Forming Heterojunctions at the Nanoscale for Improved Photoelectrochemical Water Splitting by Semiconductor Materials: Case Studies on Hematite

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CONSPECTUS

In order for the future energy needs of humanity to be adequately and sustainably met, alternative energy techniques such as artificial photosynthesis need to be made more efficient and therefore commercially viable. On a grand scale, the energies coming to and leaving from the earth are balanced. With the fast increasing waste heat produced by human activities, the balance may be shifted to threaten the ecosystem in which we reside. To avoid such dire consequences, it is necessary to power human activities using energy derived from the incoming source, which is predominantly solar irradiation. Indeed, most life on the surface of the earth is supported, directly or indirectly, by photosynthesis that harvests solar energy and stores it in chemical bonds for redistribution. Being able to mimic the process and perform

it at high efficiencies using low-cost materials has significant implications. Such an understanding is a major intellectual driving force that motivates research by us and many others.

From a thermodynamic perspective, the key energy conversion step in natural photosynthesis happens in the light reactions, where H_2O splits to give O_2 and reactive protons. The capability of carrying out direct sunlight-driven water splitting with high efficiency is therefore fundamentally important. We are particularly interested in doing so using inorganic semiconductor materials because they offer the promise of durability and low cost. In this Account, we share our recent efforts in bringing semiconductor-based water splitting reactions closer to reality. More specifically, we focus on earth-abundant oxide semiconductors such as Fe_2O_3 and work on improving the performance of these materials as photoelectrodes for photoelectrochemical reactions.

Using hematite (α-Fe_2O_3) as an example, we examine how the main problems that limit the performance, namely, the short hole collection distance, poor light absorption near the band edge, and mismatch of the band edge energetics with those of water redox reactions, can in principle be addressed by adding nanoscale charge collectors, forming buried junctions, and including additional light absorbers. These results highlight the power of forming homo- or heterojunctions at the nanoscale, which permits us to engineer the band structures of semiconductors to the specific application of water splitting. The key enabling factor is our ability to synthesize materials with precise control over the dimensions, crystallinity, and, most importantly, the interface quality at the nanoscale. While being able to tailor specific properties on a simple, earth-abundant device is not straightforward, the approaches we report here take significant steps towards efficient artificial photosynthesis, an energy harvesting technique necessary for the well-being of humanity.
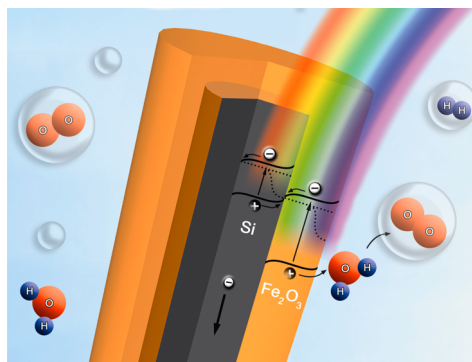
1. Introduction

Under standard conditions, the splitting of H_2O into H_2 and O_2 requires approximately 1.23 eV of energy per electron. More than 50% of photons in the solar spectrum are sufficiently energetic to power this reaction. To do so, one needs an absorber to harvest the energy carried by the photons and transform it into excited electrons. One also needs a mechanism to transfer the excited charges to sites where they can drive reduction and oxidation reactions, preferably at locations that are physically separated to minimize the annihilation of excited electrons. In natural photosynthesis, this process is carried out by the complex
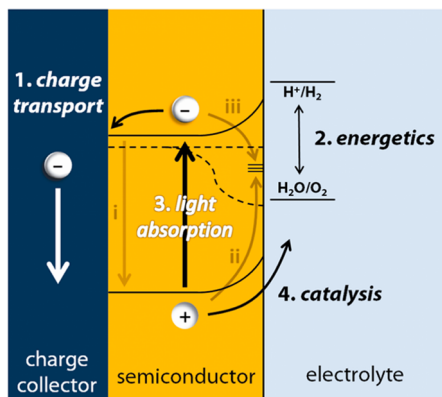
FIGURE 1. Semiconductor-based photoelectrochemical H_2O splitting on an n-type electrode. Important processes to consider include (1) charge transport, (2) the energetics relative to H_2O redox potentials, (3) light absorption (spectral response), and (4) catalytic activities. Competing detrimental processes include (i) bulk recombination and (ii, iii) surface trapping and recombination.

machinery of photosystems, which includes two absorbers, an intricate route of charge transfer to separate charges, and efficient catalysts for reduction and oxidation reactions at fast turnover rates.[1] In principle, all these functionalities, including light absorption, charge separation, and catalytic reactions, can be realized on a single semiconductor, as has been demonstrated in 1972 by Honda and Fujishima.[2] Schematically illustrated in Figure 1, a semiconductor absorbs light because it has a gap between its energy bands (the energy band gap). When in contact with an electrolyte, a Schottky-type diode is formed due to surface potential buildup, resulting in band bending near the surface that helps separate photogenerated charges.[3] Typically, the bending is such that minority charges are moved to the surface to perform oxidation (holes in n-type) or reduction (electrons in p-type) reactions. In addition to the relative simplicity as compared with natural photosystems, semiconductor-based water splitting also holds the potential of being durable and low-cost. For these reasons, photon-driven water splitting using semiconductors has attracted significant research attention in the past four decades.[4−6]

