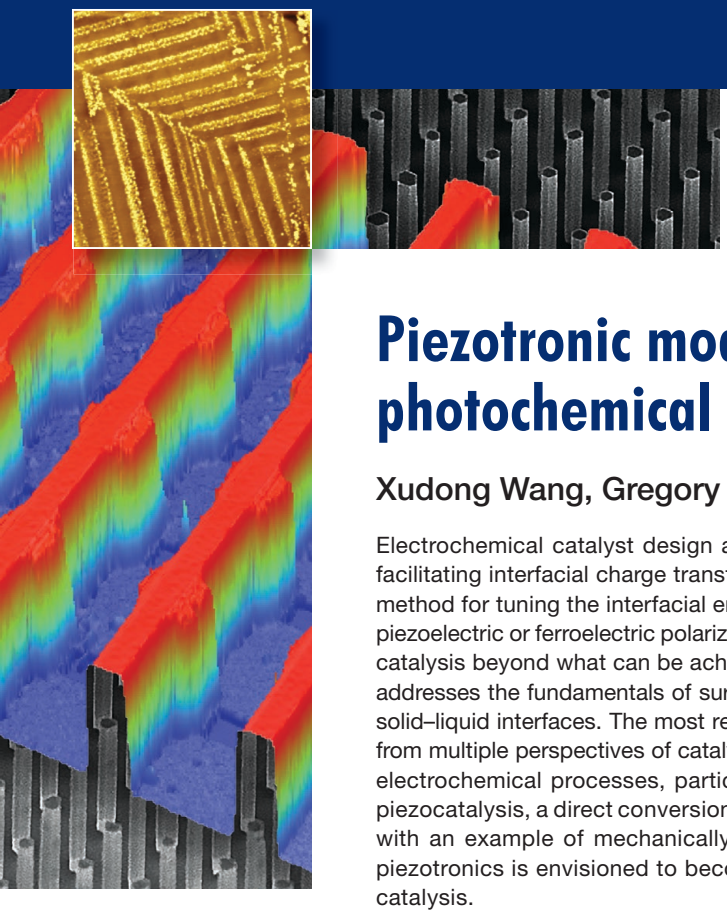


Piezotronic modulations in electro- and photochemical catalysis

Xudong Wang, Gregory S. Rohrer, and Hexing Li

Electrochemical catalyst design and optimization primarily relies on understanding and facilitating interfacial charge transfer. Recently, piezotronics have emerged as a promising method for tuning the interfacial energetics. The unique band-engineering capability using piezoelectric or ferroelectric polarization could lead to performance gains for electrochemical catalysis beyond what can be achieved by chemical or structural optimization. This article addresses the fundamentals of surface polarization and corresponding band modulation at solid–liquid interfaces. The most recent advances in piezotronic modulations are discussed from multiple perspectives of catalysis, including photocatalytic, photoelectrochemical, and electrochemical processes, particularly for energy-related applications. The concept of piezocatalysis, a direct conversion of mechanical energy to chemical energy, is introduced with an example of mechanically driven water splitting. While still in the early stages, piezotronics is envisioned to become a powerful tool for revolutionizing electrochemical catalysis.

Introduction

Research on advanced catalysts for electrochemical processes, particularly relevant to energy and the environment, is currently attracting increasing attention in various science and technology disciplines. Understanding and facilitating the charge-transfer kinetics at heterogeneous interfaces are the predominate strategy to advance electrochemical catalyst design and performance.

Piezotronics is an emerging concept to tune the charge separation and transport properties at heterojunctions.[1–3] The core of piezotronics lies in the coupling between electrical polarizations and the internal electric field formed at the heterojunction interfaces.[4–6] The unique band-tuning ability of the piezotronic effect provides a revolutionary paradigm to exceed the performance cap in many electrochemical systems.[7] As electrochemical catalysis is sensitive to the electronic band structure at the solid–liquid interface, introducing an additional polarization to that interface can help manipulate the interfacial energy landscape, and thereby modulate the catalytic performance. Such a unique coupling opens a promising application direction for piezotronics leading a new route toward ultimate performance gain of electrochemical catalysis.

