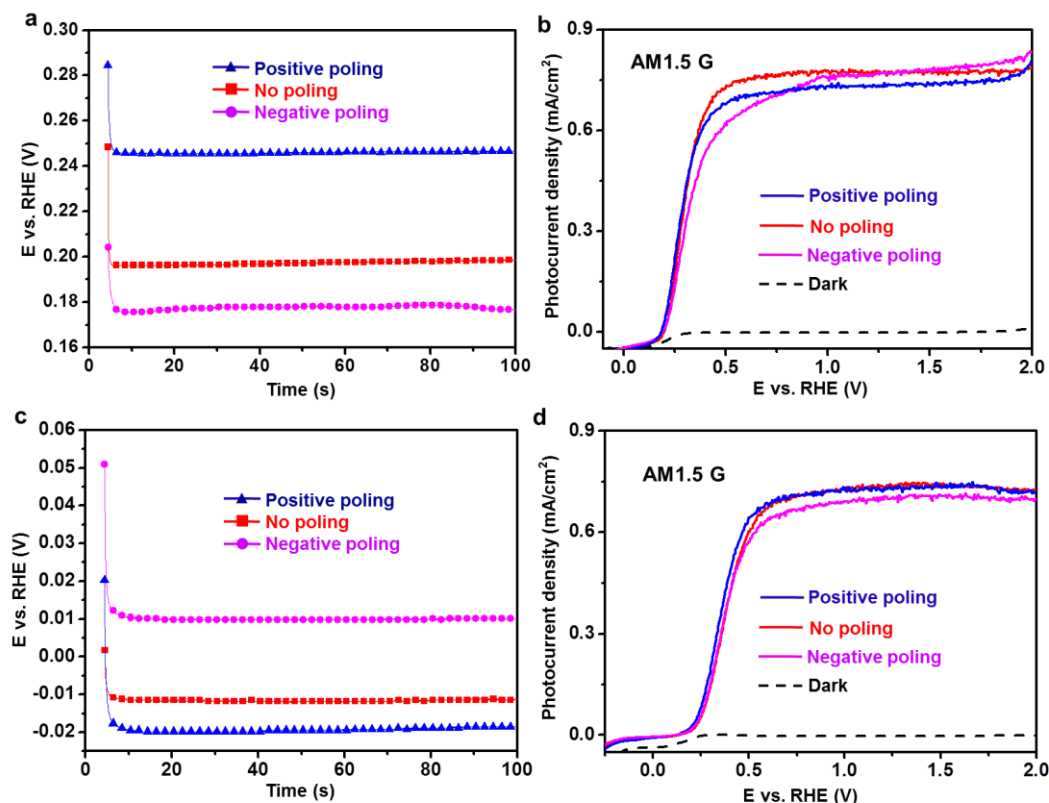


Figure 41. (a) Chronopotentiometric curves of the as-prepared (red), positively poled (blue) and negatively poled (magenta) 150 °C TiO₂/BTO NWs measured in 1 M NaOH electrolyte under AM1.5 G illumination with a constant current of zero, demonstrating their onset potentials were 197, 246 and 178 mV, respectively. (b) *J*-*V* curves of the as-prepared (red), positively poled (blue) and negatively poled (magenta) TiO₂ NWs under one sun illumination. TiO₂ NWs were poled under 3 and -2 V by solution method. (c) Chronopotentiometric curves of the as-prepared (red), positively poled (blue) and negatively poled (magenta) 210 °C TiO₂/BTO NWs measured in 1 M NaOH electrolyte under AM1.5 G illumination with a constant current of zero, demonstrating their onset potentials were -12, -19 and 10 mV, respectively. (d) *J*-*V* curves of the as-prepared (red), positively poled (blue) and negatively poled (magenta) TiO₂ NWs under one sun illumination. TiO₂ NWs were poled under ± 100 V in air.[352]

For thick BTO shells as the situation shown in Figure 37b, negative poling would enhance the PEC performance. This prediction was confirmed experimentally from the 210 °C sample. 210 °C TiO₂/BTO NWs were poled using FTO glass as the counter electrode in air. As shown in Figure 37d, negative poling raised J_{ph} from 0.74 to 0.96 mA/cm², corresponding to 29.7 % enhancement. On the contrary, positive poling reduced J_{ph} to 0.65 mA/cm², corresponding to 12.2 % decreasing.

The much larger amplitude of PEC performance gain also could be attributed to the pre-aligned polarization of the as-synthesized BTO, which was not favorable for charge separation in this case. In general, the onset potential of the 210 °C TiO₂/BTO NWs was less influenced by the poling treatment compared to 150 °C TiO₂/BTO NWs (Figure 41c). It is worth noting that after poling, the 210 °C BTO/TiO₂ photoanode significantly outperformed the pristine TiO₂ photoanode, which exhibited negligible performance change under the same poling condition (Figure 41d), suggesting the ferroelectric polarization could contribute extra performance gain in addition to chemistry and structure optimization.

In summary, we developed a ferroelectric polarization-enhanced PEC photoanode based on TiO₂/BTO NW arrays. The BTO shell was formed by locally converting TiO₂ NWs surface via a hydrothermal reaction, which was able to yield a uniform, epitaxial, and spontaneously poled BTO layer on TiO₂ NW surfaces. The 5 nm BTO coating yielded the highest J_{ph} of water oxidation (1.30 mA/cm²) that was 67% higher than pristine TiO₂ NWs (0.78 mA/cm²). The PEC performance gain was attributed to the improved charge separation efficiency by investigating and comparing the light absorption, charge injection and separation properties of TiO₂ and TiO₂/BTO NWs. Calculating the potential distribution across TiO₂/BTO/electrolyte heterojunctions quantitatively presented the effectiveness of ferroelectric BTO in tuning the interfacial electronic band structure of TiO₂. PE hysteresis loop, DC-EFM characterization, and electric poling further confirmed strong ferroelectricity of the BTO thin film, and the predominating role of ferroelectric polarization in controlling the PEC performance. This research evidenced that the ferroelectric or piezoelectric polarization could be an effective approach to tune the performance of semiconductor heterojunction-based devices beyond the limitation of chemistry and structure optimization.

3.3 Piezoelectric Semiconductor/Insulator/Solution

Controlling the interface electronic band structure in heterostructures is essential for developing highly efficient photoelectrochemical (PEC) photoanodes. Here, we presented an enhanced oxygen evolution reaction (OER) by introducing the piezotronics concept, i.e. piezoelectric polarization (P_{pz})-induced band engineering. In a Ni(OH)_2 decorated ZnO photoanode system, appreciably improved photocurrent density of sulfite (SO_3^{2-}) and hydroxyl (OH^-) oxidation reactions were obtained by physically deflecting the photoanode. Both theoretical and experimental results suggested that the performance enhancement was a result of the piezoelectric P_{pz} -endowed enlargement of the built-in electric field at the ZnO/Ni(OH)_2 interface, which could drive additional amount of photoexcited charges from ZnO toward the interface for OER. This strategy demonstrates a new route for improving the performance of inexpensive catalysts-based solar-to-fuel production.

Photoelectrochemical (PEC) water splitting is a promising strategy for converting solar energy to chemical fuels[442]. In a PEC system, the energy discontinuity at the semiconductor/electrolyte interface provides necessary driving force to separate photoexcited charges.[399, 412] Corresponding oxidation and reduction reactions are referred as the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively. Thermodynamically, the minimum energy required for splitting H_2O into H_2 and $\frac{1}{2}\text{O}_2$ is 1.23 eV. Additional activation energy is also needed to overcome the kinetic barrier and increase the rate of electrochemical reaction. To minimize the requirement of activation energy, OER and HER catalysts are frequently applied to the surface of semiconductor photoelectrodes. Noble metals such as platinum and iridium have shown excellent catalytic performance in both OER[403, 443] and HER[404, 444] processes. However, large-scale industrial application of these catalysts has

been severely limited by their high cost. Recently, pure transition-metals, transition-metal oxides, and hydroxides have emerged as promising low-cost catalysts, especially for OER.[413, 445-448] These catalysts are predominantly insulators, which would induce a significant drop of the total potential (defined by the initial Fermi level difference between semiconductor and electrolyte, denoted as φ_0) in the catalyst layer, and thus reduce the built-in potential (φ_{bi}) and depletion width (L_d) in the semiconductor. The reduced φ_{bi} and L_d impairs the efficiency of photoexcited charge separation and hole injection. To alleviate these drawbacks of the insulating catalysts, additional consideration should be given to improving the semiconductor/catalyst interfacial electronic structure and properties.

The piezotronic effect is a recently-proposed principle for locally engineering the band structures of heterojunctions using piezoelectric polarization (P_{pz}). [449-451] P_{pz} can considerably influence the free charge distribution and the band structure at the piezoelectric/semiconductor interface. Applying P_{pz} to control the charge transport properties of semiconductor devices has been employed in gating field-effect transistors (FET), [418, 452] manipulating electro- or photoluminescence, [445, 451, 453, 454] optimizing photovoltaics performance, [455] and facilitating electrochemical reactions. [456-458] Here, we studied the application of the piezotronic concept to enhancing the performance of inexpensive catalysts in OER. In a ZnO/Ni(OH)₂ photoanode, P_{pz} was introduced to increase the electric field strength in the vicinity of the semiconductor/electrolyte heterojunction, expanding the depletion length, and thus driving additional amount of photoexcited charges toward the interface for the OER. By physically deflecting a laminate ZnO/Ni(OH)₂ photoanode, appreciably improved the photocurrent density (J_{ph}) of sulfite (SO_3^{2-}) and OH^- oxidation reactions were obtained. Both theoretical and experimental results suggested that the performance gain was a result of the piezotronic-induced

enlargement of the built-in electric field at the ZnO/Ni(OH)₂ interface. This strategy demonstrates a new route for improving the performance of OER catalysts for achieving efficient PEC water splitting.

To investigate the influence of P_{pz} on OER performance, the potential distribution across the ZnO/Ni(OH)₂/H₂O heterojunction was first calculated numerically.

Calculation of electric potential profile at the ZnO/Ni(OH)₂/H₂O heterojunction.

At thermodynamic equilibrium, the total electrical potential (V) change across a heterojunction (in the absence of piezoelectric charge) is equal to the total Fermi energy (E_F) difference between the materials composing the junction. It is important to emphasize that while charge conservation is always a key constraint in the system, material parameters such as electrical permittivity, free charge density, and (insulator) layer thickness can dramatically change the total amount of charge transfer necessary to create a specific magnitude of V.

Calculating the electrical potential distribution begins with an accounting of the physical properties of the materials composing the heterojunction before any charge exchange occurs (Figure 42, Table 3).

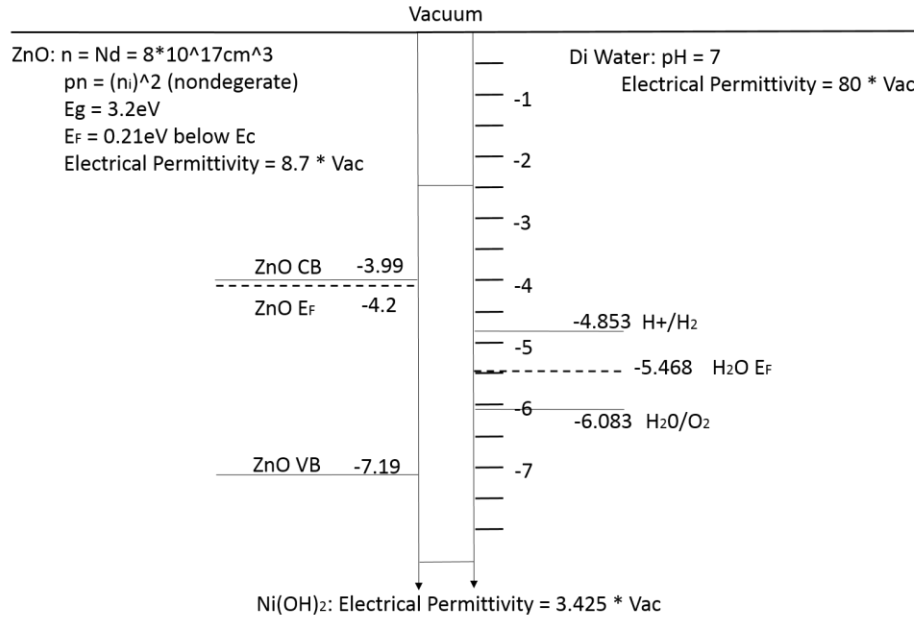


Figure 42. The relative band and Fermi energy (E_F) positions of relevant materials. Vacuum energy is chosen as a convenient universe reference. The band positions of $\text{Ni}(\text{OH})_2$ are arbitrarily selected to exemplify the material's resistive properties.[257]

Material	ϵ_r	$d_{31}(\frac{\text{Coulomb}}{N})$	Thickness	$V_{EF_{Bulk}}$ (eV vs Vacuum)	$Nd (\frac{\text{ions}}{m^3})$	$n_b(\frac{\text{ions}}{m^3})$	$p_b(\frac{\text{ions}}{m^3})$	$Y(\frac{N}{m^2})$
ZnO	8.7	$-3.3 \cdot 10^{-12}$	infinite ($> 100nm$)	-4.2 (at pH 7)	$8 \cdot 10^{237}$	$8 \cdot 10^{23}$	Mass action*	$150 \cdot 10^9$
$\text{Ni}(\text{OH})_2$	3.425	-	(varied)	-	-	-	-	-
H_2O	80	-	infinite ($> 8\mu m$)	-4.642	-	6.022×10^{19}	6.022×10^{19}	-

Table 3. Parameters used and calculated concentrations of various ions from equation (2.71) assuming no physical size of ions.[257]

***Concentration of holes at every location was determined by law of mass action.**

***Bulk concentration of charges in H_2O was set to equilibrium concentration of hydronium and hydroxyl ions at $\text{pH} = 7$.**

When the materials composing the heterojunction are placed in intimate contact with one another, entropy drives charge exchange between the conductive phases (i.e. ZnO and the H_2O solution). This charge exchange continues until the imbalance of electrical charge creates an electrical potential difference between the two phases that is equal to the bulk E_F difference between the two phases. Free and bound charges in the ZnO and H_2O are pushed and pulled by

the electric field (potential gradient $\frac{dV}{dx}$) this charge exchange creates, causing accumulation and depletion of charge in the vicinity of the heterojunction. These charge accumulation regions act to screen the junction's electric field from the bulk. To understand the potential distribution in the vicinity of the heterojunction we must understand how electrical potentials effect charge distributions.

From electrostatics, the Poisson equation describes how the charge density at location x ($\rho(x)$) is influenced by the potential at location x ($V(x)$):

$$\frac{d^2V(x)}{dx^2} = \frac{-\rho(x)}{\epsilon_0\epsilon_r} \quad (2.70)$$

Where ϵ_0 and ϵ_r are the electrical permittivity of vacuum and the medium inhabited by the charge, respectively. $V(x)$ is be solved for all x by twice integrating $\rho(x)$, but we first must get ρ as a function of $V(x)$.

In the ZnO semiconductor, the charge density is comprised of mobile electrons and holes as well as the immobile charged atoms that we attribute to dopant atoms:

$$\rho_{ZnO}(x) = (z_n)(n(x)) + (z_p)(p(x)) + z_dNd_{ZnO} \quad (2.71)$$

Where z_n , z_p and z_d are the charge of an electron (-1), hole (1) and dopant atom (1) in ZnO, respectively, and $n(x)$, $p(x)$ and Nd_{ZnO} are the charge density of electrons, holes, and dopant atoms, respectively. The charge density of electrons and holes varies with position because the electrical potential (relative to bulk potential in ZnO) varies as x approaches the heterojunction.

In both semiconductors and solutions, the ratio of concentrations of charged species i in bulk (n_i^0) at bulk potential ($\phi^0=0$) to its concentration (n_i) found at any other potential (ϕ) is taken to depend upon the Boltzmann factor in the following way:

$$n_i = n_i^0 e^{\left(\frac{-z_i e \phi(x)}{kT}\right)} \quad (2.72)$$

where z_i is the charge of ion i , and e is the charge of the electron, ϕ is the potential relative to bulk solution, x is a measure of distance into solution and perpendicular to the monolayer surface, k is the Boltzmann constant, and T is absolute temperature.

Combining equation (2.71) and (2.72) results in the following expression for charge density in the semiconductor:

$$\rho_{ZnO}(x) = (z_n)(n_b)e^{\frac{(z_n)V(x)e}{kT}} + (z_p)(p_b)e^{\frac{(z_p)V(x)e}{kT}} + z_dNd_{ZnO} \quad (2.73)$$

Where n_b and p_b are the bulk concentrations of electrons and holes, respectively.

Applying this same treatment to the DI-H₂O medium, where H⁺ and OH⁻ ions comprise the charge density, yields the following expression for the charge density in the aqueous medium:

$$\rho_{H_2O}(x) = (z_{H^+})(H^+_b)e^{\frac{(z_{H^+})V(x)e}{kT}} + (z_{OH^-})(OH^-_b)e^{\frac{(z_{OH^-})V(x)e}{kT}} \quad (2.74)$$

Where z_{H^+} and z_{OH^-} are the charge of hydronium (1) and hydroxyl (-1) ions, respectively, and H^+_b and OH^-_b are the bulk concentrations of hydronium and hydroxyl ions in DI-H₂O, respectively.

Equations (2.73) and (2.74) can be combined with equation (2.70) to yield the following expressions that describe how potential and charge density are interrelated in both the DI-H₂O and ZnO:

$$\text{In the Semiconductor: } \frac{d^2V}{dx^2} = \frac{-((z_n)(n_b)e^{\frac{(z_n)V(x)e}{kT}} + (z_p)(p_b)e^{\frac{(z_p)V(x)e}{kT}} + z_dNd_{ZnO})}{\epsilon_0\epsilon_r} \quad (2.75)$$

$$\text{In the Solution: } \frac{d^2V}{dx^2} = \frac{-((z_{H^+})(H^+_b)e^{\frac{(z_{H^+})V(x)e}{kT}} + (z_{OH^-})(OH^-_b)e^{\frac{(z_{OH^-})V(x)e}{kT}})}{\epsilon_0\epsilon_r} \quad (2.76)$$

To solve these second order differential equations requires two boundary conditions for each expression. In the semiconductor, the boundary conditions are as follows:

3. The electric field ($\frac{dV}{dx}$) in the bulk of the ZnO is zero.

$$\left(\frac{dV}{dx}\right)_{x=-\infty} = 0 \quad (2.77)$$

4. The electrical potential in the bulk is equal to the Fermi energy of ZnO ($V_{EF_{ZnO}}$)

$$V_{x=-\infty} = V_{EF_{ZnO}} \quad (2.78)$$

In the solution phase, the boundary conditions are similar:

3. The electric field ($\frac{dV}{dx}$) in the bulk of DI-H₂O is zero.

$$\left(\frac{dV}{dx}\right)_{x=\infty} = 0 \quad (2.79)$$

4. The electrical potential in the bulk is equal to the Fermi energy of DI-H₂O ($V_{EF_{H_2O}}$).

$$V_{x=\infty} = V_{EF_{H_2O}} \quad (2.80)$$

Applying boundary conditions (2.77) and (2.72) to expression S6 during integration yields the following expression for the potential gradient in the ZnO:

$$\frac{dV}{dx} = \sqrt{-\frac{2kT}{\epsilon_0 \epsilon_{ZnO}} \left[\left(n_b \left[e^{\frac{z_n V_e}{kT}} \right] - 1 \right) + \left(p_b \left[e^{\frac{z_p V_e}{kT}} \right] - 1 \right) + \frac{z_{Nd} N_{dZnO} V_e}{kT} \right]} \quad (2.81)$$

Applying boundary conditions (2.79) and (2.80) to expression (2.76) during integration yields the following expression for the potential gradient in the DI-H₂O:

$$\frac{dV}{dx} = \sqrt{-\frac{2kT}{\epsilon_0 \epsilon_{ZnO}} \left[\left(n_b \left[e^{\frac{z_n V_e}{kT}} \right] - 1 \right) + \left(p_b \left[e^{\frac{z_p V_e}{kT}} \right] - 1 \right) \right]} \quad (2.82)$$

Up to this point, the derivation of the potential profile in the ZnO (equation (2.81)) and DI-H₂O (equation (2.82)) have remained independent from one another. However, the electrical potential at the heterojunction only exists because the materials have exchanged mobile charges in order to come to equilibrium with each other. In order to physically couple the ZnO and H₂O systems, two conditions are applied:

1. The electric field at the interface between the ZnO and H₂O must have the same magnitude and direction when calculated from both the ZnO or H₂O side:

$$\left(\frac{dV_{ZnO}}{dx}\right)_{x=0} = \left(\frac{dV_{H_2O}}{dx}\right)_{x=0} \quad (2.83)$$

2. The total charge of the system must be:

$$Q_{ZnO} + Q_{Piezo} = Q_{H_2O} \quad (2.84)$$

Where Q_{ZnO} and Q_{H_2O} are the net charge in the ZnO and H₂O, respectively. Q_{Piezo} is the first instance thus far to introduce a piezoelectric component to our calculation. Q_{Piezo} represents the charge density present at the interface ZnO interface due to the direct piezoelectric effect.

To calculate Q_{Piezo} we assume the linear piezoelectric equation of state applies. In this case, the charge density (Q_{Piezo}) introduced by straining (E) the piezoelectric perpendicular to the (0001) axis will be uniform across the ZnO surface and given by:

$$Q_{Piezo} = (d_{31})(E)(Y) \quad (2.85)$$

Where d_{31} is the direct piezoelectric coefficient ($\frac{Coulomb}{N}$) and Y is Young's modulus ($\frac{N}{m^2}$).

We assume a simple, planer heterojunction at the interface. Thus, the charge in the medium can be related to the electric field at the interface by the following expression:

$$Q = \epsilon_0 \epsilon_r \left(\frac{dV}{dx}\right)_{x=0} \quad (2.86)$$

Combining (2.84), (2.85) and (2.86) yields the final expression for our second coupling condition:

$$\epsilon_0 \epsilon_{ZnO} \left(\frac{dV_{ZnO}}{dx}\right)_{x=0} + (d_{31})(E)(Y) = \epsilon_0 \epsilon_{H_2O} \left(\frac{dV_{H_2O}}{dx}\right)_{x=0} \quad (2.87)$$

Taken together, equation (2.83) and (2.87) couple the physical phenomena occurring in the ZnO (equation (2.81)) and DI-H₂O (equation (2.82)) systems.

In order to stitch the potential profiles generated by integrating equation (2.81) and equation (2.82) together into a single, cohesive picture, it is necessary to track the potential change as the calculations move from one medium to the next.

In our experiments there are four potentials (referenced to vacuum) that must be stitched together, these potentials include: V1, the bulk potential of ZnO ($V_{EF_{ZnO}} \pm V$ vs. SCE); V2, the potential at the interface between ZnO and Ni(OH)₂; V3, the potential at the interface between Ni(OH)₂ and DI-H₂O; and V4, the bulk potential of DI-H₂O ($V_{EF_{H_2O}}$). These potentials are schematically represented in Figure 43.

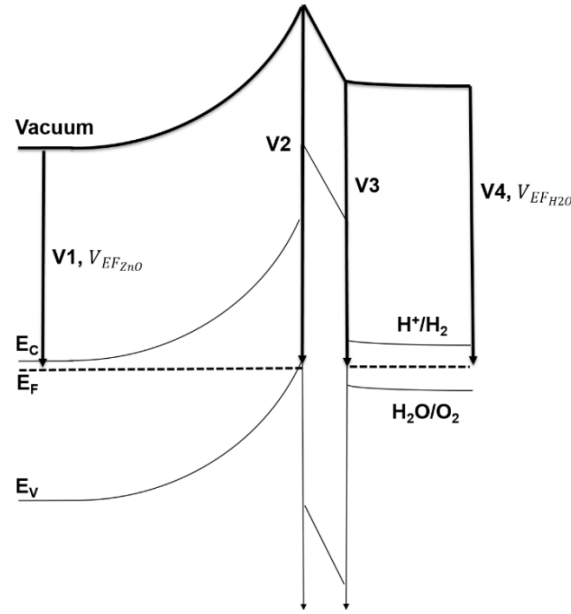


Figure 43. Energy diagram of the ZnO/Ni(OH)₂/DI-H₂O heterojunction (with piezoelectric charge present at the ZnO/Ni(OH)₂ interface). V1, V2, V3 and V4 denote potentials that define the interfaces between materials and thus need to be combined when generating band diagrams. [257]

The Ni(OH)₂ layer is taken as a perfect insulator. Thus, the voltage change between V2 and V3 is equal to the electric field inside the Ni(OH)₂ layer ($\left(\frac{dV_{ZnO}}{dx}\right)_{x=0} = \left(\frac{dV_{H_2O}}{dx}\right)_{x=0}$) multiplied by the Ni(OH)₂ thickness (equation (2.88)).

$$V3 = V2 - \frac{(Q_{ZnO} + Q_{Piezo})}{(\text{Ni(OH)}_2 \text{ Thickness})\epsilon_{\text{Ni(OH)}_2}} \quad (2.88)$$

The values of material properties used in the calculation are aggregated in Table 3.

To calculate the potential profiles when electrolyte Na_2SO_3 was added to solution, equations (2.74) and (2.76) were changed to reflect the addition of Na^+ and SO_3^{2-} to the expression of charge density. CV measurement of electrolyte Na_2SO_3 solution revealed a strong oxidation peak (SO_3^{2-} oxidation) at -4.831V vs Vacuum, this potential was well defined and used as the potential of electrolyte solution (V4).

The pH of electrolyte Na_2SO_3 solution was measured after preparation and found to be 10. For systems where the ZnO electrode was directly exposed to the Na_2SO_3 solution, a change of 0.059eV per pH unit was applied to the flat band potential of the electrode. If the ZnO wasn't in contact with solution (because of a Ni(OH)_2 coating), the $V_{EF_{Bulk}}$ of ZnO at pH =7 was used. This flat band potential shift is the reason for the discrepancy in total potential difference between ZnO and solution in the two conditions depicted in Figure 44C.

Checking for physically reasonable values

During every step of the calculation, the properties of the physical environment were checked to ensure that physically reasonable quantities were being produced. Of particular concern was ensuring that the atomic density in solution, adjacent to the ZnO/ DI- H_2O or Ni(OH)_2 / DI- H_2O interface, never exceeded the atomic density of a condensed phase.

To calculate the maximum charge densities we could physically expect, we modeled the hydrated ions (Na^+ , SO_3^{2-} , H^+ , and OH^-) as hard spheres and fit them into the maximum packing

density possible, the close packing structure. Taking SO_3^{2-} ions as an example, each with a hydration diameter (d) of 4 Å, the maximum 3D packing density possible is given by:

$$\text{Maximum 3D Density} = \frac{\text{Total ions}}{\text{Volume}} = \frac{\left(\frac{3}{2}\right) + 3 + \left(\frac{3}{2}\right)}{\frac{3\sqrt{3}}{2}a^2c} = \frac{6}{\frac{3\sqrt{3}}{2}(d)(2d\sqrt{\frac{2}{3}})} = 2.20971 * 10^{28} \frac{\text{ions}}{\text{m}^3} \quad (2.89)$$

Thus, the total of all ion concentrations at the closest approach to the interface must be approximately equal to or less than this atomic density.

$$n_{\text{max}} \leq 2.20971 * 10^{28} \frac{\text{ions}}{\text{m}^3} \quad (2.90)$$

Summing up the concentration of all hydrated ions in solution at the interface means summing up the value from equation (2.72) for each ion:

$$\sum n_i = \sum n_i^0 e^{\left(\frac{-z_i e \phi (V_3 - V_4)}{kT}\right)} \quad (2.91)$$

Table 4 displays the atomic density at the ZnO/H₂O interface as a function of strain and insulator thickness. At no point did our model exceed the maximum charge atomic density n_{max} .

V1 SCE	Vs.	NiOH (nm)	Thickness	Na ₂ SO ₃ concentration (Molar)	Strain (%)	n_i ($\frac{\text{ions}}{\text{m}^3}$)
1		0		0	-0.2	5.79473×10^{24}
1		0		0	0	4.01274×10^{24}
1		0		0	0.2	2.56275×10^{24}
1		0		1	-0.2	1.8144×10^{27}
1		0		1	0	1.81228×10^{27}
1		0		1	0.2	1.81051×10^{27}
1		10		0	-0.2	1.56527×10^{24}
1		10		0	0	1.17801×10^{24}
1		10		0	0.2	8.07261×10^{23}
1		10		1	-0.2	1.80879×10^{27}
1		10		1	0	1.80828×10^{27}
1		10		1	0.2	1.8078×10^{27}

Table 4. Concentration of solution ions as a function of insulator thickness, electrolyte concentration and ZnO strain when ZnO is under a bias of 1V vs SCE.[257]

As shown in Figure 44a, for a photoanode held at 1V vs SCE, without Ni(OH)_2 (i.e., a ZnO/ H_2O junction), ZnO and H_2O share 80.9% and 19.1% of φ_0 , respectively. After adding a 10 nm-thick Ni(OH)_2 layer between the ZnO and H_2O , the majority (58%) of φ_0 is dropped within the insulating Ni(OH)_2 . The electric potential shared by ZnO and H_2O decreased to 25% and 17%, respectively. Meanwhile, L_d of ZnO was reduced from 37.6 nm to 20.3 nm. This calculation suggests that an insulating Ni(OH)_2 layer between the ZnO and H_2O will cause a deterioration of φ_{bi} and L_d in the photoactive ZnO film.

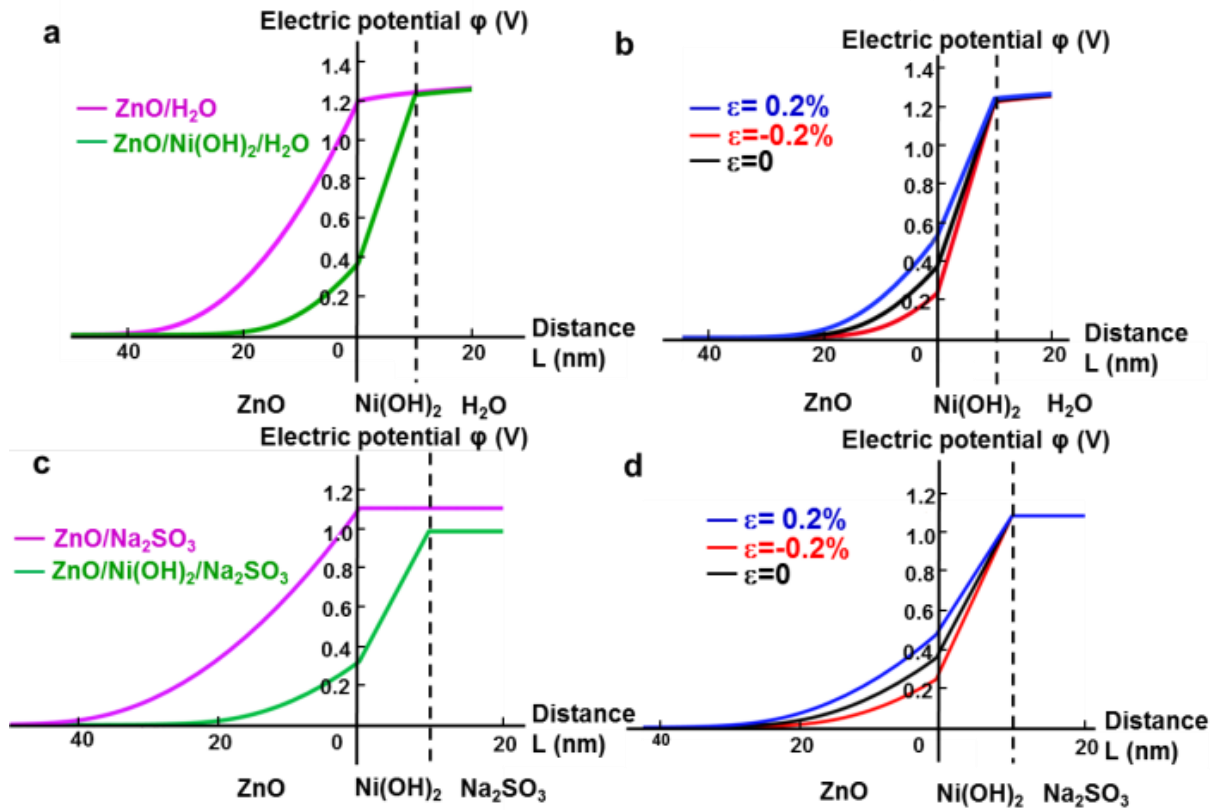


Figure 44. Calculated electric potential (φ) distribution in response to Ni(OH)_2 and P_{pz} . (a) φ distribution of ZnO/ H_2O with (green) and without (magenta) Ni(OH)_2 catalyst layer. (b) φ distribution of ZnO/ Ni(OH)_2 / H_2O under different strain conditions (denote strain as ε). (c) φ distribution of ZnO/ Na_2SO_3 with (green) and without (magenta) Ni(OH)_2 catalyst layer. (d) φ distribution of ZnO/ Ni(OH)_2 / Na_2SO_3 under different strain conditions.[257]

We next introduced strain to the model to investigate the influence of P_{pz} . Figure 45 presents the potential distribution of the ZnO/H₂O junction, under uniform positive (tensile) and negative (compressive) strain, perpendicular to the ZnO/H₂O interface, when a bias of 1V vs SCE applied to the ZnO anode. It was found that when the ZnO layer is strained, P_{pz} has little effect on the band positions at the interface, changing the junction potential by less than 21 mV. When an insulating Ni(OH)₂ layer with low dielectric constant (~ 3.4)[459] is introduced between ZnO and H₂O (Figure 44b), the impact of the strain-induced P_{pz} on the energetics of ZnO is intensified. The insulating Ni(OH)₂ layer increases the energetic penalty of redistributing charge in H₂O relative to redistributing charge in ZnO, thus ZnO provides the majority of charge redistribution and compensation necessary to balance P_{pz} . Under these conditions, a uniform tensile strain of 0.2%, perpendicular to the junction, increased the ϕ_{bi} and L_d of ZnO from 0.37 eV to 0.53 eV and 20.3 nm to 24.6 nm, respectively. A compressive strain of -0.2% reduced the ϕ_{bi} and L_d to 0.23 eV and 15.7 nm, respectively.

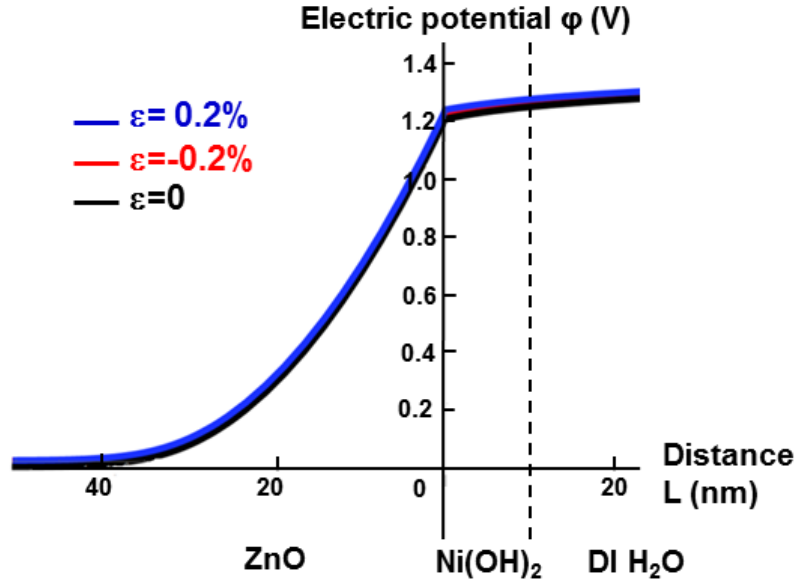


Figure 45. ϕ distribution of ZnO/H₂O heterojunction under different strain conditions, showing piezoelectric polarization can barely change the depletion of ZnO without Ni(OH)₂. [257]

The effect of increasing the electrolyte concentration on the expression of P_{pz} was then investigated. Figure 44c shows the electrical potential profiles for a ZnO/Na₂SO₃ solution (1 M in H₂O) junction with and without a 10 nm thick insulating Ni(OH)₂ layer. Without the Ni(OH)₂, the majority (<99.9%) of electrical potential change across the interface is within ZnO. After adding a 10 nm-thick Ni(OH)₂ layer between the ZnO and Na₂SO₃ solution, the majority (67.1%) of ϕ_0 is found to drop within the insulating Ni(OH)₂. The electric potential shared by ZnO and Na₂SO₃ solution decreased to 32.8% and 0.05%, respectively. Meanwhile, L_d of ZnO was reduced from 44.3 nm to 23.5 nm. Applying strain directly to a ZnO/Na₂SO₃ junction was found to have no effect (<1 mV) on the potential distribution (Figure 46) because P_{pz} is completely screened by charge redistribution (stern layer formation) in the 1 M Na₂SO₃ solution. Applying an insulating Ni(OH)₂ layer between ZnO and Na₂SO₃ revives the energy penalty of screening P_{pz} via charge redistribution in the solution phase (Figure 44d). For the ZnO/Ni(OH)₂/Na₂SO₃ interface, a tensile

strain of 0.2%, increased the ϕ_{bi} and L_d of ZnO from 0.49 eV to 0.65 eV and 23.5 nm to 37.4 nm, respectively. A compressive strain of -0.2% reduced the ϕ_{bi} and L_d to 0.34 eV and 19.3 nm, respectively. Under proper conditions (e.g. an $\text{Ni}(\text{OH})_2$ layer and positive strain), both the increased electric field strength at the ZnO interface and the greater depth of the electric field into the bulk of ZnO are expected to contribute to an increase in the total number of photoexcited charges that are successfully separated and driven toward the water interface, resulting in higher J_{ph} and OER performance.

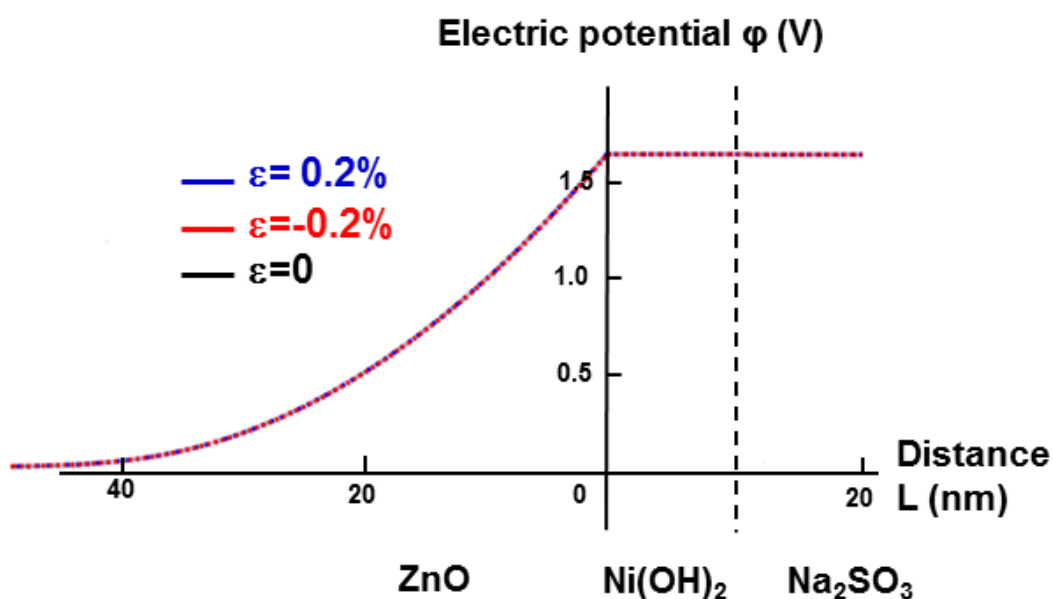


Figure 46. ϕ distribution of $\text{ZnO}/\text{Na}_2\text{SO}_3$ heterojunction under different strain conditions, showing little effect can be induced by piezoelectric polarization without $\text{Ni}(\text{OH})_2$. [257]

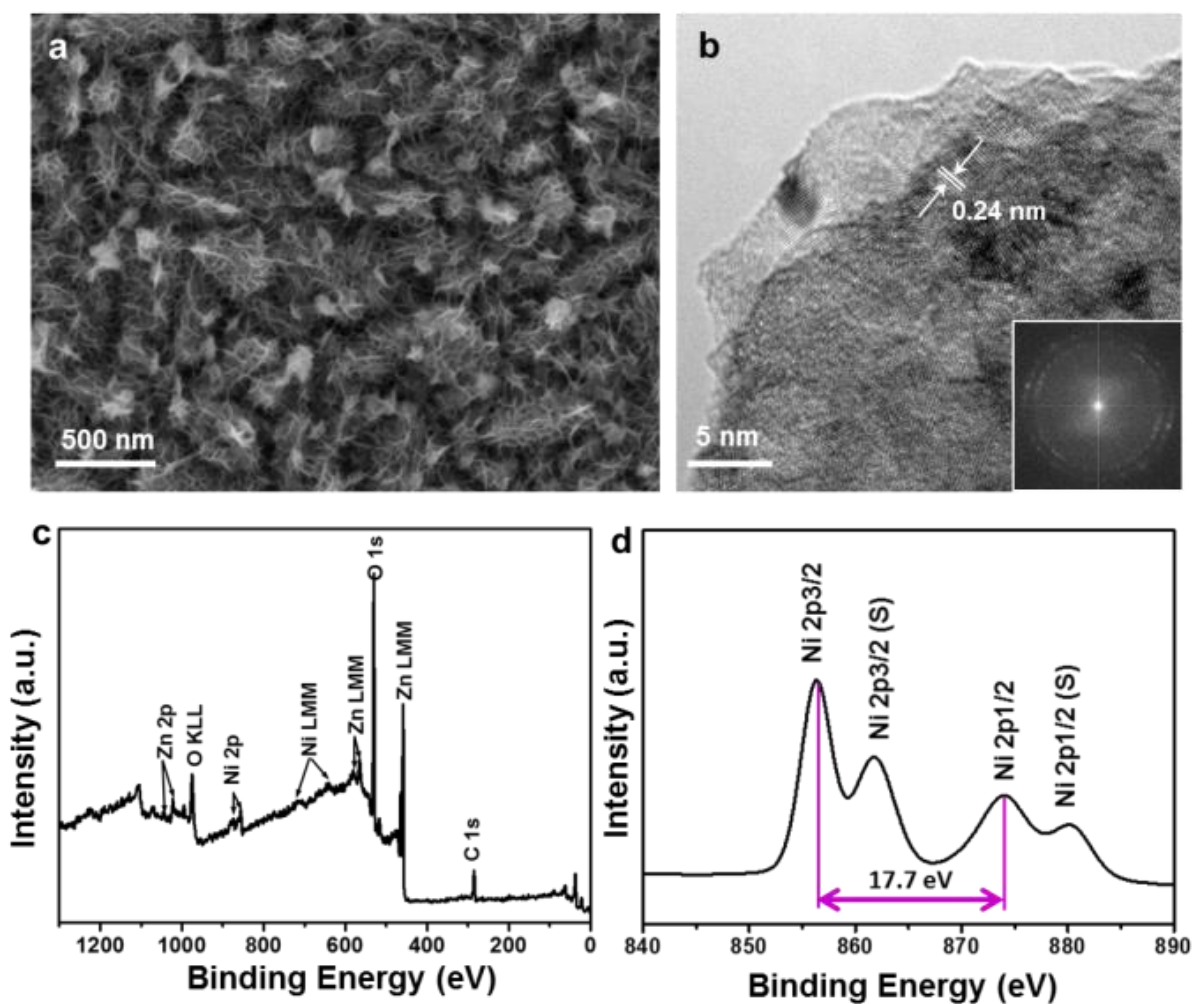


Figure 47. Structure and elemental characterizations of a ZnO/Ni(OH)₂ heterostructures. (a) SEM image of electrodeposited sheet-like Ni(OH)₂ uniformly covering entire ZnO surface. (b) TEM of an individual Ni(OH)₂ sheet. Inset is the FFT revealing the polycrystalline feature of Ni(OH)₂. (c) Full range XPS spectrum acquired from a ZnO/Ni(OH)₂ heterojunction. (d) Ni 2p scan verified the Ni(OH)₂ composition.[257]

The calculated piezotronic enhancement was then tested in a strained PEC water splitting system. The piezo-photoanode comprised three layers: a flexible indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrate; a radio frequency sputtered ZnO film; and a layer of electrodeposited Ni(OH)₂ catalyst. The morphology of the Ni(OH)₂ film was characterized using scanning electron microscopy (SEM). The rough Ni(OH)₂ layer had a sheet-like structure with wrinkled surface features and a uniform coverage over the ZnO photoanode (Figure 47a). A high-

resolution TEM image (Figure 47b) and its corresponding fast Fourier transform (inset of Figure 47b) revealed that the Ni(OH)_2 film was polycrystalline. The lattice distance was measured to be 0.24 nm, agreeing well with the (011) plane of $\beta\text{-Ni(OH)}_2$.^[460] Elemental characteristics of the ZnO/Ni(OH)_2 heterojunction were further studied by X-ray photoelectron spectroscopy (XPS). The full XPS spectrum (Figure 47c) showed good agreement with all the elements expected in a ZnO and Ni(OH)_2 sample. The two major peaks with binding energies of 856.3 eV and 874 eV, and their associating satellite peaks located at higher binding energies, were attributed to the Ni 2p_{3/2} and Ni 2p_{1/2} binding energies, respectively (Figure 47d). The spin-energy separation of 17.7 eV between the Ni 2p_{3/2} and Ni 2p_{1/2} peaks confirmed the Ni(OH)_2 composition.^[461]

The influence of P_{pz} on the PEC performance was first studied in 1 M Na_2SO_3 electrolyte, which acted as a photoexcited hole scavenger.^[405] Though the fundamental principles are the same, sulfite (SO_3^{2-}) oxidation is thermodynamically and kinetically more favorable compared to OER. The device and measurement setup are schematically shown in Figure 48a. The working area of the PEC cell was confined to $\sim 0.1 \text{ cm}^2$. The entire device was attached to a poly(methyl methacrylate) (PMMA) cantilever, which can be deformed to produce different strains to the photoanode. A three electrode configuration was adopted for PEC measurement with a platinum wire and a saturated calomel electrode (SCE) as the counter and reference electrode, respectively. Upon 150 W Xe lamp illumination, the J_{ph} of a pristine ZnO photoanode, exposed directly to the Na_2SO_3 solution, reached $\sim 1.4 \text{ mA cm}^{-2}$ at a bias of 0.5 V versus SCE (Figure 48b). This J_{ph} is 2.8 times larger than that of $\text{ZnO/Ni(OH)}_2/\text{Na}_2\text{SO}_3$ heterojunction ($\sim 0.5 \text{ mA cm}^{-2}$ at bias of 0.5 V versus SCE) under the same conditions. According to the calculated potential distribution, the pronounced decline of J_{ph} after adding Ni(OH)_2 to the surface of ZnO is attributed to the significant

reduction of φ_{bi} and L_d in the ZnO (see Figure 44c), thus reducing the efficiency of photoexcited charge separation and reducing the concentration of charges at the interface.