Depending on the design, semiconductors can be used in either *photocatalytic* (defined as particulate or colloidal suspension-based)[7] or *photoelectrochemical* (PEC; defined as discrete photoelectrodes connected by external circuit with spatially separated reduction and oxidation processes) systems.[3] Here we choose to concentrate on PEC systems because they permit us to examine the properties of the electrode materials in great detail. In other words, a PEC system may be viewed as a study tool for material characterization. It is, nonetheless, a tool that has potential for

practical water splitting applications. Presently, the main challenge faced by the community is the dilemma between efficiency and cost: materials that can deliver high efficiencies are either too expensive or too short-lived or both; those that are stable and inexpensive typically do not split water efficiently or cannot split water at all without externally applied potentials. Here one has two choices: focusing on efficient materials and trying to reduce the cost, or choosing low-cost materials and working on improving their efficiencies. With the foresight that water splitting will need to be carried out on an extremely large scale to rival that of natural photosynthesis, we elected to follow the second route and study inexpensive and stable semiconductors. The material candidates that stand out are metal oxides,[6,8,9] such as TiO_2, WO_3, and Fe_2O_3. Our goal is to identify problems presented by these materials and come up with solutions to these issues through band structure engineering and controlled syntheses.

Consider hematite (α-Fe_2O_3) as an example.[10−12] Its main advantages include its low cost, its stability against photocorrosion in aqueous solutions, and its suitable band gap for complete water splitting. Its absorption, for example, extends deep into the visible range ($\lambda_{max} \approx 610$ nm), which can potentially offer energy conversion efficiencies greater than 12%.[13] However, hematite is also a semiconductor with big problems. For instance, holes have been reported to diffuse just a few nanometers in hematite.[14] This means that most photogenerated holes cannot be collected unless the film is sufficiently thin (a few to tens of nanometers). But hematite this thin will only absorb a small portion of photons in regions of the solar spectrum where photons are most abundant (λ = 500−600 nm), whereas effective absorption would require films upward of 600 nm thick.[11] To make the problem more severe, water oxidation on the hematite surface requires holes with lifetimes on the order of milliseconds to seconds, far longer than most photogenerated holes can live in the material.[15] Additionally, the band edges of hematite are too positive to reduce water. Taken as a whole, hematite is a material with great promise but huge problems, which makes it an ideal model system to study for the purpose of testing material design and synthesis principles. For this reason, we choose to examine hematite in this Account, and our approaches to combating the variety of problems listed above are discussed herein.

2. Charge Transport Using Heteronanostructures

In general, the collection efficiency of photogenerated charge carriers is determined by the distance that carriers have to travel, their overall lifetime, and their bulk
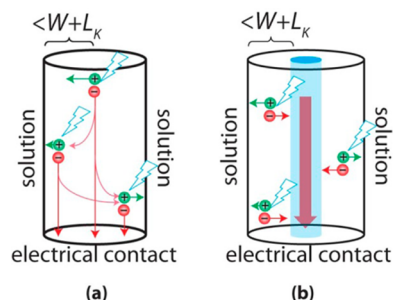
FIGURE 2. Charge collection and recombination mechanisms within nanostructures in a photoelectrochemical system. (a) To ensure effective hole collection, the smallest dimension of the nanostructure needs to be shorter than the sum of depletion width (W) and the diffusion distance of holes (L_K). Nevertheless, electron−hole recombination may still take place on the electron-transport pathway, which will result in reduced efficiencies. (b) When a dedicated charge transporter is added (shaded region in the center), the electron−hole recombination can be greatly reduced, enhancing the measurable efficiencies. Adapted with permission from ref 5. Copyright 2011 Elsevier.

FIGURE 3. TiSi$_2$ nanonet-based hematite nanostructure. (a) The structure is essentially a core/shell arrangement where the core is the nanonet for good charge collection and the shell is hematite for photocatalytic functionalities. (b) Low and (c) high magnification transmission electron micrographs showing the conformal coverage and crystallinity of hematite. Reprinted with permission from ref 19. Copyright 2011 American Chemical Society.

recombination rate. Because hematite's absorption depths are large within the visible range, a short collection distance, long lifetime, and low recombination rate favor charge collection. Among these considerations, the lifetime and the recombination rate are determined by the electronic structure of the semiconductor and are difficult to manipulate. However, the distance the carriers have to travel, being defined by the depth at which light absorption takes place, can be minimized by modifying the morphologies of the semiconductor through synthesis control aimed at decoupling the directions of light absorption and charge collection. This realization has led to the proposal of using nanostructures such as nanowires to improve charge collection efficiencies.[16] It is important to keep the characteristic dimensions within the nanoscale because charge diffusion distances typically fall within this range. As far as hematite is concerned, the best-known example is found in Grätzel et al.'s success in using nanoscale "cauliflower"-shaped hematite to measure record-high photocurrents in PEC water splitting systems.[17] In their demonstration, the light absorption by hematite is ensured by having a nanostructured film over a few hundred nanometers thick. The distance the photogenerated holes need to diffuse, by contrast, is only a few nanometers, enabling high collection efficiencies of the minority carriers. At 1.23 V vs the reversible hydrogen electrode (RHE), 2.3 mA/cm^2 photocurrent was measured when no catalyst was used, which is still the benchmark of hematite performance as of today.[18]