Piezotronics modulation can be implemented by using strained piezoelectric materials or the permanent polarization of ferroelectric materials, both of which are generally treated as surface polarization in this article. The operational conditions of piezotronics are not restricted by other factors, such as with or without light or an external bias. All of these conditions are discussed here. In addition, the piezoelectric polarization can be directly used as an exclusive driving force to catalyze electrochemical reactions—this has been called piezocatalysis, a new concept in energy transformation and catalysis.[8]

Piezoelectric polarization—Influence on near-surface energetics

Charged oxide surfaces support subsurface space-charge layers that can enhance the separation of photogenerated carriers and thereby reduce recombination losses. Beyond the trivial solution of polarizing the oxides with an external bias, there are two mechanisms for creating charged oxide surfaces. The first is to alter the pH of the solution that is in contact with the oxide surface.[9,10] This uniformly changes the charge state on the surface, similar to an external bias, and can be used with samples of any form factor. The second mechanism is to select materials that naturally have charged domains on their surfaces because of their crystallography or microstructure.

There are three types of complex oxides that intrinsically have charged surface domains. The first type is comprised of

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doi:10.1557/mrs.2018.264

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crystals with noncentrosymmetric structures that exhibit polar behavior. This includes piezoelectric materials such as ZnO[11] and tourmaline (a boron silicate mineral),[12] and ferroelectrics such as $BiFeO_3$,[13] $BaTiO_3$ (BTO),[14] and lead zirconate titanate (PZT).[15] Polar materials have a fixed polarization throughout their volume that creates uncompensated charge at the surface. When a ferroelectric material is cooled below its Curie temperature, a rich microstructure of ferroelectric domains is created such that at the surface, regions with uncompensated positive and negative charge develop.

The second type of these materials is ferroelastics, which also have a domain structure, such as WO_3[16] and $BiVO_4$.[17] While these materials do not have polarity in the bulk, they exhibit polarity at the surface, likely from the flexoelectric effect. The third type of complex oxides that have charged surfaces are those whose crystal structures create charged surface terminations. For example, cubic perovskite-structured $SrTiO_3$ (STO) consists of alternating layers of Ti^{4+} and $(SrO_3)^{4-}$ along ⟨111⟩. A (111) surface will therefore have a positive or negative charge.

In practice, the surface is composed of domains of positive and negative charge separated by surface steps. When the surface is made of oppositely charged regions (from any of the previously mentioned sources), the subsurface band bending will differ in each region (**Figure 1**a), leading, for instance, to relatively photoanodic and photocathodic areas and selective electrochemical deposition (Figure 1b).[18] Of the three types of oxides previously discussed with charged surface domains, those that have charge arising from the termination layer are the most practical to control because they can be easily adjusted through chemical treatments.[19]

One important criterion for a photocatalyst used in aqueous solutions (e.g., water splitting) is long-term stability. The main strategy that has been used to protect surface charges on photocatalysts is to deposit a thin layer of TiO_2 on the surface. TiO_2 has excellent stability in aqueous solutions and preserves the charge at the interface between the oxide and titania overlayer. For example, pulsed laser deposition (PLD) deposited TiO_2 has been shown to stabilize the buried charge at interfaces with $BaTiO_3$,[20] $BiFeO_3$,[21] and $SrTiO_3$.[22] More importantly, sol-gel-deposited titania layers have been used to stabilize charge at buried interfaces with $BaTiO_3$[23] and $PbTiO_3$[24] particulate catalysts, illustrating a practical path to scalable production of such heterostructured catalysts.

Alteration of surface charge will directly impact the near-surface electron-energy landscape (e.g., barrier height and depletion width), which in turn influences the interfacial charge exchange behavior (i.e., electrochemical processes). Quantification of the interfacial electronic band diagram is therefore essential to conceive a clear picture of piezotronics modulations in electrochemical catalysis. The Poisson's equation is typically used for such quantification on the basis of equal interface potential and neutralized interfacial charges.[25] In an electrochemical system, the semiconductor–liquid interface plays the most significant role in performance control. In addition, insulating layers, such as a surface protection layer or a catalyst layer, are often involved, which can impose additional influences on the interfacial charge balance and electronic-band alignment. Therefore, quantification of piezotronic regulation necessitates considering the influences of the solution's pH, the isoelectric point (pH_{iso}, the pH at which there is a net zero charge on the surface) of the solution-facing material, the insulating layer's permittivity (ε_{ins}), and the surface charge induced by the semiconductor.