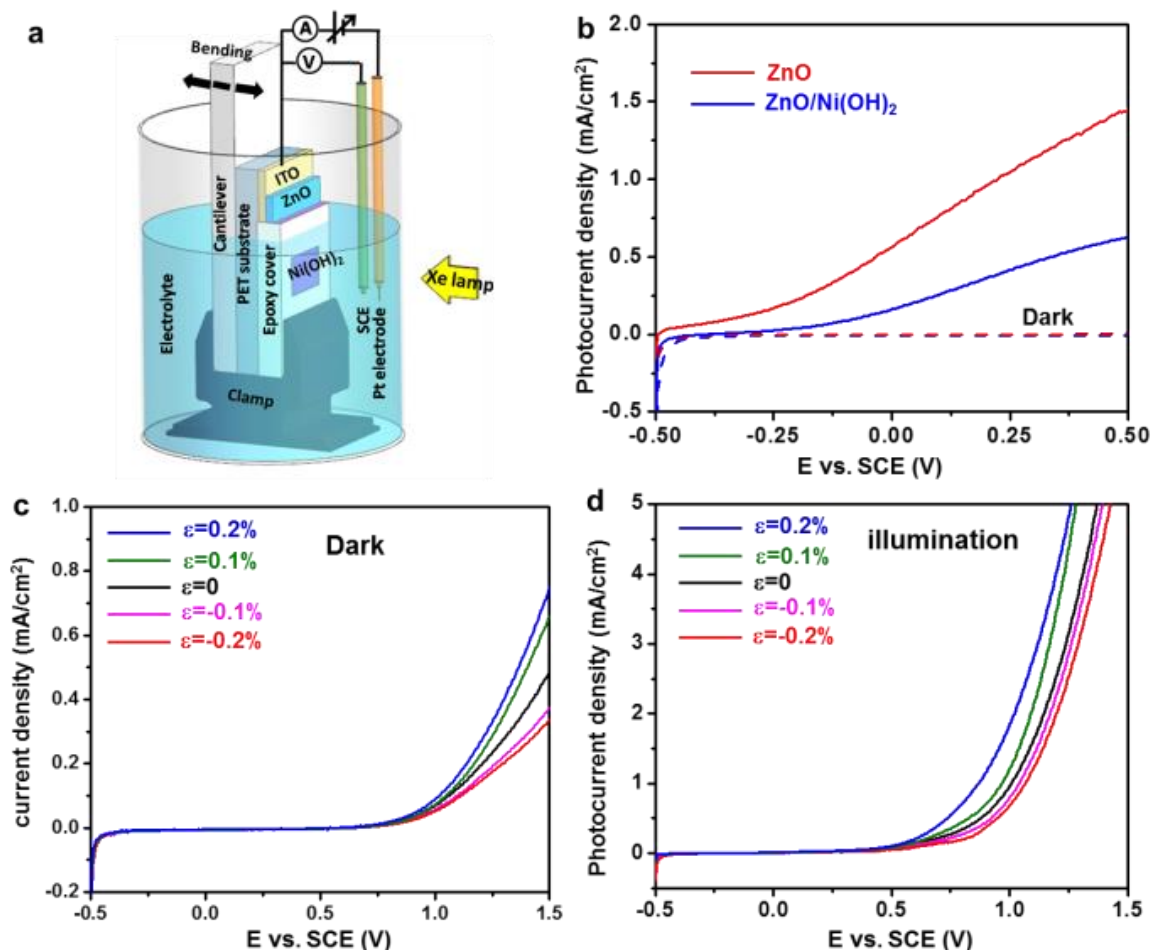


Figure 48. P_{pz} enhanced sulfite oxidation based on ZnO/ Ni(OH)_2 photoanode. (a) Schematic experiment setup for studying the influence of P_{pz} on sulfite oxidation and OER. (b) J_{ph} -V curves of ZnO (red) and ZnO/ Ni(OH)_2 (blue) photoanode for sulfite oxidation (c, d) J -V characteristics of strained ZnO/ Ni(OH)_2 under dark (c) and 150 W Xe lamp illumination(d). [257]

Calculations suggested that the unfavorable change in interfacial band structure caused by adding a Ni(OH)_2 film onto the ZnO surface (Figure 44a) can be compensated by the P_{pz} created by straining the ZnO (Figure 44c). Figure 48c shows the current density-potential (J - V) curve of the ZnO/ Ni(OH)_2 / Na_2SO_3 PEC anode under different straining conditions without light illumination. In general, positive strain increased J and negative strain decreased J , in agreement

with predictions made from calculation. Specifically, 0.1% and 0.2% strain increased J from 0.482 mA cm⁻² to 0.654 mA cm⁻² and 0.740 mA cm⁻² at bias of 1.5 V versus SCE, corresponding to an improvement of ~36% and ~85%, respectively. Applying -0.1% and -0.2% strain decreased J from 0.482 mA cm⁻² to 0.374 mA cm⁻² and 0.338 mA cm⁻², corresponding to a reduction of ~22% and ~30%, respectively. Under Xe lamp illumination, the absolute values of J_{ph} are significantly increased (Figure 48d). At a bias range of 0.5 V-1.5 V versus SCE, SO₃²⁻ oxidation occurred and J_{ph} responded to the applied strain in the same manner as in the dark condition, where an increase and decrease of J_{ph} are clearly identified upon positive and negative strains, respectively. These mechanical strain-induced variations to J and J_{ph} are believed to be the consequence of altered electron-hole separation and holes injection efficiency, reinforcing the conclusion that P_{pz} is capable of significantly manipulating the interfacial band structure of the ZnO/Ni(OH)₂ heterojunction.

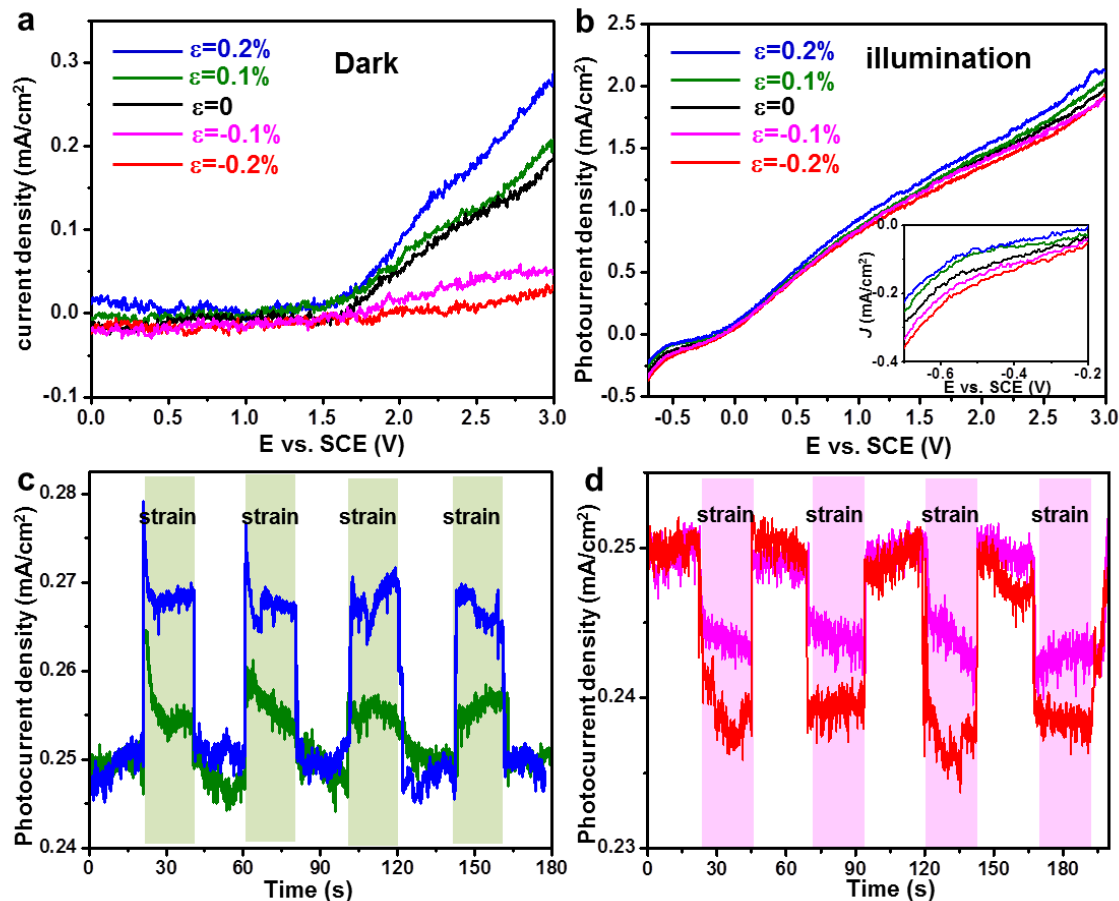


Figure 49. Strain-related OER performance of ZnO/Ni(OH)₂ photoanode. (a, b) J - V curves of ZnO/Ni(OH)₂ photoanode for OER under different strain conditions in dark circumstance (a) and 150 W Xe lamp illumination (b). (c, d) J_{ph} of ZnO/Ni(OH)₂ photoanode under periodic positive (c) 0.1% (green) and 0.2% (blue) strains, and negative (d) 0.1% (magenta) and 0.2% (red) strains at a constant bias of 1 V versus SCE. The positive and negative strained regions are marked with light green and pink, respectively. J_{ph} were collected under 150 W Xe lamp illumination.[257]

To reveal the influence of P_{pz} on the OER, the Na₂SO₃ electrolyte was replaced with de-ionized (DI)-H₂O. For a typical ZnO/Ni(OH)₂ photoanode, the driving force for separating photogenerated charges originates in the energy difference between the Femi level of ZnO and electrolyte solution. With the addition of mechanical strain as a variable, P_{pz} is expected to augment the driving force for electron transfer reactions at the interface. As shown by the calculated band diagram (Figure 44b), positive strain in ZnO film will generate a P_{pz} with a direction pointing

toward the ZnO/Ni(OH)₂ interface.[462] The low conductivity and low dielectric constant Ni(OH)₂ film increases the energetic penalty of screening the P_{pz} via charge redistribution in the DI-H₂O as compared to the ZnO. As charge redistribution takes place in the ZnO to screen P_{pz} , ϕ_{bi} and L_d in the ZnO increases. This enhanced band bending is expected to speed up the efficiency of photoexcited charge separation and accelerating the rate of holes injection into Ni(OH)₂, therefore increasing the J_{ph} .

To investigate this effect, the PEC performance of the ZnO/Ni(OH)₂ anode was measured in DI-H₂O under different straining conditions. Without applying any strain or light, the current remained at a low level between a bias of -0.5 V and 1.5 V versus SCE (Figure 49a). When the bias was greater than 1.5 V, the OER began. Similar to SO₃²⁻ oxidation, the largest and smallest J were measured with 0.2% and -0.2% strain, respectively, indicating that P_{pz} has an influence on hole-injection capability under a constant bias. Both in the dark and when illuminated by a Xe lamp (Figure 49b), J had an approximately linear relationship to both potential and strain. This linear response of both J and J_{ph} to the applied potential is likely because the OER in DI H₂O is both extremely kinetically and diffusion limited. These factors are not strongly influenced by the energetic landscape on the electrode-side of the junction, and thus the effect of strain on J and J_{ph} remained small. It's useful to compare J and J_{ph} as a function of strain, where strain had a greater effect on J than on J_{ph} . This phenomenon was also observed in P_{pz} modulated PVs and was known as a consequence of photoexcited charges screening the P_{pz} .[463] Photoexcited charges are expected to most prominently screen P_{pz} when the charges don't have an efficient electron source and sink to reduce their concentration in the vicinity of the interface. This situation is exactly what was encountered under our DI H₂O experimental condition. A magnified J_{ph} - V curve in the negative bias region (inset of Figure 49b) shows a reversal of the strain-related current deviation

trend as compared to the positive bias region (*i.e.* positive strain reduced J_{ph}). This observation is evidence that the observed current variation is a result of band engineering rather than piezo-induced resistance change,[418] which would exhibit a linear J_{ph} - V curve.

J_{ph} was further characterized at a fixed external bias of 1 V versus SCE as a function of periodic strain. Figures 49c and 49d present the J_{ph} -strain curves measured when strain was periodically applied to the ZnO/Ni(OH)₂ heterojunction. In general, J_{ph} exhibited a quick response to the strain. Under a tensile strain of 0.1% and 0.2%, J_{ph} increased from 0.249 mA cm⁻² to 0.256 mA cm⁻² and 0.268 mA cm⁻², respectively, demonstrating an enhanced OER activity under a constant bias but increased tensile strain. When subjected to a compressive strain of -0.1% and -0.2%, J_{ph} decreased from 0.249 mA cm⁻² to 0.244 mA cm⁻² and 0.239 mA cm⁻², respectively. These J_{ph} -strain characterizations are further evidence that P_{pz} is an effective approach to control the OER performance of Ni(OH)₂ decorated ZnO photoanodes.

In summary, we report a novel strategy for manipulating the interfacial band structure of a ZnO/Ni(OH)₂ heterojunction using strain induced P_{pz} . Electrical potential distributions calculated for ZnO/Ni(OH)₂ heterojunctions suggested that P_{pz} is able to largely increase the ϕ_{bi} and L_d of ZnO at the ZnO/Ni(OH)₂ interface, improving the PEC performance. Experimentally, tensile strain on ZnO films increased both J and J_{ph} for sulfite and water oxidation reactions. These enhancements were attributed to the increased depth of electric field into the bulk of the ZnO and increased strength of the interfacial electric field, both contributing to an increased efficiency of photoexcited charge separation in ZnO. These results have shown the promise of using the piezotronic effect to improve the performance of OER catalysts on semiconductor photoelectrodes.

Chapter 4: Application of Band Diagram Calculator to designing experiments

4.1 Piezoelectric-Enhanced Quantum Dot Solar Cell.

Colloidal quantum-dots (QD) photovoltaics (PVs) have shown promising future with merits of low-cost processing, tunable spectral absorption, long-lifetime hot carriers, and multiple exciton generation by single photon.[464-468] For instance, tailoring the semiconductor bandgap of QDs by quantum size effect enables multi-junction PVs in single junction QD solar cells (QDSCs).[467] Ability of collecting hot carriers could theoretically raise the solar energy conversion efficiency of QDSCs to as high as 66%.[467, 469] However, the performance of QDSCs is seriously hampered by the charge extraction/transport problem due to the material and electrical discontinuity among organic molecule-capped QDs. Endeavors have been carried out to mitigate electron-hole recombination and improve charge extraction efficiency from various aspects. To alleviate charge recombination at the QDs-anode interface, ultra-deep-work-function layer such as MoO₃ was utilized to provide a back surface field to repel electrons.[470] Depletion heterojunction (DH) QDSCs have been developed with the highest 7% solar energy conversion efficiency using p-type QDs as absorbers and n-type wide bandgap semiconductors as electron collectors.[471] The built-in electric field at the p-n junction effectively facilitates the dissociation of excitons and extraction of electrons from the QDs thin film.[472] One critical obstacle for achieving highly efficient DH QDSCs is the divergence between their effective regions of charge extraction (effective depletion width 100 ~ 150 nm) and light absorption (1 ~ 2 μm thick film to fully absorb above-band gap solar illumination).[473] Addressing this issue requires either a wider and steeper depletion region in the QDs layer or a well-designed photo-management structure of the charge collecting electrode. Depletion bulk heterojunction (DBH) QDSCs were exploited to

reduce the compromise between light absorption and charge extraction using porous charge collector.[474] However the very large QDs/electrode interfacial area significantly increased the bimolecular recombination rate and thus reduced the charge extraction efficiency.

A great number of researches have shown that the interfacial electronic band structure can be engineered by the permanent polarization induced by ionic displacement, e.g. ferroelectric or piezoelectric effect.[475-480] It is typically implemented via straining either from lattice mismatching or mechanical deformation. In a heterojunction structure involving a piezoelectric semiconductor material, appearance of piezoelectric polarization (P_{pz}) will lead to a considerable change of free carrier distributions in both the piezoelectric material and its adjacent semiconductor or metal contacts. Accordingly, there will be a corresponding band structure change following the charge redistribution. Combination of P_{pz} and redistribution of free charge could effectively modulate the performance of practical heterojunction-based devices. For example, in wurtzite nitrides-based quantum well lasers, P_{pz} can largely deform the potential profiles of the superlattice structure and affect the quantum efficiency by regulating the spatial overlapping between electrons and holes.[476] The application of P_{pz} to semiconductor functionalities has recently been explored to a much broader extent.[234, 242, 307, 309, 481, 482] This interaction is denoted as the piezotronic effect, which implements P_{pz} -induced charge redistribution to locally tune the interfacial band structure, and thus engineer the charge transport properties without altering the interface structure or chemistry. Piezotronics has demonstrated great promises in augmenting the quantum efficiency of n-ZnO/p-GaN light emitting diodes (LEDs), gating the nanowire-based field effect transistor (FET), manipulating the metal-semiconductor contact type, and optimizing the interfacial band alignment in heterojunction systems.[242, 303, 483, 484] Introducing the piezotronic concept to PV devices could also

arbitrarily adjust the band structure at the interface, and thus modulate their performance. This unique capability may find great promises for improving the effectiveness of charge extraction in a QD-ZnO system.

The work conducted in our lab [[463]] is some of the only work yet done in the area of using piezoelectric surface charge to extend the depletion width within a QD solar cell. Being an area that lacks significant experimental data to base future experiments on[485], piezotronic QD solar cells are an area ideal for exploring with our simulation software. An interesting design to explore for a piezotronic solar cell is depicted in Figure 50.

There are many factors to consider when designing this solar cell: The transparency of the piezoelectric material; the piezoelectric response of the piezoelectric material; the strain and fracture strength of the piezoelectric material; the screening potential of the thin conductive layer (electrode); the QD material, the ligands chosen, particle size, and dopant density. The importance of the piezoelectric materials' transparency and piezoelectric coefficient are self-evident: absorption of light in this layer will lead to a loss in solar cell efficiency and the stronger the piezoelectric coefficient the greater surface charge (and band bending) which will result from strain. The screening potential of the conductive electrode determines how much of the piezoelectric's surface charge is able to effect the band bending in the QD film. As for the quantum dot material, the choice of ligands will influence the conductivity of the film, as well as the dielectric constant. The QD particle size will influence the material's band gap, which in turn will influence the free charge density in the film and the material's ability to create an accumulation or depletion region in response to an applied field.

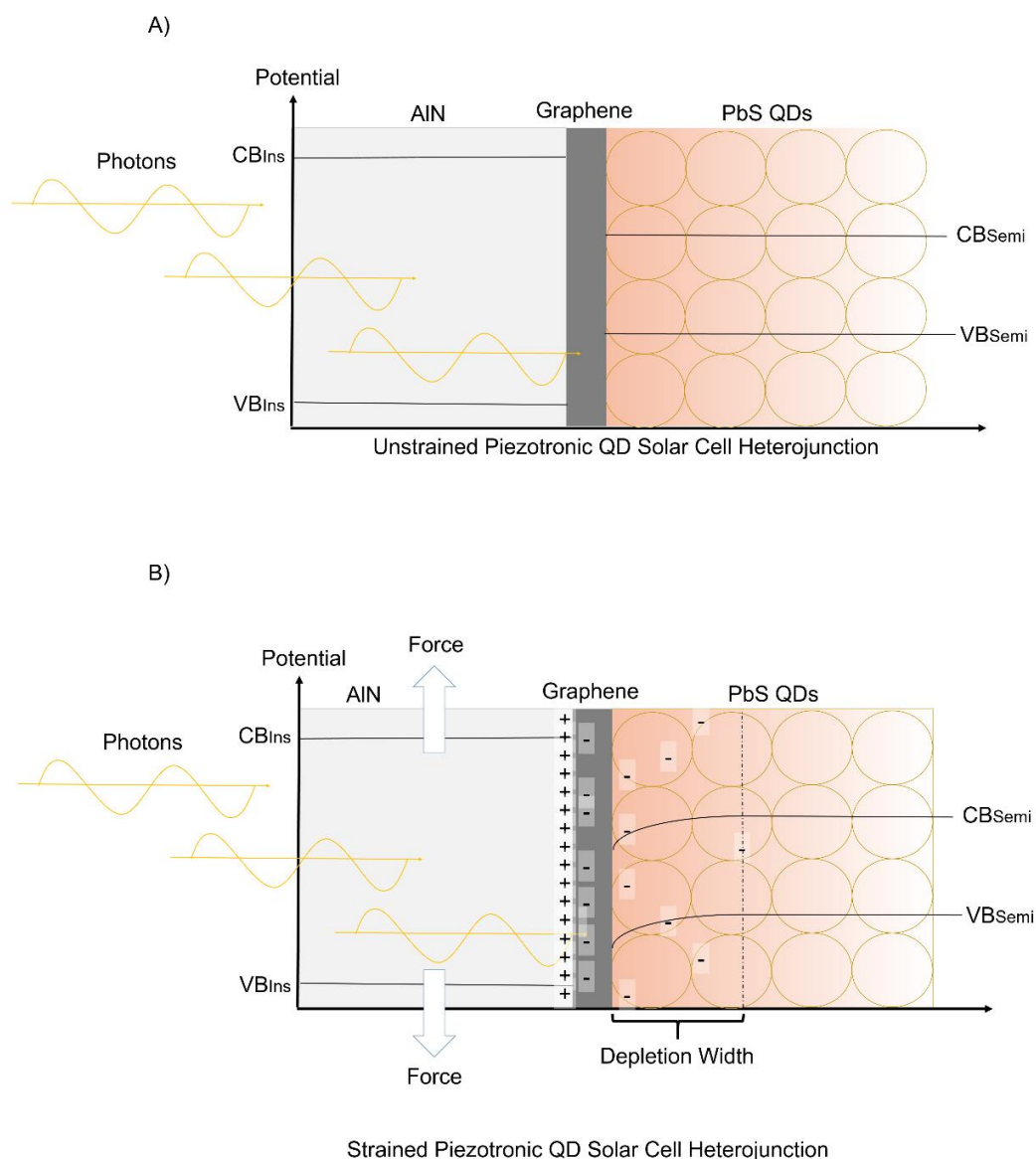


Figure 50. A Piezotronic QD solar cell. (A) The general structured of the solar cell. The photoactive QD material, such as PbS, is placed behind a single piece of conductive graphene and a slab of (transparent) piezoelectric Aluminum Nitride (AlN). (B) Upon straining the AlN, piezoelectric surface charge forms at the interface. The single atomic plane of graphene is incapable of completely screening the surface AlN surface charge, the PbS QDs respond to the remaining surface charge by forming a depletion region.

With a photoactive material like PbS as the QD material, a depletion width on the order of two microns would be sufficient for absorbing all incoming light from the sun. Can piezotronics help us achieve a solar cell with that type of depletion width within the PbS film? Taking the solar cell structure above and analyzing it with our Mathematica software, we find that is quite difficult to achieve. Figure 51 demonstrates the effect of AlN strain on the electrical potential profile in the PbS QD film. Figure 52 shows the effect of increasing strain from -0.5% to -1.0% in the AlN film.

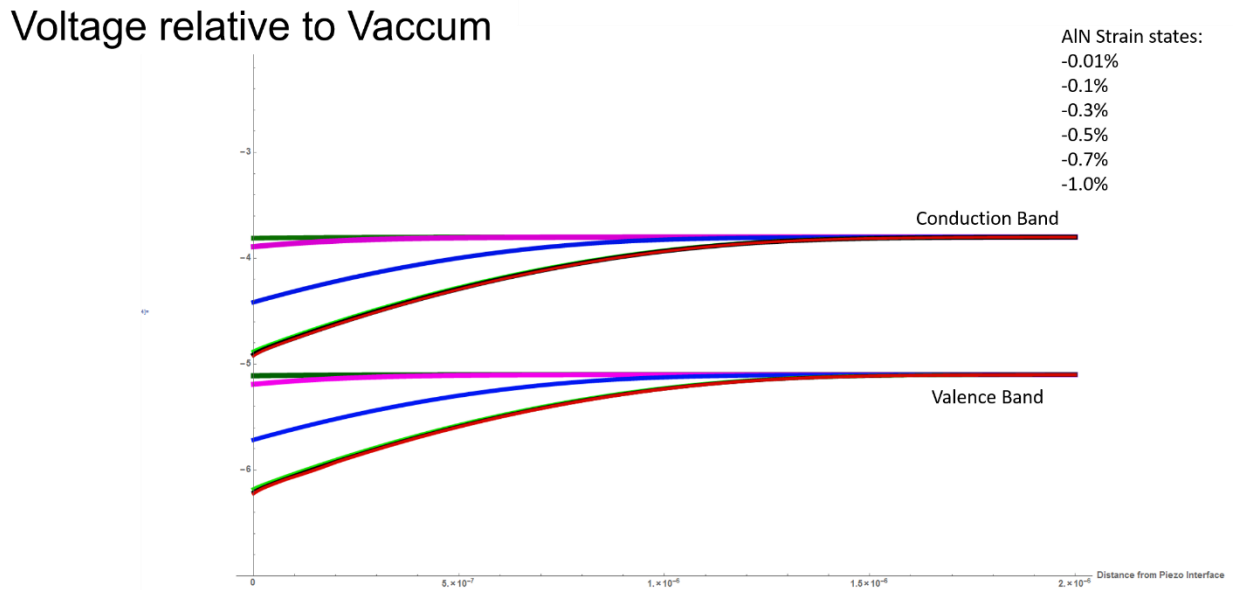


Figure 51. The effect of piezoelectric strain on the QD layer depletion width. Greater band bending occurs with greater strain. However, all strain values result in band bending which ends before 2 microns in length

Voltage relative to Vacuum

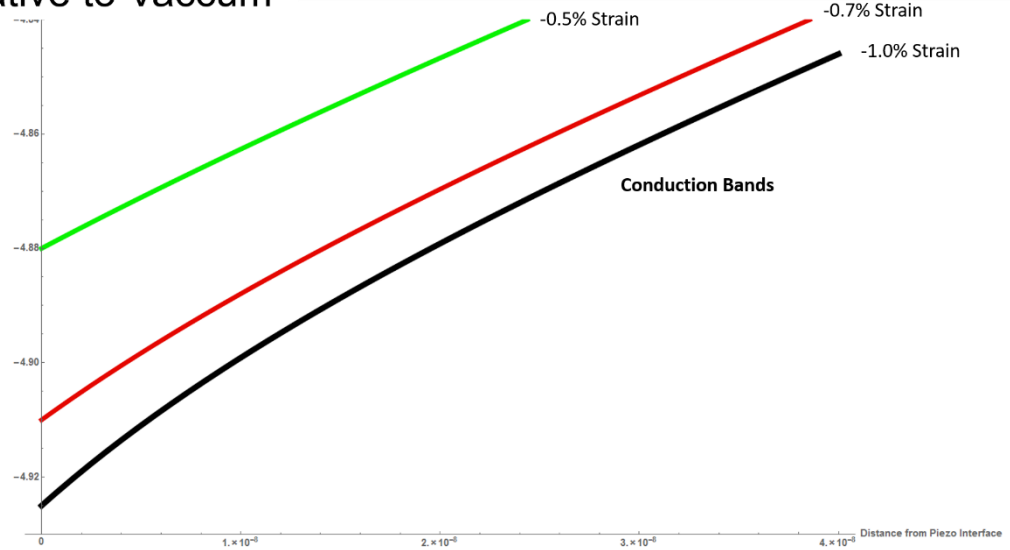


Figure 52. The effect of increasing strain from -0.5% to -1.0% in the AlN causes an increased band bending of less than 0.1 Volts.

The reason for the small change is that by the AlN has been strained to $\sim -0.5\%$, the QD film has begun to go into accumulation of free charge. Table 5 shows the effect of AlN strain on depletion width within the QD film

AlN strain	depletion width (m)	width to 0.0257eV
-0.010000%	5.88577×10^{-8}	0
-0.100000%	3.61445×10^{-7}	2.66×10^{-7}
-0.300000%	1.08601×10^{-6}	9.917×10^{-7}
-0.500000%	1.84298×10^{-6}	1.35374×10^{-6}
-0.700000%	2.52107×10^{-6}	1.36785×10^{-6}
-1.000000%	3.12243×10^{-6}	1.3733×10^{-6}

Table 5. Depletion Width (as calculated by our Mathematica code) as a function of AlN strain.

The depletion width calculated in Table 1 by the Mathematica code is determined when slope in the electrical potential profile becomes zero. However, technologically speaking, this

definition is not particularly useful. A more technologically useful value of depletion width is the distance from the heterojunction interface over which the electrical potential value differs from bulk values by greater than thermal energy ($\sim 25\text{mV}$). We can also determine this value of depletion width by analyzing the code. As can be seen in table 1, after $\sim -0.5\%$ of strain is achieved in the AlN, the practical value for depletion width doesn't vary significantly. This same type of behavior is seen in Figure 53, where the strain of the AlN is held constant but the screening capability of the thin conductive electrode is varied[486-494].

For our calculation, we looked to the literature to see what the screening capabilities are of a graphene sheet. Numerous attempts to calculate the screening length in 2D graphene-like systems have been made, with results that typically range between the 2 layers ($.7\text{nm}$) to 5 layers (1.7nm) deep.[487, 488, 490, 493, 494] Experimentalists have measured screening lengths in thin-graphite and graphene materials varying from 1 to 4 graphene layers by techniques including angle-resolved photoemission spectroscopy[491], plasmonic resonance[492] and field effect devices[489, 491]. The shortest screening length was obtained for highly doped ($10^{13}/\text{cm}^2$) graphene grown on SiC [491], whereas low $10^{12}/\text{cm}^2$ carrier concentrations resulted in longer (2-4 layer) screening lengths. The confluence of theoretical and experimental work conducted on graphene's electric field screening capability suggests that electric field is indeed capable of penetrating a single layer of graphene and effecting energetics of a material adjacent to it.

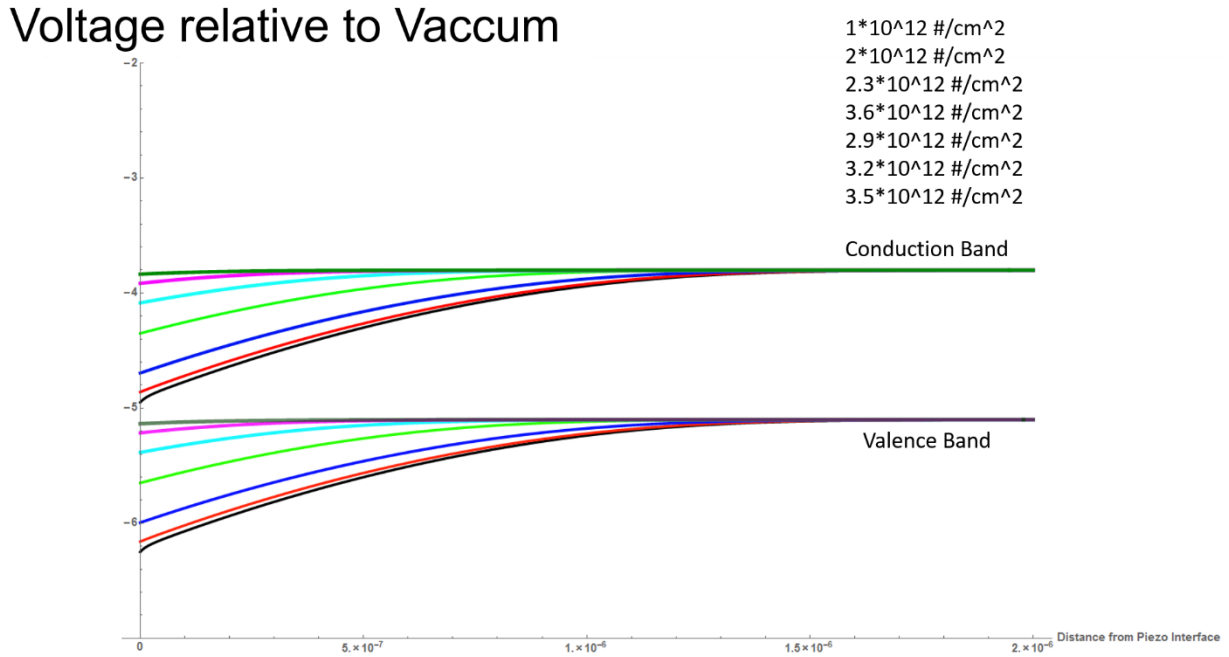


Figure 53. The electrical potential profile in the QD film as a function of the thin conductive electrode's charge density.

The behavior in Figure 53 is much that same as that seen in figure 52. Figure 54 shows the behavior of the electrical potential for the smallest quantities of charge density. Again, very little potential change at the wall is possible after the potential has been changed by approximately 1 Volt. The reason for this behavior in both cases is due to the QD bandgap.

The bandgap of the QD material sets a limit on how much potential change can occur within the film before there is an accumulation of minority carriers (electrons, in this case) at the interface. Once there is an accumulation of charges at the interface, the material is capable of very efficiently screening any additional electric field from the AlN layer that impinges on the surface of the material. For the most part, even if the material is only slightly conductive, accumulation of minority or majority carriers will occur once the potential change at the surface approaches the

value of the material's bandgap. For solar cell applications, there is an optimum range for the bandgap of the material in order for it to absorb sufficient light.

Voltage relative to V_{vacuum}

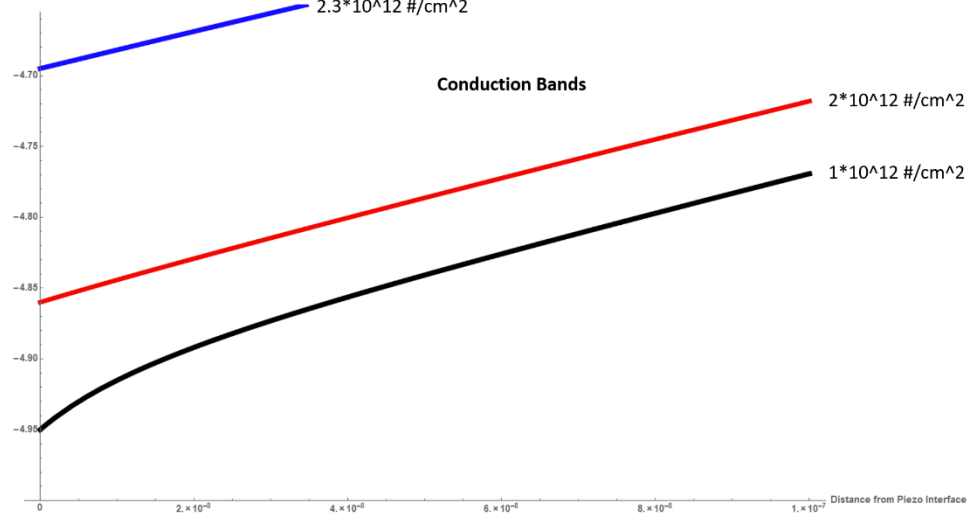


Figure 54. The effect of electrode charge density on the electrical potential profile in the QD film.

The depletion region of the material does respond approximately linearly in response to the electrical permittivity of the QD material. The larger the electrical permittivity of the QD film. The longer the depletion width. In QD films, electrical permittivity can be tailored by changing the ligand that attached to the crystals [495-497]. The band gap restriction and the electrical permittivity effect can work together to produce a better QD solar cell. Our calculations suggest that a high electrical permittivity, small bandgap materials should be chosen as the light absorber, while quantum confinement effects should then be used to increase the materials bandgap [497-499] into the range that is desirable for solar energy harvesting.

Chapter 5. Piezochemistry: Piezoelectrics for Driving Electrochemical Reactions

5.1 Introduction to Piezochemistry: Coupling of piezoelectric effect with electrochemical processes

The coupling effect between piezoelectric polarization and electrochemical processes depicts the engineering of charge-carrier conduction characteristics at the heterojunction between a strained piezoelectric material and a chemical solution. It is a unique subcategory of piezotronics. Applications of this coupling effect include selective etching enabled by piezo(ferro)-electric polarization; selective (photo)electrochemical deposition directed by piezo(ferro)-electric potential; and the directly utilization of piezoelectric potential to drive electrochemical reactions (piezocatalysis).

Piezoelectrics are a class of materials that create an electric field in response to mechanical deformation. The origin of the electric field (i.e. piezoelectric field) is a break in the inversion symmetry which lead to electric dipoles within the material, the strength of which changes as the material is strained. The changing dipole field leads to a change in the electric field which permeates the material (Figure 55). Piezoelectrics as a phenomenological description encompasses three subcategories of materials: ferroelectrics, pyroelectrics and piezoelectrics (Figure 56)[500, 501]. Piezoelectric materials that are non-ferroelectric and non-piezoelectric (e.g. SiO_4) have no electric dipoles when under no strain, but upon strain there is a separation between the positive and negative charge centers which results in an non-zero electric field. Pyroelectric materials that are non-ferroelectric (e.g. LiTaO_3) exhibit spontaneous polarization: even in the absence of mechanical deformation or an electric field, the positive and negative charge centers in each unit cell do not coincide, giving rise to a resultant electric dipole. Upon strain, the separation between

charge centers changes and thus the electric field changes. Pyroelectric materials will also experience a change to their dipoles when subjected to a change in temperature. The polarization in piezoelectric materials that are not ferroelectric is not permanently changeable by applying an external electrical field. Ferroelectric materials (all of which are piezoelectric) also contains a spontaneous polarization in the absence of strain, as well as a temperature-sensitive polarization, but differ from the other classes of materials in that a ferroelectric material's spontaneous dipoles need not necessarily align from one unit cell to the next. Regions in which neighboring dipoles are aligned with one another are called domains. The direction of spontaneous polarization in a ferroelectric's unit cell can be changed if exposed to a sufficiently strong electric field.

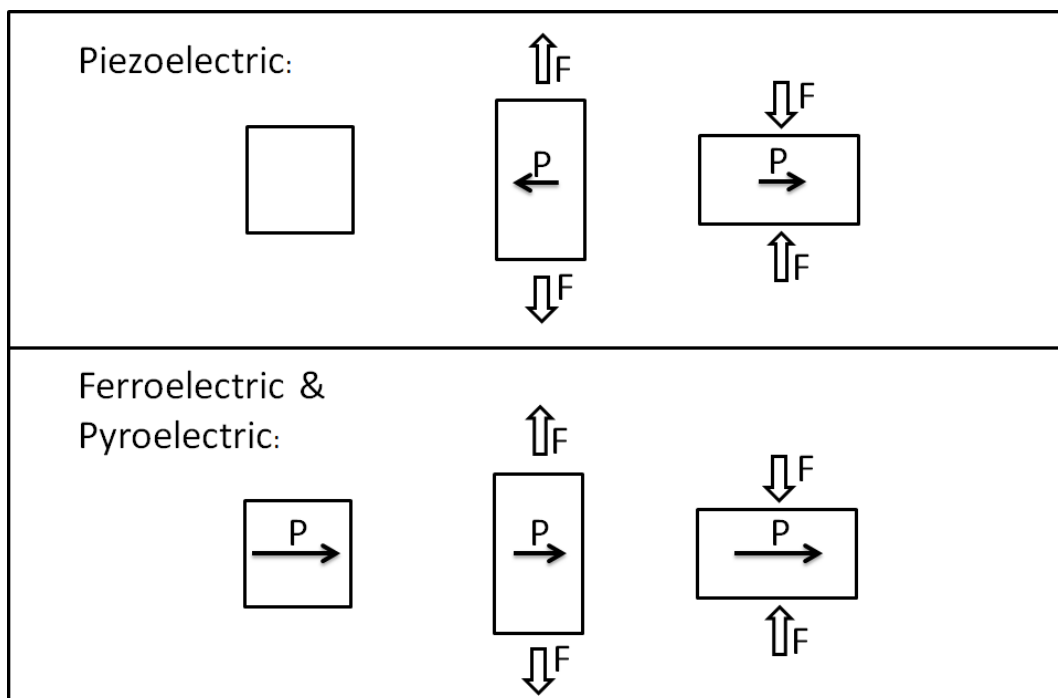


Figure 55. a) Piezoelectric materials that are non-ferroelectric and non-pyroelectric being with zero internal dipole. When these materials are strained, the lattice displacement creates dipole moments that create an electric field across the material. b) Ferroelectric and pyroelectric materials have spontaneous dipoles without strain. When these materials are strained, their dipoles change in strength, again changing the electric field saturating the material.[502]

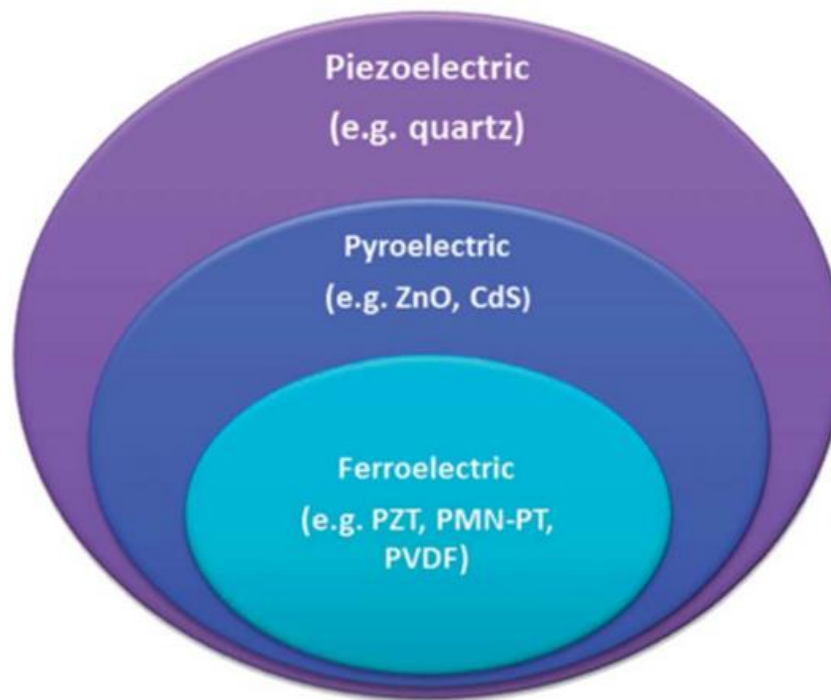


Figure 56. Piezoelectric materials experience a change in internal dipole moment when mechanically deformed. Pyroelectrics are kind of piezoelectric material which have spontaneous dipoles in the absence of mechanical deformation. The dipoles cannot be made to permanently switch direction by applying an external electric field. The spontaneous dipoles of pyroelectric materials changes as a function of temperature. Ferroelectric materials are a special subclass of pyroelectrics. The spontaneous dipole in ferroelectric materials can be made to permanently change orientation by applying a strong enough external electric field.[503]

The electric field exhibited by piezoelectric materials, whether strain induced, temperature induced, or spontaneously realized, can have a dramatic effect on the electronic properties both inside and outside of the material. Electric fields disrupt the energy of electronic states throughout the material (Figure 57a) and can cause the rearrangement of free charge inside and outside of the material (Figure 57b). This electronic rearrangement can dramatically affect charge-carrier conduction characteristics at the heterojunction between a piezoelectric material and another medium, because these characteristics depend sensitively upon the continuity of occupiable electronic states from one medium to the other and on the number of charges free to move between

the mediums. This phenomenon is known as the piezotronics effect [234, 307, 450]. One such heterojunction that is particularly dynamic is that which exists between a piezoelectric material and a chemical solution[504, 505]. Piezoelectric fields have been used to control the corrosion rate of materials exposed to etchant solutions[506-516], selectively control the energetics and spatial separation of adsorbed[517, 518] and photo-deposition materials[519-526], and have even been used to directly drive electrochemical reactions across piezoelectric/solution interface[504, 505, 527-529].