The strategy of using simple nanostructures faces inherent limitations, however. The limit comes from the fact that one still relies on a single material to carry out the functions
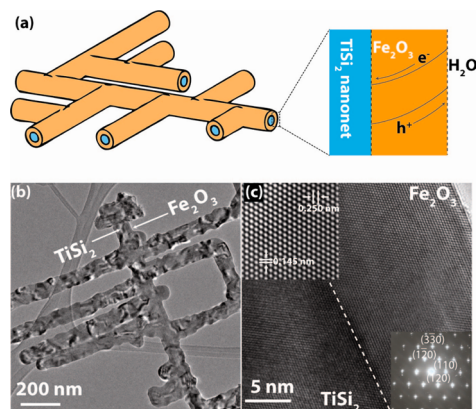
of both light absorption and charge transport. As shown in Figure 2a, along their path to be collected by an electrical contact, the majority charges (electrons in the case of n-type hematite) may still recombine with holes to reduce the achievable efficiencies. To mitigate this problem, we proposed and tested the idea of forming heterojunctions, combinations of two material components with different properties. In a simplistic form, a heterojunction design can be a core/shell structure (Figure 2b), with the core being a dedicated charge transporter while the shell absorbs light and separates charges. Such a design should enable us to address challenges associated with poor charge collection, which are common among metal oxide semiconductors due to their relatively low conductivity and short minority charge diffusion distance.[8] From a practical standpoint, the core material is desired to be of high conductivity, high surface area, and low light absorption.

Our first proof-of-concept demonstration was carried out on the unique platform of TiSi$_2$ nanonets, as shown in Figure 3.[19] A nanonet differs from the more widely studied nanowire in its two-dimensional connectivity as depicted in Figure 3a and b. The connectivity offers better charge transport and increased surface area. We typically produced the nanonets by chemical vapor deposition (CVD) reactions,[20−22] and the nanonets spontaneously grew into vertically packed arrangements with one end connected to the charge collecting substrate (e.g., a metal foil). Next, we deposited a thin layer of hematite on the surface of the nanonets. To realize the design as shown in Figure 2b, we desired a conformal coating that could cover the nanonet core completely. We also wanted the interface between the nanonet
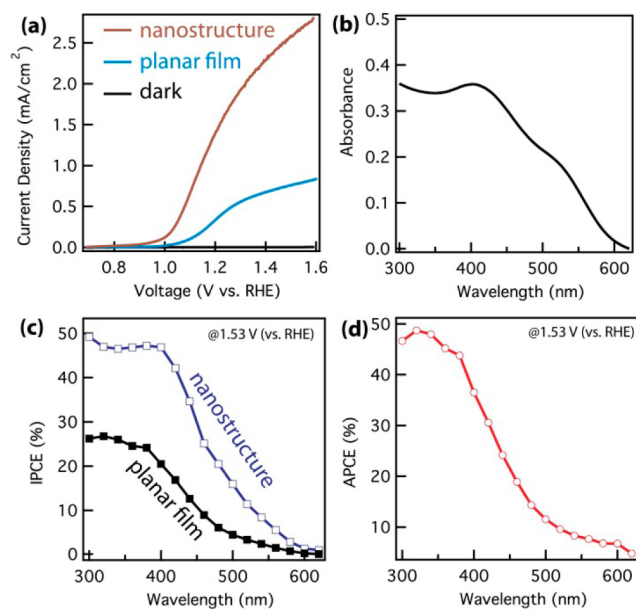
FIGURE 4. PEC characteristics of Fe_2O_3/$TiSi_2$-nanonet heteronanostructures in water splitting reactions. (a) A stark contrast in the measured photocurrents is seen between planar hematite (0.5 mA/cm^2 at 1.23 V vs RHE) and that on $TiSi_2$ nanonets (1.6 mA/cm^2 at 1.23 vs RHE). (b) The absorption spectrum of the nanostructure. (c) IPCE comparison of the planar and nanonet-based hematite. (d) The measured absorbed photon to charge conversion efficiency matches the IPCE of the nanonet-based hematite, suggesting the inclusion of the nanonet maximizes the performance of hematite. Reprinted with permission from ref 19. Copyright 2011 American Chemical Society.

and hematite to be of low density of trap states ($<10^{12}$ cm^{-2}), which would otherwise act to trap charges and invalidate the benefits expected from the design. Among various available oxide growth methods, atomic layer deposition (ALD) caught our attention as it promised the characteristics we were looking for.

To our delight, a high-quality heteronanostructure consisting of a two-dimensional nanonet as the core and a thin, crystalline hematite film as the shell was indeed created by the simple synthesis (Figure 3b). As evident from the high-resolution transmission electron micrograph (TEM) shown in Figure 3c, the interface between Fe_2O_3 and $TiSi_2$ was uniform and free of major defects. Work function considerations predict ohmic contact between n-type Fe_2O_3 and metallic $TiSi_2$, and electrochemical impedance spectroscopy and photocurrent−voltage data confirmed that the heterojunction produced no significant interfacial barrier or series resistance increase. The PEC performance of this heteronanostructure and its planar counterpart are compared in Figure 4. The optimum thickness of Fe_2O_3 was identified as 25 nm, consistent with the depletion depth predicted for Fe_2O_3 in water,[11] but thicker than that which is expected to

produce quantum confinement effects.[23] By introducing the $TiSi_2$ nanonet array as a dedicated charge transporter, the photocurrent increased from 0.78 to 2.7 mA/cm^2 at 1.53 V vs RHE, representing a 200% improvement. The improved performance of charge collection was also verified by incident photon to charge conversion efficiency (IPCE) measurements. The most pronounced improvement of IPCE for the heteronanostructure was achieved in the long wavelength range, where the penetration depth in Fe_2O_3 is large and the absorption is typically poor.