Figure 1c illustrates calculated electric potential profiles across a semiconductor/insulator/solution heterojunction and compares how the potential is influenced by other factors. The amount of charge accumulation (or depletion) in the semiconductor increases with an increase in the difference between pH and pH_{iso}, as well as with an increase in the value of ε_{ins}. While this calculation is based on piezoelectric ZnO, significant polarization tuning can be expected if the semiconductor is replaced by high-performance piezoelectric or ferroelectric materials, such as PZT. In most practical electrochemical systems, the piezoelectric surface charge could induce band bending on the order of tens to hundreds of meV, which may introduce significant electrochemical performance variation. Based on the electrochemical system used, and the physical limits of the materials used therein, one may exploit different pathways of manipulating these variables to optimize the device performance by implementing the piezotronic effect.

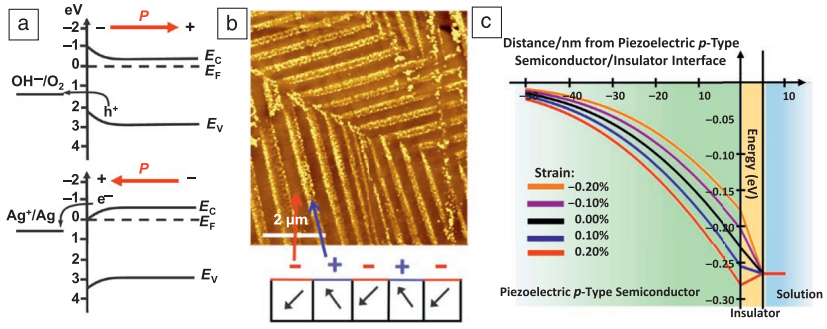


Figure 1. Surface polarization and the influence on interfacial band structure. (a) Schematic energy-level diagrams for $BaTiO_3$ in contact with a solution showing surface polarization-determined photochemical reactions (top: water oxidation; bottom: Ag^+ reduction). (b) Topographic atomic force micrographs of ferroelectric $BaTiO_3$ surfaces after the photochemical reduction of silver. The surface has photocathodic domains (bright contrast) that reduce Ag^+ from an aqueous solution and photoanodic domains (dark contrast) that do not. The rise of surface charges is illustrated by the schematic below the images.[18] (c) Calculated electrical potential profiles at a piezoelectric *p*-type semiconductor/insulator/solution heterojunction. The interfacial electronic band structure can be effectively tuned by straining a piezoelectric semiconductor.[25] Note: *p*, polarization; E_C, conduction band energy; E_F, Fermi energy; E_V, valence band energy.

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Effects of piezoelectric polarization on photochemical reaction rates

Two of the principal losses associated with photochemical reactions are the recombination of the photogenerated carriers and the back reactions of intermediate species. Charged surfaces can ameliorate both of these losses. First, the subsurface space charges below differently charged domains move electrons and holes in opposite directions so they are less likely to recombine. Second, the photocathodic and photoanodic half reactions take place on different surface domains and make the recombination of intermediate species less likely.

Evidence from experiments and simulations for the influence of charged surfaces on charge-carrier dynamics and photochemical reaction rates is abundant.[26–29] For example, it has been reported that the charge-carrier lifetime in $BaTiO_3$ in the ferroelectric state is 10^4 times larger than in the nonferroelectric state.[30] Simulations have shown that charge carriers are separated by charged surface domains, so that photogenerated carriers driven away from the surface in one domain can be collected at the surface of the neighboring domain and participate in surface reactivity rather than recombining.[31] Experiments comparing the photochemical reactivity of similar samples with and without charged surface domains have also concluded that the ferroelastic samples were more reactive.[32] Studies of $BaTiO_3$ powders with varying degrees of the tetragonal ferroelectric phase have shown that powders with more of the ferroelectric phase have the highest reactivity.[33] The surface-polarization-enhanced photocatalysts can be further improved by applying additional strain to the ferroelectrics. In a Ag_2O-$BaTiO_3$ hybrid photocatalyst, applying ultrasonic waves generated an alternating internal electric field, thereby facilitating the separation of photoinduced charges and providing a significant performance gain to the photocatalytic activity (**Figure 2**a).[34]

Such strain-based polarization is also often seen in piezoelectric materials, which can arbitrarily switch the direction and intensity of surface polarization and offer more flexible tuning capability. Wurtzite ZnO, owing to its appreciable piezoelectric response and photoactivity, has been studied intensively in this regard.[35] Taking into account the potential applications of photocatalysis in cleaning water and air, flow- or wind-driven piezo-promoted photochemical processes offer intriguing application opportunities for piezotronics in environmental engineering.