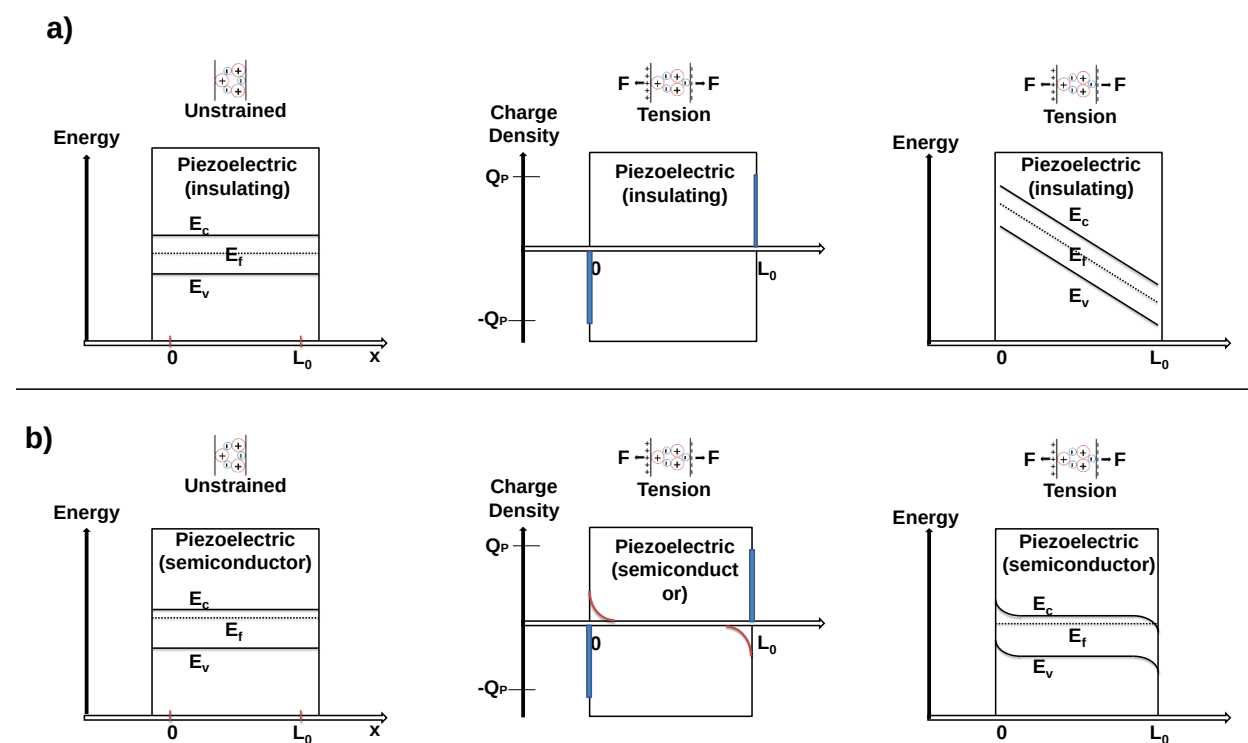


Figure 57. The electric field created by straining a piezoelectric material effects the energetics of electronic states throughout the material. a) In a perfect insulator, no charge is able to move in response to the piezoelectric field and the electric field linearly augments the energy of occupied (valence band) and unoccupied (conduction band) states across the material. b) In a semiconducting piezoelectric, the piezoelectric field pushes mobile charge carriers to opposite sides of the material. The mobile charges continue to migrate under the influence of the piezoelectric field until the enough mobile charge accumulates on opposite sides of the material to create an electric field which counters that of the piezoelectric and effectively screens the bulk of the material for the piezoelectric potential shift.[502]

Using piezoelectric fields to influence chemical reactions happening at the material's surface is closely related to electrochemical processes which typically take place at the surface of an electrode in contact with solution, influenced by an outside voltage source (Figure 58). A chemically stable electrode material in contact with solution containing electroactive species will arrive at a steady state electrochemical equilibrium between the electrode and solution (Figure 4a). Applying a voltage to a metal electrode can have one of two results: (1) the electrode potential rises above that of unoccupied states in solution, or (2) the electrode potential drops below that of occupied states in solution. In the first case it is now energetically favorable for there to be a net electron flow from occupied states in the electrode to unoccupied states of electroactive species in solution (i.e. cathodic current, Figure 58b). In the second case it is energetically favorable for a net flow of electrons to come from occupied states of species in solution into the unoccupied states in the electrode (i.e. anodic current, Figure 58c). In the case of an insulating piezoelectric material (Figure 58d) the piezoelectric field, induced by mechanically deforming the piezoelectric material, exerts an energy shift on the occupied (valence band) and unoccupied (conduction band) states throughout the material. With sufficient shifts in the energies of these states, it is possible to drive the flow of electrons from the piezoelectric's surface to species in solution or from species in solution to the piezoelectric's surface (Figure 58e)[505]. In pyroelectric and ferroelectric materials, the presence of a spontaneously dipole means an electric field, and its associated electronic distortion, is present throughout the material even in the absence of an applied strain. It is the presence of these spontaneous dipoles that allows pyroelectric and ferroelectric materials to exhibit useful corrosion, photochemical and electrochemical properties.

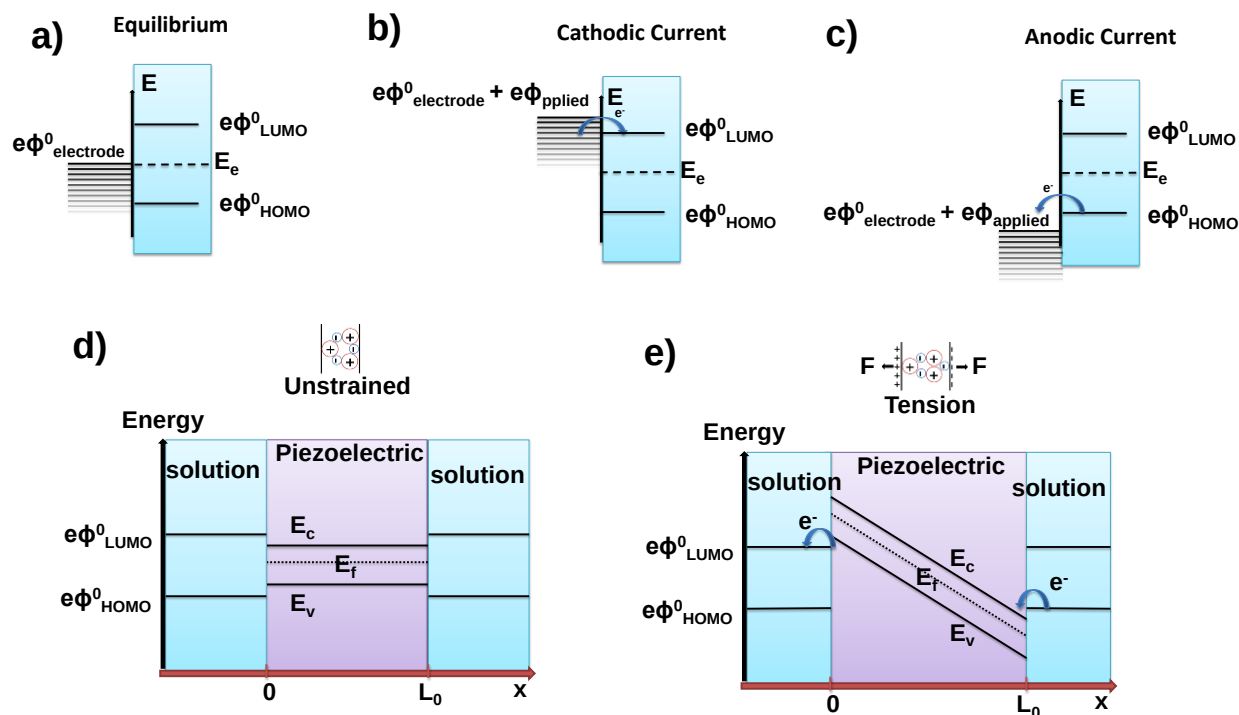


Figure 58. Changes in electrical potential between and electrode and solution and drive electrochemical reactions. a) A metal electrode is at equilibrium with its chemical surroundings. b) a potential is applied to the electrode, living up the energy of electrons in its orbitals above that of unoccupied states in solution. Electrons leave the electrode and go into solution, reducing the systems energy (cathodic current). c) a potential is applied to the electrode that lowers the energy of electrons in its orbitals below that of occupied states in solution. Electrons leave the solution and go into the electrode, reducing the systems energy (anodic current). d) A insulating piezoelectric is unstrained and in equilibrium with its chemical surroundings. e) The strained piezoelectric has dramatically changed the energy state of occupied and unoccupied states across the material, making electron transfer possible out of the valence band and into the conduction band.[502]

5.1.1 Piezopotential used for material removal

The selective removal of a material can have disastrous effects, such as in the case of corrosion, or being used to craft useful, precisely engineered structures like undercut etching in microelectromechanical (MEM) or nanoelectromechanical (NEM) device fabrication[530-539]. Regardless whether the process is purely chemical (electro-less) dissolution (Figure 59a),

electrochemical (Figure 59b) or photoelectrochemical etching (Figure 59c), the selective removal of material is a two-step process:

- 1) The bonds that hold an atom to the surface of the material are broken. In solid state materials like semiconductors, the valence band represents the energy states of the electrons bonding the atoms of the material together. A broken bond is represented as a hole and thus processes that create holes (e.g. thermal or photoexcitation, electron extraction, etc.) or increase the concentration of holes (e.g. inversion regions) weaken the cohesive forces holding the materials constituent parts together.
- 2) The saturation of a dangling atom by nucleophilic species in solution (e.g. OH^-). When the bonds holding an atom to the surface of a material are broken, the atom is susceptible to having its broken bonds satisfied either by nucleophilic species from solution, that can then surround and shepherd the dangling atom away from the surface, or by an native electron from elsewhere in the material (and thus mending the material).

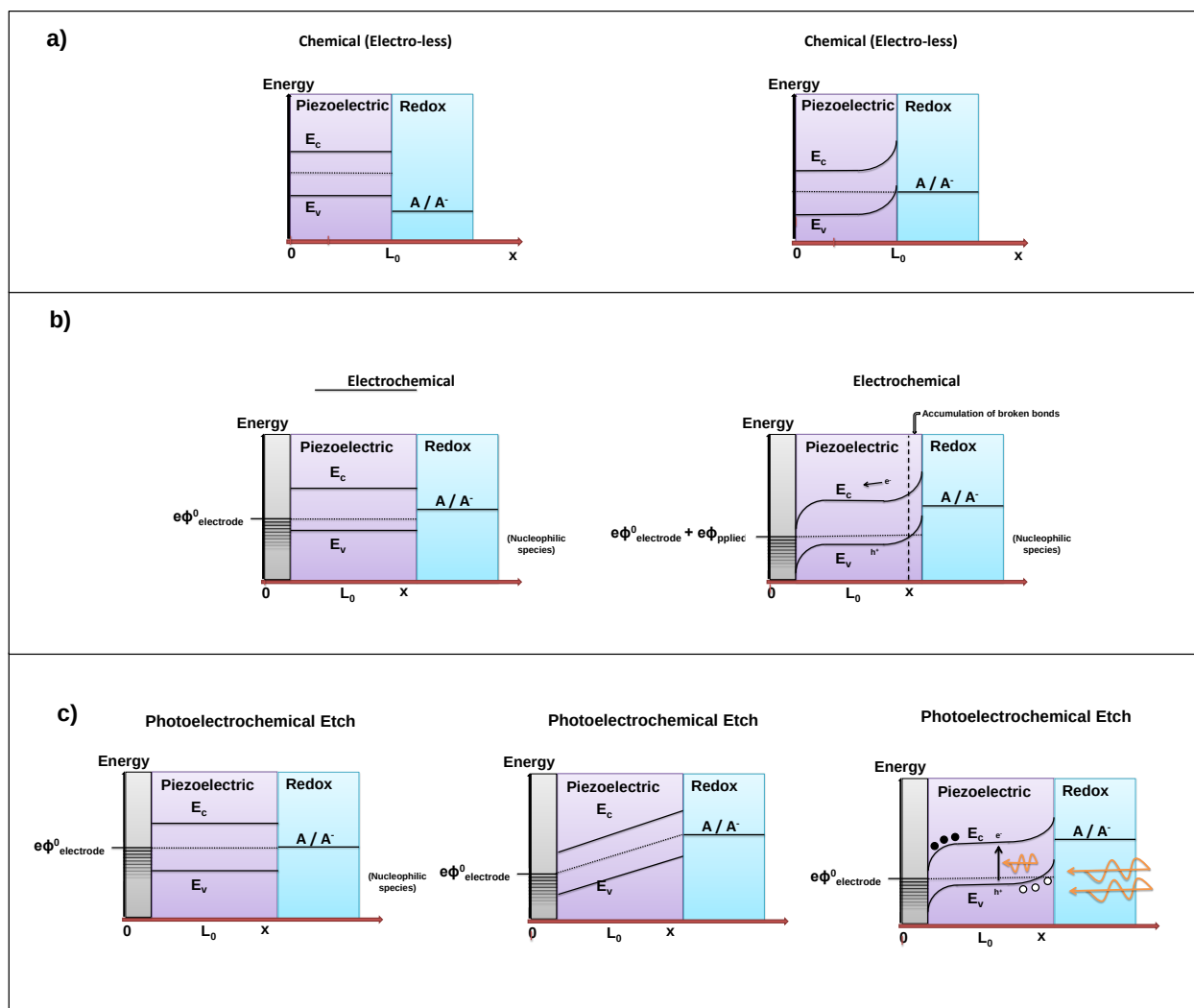


Figure 59. Etching can take place spontaneously or under an external bias. a) In pure chemical etching, the energetics of electroactive species in solution are naturally such that they are able to interface with the material, donating or extracting electrons as is necessary to isolate and extract atoms out from the surface and into solution. b) In electrochemical etching, and external bias is applied to a material, typically a metal or semiconductor, such that the energy of electronic states at the surface are made to be unoccupied (full of holes) and thus available for electroactive species in solution to donate to and interact with surface atoms. c) Photoelectrochemical etching is typically used in insulating materials, where the application of a bias alone is insufficient to drive the electrochemical etching process. Applying a potential to an insulating material results in a relatively diffuse electric field permeating the material. This field may be insufficient to focus a high concentration of charge carriers at the material/solution interface. Photoexciting mobile charges within the material allows charge to migrate throughout the material, concentrating at the material's walls. As broken bonds accumulate at the material/solution interface, the surface atoms are made available for electron donation and interaction from electroactive species in solution.[502]

The electric dipoles present in piezoelectric materials influence the rate of dissolution by acting to enhance process 1. The electric field present within the material applies a force to all of the material's charges, causing segregation of broken (holes) and unbroken bonds to opposite sides of the material. The side of the material that accumulates the broken bonds is more damaged, experiences more dangling atoms and is more susceptible to dissolution. In addition to concentrating broken bonds, the piezoelectric field also shifts the relative energies of occupied and unoccupied states across the material. Where the piezoelectric field increases the energy of electronic states occupied by electrons, the thermodynamic driving force for electron extraction by electroactive species in solution is increased and thus the number of broken bonds is increased, making more opportunities for nucleophilic attack.

The precise manufacturing of fine ferroelectric structures has found use in MEM devices[530-538], NEM devices[539], non-volatile memories[540-542] and integrated optics[511, 514, 515]. Conventionally, piezoelectric elements have been processed by chemical wet etching or argon milling techniques. In ferroelectric materials, anisotropic etching is widely observed between regions of differing polarization (i.e. domains)[543-549]. The prototypical case for domain specific etching is in the widely studied optoelectronic material, ferroelectric LiNbO_3 , etched by a HF:HNO_3 solution[550]. Figure 60 is a schematic showing what one would expect to see if a free-standing LiNbO_3 film with a periodic domain structure, as is typically used in optoelectronic applications, were exposed to an etchant solution. In LiNbO_3 , negative domains (areas with a negative surface charge) etch appreciable faster than positive domains.

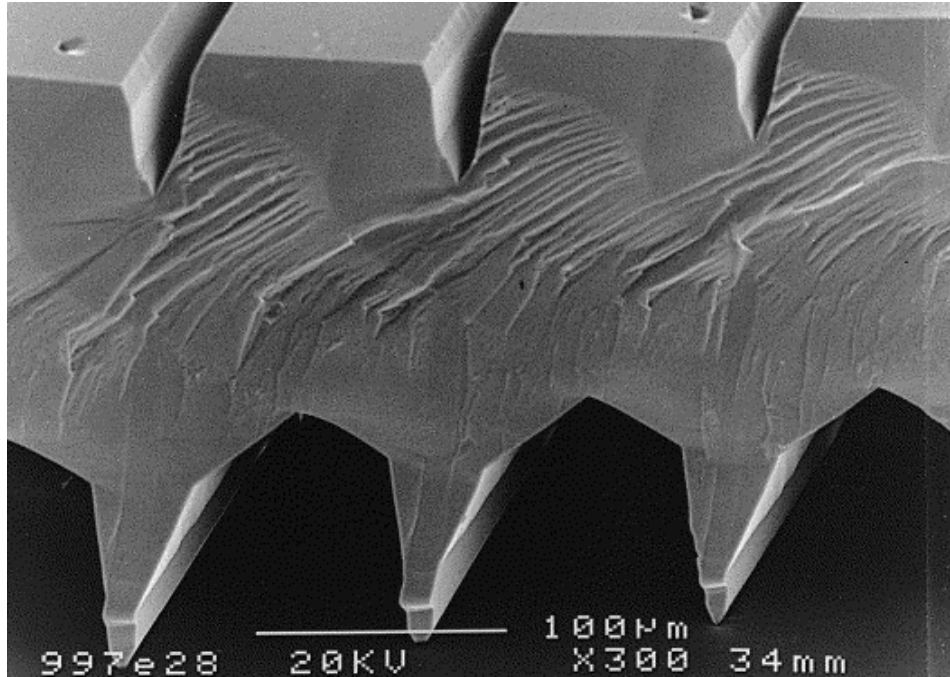


Figure 60. Etching rates of ferroelectrics depend on the local polarization. Here, a free-standing ferroelectric LiNbO_3 is etched from both sides. Negative domains etch faster than positive domains, resulting in this jagged structural formation.[551]

LiNbO_3 is a wide bandgap material that has negligible free charge carriers. The different etching rates observed on the positive and negative domain surfaces are due to the energetic difference between the electroactive etchant species in solution and the valence band position on the negative and positive domain's surface. At the negative domain's surface, the energy of occupied electronic states is elevated, making them more easily accessible to electron extraction by etchant species. There is a reversed effect on the positive domain's surface, where the energy of occupied electronic states is reduced with respect to the unoccupied states that characterize etchant species.

5.1.2 Piezopotential used for selective deposition

The piezoelectric field's augmentation of electronic states can be wielded to enable the selective growth of new material on the piezoelectric's surface. The adhesive forces that define the bond between the new material and the piezoelectric's surface come in two forms, secondary bonding and primary bonding. Secondary bonds are defined by their weak cohesive forces, e.g. electrostatic and van der Waals bonds. Material additions made to the piezoelectric that have this bonding character may subsequently experience a desorption process with an energy barrier dependent on piezoelectric potential. Primary bonds experience a strong ionic or covalent character. These strong inter-material bonds mean they experience intimate electrical and mechanical relationships with the piezoelectric and may readily be used to enhance or inhibit one or more of the piezoelectric's native surface properties.

5.1.3 Effect of polarization on absorption and desorption energy of polar and nonpolar molecules

Electrostatic and van der Waals forces can characterize the attractive forces bonding polar and nonpolar molecules to piezoelectric's surface [552-557].

Experiments carried out by Altman and Yun evaluated the influence of ferroelectric domain polarization on the absorption and desorption energy of polar acetic acid and 2-propanol and nonpolar dodecane on the (0001) surface of ferroelectric LiNbO_3 [517]. Careful absorption and desorption cycles were carried out in an ultrahigh vacuum (UHV) chamber equipped with a differentially pumped microwave electron cyclotron resonance plasma source, an X-ray source, a cylindrical mirror analyzer, and a quadrupole mass spectrometer. The two polar molecules were found to adsorb significantly more strongly on the positive surface (Figures 61a, b). Temperature-programmed desorption (TPD) data yielded desorption energies of the two polar molecules more

than 11 orders of magnitude lower than expected. The non-polar dodecane adsorption/ desorption energies were independent of surface polarity (Figures 61c, d).

Absorption and desorption experiments were conducted at multiple temperatures. These experiments demonstrated a dependence of the polar molecules' desorption energies on temperature. Altman and Yun analyzed the trend of desorption with temperature and determined the difference to be due to the pyroelectric property of LiNbO_3 , where the spontaneous dipole (and the corresponding surface charge) change as a function of temperature. In the end, electrostatic interaction between the pyroelectric surface and the polar molecules were shown to effect surface absorption properties, encourage or discourage desorption of surface molecules.

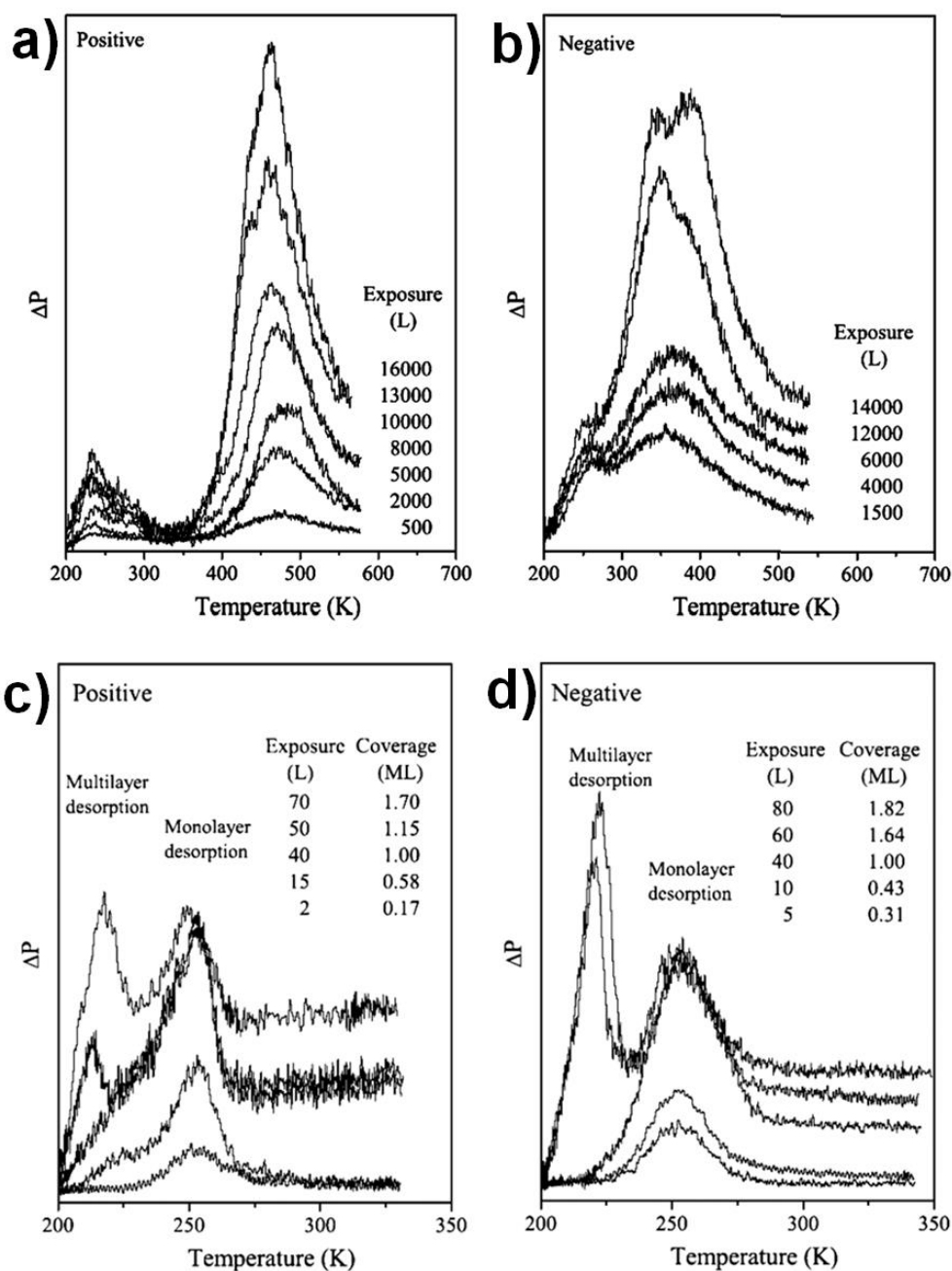


Figure 61. The bonding energy of surface absorbed molecules depends on both the polarization of the molecules and the surface. a) and b) are desorption curves for acetic acid on positively and negatively poled $\text{LiNbO}_3(0001)$ surfaces, respectively. Acetic acid desorbs from both surfaces. The desorption peak for acetic acid on the positive face is ~ 101 K higher than on the negative face, indicating that acetic acid adsorbs more strongly on the positive surface. c) and d) show that the desorption peaks for the nonpolar dodecane are approximately equal.[517]

5.1.4 Piezopotential-engineered photo deposition

The coincidence of piezoelectric domain structures being on the order of nanometers and the persistent interest in the bottom-up manufacturing of miniscule electrical components for integrated circuit, memory and sensing applications has encouraged the investigation of how piezoelectric potentials, and in particular ferroelectric domain structure engineering, can be used to control the atomic deposition and growth of new materials. In this instance, the ferroelectric polarization acts as a kind of ‘mask’, dictating the locations of material deposition and growth. A number of experiments have been carried out on both ferroelectric particles and films to explore the feasibility of this possibility [519-526]. Bulk ferroelectric materials exhibit a complicated arrangement of spontaneous electrical polarization orientations. In small ferroelectric particles, it is often observed that a single polarization orientation (domain) dominates the entire particle (Figure 62)[558]. Because of their simple dipole arrangement, ferroelectric particles make an ideal system for testing polarization’s influence on material deposition processes.

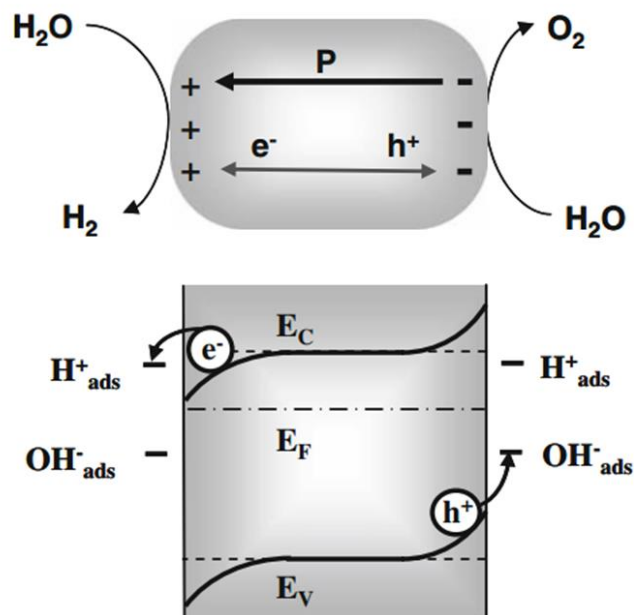


Figure 62. The spontaneous polarization in ferroelectric particles influences how mobile charges move about the particle, as well as the energetics of occupied and unoccupied states at the interface of the material and its surroundings. The polarization can dramatically affect how one end of the material reacts with its environment compared to the other.[559]

Studies conducted by Rohrer and Giocondi on ferroelectric BaTiO_3 particles less than 5 microns in diameter demonstrated the ability of the spontaneous polarization within these particles to spatially segregate photodeposition reactions occurring on their surfaces (Figure 63). In a series of experiments, BaTiO_3 particles were suspended in an aqueous solution containing 0.115 M aqueous AgNO_3 (for the oxidation reaction) and 0.0115 M aqueous $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ (for the reduction reaction). These reagents were chosen because of the energies of the Ag^+ and Pb^{2+} redox potentials, which are within BaTiO_3 's bandgap (Figure 64).

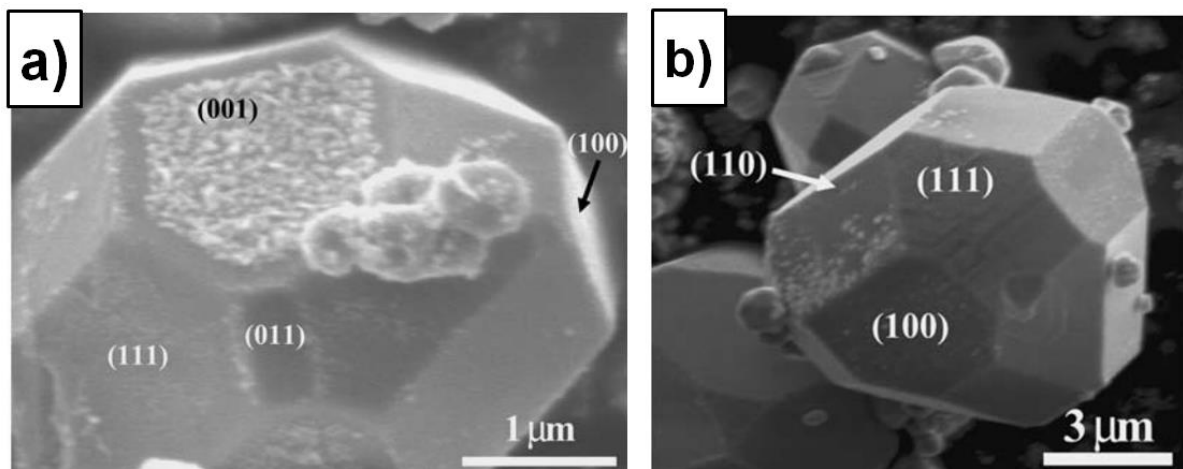


Figure 63. The effect of a single polarization within small ferroelectric particles can be seen in photodeposition experiments. a) An SEM of a ferroelectric BaTiO₃ particle exposed to aqueous AgNO₃ and photo-excited into reacting with its environment. The photodeposited silver deposits are primarily on the (001) facet. b) An SEM of a small BaTiO₃ particle after it was exposed to aqueous Pb(C₂H₃O₂)₂ and driven by light to photo-react with its environment. The deposits seen in the picture contain oxidized lead and also primarily fall on a single facet, (100).[559]

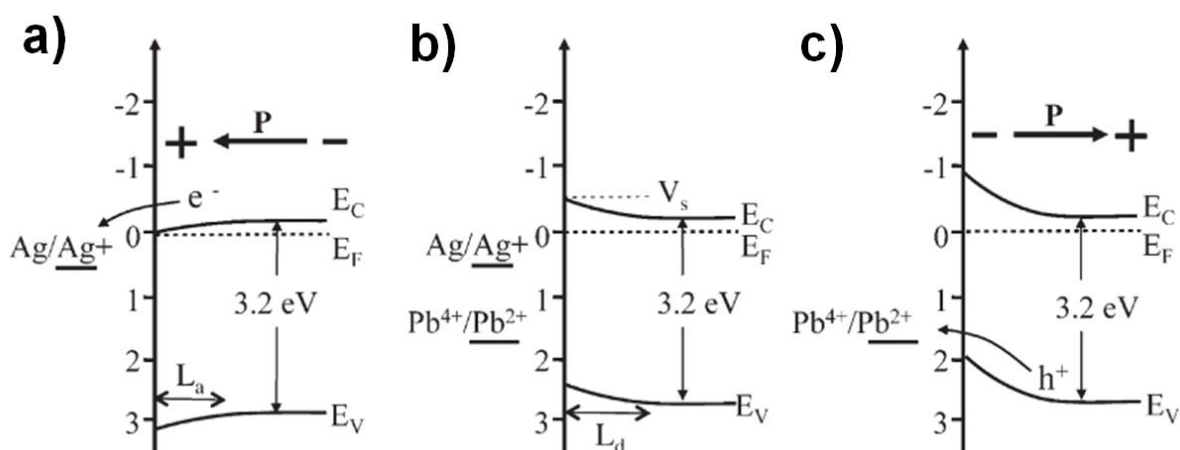
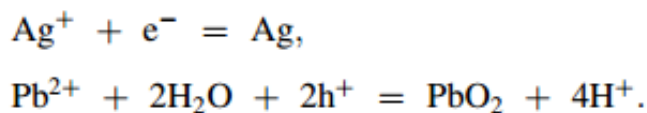


Figure 64. The spontaneous polarization of ferroelectric materials can effect what reactions take place on their surfaces. a) Is an energy diagram depicting what the energy landscape looks like on a positive BaTiO₃ domain. b) and c) depict the energetic landscape for a nonpolar and negative BaTiO₃ domain, respectively. Both Ag⁺/Ag and Pb⁴⁺/Pb²⁺ are accessible redox potentials for BTO. [560]

The reactions expected to occur on opposite facets of the particles are as follows:



The BaTiO₃ solution was continuously stirred and exposed to a UV lamp capable of photoexciting charges within the BaTiO₃ particles. Careful investigation of the particles' surfaces after UV exposure revealed that the particles photochemically reacted with the electroactive species in their surroundings. Evidence for lead oxidation was found on the [248], [474]_v, and [561] surfaces. Silver reduction was most prominently found on the [473] surface. Giocondi et al attribute the photodeposition selectivity of the BaTiO₃ particles to their spontaneous polarization. The spontaneous polarization is theorized to influence photodeposition of solid Ag and PbO by controlling the migration direction of photoexcited electrons and broken bonds (holes) in the particles (Figure 65).

In the large band gap material BaTiO₃, photoexcited electrons occupy conduction band states that are at higher potential energy than the reduction potential of the electroactive Ag⁺ cations in solution. These energetic, photoexcited electrons can lower the systems energy by transferring to the electroactive cations, in this case reducing them from Ag⁺ to solid Ag metal. On the other end of the particle, broken bonds (holes in the valence band) accumulate and are able to accept electron injection from any number of courses, including water moles.

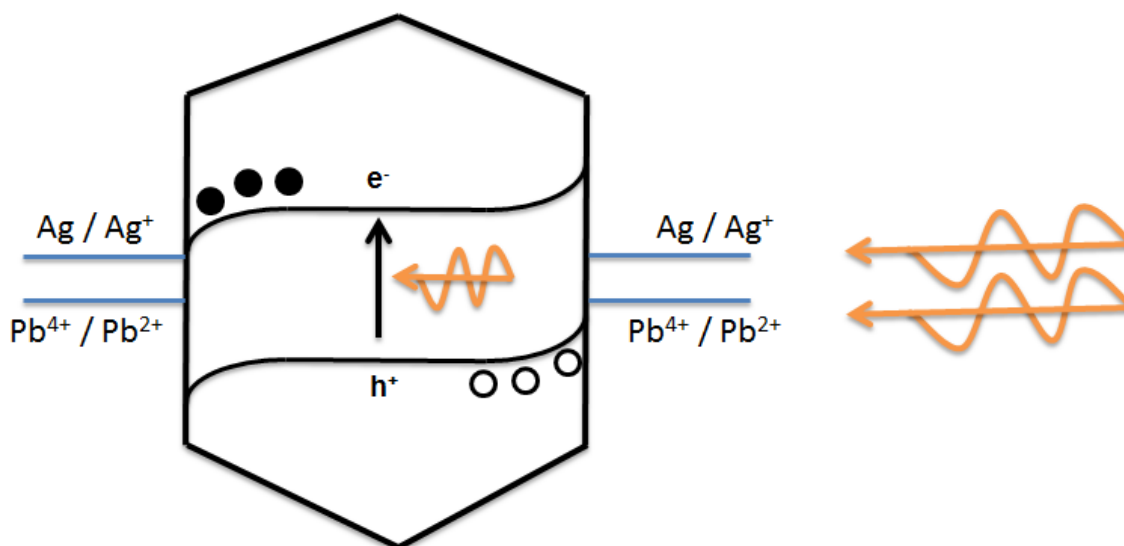


Figure 65. The spontaneous polarization of ferroelectric particles causes charge migration within the particles, resulting in reduction and oxidation reactions occurring on opposite sides of the material.[502]

The ability of spontaneous dipoles to orchestrate the photodeposition process was further investigated by Zhang, Dunn et al[521, 524]. In a series of carefully conducted experiments, Q. Zhang and Dunn showed that for ferroelectric lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) films, photoreduction and photo-oxidation reactions occur nearly exclusively on the positive and negative domain surfaces, respectively (Figure 66). Zhang and Dunn were able to show that poling the ferroelectric with an AFM tip is capable of engineering the shape of photodeposited structures. Checkerboard patterns, nested squares and wire shapes were all poled in the surface of a PZT film and shown to predictably control the photodeposition of structures on its surface.

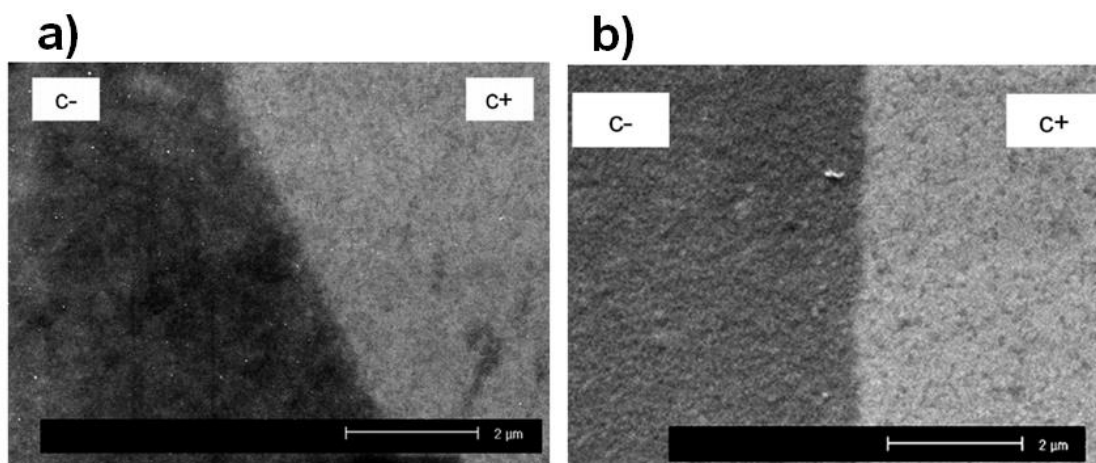


Figure 66. Ferroelectric domains dramatically effect the result of photodeposition experiments taking place on films. a) an SEM image of an interface between a negative and positive ferroelectric domain, after a photodeposition experiment. Sn deposited on the c+ domain from an aqueous SnCl_2 solution. The surface of the c- domain was unaffected by the photoexcitation. b) Fe deposited on c+ in from an aqueous FeCl_2 solution. The surface of the c- domains remained unaffected in this sample.[562]

Subsequent work by Rohrer et al examined the influence of ferroelectric dipoles on photochemical processes occurring beyond the ferroelectric/solution interface [560, 563]. Rohrer conducted a series of studies to examine how the ferroelectric dipoles effected the photochemical reactivity of TiO_2 films of varying thicknesses deposited by pulsed laser deposition on the surface ferroelectric BaTiO_3 . The influence of spontaneous polarization was indeed seen in the patterns of photodeposited Ag on the TiO_2 surface, even when the TiO_2 film thickness extended 100nm away from the buried ferroelectric's surface (Figure 67). A careful set of characterization experiments was able to confirm that it was the domain polarization alone, and not other surface features correlated with polarization, which determined the photodeposition behavior of the TiO_2 coating.

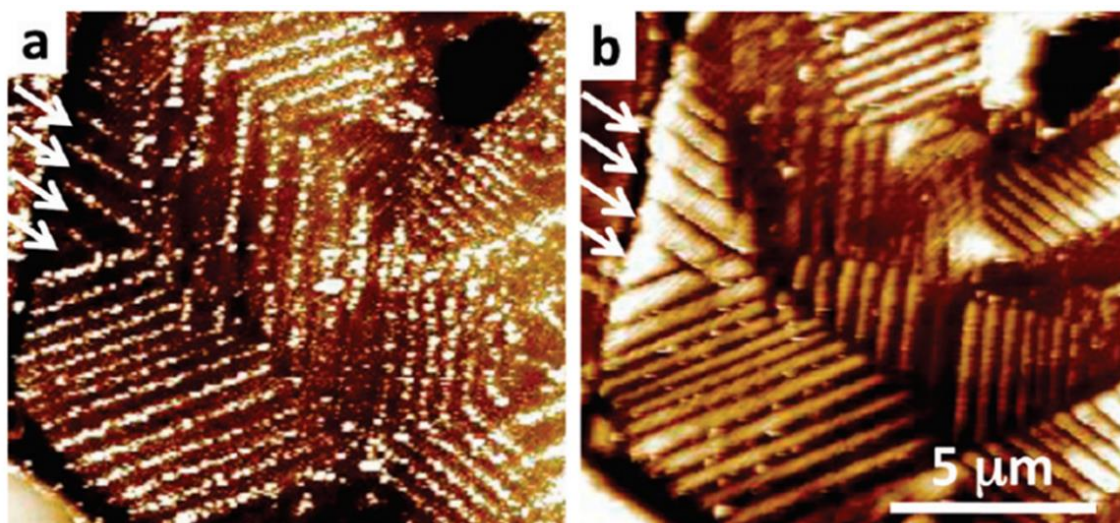


Figure 67. A 15 nm thick TiO_2 coated, multi-domain ferroelectric substrate exposed to photodeposition experiments. a) A topographic AFM images of the film after reaction with aqueous AgNO_3 solution. Ag is deposited on top of the TiO_2 coating in the same pattern as the ferroelectric domains beneath the surface. b) A topographic AFM images of the film after reaction with a Pb solution. The arrows in Figure a) and b) direct attention to domains that avoid deposition reactions under one experimental condition while encouraging it under another.[560]

5.1.5 Piezopotential-driven materials evolution

In the subsequent section we reviewed how the dipoles present in piezoelectric materials could influence material dissolution, the condensation and evaporation of a gas phase, and the photodeposition of an electro active species in solution. The same process that physically segregates reduction and oxidation photodeposition reactions can also be used to separate concurrent gas evolution reactions, such as the photolysis of water into H_2 and O_2 , where back reactions can be parasitic to the energy conversion process.

5.1.6 Piezopotential-engineered photoelectrochemical material evolution

The conversion of renewable energy sources, especially solar, into chemical fuels that can provide drop-in, sustainable drivers for our energy intensive economy has been a scientific pursuit for decades[564-570]. One of the many ensembles currently pursued for achieving this goal is the

‘photocatalytic’ approach, whereby a semiconductor or a series of semiconductor heterojunctions absorbs light from the sun and uses the photoexcited carriers to simultaneously electrochemically reduce and oxidize water to H_2 and O_2 gas, respectively[567, 570-589]. The H_2 and O_2 gas can then be extracted and used by fuel cells to generate electricity, or the H_2 can be used to synthesize carbon based fuels by combining it with reduced CO_2 . Many designs have been proposed for the photocatalytic approach. One of the economically inexpensive of the proposed approaches consists of a suspension of light sensitive semiconductor particles in a transparently encapsulated pool of water where the particles have direct access to both the sunlight and H_2O (Figure 68). This approach has encountered a number of challenges, including a high recombination rate of photoexcited charges within the semiconductor particles themselves and the back reaction of $2H_2$ and O_2 molecules into $2H_2O$ in the moments immediately following the electrochemical splitting of water on the particles surface.

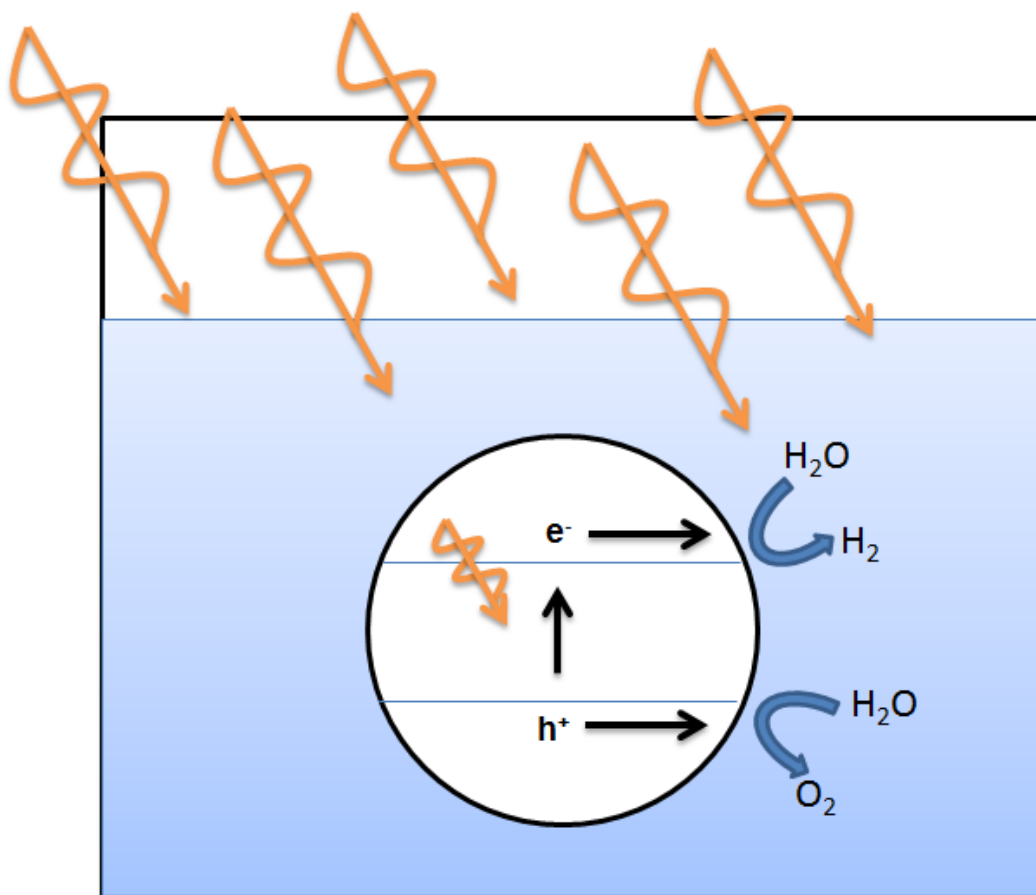


Figure 68. Free floating, semiconducting particles absorb light from the sun and use it to split water into H_2 and O_2 gas.[502]

Semiconducting ferroelectric particles employed for the photolysis of H_2O offers an eloquent solution to both of these challenges [590-595]. In small particles, electrons and holes are spatially confined resulting in a high rate of photoexcited charge recombination. The spontaneously polarization present throughout a ferroelectric particle pushes the electrons and holes to opposite sides of the material, reducing their wave function overlap and thus reducing their probability of recombination. A reduced recombination rate leads to a longer carrier lifetime and subsequently a greater number of attempts for the photoexcited electron and hole to react with their chemical environment. In addition to reducing the recombination rate and increasing the likelihood that a photoexcited carrier will react with its chemical environment, the segregation of

electrons and holes also ensures that the electrochemical reduction and oxidation of water will happen on spatially segregated surfaces. The separation of reaction products (H_2 and O_2 in this case) dramatically reduces the likelihood that these chemical species will immediately back-react to form water.