Because the idea of a heteronanostructure design is to combine multiple components in one electrode material, the approach is highly versatile and should allow tuning of the properties of each component individually. We further demonstrated this understanding by substituting vertically aligned aluminum-doped zinc oxide (AZO) nanotube arrays as the charge transport component.[24] AZO is a low-cost and promising transparent conductive oxide which has little absorption competition with Fe_2O_3. The Fe_2O_3−AZO nanotube arrays indeed greatly improved the solar water splitting performance compared with Fe_2O_3 on planar AZO substrate. Despite the challenge of low conductivity exhibited by AZO after thermal annealing, the IPCE of Fe_2O_3 on nanotubes was higher than on nanonets, specifically in the long wavelength region close to the Fe_2O_3 band edge ($\lambda = 500-590$ nm). The difference could be attributed to the transparent nature of AZO or the vertical arrangement of the structure to enhance light trapping or both.

The strategy of using a conductive structure to assume the role of long-range charge transporter should be widely applicable for use with other PEC-active materials. The criteria for selecting a suitable transport material should include, ideally, an electronic structure which allows lossless interfacial charge transport, a light absorption profile which does not compete with that of the active material, and an earth-abundant and nontoxic composition.

3. Additional Photovoltage from Buried n−p Junctions

A central challenge of water splitting by semiconductor PEC means is to generate sufficient photovoltage to drive the reactions without requiring an external power source. This is because the electrolysis of water requires a sizable voltage. In addition to the 1.23 V minimum thermodynamic requirement, one has to factor in the difference between free energy and internal energy, as well as overpotentials due to concentration and kinetic considerations, leading to practical requirements of 1.6−2.4 V in real devices.[3,13]
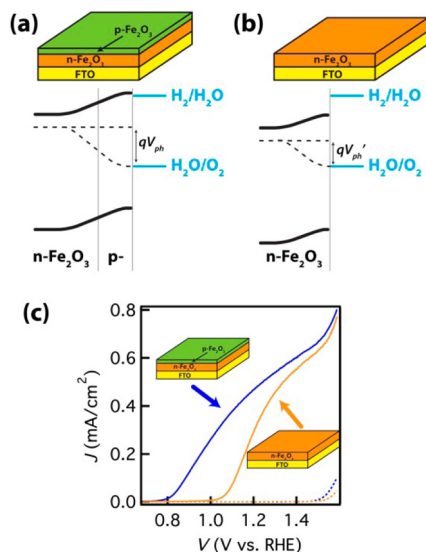
FIGURE 5. Improved water splitting by buried n−p junctions within hematite thin films. The existence of a thin (∼5 nm) p-type layer through Mg-doping helps create additional photovoltage (a) that is greater than hematite without such layer (b). The effect is observed in the significantly reduced turn-on voltages in the PEC plots (c). Reprinted with permission from ref 26. Copyright 2012 American Chemical Society.

In laboratory demonstrations, the requirement is rarely met by photoelectrodes alone. Instead, additional power from an external source (e.g., a photovoltaic module or battery) is employed to enable complete water splitting. So-called *unassisted* water splitting, meaning one without any external bias, remains elusive other than examples where the efficiencies are impractically low or the cost of materials or fabrication is prohibitively high. The goal is made difficult by the intricate balance between band gap energies, light absorption characteristics, and band edge positions.

To understand the challenge, let us again consider hematite as a model system. Its band gap of 2.0−2.2 eV should in principle enable complete water splitting because its ideal maximum achievable photovoltage exceeds the minimum requirement of 1.6 V. In practice, however, the experimental photovoltages attained on hematite devices have failed to exceed about 0.4 V.[18] Additionally, the band edge positions relative to water redox potentials are also critically important. Since the conduction band edge of hematite is too positive to reduce water (Figure 5b), hematite-based water splitting often requires a significant applied potential, which is not ideal. The capability to reduce the demand for applied potential is important, which would signify a higher overall energy conversion efficiency and move closer to the goal of unassisted water splitting.

With this understanding in mind, we proposed to change the band edge positions by forming a buried n−p junction. The idea was to use the photovoltage produced in situ to augment water splitting, thereby decreasing the reliance on externally applied bias. In other words, we sought to create a homojunction that drives charge separation and produces a photovoltage. If the photovoltage from this solid−solid n−p junction is larger than that from the original solid−liquid junction (on n-type hematite), additional voltage goes toward reducing the external bias needed to drive water splitting. Such a junction could also act to suppress recombination near the surface, a process believed to be significant in limiting hematite's efficiency.[25] To this end, we took advantage of the synthetic control offered by ALD and introduced small amounts of Mg as a dopant to generate films of p-type hematite. By depositing a thin p-type layer over undoped hematite (intrinsically n-type due to oxygen vacancies), an n−p homojunction device was formed, as illustrated in Figure 5.[26] The photocurrent onset potential for n−p Fe_2O_3 at 0.8 V vs RHE was one of the lowest values for hematite synthesized by vapor phase chemistries,[27] and the improvement was comparable to what has been achieved by using surface catalyst treatments[18] but through a fundamentally different mechanism.