In a nanocomposite consisting of arrays of vertical ZnO nanorods on a three-dimensional (3D) Ni foam, piezoelectric polarization induced by deformation of the ZnO nanorods was used to separate photoelectrons and holes, promoting photocatalytic activity (Figure 2b).[36] This piezotronic effect raised the quantum efficiency of the ZnO nanorod–3D Ni foam structure more than 5×, where the enhancement was directly related to the velocity of the water flow in the testing system. Meanwhile, the 3D porous structure could further enhance the piezoelectric effect owing to some small water turbulence on the inner surface of the Ni foam. On the other hand, such a 3D structure is favorable for reactant diffusion and photocharge migration. This work showed that the piezotronic effect can be effectively integrated with other physical or chemical improvement strategies and optimize the performance of many practical photochemical processes.

Effects of piezoelectric polarization on photoelectrochemical performance

When the piezoelectric component is semiconducting, the piezotronic modulation can be further applied to the photoelectrochemical (PEC) process, where an external bias is involved to drive charge separation. In a typical PEC oxygen evolution reaction (OER) or hydrogen evolution reaction (HER), the piezoelectric polarization is able to expedite charge transfer and thus facilitate the catalyst performance. Since electrochemical catalysts are primarily insulators, the interfacial band structures showing the piezotronic influences can be closely represented by Figure 1c. ZnO is often examined as a model system of the piezotronic PEC effect, where the piezoelectric polarization is introduced by straining the electrode. As illustrated by a ZnO/$Ni(OH)_2$ OER system, enhanced photocurrent density (J_{ph}) was obtained under tensile strain, demonstrating enhanced OER activity, while a compressive strain led to a decreased J_{ph}.[37]

Higher interfacial charge density can be introduced by ferroelectric materials, and significant piezotronic modulation can be expected. Since ferroelectric polarization is a spontaneous effect, it does not require an external strain to activate the modulation, making it more applicable for PEC catalytic systems. While charge transfer is still the main concern in this system, the insulating ferroelectric material has to be made with a small thickness (<30 nm) to allow charge tunneling. In this regard, a semiconductor core–ferroelectric shell nanowire (NW) structure is particularly advantageous. As shown by a TiO_2/BTO core–shell NW-based photoanode, the PEC performance in 1 M NaOH solution under 1 Sun illumination was raised by 67% compared to pristine TiO_2 NWs, when the ferroelectric BTO thickness was only ~5 nm (Figure 2c).[38] The enhancement was attributed to the improved charge-separation efficiency enabled by the ferroelectric polarization. Thicker BTO shells yielded much lower J_{ph} due to the significant increase in film resistance, although higher polarization was introduced. A similar performance gain was also discovered for a ferroelectric poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) thin-film-coated Si photoanode. Under positive poling, the onset potential could be reduced by 80 mV as the ferroelectric dipoles were favorably aligned with the charge-transfer direction, which led to a 110% increase of the saturated J_{ph}.[39]

While the piezotronic modulation shows great promise to raise the material's PEC efficiency, most piezotronic PEC systems still offer relatively low overall efficiency. The key challenge lies in the long-standing contradiction between the dielectric nature of piezoelectric/ferroelectric materials and the high conductivity requirement of a PEC system. Using a