5.1.7 Piezopotential-driven electrochemistry

The use of piezoelectric materials in chemical systems was classically restricted to their ‘static’ deployment. In these cases, the piezoelectric would be un-poled, poled, or statically strained and the resulting spontaneous or strain-induced piezoelectric field would modify the energetics of electric states and the direction of migrating charges, to achieve some engineered goal[248, 483, 590-595]. Recently there have been investigations into the use of dynamic applications, where a piezoelectric material is continuously and alternately strained between a tensile and compressive state resulting in a large and rapidly varying piezoelectric field within the material. This continuously varying system is prevented from achieving thermodynamic (electrochemical) equilibrium with its environment, the result of which is an enduring, though fluctuating, exchange of charge between the piezoelectric and its environment[504, 505, 527, 528].

The procedure of a typical electrochemistry experiment includes submerging an electrode of interest in a chemical environment of interest and then using an external power source to control the flow of charge between the electrode/environment interfaces. Li et al explored a set of experiments that combined the power source and electrode into a single material [527, 528]. Using an ultrasonic bath and water based solutions, Li subjected suspensions of wire-like ZnO and $BaTiO_3$ to ultrasonic vibration and micro-cavitation forces with the objective of getting them to bend and strain, generate a piezoelectric field, and piezoelectrochemically split water into H_2 and

O₂. While a number of questions remain as to what kinds of forces the piezoelectrics were subjected to and what magnitude of piezoelectric potentials were created, the H₂ and O₂ evolution as a function of piezoelectric ultrasonication were clearly correlated (Figure 69).

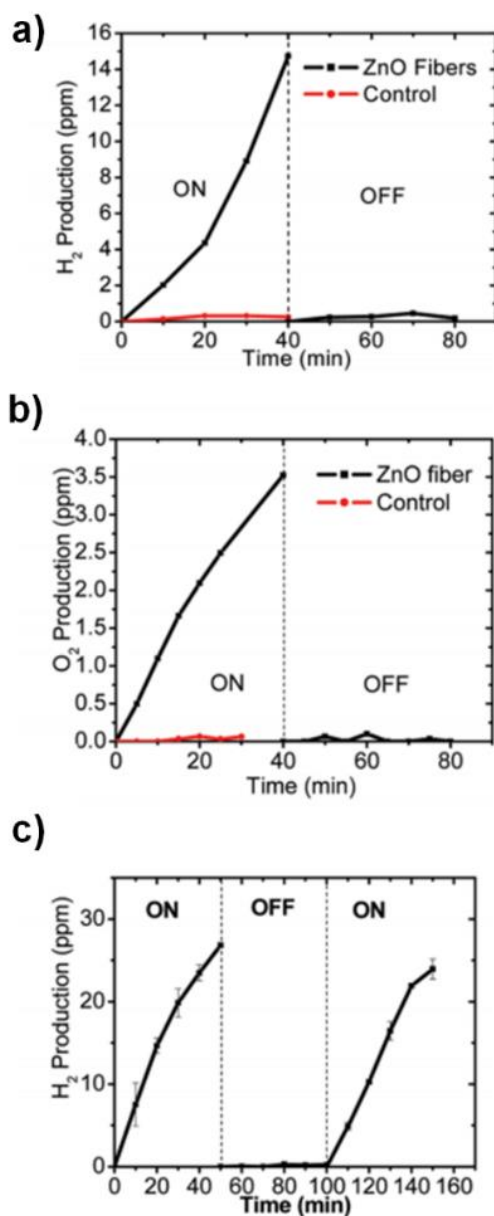


Figure 69. Ultrasonication of piezoelectric sires suspended in a water solution show a correlation with evolved H₂ and O₂ gas. A) and B) show the H₂ and O₂ production are both dependent on the piezoelectric nature of the material and the mechanical agitation to solution. C) The system is repeatable. Here, where the environment is refreshed, the system continues to convert mechanical energy into H₂ and O₂ evolution. [596]

5.1.7.1 Piezocatalysis on metal surfaces

Study of the piezocatalytic effect was conducted on a single-crystalline ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}32\text{PbTiO}_3$ (PMN-PT) cantilever in a sealed chamber (Figure 70). The voltage output of the PMN-PT slab was first characterized in air (Figure 71a). The cantilever was mechanically oscillated with a fixed frequency and amplitude. When the piezoelectric cantilever was transitioned to the DI water environment, the voltage amplitude decreased while the mechanical oscillation frequency and amplitude remained constant. In order to encompass the entire piezocatalytic system into a cohesive being, an analog circuit was constructed as shown in Figure 71b. Here, opposite and iteratively alternating sides of the piezoelectric material serve as both the working and counter electrodes, respectively. A strained piezoelectric material can be considered a charged capacitor, and thus the change in measured voltage is correlated with a change in piezoelectric-induced surface charge (ΔQ_p). When a strained piezoelectric material is placed within an aqueous medium of finite conductivity and polarizability, its piezoelectric-induced surface charge can be depleted via two primary pathways: Faradic (I_f) and capacitive ($I_c = dC_d V_d / dt$, where C_d and V_d are the double layer capacitance and voltage drop across the double layer, respectively) currents (equation (3.1)):

$$\Delta Q_p = \int I_f dt + C_d \cdot V_d \quad (3.1)$$

The capacitive current leads the formation of double layers in the vicinity of piezoelectric surfaces, screening the surface charge. The Faradic current involves charge transfer between the solution and piezoelectric surfaces, which is possible under bias and responsible for electrochemical reactions.

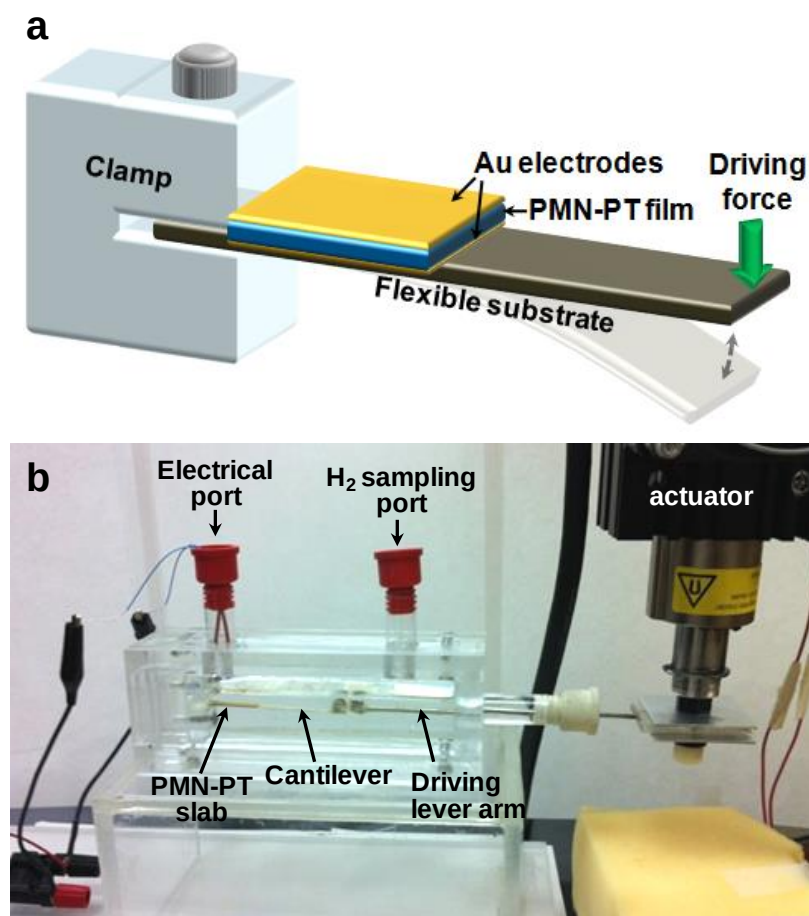


Figure 70. Experimental setup. a, The piezoelectric cantilever setup for studying the piezocatalytic effect. It consists of a flexible substrate for strain induction, a piezoelectric element for generation of piezoelectric potential, and a clamp for securing the cantilever's base. b, Photo of the experimental setup and reaction apparatus used for studying piezocatalyzed hydrogen evolution from water. [450]

Figure 71c demonstrates a means by which piezoelectric potential is sufficient to create a favorable energetics landscape for generating Faradic currents on opposite electrode surfaces, promoting both the reduction of protons in solution (evolving H_2) and the oxidation of water. In the limit where the piezoelectric material is a perfect dielectric, the appearance of piezoelectric potential induces a linear shift of the Fermi level. The electron energy levels of both electrodes follow the shift and the difference is the observed piezoelectric voltage output (V_{pz}). Because neither of the electrodes is grounded, their absolute electrochemical potentials are considered

“floating” and in intimate electrical contact with the pure water environment. Thus V_{pz} will shift the potential of both Au electrodes by an equal and opposite amount of $1/2eV_{pz}$ and $-1/2eV_{pz}$, respectively (shown by red lines in Figure 71c). This electronic perturbation induced by the mechanical deformation modifies the electrons’ energy in the Au electrodes and moves it away from equilibrium. The electrochemical potential differences between the electrode and solution are a driving force for electron transfer across the electrode/solution interface and thus induce electrochemical reactions. This process is similar to that which occurs in an electrolysis system, where an applied bias disrupts the fermi-level equilibrium across the interface resulting in a driving force for electrochemical reactions.

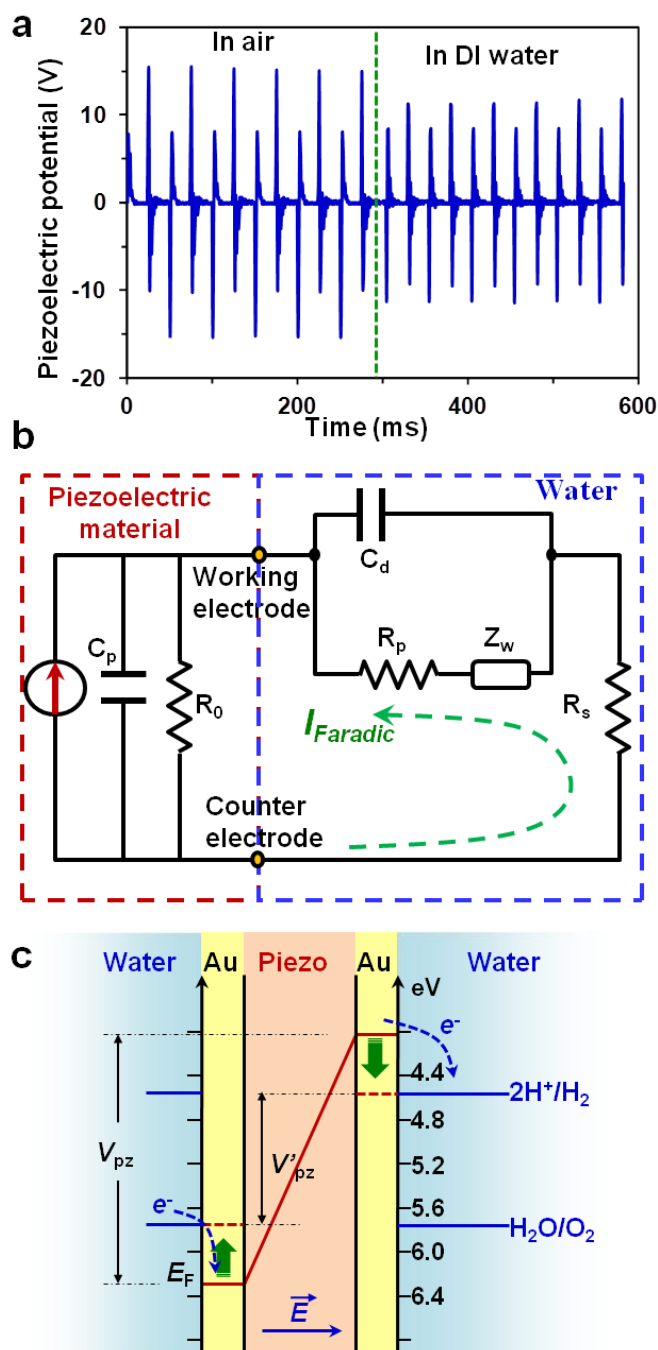


Figure 71. Fundamentals and preliminaries of piezocatalysis. a) The effect of environment on the measured piezoelectric potential. A marked decrease in potential-difference is observed when the piezoelectric cantilever is submerged in DI water versus air. b) A proposed equivalence circuit based upon a first approximation combination of both a piezoelectric circuitry element and a charge-transfer/double layer analog for an electrochemical system. c) A proposed mechanism for the occurrence of piezoelectric-potential-driven Faradic currents at the piezoelectric/water interface.[450]

Therefore, when the potential on the negative electrode exceeds the proton reduction potential (right Au electrode in Figure 71c), electrons of sufficient energy could transfer from the electrode to protons on or near the surface, producing hydrogen. Similarly, when unoccupied electron energy levels of the electrode are made sufficiently positive in potential so as to exist below the water oxidation potential (left Au electrode in Figure 71c), electrons could transfer from water molecules to the electrode, producing O_2 . Such piezoelectric-potential-driven electrochemical reactions create Faradic currents in the electrolyte and deplete piezoelectric-induced surface charge. Therefore, the piezoelectric potential drops accordingly and eventually the reactions cease when the electron energy levels are no longer energetically favorable for net charge transfer (shown by dashed red lines in Figure 71c). The Faradic capability of piezoelectric potential was experimentally demonstrated by characterizing the electrode potential relative to a saturated calomel electrode (SCE) via a potentiostat. Even under conditions of DI water solution resistance (R_s) and modest strain, the potential present on the electrode is sufficiently negative to thermodynamically engage the H_2 evolution reaction (Supplementary Figure 72a-d).

Experimental setup

The piezoelectric cantilever used a PMN-PT single crystal slab as the piezoelectric component. The PMN-PT slabs were poled along the $\langle 001 \rangle$ direction, and exhibit piezoelectric coefficients of 2200-2700 pC/N. Cantilever construction and encapsulation was accomplished with ECCOBOND® 45 epoxy. The entire assemblage was emerged in DI water and $NaNO_3$ electrolytes within a sealed chamber with access ports for piezoelectric actuation and monitoring, environmental purging, and atmospheric sampling. Straining of the piezoelectric cantilever was achieved by a computer controlled vibrator (for high-frequency oscillation) and linear actuator (for controlling straining state). The H_2 concentration was determined by measuring the atmosphere

sample in the reactor using an AMETEK Analyzer ta3000F H₂ gas analyzer. A background baseline for atmospheric H₂ concentration was established before every experiment via a 10-minute nitrogen purging to the apparatus. The piezoelectric potential and the surface electrochemical potential were measured by a digital oscilloscope and a potentiostat, respectively.

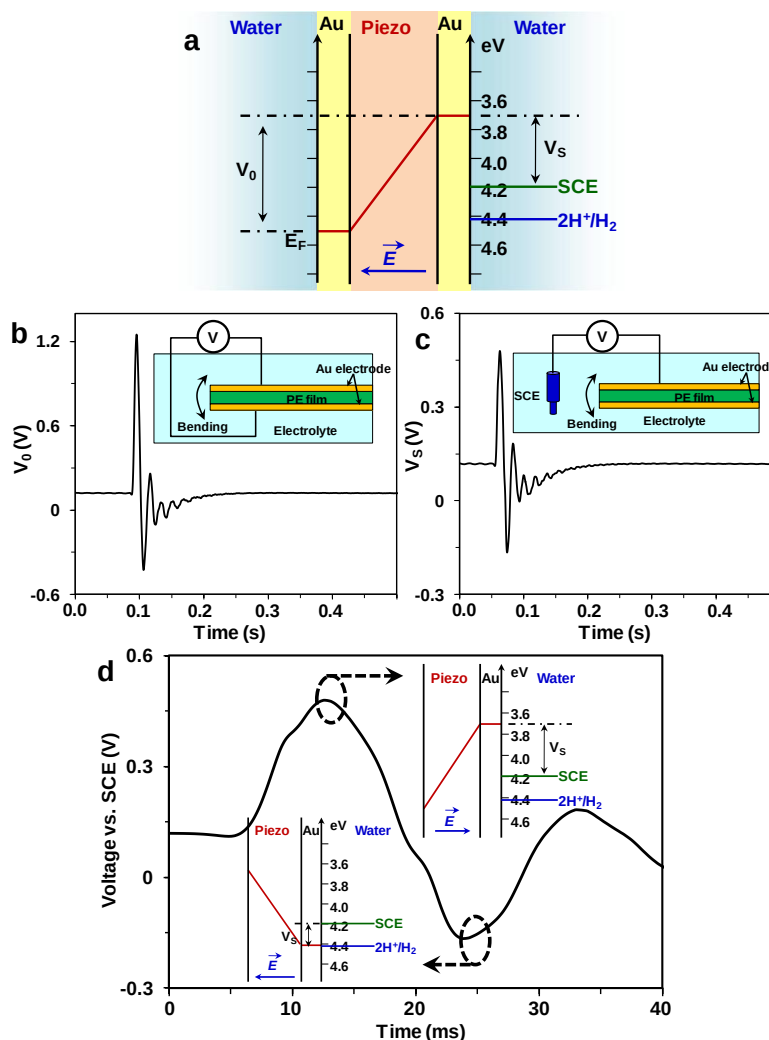


Figure 72. Electrical potential characterization of the piezoelectric material with respect to a saturated calomel electrode (SCE). a, diagram of the potential profile across the piezoelectric element under minor strain as elucidated by reference to the SCE. V_0 represents the piezoelectric potential observed between the two electrodes; while V_S represents the potential difference between one electrode and the standard SCE. b, The piezoelectrical potential measured across the piezoelectric material that was under a sudden impact-load of strain pulse and then released for damped oscillation. The maximum potential difference was ~ 1.2 V. c, The potential profile measured on a single electrode of the piezoelectric material versus SCE. The applied strain was the same as that used in b. The maximum potential was ~ 0.5 V, demonstrating the potential difference between the counter electrode and SCE as that illustrated in a. d, The potential measured on one side of the piezoelectric material versus SCE during an oscillatory period of strain. The positive and negative values of the potential suggest that the relative electrochemical potential of the electrode can be driven higher and lower than the standard SCE level by the direct piezoelectric effect. The potential appearing on the electrode surface is thermodynamically capable of driving proton reduction reactions in its immediate vicinity. [450]

Having verified that piezocatalyzed proton reduction is thermodynamically accessible, H₂ gas evolution was measured as a function of time, during mechanical oscillation of the piezoelectric cantilever in DI water at given frequencies (Figure 73a). The strain amplitude was kept constant, generating a piezoelectric potential of 20 Volts throughout the entire experimental set. The green triangles in Figure 73a represent H₂ concentrations in the reactor when the piezoelectric cantilever was oscillating at 10 Hz. Higher H₂ concentrations can be clearly observed at longer oscillation times. A linearized fit indicates the rate of H₂ concentration increase was ~0.22 ppb/s. By raising the oscillation rate to 20 Hz, the H₂ concentration was strikingly higher at given sampling times, though the data also exhibited a much wider distribution, as shown by the blue diamonds in Figure 73a. The rate of H₂ concentration increase suggested by the linearized fit was ~0.68 ppb/s. These H₂ production rates far exceeded (by at least an order of magnitude) that exhibited by the control, which consisted of a non-piezoelectric (silicon) cantilever manufactured in an identical manner and mechanically oscillated at equal amplitude and frequency (red circles in Figure 73a).

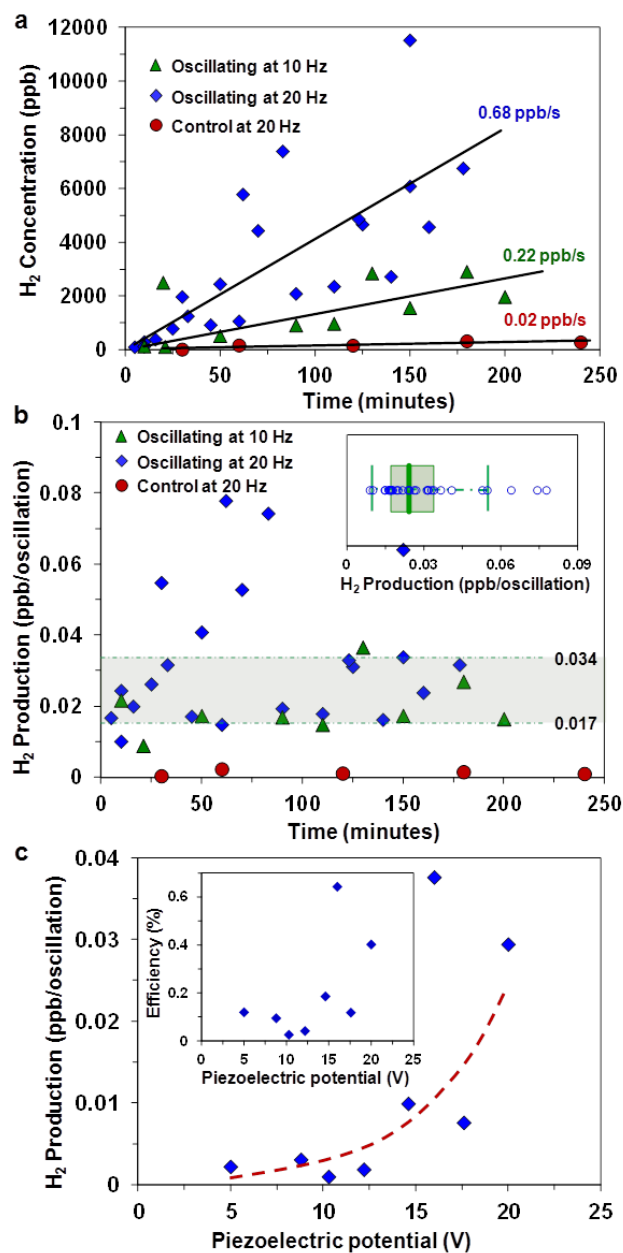


Figure 73. H₂ evolution correlated with the direct piezoelectric effect. a) H₂ concentrations measured as a function of oscillating time of the piezoelectric beam in DI water medium with a frequency of 10 Hz (green triangles) and 20 Hz (blue diamonds). A Si cantilever with identical configuration was used as a control and the corresponding H₂ concentrations are marked by red circles. b) H₂ production per oscillation values derived from experiments shown in a. Inset is a box-whisker plot of the data shown in b representing a reference for the dispersion. c) H₂ production per oscillation as a function of peak piezoelectric potential, where an exponential dependence was identified (red dashed line), consistent with the application of the Butler-Volmer relationship. Inset is the corresponding piezocatalytic efficiency calculated as a function of peak piezoelectric potential.[450]

Figure 73b summarizes all the acquired data from both 10 Hz and 20 Hz normalized by the number of oscillation cycles. Although a wide distribution (from ~ 0.01 to ~ 0.08 ppb/oscillation) was obtained, the rate of H_2 production remained within a constant range throughout an operation time exceeding 3 hours (or $>220,000$ cycles), indicating a stable H_2 evolution capability from the piezoelectric material. The H_2 production data were also analyzed by the Box-Whisker plot (inset of Figure 73b). The sample median has a value of ~ 0.024 ppb/oscillation. The upper and lower borders of the green box represent the largest 25% and smallest 25% of the observations, corresponding to upper and lower limits of 0.034 and 0.017 ppb/oscillation, respectively. The data points outside the green lines are classified as outliers.

H_2 output per oscillation was further investigated as a function of the piezoelectric potential. As shown in Figure 73c, the H_2 production as a function of voltage is non-linear and indeed follows an exponential relationship. This is indicative of a non-diffusion limited case, likely due to the low current density (or H_2 production rate) and oscillation-self-induced agitation. The dependency of current density j on applied potential η is similar in form to that given by the Butler-Volmer equation (3.2) [597]:

$$j = j_0 e^{\frac{\alpha_c n F \eta}{RT}} \quad (3.2)$$

Fitting the data to such an exponential dependence yields exchange current j_0 of 0.4 mA/cm² and the cathodic transfer coefficient α_c of 0.002651. The small α_c possibly suggests that high over potential would be necessary to drive the piezocatalytic process in the DI water environment[597]. The agreement between trend articulated by theory and the experimental results is indicative of an accord in basic principles. However, the time-dependent voltage-current relationship throughout an oscillation cycle would require a more complex, dynamic- j analysis to reveal the piezocatalysis mechanisms and kinetics with higher precision.

The electrical-to-chemical energy conversion efficiency (*i.e.* piezocatalytic efficiency) was estimated by comparing the total surface charge generated on the strained piezoelectric material to the amount of H_2 produced (inset of Figure 73c). The efficiency per oscillation is less than 0.7% even under the favorable condition of high piezoelectric potential. Possible reasons for this inefficiency are: (1) voltage losses due to a capacitive current; and (2) an inability to carry out the electrochemical reaction to completion due to the insufficient time allotted for the piezoelectric-induced surface charge to fully diminish via Faradic and/or capacitive currents.

Therefore, if the time between one straining action to the next is less than the time necessary for the available energized surface charges to fully take part in the reaction, the ability of these charges to generate reaction products will be retarded. In order to demonstrate this influence toward the piezocatalytic efficiency, a new straining procedure was devised (Supplementary Figure 74). In this instance, the piezoelectric cantilever was put through a straining action in time t_1 , held statically in the strained state for a time t_2 , unstrained in a time $t_3 = t_1$, and held for a time $t_4 = t_2$. A typical voltage output *via* this manner of operation is shown in the inset of Figure 75a, where $t_1 = t_3 = 50$ ms, and $t_2 = t_4 = 2$ s. Holding the strain for an extended period of time (~ 2 s) allowed the piezoelectric-induced surface charge to fully deplete before the occurrence of an opposite strain and thus the revival of piezoelectric potential. The voltage-drop curve during one straining cycle is shown in Figure 75a. The majority (90%) of voltage decrease occurred within the first ~ 0.06 s, with 99% voltage drop having occurred by 1.46 s. To reveal the holding-time dependent H_2 evolution, a series of experiments were conducted under various t_2 ($= t_4$) values ranging from 0.05 to 2 s and a fixed $t_1 = t_3 = 50$ ms to ensure the same strain rate. From the output voltage profiles (Figure 76), the quantity of charge depleted from each straining action was calculated (see Figure 77 for details) and plotted as a function of strain holding time (red triangles

in Figure 75b). Also on this plot is depicted the number of H₂ molecules produced during each straining cycle as a function of holding time (blue diamonds). Due to the rapid voltage drop, small variations of the released charge were observed at $t_2 > 0.2$ s; whereas the ability of the piezoelectric potential to drive the H₂ evolution reactions markedly improved as t_2 increased beyond 0.5 s and approached its asymptote when $t_2 > \sim 1$ s. The discrepancy between the amounts of released charge and produced H₂ molecules at shorter t_2 indicates that the initial voltage drop may be mostly attributed to capacitive current, whilst Faradic charge transfer would occur in a steady but slow manner and may only become dominating after the double layer has formed.

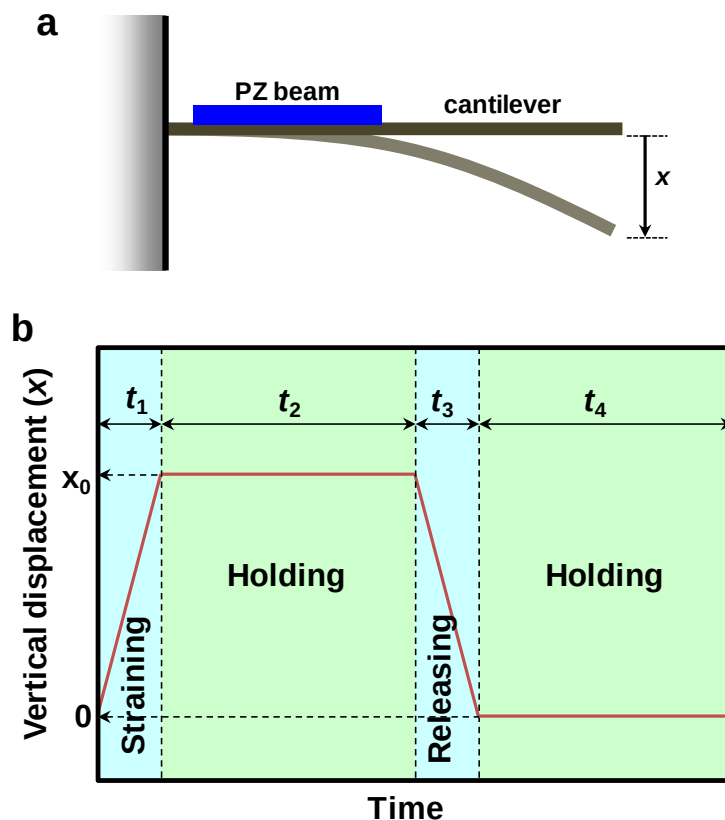


Figure 74. Experimental design of the straining and holding control. a, A diagram demonstrating how strain was imposed on the piezoelectric cantilever via vertical displacement of the cantilever tip by a distance of x . b, One straining cycle depicted by the displacement of the piezoelectric cantilever tip (x) as a function of time. One cycle includes four segments: (1) straining: an enforced linear increase of x , reaching the maximum displacement of x_0 over time t_1 ; (2) holding: the piezoelectric cantilever held at the maximum displacement x_0 for time t_2 ; (3) releasing: a linear return of the displacement back to 0 over a time t_3 ; (4) holding: the piezoelectric cantilever held at the displacement 0 for time t_4 . The displacement was program controlled and repeated for designed cycles. In all experiments, straining times t_1 and t_3 were set equal and their value held constant; while t_2 and t_4 were set equal but their value varied for investigating the holding time influence toward the piezocatalyzed hydrogen evolution. [450]

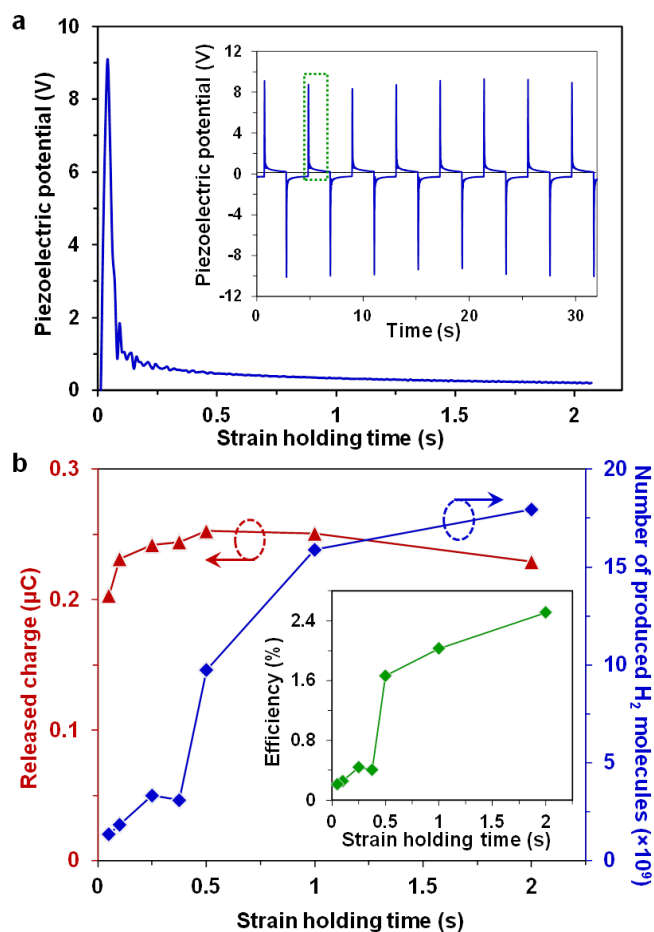


Figure 75. H_2 evolution correlated with the piezoelectric charge release. a) A piezoelectric potential curve obtained from the piezoelectric beam, when it was held under a constant strain within DI water medium. Inset is a typical piezoelectric potential profile with a 2 second strain holding time. The green dashed box highlights the potential decreasing cycle shown in a. b) The total quantity of released charge (red triangles) and the corresponding number of H_2 molecules produced (blue diamonds) as functions of the strain holding time, where the peak piezoelectric potential was kept at ~ 10 V. Inset: The piezocatalytic efficiency of H_2 evolution per straining as a function of holding time. [450]

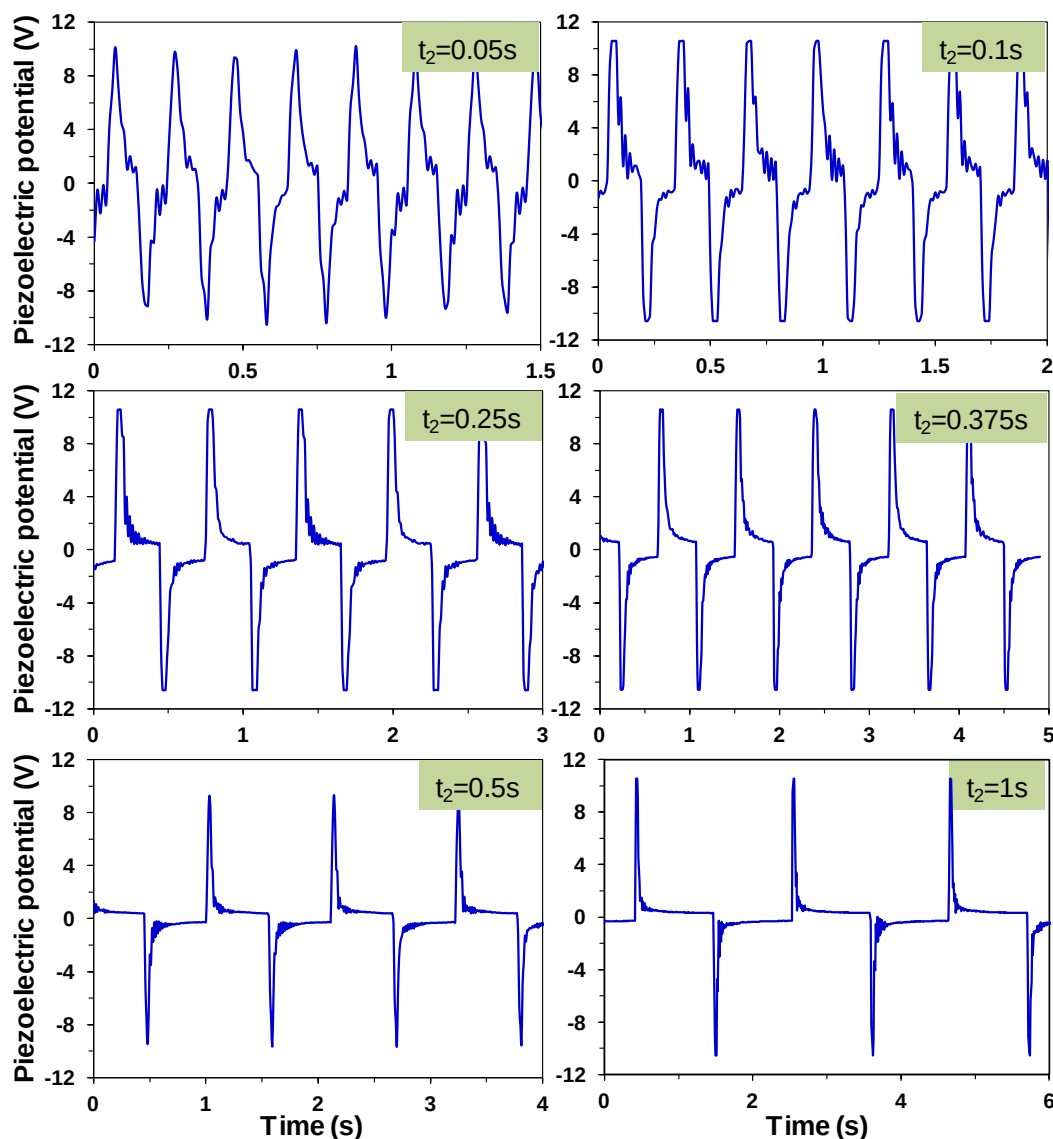


Figure 76. The piezoelectric potential profiles measured under different straining patterns for studying the influence of holding time toward the piezocatalyzed hydrogen evolution. In all experiments, the straining and releasing times were set equal ($t_1 = t_3 = 50$ ms). The holding times ($t_2 = t_4$) were varied from 0.05 to 2.0 s as marked in the top-right corner of each figure (the 2.0 s curve is shown in Figure 72A). Because of the constant straining time t_1 , the piezoelectric material experienced the same strain rate, and thus nearly identical peak piezoelectric potentials were obtained. From these curves, the quantity of charges depleted from the piezoelectric material can be calculated as a function of the holding time.[450]

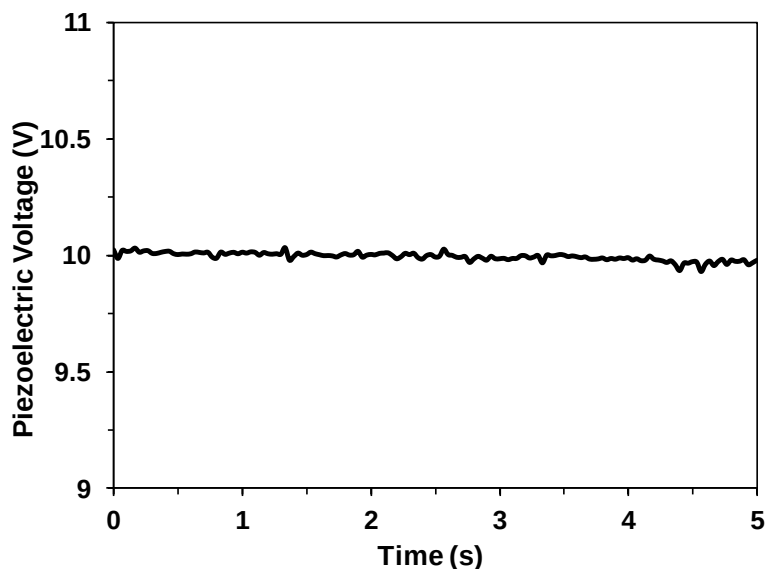


Figure 77. Method for calculating the number of released charges from the piezoelectric potential profiles. Above curve is the piezoelectric potential profile when the piezoelectric beam was strained and held in air. This curve reveals the rate of piezoelectric charge leakage due to the measurement system. Starting from a piezoelectric potential of ~ 10 V (identical to the holding experiments), the magnitude of potential drain was within the noise level during a 5 second period. Therefore, when calculating the quantity of charge drained in an aqueous environment for a maximum 2 second period, the charge drained through the measurement equipment is negligible. Hence, the piezoelectric potential drop was attributed completely to charge depletion mechanisms in the aqueous environment (i.e. capacitive or Faradic currents). Thus, total charge released from the piezoelectric surface over a single straining cycle was determined by: $\Delta Q = \frac{\Delta V \epsilon_m}{2d}$. ΔQ is the

total charge removed from a single side of the piezoelectric material. ΔV is the piezoelectric potential difference between the peak value and the value right before the opposite strain was applied. They were determined from the voltage curves shown in Figure 76. ϵ_m and d are the electrical permittivity and thickness of the PMN-PT slab with values of 6.6406×10^{-8} F/m and 0.25 mm, respectively. [450]

Comparing the values of released charges to produced H_2 molecules, the piezocatalytic efficiency per straining action as a function of t_2 was obtained (inset of Figure 75b). The efficiency results are consistent with those of reaction kinetics hindering the productivity of hasty oscillations, which clearly shows that the introduction of a holding period did largely facilitate the H_2 generation. Given the same peak piezoelectric voltage (~ 10 V), a 50 ms holding-time improved the piezocatalytic efficiency from $\sim 0.02\%$ to $>0.2\%$. With longer t_2 (1–2 s), the piezocatalytic

efficiency reached $\sim 2\text{--}2.4\%$. These values exceeded those of the 20 Hz oscillations by two orders of magnitude.

According to equation (3.1), the double layer capacitance (C_d) could also significantly impact the efficiency. Therefore, in piezocatalytic systems, a concentrated electrolyte might critically limit the effectiveness of the piezocatalytic process through an increase in C_d and thus screening the piezoelectric potential, detrimentally sapping the free energy available for driving electrochemical reactions. In order to reveal the influences of electrolyte in piezocatalytic systems, piezocatalyzed H_2 evolution was conducted in NaNO_3 solution with concentrations varying from $1\text{ }\mu\text{M}$ to 1 mM . All the experiments were performed under the straining condition of $t_1 = t_3 = 50\text{ ms}$ and $t_2 = t_4 = 1\text{ s}$. Figure 78a shows the peak piezoelectric voltages and corresponding H_2 production rates as functions of electrolyte concentration together with the results from DI water under the identical straining conditions.

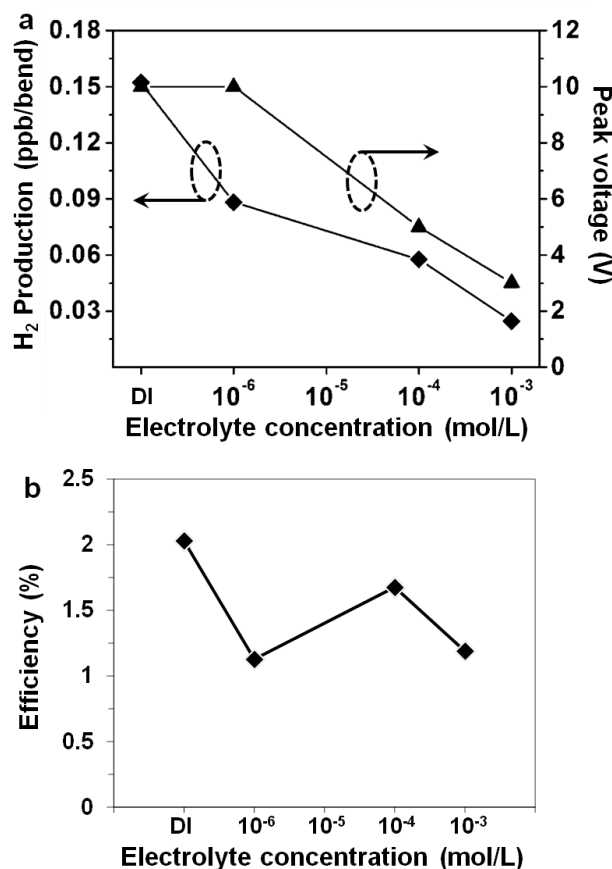


Figure 78. H₂ evolution correlated with electrolyte concentration. c) The peak piezoelectric voltage (triangles) and H₂ production rate (diamonds) as functions of the electrolyte concentration. b) Corresponding piezocatalytic efficiency of H₂ production per strain as a function of electrolyte concentration.[450]

The H₂ production rate dropped monotonically with the increase of electrolyte concentration. This clearly shows that the increased screening-charge resultant from a large C_d is capable of severely subduing the free energy difference between the electrodes and thus reducing the quantity of work possible in the form of electrochemical processes. This result is also manifest in the reduced maximum piezoelectric voltage at higher electrolyte concentrations, which indicates a reduction in the number of surface charges. The calculated piezocatalytic efficiency therefore still exhibited comparable values (~1-2%, Figure 78b) as the case in DI water. These are significantly high efficiencies given the low piezoelectric voltages (3-5 V), which are attributed to

the improved R_s . Therefore, due to the finite amount of energized surface electrons and the charge-dictated potential amplitude, the piezocatalyzed H_2 evolution is heavily influenced by the magnitude of piezoelectric potential, the rate of charge exchange, and the formation of double layers.

5.1.7.2 Piezocatalysis on bare piezoelectric surfaces

Recently, a piezocatalysis process was demonstrated by our study of a strained ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$ -32 $PbTiO_3$ (PMN-PT) beam in a deionized (DI) water system, from which a strong dependence of hydrogen evolution from the aqueous surroundings on the material's piezoelectric potential was observed.[504] In addition, numerous recent works have confirmed the correlation between electrochemical activity and piezoelectric or ferroelectric polarization in a broader sense. For example, a study conducted using ferroelectric poly(vinylidene fluoride) (PVDF) has demonstrate that *in-situ* piezopotential can influence lithium battery charging behavior. [598] Electrochemical deposition was found to be selectively activated by ferroelectric domain polarization.[519-521, 560, 599-602] However, to date there is no general theoretical analysis of the piezopotential's effect on electrochemical activities, e.g. how one piezoelectric material's activity differs from another; the influence of metallic electrodes as compared to a bare piezoelectric surface on reaction output, and how free charge in piezoelectric material systems affects the piezocatalysis process. In this paper, we address the piezocatalysis system in generality to elucidate the details underlying these open questions and illuminate trends for further experimental study.

In order to clearly understand the piezocatalysis process, a conventional electrocatalysis process is discussed first, where the application of electrical potential from an external power

source is a typical means of driving the electron transfer reactions (Figure 79a). The applied potential can result in one of the following two processes: (1) lowering electronic energy levels of unoccupied states within the electrode to a magnitude less than that of the highest occupied molecular orbital (HOMO) in solution; (2) raising occupied states within the electrode above the lowest unoccupied molecular orbital (LUMO) in solution. Under the first condition, electrons will leave the HOMOs in solution and transfer to the unoccupied states within the electrode – oxidizing the solution (center panel of Figure 79a). Under the second condition, electrons will leave the occupied states in the electrode and transfer to the LUMOs in solution – reducing the solution (right panel of Figure 79a). When the electrode is a non-metallic solid, the $e\phi_{\text{HOMO}}$ and $e\phi_{\text{LUMO}}$ logic extends to the materials valence ($e\phi_{\text{VB}}$) and conduction band ($e\phi_{\text{CB}}$) edges, respectively.