Various control experiments were performed to verify that the observed effect was a result of the formation of an n−p junction rather than effects such as surface passivation, catalysis, or simply a variation of hematite film thickness. Our studies confirmed the formation of n−p Fe_2O_3 and its function in improving water oxidation performance. It is worth noting that exposing a p-type layer to an oxidation reaction is an unorthodox approach; rather, p-type materials are more conventionally used for reduction reactions. This was precisely why we had to keep the p-type layer thin. A thicker p-coating, or placing the p-layer between n-type hematite and the charge collector, resulted in potential wells in the electronic structure, and hence, worse performance resulted, as evidenced by a diminished or abolished photovoltage.[26] Therefore, the construction of an n−p homojunction photoelectrode requires great synthetic control, here enabled by the ALD technique. The concept is analogous to that demonstrated recently by Lewis et al., for PEC hydrogen evolution on p−n^+ Si microwire arrays.[28] The achievement of a built-in junction within a single metal oxide semiconductor material was, to the best of our knowledge, a novel demonstration, signifying a promising new direction for enhancing the PEC performance of earth-abundant materials.
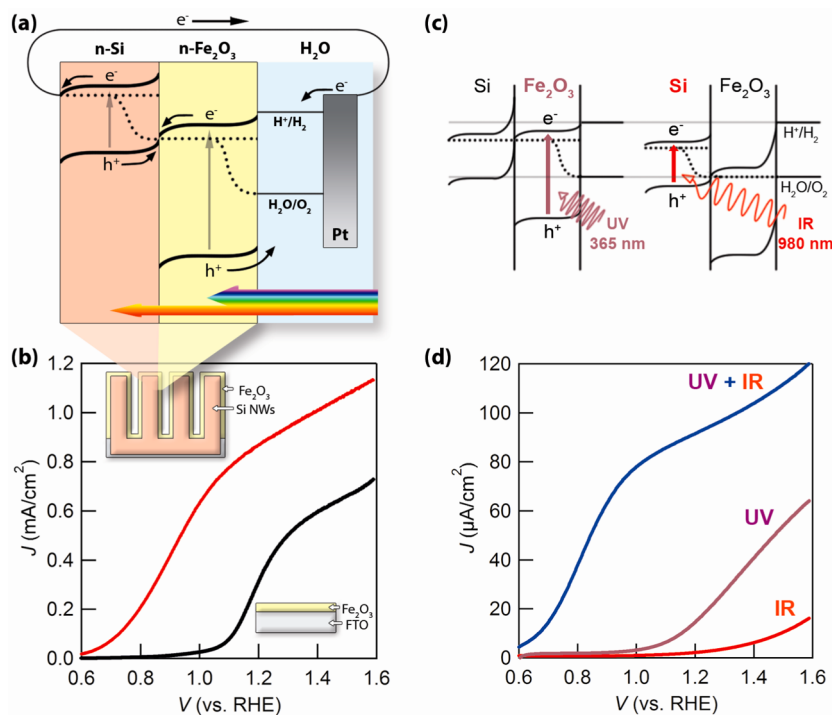
FIGURE 6. Heterojunctions of Si and hematite. (a) Hematite absorbs in the UV and visible region up to yellow ($\lambda < 600$ nm); Si absorbs what passes through hematite up to $\lambda \sim 1100$ nm and uses the energy to produce an additional photovoltage for improved water splitting. (b) A significant cathodic shift of 400 mV is measured when the Si nanowires are present. (c) Under monochromatic illumination, Fe_2O_3 and Si can be excited individually or simultaneously, and the resulting $J-V$ responses (d) prove the synergistic dual-absorber mechanism. Adapted with permission from ref 30. Copyright 2012 American Chemical Society.

4. Enhanced Light Absorption by Adding Absorbers

While the creation of an n−p homojunction serves the purpose of producing additional photovoltage, it relies on light absorption within the same region ($\lambda \leq 610$ nm). It would be even better if the additional voltage was produced by an absorber that does not compete with hematite in light absorption. That is, we need a semiconductor that is capable of absorbing in the red and near-infrared region ($\lambda > 610$ nm) and transforming the harvested energy into additional photovoltage to assist hematite-based water splitting. This idea coincides with the better-known "Z-scheme" in natural photosystems and is similar to Turner's demonstration of tandem junctions over a decade ago.[29] The key value added by our approach was the ability to realize such a design on oxide semiconductors, whose synthesis was much less studied than those of molecular systems or III−V photovoltaic materials.

To follow our pursuit of studying earth-abundant and nontoxic materials, we chose to prove the concept on Si.[30] The nanowire form of Si was chosen for its ease of preparation and its increased surface area that are believed to enable better charge collection, as discussed in section 2.

With a band gap of 1.1 eV and a conduction band edge around 700 mV more negative than that of hematite, Si should be capable of absorbing lower-energy solar photons (λ up to $\sim$1100 nm) which pass through hematite, using them to promote electrons to greater potentials than can be achieved within hematite itself. The ALD technique allowed conformal deposition to completely cover the Si nanowires. Such coverage is extremely important because otherwise the exposed Si would be susceptible to photocorrosion. The resulting PEC performance, as shown in Figure 6, was greatly enhanced as compared to standard devices of planar hematite. The improvement from the nanostructured surface was evidenced by the increase in the plateau photocurrent, benefiting from a combination of improved light absorption, better charge separation, and overall higher solid−liquid junction area. More significantly, the Si/Fe_2O_3 heterojunction device produced a considerably enhanced photovoltage, as seen from the low onset potential of $\sim$0.6 V vs RHE, representing a cathodic shift of approximately 400 mV resulting from the utilization of low-energy photons by the Si (Figure 6c,d). It is important to note that this was achieved without the use of hematite doping or oxygen-evolution catalysts.