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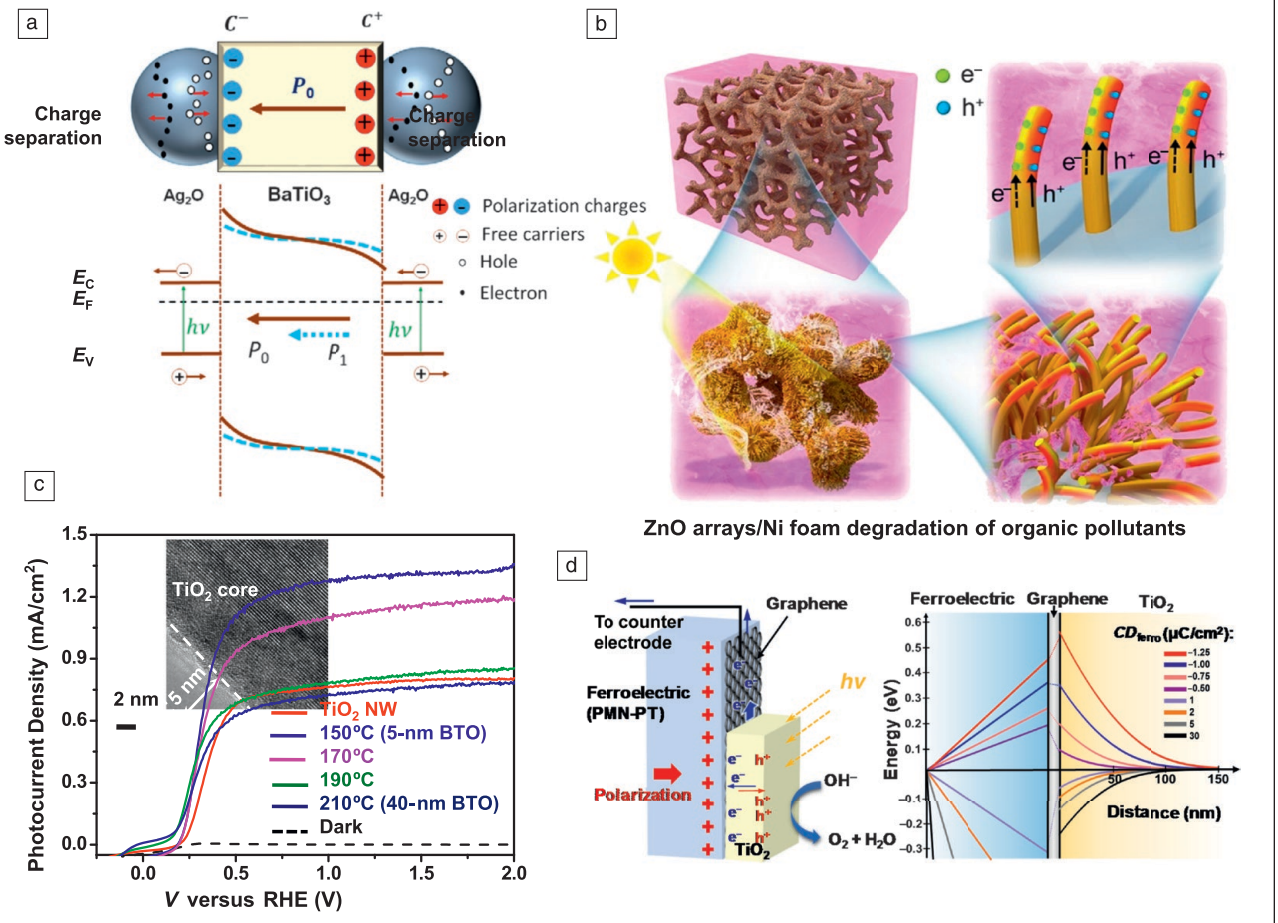


Figure 2. Piezotronics modulation on photoelectrochemical (PEC) processes. (a, upper) The separation of electrons and holes in Ag_2O nanoparticles attached to the two opposite surfaces of a $BaTiO_3$ (BTO) nanoparticle that have opposite polarization charges due to the piezoelectric effect and (lower) the corresponding tilting in the bands.[34] (b) Synergetic effects between the piezoelectric field and photocatalysis of ZnO nanorod arrays/Ni foam. Top left: ZnO nanorods on 3D Ni foam. Bottom left: This 3D structure is under light illumination. Bottom right: Turbulence and eddies created at the ZnO/Ni interface by stirring the solution, which deforms the ZnO nanorods and generates a piezoelectric field. Top right: The piezoelectric field promotes separation of photogenerated electrons and holes, leading to enhanced photocatalytic activity.[36] (c) Positive ferroelectric polarization in BTO can largely enhance the PEC performance of TiO_2 photoanodes. The plot shows the J_{ph}-V curves of TiO_2/BTO core–shell nanowire photoanodes. Inset is a high-resolution transmission electron microscope image showing the TiO_2/BTO interface.[38] (d) Graphene charge collector has negligible influence on the electronic energy level shifting in the TiO_2 photoanode. Left panel schematically shows the PMN-PT/graphene/TiO_2 heterojunction for the piezotronic PEC setup; right panel is the calculated interfacial electronic energy level when the graphene layer was assumed to have a charge density of 1–10 × 10^{12} cm^2 and the ferroelectric polarization was held constant at 15 μC/cm^2.[41] Note: NW, nanowire; P_0, initial polarization; P_1, polarization after Ag_2O attachment; E_C, conduction-band energy; E_V, valence-band energy; E_F, Fermi energy; h, Planck's constant; ν, frequency; C^-, negative surface charge ; C^+, positive surface charge; PMN-PT, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$; CD_{ferro}, ferroelectric charge density; V, voltage; RHE, reference hydrogen electrode.