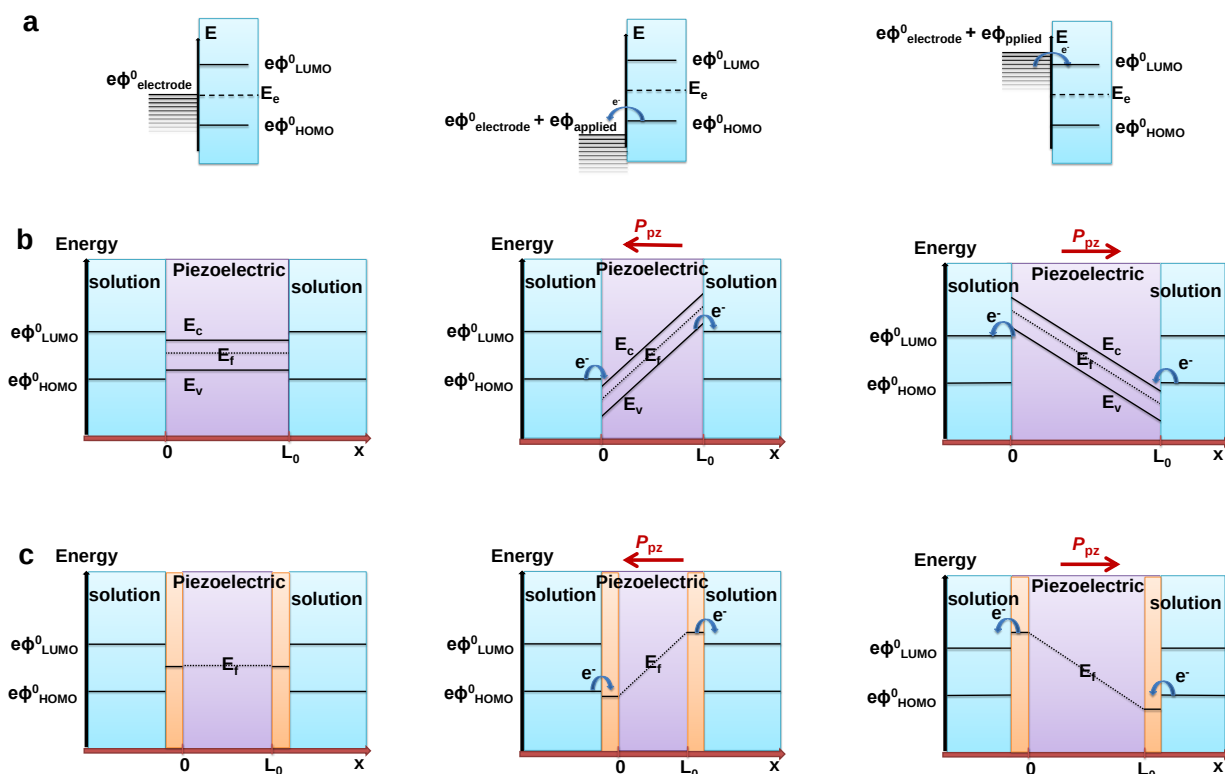


Figure 79. Energy diagrams describing the electrochemistry and piezocatalysis process. a, The effect of applying a sufficient positive or negative bias to an electrode is to increase anodic and cathodic current, respectively. b, In the case of a bare piezoelectric, conduction and valence bands act as the reservoirs for electrons donated or accepted from molecules in solution. The piezoelectric polarization (P_{pz}) applies a variable bias across the material, lifting and lowering valence band and conduction band energies. c, Applying electrodes to the piezoelectric simplifies the electron reservoir to that of the metal's Fermi energy, while maintaining the piezoelectric potential as the source of bias.[603]

For piezocatalysis, the external power source is replaced by piezoelectric potential which results from the piezoelectric polarization (P_{pz}). A perfectly insulating piezoelectric material is the most ideal and simplest case and it will be analyzed first. For such a material, mechanical deformation creates a perfuse electric field inducing a total energy shift across the material, V_{pmax} , given by:

$$V_{p_{max}} = \frac{w_x T_k d_{xk}}{\epsilon_0 \epsilon_{r,x}} \quad (3.3)$$

where T_k is an applied stress in the k dimension, d_{xk} are the piezoelectric moduli, ϵ_0 is the electrical permittivity of free space, and $\epsilon_{r,x}$ is the relative permittivity in the x dimension and w_x is the width of the piezoelectric material in the x dimension. In a one-dimensional case, x and k are equal and the subscripts are dropped.

This piezoelectric potential, which changes the energetics of the valence band (VB) and conduction band (CB) across the piezoelectric material, can have a dramatic effect on the material's interaction with its environment (Figure 79b). In this model it is assumed that strain does not change the magnitude of the band gap. If the $e\phi_{VB}$ approaches $e f_{LUMO}$, it becomes energetically favorable for electrons to leave the VB and enter the LUMO (center panel of Figure 79b). If the $e\phi_{CB}$ approaches $e\phi_{HOMO}$, it becomes energetically favorable for electrons to leave the HOMO and enter the CB (right panel of Figure 79b). Placing metal electrodes between the piezoelectric and solution, with their continuous density of states about their Fermi energies, simplifies this situation: the piezopotential now acts as a bias, lifting and lowering the metal's Fermi energy $e\phi_M$ (Figure 79c).

Piezoelectric materials, which are the source of bias in the case of piezocatalysis, are capable of achieving extremely high potentials (tens to hundreds of volts) when subjected to moderate to severe strain.[604] Under such circumstances (*i.e.* where electrode potentials versus standard hydrogen electrode (SHE) exceeding ~3 volts) many chemical species in contact with the piezoelectric will be thermodynamically capable of undergoing reduction or oxidation reactions.

In order to deduce the maximum quantity of oxidation or reduction reactions possible for a given deformation, it is necessary to quantify the interaction between charge exchange at the

piezoelectric/electrolyte interface and the effect of charge exchange on the piezopotential. A characteristic of piezocatalytic systems is the piezopotential drop that takes place during charge transfer to and from its surfaces (or electrodes). In this way the system acts as a capacitor. The rate of piezopotential drop is dependent upon both the piezoelectric material's properties and the nature of the solution in which it is submerged. In the case where the concentration of reactive species in solution is low, e.g. when pure Milli-Q water is used for the hydrogen reduction reaction, and the power available for driving electron-transfer reactions is sufficiently high, the rate of electrochemical reactions at the electrode is dominated by the diffusion rate of redox species to the electrode. In the case of Milli-Q water, the redox species are protons, hydroxide and impurity species. Mass transfer to the electrode is described by the Nerst-Planck equation, which in its one-dimensional form along the x-axis is written as:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{F}{RT} D_i C_i(x) \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad (3.4)$$

where $J_i(x)$ is the flux of species i at distance x from the surface, D_i is the diffusion coefficient, $\frac{\partial C_i(x)}{\partial x}$ is the concentration gradient at distance x , F is the Faraday constant, R is the gas constant, T is absolute temperature, $\frac{\partial \phi(x)}{\partial x}$ is the potential gradient, C_i is the concentration of species i , and $v(x)$ is the velocity with which a volume element in solution moves along the axis.[605] The expression describes the contributions of diffusion, migration and convection, respectively, to the flux of species i .

Neglecting migration and convective phenomena, the flux of species i is dependent upon diffusion alone. In the diffusion limited regime, the maximum rate of electron transfer from the

piezoelectric is equal to the rate of reactant diffusion to the piezoelectric, resulting in a current density j given by:

$$j_i(x) = -n_i F D_i \frac{\nabla C_i(x)}{\nabla x} \quad (3.5)$$

where n_i is the number of electrons per reaction event with species i . [605]

Applying appropriate boundary conditions to equation (3.5) and taking account of the capacitive nature of the piezoelectric bias source, yields an expression of the piezopotential V_p as a function of time (a variant on the Cottrell equation):

$$\frac{\partial V_p}{\partial t} = - \frac{w_x F \sum n_i D_i^{1/2} c_i f_i}{t^{1/2} \epsilon_0 \epsilon_{r,x} \pi^{1/2}} \quad (3.6)$$

where c_i is the bulk concentration of species i , f_i is a parameter taking on a value between 0 and 1 that toggles the kinetics of the electrodes' reactivates with species i , and t is time.[606]

Under conditions of low reactant and electrolyte concentrations and high positive electrode potential ($e f_{LUMO} > 2\text{eV}$ vs SHE), a kinetics parameter (f_i) less than 1 causes a semi-diffusion controlled regime to form where charged reactant species (e.g. protons and metal ions) capacitively couple to the electrode's surface, effectively reducing the surface potential before they are electrochemically reduced or oxidized (Figure 80a). Under the application of a large positive electrode potential, a dilute (e.g. Milli-Q water) system's capacitance is well approximated by the Helmholtz model. [605] The voltage drop expected in time t by both electron transfer reactions and capacitive effects is given by integrating equation (3.6):

$$V_p = - \frac{2 F t^{1/2}}{\epsilon_0 \epsilon_{r,x} \pi^{1/2}} \left[w_x \sum_{i=1}^{i=l} n_i D_i^{1/2} c_i f_i + w_H \sum_{i=1}^{i=l} z_i n_i D_i^{1/2} c_i (1 - f_i) \right] \quad (3.7)$$

where z_i is the charge sign (1 for cation, -1 for anion) of species i , w_H is the thickness of the Helmholtz layer, and l is the number of different species in solution. The positive potential of the

electrode dictates that a positive charge in solution will contribute to a positive capacitive current, lowering the piezopotential. The first term in equation (3.7) describes the piezopotential change as redox reactions proceed, the second term describes the potential change due to capacitive coupling of not yet reacted species at the piezoelectric material's surface.

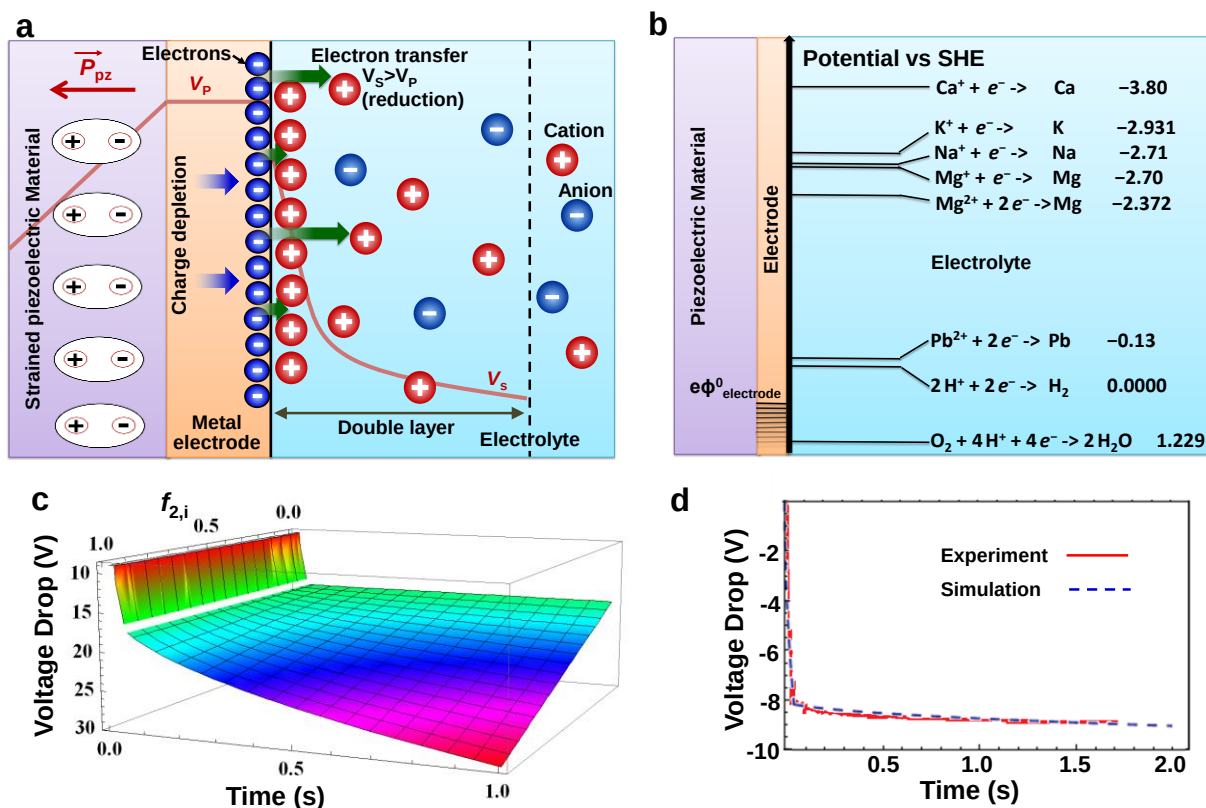


Figure 80. The voltage drop across a strained piezoelectric is dependent upon the rate of capacitive and Faradic effects. (a) The charged piezoelectric's surface induces both capacitive double layer effects and electron transfer events across the interface. (b) At high negative piezoelectric potentials, the electrode is thermodynamically capable of reducing all reported impurity ions in solution. As the potential increases below -2.0 volts, the majority of side reactions are no longer possible. (c) Depending on t_p and the values of kinetic parameters $f_{i,1}$ and $f_{i,2}$, the rate of voltage drop experienced as a function of time can take on a wide range of values. (d) Applying a recursion procedure to the data obtained by Wang et al, values of $t_p = 0.042$ s, $f_{i,1} = 0.715$ and $f_{i,2} = 0.07$ are determined.[603]

Equation (3.7) governs how the potential on the piezoelectric's wall should drop from the time ($t=0$) of initial mechanical deformation, when the piezopotential can be a value of tens or

hundreds of volts, to a time ($t = t_p$) when the potential has been reduced to a reasonable value about the SHE (e.g. $\pm 2V$ vs SHE). Between time $0 < t < t_p$, the electrode potential is sufficiently high as to reduce or oxidize species within solution in an effectively nonselective manner. At $t > t_p$, the piezoelectric potential falls within the range of typical $e\phi_{HOMO}$ and $e\phi_{LUMO}$ values of ions in solution resulting in a more selective reduction and oxidation process (Figure 80b).

The processes described above pertain to both surfaces of the piezoelectric material; on one surface oxidation dominates while reduction dominates on the other. The full voltage change, as measured across the piezoelectric material, is a combination of both of these processes happening simultaneously. An electrode potential above (in the case of oxidation current) or below (reduction current) the selective potential window of $\sim \pm 2V$ versus SHE here are treated identically. This results in a total voltage reduction across the piezoelectric material of twice the expected magnitude from a single wall (equation (3.7)).

As the piezopotential reaches a modest range about $0V$ ($t = t_p$), the electrochemical activity of some ions is effectively switched off while others will remain highly active. Those ions which are no longer electrochemically active are still free to participate in capacitive effects (Figure 80b and second term in equation (3.7)). The voltage decrease across the piezoelectric from $t_p \leq t \leq \infty$ is thus due to a separate set of electrochemical and capacitive effects conducted by a subset ($i \dots m$) of the total chemical species present ($i \dots l$). By applying equation (3.7) to both the selective and unselective regime we can describe the magnitude of piezopotential at all times by the following derived expression:

$$\begin{aligned}
V_p = & -H(t_p - t) \left(\frac{4Ft^{1/2}}{\varepsilon_0 \pi^{1/2}} \left[\frac{w_x}{\varepsilon_{r,x}} \sum_{i=l}^{i=1} n_i D_i^{1/2} c_i f_{1,i} + \frac{w_H}{\varepsilon_H} \sum_{i=l}^{i=1} z_i n_i D_i^{1/2} c_i (1 - f_{1,i}) \right] \right) - \\
& H(t - t_p) \left(\frac{4Ft^{1/2}}{\varepsilon_0 \pi^{1/2}} \left[\frac{w_x}{\varepsilon_{r,x}} \sum_{i=m}^{i=1} n_i D_i^{1/2} c_i f_{2,i} + \frac{w_H}{\varepsilon_H} \sum_{i=m}^{i=1} z_i n_i D_i^{1/2} c_i (1 - f_{2,i}) + \frac{w_H}{\varepsilon_H} \sum_{i=l}^{i=m+1} z_i n_i D_i^{1/2} c_i \right] + \right. \\
& \left. \left(\frac{4Ft^{1/2}}{\varepsilon_0 \pi^{1/2}} \left[\frac{w_x}{\varepsilon_{r,x}} \sum_{i=l}^{i=1} n_i D_i^{1/2} c_i f_{1,i} + \frac{w_H}{\varepsilon_H} \sum_{i=l}^{i=1} z_i n_i D_i^{1/2} c_i (1 - f_{1,i}) \right] - \right. \right. \\
& \left. \left. \left(\frac{4Ft^{1/2}}{\varepsilon_0 \pi^{1/2}} \left[\frac{w_x}{\varepsilon_{r,x}} \sum_{i=m}^{i=1} n_i D_i^{1/2} c_i f_{2,i} + \frac{w_H}{\varepsilon_H} \sum_{i=m}^{i=1} z_i n_i D_i^{1/2} c_i (1 - f_{2,i}) + \frac{w_H}{\varepsilon_H} \sum_{i=l}^{i=m+1} z_i n_i D_i^{1/2} c_i \right] \right) \right) \right) \quad (3.8)
\end{aligned}$$

where $H(x)$ is the Heaviside function defined as 0 when x is less than 0, and 1 when x is equal to or greater than 0. ε_H is the electrical permittivity of the Helmholtz layer. The third and fourth terms in equation (3.8) acts to add continuity between the selective and unselective regimes.

Equation (3.8) is a simplification of the activity occurring around the piezoelectric as the piezopotential drops to within the vicinity of $e\varphi_{\text{HOMO}}$ and $e\varphi_{\text{LUMO}}$ of species in solution. As the energetic advantage for electron transfer diminishes, the current density j begins to show its exponential dependence upon driving force ($e\varphi_{\text{HOMO}} - e\varphi_{\text{LUMO}}$). The current density exponentially depends upon applied potential about E_e :

$$j = j_0 \left(\exp \frac{\alpha_a n F \eta}{RT} - \exp \frac{(1-\alpha_a) n F \eta}{RT} \right) \quad (3.9)$$

where j_0 is the exchange current density and is equal to:

$$j_0 = n F k_a^0 C_R \exp \frac{\alpha_a n F E_e}{RT} = n F k_C^0 C_O \exp \frac{(1-\alpha_a) n F E_e}{RT} \quad (3.10)$$

n is the number of electrons transferred in the reaction, k_a^0 and k_C^0 are the rate constants for the anodic and cathodic current, respectively, C_R and C_O are the concentrations of the reduced and oxidized species, respectively, α_a is the anodic transfer coefficient, E_e is the redox potential of a species in solution, and η is the applied bias (*i.e.* Fermi energy difference between $e\varphi_m$ and

E_e).[606] For the purposes of simplification, the effects of equation (3.9) will be approximated by utilizing two different kinetics constants acting in equation (3.8) for $1 \geq i \geq m$: $f_{1,i}$ and $f_{2,i}$ for the nonselective time interval $0 \leq t \leq t_p$ and the selective interval $t_p \geq t \geq \infty$, respectively.

To elucidate the behavior of the system, Figure 80c is a plot of equation (3.8) as it is applied to the case of a piezoelectric material (PMN-PT) strained in Milli-Q water. We take a value of electrical permittivity $\epsilon_{PMN-PT,x} = 8000$ and a thickness of PMN-PT $w_{th} = .23\text{mm}$. [607] The value of the Helmholtz layer thickness (w_H) was fixed to $2.75\text{\AA}$ with a $\epsilon_H = 80$. Under standard conditions, Milli-Q water has a resistivity value of $18\ \Omega \cdot \text{cm}$ due to the contribution of l “impurities”, including hydroxide and hydronium ($c_{1,2} = \sim 0.100\ \text{ppb} \cdot \text{mol} \cdot \text{cm}^{-3}$, $D_{1,2} = 9.3 \cdot 10^{-5}\ \text{cm}^2\ \text{sec}$), organics ($c_3 = 1.106\ \text{ppb} \cdot \text{mol} \cdot \text{cm}^{-3}$, $D_3 = 0.52 \cdot 10^{-5}\ \text{cm}^2\ \text{sec}$), silicates ($c_4 = 0.5534\ \text{ppb} \cdot \text{mol} \cdot \text{cm}^{-3}$, $D_4 = 1.28 \cdot 10^{-5}\ \text{cm}^2\ \text{sec}$), and heavy metal ions (calcium, sodium, chloride, etc; $c_5 = 0.1106\ \text{ppb} \cdot \text{mol} \cdot \text{cm}^{-3}$, $D_5 = 1.2 \cdot 10^{-5}\ \text{cm}^2\ \text{sec}$). [608] Based on experimental measurements discussed in the following section, t_p is chosen to be $0.042\ \text{s}$ and f_{1i} is 0.715 (between $0 \geq t > t_p$, 71.5% of all species immediately undergo redox reactions upon their contact with the electrode, 28.5% of species first capacitive couple to the electrode).

The physical consequences of the voltage decrease described by equation (3.8) are: (1) the creation of reaction byproducts in the medium surrounding the piezoelectric material (e.g. hydrogen gas, oxygen gas, chlorine gas, oxidized organics, etc); (2) the buildup of a capacitive layer in solution alongside the piezoelectric material; and (3) a reduction in the electric field present inside the piezoelectric material. These effects will continue to change with time until the potential decrease (equation (3.8)) approaches the total potential originally generated (equation (3.3)). The rate of these effects depend sensitively upon the rate constants f_{1i} and f_{2i} , the

concentration of reactive species and their diffusion coefficients. The natural driving force for these chemical changes is the piezopotential which, as described by equation (3.3), depends upon the electrical permittivity, mechanical strain, Young's moduli and piezoelectric moduli. This is true regardless of whether the electrochemically active medium is in contact with metallic electrodes or the piezoelectric material's bare surfaces. In the case of bare piezoelectric surfaces, the band gap and positions of $e\mathbf{f}_{CB}$ and $e\mathbf{f}_{VB}$ relative to $e\varphi_{HOMO}$ and $e\mathbf{f}_{LUMO}$ also determine the nature of what happens during straining.

When comparing the piezocatalytic abilities of various piezoelectric materials, it is useful to choose a performance metric from equation (3.8) such as the quantity of a reaction byproduct, e.g. H_2 gas. This value depends sensitively upon the parameters we choose. Previous work reported the production of hydrogen gas *via* piezocatalysis between a PMN-PT single crystal slab ($2\text{mm} \times 10\text{ mm}$ in size) and Milli-Q water.[504] Using recursion we are able to fit equation (3.8) to the piezopotential verses time profile obtained from a working electrode on a PMN-PT surface under one strain (Figure 80d). The results yield $t_p = 0.042\text{ s}$, $f_{1i} = 0.715$, and $f_{2i} = 0.07$ under the constraints that after $t = t_p$ only H^+ reduction and H_2O oxidation were possible at the electrodes, whilst unreacted H^+ , OH^- , silicate and heavy metal ions only acted capacitively. These low kinetics values likely resulted from a low concentration of electrolyte. The switch over at $t_p = 0.042\text{s}$ from one reaction regime to the other occurred at a potential (difference) value between the electrodes of approximately 2 V. A gold electrode in equilibrium with pH 7 Milli-Q water is in equilibrium with the H^+ reduction and H_2O oxidation reactions. This places the Au electrode's potential ($\varphi_{\text{Electrode HOMO}}$) at 0.41V vs. SHE (0.615V below the $e\varphi_{LUMO}$ of H^+ and -0.615 above the $e\varphi_{HOMO}$ of H_2O). A symmetric voltage shift applied to both Au electrodes of 1V at t_p means an overpotential ($\varphi_{\text{Electrode HOMO}} - \varphi_{LUMO}$) of -0.385V for the H^+ reduction reaction and an

overpotential ($\varphi_{\text{ElectrodeHOMO}} - \varphi_{\text{HOMO}}$) of 0.385V for the H_2O oxidation reaction. These are the potential values taken at which the system switches from a nonselective regime to a selective regime.

In order to derive a function of H_2 evolution dependency on strain, the minimum strain $S_{\text{min},1}$ capable of driving electrochemical reactions for an arbitrary piezoelectric is necessary and determined by augmenting equation (3.3):

$$S_{\text{min},1} = \frac{\varepsilon_0 \varepsilon_{r,x} (\varphi_{\text{Electrode HOMO}} - \varphi_{\text{LUMO}})}{2w_x Y d_{xk}} \quad (3.11)$$

where Y is the Young's modulus of the material. For metallic Au electrodes, the preceding analysis determined the potential necessary to drive electrochemical H_2 production under the observed conditions to be 0.615 ($\varphi_{\text{Electrode HOMO}} - \varphi_{\text{LUMO}}$). In the case of a bare piezoelectric, ($\varphi_{\text{Electrode HOMO}} - \varphi_{\text{LUMO}}$) becomes ($\varphi_{\text{VB}} - \varphi_{\text{LUMO}}$). $S_{\text{min},2}$ is denoted as the strain necessary to transition from the selective to nonselective regime, e.g. where ($\varphi_{\text{Electrode HOMO}} - \varphi_{\text{LUMO}}$) in equation (3.11) becomes ($\varphi_{\text{Electrode HOMO}} - \varphi_{\text{LUMO}} + 0.385 \text{ V}$). Using the value parameters fit from experiment in conjunction with the values of piezoelectric materials' parameters listed in Table 6, the H_2 generation capacity per straining event ($H_{\text{Metal,Total}}$) for a multitude of Au-electrode coated piezoelectric materials is depicted in Figure 81a and is given by a manipulation of equation (3.8):

$$H_{\text{Metal,Total}} = H(S - S_{\text{min},1})H_{\text{Metal,SmallS}} + H(S_{\text{min},2} - S)H_{\text{Metal,LargeS}} \quad (3.12)$$

$H_{\text{Metal,SmallS}}$ is the H_2 production for piezopotentials that fall within the selective regime and is given by:

$$H_{Metal, SmallS} = \frac{AC_e 2FD_H^{1/2} C_H f_{2,H} n \sqrt{t_1}}{\sqrt{\pi}} \quad (3.13)$$

where t_1 is the time required to exhaust the hydrogen production capability for a piezoelectric operating only within the selective regime ($S_{min,1} < S < S_{min,2}$) and is given by:

$$t_1 = \left(\frac{\left[\frac{V_{pmax}}{2} - (\varphi_{Electrode\ HOMO} - \varphi_{LUMO}) \right] \varepsilon_0 \sqrt{\pi}}{F \frac{n_{H^+} w_x D_{H^+}^{1/2} C_{H^+} f_{2,H^+}}{\varepsilon_{r,x}} + \frac{w_H}{\varepsilon_{H_2O}} \left(\sum_{i=m}^{i=1} D_i^{1/2} C_i (1 - f_{2,i}) + \sum_{i=l}^{i=m+1} D_i^{1/2} C_i \right)} \right)^2 \quad (3.14)$$

where ε_{H_2O} is the electrical permittivity of water. $H_{Metal, LargeS}$ is the H_2 production for piezopotentials that reach the unbiased regime ($S > S_{min,2}$) and is given by:

$$H_{Metal, LargeS} = \frac{AC_e 2FD_{H^+}^{1/2} C_{H^+} n_{H^+}}{\sqrt{\pi}} (f_{1,H^+} \sqrt{t_2} + f_{2,H^+} (\sqrt{t_3} - \sqrt{t_2})) \quad (3.15)$$

where t_2 (equation (3.16)) is the time it takes for the piezopotential to fall from an arbitrarily large potential (V_{pmax}) to that which brings it into the selective regime ($\varphi_{LUMO} + \varphi_{Op}$, where φ_{Op} is the overpotential necessary to transition between reaction regimes, e.g. 0.385V), and t_3 (equation (3.17)) is the time it takes for that same piezoelectric to reduce its potential from $\varphi_{LUMO} + \varphi_{Op}$ to φ_{LUMO} .

$$t_2 = \left(\frac{\left[\frac{V_{pmax}}{2} - ((\varphi_{Electrode\ HOMO} - \varphi_{LUMO}) + \varphi_{Op}) \right] \varepsilon_0 \sqrt{\pi}}{4F \frac{n_{H^+} w_x}{\varepsilon_{r,x}} \sum_{i=l}^{i=1} D_i^{1/2} C_i f_{1,i} + \frac{w_H}{\varepsilon_{H_2O}} \sum_{i=l}^{i=1} D_i^{1/2} C_i (1 - f_{1,i})} \right)^2 \quad (3.16)$$

and

$$t_3 = \left(\sqrt{t_2} - \frac{\frac{\varphi_{Op} \varepsilon_0 \sqrt{\pi}}{2F}}{\frac{2n_{H^+} w_x D_H^{1/2} C_H f_{2,H}}{\varepsilon_{r,x}} + \frac{w_H}{\varepsilon_{H_{2O}}} \left(\sum_{i=m}^{i=l} D_i^{1/2} C_i (1 - f_{2,i}) + \sum_{i=l}^{i=m+1} D_i^{1/2} C_i \right)} \right)^2 \quad (3.17)$$

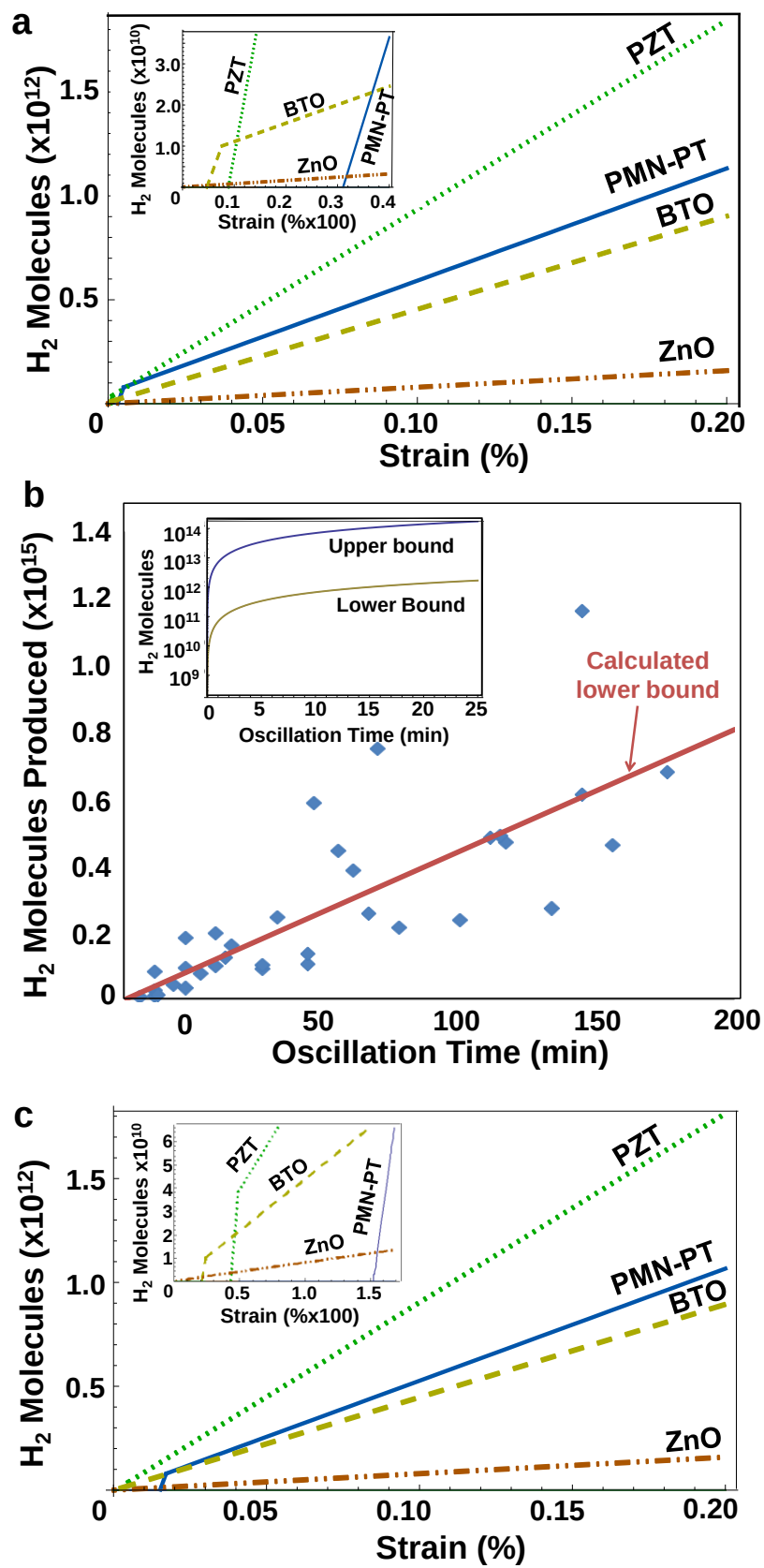


Figure 81. The H₂ production per straining event predicted as a function of strain magnitude. a, In the case of piezoelectric materials with metal electrodes on their surfaces. Inset shows the turn-on strain value is dependent on the ratio of $\frac{\varepsilon_{r,x}}{d_{xk}}$. b, Comparison between experimental data of hydrogen generation over the course of an oscillating PMN-PT cantilever experiment and the predicted results from simulation under the conditions of poor kinetics ($f_i = 0.07$). Inset shows the envelope of hydrogen generation predicted from simulation under the case of good kinetics ($f_i = 0.715$) and poor kinetics. c, In the case of bare surfaced piezoelectric materials. Inset shows the turn-on strain values depends upon both the ratio of $\frac{\varepsilon_{r,x}}{d_{xk}}$ and the value of φ_{Op} . [603]

Piezoelectric Material	Reduction Overpotential $e\varphi_{VB} - e\varphi_{LUMO}$	Oxidation Overpotential $e\varphi_{CB} - e\varphi_{HOMO}$	BandGap E_g	$\varepsilon_{r,x}$	$d_{xk} (CN^{-1})$
ZnO	3.84	-0.52	3.37	8.8	$11 \cdot 10^{-12}$
PZT	3.01	-1.13	3.27	3850	$300 \cdot 10^{-12}$
PMNPT	3.01	-1.13	3.4	8000	$374 \cdot 10^{-12}$
BTO	2.78	-1.72	3.4	1000	$93 \cdot 10^{-12}$

Table 6. Overpotential and material property values for various piezoelectric materials.[601, 603, 607, 609-614]

At large strains (strain > .00025), PZT dominates H₂ gas production per unit strain with a value of 9.1×10^{14} H₂·strain, PMN-PT and BTO have similar production rates of 5.4×10^{14} H₂·strain and 4.5×10^{14} H₂·strain respectively, while ZnO maintains a modest H₂ production rate of 79×10^{13} H₂·strain. From equation (3.15) it can be determined that the H₂ production depends upon the relative weight of f_{1,H^+} to f_{2,H^+} , d_{xk} and $\varepsilon_{r,x}$. When f_{1,H^+} is much larger than f_{2,H^+} , $\sqrt{t_2}$ dominates the expression where a large $\sqrt{t_2}$ value results from a larger V_{pmax} combined with a large $\varepsilon_{r,x}$. However $\varepsilon_{r,x}$ is contained within the denominator of the expression determining V_{pmax} (equation (3.3)). Thus, while a large d_{xk} is always valuable to the piezocatalysis process, a balance

must be achieved with $\varepsilon_{r,x}$. This is why PZT, possessing both large d_{xk} and moderately large $\varepsilon_{r,x}$, has the largest H_2 production rate. Physically this competition represents a balancing between the piezoelectric, voltage generating capabilities of the material, and the capacitive nature of the material. The inset in Figure 81a enlarges the small strain region (strain < 0.00004), demonstrating the dynamics of initiating H_2 production. Materials with the smallest $\frac{\varepsilon_{r,x}}{d_{xk}}$ ratio, the most prominent being ZnO, begin H_2 production at strains far smaller than a material like PMN-PT. This is because the thermodynamic accessibility of electrochemical reactions depends upon the relative energetics of donor ($e\phi_{HOMO}$) and acceptor (ef_{LUMO}) states and a high ratio of piezoelectric moduli to electrical permittivity strongly couples the strain state of the material to these state energetics (equation (3.11)).

The predicted H_2 production capacity is compared to experimental data obtained from an oscillating gold coated PMN-PT cantilever with a peak piezopotential of 20 volts (Figure 81b).[450] At 20Hz, each straining action takes place during 0.025 seconds, which is insufficient for depleting all piezopotential and reaching a thermodynamic equilibrium. Nonetheless, an approximation of the experiment can be constructed by truncating the nonselective regime at 0.025 seconds and applying a window of acceptable values on the kinetics parameter f_i from 0.07 to 0.715 (inset of Figure 81b). Experimental data exhibit good agreement, falling around the lower bound of predicted H_2 evolution rate. This indicates that there remains much room for experimentally improving the H_2 production rate by means of adding a proton reduction co-catalyst and thus increasing the f_i value.

Several factors change when comparing a piezoelectric material coated with metal electrodes to a naked, insulating one. In general, a naked and perfectly insulating piezoelectric

material does not necessarily possess a continuum of states about the redox potentials in solution. To achieve piezocatalysis (including H₂ production) with such a piezoelectric material, the conduction band and valence band must be moved sufficiently in potential so that their energies coincide with redox potentials under examination. Taking the production of H₂ as our prototypical case, the energetics of top-most valence band electrons ($e\phi_{VB}$) must be lifted above the (ef_{LUMO}) of H₂. The minimum strain, and thus potential, required to achieve this criteria is again given by equation (3.11), except in the case of a bare piezoelectric $\phi_{\text{Electrode HOMO}}$ becomes ϕ_{VB} . The values of potentials necessary to cause the reduction of H⁺ and oxidation of H₂O for various piezoelectric materials can be found in Table 1. The hydrogen production capacity of a bare piezoelectric material can be calculated by modifying equation (3.12):

$$H_{Insulator, Total} = H(S_{\min, 1} - S)H_{Insulator, SmallS} + H(S - S_{\min, 2})H_{Insulator, LargeS} \quad (3.18)$$

where $H_{Insulator, SmallS}$ is the H₂ production for piezopotentials that fall within the selective regime ($S_{\min, 1} < S < S_{\min, 2}$), $H_{Insulator, LargeS}$ is the H₂ production for piezopotentials capable to reaching the nonselective regime ($S > S_{\min, 2}$).

Applying the values from Table 1 and the same kinetic parameters as in the metal electrode case ($f_{1i} = 0.715$, $f_{2i} = 0.07$, and $\phi_{Op} = -0.385V$), Figure 81c shows the H₂ production rate for various naked piezoelectric materials. Subjected to large strains (strain>.001), both naked and Au coated piezoelectric materials perform consonantly. Discrepancies between these two are more prominent under small strain (strain<0.0002), which are a result of the difference in the band structures of individual piezoelectric materials. Under small strain, each piezoelectric's H₂-production's turn-

on strain depends not only upon the $\frac{\varepsilon_{r,x}}{d_{xk}}$ ratio but also upon the value of the individual piezoelectric material's ($e\phi_{VB} - e\phi_{LUMO}$) value.

Concerns over the stability of a piezocatalysis system comprising a bare piezoelectric material can be addressed by comparing piezocatalysis with a controlled corrosion process, where reduction reactions take place through the piezoelectric's oxidation and vice versa. The maximum piezoelectric charge density at the surface is on the order of 10^{13} charge·cm², two orders of magnitude lower than the average atomic density of a solid-state surface. With oxidation events of this magnitude, it is expected that a piezoelectric capable of withstanding photocatalytic reactions with water is also able to survive the piezocatalysis process.

In contrast to the previous analysis, most piezoelectric materials are not perfect insulators, mobile electrical charges inside the piezoelectric material respond to and rearrange according to its internal electric field. In bulk systems, these mobile charges act as extremely effective screening agents of the piezopotential, resulting in an effective piezopotential given by a manipulation of the Gouy-Chapman capacitance model:

$$V_{Semi} = \frac{2kT \sinh^{-1}[d_{xk} S_k Y \sqrt{\varepsilon_0 \varepsilon_{r,x} k n_0 T}]}{2\sqrt{2} \varepsilon_0 \varepsilon_{r,x} k n_0 T} \quad (3.19)$$

where k is Boltzmann's constant,, and n_0 is the bulk concentration of free charge. According to equation (3.19), a highly insulating bulk piezoelectric is required to reach an appreciable potential (Figure 82a). Taking the values from Table 1 for various piezoelectric materials subjected to a strain of 0.002, the maximum concentration of free charges allowed in order for the piezoelectric materials' surfaces to obtain the H₂ production potential were 5.22×10^{-40} , 2.33×10^{-27} , 9.37×10^{-23} , and 1.38×10^{-26} m⁻³, for ZNO, PMNPT, BTO and PZT respectively. The H₂ production capacity

for these piezoelectric materials subjected to 0.2% strain was determined as a function of free charge by manipulating equation (3.18):

$$H_{Semi,Total} = H(n_{\max,1} - n_0)H_{Highn_0}H(n_0 - n_{\max,2}) + H(n_0 - n_{\max,2})H_{Lown_0} \quad (3.20)$$

where H_{Highn_0} is the expression for H_2 production while the piezopotential is within the selective regime and H_{Lown_0} describes the H_2 production for a piezoelectric that has achieved a potential for accessing the nonselective regime. $n_{\max,1}$ is the maximum number of free charges allowed for a given piezoelectric material under 0.2% strain to reach the threshold potential $(\phi_{VB} - \phi_{LUMO})$ for driving H_2 production. $n_{\max,2}$ is the charge concentration necessary to reach the potential threshold between the two reaction regimes $[(\phi_{VB} - \phi_{LUMO}) + \phi_{OP}]$. In equation (3.20) the dependence of H_2 production on n_0 comes exclusively from the fact that in the case of a semiconducting piezoelectric material, $V_{p,\max}$ [equation (3.15) & (3.16)] becomes V_{Semi} [equation (3.19)].

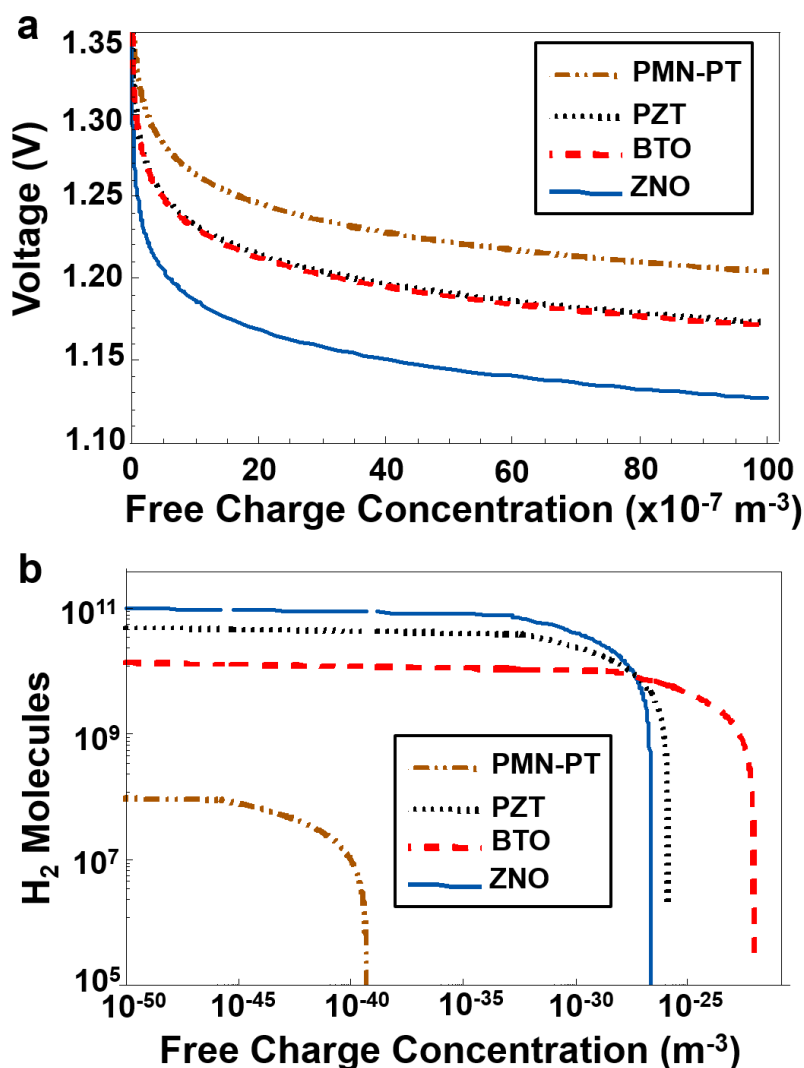


Figure 82. Free charge can dramatically affect the piezocatalytic ability of a strained piezoelectric. For a strain=.0.002, the effect of free charge on (a) piezoelectric potential and (b) H₂ production for various piezocatalysis systems.[603]

The effect of free charge on H₂ production for various piezoelectric materials is demonstrated in Figure 82b, where the hydrogen production for a strain of 0.2% is shown as a function of mobile charge concentration, n_0 . Behavior of note is the dramatic increase in H₂ production that results from decreasing the mobile charge concentration ~5 orders of magnitude below the minimum concentration required to reach the H₂ potential for the piezoelectric materials.

Additional mobile charge reduction beyond that initial 5 orders reduction has relatively little effect on H₂ evolution.

Discussion

A number of factors have been shown to augment the efficacy of strain to induce electrochemical reactions. The relative energies of states within the electrode with respect to HOMO and LUMO energies in solution can both dramatically change the rate of chemical reactions and be a determining factor in which chemical reactions are allowed to proceed. These energy state positions depend directly on the magnitude of strain and piezoelectric coefficient while depending inversely upon the electrical permittivity. In the presence of free-charge, generated either by doping, photo or thermal excitations, the piezopotential can be markedly decreased with direct repercussions on reactivity. In order to increase the electrochemical activity of a strained piezoelectric, the electrical permittivity needs to be optimized. The piezoelectric, semiconductor and molecular orbital frameworks discussed herein have historically and successfully been applied to solid state and electrochemical systems. It is expected that these frameworks can be extended to the piezocatalysis theory. The theoretical work presented here can provide fundamental guidance for designing and understanding the novel piezocatalysis phenomenon from broad electrochemistry and piezoelectric material systems.

5.2 Perspective on Piezochemistry

As long as electrical charges play a role in the removal, addition, or evolution of chemical species from the surfaces of a piezoelectric, an electric field inside the piezoelectric will affect the directionality and locality of these chemical processes. Photoexcited charges are one way of driving chemical reactions, and the dipoles in unstrained ferroelectrics have been used to direct their flow. A piezoelectric that is non-ferroelectric can be strained to induce dipoles that can be used to influence photoexcited charges. However, these materials can never be poled like ferroelectrics and thus the spatial locality of chemical reactions cannot be intricately written into their surface, which is a useful property when making a polarization ‘mask’ for depositing intricate micro and nanostructures.