The key result produced by this heterostructure (and also by the n−p homojunction) was the attainment of greater photovoltages without the use of a large-band-gap semiconductor. Furthermore, this approach made better use of the total solar spectrum by utilizing the large number of photons with energies too small to excite hematite. For the purpose of harvesting lower energy photons, an alternative approach is to use upconversion (UC) materials such as rare-earth nanoparticles. The UC nanoparticles function through an anti-Stokes shift mechanism, absorbing in the IR region and emitting in the visible range. We recently demonstrated that the re-emission could indeed be harvested by hematite for water splitting using IR light, a process which otherwise would not be possible from a thermodynamic perspective.[31] The main challenge here is the low efficiencies of the UC processes; nevertheless, it demonstrates another tactic to broadening the PEC response of materials like hematite.

5. Catalysis for Water Splitting

Another critical challenge presented by hematite when used for water splitting is the slow kinetics of hole transfer to the solution, requiring lifetimes on the order of milliseconds to seconds. Durrant et al. recently argued that the requirement is an important reason why high applied potentials are needed for hematite-based water splitting.[32] In principle, the kinetics can be improved by application of catalysts that better facilitate the complex four-electron process of water oxidation, with an ideal catalyst predicted to allow photocurrent onsets as low as 0.6 V vs RHE.[33] Recent examples of catalysts on hematite include IrO_2[18] and Co-Pi.[34,35] To this end, our effort in studying hematite/catalyst interfaces has just begun. For the completeness of discussions, here we resort to our recent study on a similar metal oxide system, WO_3, to present our insights.

The effort was guided by similar principles as outlined above, which is to use earth-abundant materials and preparation methods that permit the creation of thin and conformal coatings. The catalyst system that caught our attention was a derivative of the Brudvig−Crabtree catalyst, which is essentially a precipitate of the Mn-oxo monomers, because its preparation conditions are compatible with that of WO_3 photoelectrodes.[36] When deposited on the surface of WO_3 to form a 2 nm thick coating, the catalyst was shown to stabilize WO_3 against dissolving near pH 7.[37] The catalyst did so by physically separating WO_3 from H_2O. Important to our purpose, the hole transfer to H_2O for O_2 evolution was not compromised. Instead, a measurable improvement was observed, strongly suggesting that the catalyst had

fundamentally changed the O_2 evolution mechanism on the surface of WO_3.

6. Conclusions and Future Directions

When presented with an abundant form of energy, solar light, and a readily available chemical, H_2O, nature devised an ingenious reaction route of photosynthesis to harvest that energy for easy storage and redistribution. There is a great deal to learn from natural photosynthesis in order for us to develop methods to efficiently harvest and utilize solar energy. Despite apparent differences in various existing approaches, including molecular-based reactions, PEC methods, and slurry-based photocatalysis, the need for good light absorber, effective charge separator, and efficient catalyst is shared. As such, the main challenge can be regarded as a materials one. Because in semiconductor-based PEC reactions the photoelectrode is expected to perform all three functions of absorbing light, separating charge, and catalyzing specific chemical reactions simultaneously, we regard the PEC system as an ideal platform where the various concepts regarding different aspects of photosynthesis can be tested on a single material.

Within this context, we presented in this Account our attempts to improve the performance of hematite-based PEC devices. The main idea we have tested is to use additional material components to complement hematite's properties. When good charge collection is desired, a highly conductive $TiSi_2$ nanonet proves effective; when additional photovoltages are required, homo- or heterojunctions can help achieve the goal. Additions of material components also enable the absorption of photons whose energies are not sufficient to split water when used alone. It is important to realize, however, that even when efficient water splitting by stable and low-cost materials such as hematite becomes possible, we would have only solved the first step of the problem. The storage, transportation, and utilization of H_2 remain outstanding scientific and technological challenges. Why can we not learn from nature and use the harvested solar energy to produce other chemicals? This appears to be a logical next step to pursue.

There have indeed been significant efforts devoted toward similar goals. For instance, a large number of reports on attempts to reduce CO_2 to fuels exist.[38−40] The key challenge in doing so is the poor selectivity due to the richness of C oxidation states, the relatively high energetic barriers between different forms of hydrocarbon products, and the competitive side reaction of hydrogen formation. As a result, the controls over what one produces remain poor.
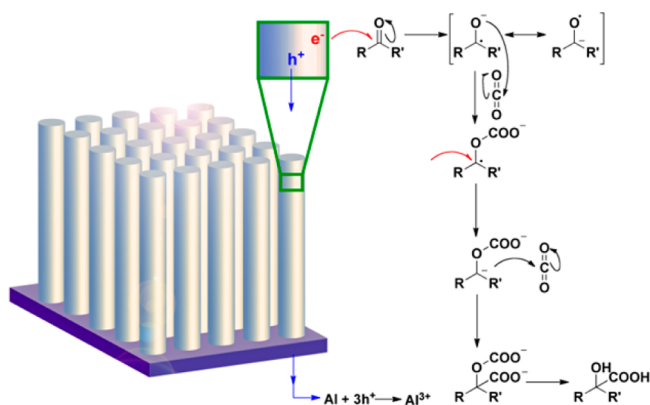
FIGURE 7. The reaction mechanism of Si nanowire-based CO_2 photo-fixation. Red arrows represent electron transfer from Si nanowires to organic substrates. Adapted with permission from ref 41. Copyright 2012 John Wiley & Sons.

To understand why the reactions in natural photosynthesis are so specific, we examined the mechanistic steps of the dark reactions and found that nature bypasses the challenge outlined above by avoiding directly reducing CO_2. Instead, the reaction proceeds through the creation of reactive intermediates (e.g., ribulose-1,5-bis-phosphate, or RuBP) that bind with CO_2 in a highly specific fashion. Inspired by this finding, we recently demonstrated that highly specific CO_2 fixation reactions could indeed be readily carried out.[41] To do so, we used p-type Si nanowires as a photocathode, which harvested photons and produced excited electrons. As shown in Figure 7, the electrons were then transferred to aromatic ketones (e.g., benzophenone) to produce a reactive radical; the radical subsequently bound with CO_2. After another electron transfer and followed by a fragmentation, α-hydroxy acid was produced, which could serve as precursors to nonsteroidal anti-inflammatory drugs (NSAID) such as ibuprofen and naproxen.