more conductive component to support surface charges (e.g., STO) would alleviate the charge-transport problem and allow a thicker layer to be applied, thus higher interfacial polarization.[40] This strategy, however, does not fundamentally resolve the challenge where polarization and charge transport are still coupled. An ultimate solution is to completely circumvent the piezo-/ferroelectric material of charge transport.

A single layer of graphene was recently proposed as a dedicated charge collector in a ferroelectric PEC system (Figure 2d).[41] In this case, an insulating lead magnesium niobate-lead titanate (PMN-PT) slab with strong polarization was used only for interfacial band-structure tuning. The band-structure change could be well preserved after inserting a graphene layer due to its orders of magnitude lower charge density compared to the ferroelectric polarization. Therefore, the contradictory requirement of conductivity was decoupled, and significant enhancements of both J_{ph} and onset potential were obtained for PEC water splitting under one sun illumination.[41]

Electrochemical reaction enabled by piezoelectric polarization

Given the strong capability of inducing electronic-band shifting, piezoelectric polarization can provide the electrochemical

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driving force for the reaction through transformation of mechanical energy. This is known as piezocatalysis.[8]

The fundamental concern of a piezocatalytic process is to couple the piezoelectric potential to the force driving charges across the semiconductor/solution interface, where the accepting or donating of electrical charge from the solution occurs via chemical reactions at the interface. **Figure 3**a demonstrates a means by which piezoelectric potential is sufficient to create a favorable energetic landscape for generating faradic currents on opposite Au electrode surfaces, promoting both HER and OER in solution.[42] The appearance of a piezoelectric potential induced by mechanical deformation shifts the Fermi level and modifies the electron energy in the Au electrodes. 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. Such piezoelectric-potential-enabled 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.

In an experimental demonstration, a gold-coated PMN-PT cantilever was used as the piezoelectric component. H_2 gas evolution was measured as a function of time during mechanical oscillation of the cantilever in deionized water at given frequencies (Figure 3b). A linearized fit indicates that the rate of H_2 concentration increase was ~0.22 ppb/s at a 10 Hz oscillation rate, which was further raised to ~0.68 ppb/s at 20 Hz, demonstrating that more straining cycles could result in a higher hydrogen output per unit time. Quantitative analysis revealed that the majority of the piezoelectric potential was consumed by surface capacitive charge. Holding the polarization over one second was found to significantly enlarge the faradic currents and thus improve the piezocatalysis efficiency.

Similar piezocatalysis processes can also be expected from uncoated piezoelectric surfaces. Most piezoelectric materials are wide-bandgap semiconductors or insulators. This requires the valence/conduction bands of the piezoelectric to be higher/lower than the redox energy level of hydrogen/hydroxyl ions.[42] Without including electrodes, the piezocatalysis process can be more conveniently implemented under many different circumstances using nanomaterials. PZT nanoparticles were recently used to investigate the piezocatalysis process via the degradation of dye molecules rhodamine B.[43] The PZT nanoparticles were doped with a narrow bandgap semiconductor bismuth ferrite to introduce free charges. Mechanical strain was introduced by stirring the solution, and the strain-induced polarization drove internal free charges toward the surface to participate in the redox reactions (Figure 3c). Effective dye molecule degradation was observed within 150 min. This research confirmed a successful piezocatalysis process on exposed piezoelectric surfaces independent of the geometry. In addition, it was found that if only nonmobile polarization was evolved in a strained piezoelectric material, redox reactions may not be activated. Free charges in the piezoelectric material are crucial for piezocatalysis to occur, because it may largely reduce the activation energy to drive charge transfer at the interface.