Some instances require strain in order to drive chemical reactions between the piezoelectric and the environment. For example, when a piezoelectric is in equilibrium with its surroundings and there is no illumination to provide photoexcited charges to drive chemical reactions, then an electronic perturbation, such as that which accompanies the mechanical strain of a piezoelectric, is required to push or pull electrons out of or into the surface of the piezoelectric.

Much of the work done to date for exploring the use of piezoelectric polarization for influencing chemical reactions at the surface of the piezoelectric, or within the vicinity of the piezoelectric, have focused on simple system and delivered proof of principle results. Extending the work of polarization’s effect on corrosion rate beyond the development of a characterization technique for confirming domain structure orientation, for example to applications in corrosion prevention, is a natural but meaningful progression of this work. Rohrer’s work with ferroelectric BTO coated with TiO_2 films demonstrates that the effect of ferroelectric polarization can extend well beyond the piezoelectric’s surface, affecting the chemical reactivity of its surroundings. This

work points the way to developing paints and other coating materials impregnated with polarized piezoelectric materials that imbue the objects they coat with enhanced corrosion resistance properties.

The selectively photo deposition of precise nanostructures on specific ferroelectric domains may have important applications for device manufacturing if several difficulties can be overcome. In practice, an AFM can be used to ‘write’ extremely small and intricate polarization structures on the surface of a ferroelectric, and the use of photochemistry triggered by broad UV exposure opens up the possibility of large area, simultaneous growth of photodeposited nanostructures across an entire wafer. However, the AFM writing process is slow, akin to the slow and expensive process of using electron beams to make fine-featured photolithography masks. Like in current photolithographic schemas, the ferroelectric polarization ‘masks’ made by AFM will be expensive and viewed as a non-consumable. Today, photodeposition of nanostructures on written ferroelectric domains proceeds directly on the surface of the ferroelectric, with no regard to how these structures could be securely removed and transferred without irreversibly damaging the expensive ferroelectric mask. A possibility forward is to focus work on developing film coatings for the ferroelectric masks that will be strongly photochemically influenced by the ferroelectric domains (such as in Rohrer’s work with TiO_2 films) and may also be easily removed as a sacrificial layer, making transferability of the photochemically deposited nanostructures possible. Following the nanostructure transfer step, the process could again be repeated with a new sacrificial film being grown on top of the ferroelectric mask and the photodeposition step proceeding. Realizing a process like this means the expensive ferroelectric polarization mask could be used many times, reducing the cost of using this strategy for nanoarchitecture growth.

The use of ferroelectric particles as a single material system for simultaneously 1) absorbing solar energy, 2) separating photoexcited electrons and holes to reduce charge recombination, and 3) spatially segregating reaction products and thereby reducing the probability of back reactions, is a tantalizing prospect. Additional measures are needed to overcome these obstacles when using non-ferroelectric material systems, such as binary phase particles and artificial membranes to help separate photoexcited charges and reaction products. Ferroelectric water photolysis systems still face many challenges, such as large bandgaps and low activity with respect to water splitting, but a renewed interest in perovskite light absorbers that has recently taken to the literature and will no doubt be accompanied by the creation of novel ferroelectric materials for future photolysis systems to exploit.

When applying the direct piezoelectric effect as the driving force for electrochemical reactions on bare piezoelectrics, whether it be a nanomaterial's facet or a bulk slab's polished surface, the biggest questions that remain pertain to what exactly is the energetic effect of the piezoelectric field on the surface electronic states and what is the exact nature of the interaction between electroactive species in solution and the piezoelectrics' surface atoms. These systems have promise, directly leveraging the ubiquity of mechanical energy for use in energy storage or environmental chemical remediation applications. The presence of metal films on the piezoelectric's surfaces greatly reduces the complexity of these systems, and perhaps makes the systems immediately suited for some applications, but these films also obscure our ability to observe novel phenomena in this unexplored field. If we don't know how the systems work, we cannot intelligently engineer better systems.

Until recently it would be impossible to probe the electronic nature of the surface of these piezoelectric materials, under strain, while exposed to various solution chemistry. Developments

in the field of ambient pressure x-ray photoelectron spectroscopy (AP-XPS) are beginning to shine light on once unseen electronical and chemical phenomena occurring in-situ in fuel cells during their operation. These new AP-XPS techniques can be extended to strained piezoelectric systems, where the electronic evolution of a piezoelectric surface can be observed in real-time, during mechanical strain and exposed to a condensed liquid phase. These results can feedback in the materials design process, focusing on elemental compositions that most readily react with desired electroactive species without going as far as to irreversibly deconstruct the piezoelectrics bonds.

In addition to characterizing the piezoelectric's electronic structure using spectroscopy techniques, under proper conditions electrochemistry techniques can also be used to analyze the nature of the piezoelectric/solution interface. Catalysis is an area of significant scientific and commercial interest, studying the influence of piezoelectric potential of the catalytic properties of surfaces (piezocatalysis) may yield surprising and useful results.

Chapter 6. Future Work: Piezocatalysis

6.1 Introduction to Piezocatalysis

Enhancing the rate of electrochemical reactions in a solution is of growing interest in several domains, including the solar fuel production effort[565, 570, 615-621], batteries[622-626], fuel cells[627-630] and flow cells[631-633]. In these applications, many methods are being pursued to augment the kinetics of electron transfer at heterointerfaces, including encouraging ‘active site’ formation at surface defects[634, 635] or at metal/oxide interfaces[561, 634, 636]. In addition to direct chemical means, mechanical forces have been used for changing reaction rate[637-642]. Piezocatalysis is the use of piezoelectric potential to manipulate the energetics of an electron-transfer reaction occurring at the surface of a piezoelectric electrode.

6.1.1 Interfacial Charge-Transfer at Semiconductor/solution interfaces

The use of semiconductor materials as the electron donor or acceptor species in electrochemical reactions is of intense interest due to these materials’ ability to make use of photons as a driving force for electron transfer reactions (i.e. photoelectrochemistry) and the potential offered by this material class’s largely unexplored electrochemical variability and tunability.

Semiconductor electrodes can behave much differently than their metallic counterparts and this is primarily due to the differences in the arrangement of electronic states in these materials. Metallic electrodes have a continuum of electronic states about their Fermi energy (Figure 83a,b), each of which potentially act as a donor state for an electron to solution or as an acceptor state for an electron from solution. Each of these individual states possess its own electron transfer rate constant (k_{et}), unique to its own energy level, between itself and an electroactive state in solution

(e.g. $E(A/A^-)$). For a metal electrode in contact with a solution containing electroactive species, the total empirically measured current density (J) as a function of applied potential (ϕ_{Ap}) is a summation of the individual currents contributed by each energy level (Figure 83b). The current density we expect between any one state in the metal, e.g. at energy E_1 , and the state in solution at energy $E(A/A^-)$ is described by the following equation (4.1) [643]:

$$J_{E_1, E(A/A^-)} = -e[k_{et, E_1, E(A/A^-)}][A][n_{s, E_1}] \quad (4.1)$$

Where $J_{E_1, E(A/A^-)}$ is the current density ($A\ cm^{-2}$), e is the charge of an electron, $k_{et, E_1, E(A/A^-)}$ is the electron transfer rate constant the between states E_1 and $E(A/A^-)$ in units ($cm^4\ s^{-1}$), $[A]$ is the acceptor concentration (cm^{-3}) in solution, and n_{s, E_1} is the concentration (cm^{-3}) of electrons that simultaneously occupy a state at energy E_1 in the electrode and are available to participate in the reaction (e.g. the electrons are located at the surface of the material).

A typical semiconductor differs from a metal in that it does not possess a continuum of occupiable electronic states about its Fermi energy, this gap in electronic states is referred to as the bandgap. When an n-type semiconductor is in contact with a solution containing electroactive species, charge exchange occurs between the semiconductor and the solution. This charge exchange results in a region in the vicinity of the semiconductor/solution interface depleted of mobile charges, i.e. the depletion region. The depletion region possess a non-zero charge density that is time independent and approximately equal to that of the immobile charge centers (dopant sites, N_d) left behind by the evacuated mobile charges. The non-zero charge density in this region results in an electric field, causing band bending at the interface (see Figure 83c) and a built in potential energy difference (ϕ_{bi}) between the bulk of the semiconductor and the surface .

To drive additional (net) electron transfer from the semiconductor to solution, after the formation of a deletion region, 2 conditions must be met:

- 1) An electron must occupy a state in the conduction band. If the semiconductor is not degenerately doped, only electronic states within $\sim 3k_bT$ of E_{CB} should be occupied by mobile electrons. Even as potential is applied to the electrode (ϕ_{Ap}), it will only be the states about the bottom of the conduction band (the conduction band edge) which transfer electrons from the semiconductor electrode to $E(A/A^-)$ in solution.
- 2) An electron in the conduction band must be at the electrode/solution interface to transfer to the state at $E(A/A^-)$ in solution. Electron transfer from one entity to another is a quantum mechanical, short-range process. In order for electrons to transfer from the semiconductor to solution they must be at the semiconductor's surface.

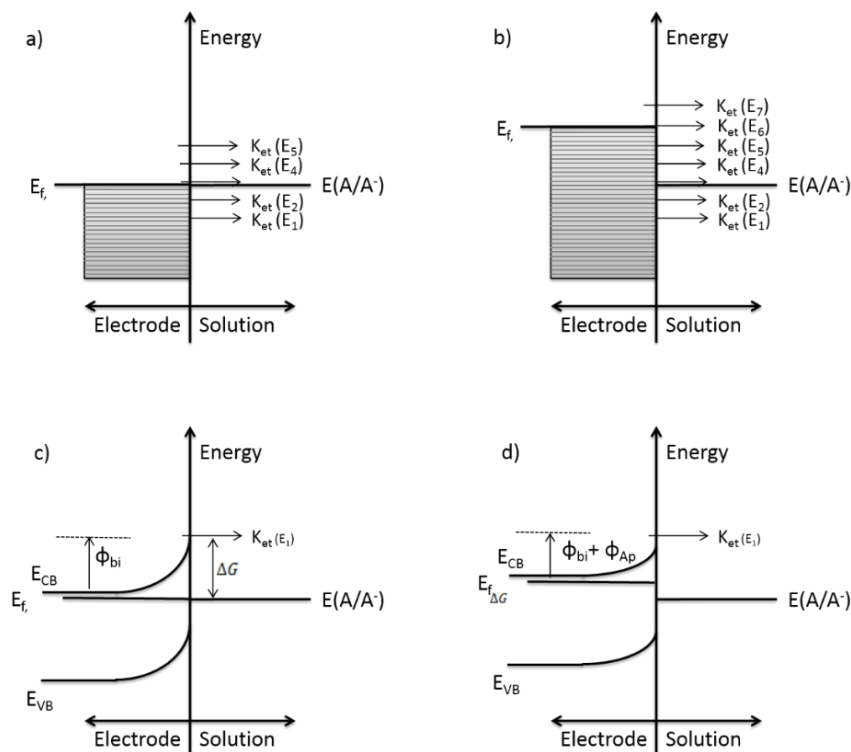


Figure 83. Electron transfer processes from electrodes to electroactive species in solution begin and end at specific energy states, each with its own electron transfer rate (k_{et}). a) A metal electrode in equilibrium with species in solution. After equilibrium is established, no net current travels between the two. b) A negative potential applied to the metal electrode increases the energy of occupied states in the metal, driving electrons across the electrode/solution interface, to solution. Each state in the metal participates in electron transfer between the two mediums, each state has its own rate constant. c) A n-type semiconductor electrode in equilibrium with electroactive species in solution. About the Fermi energy, the absence of states occupiable by electrons at the interface means that the majority of electron transfer events take place from an energy state at the bottom of the conduction band. Little current is exchanged between the semiconductor and solution because the occupancy of the conduction band state at the interface is low (due to a built in potential ϕ_{bi}). d) When a negative potential (ϕ_{Ap}) is applied to the semiconductor, the bias acts to reduce the potential at the surface relative to the bulk, increasing the occupancy of the conduction band state and driving electron flow from the semiconductor to solution. The typical way to drive current through a semiconductor/solution interface is by applying a potential (ϕ_{Ap}) to the semiconductor. When ϕ_{Ap} is applied across a semiconductor/solution interface, the majority of potential difference between the semiconductor and solution is ‘dropped’ in the semiconductor because its capacitance is much smaller than that of solution. Thus, applying ϕ_{Ap} to a semiconductor electrode causes a change to the potential difference between the bulk of the semiconductor and its interface by the amount ϕ_{Ap} (Figure 83d)). The application of ϕ_{Ap} drives current through the interface primarily by change the concentration of electrons at the interface ($n_{s,E_{CB}}$) at energy state E_{CB} at the interface.

The concentration of electrons at the surface of the semiconductor ($n_{s,ECB}$) is influenced by the equilibrium concentration of electrons in the bulk (n_b) and the potential energy difference between surface and bulk of the semiconductor ($\varphi_{Surface}$), as given by the following equation (4.2):

$$n_{s,ECB} = n_b \cdot \exp \frac{(\varphi_{Surface})}{k_b T} \quad (4.2)$$

Where k_b is Boltzmann's constant, T is temperature in Kelvin, and the potential energy at the surface is related to the built-in and applied potential by equation (4.3):

$$\varphi_{Surface} = \varphi_{bi} + \varphi_{Ap} \quad (4.3)$$

and thus equation (4.4)

$$n_{s,ECB} = n_b \cdot \exp \frac{(\varphi_{bi} + \varphi_{Ap})}{k_b T} \quad (4.4)$$

When a semiconductor/solution junction has formed a depletion region and is under zero applied potential ($\varphi_{Ap} = 0$, Figure 83c), the concentration of electrons at the surface of the semiconductor (described by equation (4.4)) are non-zero and in equilibrium with the concentration of electroactive species in solution at the surface ($[A]_s$, Figure 84a)).

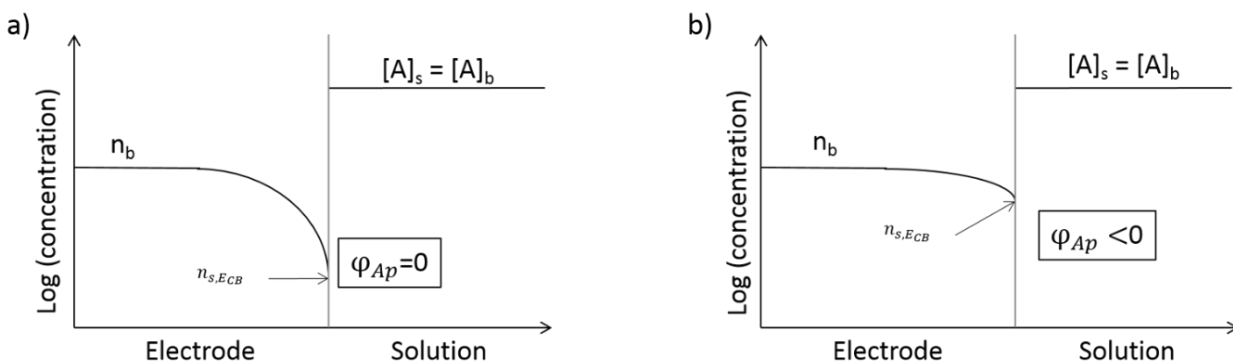


Figure 84. The free charge density in the semiconductor is non-uniform, depending exponentially on potential (equation (4.4)). a) Under zero applied potential, a non-zero surface potential exists which acts to reduce $n_{s,ECB}$ relative to n_b . b) Applying a potential to the semiconductor can change the distribution of free charge by modulating the built-in potential established during depletion-region formation. The new $n_{s,ECB}$ is out of equilibrium with $[A]_s$ and charge transfer across the semiconductor/solution interface is the result.

Applying potential ϕ_{Ap} to the surface causes electrons to cross the semiconductor/solution interface by acting to change the energy barrier ($\phi_{surface}$) between the bulk and surface of the semiconductor and thus change the concentration of electrons at that surface (equation (4.4)). Under forward bias, $n_{s,ECB}$ increase exponentially with ϕ_{Ap} , which perturbs equilibrium at the interface ($n_{s,ECB}$ is no longer in equilibrium with $[A]_s$) and this drives a net current across the semiconductor/solution interface (equation (4.1)).

Under the condition of constant $\phi_{surface}$, the current can be increased further by increasing the concentration of acceptor species, $[A]$, in solution or by increased and the electron transfer rate constant, k_{et} (equation (4.1)). **If the practical goal is to reduce the energy requirements necessary for driving electrochemical reactions then an ϕ_{Ap} as small as necessary is desired for achieving a high $J_{E,E(A/A^-)}$.** In a system where the current density is sufficiently low such that the current is not limited by the diffusion of acceptor species to the interface, **increasing $k_{et,E1,E(A/A^-)}$ is the only remaining option for increasing $J_{E,E(A/A^-)}$** (equation (4.1)).

6.1.2 Rate constant ($k_{et,E_1,E(A/A^-)}$) of Interfacial Charge Transfer Reactions for a Semiconducting Electrode.

In 1956 Rudolph A. Marcus formulated a theory for explaining the rates of electron transfer between two chemical species solvated in solution: a donor and an acceptor. In the case originally examined by Marcus' theory, the charge exchange between the two chemical species results in only a change of the electrical charge of the donor and acceptor species (e.g. Mn^{3+} to Mn^{4+} , Fe^{2+} to Fe^{3+} , etc.), no chemical bonds are formed or broken and thus there is no structural change to the species themselves. These types of electron transfer reactions are called “outer sphere electron transfer” reactions because the only physical rearrangement that takes place is with the orientation of the molecules in the outer hydration-shell (i.e. the polarization of the solvent) (figure 85) and the internal vibration modes of the donor and acceptor species.

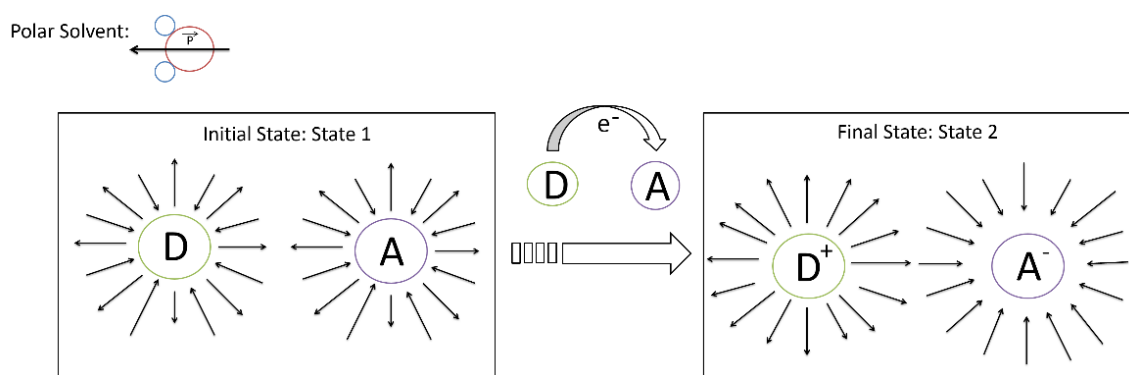


Figure 85. Outer Sphere Electron Transfer Reaction. Redox reactions that take place in polar solvents result in rearrangement of solvation shells around the donor and acceptor species.

In outer sphere electron transfer reactions, the energy required to reorganize the solvent's polarization plays a dominant role in determining the free energy of activation for the electron transfer reaction.

The electron transfer process is governed by quantum mechanical rules. These rules dictate that the energy of a system cannot change *during* the electron transfer event. In addition, the electron transfer event is expected to occur much faster than the molecular motion of the solvated molecules, meaning there will be identical solvent polarization immediately before and directly after the electron transfer event (Franck–Condon principle)[644]. For both of these criteria to be valid during a general case of electron transfer, the state of solvent polarization around the acceptor and donor species cannot be their minimum-energy states. The non-equilibrium solvent polarization state needed for the electron transfer process to enact no change to the system's energy is a salvation state resembling an intermediary between the minimum-energy states both pre- and post- electron transfer. Because electron transfer occurs in a non-equilibrium (solvent) polarization state (i.e. a transition state), energy is required to rearrange the solvent polarization away from its pre-transfer equilibrium orientation. Thermal fluctuations in the solvent can provide the energy necessary to change the polarization from the equilibrium state to that of the non-equilibrium transition state. Once this transition state is achieved, electron transfer can occur.

Marcus calculated the Gibbs free energy ΔG of a system of two chemical species as a combined function of: 1) ΔG_{in} the electrical polarization in the solvent surrounding the species (i.e. outer sphere reorganization energy, equation (4.5)); and 2) ΔG_{out} , the vibration modes of the species with their inner solvated water molecules (i.e. inner sphere reorganization energy, equation (4.6)).

ΔG_{in} , a function of polarization energy, is given by:

$$\Delta G_{in} = \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \cdot \left(\frac{1}{\epsilon_{OP}} - \frac{1}{\epsilon_S} \right) \cdot (\Delta e)^2 \quad (4.5)$$

where r_1 and r_2 are the radii of the spheres that approximate the dimensions of acceptor and donor species, R is the distance between acceptor and donor, ϵ_S and ϵ_{OP} are the static and high optical dielectric constants of the solvent, and Δe is the magnitude of charge transferred between donor and acceptor.

If we only consider the symmetric breathing vibrations of the (6) water molecules surrounding donor and acceptor species, and assume harmonic conditions, the energy of the system with respect to the inner sphere reorganization energy (ΔG_{out}) is given by[645]:

$$\Delta G_{out} = \frac{3f_D f_A}{f_D + f_A} (q_{0,D} - q_{0,A})^2 \quad (4.6)$$

Where f_D and f_A are force constants of the bonds between the donor species and its solvated water molecules and acceptor species and its solvated water molecules, respectively. $q_{0,D}$ and $q_{0,A}$ are the equilibrium normal coordinates of the water molecules solvated around the donor and acceptor species, respectively.

In these expressions, both the inner sphere and outer sphere have same quadratic form which means their general form doesn't change when added together and plotted, as in Figure 86.

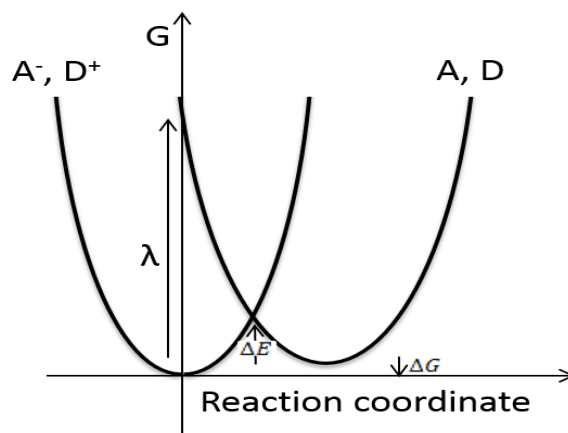


Figure 86. The two parabolas represent the free energies of two different states of the system pre- and post-electron transfer. The parabola on the right, (A, D), represents how the free energy of the (A, D) system varies as a function of the surrounding solvent's polarization and molecular vibration in the system's initial state before electron transfer takes place. The parabola on the left, (A^- , D^+), represents how the free energy of a different system, the one where an electron-transfer has occurred by donor and acceptor, varies as a function of the same variables.

From Figure 86 it can be seen that if the solvent and vibration modes of the (A,D) system take on conformations that change the energy of the (A,D) system by an amount λ , then upon an electron transfer event the system would conform to the lowest energy state of the (A^- , D^+) system. λ is called the reorganization energy because it is the amount of energy necessary to transform the environment around A and D into a state necessary for electron-transfer to take place.

A mismatch between the free energy change of the system going from one state to the other (ΔG) and the reorganization energy (λ) necessary to get from one state to the other represents an energetic barrier and impediment to the electron-transfer process. If $\Delta G < \lambda$ then additional energy from the environment is necessary to reorganize the polarization of solvent in order to drive the electron-transfer process in the (A,D) system. If $\Delta G > \lambda$ then an energy *sink* in the environment is necessary to expel the excess energy for the electron-transfer process to be successful. Energy *sources* and *sinks* are a third member in the two-member (A,D) system, and the precise coordination of energy transfer between three bodies is far less likely than two. As the

magnitude of energy transferred between the members increases (*e.g.* $\Delta G \ll \lambda$ or $\Delta G \gg \lambda$), the probability of three members successfully coordinating energy transfer between themselves through stochastic atomic ensembles decreases precipitously. This leads to the counter intuitive result that is a key prediction of Marcus theory: increasing the driving force for electron transfer ($\Delta G \gg \lambda$) can have a detrimental effect on the electron-transfer process by reducing its probability of success. The maximum rate of electron-transfer ($k_{et,Max}$) takes place when the driving force for electron transfer is equal to the solvent reorganization energy of the system: when $\Delta G = \lambda$ (Figure 87).

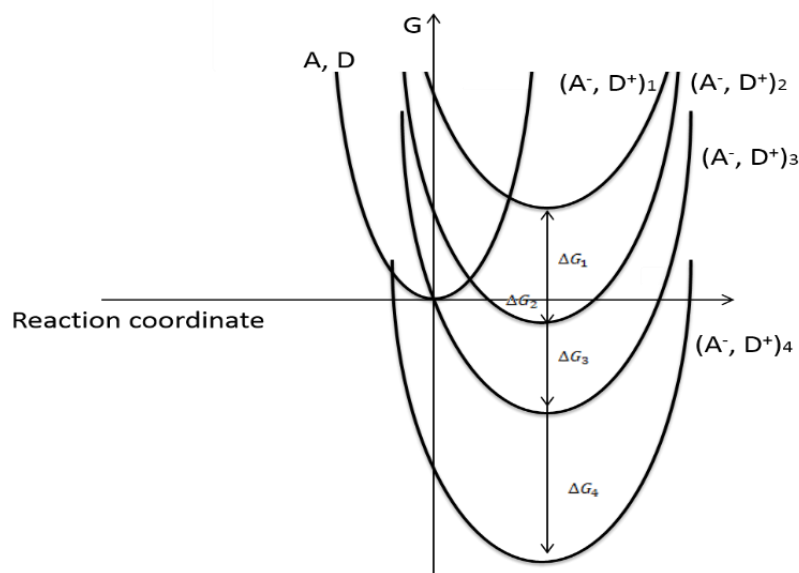


Figure 87. All other factors remaining constant, changing the free energy difference between the pre- and post- electron transfer state acts to vertically shift the two curves relative to each other. When the free energy difference (ΔG) between the two is equal to the reorganization energy of the solvent (λ), the system can efficiently switch from one state into the other.

The rate of electron transfer, k_{et} , is therefore a function of the potential energy curves of the system because the easier it is for the system to access the energy to transition from one state to the other, the more likely the electron-transfer process will occur and thus the faster the rate.

The basic equation for k_{et} , derived from Marcus theory for a molecular donor and acceptor species in solution, is given by equation (4.7):

$$k_{et} = \frac{(2\pi)^2}{h} \cdot |H_{AB}|^2 \cdot \frac{1}{\sqrt{4\pi\lambda k_b T}} \cdot \exp\left(-\frac{(\lambda + \Delta G)^2}{4\lambda k_b T}\right) \quad (4.7)$$

Where h is Plank's constant, H_{AB} is the electron coupling between initial and final state, and ΔG is the Gibbs free energy of the electron transfer reaction.

In 1997, Lewis et al.[646] broadened Marcus' theory of charge-transfer kinetics to the semiconductor/solution interface (Figure 84c & 84d). In their work, they found the expression for the rate constant (k_{et}) of interfacial charge-transfer reactions for a semiconductor electrode in contact with a random distribution of acceptor species ($[A]$) in solution to be:

$$k_{et} = k_{et,max} \cdot \exp\left(-\frac{(\lambda_{SC} + \Delta G)^2}{4\lambda_{SC} k_b T}\right) \quad (4.8)$$

Where λ_{SC} is the reorganization energy of the acceptor species near the semiconductor electrode, and the prefactor, $k_{et,max}$, is the rate constant at optimum exoergicity, obtained when $\Delta G = \lambda_{SC}$, with typical k_{et} values ranging between $\sim 10^{-17} - 10^{-16} \text{ cm}^4 \text{ s}^{-1}$ [646-649].

For a typical semiconductor/solution interface, $k_{et,max}$, ΔG , and λ_{SC} are constant values for a fixed pH and a given combination of semiconductor/acceptor species. By altering the acceptor species or solution pH, values $E(A/A^-)$ or the conduction band edge position (for oxides) are changed, respectively, and thus ΔG is changed (Figure 84c). pH influences the protonation/deprotonation equilibrium of $-\text{OH}$ sites on the oxide surface[643], thus effecting the semiconductor's surface charge density and so shifting its band-edge position at the interface, E_{CB} . Experiments conducted on n-ZnO semiconductor electrodes have confirmed the dependence of k_{et} on λ_{SC} [649] and $\Delta G^{0'}$ by modifying $E(A/A^-)$ [648] and pH[650] respectively.

These previous investigations of semiconductor/solution interfaces have all confirmed the link between k_{et} , ΔG and λ_{SC} as first discussed by Marcus, Lewis and others, namely that k_{et} behaves exponentially as a function of ΔG and λ_{SC} (Figure 88a & 88b).

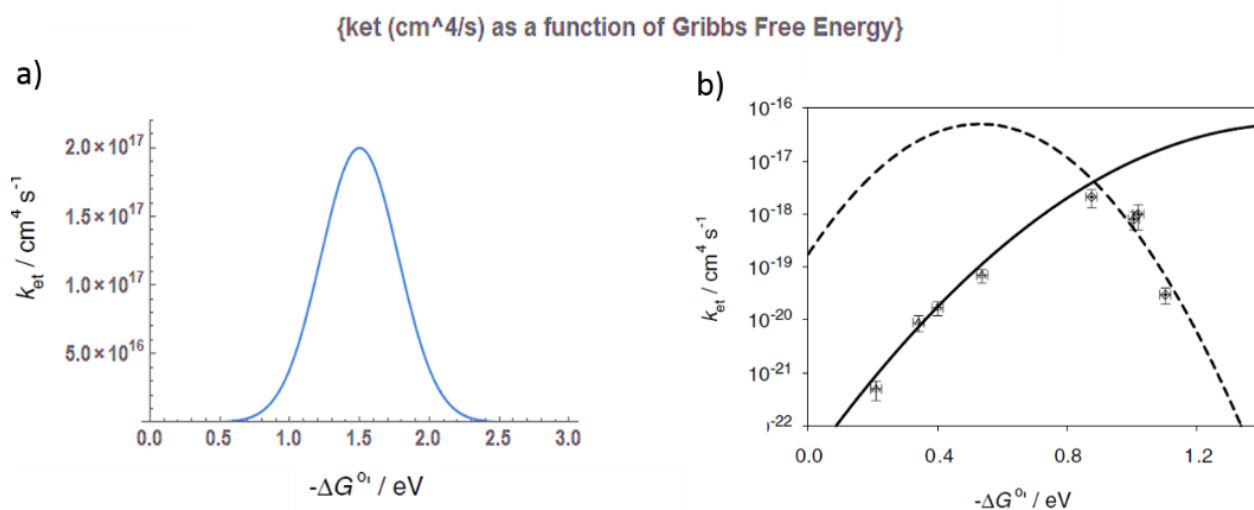


Figure 88. The electron transfer rate, k_{et} , is calculated to be an exponentially dependent on ΔG and λ_{SC} , with a maximum value of k_{et} when $\Delta G^0' = \lambda_{SC}$. a) A plot of equation (4.8) for a n-ZnO/ $\text{K}_2\text{Fe}(\text{CN})_6$ system, where $k_{et,max} = 2 \times 10^{-17} \text{ cm}^4 \text{s}^{-1}$, $\lambda_{SC} = 1.5 \text{ eV}$, $k_b = 8.61 \times 10^{-5} \text{ eV K}^{-1}$ and $T = 295.15 \text{ K}$. b) Data obtained by Lewis et al. of two pairs of electroactive species in contact with a n-ZnO electrode. The n-ZnO/solution interfaces tested therein adhered well to the behavior adapted from Marcus theory.

Investigating other means of increasing k_{et} is valuable as both λ_{SC} and $E(A/A^-)$ are functions of the electroactive species involved and may not be varied depending on application. Varying pH has proven effective at modulating k_{et} [651], but the freedom to vary pH depends upon the pH stability range of both the electrode and acceptor species of interest. Discovering other means of changing k_{et} are of particularly high interest if they are relatively easy to control, easy to implement, and potentially dynamically tailorable to the functioning environment of the electrochemical system. Proposed in this study is the exploration of modulating k_{et} via the direct piezoelectric effect.

6.2 The Application of Piezoelectrics to the Kinetics of Electron Transfer Reactions.

Piezoelectric materials have the property such that, upon the application of stress (T), an electric dipole density (D) is induced in the material. This transduction of mechanical energy into electrical energy is called the direct piezoelectric effect. The constitutive equation describing the dipole density resultant from a piezoelectric material undergoing stress (σ_{jk}) is given by equation (4.9):

$$P_i = d_{ijk}\sigma_{jk} + \epsilon_{ijk}E_{jk} \quad (4.9)$$

Where ϵ_{ijk} is the materials' electrical permittivity and E_{jk} is the electric field strength.

In the case of a perfectly-*insulating* piezoelectric material strained along a principal axis, the dipole field will linearly augment the energetics of electronic states throughout the material, as depicted in Figure 89a & 89b.

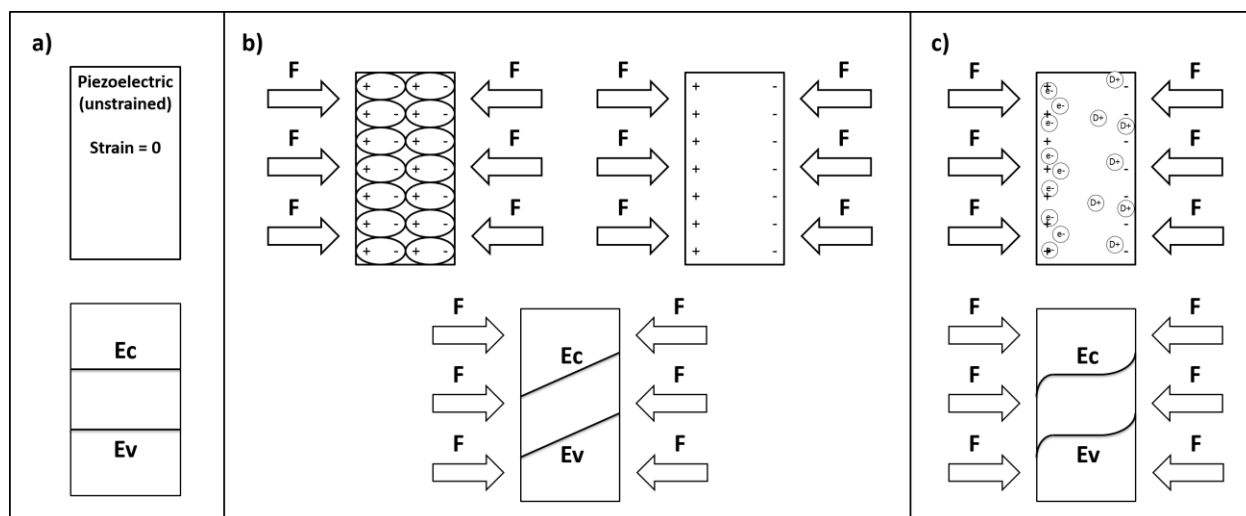


Figure 89. a) In a perfectly insulating piezoelectric material subject to no forces, the conduction and valence band states are flat across the material. b) The electric dipoles induced by mechanically straining a perfectly insulating piezoelectric material cause a linear voltage change across the material. c) mechanically deforming a piezoelectric semiconductor causes free charges to migrate to the boundaries of the material and produce depletion and accumulation regions.

In the more general case of a strained piezoelectric *semiconductor*, mobile charges will migrate in response to the strain-induced dipole field and act to diminish the effects of the dipole field on the material's energetic landscape (Figure 88c). The magnitude of screening effect will differ between the two sides of the material as the majority carriers will be capable of forming a higher density charge-screening layer in the accumulation region as compared to the depletion region.

Studies of piezotronic systems, where strain is used in conjunction with an electronic device composed of at least one piezoelectric material, have cited the direct piezoelectric effect's ability to change the conduction and valence band edge positions (Figure 89b, c) as an explanation for observed changes in electron conduction characteristics across heterojunctions with strain[604, 652, 653] If effect as it extends beyond semiconductor/metal or semiconductor/semiconductor junctions to semiconductor/solution interfaces then it should directly influence the rate of electrochemical reactions at the interface (Figure 90).

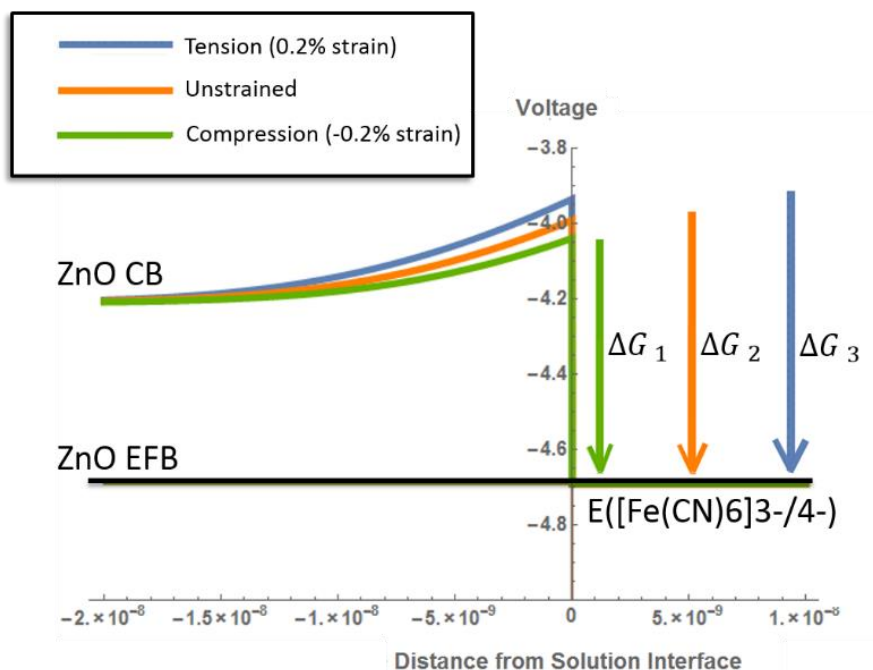


Figure 90. A piezoelectric semiconductor is placed in contact with a solution containing electroactive species, forming a depletion region within the semiconductor. Upon straining the piezoelectric, dipole fields act on the conduction and valence band positions in the semiconductor and thus act to change the ΔG of electron transfer between the E_{CB} in the semiconductor and $E(A/A^-)$ in solution. ($\Delta G_1 = 0.428 eV$, $\Delta G_2 = 0.6 eV$, $\Delta G_3 = 0.876 eV$)

It is the thesis of this work that the band-augmenting capability of strain-induced dipole charges in piezoelectric semiconductor electrodes is a means of using strain as a non-chemical means of manipulating ΔG (Figure 83c & 90) and thus enhance or suppress k_{et} (equation (4.8)).

6.2.1 Proposed Experimental Procedure

n-ZnO is a piezoelectric semiconductor that has previously been shown to obey the J-V characteristics expected of an ideal semiconductor in contact with a solution of randomly distributed, outer shell, single electron acceptor species (equation (4.3)) [648-650, 654, 655]. In the proposed experiments, a n-ZnO electrode will be submerged in a solution containing

electroactive $\text{Fe}(\text{CN})_6^{3-/4-}$. The k_{et} of electron-transfer reactions across the semiconductor/solution interface will be measured as a function of strain applied to the n-ZnO electrode.

A n-ZnO (0001) single crystal 1-side (O) polished substrates ($d_{31} = -3.3 * 10^{-12} \text{CN}^{-1}$) will be attached to a ridged beam (Figure 91a) that will act to transfer a precise magnitude of strain from a 4-point bending fixture (Figure 19b) to the n-ZnO electrode (Figure 91c). The entire ensemble will be submerged in a solution containing 0.002M $\text{K}_2\text{Fe}(\text{CN})_6$, 1M KCl, and buffered to pH=8.7 for subjection to electrochemical analysis (Figure 91d).

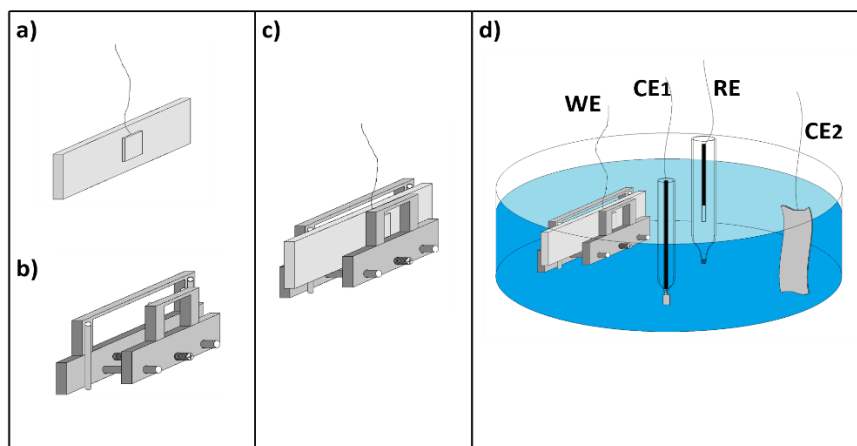


Figure 91. a) A beam with a single crystal n-ZnO electrode fixed to its surface, b) the 4-point bending apparatus used for applying precision strain, c) the beam fixed to the 4-point bending apparatus, d) the 4-point bending apparatus submerged in an electroactive solution and monitored by a potentiostat.

In each strain state, the n-ZnO semiconductor/solution system will be approximated by the equivalence circuit used in previous work to describe this n-ZnO/ $\text{K}_2\text{Fe}(\text{CN})_6$ system (Figure 92) [648-650, 654, 655].

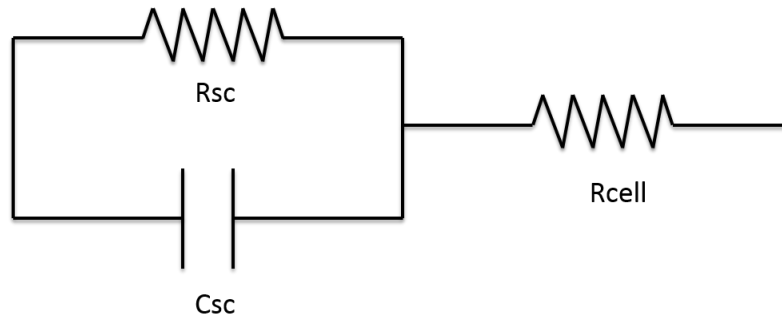


Figure 92. An equivalence circuit used to simulate the J-V results from the n-ZnO/ K₂Fe(CN)₆ system. R_{SC} is a resistor element with the resistance of the n-ZnO, C_{SC} a capacitor element with the capacitance of the n-ZnO depletion region and R_{cell} is a resistor element with the resistance of the K₂Fe(CN)₆ solution.

Electrochemical impedance spectroscopy and Mott-Schottky plot analysis will be used to determine the electrode's dopant density (N_d) and flat band potential (V_{fb}). During this analysis, differential capacitance data is gathered for the semiconductor while it is under depletion and the results are compared to the Mott-Shottky expression (equation (4.10)):

$$\frac{1}{C^2} = \frac{2}{\epsilon_{SC}\epsilon_0 A^2 e N_D} \cdot \left(V - V_{fb} - \frac{k_B T}{e} \right) \quad (4.10)$$

Where C is the interfacial capacitance and A is the interfacial area, ϵ_{SC} is the electrical permittivity of the semiconductor and ϵ_0 is the permittivity of free space. N_D is the doping density in the semiconductor, V is the applied voltage and V_{fb} is the flat band potential. A plot of $\frac{1}{C^2}$ against V should yield a straight line from which V_{fb} can be determined from the intersection with the abscissa. With knowledge of ϵ_{SC} and A, N_D can be determined from the slope.

In the piezoelectric/solution system, strain is expected to change V_{fb} by acting to change the band-edge positions at the interface (Figure 90). The change in the band-edge position of E_{CB} relative to $E(A/A^-)$ changes ΔG of the electron transfer reaction and thus changes the electron transfer rate constant k_{et} (equation (4.7)). Changing V_{fb} also effects $\phi_{surface}$ (the potential at the interface of the semiconductor relatively to the bulk of the semiconductor) and thus affects n_s

(equation (4.1)). Since a change to n_s will effect current density (J) across the junction independently of k_{et} (equation (4.3)), characterization of n_s and normalization of J with respect to n_s must be done under every straining condition in order to isolate the effect of strain on k_{et} .

6.2.2 Trends Expected from Theory

By combining piezoelectric theory with Marcus theory and extending its conclusions to semiconductor/liquid junctions, it is expected that the strain will exponentially effect the kinetics of electron-transfer via the modulation of ΔG (Figure 93).