The result was enabled by another line of research on the photoelectrochemical properties of Si nanowires that was not discussed in this Account.[42,43] Consistently high yields and up to 98% selectivities were obtained for the substrates studied. To broaden the scope of the reactions, we envision that other species such as catalysts of various natures can be introduced to replace aromatic ketones as the electron receiver. In a way, these intermediates act as a temporary energy storage unit, much like ATP in natural photosynthesis. Our strategy may open doors to a wide range of light-powered chemical reactions that mimic photosynthesis but have not been studied to date.

BIOGRAPHICAL INFORMATION

Matthew T. Mayer grew up in Alaska, received a B.S. in Chemistry from Boise State University (2008), and is a Ph.D. candidate in Chemistry at Boston College. His research focuses on the synthesis and applications of earth-abundant semiconductor materials with photovoltaic and photoelectrochemical applications.

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FOOTNOTES

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The authors declare no competing financial interest.

REFERENCES

1 Barber, J. Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.* **2009**, *38*, 185–196.

2 Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.

3 Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar water splitting cells. *Chem. Rev.* **2010**, *110*, 6446–6473.

4 Nocera, D. G. The Artificial Leaf. *Acc. Chem. Res.* **2012**, *45*, 767–776.

5 Lin, Y.; Yuan, G.; Liu, R.; Zhou, S.; Sheehan, S. W.; Wang, D. Semiconductor nanostructure-based photoelectrochemical water splitting: A brief review. *Chem. Phys. Lett.* **2011**, *507*, 209–215.

6 Youngblood, W. J.; Lee, S. H. A.; Maeda, K.; Mallouk, T. E. Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors. *Acc. Chem. Res.* **2009**, *42*, 1966–1973.

7 Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.

8 Valdes, A.; Brillet, J.; Grätzel, M.; Gudmundsdottir, H.; Hansen, H. A.; Jonsson, H.; Klupfel, P.; Kroes, G. J.; Le Formal, F.; Man, I. C.; Martins, R. S.; Norskov, J. K.; Rossmeisl, J.; Sivula, K.; Vojvodic, A.; Zach, M. Solar hydrogen production with semiconductor metal oxides: new directions in experiment and theory. *Phys. Chem. Chem. Phys.* **2012**, *14*, 49–70.

9 Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-based Photocatalytic Hydrogen Generation. *Chem. Rev.* **2010**, *110*, 6503–6570.

10 Sivula, K.; Le Formal, F.; Grätzel, M. Solar water splitting: progress using hematite (α-Fe_2O_3) photoelectrodes. *ChemSusChem* **2011**, *4*, 432–449.

11 Katz, M. J.; Riha, S. C.; Jeong, N. C.; Martinson, A. B. F.; Farha, O. K.; Hupp, J. T. Toward solar fuels: Water splitting with sunlight and "rust"? *Coord. Chem. Rev.* **2012**, *256*, 2521–2529.

12 Hamann, T. W. Splitting water with rust: hematite photoelectrochemistry. *Dalton Trans.* **2012**, *41*, 7830–7834.

13 Hanna, M. C.; Nozik, A. J. Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. *J. Appl. Phys.* **2006**, *100*, 074510–074518.

14 Kennedy, J. H.; Frese, K. W. Photooxidation of Water at α-Fe$_2$O$_3$ Electrodes. *J. Electrochem. Soc.* **1978**, *125*, 709–714.

15 Pendlebury, S. R.; Cowan, A. J.; Barroso, M.; Sivula, K.; Ye, J.; Grätzel, M.; Klug, D. R.; Tang, J.; Durrant, J. R. Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes. *Energy Environ. Sci.* **2012**, *5*, 6304–6312.

16 Kayes, B. M.; Atwater, H. A.; Lewis, N. S. Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells. *J. Appl. Phys.* **2005**, *97*, 114302–114311.

17 Kay, A.; Cesar, I.; Grätzel, M. New benchmark for water photooxidation by nanostructured alpha-Fe$_2$O$_3$ films. *J. Am. Chem. Soc.* **2006**, *128*, 15714–15721.

18 Tilley, S. D.; Cornuz, M.; Sivula, K.; Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chem., Int. Ed.* **2010**, *49*, 6405–6408.

19 Lin, Y.; Zhou, S.; Sheehan, S. W.; Wang, D. Nanonet-based hematite heteronanostructures for efficient solar water splitting. *J. Am. Chem. Soc.* **2011**, *133*, 2398–2401.

20 Zhou, S.; Liu, X.; Lin, Y.; Wang, D. Spontaneous Growth of Highly Conductive Two-Dimensional Single-Crystalline TiSi$_2$ Nanonets. *Angew. Chem., Int. Ed.* **2008**, *47*, 7681–7684.

21 Zhou, S.; Liu, X.; Lin, Y.; Wang, D. Rational Synthesis and Structural Characterizations of Complex TiSi$_2$ Nanostructures. *Chem. Mater.* **2009**, *21*, 1023–1027.

22 Zhou, S.; Xie, J.; Wang, D. Understanding the Growth Mechanism of Titanium Disilicide Nanonets. *ACS Nano* **2011**, *5*, 4205–4210.