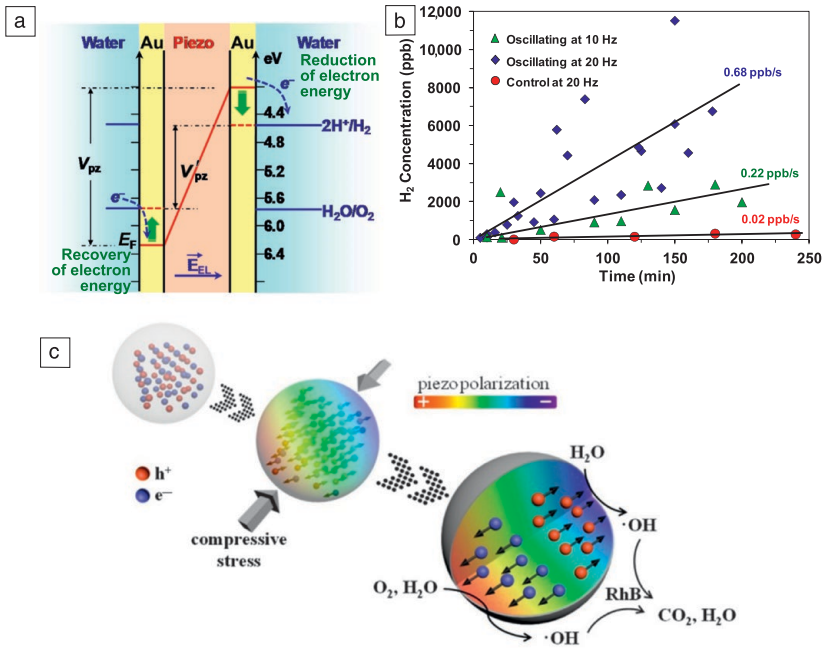


Figure 3. (a) Schematic energetic diagram for the occurrence of piezoelectric-potential-driven faradic currents at the piezoelectric/water interface. The piezoelectric potential shifts the electron energy level in the two Au electrodes toward different directions, and the resulting difference in electrochemical potentials between the electrode and the solution serves as the driving force for the redox reactions at Au surfaces.[8] (b) H_2 produced by straining a piezoelectric film in aqueous electrolyte. H_2 concentrations measured as a function of oscillating time of the piezoelectric cantilever in de-ionized water with a frequency of 10 Hz (triangles) and 20 Hz (diamonds). A Si cantilever with identical configuration was used as a control (circles).[8] (c) Schematic piezocatalysis processes at lead zirconate titanate (PZT) nanoparticle surface. Under compression, the piezoelectric material produces an internal electric field to separate free charges. The free charges activate the redox reaction on the surface of piezoelectric material and produce hydroxyl radicals. The hydroxyl radicals help with the decomposition of dye molecules into carbon dioxide and water. Note: V_{pz}, piezoelectric potential; V'_{pz}, minimal piezoelectric potential for piezocatalytic water splitting; E_{EL}, electric field; E_F, Fermi energy; RhB, rhodamine B dye molecule.[43]

Conclusion and perspectives

Piezotronics have shown an intriguing ability to manipulate the interfacial energetic landscape of solid/liquid junctions in electrochemical systems. This unique capability promises to surpass the limit of electrochemical catalysis imposed by material chemistry and

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provides a higher degree of freedom for designing an electrochemical system. At this point, piezotronics-modulated electrochemical catalysis is still in the early stages. To further extend the frontier of this promising research area, many challenges and opportunities still exist. These include well-controlled synthesis of piezoelectric/semiconductor heterostructures with well-engineered interfaces and properties; fundamental understanding of charge dynamics at the interface of piezoelectrics and electrolytes; and overarching knowledge of the piezotronic effect in general electrochemical reactions beyond water splitting. Deep understanding and novel design along these perspectives may eventually make piezotronics a powerful tool for revolutionizing electrochemical catalysis systems.

Acknowledgments

X.W. is grateful for the support of the National Science Foundation (NSF) under Award No. DMR-1709025. G.R. acknowledges support from the NSF under Grant No. DMR 1609369. X.L. acknowledges the support of the National Natural Science Foundation of China (21761142011) and Singapore National Research Foundation under Grant No. NRF2017NRF-NSFC001-007.

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