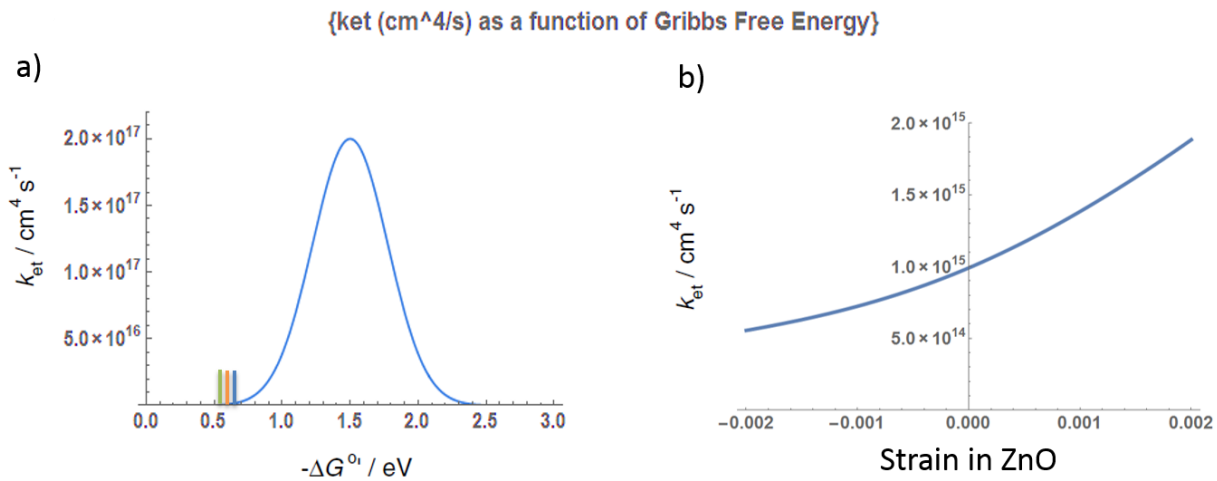


Figure 93. Straining the piezoelectric semiconductor induces dipole fields which in turn effects the ΔG of electron transfer reactions occurring at the semiconductor/solution interface. a) Expected behavior of k_{et} as ΔG varies with strain in the n-ZnO/ $K_2Fe(CN)_6$ system . b) The calculated effect of electrode strain on k_{et} for strain between -0.2% ($\Delta G_1 = 0.552eV, k_{et} = 5.55 * 10^{14} \frac{cm^4}{s}$) and 0.2% ($\Delta G_3 = 0.656eV, k_{et} = 1.88 * 10^{15} \frac{cm^4}{s}$).

Chapter 7. Conclusion

Energy band diagrams have proven themselves extremely useful to scientists and engineers for predicting, tinkering with, and explaining the behavior of heterojunction devices. While today many of these diagrams are schematics and generated from intuition, it follows that because of the immense predictive and interrogative capabilities of these diagrams, automating their creation process will have a significantly positive impact on the scientific process. In addition to time savings, automation can also increase the qualitative and quantitative accuracy of these diagrams and thus empower them, and the researchers who use them, with a greater ability to interrogate physical systems. Even given their existing prevalence, energy band diagrams are arguably a underutilized tool for interrogating research hypotheses. Often when new combinations of materials are being grown, questions remain as to that composite's electronic properties because common characterization techniques tend to sample the entire ensemble of the material stack. In a typical investigation today, energy band diagrams (including: bandgaps, band edge off-sets, fermi energies and depletion region lengths) are then more or less guessed until a qualitatively plausible one is conjured which is then used as supporting information for a hypothesis that explains the results. However, because of the physical processes involved, the diagrams are often times both qualitatively and quantitatively inaccurate given the physical properties prescribed to the materials composing the heterojunction, and thus inaccurate hypotheses are settled upon. This problem is exacerbated when piezoelectric materials are used in the materials ensemble (i.e. piezotronics) because the roles charge conservation and energy minimization play within non-trivial heterojunctions can be particular unintuitive.

The code generated within this thesis, by removing human intuition from the energy band diagram generation process, can add tremendous value to researchers pursuing this line of

investigation. The automated generation of these diagrams can not only be used for efficiently communicating the electronic nature of a researcher's heterojunction device, it can also be used to interrogate it. If one believes they have sufficiently characterized the materials of their device, but plotting their heterojunction's energy band diagram (given those characterized parameters) produces an energy band landscape inconsistent with their experimental results, then taking note of where the two conflict could point the way to discovering the true nature of the device and where one should conduct follow-up experiments. I expect the future of science will be a growing of the collaboration between humans' and machines' in data analysis and result prediction. Therefore my contribution contained herein to the open-source automation of energy band diagrams is a valuable contribution to the field of materials science.

My theoretical and experimental work on piezochemistry was the first systematic synthesis of the piezoelectrics, electrochemistry and solid state physics (i.e. piezochemistry). Previous work alluded to strained piezoelectrics driving chemical reactions, or ferroelectric domains influencing chemical etching and electrochemical oxidation/reduction reactions, but didn't necessarily regard the details of where and how the electrons would transfer, or quantify the effect of strain on the energetics at the heterointerface. Without bringing these disciplines together under a single theoretical framework, these previous studies were unable to make quantifiable predictions and at times proposed impossible hypotheses. Our experimental work on gold coated piezoelectric PMN-PT beams was the first to carefully compare the influence of magnitude and frequency of piezoelectric straining action on the production of electrochemical byproducts. Our measurements demonstrated a trend that agrees with our piezochemistry model. This general agreement between theory and experiment lends confidence to the notion that our model captures the basic physics happening to the gold-coated piezoelectric beam. My subsequent theoretical analysis of multiple

piezoelectric materials (PMN-PT, PZT, BTO, ZnO) and their ability to drive electrochemical reactions as a function of the material's strain and frequency elaborates a theoretical groundwork for understanding how arbitrary piezoelectric materials may be used to drive arbitrary electrochemical reactions. Taken together, the theoretical framework created herein provides a conduit for directly transducing energy between the macroscopic mechanical world of the piezoelectric beams and the nanoscopic chemical domain of atoms and molecules.

Finally, by applying our automated code for generating quantified energy band diagrams to piezoelectric-semiconductor/solution interfaces, I discovered the potential of the piezoelectric effect to directly influence the ability of piezoelectric surfaces to undergo electrochemical reactions. The effect reveals itself to work directly on the rate constant of the electron transfer process by changing the free energy of electron transfer, and does not simply increase the rate of electron transfer by increasing an adjacent electrochemical parameter (e.g., charge carrier concentration). There are various reports in the literature of strain effecting the electronic properties through piezoelectric electrochemical heterojunctions, however they give no systematic explanation for the results. I call this process of strain in a piezoelectric material influencing the rate of electrochemical reactions happening on its surface "piezocatalysis". I have also proposed a model system for testing this theory. If confirmed, strain transduced via the piezoelectric effect could reveal itself to be another means of engineering catalytic materials for industrial applications.

Appendix: Mathematica Code for Plotting Energy Band Diagrams of Piezoelectric Heterojunctions

```

"-----";
"CODE FOR PLOTTING POTENTIAL PROFILE CURVES V1:
METAL/INSULATOR/N-TYPE/INSULATOR/P-TYPE/INSULATOR/SOLUTION";
"-----";

"We begin by cleaing all variabes and functions defined within the code:";
Clear[k]
Clear[T]
Clear[Cel]
Clear[e]
Clear[zn]
Clear[zp]

Clear[MetalWF]

Clear[d31ZnO]
Clear[EZnO]
Clear[YZnO]

Clear[Semi1WF]
Clear[epsZnO]
Clear[EgZnO]
Clear[NcZnO]
Clear[niSemi1]
Clear[nbSemi1]
Clear[pbSemi1]

Clear[Semi1LeftDFromStrainPiezo]
Clear[CBSemi1]
Clear[VBSemi1]
Clear[epsSemi1]
Clear[zNdSemi1]
Clear[NdSemi1]
Clear[NdZnO]
Clear[Semi1WFBulk]
Clear[BulkZeroofSemi1]

Clear[d31InsPiezo]
Clear[EInsPiezo]
Clear[YInsPeizo]
Clear[InsDFromStrainPiezo]
Clear[Insulator1DFromRemnantAndStrainPiezo]

```



```

Clear[EpsBTO ]
Clear[d31SemiPiezo]
Clear[YSemiPeizo ]
Clear[ESemiPiezo]
Clear[d31BTO ]
Clear[EBTO ]
Clear[YBTO]
Clear[DSpontaneousSemi1Left]
Clear[DSpontaneousZnO]

```

```

Clear[dIns1]
Clear[epsIns1]
Clear[DSpontaneousBTO]

```

```

Clear[Semi2WF]
Clear[CBSemi2]
Clear[VBSemi2]
Clear[niSemi2]
Clear[nbSemi2]
Clear[pbSemi2]
Clear[NdSemi2]
Clear[zNdSemi2]
Clear[dIns2]
Clear[epsIns2]
Clear[epsSemi2]
Clear[BulkZeroofSemi2]
Clear[d31Semi2Piezo]
Clear[YSemi2Peizo]
Clear[ESemi2Piezo]
Clear[Semi2LeftDFromStrainPiezo]
Clear[Semi2RightDFromStrainPiezo]
Clear[DSpontaneousSemi2Right]
Clear[DSpontaneousSemi2Left]
Clear[Semi2RightChargeSign]

```

```

Clear[epsIns3]
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Clear[NdSemi2]
Clear[epsH2O]
Clear[EpsBTO]
Clear[EpsTiO2]

```

```

Clear[IsoelectricFermiOfSemi2]
Clear[IsoelectricFermiOfZnO]
Clear[IsoelectricHofsurface]
Clear[IsoelectricZnO]

```

```
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Clear[MHb]
Clear[nHbSol1]
Clear[pHb]
Clear[pOHb]
Clear[MOHb]
Clear[zOH]
Clear[nOHbSol1]
Clear[zNa]
Clear[MNab]
Clear[nNabSol1]
Clear[epsSol1]
Clear[epsH2O]
Clear[Mole]
Clear[nTotal]
Clear[SolWF]
```

```
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Clear[nOHb2Sol1]
Clear[nNab2Sol1]
Clear[IonDiameter]
Clear[HydratedNaDiameter]
Clear[IonRadius ]
Clear[volume]
Clear[atomsv]
Clear[densityv]
Clear[nHb22Sol1test]
Clear[nOHb2Sol1test]
Clear[nNab2Sol1test]
Clear[nTotaltseet]
Clear[Vmax ]
Clear[gradientinSol1Lefttest]
Clear[qsol1leftperareatest]
Clear[qsternlayer]
```

```
Clear[q1]
Clear[p1]
Clear[p2]
Clear[p3]
Clear[s1]
Clear[s2]
Clear[s3]
Clear[s4]
Clear[s5]
```

```

Clear[Vsemi1]
Clear[VSemi1Right]
Clear[VSemi2Left]
Clear[VSemi2Right]
Clear[VSol1Left]
Clear[Semi2LeftChargeSign]
Clear[gradientinSemi2Left]
Clear[qsemiconductor2Leftperarea]

```

```

Clear[V1]
Clear[V2]
Clear[V3]
Clear[V4]
Clear[V5]
Clear[V6]
Clear[V7]
Clear[V7iso]
Clear[V8]
Clear[V9]
Clear[V10]

```

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Clear[MetalBandPotentialProfile]
Clear[WorkFunctionOfMetal]
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Clear[PotentialProfileCurve3]
Clear[PotentialProfileCurve4]
Clear[PotentialProfileCurve5]

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```

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Clear[VBZnO]
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```

```

Clear[EndofDepletionWidth]
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Clear[EndofDepletionWidth4i]
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Clear[EndofDepletionWidth5i]
Clear[EndofDepletionWidth5]

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Clear[VacuumPotentialinMetal]

```

```

Clear[Vacuumpotentialininsulator1]

```

```
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Clear[Insulator1BandPotentialProfile]
Clear[DSpontaneousIns]
```

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Clear[qsemiconductor1Leftperarea]
Clear[Semi1LeftChargeSign]
Clear[gradientinSemi1Left]
Clear[SemiCBPotentialinDepletionRegion1]
Clear[SemiVBPotentialinDepletionRegion1]
Clear[VacuumPotentialinDepletionRegion1]
Clear[DepletionRegionPotentialProfile]
Clear[Semi1RightChargeSign]
Clear[gradientinSemi1Right]
Clear[Semi1RightDFromStrainPiezo]
Clear[DSpontaneousSemi1Right]
Clear[qsemiconductor1Rightperarea]
```

```
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Clear[SemiCBPotentialinSemiandOutOfDepletionRegion]
Clear[SemiVBPotentialinSemiandOutOfDepletionRegion]
Clear[BulkSemi1PotentialProfilesinBulk]
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```
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Clear[Junction1VBPotential]
Clear[Junction1VacuumPotential]
```

```
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Clear[SemiCBPotentialinSemi1inDepletionRegionRight]
Clear[SemiVBPotentialinSemi1inDepletionRegionRight]
```

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Clear[VacuumPotentialinInsulator2]
Clear[Insulator2BandPotentialProfile]
```

```
Clear[Semi2LeftChargeSignChargeSign]
Clear[gradientinSemi2Right]
Clear[VacuumPotentialinSemi2inDepletionRegionLeft]
Clear[SemiCBPotentialinSemi2inDepletionRegionLeft]
Clear[SemiVBPotentialinSemi2inDepletionRegionLeft]
Clear[Semi2PotentialProfilesInDepregion]
Clear[qsemiconductor2Rightperarea]
```

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Clear[Semi2CBPotentialinSemi2andOutOfDepletionRegion]
Clear[Semi2VBPotentialinSemi2andOutOfDepletionRegion]
```

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```
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```
Clear[Junction2VBPotential]
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```
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```
Clear[Junction2WFs]
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```
Clear[VacuumPotentialinSemi2inDepletionRegionRight]
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```
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```
Clear[SemiVBPotentialinSemi2inDepletionRegionRight]
```

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```
Clear[Insulator3BandPotentialProfile]
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```

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```

```
Clear[gradientinSol1Left]
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```
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Clear[Sol1PotentialProfilesOutOfDepletionRegion]
```

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```

```
Clear[Junction3VBPotential]
```

```
Clear[Junction3VacuumPotential]
```

```
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```

```
"MATERIALS PARAMETERS";
```

```
"-----";
```

```
"Cel is temperature of system in Celcius:";
```

```
Cel=22;
```

```
"-----";
```

```
"Metal/Insulator1/Semiconductor 1:";
```

```
"Metal:";
```

```
"Metal WF is the work function of gold metal, taken as an example";
```

```
MetalWF = -5.1;
```

```
"-----";
```

```
"Semiconductor 1:";
```

```
"Semi1WF is the work function of ZnO, taken as an example";
```

```
Semi1WF=-4.1;
```

"EgZnO is the bandgap of Zinc Oxide, taken as an example";
 EgZnO=3.3;

"NcZnO is the density of states in the conduction band of ZnO, taken as an example";
 NcZnO=(3.8*10¹⁸)*(1*10⁶);

"CBZnO and VBZnO define the bulk conduction and valence band positions of the semiconductor, respective, taking Zinc Oxide as the example." ;
 CBZnO=-3.99;
 VBZnO=-7.19;

CBSemi1=CBZnO;
 VBSemi1=VBZnO;

"epsZnO is relative electrical permittivity of Zinc Oxide semiconductor, taken as an example";
 epsZnO=8.7;

"NdZnO is the dopant density of Zinc Oxide, taken as an example";
 NdZnO=(8*10¹⁶)*(1*10⁶);

"zNd is the unit charge of the dopant atom in the semiconductor";
 zNdSemi1=1;

"d31ZnO is the direct piezoelectric coefficient of ZnO, taken as an example material.";
 d31ZnO = -3.3*10⁻¹²;

"YZnO is the Young's modulus of ZnO, taken as an example Pieoelectric material";
 YZnO =150*10⁹;

"EZnO is the Strain in the ZnO piezoelectric semiconductor, taken as an example material";
 EZnO =0;

"DSpontaneousZnO is the Spontaneous (Remnant) polarization (density) of ZnO = 0 C/cm². 1, 0, or -1 before the Remenant value is about on/off/&direction of field.";
 DSpontaneousZnO = 0*(1*10⁻⁶)*(1*10⁴);

"-----";
 "Insulator 1:";

"EpsBTO is the relative permittivity of the Insulating layer, taking BTO as an example material.";
 EpsBTO =1500;

"dIns1 is the thickness of the insulating material";
 dIns1=100*10⁻⁹;

"D_{SpontaneousBTO} is the Spontaneous (Remnant) polarization (density) of BTO = 7×10^{-6} C/cm². 1, 0, or -1 before the Remenant value is about on/off/&direction of field.";
 $D_{SpontaneousBTO} = 0 \times (7 \times 10^{-6}) \times (1 \times 10^4)$;

"d_{31BTO} is the direction piezoelectric coefficient of BTO";
 $d_{31BTO} = -79 \times 10^{-12}$;

"Y_{BTO} is the Young's Modulus of BTO
 (https://www.citrination.com/?from=0&per_page=10&term=barium%20titanate)";
 $Y_{BTO} = 120 \times 10^9$;

"E_{BTO} is the Strain in the BTO";
 $E_{BTO} = 0$;

"-----";
 "-----";

"Semiconductor 1/Insulator 2/Semiconductor 2:";

"Semiconductor 1:
 Parameters are outlined above.";

"-----";
 "Insulator 2:";

"d_{Ins2} is the thickness of the insulating material";
 $d_{Ins2} = 5 \times 10^{-9}$;

"E_{psBTO} is the relative permittivity of the Insulating layer, taking BTO as an example material.";
 $E_{psBTO} = 1500$;
 $eps_{Ins2} = E_{psBTO} \times 8.854 \times 10^{-12}$;

"-----";
 "Semiconductor 2:";

"Semi2WF is the work function of ZnO, taken as an example";
 $Semi2WF = -7$;

"CB_{ZnO} and VB_{ZnO} define the bulk conduction and valence band positions of the semiconductor, respective, taking Zinc Oxide as the example." ;
 $CB_{Semi2} = CB_{ZnO}$;
 $VB_{Semi2} = VB_{ZnO}$;

"eps_{ZnO} is relative electrical permittivity of Zinc Oxide semiconductor, taken as an example";
 $eps_{ZnO} = 8.7$;
 $eps_{Semi2} = eps_{ZnO} \times 8.854 \times 10^{-12}$;

"NdZnO is the dopant density of Zinc Oxide, taken as an example";
 NdSemi2=NdZnO;
 pbSemi2=NdSemi2;

"zNd is the unit charge of the dopant atom in the semiconductor";
 zNdSemi2=-1;

"-----";
 "-----";
 "Semiconductor 2/Insulator 3/Solution:";

"Semiconductor 2:";
 V7iso=Semi2WF;
 "All other parameters are outlined above";

"-----";
 "Insulator 3:";

"Ins thickness";
 dIns3=5*10⁻⁹;
 EpsBTO = 1500;

"-----";
 "Solution:";

"SolWF is the work function of the solution. V10 (the work function of solution) is taken to be approximately equal to V7iso for simplicity:";
 SolWF=V7iso+.0001;
 V10=SolWF;

"pHb is the bulk pH of the solution";
 pHb=14;

"IsoelectricZnO is the isoelectric point of ZnO, taken as an example";
 IsoelectricZnO=9.5;

"epsH2O is the relative electrical permittivity of the solution, H2O as example";
 epsH2O=80;

"-----"
 "Metal/Insulator 1/Semiconductor 1 Junction"
 "-----"
 "Constants and Propagation of Conditions";
 "-----";

"k is Boltzmann constant";
 $k=1.3806488 \times 10^{-23}$;

"T is absolute temperature";
 $T=273.15+Cel$;

"epsSemi1 is the electrical permittivity of the semiconductor";
 $epsSemi1=epsZnO \times 8.854 \times 10^{-12}$;

"e is number of elementary charges";
 $e=1$;

"niSemi1 is the intrinsic concentration of electrons in the semiconductor";
 $niSemi1=NcZnO \times \exp[-((1.60217646 \times 10^{-19}) \times (EgZnO/2))/(k \times T))]$;

"nbSemi1 is the bulk concentration of mobile electrons";
 $NdSemi1=NdZnO$;
 $nbSemi1=NdZnO+niSemi1$;

"pbSemi1 is the bulk concentration of holes in the semiconductor";
 $pbSemi1=((niSemi1)^2)/nbSemi1$;

"zn is the unit chage of the electron";
 $zn=-1$;

"Vsemi1 is the potential inside the semiconductor";
 $Vsemi1$;

"zp is the unit charge of the hole";
 $zp=1$;

"V1 is the work function of the metal";
 $V1=MetalWF$;

"V2 is the electrical potential at the interface between the Metal and the Insulator";
 $V2$;

"V3 is the electrical potential at the interface between the Insulator and the Semiconductor";
 $V3$;

"V3 is the work function of the semiconductor";
 $V4=Semi1WF$;

"epsIns1 is the electrical permittivity of the Insulating layer, taking ZnO as an example Insulator material.";

$\epsilon_{\text{Ins1}} = \epsilon_{\text{BTO}} * 8.854 * 10^{-12};$

"d31SemiPiezo is the direct piezoelectric coefficient of the semiconducting Piezoelectric, taking ZnO as an example material. A negative d31SemiPiezo value means electric field due to piezo charge points to the left and thus charge density on left is negative. ";
 $d31\text{SemiPiezo} = d31\text{ZnO};$

"Ypiezo is the Young's Modulus of the semiconducting Piezoelectric material.";
 $Y\text{SemiPiezo} = Y\text{ZnO};$

"Epiezo is the Strain in the semiconducting Piezoelectric";
 $E\text{SemiPiezo} = E\text{ZnO};$

"DSpontaneousBTO is the Polarization density (surface charge density) of the piezoelectric semiconductor";

$\text{Semi1LeftDFromStrainPiezo} = d31\text{SemiPiezo} * (E\text{SemiPiezo}) * (Y\text{SemiPiezo});$
 $\text{Semi1RightDFromStrainPiezo} = -\text{Semi1LeftDFromStrainPiezo};$

"DSpontaneousSemi1Left is the Spontaneous (Remnant) polarization in the ferroelectric semiconductor. Positive means electric field points to right, which means positive charge density on interface between insulator and semiconductor";

$D\text{SpontaneousSemi1Left} = D\text{SpontaneousZnO};$
 $D\text{SpontaneousSemi1Right} = -D\text{SpontaneousSemi1Left};$

"DSpontaneousIns is the Spontaneous (Remnant) polarization in the ferroelectric. Positive means electric field points to left, which means positive charge density on left side and negative charge density on right side of insulator. BTO is taken as the example material";
 $D\text{SpontaneousIns} = D\text{SpontaneousBTO};$

"d31piezo is the direct piezoelectric coefficient of the insulating piezoelectric, taking BTO as an example material.";
 $d31\text{InsPiezo} = d31\text{BTO};$

"Epiezo is the Strain in the insulating Piezoelectric semiconductor. BTO is taken as the example material";
 $E\text{InsPiezo} = E\text{BTO};$

"Ypiezo is the Young's Modulus of the insulating Piezoelectric material. BTO is taken as the example material";
 $Y\text{InsPiezo} = Y\text{BTO};$

"InsDFromStrainPiezo is the piezoelectric charge density contributed by staining the ferroelectric (and thus piezoelectric) insulator";
 $\text{InsDFromStrainPiezo} = d31\text{InsPiezo} * (E\text{InsPiezo}) * (Y\text{InsPiezo});$

"positive value means electric field points to the right, means + charge density is on the left side of the semiconductor and - charge density on the right)";

Insulator1DFromRemnantAndStrainPiezo=DSpontaneousIns+InsDFromStrainPiezo;

"-----";

"Setting up and solving for potential profiles in semiconductor 1";

"-----";

"p1 is a common factor from the previous integration step and is pulled out to simplify the appearance of the expression. Note that the electrical permittivity of the semiconductor is contained within it";

$p1 = (2 * k * T) / \epsilon_{psSemi1}$;

"q1 is a common factor of two of the expressions in the integrated expression and is pulled out to simplify the appearance of the expression.";

$q1 = -(e * (1.60217646 * 10^{-19})) / (k * T)$;

"Semi1LeftChargeSign is a way of determine what the sign of the charge is in the semiconductor by looking at the difference between potential in the bulk of the semiconductor and potential at the interface. This is useful for book keeping.";

$Semi1LeftChargeSign = -((V4 - V3) / Abs[V4 - V3])$;

"Vsemi1 is the voltage change between the bulk of the semiconductor and the it's surface.";

$Vsemi1 = V4 - V3$;

"gradientinSemi1Left is the strength of the Electric field going into the semiconductor at the interface between the semiconductor and the insulator";

$gradientinSemi1Left = -(p1 * (nbSemi1 * (Exp[-zn * Vsemi1 * q1])) + (pbSemi1 * (Exp[-zp * Vsemi1 * q1])) + (-zNdSemi1 * NdSemi1 * Vsemi1 * q1) - (nbSemi1 + pbSemi1))^{(1/2)}$;

"qsemiconductor1Leftperarea is the charge density contained within the semiconductor";

$qsemiconductor1Leftperarea = (\epsilon_{psSemi1} * gradientinSemi1Left * Semi1LeftChargeSign)$;

"V2 is the electrical potential at the interface between the metal and the insulator. NOTE: THE CHARGE INTRODUCED BY STRAINING THE PIEZOELECTRIC IS PRESENT HERE. Both the Semiconductor and Piezoelectric charge density must be balanced by the charge at the metal's surface, thus the sum of these two charges is all that is needed when applying Gauss's law to the interface to deduced V2. The term (Insulator1DFromRemnantAndStrainPiezo*dIns1/epsIns1) is to adjust for the electric field inside the ferroelectric insulator due to remenant polarization and piezoelectric charge";

$V2 = V3 + ((- (qsemiconductor1Leftperarea + Semi1LeftDFromStrainPiezo + DSpontaneousSemi1Left) * dIns1) / \epsilon_{psIns1}) + (Insulator1DFromRemnantAndStrainPiezo * dIns1 / \epsilon_{psIns1})$;

```

"FindRoot is used to determine the value of V3, the potential at the interface between the
insulator and the semiconductor";
V3 = V3 /. FindRoot[V2-V1, {V3, -4},MaxIterations->100000];

"-----";
"Plotting potential profiles in metal";
"-----";
"Now it's time to construct the potential profiles of the heterointerface. We start with the Metal";

"WorkFunctionOfMetal is the work function of the metal, defined within the region where the
metal is positioned (x<=0)";
WorkFunctionOfMetal[x_]= V1;

"VacuumPotential is the Vacuum level, defined within the region where the metal is positioned
(x<=0)";
VacuumPotentialinMetal[x_]= 0;

"MetalPotential is a grouping of these two functions together, which describe the Vacuum and
work function of the metal together.";
MetalBandPotentialProfile[x_]= {WorkFunctionOfMetal[x],VacuumPotentialinMetal[x]};

"The plot below is an example of what this metal's band potential profile looks like within 10
meters in both directions of the metal/semiconductor)";
"Potential profile in metal test:"
Plot[MetalBandPotentialProfile[x]*HeavisideTheta[ - x], {x, -10, 10}]

"-----";
"Plotting potential profiles in semiconductor 1";
"-----";

Clear[Vsemi1]
"NDSolve finds a numerical solution to the ordinary differential equations for the function
Vsemi1[x] with the independent variable x in the range {x,xmin,xmax}
We use the following function to numerically solve the integration of electric field (potential
gradient) as a function of distance from the interface (Eq. 14 in the main text)";
s1[x_]=NDSolve[{Vsemi1'[x]==-((V4-V3)/Abs[V4-V3])(p1*(
    (nbSemi1*(Exp[-zn*Vsemi1[x]*q1]))+
    (pbSemi1*(Exp[-zp*Vsemi1[x]*q1]))+
    (-zNdSemi1*NdSemi1*Vsemi1[x]*q1)-(nbSemi1+pbSemi1)))^(1/2),Vsemi1[0]==V4-
V3},Vsemi1,{x,0,100000*10^-9},MaxSteps->10000000];

"PotentialProfileCurve1 is the name of the function that describes the potential profile within the
semiconductor as a function of distance from the Insulator/Semiconductor interface";
PotentialProfileCurve1[x_]=Evaluate[Vsemi1[x]/. s1[x]];

```

"This plot generates a graph of the points generated above. You can use it to check whether things looks like they are expected to or if an error has occured";

"-----"

"Semiconductor 1 (left;metal/insulator 1/semiconductor 1 junction) depletion region potential profile test :"

"-----"

```
Plot[PotentialProfileCurve1[x],
  {x,0,200*10^-9},
  PlotRange->{-2,5},AxesLabel->{"Distance from Metal/Semiconducutor Interface","Elecrical
  Potential,V"},BaseStyle->{FontWeight->"Bold",FontSize->15}]
```

"-----";

"Plotting potential profile in insulator 1";

"-----";

"Electric field in the insulator ('ElectricFieldInInsulator1') is deduced by applying Gauss's Law to the charge contained at the insulator interfaces.";

```
ElectricFieldInInsulator1= -
(qsemiconductor1Leftperarea+Semi1LeftDFromStrainPiezo+DSpontaneousSemi1Left-
Insulator1DFromRemnantAndStrainPiezo)/epsIns1;
```

"Vacuumpotentialininsulator1 is the potential of vacuum within the insulating material as a function of distance";

```
Vacuumpotentialininsulator1[x_]= (ElectricFieldInInsulator1*x);
```

"Insulator1BandPotentialProfile is a name change to maintain consistancy";

```
Insulator1BandPotentialProfile[x_]=Vacuumpotentialininsulator1[x];
```

"This is a plot of the potential profile of vacuum within the insulating layer, glancing at it makes a good check to see if anything unexpected is happening";

"-----"

"Potential profile in insulator 1 test:"

"-----"

```
Plot[Insulator1BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[ x-dIns1]), {x, -
10*10^-9, dIns1*2}]
```

"-----";

"Calculating and plotting within and out of depletion width: semiconductor 1(left):

Note: This is for the potential profile in semiconductor 1 at the metal/insulator/semiconductor interface (designated left side of semiconductor 1);

"-----";

"Next we need to create a function that describes the potential profile of the semiconductor and vacuum level within the depletion region of the semiconductor. To do this, we must first

determine the distance x that defines the boundry of the depletion region. We can define this boundary as the distance at which potential gradient becomes zero and the potential of the depletion equals that of bulk semiconductor.";

"To determine where the potential in the depletion region equals the bulk semiconductor potential, we instruct Mathematica to find the root of PotentialProfileCurve1[x]";

"This function automatically looks for the root of PotentialProfileCurve1[x], starting at the value $x = 0$, and stores that x value in the variable 'EndofDepletionWidth'";

EndofDepletionWidth = x /. FindRoot[PotentialProfileCurve1[x], {x, 0}, MaxIterations->1000];

"numerical solution can result in small deviations from phsyicallity, this ensures that the result is a completely real number";

"This is the end of the depletion width"

EndofDepletionWidth = Re[EndofDepletionWidth]

"We can now use EndofDepletionWidth in combination with a heaviside function to create a function that defines the potential profile of the vacuum level and the semiconductor's conduction and valence bands within the depletion region. NOTE: THESE POTENTIAL PORFILES ARE OFFSET IN SPACE BY THE INSULATING LAYER AND OFFSET IN POTENTIAL BY THE POTENTIAL DROP THAT OCCURS IN THE INSULATING LAYER";

VacuumPotentialinDepletionRegion1[x_]=(PotentialProfileCurve1[x]-(V4-V3)+(ElectricFieldInInsulator1*dIns1));

SemiCBPotentialinDepletionRegion1[x_]=(CBZnO+VacuumPotentialinDepletionRegion1[x]);

"SemiVBPotentialinDepletionRegion1=HeavisideTheta[x-dIns1]*(VBZnO+VacuumPotentialinDepletionRegion1)*HeavisideTheta[EndofDepletionWidth- (x-dIns1)];";

SemiVBPotentialinDepletionRegion1[x_]=(VBZnO+VacuumPotentialinDepletionRegion1[x]);

"DepletionRegionPotentialProfile is a grouping of these three functions together, which describes the Vacuum and band positions of the semiconductor in the depletion region.";

DepletionRegionPotentialProfile[x_] =

{VacuumPotentialinDepletionRegion1[x],SemiCBPotentialinDepletionRegion1[x],SemiVBPotentialinDepletionRegion1[x]};

"These plots can be used as checks to make sure that nothing unexpected is going on";

"-----"

"Potential profiles in Semiconductor 1 (left) in depletion width:"

"-----"

```
Plot[(HeavisideTheta[ x-dIns1]-HeavisideTheta[x-
(EndofDepletionWidth+dIns1)])*{DepletionRegionPotentialProfile[x-dIns1]},{x,-200*10^-
9,2*dIns1+EndofDepletionWidth},PlotRange->
{2*(VBZnO+VacuumPotentialinDepletionRegion1),2}]
```

"Next we need to create function that describes the potential profiles of the semiconductor and vacuum level outside of the depletion region ($x > \text{EndofDepletionRegion}$). Note: These potential profiles are offset in space by the insulating later and offset in potential by the potential drop that occurs in the insulating layer.";

```
VacuumPotentialinSemiandOutOfDepletionRegion[x_]=
0-(V4-V3)+(ElectricFieldInInsulator1*dIns1);
```

```
SemiCBPotentialinSemiandOutOfDepletionRegion[x_]=
CBZnO-(V4-V3)+(ElectricFieldInInsulator1*dIns1);
```

```
SemiVBPotentialinSemiandOutOfDepletionRegion[x_]=
VBZnO-(V4-V3)+(ElectricFieldInInsulator1*dIns1);
```

```
Semi1WFBulk[x_]=Semi1WF-(V4-V3)+(ElectricFieldInInsulator1*dIns1);
```

"BulkSemiPotentialProfiles is a grouping of these three functions together, which describes the Vacuum and band positions of the semiconductor in the Bulk of the semiconductor.";

```
BulkSemiPotentialProfiles[x_] =
{VacuumPotentialinSemiandOutOfDepletionRegion[x],SemiCBPotentialinSemiandOutOfDeplet
ionRegion[x],SemiVBPotentialinSemiandOutOfDepletionRegion[x]};
```

"These plots can be used as checks to make sure that nothing unexpected is going on";

```
"-----"
```

"Bulk potential profiles in semiconductor 1:"

```
"-----"
```

```
Plot[{BulkSemiPotentialProfiles[x]*HeavisideTheta[ x-
(EndofDepletionWidth+dIns1)],Semi1WFBulk[x]},{x,-200*10^-9,2000*10^-9},PlotRange-> {-
10,5}]
```

```
"-----";
```

"Plotting band diagram of metal/insulator 1/semiconductor 1";

```
"-----";
```

"We can now stitch together the functions that contain the potential profile information within the metal, insulator, depletion region, and the bulk of the semiconductor.";

```
Junction1VBPotential=
```

```
VacuumPotentialinMetal[x]*HeavisideTheta[-x]+
```

```
Vacuumpotentialininsulator1[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns1])+
```

```

SemiVBPotentialinDepletionRegion1[x-dIns1]*HeavisideTheta[x-dIns1]+

SemiVBPotentialinSemiandOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns1+EndofDepletionWidth)]);

Junction1CBPotential=

VacuumPotentialinMetal[x]*HeavisideTheta[-x]+

Vacuumpotentialininsulator1[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns1])+

SemiCBPotentialinDepletionRegion1[x-dIns1]*HeavisideTheta[x-dIns1]+

SemiCBPotentialinSemiandOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns1+EndofDepletionWidth)]);

Junction1VacuumPotential=

VacuumPotentialinMetal[x]*HeavisideTheta[-x]+

Vacuumpotentialininsulator1[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns1])+

VacuumPotentialinDepletionRegion1[x-dIns1]*HeavisideTheta[x-dIns1]+

VacuumPotentialinSemiandOutOfDepletionRegion[x-dIns1]*HeavisideTheta[x-
(dIns1+EndofDepletionWidth)];
"-----"
"Band diagram of the metal/insulator 1/semiconductor 1 junction:"
"-----"
Plot[{WorkFunctionOfMetal[x]*HeavisideTheta[-x],

Junction1CBPotential,

Junction1VBPotential,

Semi1WFBulk[x]*HeavisideTheta[x],

Junction1VacuumPotential},{x,-(EndofDepletionWidth*2+5*10^
8),EndofDepletionWidth*2+5*10^8},PlotRange->{8,-10},AxesLabel->{"Distance from
Metal/Semiconductor Interface","Band Diagram"},BaseStyle->{FontWeight->"Bold",FontSize-
>15},PlotStyle->
{Black,Red,Blue,{Black,Dashed},{Black,Thickness[0.007]}}]

```


"This may be offset by some amount depending what happens on the left side";
 BulkZeroofSemi1=MetalWF-Semi1WF;

"-----"

"Semiconductor 1/Insulator 2/Semiconductor 2 Junction"

"-----"

"Additional Constants and Conditions:";

"niSemi2 is the intrinsic concentration of electrons in the semiconductor";

$niSemi2 = N_{cZnO} * \exp[-((1.60217646 * 10^{-19}) * (E_{gZnO}/2))/(k * T))];$

"pbSemi1 is the bulk concentration of holes in the semiconductor";

$nbSemi2 = ((niSemi2)^2)/pbSemi2;$

"V5";

V5;

"V6";

V6;

"V7";

V7=Semi2WF;

BulkZeroofSemi1=0;

"-----";

"Setting up and solving for potential profiles in semiconductor (right)";

"-----";

$p1 = (2 * k * T)/epsSemi1;$

$q1 = -(e * (1.60217646 * 10^{-19})) / (k * T);$

$V_{Semi1Right} = -(V5 - V4);$

$Semi1RightChargeSign = -(V5 - V4) / Abs[(V5 - V4)];$

"gradientinSemi1Left is the strength of the Electric field going into the semiconductor at the interface between the semiconductor and the insulator";

$gradientinSemi1Right = -(p1 * (nbSemi1 * (\exp[-z_n * V_{Semi1Right} * q1])) + (pbSemi1 * (\exp[-z_p * V_{Semi1Right} * q1])) + (-z_{NdSemi1} * NdSemi1 * V_{Semi1Right} * q1) - (nbSemi1 + pbSemi1))^{(1/2)};$

$q_{semiconductor1Rightperarea} = (epsSemi1 * gradientinSemi1Right * Semi1RightChargeSign);$

"I REMOVED THE NEGATIVE SIGN FROM IN FRONT OF QSEIMCONDUCTOR, AND IT FIXED WTF WAS GOING ON, WHY???";

$V6 = Re[V5 + (((q_{semiconductor1Rightperarea} + Semi1RightDFromStrainPiezo + D_{SpontaneousSemi1Right}) * d_{Ins2}) / eps_{Ins2})];$

"Voltage is referenced to a negative test charge. Increases in voltage mean an increase in negative charge density";

$p2 = (2 * k * T)/epsSemi2;$

$V_{Semi2Left} = -(V6 - V7);$

```

Semi2LeftChargeSign=-((V6-V7)/Abs[(V6-V7)]);
gradientinSemi2Left=-(p2*(
    (nbSemi2*(Exp[-zn*VSemi2Left*q1]))+
    (pbSemi2*(Exp[-zp*VSemi2Left*q1]))+
    (-zNdSemi2*NdSemi2*VSemi2Left*q1)-(nbSemi2+pbSemi2)))^(1/2);

qsemiconductor2Leftperarea=(epsSemi2*gradientinSemi2Left*Semi2LeftChargeSign);

"-----"
"Plot used to visually identify net charge neutrality;also used as a quality control to see if the
function describing net charge does not have anomolies(e.g. step functions, holes, etc.):"
"-----"
Plot[qsemiconductor1Rightperarea+qsemiconductor2Leftperarea+Semi1RightDFromStrainPiezo
+DSpontaneousSemi1Right,{V5,-30,30},
    PlotRange->{-0.01,.01},AxesLabel->{"V5","Qnet"}}
V5 = V5 /.
FindRoot[qsemiconductor1Rightperarea+qsemiconductor2Leftperarea+Semi1RightDFromStrain
Piezo+DSpontaneousSemi1Right, {V5, V4+.00001},MaxIterations->100000];
"V5 is:"
V5
"Strain is:"
EZnO
"-----";
"Plotting potential profiles in semiconductor 1 (right)";
"-----";

Clear[VSemi1Right]
Semi1RightChargeSign=-(V5-V4)/(Abs[V5-V4]);
s2[x_]=NDSolve[{VSemi1Right[x]==Semi1RightChargeSign (p1*(
    (nbSemi1*(Exp[-zn*VSemi1Right[x]*q1]))+
    (pbSemi1*(Exp[-zp*VSemi1Right[x]*q1]))+
    (-zNdSemi1*NdSemi1*VSemi1Right[x]*q1)-
    (nbSemi1+pbSemi1)))^(1/2),VSemi1Right[0]==V5-V4},VSemi1Right,{x,0,1000*10^-
9},MaxSteps->10000000];PotentialProfileCurve2[x_]=Evaluate[-VSemi1Right[-x]/. s2[x]];
"-----"
"Semiconductor 1 (right;semiconductor 1/insulator 2/semiconductor 2 junction) depletion region
potential profile test:"
"-----"
Plot[PotentialProfileCurve2[x],{x,-200*10^-9,0},
    PlotRange->{-2,2},
    AxesLabel->{"Distance from Semiconductor/Insulator Interface","Electrical Potential Deviation
From Bulk Semi Value"},BaseStyle->{FontWeight->"Bold",FontSize->15}]

"-----";
"Solving depletion width in semiconductor 1 (right)";
"-----";

```

"Find the end of the depletion width for this semiconductor. This value, + the value of the depletion width on the other side will be the spatial limit defining the bulk case.";
 EndofDepletionWidth2= x /. FindRoot[PotentialProfileCurve2[x], {x, 0}, MaxIterations->1000];

"Numerical solution can result in small deviations from physicality, the following ensures that the result is a completely real number";
 "This is the end of the depletion width"
 EndofDepletionWidth2=Re[EndofDepletionWidth2]

"Create the potential profile in the bulk of the semiconductor1";
 VacuumPotentialinSemi1andOutOfDepletionRegion[x_]=(0+BulkZeroofSemi1);

SemiCBPotentialinSemiandOutOfDepletionRegion[x_]=CBSemi1+BulkZeroofSemi1;

SemiVBPotentialinSemiandOutOfDepletionRegion[x_]=VBSemi1+BulkZeroofSemi1;

BulkSemi1PotentialProfilesinBulk[x_]={ VacuumPotentialinSemi1andOutOfDepletionRegion[x], SemiCBPotentialinSemiandOutOfDepletionRegion[x], SemiVBPotentialinSemiandOutOfDepletionRegion[x]};

"-----"

"Bulk potential profiles in semiconductor 1 relative to semiconductor 1/insulator 2 interface:"

"-----"

Plot[{ VacuumPotentialinSemi1andOutOfDepletionRegion[x]*(1-HeavisideTheta[x-EndofDepletionWidth2]),

SemiCBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x-EndofDepletionWidth2]),

SemiVBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x-EndofDepletionWidth2])},

{x,-2000*10⁻⁹,5000*10⁻⁹},PlotRange-> {-10,5},PlotStyle->{{Black,Thickness[0.01]},Red,Blue}]

Clear[VacuumPotentialinSemi1inDepletionRegionRight,SemiCBPotentialinSemi1inDepletionRegionRight,SemiVBPotentialinSemi1inDepletionRegionRight]

"Create the potential profile in the depletion of the semiconductor1Right";
 VacuumPotentialinSemi1inDepletionRegionRight[x_]=(0+PotentialProfileCurve2[x]+BulkZeroofSemi1);

SemiCBPotentialinSemi1inDepletionRegionRight[x_]=(CBSemi1+PotentialProfileCurve2[x]+BulkZeroofSemi1);

SemiVBPotentialinSemi1inDepletionRegionRight[x_]=(VBSemi1+PotentialProfileCurve2[x]+BulkZeroofSemi1);

```
Semi1PotentialProfilesinDepRegion[x_]={ VacuumPotentialinSemi1inDepletionRegionRight[x],
SemiCBPotentialinSemi1inDepletionRegionRight[x],SemiVBPotentialinSemi1inDepletionRegionRight[x]};
```

```
"-----"
```

```
"Band diagram of semiconductor 1 (right):"
```

```
"-----"
```

```
Plot[ { VacuumPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-EndofDepletionWidth2]-HeavisideTheta[x]),SemiCBPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-EndofDepletionWidth2]-HeavisideTheta[x]),SemiVBPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-EndofDepletionWidth2]-HeavisideTheta[x])},{x,-300*10^-9,0*10^-9},PlotRange-> {-9,1},PlotStyle->{Black, Red, Blue}]
```

```
"-----";
```

```
"Potential profile in insulator 2:";
```

```
"-----";
```

```
ElectricFieldInInsulator2= -
```

```
(qsemiconductor1Rightperarea+Semi1RightDFromStrainPiezo+DSpontaneousSemi1Right)/epsIns2;
```

```
"VacuumPotentialinInsulator is the potential of vacuum within the insulating material as a function of distance";
```

```
VacuumPotentialinInsulator2[x_]=((ElectricFieldInInsulator2*x)+(V4-V5)+BulkZeroofSemi1);
```

```
"InsulatorBandPotentialProfile is a name change to maintain consistency";
```

```
Insulator2BandPotentialProfile[x_]=VacuumPotentialinInsulator2[x];
```

```
"This is a plot of the potential profile of vacuum within the insulating layer, glancing at it makes a good check to see if anything unexpected is happening";
```

```
"-----"
```

```
"Potential profile in insulator 2 test:"
```

```
"-----"
```

```
Plot[Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2]), {x, -10*10^-9, dIns2*2}]
```

```
"-----";
```

```
"Potential profile in semiconductor 2 (left):";
```

```
"-----";
```

```
"Generate the potential profile in Semiconductor 2 on left.";
```

```
Clear[VSemi2Left]
```

```
Semi2LeftChargeSignChargeSign=-(V6-V7)/(Abs[V6-V7]);
```

```
s3[x_]=NDSolve[{VSemi2Left'[x]==Semi2LeftChargeSignChargeSign (p2*(
```

```

(nbSemi2*(Exp[-zn*VSemi2Left[x]*q1]))+
(pbSemi2*(Exp[-zp*VSemi2Left[x]*q1]))+
(-zNdSemi2*NdSemi2*VSemi2Left[x]*q1)-
(nbSemi2+pbSemi2))^(1/2),VSemi2Left[0]==V6-V7},VSemi2Left,{x,0,1000*10^-
9},MaxSteps->1000000];PotentialProfileCurve3[x_]=Evaluate[-VSemi2Left[x]/. s3[x]];
"-----"
"Semiconductor 2 (left;semiconductor 1/insulator 2/semiconductor 2 junction) depletion region
potential profile test : "
"-----"
Plot[PotentialProfileCurve3[x],{x,0,50.00*10^-9},
PlotRange->{-0.5,0.5},
AxesLabel->{"Distance from Semiconductor/Insulator Interface","Electrical Potential Deviation
From Bulk Semi Value"},BaseStyle->{FontWeight->"Bold",FontSize->15}]