23 Beermann, N.; Vayssieres, L.; Lindquist, S. E.; Hagfeldt, A. Photoelectrochemical studies of oriented nanorod thin films of hematite. *J. Electrochem. Soc.* **2000**, *147*, 2456–2461.

24 Lin, Y.; Yuan, G.; Sheehan, S.; Zhou, S.; Wang, D. Hematite-based solar water splitting: challenges and opportunities. *Energy Environ. Sci* **2011**, *4*, 4862–4869.

25 Cowan, A. J.; Durrant, J. R. Long-lived charge separated states in nanostructured semiconductor photoelectrodes for the production of solar fuels. *Chem. Soc. Rev.* **2013**, DOI: 10.1039/c2cs35350a.

26 Lin, Y.; Xu, Y.; Mayer, M. T.; Simpson, Z. I.; McMahon, G.; Zhou, S.; Wang, D. Growth of p-type hematite by atomic layer deposition and its utilization for improved solar water splitting. *J. Am. Chem. Soc.* **2012**, *134*, 5508–5511.

27 It is noted that hematite synthesized by solution phase chemistries often exhibits lower turn-on potentials and poorer fill factors. See, for example: Li, L.; Yu, Y.; Meng, F.; Tan, Y.; Hamers, R. J.; Jin, S. Facile solution synthesis of α-FeF$_3$·3H$_2$O nanowires and their conversion to α-Fe$_2$O$_3$ nanowires for photoelectrochemical application. *Nano Lett.* **2012**, *12*, 724–731.

28 Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.; Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.; Lewis, N. S. Photoelectrochemical hydrogen evolution using Si microwire arrays. *J. Am. Chem. Soc.* **2011**, *133*, 1216–1219.

29 Khaselev, O.; Turner, J. A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting. *Science* **1998**, *280*, 425–427.

30 Mayer, M. T.; Du, C.; Wang, D. Hematite/Si Nanowire Dual-Absorber System for Photoelectrochemical Water Splitting at Low Applied Potentials. *J. Am. Chem. Soc.* **2012**, *134*, 12406–12409.

31 Zhang, M.; Lin, Y.; Mullen, T. J.; Lin, W.-f.; Sun, L.-D.; Yan, C.-H.; Patten, T. E.; Wang, D.; Liu, G.-y. Improving Hematite's Solar Water Splitting Efficiency by Incorporating Rare-Earth Upconversion Nanomaterials. *J. Phys. Chem. Lett.* **2012**, *3*, 3188–3192.

32 Barroso, M.; Mesa, C. A.; Pendlebury, S. R.; Cowan, A. J.; Hisatomi, T.; Sivula, K.; Grätzel, M.; Klug, D. R.; Durrant, J. R. Dynamics of photogenerated holes in surface modified α-Fe$_2$O$_3$ photoanodes for solar water splitting. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15640–15645.

33 Dotan, H.; Sivula, K.; Grätzel, M.; Rothschild, A.; Warren, S. C. Probing the photoelectrochemical properties of hematite (α-Fe$_2$O$_3$) electrodes using hydrogen peroxide as a hole scavenger. *Energy Environ. Sci.* **2011**, *4*, 958–958.

34 Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with "Co—Pi"-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **2012**, *134*, 16693–16700.

35 Gamelin, D. R. Water splitting: Catalyst or spectator? *Nat. Chem.* **2012**, *4*, 965–967.

36 Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W. A functional model for O-O bond formation by the O$_2$-evolving complex in photosystem II. *Science* **1999**, *283*, 1524–1527.

37 Liu, R.; Lin, Y.; Chou, L.-Y.; Sheehan, S. W.; He, W.; Zhang, F.; Hou, H. J. M.; Wang, D. Water splitting by tungsten oxide prepared by atomic layer deposition and decorated with an oxygen-evolving catalyst. *Angew. Chem., Int. Ed.* **2011**, *50*, 499–502.

38 Dubois, M. R.; Dubois, D. L. Development of Molecular Electrocatalysts for CO$_2$ Reduction and H$_2$ Production/Oxidation. *Acc. Chem. Res.* **2009**, *42*, 1974–1982.

39 Morris, A. J.; Meyer, G. J.; Fujita, E. Molecular Approaches to the Photocatalytic Reduction of Carbon Dioxide for Solar Fuels. *Acc. Chem. Res.* **2009**, *42*, 1983–1994.

40 Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. Photochemical and Photoelectrochemical Reduction of CO$_2$. *Annu. Rev. Phys. Chem.* **2012**, *63*, 541–569.

41 Liu, R.; Yuan, G.; Joe, C. L.; Lightburn, T. E.; Tan, K. L.; Wang, D. Silicon Nanowires as Photoelectrodes for Carbon Dioxide Fixation. *Angew. Chem., Int. Ed.* **2012**, *51*, 6709–6712.

42 Yuan, G. B.; Aruda, K.; Zhou, S.; Levine, A.; Xie, J.; Wang, D. W. Understanding the Origin of the Low Performance of Chemically Grown Silicon Nanowires for Solar Energy Conversion. *Angew. Chem., Int. Ed.* **2011**, *50*, 2334–2338.

43 Yuan, G. B.; Zhao, H. Z.; Liu, X. H.; Hasanali, Z. S.; Zou, Y.; Levine, A.; Wang, D. W. Synthesis and Photoelectrochemical Study of Vertically Aligned Silicon Nanowire Arrays. *Angew. Chem., Int. Ed.* **2009**, *48*, 9680–9684.