"-----";
"Calculating and plotting within and out of depletion width: semiconductor 2(left)";
"-----";

"Find the end of the depletion width for this semiconductor. This value, will be the spatial limit
defining the bulk case.";
EndofDepletionWidth3i= x /. FindRoot[PotentialProfileCurve3[x], {x, 10^-8},MaxIterations-
>10000];
"numerical solution can result in small deviations from physycallity, this ensures that the result is
a completely real number";
"This is the end of the depletion width:"
EndofDepletionWidth3=Re[EndofDepletionWidth3i]

"Create the potential profile in the depletion of the semiconductor2Left";
VacuumPotentialinSemi2inDepletionRegionLeft[x_]=((PotentialProfileCurve3[x])+(V6-
V7)+(ElectricFieldInInsulator2*dIns2)+(V4-V5)+(BulkZeroofSemi1));

SemiCBPotentialinSemi2inDepletionRegionLeft[x_]=(CBSemi2+(PotentialProfileCurve3[x])+(
V6-V7)+(ElectricFieldInInsulator2*dIns2)+(V4-V5)+(BulkZeroofSemi1));

SemiVBPotentialinSemi2inDepletionRegionLeft[x_]=(VBSemi2+(PotentialProfileCurve3[x])+(
V6-V7)+(ElectricFieldInInsulator2*dIns2)+(V4-V5)+(BulkZeroofSemi1));

Semi2PotentialProfilesInDepregion[x_]={ VacuumPotentialinSemi2inDepletionRegionLeft[x],Se
miCBPotentialinSemi2inDepletionRegionLeft[x],SemiVBPotentialinSemi2inDepletionRegionLe
ft[x]};
"-----"
"Band diagram of semiconductor 2 (left) within depletion width:"
"-----"
Plot[{ VacuumPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-
HeavisideTheta[x-(dIns2+EndofDepletionWidth3)])],

```

```

SemiCBPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-
HeavisideTheta[x-(dIns2+EndofDepletionWidth3)]),
SemiVBPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-
HeavisideTheta[x-(dIns2+EndofDepletionWidth3)]),{x,.99*10^-8,30.005*10^-8},PlotRange->
{-10.3,2.4},PlotStyle->{Black, Red, Blue}]

```

"Next we need to create a function that describes the potential profile of the semiconductor and vacuum level within the semiconductor but outside of the depletion region EndofDepletionWidth <= x. NOTE: THESE POTENTIAL PORFILES ARE OFFSET IN SPACE BY THE INSULATING LAYER AND OFFSET IN POTENTIAL BY THE POTENTIAL DROP THAT OCCURS IN THE INSULATING LAYER";

```

VacuumPotentialinSemi2andOutOfDepletionRegion[x_]=(BulkZeroofSemi1+(V6-
V7)+(ElectricFieldInInsulator2*dIns2)+(V4-V5)+(BulkZeroofSemi1));

```

```

Semi2CBPotentialinSemi2andOutOfDepletionRegion[x_]=(CBSemi2+(V6-
V7)+(ElectricFieldInInsulator2*dIns2)+(V4-V5)+(BulkZeroofSemi1));

```

```

Semi2VBPotentialinSemi2andOutOfDepletionRegion[x_]=(VBSemi2+(V6-
V7)+(ElectricFieldInInsulator2*dIns2)+(V4-V5)+(BulkZeroofSemi1));

```

```

Semi2WFBulk=V7;

```

"BulkSemiPotentialProfiles is a grouping of these three functions together, which describes the Vacuum and band positions of the semiconductor in the Bulk of the semiconductor.";

```

BulkSemi2PotentialProfiles[x_] =
{ VacuumPotentialinSemi2andOutOfDepletionRegion[x],Semi2CBPotentialinSemi2andOutOfDe
pletionRegion[x],Semi2VBPotentialinSemi2andOutOfDepletionRegion[x]};

```

"These plots can be used as checks to make sure that nothing unexpected is going on";

```

"-----"

```

"Band diagram of bulk semiconductor 2 (left):"

```

"-----"

```

```

Plot[{ VacuumPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns2+EndofDepletionWidth3)]),
Semi2CBPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns2+EndofDepletionWidth3)]),
Semi2VBPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns2+EndofDepletionWidth3)]),
SemiWFBulk},{x,-20*10^-9,500*10^-9},PlotRange-> {-10,5},PlotStyle->{Black, Red,
Blue,{Black,Dashed}}]

```

```

"-----";

```

"Plotting band diagram of semiconductor 1/insulator 2/semiconductor 2";

```

"-----";

```

"We can now stitch together the three functions that contain the potential profile information within the semiconductor1Bulk, semiconductor1right, insulator, semiconductor2left, and semiconductor2Bulk regions of the semiconductor.";

Junction2VacuumPotential=

VacuumPotentialinSemi1andOutOfDepletionRegion[x]*(1-HeavisideTheta[x-EndofDepletionWidth2])+

VacuumPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-EndofDepletionWidth2]-HeavisideTheta[x])+

Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2])+

VacuumPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-HeavisideTheta[x-(dIns2+EndofDepletionWidth3)))+

VacuumPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-(dIns2+EndofDepletionWidth3)]);

Junction2CBPotential=

SemiCBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x-EndofDepletionWidth2])+

SemiCBPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-EndofDepletionWidth2]-HeavisideTheta[x])+

Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2])+

SemiCBPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-HeavisideTheta[x-(dIns2+EndofDepletionWidth3)))+

Semi2CBPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-(dIns2+EndofDepletionWidth3)]);

Junction2VBPotential=

SemiVBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x-EndofDepletionWidth2])+

SemiVBPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-EndofDepletionWidth2]-HeavisideTheta[x])+

Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2])+

SemiVBPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-HeavisideTheta[x-(dIns2+EndofDepletionWidth3)))+

Semi2VBPotentialInSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-(dIns2+EndofDepletionWidth3)]);

Junction2WFs=

Semi1WF*(1-HeavisideTheta[x])+

(Semi2WF-(V7-V4))*HeavisideTheta[x];

"-----"

"Band diagram of the semiconductor 1/insulator 2/semiconductor 2 junction"

"-----"

Plot[{Junction2CBPotential,Junction2VBPotential,Junction2VacuumPotential,Junction2WFs},{x,-100*10⁻⁹,100*10⁻⁹},PlotRange->{5,-8},AxesLabel->{"Distance from Metal/Semiconductor Interface","Band Diagram"},BaseStyle->{FontWeight->"Bold",FontSize->15},PlotStyle->{Red, Blue,{Black,Thickness[0.006]},{Dashed,Black}}]

"-----"

"Semiconductor 2/Insulator 3/Solution Junction"

"-----"

"Additional Constants and Conditions:";

"-----";

Clear[V7]

"epsIns3 is the electrical permittivity of insulator 3, BTO as an example";

epsIns3=EpsBTO*8.854*10⁻¹²;

"IsoelectricpHofsurface is the pH of solution that produces neutral charge on the surface making contact with solution, assuming insulator thickness is 0, then the iso pH of surface is just the isopH of the semiconductor, which in the case is taken to be p-type ZnO";

IsoelectricFermiOfZnO = V7iso;

IsoelectricpHofsurface = IsoelectricZnO;

IsoelectricFermiOfSemi2 =IsoelectricFermiOfZnO;

V7 =IsoelectricFermiOfSemi2 - (0.059)*(pHb-IsoelectricZnO);

"epsSol1 is the electrical permittivity of the solution, H2O as example";

epsSol1=epsH2O*8.854*10⁻¹²;

BulkZeroofSemi2=0;

""Mole' is Avogadro's number";

Mole=6.02214129*10²³;

"The concentration (#/m³) of H⁺ ions is determined from pH";

zH=1;

MHb=10^{-pHb};
 nHbSol1=MHb*(1/(0.001))*Mole;

"The concentration (#/m³) of OH⁻ ions is determined from pOH";
 zOH=-1;
 pOHb=14-pHb;
 MOHb=10^{-pOHb};
 nOHbSol1=MOHb*(1/(0.001))*Mole;

zNa=+1;
 MNab=MOHb;
 nNabSol1=MNab*(1/(0.001))*Mole;

"d31SemiPiezo is the direct piezoelectric coefficient of the semiconducting Piezoelectric, taking ZnO as an example material. A negative d31SemiPiezo value means electric field due to piezo charge points to the left and thus charge density on left is negative. ";
 d31Semi2Piezo = d31ZnO;

"Ypiezo is the Young's Modulus of the semiconducting Piezoelectric material.";
 YSemi2Peizo = YZnO;

"YZnO is the Young's modulus of ZnO, taken as an example Pieoelectric material";
 YZnO =150*10⁹;

"Epiezo is the Strain in the semiconducting Piezoelectric";
 ESemi2Piezo = EZnO;

"DSpontaneousBTO is the Polarization density (surface charge density) of the piezoelectric semiconductor";
 Semi2LeftDFromStrainPiezo = d31Semi2Piezo*(ESemi2Piezo)*(YSemi2Peizo);

Semi2RightDFromStrainPiezo=-Semi2LeftDFromStrainPiezo ;

DSpontaneousSemi2Right = -DSpontaneousSemi2Left;

"DSpontaneousZnO is the Spontaneous (Remnant) polarization (density) of ZnO = 0 C/cm². 1, 0, or -1 before the Remenant value is about on/off/&direction of field.";
 DSpontaneousSemi2Left = DSpontaneousZnO;
 DSpontaneousZnO = 0*(1*10⁻⁶)*(1*10⁴);

"-----";
 "Setting up and solving for potential profiles in semiconductor 2(right)";
 "-----";

VSemi2Right=-(V7-V8);
 Semi2RightChargeSign=(V7-V8)/(Abs[V7-V8]);

```

"gradientinSemi2Left is the strength of the Electric field going into the semiconductor at the
interface between the semiconductor and the insulator";
"gradientinSemi2Right";
gradientinSemi2Right=Re[(p2*(
    (nbSemi2*(Exp[-zn*VSemi2Right*q1]))+
    (pbSemi2*(Exp[-zp*VSemi2Right*q1]))+
    (-zNdSemi2*NdSemi2*VSemi2Right*q1)-(nbSemi2+pbSemi2)))^(1/2)];
"qsemicharge2rightperarea";
qsemiconductor2Rightperarea=(epsSemi2*gradientinSemi2Right*Semi2RightChargeSign);

"Incorperate voltage drop across insulator";
"postivity DSpontaneousBTO will increase |V9| relative to |V8|";
V9=V8+((-
(qsemiconductor2Rightperarea+Semi2RightDFromStrainPiezo+DSpontaneousSemi2Right)*dIns
3)/epsIns3);

"Voltage is referenced to a negative test charge. Increases in voltage mean an increase in
negative charge density";
p3=(2*k*T)/epsSol1;
VSol1Left=-(V9-V10);
Sol1LeftChargeSign=-(V9-V10)/(Abs[(V9-V10)]);
gradientinSol1Left=Re[(p3*(
    (nHbSol1*(Exp[-zH*VSol1Left*q1]))+
    (nOHbSol1*(Exp[-zOH*VSol1Left*q1]))+
    (nNabSol1*(Exp[-zNa*VSol1Left*q1]))-
    (nHbSol1+nOHbSol1+nNabSol1)))^(1/2)];

qsol1leftperarea=(epsSol1*gradientinSol1Left*Sol1LeftChargeSign);

"-----"
"Plot used to visually identify net charge neutrality;also used as a quality control to see if the
function describing net charge does not have anomolies(e.g. step functions, holes, etc.):"
"-----"
Plot[qsemiconductor2Rightperarea+qsol1leftperarea,{V8, -10,0},PlotRange->{-
.000001,.000001}]

V8 = V8 /. FindRoot[qsemiconductor2Rightperarea+qsol1leftperarea, {V8, -10},MaxIterations-
>100000];

"V7 is:"
    V7
"V8 is:"
    VSemi2Right=V8
"Semiconductor 2 sign charge is:"
    Semi2RightChargeSign

```

"-----"

"Physicality check to determine if the use of a Stern layer is appropriate:"

"-----"

"Now to check the physicality of the result. First calculate the total atomic density of charged species at the solid/liquid interface.";

$n_{Hb22Sol1} = n_{HbSol1} * \exp[(z_H * e * V_{Sol1Left} * (1.60217646 * 10^{-19})) / (k * T)];$

$n_{OHb2Sol1} = n_{OHbSol1} * \exp[(z_{OH} * e * V_{Sol1Left} * (1.60217646 * 10^{-19})) / (k * T)];$

$n_{Nab2Sol1} = n_{OHbSol1} * \exp[(z_{Na} * e * V_{Sol1Left} * (1.60217646 * 10^{-19})) / (k * T)];$

"Total atomic Density at the interface"

$n_{Total} = n_{Hb22Sol1} + n_{OHb2Sol1} + n_{Nab2Sol1}$

"Concentration of H";

$n_{Hb22Sol1};$

"Concentration of OH";

$n_{OHb2Sol1};$

"Concentration of Na";

$n_{Nab2Sol1};$

"-----"

"3D Close-Packing Density of Charged Species in Solution at Solid-Solution Interface to Test for Maximum Potential to form Stern Layer:"

"-----"

"We can determine size of ions from resources such as
http://www.electrobionics.org/ionic_radii.pdf;

"Choose the ion with the largest size and largest concentration, in this case Na, and determine the closed packed density of that ion. Hydrated Na is $450 * 10^{-12}$ meters in diameter.";

"testing max atomic density allowed";

$IonDiameter = HydratedNaDiameter;$

$HydratedNaDiameter = 450 * 10^{-12};$

$IonRadius = IonDiameter / 2;$

$volume = ((3 * \sqrt{3}) / (2)) * ((IonDiameter)^2) * (\sqrt{(2/3)}) * (4 * (IonRadius));$

$atoms_v = 6;$

"Solid surface site density:"

$density_v = N[atoms_v / volume]$

"If the density calculated above is greater than the total density of charged species also calculated above, then total physicality of the calculation hasn't broken down and you may proceed with the calculation"

"If the charge density found at the wall is below the maximum, skip this step. This step is a means of determining what potential (V_{max}) is necessary at the solution interface to create an unphysical charge density. If the charge density at the interface is higher than the maximum charge density allowed then the potential at the interface ($V_{Sol1Left}$) is greater than V_{max} . Under these conditions, a charged hexagonal closed-packed Stern layer will form at the interface

(Figure S2). This sheet of charged hydrated ions will reduce the potential between the interface and solution so that the potential value becomes equal to $V_{\max}$ "

```

nHb2Sol1test=nHbSol1*Exp[(zH*e*VSol1Lefttest*(1.60217646*10^-
19))/(k*T)];
nOHb2Sol1test=nOHbSol1*Exp[(zOH*e*VSol1Lefttest*(1.60217646*10^-
19))/(k*T)];
nNab2Sol1test=nOHbSol1*Exp[(zNa*e*VSol1Lefttest*(1.60217646*10^-
19))/(k*T)];
"Total atomic Denisty at the interface";
nTotalseet=nHb2Sol1test+nOHb2Sol1test+nNab2Sol1test;
"Maximum potential allowed in solution before physicality breaks down:"
Vmax = VSol1Lefttest /. FindRoot[nTotalseet-densityv, {VSol1Lefttest,
0},MaxIterations->100000]
"Potential in the Solution:"
Abs[V9-V10]

```

"If physicality broke down because the potential in solution is higher then $V_{\max}$, we must determine what amount of charge to place in a stern layer to reduce the potential in solution to $V_{\max}$. We do this solving the electric field strength (gradientinSol1Lefttest) necessary to create $V_{\max}$ in solution, and then we subtract this value from the actual value of electric field strength we found at the interface (qsol1leftperarea). The resultant is the charge density that must be placed in the stern layer to:"

```

Sol1LeftChargeSign=-(V9-V10)/(Abs[(V9-V10)]);
gradientinSol1Lefttest=(p2*(
  (nHbSol1*(Exp[-zH*Vmax*q1]))+
  (nOHbSol1*(Exp[-zOH*Vmax*q1]))+
  (nNabSol1*(Exp[-zNa*Vmax*q1]))-
  (nHbSol1+nOHbSol1+nNabSol1)))^(1/2);
qsol1leftperareatest=(epsSol1*gradientinSol1Lefttest*Sol1LeftChargeSign);
"Charge needed in the stern layer"
qsternlayer =qsol1leftperareatest-qsol1leftperarea

```

```

"-----";
"Setting up and solving for potential profiles in semiconductor 2(right)";
"-----";
"Generate the potential profile in Semiconductor 2 on Right.";
Clear[VSemi2Right]

```

```

Semi2RightChargeSign=(V7-V8)/(Abs[V7-V8]);

```

```

s4[x_]=NDSolve[{VSemi2Right'[x]==Semi2RightChargeSign (p2*(
  (nbSemi2*(Exp[-zn*VSemi2Right[x]*q1]))+
  (pbSemi2*(Exp[-zp*VSemi2Right[x]*q1]))+
  (-zNdSemi2*NdSemi2*VSemi2Right[x]*q1)-
  (nbSemi2+pbSemi2)))^(1/2),VSemi2Right[0]==V8-V7},VSemi2Right,{x,0,1000*10^-
9},MaxSteps->10000000];

```

```

PotentialProfileCurve4[x_]=Evaluate[-VSemi2Right[x]/. s4[x]];

"-----"
"Potential profile test: semiconductor 2(right):"
"-----"
Plot[PotentialProfileCurve4[x],{x,0,200*10^-9},
PlotRange->{-2,2},
AxesLabel->{"Distance from Semiconductor/Insulator Interface","Electrical Potential Deviation
From Bulk Semi Value"},BaseStyle->{FontWeight->"Bold",FontSize->15}]

"-----"
"Bulk potential profiles in semiconductor 2 relative to semiconductor 2/insulator 3 interface:"
"-----"
"Create the potential profile in the bulk of the semiconductor2";

"First we must determine how far the depletion width goes into semi2, and thus where bulk
ends"

"Find the end of the depletion width for this semiconductor. This value, + the value of the
depletion width on the other side will be the spatial limit defining the bulk case.";
EndofDepletionWidth4i= x /. FindRoot[PotentialProfileCurve4[x], {x, 0},MaxIterations->1000];
"numerical solution can result in small deviations from physycallity, this ensures that the result is
a completely real number";
"This is the end of the depletion width"
EndofDepletionWidth4=Re[EndofDepletionWidth4i]

"Now lets create potential profile for the semi2 bulk";

VacuumPotentialinSemi2andOutOfDepletionRegion[x_]=(0+BulkZeroofSemi2);

SemiCBPotentialinSemiandOutOfDepletionRegion[x_]=CBSemi2+BulkZeroofSemi2;

SemiVBPotentialinSemiandOutOfDepletionRegion[x_]=VBSemi2+BulkZeroofSemi2;

Plot[{ VacuumPotentialinSemi2andOutOfDepletionRegion[x]*(1-HeavisideTheta[x]),
SemiVBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x]),
SemiCBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x])},{x,-2000*10^-
9,5000*10^-9},PlotRange-> {-10,5},PlotStyle->{{Black,Thickness[0.01]},Blue,Red}]

"-----"
"Calculating and plotting within depletion width: semiconductor 2(right)"
"-----"
"Create the potential profile in the depletion of the semiconductor2Right";

```

VacuumPotentialinSemi2inDepletionRegionRight[x_]=(0+PotentialProfileCurve4[-x]+BulkZeroofSemi2);

SemiCBPotentialinSemi2inDepletionRegionRight[x_]=(CBSemi2+PotentialProfileCurve4[-x]+BulkZeroofSemi2);

SemiVBPotentialinSemi2inDepletionRegionRight[x_]=(VBSemi2+PotentialProfileCurve4[-x]+BulkZeroofSemi2);

Plot[{SemiCBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x]),

SemiVBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x]),

VacuumPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])},{x,-400*10⁻⁹,400*10⁻⁹},PlotRange->{-8,1},PlotStyle->{Red,Blue,{Black,Thickness[0.005]}}]"Create the potential profile in the depletion of the semiconductor2Right";

VacuumPotentialinSemi2inDepletionRegionRight[x_]=(0+PotentialProfileCurve4[-x]+BulkZeroofSemi2);

SemiCBPotentialinSemi2inDepletionRegionRight[x_]=(CBSemi2+PotentialProfileCurve4[-x]+BulkZeroofSemi2);

SemiVBPotentialinSemi2inDepletionRegionRight[x_]=(VBSemi2+PotentialProfileCurve4[-x]+BulkZeroofSemi2);

Plot[{SemiCBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x]),

SemiVBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x]),

VacuumPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])},{x,-400*10⁻⁹,400*10⁻⁹},PlotRange->{-8,1},PlotStyle->{Red,Blue,{Black,Thickness[0.005]}}]

"-----"

"Potential profile in insulator 3 test:"

"-----"

"Create potential profile in insulator at the interface"

```
ElectricFieldInInsulator3=
(qsemiconductor2Rightperarea+Semi2RightDFromStrainPiezo+DSpontaneousSemi2Right)/epsI
ns3;
```

"VacuumPotentialinInsulator is the potential of vacuum within the insulating material as a function of distance";

```
VacuumPotentialinInsulator3[x_] =
((ElectricFieldInInsulator3*x)+PotentialProfileCurve4[0].{1}+BulkZeroofSemi2);
```

"InsulatorBandPotentialProfile is a name change to maintain consistency";

```
Insulator3BandPotentialProfile[x_]=VacuumPotentialinInsulator3[x];
```

"This is a plot of the potential profile of vacuum within the insulating layer, glancing at it makes a good check to see if anything unexpected is happening";

```
Plot[Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3]), {x, -
10*10^-9, dIns3*2}]
```

```
"-----"
```

"Setting up for, solving, and testing the potential profile in solution (left) within depletion width:"

```
"-----"
```

"Generate the potential profile in Semiconductor 2 on Right.:"

```
Clear[VSol1Left]
```

```
Sol1LeftChargeSign=-(V9-V10)/(Abs[(V9-V10)]);
```

```
s5[x_]=NDSolve[{VSol1Left[x]==Sol1LeftChargeSign (p2*(
  (nHbSol1*(Exp[-zH*VSol1Left[x]*q1]))+
  (nOHbSol1*(Exp[-zOH*VSol1Left[x]*q1]))+
  (nNabSol1*(Exp[-zNa*VSol1Left[x]*q1])))-
  (nHbSol1+nOHbSol1+nNabSol1))^(1/2),VSol1Left[0]==V9-
V10},VSol1Left,{x,0,1500*10^-9},MaxSteps->1000000];
```

```
PotentialProfileCurve5[x_]=Evaluate[-VSol1Left[x]/. s5[x]];
```

```
Plot[PotentialProfileCurve5[x],{x,0,600000*10^-9},PlotRange->{0,.00005},
  AxesLabel->{"Distance from Ins/Solution Interface","Electrical Potential Deviation From Bulk
Sol Value"},BaseStyle->{FontWeight->"Bold",FontSize->15}]
```

```
"-----";
```

"Solving for depletion width in solution (left):";

```
"-----";
```

"Create the potential profile in the bulk of the solution";

"First we must determine how far the depletion width goes into sol, and thus where bulk ends"

"Find the end of the depletion width for this sol. This value, + the value of the depletion width on the other side will be the spatial limit defining the bulk case.:"

```
EndofDepletionWidth5i= x /. FindRoot[PotentialProfileCurve5[x], {x, 0},MaxIterations->1000];
```

"Numerical solution can result in small deviations from physicality, this ensures that the result is a completely real number";

"This is the end of the depletion width"

EndofDepletionWidth5=Re[EndofDepletionWidth5i]

"Create the potential profile in the depletion of the solution";

VacuumPotentialinSol1inDepletionRegionLeft[x_]=

(PotentialProfileCurve5[x]+((ElectricFieldInInsulator3*dIns3+PotentialProfileCurve4[0].{1}-PotentialProfileCurve5[0].{1})+BulkZeroofSemi2));

Sol1PotentialProfilesinDepRegion[x_]=VacuumPotentialinSol1inDepletionRegionLeft[x];

"-----"

"Plotting bulk potential profile in solution (left) test:"

"-----"

Plot[{Sol1PotentialProfilesinDepRegion[x-dIns3]}*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-
(dIns3+EndofDepletionWidth5)]),{x,0,dIns3+2000*10⁻⁹};

"Here, we compensate the position of solution potential for the potential changes across semiconductor 2(right), insulator 3, and depletion width of the solution (relative position to bulk semiconductor 2)";

((ElectricFieldInInsulator3*dIns3+PotentialProfileCurve4[0].{1}-
PotentialProfileCurve5[0].{1})+BulkZeroofSemi2);

VacuumPotentialinSol1OutOfDepletionRegion[x];

Sol1PotentialProfilesOutOfDepletionRegion[x];

VacuumPotentialinSol1OutOfDepletionRegion[x_]=

((((ElectricFieldInInsulator3*dIns3+PotentialProfileCurve4[0].{1}-
PotentialProfileCurve5[0].{1})+BulkZeroofSemi2));

Sol1PotentialProfilesOutOfDepletionRegion[x_]={VacuumPotentialinSol1OutOfDepletionRegion[x];

Plot[{Sol1PotentialProfilesOutOfDepletionRegion[x]}*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)],{x,0,dIns3+60000*10⁻⁹},PlotRange->Automatic]

"-----"

"-----"

"Band diagram for semiconductor 2/insulator 3/solution junction:"

"-----"

"We can now stitch together the three functions that contain the potential profile information within the semiconductor2Bulk, semiconductor2right, insulator, Sol1left, and Sol2Bulk regions of the Solution.";

Junction3VBPotential=

SemiVBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])+

Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3])+

Sol1PotentialProfilesinDepRegion[x-dIns3]*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-(dIns3+EndofDepletionWidth5)]))+

Sol1PotentialProfilesOutOfDepletionRegion[x]*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)];

Junction3CBPotential=

SemiCBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])+

Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3])+

Sol1PotentialProfilesinDepRegion[x-dIns3]*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-(dIns3+EndofDepletionWidth5)]))+

Sol1PotentialProfilesOutOfDepletionRegion[x]*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)];

Junction3VacuumPotential=

VacuumPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])+

Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3])+

Sol1PotentialProfilesinDepRegion[x-dIns3]*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-(dIns3+EndofDepletionWidth5)]))+

Sol1PotentialProfilesOutOfDepletionRegion[x]*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)];

Plot[{Junction3VBPotential,Junction3CBPotential,Junction3VacuumPotential},{x,-10*10^-9,10*10^-9},PlotRange->{-8, 0.5},AxesLabel->{"Distance from Metal/Semiconductor Interface","Band Diagram"},BaseStyle->{FontWeight->"Bold",FontSize->15},PlotStyle->{Blue,Red,{Black,Thickness[0.008]}},
{GridLines->{{5*10^-9},{}},GridLinesStyle->Directive[Gray, Dashed]}}

“-----

Splicing the Three Junctions

-----“

“We will now extract the individual functions that make up each junction. Since more descriptive function definitions were given in their respective sections above, each function will be given simpler definitions (e.g., $f1[x]$, $f2[x]$, etc.) and translation steps for profile continuity will be given more concise definitions. This is done to simplify the stitching process.”

Clear[f1vb,f2vb,f3vb,f4vb,f5vb,f6vb,f7vb,f8vb,f9vb,f10vb,f11vb,f12vb,f13vb]

Clear[f1cb,f2cb,f3cb,f4cb,f5cb,f6cb,f7cb,f8cb,f9cb,f10cb,f11cb,f12cb,f13cb]

Clear[f1vac,f2vac,f3vac,f4vac,f5vac,f6vac,f7vac,f8vac,f9vac,f10vac,f11vac,f12vac,f13vac]

“-----
-----“

“Extracting Functions:”

“-----
-----“

“From Junction 1:”

Junction1VBPotential=

VacuumPotentialinMetal[x]*HeavisideTheta[-x]+

Vacuumpotentialininsulator1[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns1])+

SemiVBPotentialinDepletionRegion1[x-dIns1]*HeavisideTheta[x-dIns1]+

SemiVBPotentialinSemiandOutOfDepletionRegion[x]*(HeavisideTheta[x-(dIns1+EndofDepletionWidth)]);

"Extracted functions";

f1vb[x_]=VacuumPotentialinMetal[x];

f2vb[x_]=Vacuumpotentialininsulator1[x];

f3vb[x_]=SemiVBPotentialinDepletionRegion1[x];

f4vb[x_]=SemiVBPotentialinSemiandOutOfDepletionRegion[x];

Junction1CBPotential=

VacuumPotentialinMetal[x]*HeavisideTheta[-x]+

Vacuumpotentialininsulator1[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns1])+

```

SemiCBPotentialinDepletionRegion1[x-dIns1]*HeavisideTheta[x-dIns1]+

SemiCBPotentialinSemiandOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns1+EndofDepletionWidth)]);

"Extracted functions";
f1cb[x_]=VacuumPotentialinMetal[x];
f2cb[x_]=Vacuumpotentialininsulator1[x];
f3cb[x_]=SemiCBPotentialinDepletionRegion1[x];
f4cb[x_]=SemiCBPotentialinSemiandOutOfDepletionRegion[x];
Junction1VacuumPotential=

VacuumPotentialinMetal[x]*HeavisideTheta[-x]+

Vacuumpotentialininsulator1[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns1])+

VacuumPotentialinDepletionRegion1[x-dIns1]*HeavisideTheta[x-dIns1]+

VacuumPotentialinSemiandOutOfDepletionRegion[x-dIns1]*HeavisideTheta[x-
(dIns1+EndofDepletionWidth)];

"Extracted functions";
f1vac[x_]=VacuumPotentialinMetal[x];
f2vac[x_]=Vacuumpotentialininsulator1[x];
f3vac[x_]=VacuumPotentialinDepletionRegion1[x];
f4vac[x_]=VacuumPotentialinSemiandOutOfDepletionRegion[x];

"From Junction 2:"
Junction2VBPotential=

SemiVBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x-
EndofDepletionWidth2])+

SemiVBPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-
EndofDepletionWidth2]-HeavisideTheta[x])+

Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2])+

SemiVBPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-
HeavisideTheta[x-(dIns2+EndofDepletionWidth3)]))+

Semi2VBPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns2+EndofDepletionWidth3)]);

"Extracted functions";

```

```

f5vb[x_]=SemiVBPotentialinSemiandOutOfDepletionRegion[x];
f6vb[x_]=SemiVBPotentialinSemi1inDepletionRegionRight[x];
f7vb[x_]=Insulator2BandPotentialProfile[x];
f8vb[x_]=SemiVBPotentialinSemi2inDepletionRegionLeft[x];
f9vb[x_]=Semi2VBPotentialinSemi2andOutOfDepletionRegion[x];
Junction2CBPotential=

```

```

    SemiCBPotentialinSemiandOutOfDepletionRegion[x]*(1-HeavisideTheta[x-
EndofDepletionWidth2])+

```

```

    SemiCBPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-
EndofDepletionWidth2]-HeavisideTheta[x])+

```

```

    Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2])+

```

```

    SemiCBPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-
HeavisideTheta[x-(dIns2+EndofDepletionWidth3))]+

```

```

    Semi2CBPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns2+EndofDepletionWidth3)]);

```

```

"Extracted functions";

```

```

f5cb[x_]=SemiCBPotentialinSemiandOutOfDepletionRegion[x];
f6cb[x_]=SemiCBPotentialinSemi1inDepletionRegionRight[x];
f7cb[x_]=Insulator2BandPotentialProfile[x];
f8cb[x_]=SemiCBPotentialinSemi2inDepletionRegionLeft[x];
f9cb[x_]=Semi2CBPotentialinSemi2andOutOfDepletionRegion[x];
Junction2VacuumPotential=

```

```

    VacuumPotentialinSemi1andOutOfDepletionRegion[x]*(1-HeavisideTheta[x-
EndofDepletionWidth2])+

```

```

    VacuumPotentialinSemi1inDepletionRegionRight[x]*(HeavisideTheta[x-
EndofDepletionWidth2]-HeavisideTheta[x])+

```

```

    Insulator2BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns2])+

```

```

    VacuumPotentialinSemi2inDepletionRegionLeft[x-dIns2]*(HeavisideTheta[x-dIns2]-
HeavisideTheta[x-(dIns2+EndofDepletionWidth3))]+

```

```

    VacuumPotentialinSemi2andOutOfDepletionRegion[x]*(HeavisideTheta[x-
(dIns2+EndofDepletionWidth3)]);

```

```

"Extracted functions";

```

```

f5vac[x_]=VacuumPotentialinSemi1andOutOfDepletionRegion[x];
f6vac[x_]=VacuumPotentialinSemi1inDepletionRegionRight[x];

```

```
f7vac[x_]=Insulator2BandPotentialProfile[x];
f8vac[x_]=VacuumPotentialinSemi2inDepletionRegionLeft[x];
f9vac[x_]=VacuumPotentialinSemi2andOutOfDepletionRegion[x];
```

“From Junction 3:”

Junction3VBPotential=

```
SemiVBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])+
```

```
Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3])+
```

```
Sol1PotentialProfilesinDepRegion[x-dIns3]*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-(dIns3+EndofDepletionWidth5))]+
```

```
Sol1PotentialProfilesOutOfDepletionRegion[x]*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)];
```

"Extracted functions";

```
f10vb[x_]=SemiVBPotentialinSemi2inDepletionRegionRight[x];
f11vb[x_]=Insulator3BandPotentialProfile[x];
f12vb[x_]=Sol1PotentialProfilesinDepRegion[x];
f13vb[x_]=Sol1PotentialProfilesOutOfDepletionRegion[x];
```

Junction3CBPotential=

```
SemiCBPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])+
```

```
Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3])+
```

```
Sol1PotentialProfilesinDepRegion[x-dIns3]*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-(dIns3+EndofDepletionWidth5))]+
```

```
Sol1PotentialProfilesOutOfDepletionRegion[x]*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)];
```

"Extracted functions";

```
f10cb[x_]=SemiCBPotentialinSemi2inDepletionRegionRight[x];
f11cb[x_]=Insulator3BandPotentialProfile[x];
f12cb[x_]=Sol1PotentialProfilesinDepRegion[x];
f13cb[x_]=Sol1PotentialProfilesOutOfDepletionRegion[x];
```

Junction3VacuumPotential=

VacuumPotentialinSemi2inDepletionRegionRight[x]*(HeavisideTheta[x+EndofDepletionWidth4]-HeavisideTheta[x])+

Insulator3BandPotentialProfile[x]*(HeavisideTheta[x]-HeavisideTheta[x-dIns3])+

Sol1PotentialProfilesinDepRegion[x-dIns3]*
(HeavisideTheta[x-dIns3]-HeavisideTheta[x-(dIns3+EndofDepletionWidth5)]))+

Sol1PotentialProfilesOutOfDepletionRegion[x]*
HeavisideTheta[x-(dIns3+EndofDepletionWidth5)];

"Extracted functions";

f10vac[x_]=VacuumPotentialinSemi2inDepletionRegionRight[x];

f11vac[x_]=Insulator3BandPotentialProfile[x];

f12vac[x_]=Sol1PotentialProfilesinDepRegion[x];

f13vac[x_]=Sol1PotentialProfilesOutOfDepletionRegion[x];

“Note: For materials in which conduction and valence bands are not calculated (i.e. insulators and solution) the conduction and valence band profile continuums go to the vacuum potentials through Heaviside functions for the respective materials. This is for aesthetic reasons as redundant zero value lines would be plotted otherwise.”

-----“

“Translations Along the X and Y Axes:”

-----“

“In order to produce continuity between potential curves, we must define translation values that coincide with interface distances and other points of interest (i.e. ends of depletion regions in the semiconductors and the solution).”

Clear[x1,x2,x3,x4,x5,x6,x7,x8,x9]

Clear[y1,y2,y3,y4,y5,y6,y7,y8]

“Translations Along the X-axis:

X-axis translations (x1, x2, x3, etc.) are fairly straight forward. These translations correspond to the stacked thicknesses of the insulators and depletion regions within the semiconductors in the solution.

It is important to note that since we have defined the depletion regions as zero for the potential curve derivatives, we will stitch curves at the ends of those depletion regions. In other words, we will eliminate using the original line functions that end with ‘...OutOfDepletionRegion’ and their corresponding f[x] definitions (defined for consistency) for simplicity.”

x1=0;

x2=x1+dIns1;

x3=x2+EndofDepletionWidth;

```

x4=x3-EndofDepletionWidth2;
x5=x4+dIns2;
x6=x5+EndofDepletionWidth3;
x7=x6+EndofDepletionWidth4;
x8=x7+dIns3;
x9=x8+EndofDepletionWidth5;

```

“Translations Along the Y-axis:

Similar to the x-axis translations, y-axis translations(y1, y2, y3, etc.) stack as we continue to splice more functions together. However, these translations correspond to relative changes from the start of the function and to its end. Physically, these changes correspond to the change potential over their respective distances (depletion widths and insulator thicknesses).

Since the y-axis translations are relative, we can choose an arbitrary set of potential profiles that are to be spliced so long as it describes the entire set of heterojunctions. As such, the vacuum potential functions are used and are consolidated below:”

```

f1vac[x_]=VacuumPotentialinMetal[x];
f2vac[x_]=Vacuumpotentialininsulator1[x];
f3vac[x_]=VacuumPotentialinDepletionRegion1[x];
f4vac[x_]=VacuumPotentialinSemiandOutOfDepletionRegion[x];
f5vac[x_]=VacuumPotentialinSemi1andOutOfDepletionRegion[x];
f6vac[x_]=VacuumPotentialinSemi1inDepletionRegionRight[x];
f7vac[x_]=Insulator2BandPotentialProfile[x];
f8vac[x_]=VacuumPotentialinSemi2inDepletionRegionLeft[x];
f9vac[x_]=VacuumPotentialinSemi2andOutOfDepletionRegion[x];
f10vac[x_]=VacuumPotentialinSemi2inDepletionRegionRight[x];
f11vac[x_]=Insulator3BandPotentialProfile[x];
f12vac[x_]=Sol1PotentialProfilesinDepRegion[x];
f13vac[x_]=Sol1PotentialProfilesOutOfDepletionRegion[x];
Clear[f4vac,f5vac,f9vac]

```

“Note that f4vac[x], f5vac[x], f9vac[x], and f13vac[x] are cleared (omitted) in regards to ‘...OutOfDepletionRegion’ function discussed above (Translations Along the X-axis section).”

```

f1vac[x_]=VacuumPotentialinMetal[x];
f2vac[x_]=Vacuumpotentialininsulator1[x];
f3vac[x_]=VacuumPotentialinDepletionRegion1[x];

f6vac[x_]=VacuumPotentialinSemi1inDepletionRegionRight[x];
f7vac[x_]=Insulator2BandPotentialProfile[x];
f8vac[x_]=VacuumPotentialinSemi2inDepletionRegionLeft[x];

f10vac[x_]=VacuumPotentialinSemi2inDepletionRegionRight[x];
f11vac[x_]=Insulator3BandPotentialProfile[x];
f12vac[x_]=Sol1PotentialProfilesinDepRegion[x];
y1=0;

```

```

y2=Re[y1-(f2vac[0]-f2vac[dIns1])];
y3=Re[y2+(f3vac[EndofDepletionWidth]-f3vac[0]).{1};
y4=Re[y3+(f6vac[0]-f6vac[EndofDepletionWidth2]).{1};
y5=Re[y4+(f7vac[dIns2])];
y6=Re[y5+(f8vac[EndofDepletionWidth3]-f8vac[0]).{1};
y7=Re[y6+(f10vac[EndofDepletionWidth4]-f10vac[0]).{1};
y8=Re[y7+(f11vac[dIns2])];

```

“Note: Each separate junction has built-in translations that are found within their root functions so the translations defined above will only be used as needed.”

```

fvb=f1vb[x]*(HeavisideTheta[-x]-HeavisideTheta[x-x1])+

f2vb[x]*(HeavisideTheta[x-x1]-HeavisideTheta[x-x2])+

f3vb[x-x2]*(HeavisideTheta[x-x2]-HeavisideTheta[x-x3])+

(f6vb[x-x4]+y3)*(HeavisideTheta[x-x3]-HeavisideTheta[x-x4])+

(f7vb[x-x4]+y3)*(HeavisideTheta[x-x4]-HeavisideTheta[x-x5])+

(f8vb[x-x5]+y3)*(HeavisideTheta[x-x5]-HeavisideTheta[x-x6])+

(f10vb[x-x7]+(f8vac[EndofDepletionWidth3
]+y3))*(HeavisideTheta[x-x6]-HeavisideTheta[x-x7])+

(f11vb[x-x7]+(f8vac[EndofDepletionWidth3
]+y3))*(HeavisideTheta[x-x7]-HeavisideTheta[x-x8])+

(f12vb[x-x8]-(f11vac[0]-f11vac[dIns3])(f8vac[EndofDepletionWidth3
]+y3))*(HeavisideTheta[x-x8]-HeavisideTheta[x-x9])+

(f13vb[x]-(f11vac[0]-f11vac[dIns3])+(f8vac[EndofDepletionWidth3
]+y3))*(HeavisideTheta[x-x9]);

fcb=f1cb[x]*(HeavisideTheta[-x]-HeavisideTheta[x-x1])+

f2cb[x]*(HeavisideTheta[x-x1]-HeavisideTheta[x-x2])+

f3cb[x-x2]*(HeavisideTheta[x-x2]-HeavisideTheta[x-x3])+

(f6cb[x-x4]+y3)*(HeavisideTheta[x-x3]-HeavisideTheta[x-x4])+

(f7cb[x-x4]+y3)*(HeavisideTheta[x-x4]-HeavisideTheta[x-x5])+

(f8cb[x-x5]+y3)*(HeavisideTheta[x-x5]-HeavisideTheta[x-x6])+

(f10cb[x-x7]+(f8vac[EndofDepletionWidth3
]+y3))*(HeavisideTheta[x-x6]-HeavisideTheta[x-x7])+

```



```

(f11cb[x-x7]+(f8vac[EndofDepletionWidth3
  ]+y3))*(HeavisideTheta[x-x7]-HeavisideTheta[x-x8])+

(f12cb[x-x8]-(f11vac[0]-f11vac[dIns3])+(f8vac[EndofDepletionWidth3
  ]+y3))*(HeavisideTheta[x-x8]-HeavisideTheta[x-x9])+

(f13cb[x]-(f11vac[0]-f11vac[dIns3])+(f8vac[EndofDepletionWidth3
  ]+y3))*(HeavisideTheta[x-x9]);

fvac=f1vac[x]*(HeavisideTheta[-x]-HeavisideTheta[x-x1])+

f2vac[x]*(HeavisideTheta[x-x1]-HeavisideTheta[x-x2])+

f3vac[x-x2]*(HeavisideTheta[x-x2]-HeavisideTheta[x-x3])+

(f6vac[x-x4]+y3)*(HeavisideTheta[x-x3]-HeavisideTheta[x-x4])+

(f7vac[x-x4]+y3)*(HeavisideTheta[x-x4]-HeavisideTheta[x-x5])+

(f8vac[x-x5]+y3)*(HeavisideTheta[x-x5]-HeavisideTheta[x-x6])+

(f10vac[x-x7]+(f8vac[EndofDepletionWidth3]+y3))*(HeavisideTheta[x-x6]-
HeavisideTheta[x-x7])+

(f11vac[x-x7]+(f8vac[EndofDepletionWidth3]+y3))*(HeavisideTheta[x-x7]-
HeavisideTheta[x-x8])+

(f12vac[x-x8]-(f11vac[0]-f11vac[dIns3])+

(f8vac[EndofDepletionWidth3]+y3))*(HeavisideTheta[x-x8]-HeavisideTheta[x-x9])+

(f13vac[x]-(f11vac[0]-
f11vac[dIns3])+(f8vac[EndofDepletionWidth3]+y3))*(HeavisideTheta[x-x9]);

Plot[{fcb,fcb,fvac},
{x,-100*10^-9,x9+100*10^-9},
PlotRange->{-10,3},
PlotStyle->{Blue,Red,{Black,Thickness[0.008]}},
GridLines->{{x1,x2,x4,x5,x7,x8},{}},
GridLinesStyle->Directive[Gray,Dashed],
AxesLabel->{"Distance from Metal/Semiconductor Interface","Band Diagram"},
BaseStyle->{FontWeight->"Bold",FontSize->15}]
Plot[{fcb,fcb,fvac},
{x,x1-100*10^-9,x1+500*10^-9},
PlotRange->{-10,4},

```

```

PlotStyle->{Blue,Red,{Black,Thickness[0.008]}},
GridLines->{{x1,x2,x4,x5,x7,x8},{}},
GridLinesStyle->Directive[Gray,Dashed],
AxesLabel->{"Distance from Metal/Semiconductor Interface","Band Diagram"},
BaseStyle->{FontWeight->"Bold",FontSize->15}]

```

```

Plot[{fvb,fcb,fvac},
{x,x4-100*10-9,x4+100*10-9},
PlotRange->{-10,4},
PlotStyle->{Blue,Red,{Black,Thickness[0.008]}},
GridLines->{{x1,x2,x4,x5,x7,x8},{}},
GridLinesStyle->Directive[Gray,Dashed],
AxesLabel->{"Distance from Metal/Semiconductor Interface","Band Diagram"},
BaseStyle->{FontWeight->"Bold",FontSize->15}]

```

```

Plot[{fvb,fcb,fvac},
{x,x7-100*10-9,x7+100*10-9},
PlotRange->{-10,4},
PlotStyle->{Blue,Red,{Black,Thickness[0.008]}},
GridLines->{{x1,x2,x4,x5,x7,x8},{}},
GridLinesStyle->Directive[Gray,Dashed],
AxesLabel->{"Distance from Metal/Semiconductor Interface","Band Diagram"},
BaseStyle->{FontWeight->"Bold",FontSize->15}]

```

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