Water Splitting

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Hematite-Based Water Splitting with Low Turn-On Voltages**

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Sunlight-driven photoelectrochemical (PEC) water splitting offers promise as a method for effective solar-energy harvesting and storage.[1–4] To transform the reaction into economically competitive technology, we need materials that can absorb sunlight broadly, transfer the energy to excited charges at high efficiencies, and catalyze specific reduction and oxidation reactions.[5,6] Furthermore, the materials should be inexpensive and stable against photocorrosion. To date, an ideal material that satisfies all of these considerations remains elusive. This challenge can, in principle, be addressed by combining various material components, each purpose-designed to offer desired properties with respect to photovoltage generation, charge transport, and catalytic activity.[7] For example, it has recently been shown that the performance of hematite (α-Fe_2O_3)-based water splitting can indeed be improved by introducing dedicated charge collectors,[8,9] buried homo- and heterojunctions,[10,11] and oxygen-evolution catalysts.[12–15] Hematite was chosen as a prototypical system for these proof-of-concept demonstrations because it is an earth-abundant material with great promise for high-efficiency, low-cost water splitting.[16,17] To realize the potential of hematite, however, we still need to address a key issue concerning its low photovoltage (V_{ph}, typically ≤ 0.4 V), which is unreasonably low given that the bandgap of hematite is ≥ 2.0 eV. For successful integration with a small-bandgap photocathode, the photovoltage generated at the photoanode needs to be significantly higher so that a total (combined) photovoltage of 1.61 V (or greater, with a minimum overpotential of 0.38 V) is produced.[18] Herein we show that this issue may be addressed by modifying the hematite surface. When decorated with an amorphous $NiFeO_x$ layer (Figure 1), hematite produces photovoltages as high as 0.61 V, which enable the observation of turn-on voltages (V_{on}) as low as 0.62 V (versus the reversible hydrogen electrode, RHE) without the need for a second absorber (unless otherwise noted, all electrochemical potentials reported herein are relative to RHE). When a second absorber, Si, was added, a record-low turn-on voltage of 0.32 V was measured.

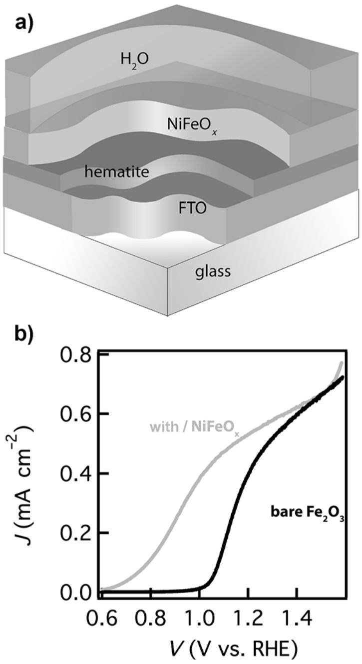

Figure 1. Effect of surface modification with a $NiFeO_x$ overlayer on the PEC performance of hematite. a) Schematic perspective view of the modification. b) Photocurrent-density–voltage plot showing the substantial cathodic shift (up to 0.38 V) observed upon the surface modification of hematite with $NiFeO_x$. FTO = fluorine-doped tin oxide.

The basis for our approach is illustrated schematically in Figure 2. The fundamental reason for the observed limited photovoltage generation by hematite lies in the relatively positive positions of its valence- and conduction-band edges.[19,20] However, even within these limits, the V_{ph} value of 0.6–0.8 V calculated for reported flat-band potentials (V_{fb}) of 0.4–0.6 V[21] has not been reached. We understand the cause of this discrepancy to be a partial Fermi level pinning effect. That is, owing to the existence of surface states, a non-negligible potential drop takes place within the Helmholtz layer (η_H, Figure 2a).[22] The effect is manifested as a more positive V_{on} value, since a significant portion of the applied potential is used to overcome the overpotential η_H (Figure 2c).[23] Appropriate surface modification enables the η_H to be minimized or eliminated (Figure 2b) and a less positive V_{on} value to be measured (Figure 2d).

The effect of the $NiFeO_x$ overlayer was profound: it led to a V_{on} shift from approximately 1.0 V to approximately 0.6 V (Figure 1b). Although the apparent effect of the cathodic V_{on} shift is similar to the effect of reducing the kinetic over-

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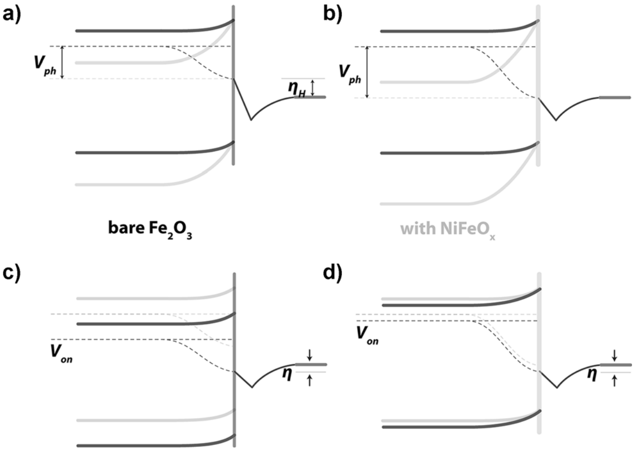

Figure 2. Band diagrams under open-circuit and turn-on conditions. a) For bare hematite under open-circuit conditions, a significant potential drop (η_H) occurs across the Helmholtz layer. The band diagram for the material in light is shown in black, and that for the material in the dark is shown in light gray. b) Surface modification by $NiFeO_x$ helps reduce the η_H value and increase the V_{ph} value. c) For the measurement of photocurrents, the quasi-Fermi level of holes needs to be made more positive than the oxidation potential of H_2O by a kinetic overpotential (η). The band diagram under open-circuit conditions is shown in light gray. d) The need for externally applied power is significantly reduced for $NiFeO_x$-decorated hematite: a less positive V_{on} value is observed.

potential through the application of cocatalysts,[12,24] our approach is distinctly different. Most importantly, with cocatalysts, one seeks to change the kinetics of the system; our approach aims to alter the thermodynamics of the system.[25] Consequently, we understand the V_{on} shift observed in Figure 1b as a result of an increase in V_{ph}, but not a reduction in η. Evidence that supports this hypothesis is presented herein. To avoid a further increase in the V_{on} value as a result of poor kinetics (and, hence, a greater η value), the decoration that we used is a recently identified oxygen-evolution catalyst, $NiFeO_x$ prepared by the photochemical metal–organic deposition (PMOD) technique.[26] Another important reason for choosing this material is that it is made of earth-abundant elements and should therefore be inexpensive for large-scale implementation.

Figure 3 shows typical transmission electron micrographs (TEM) of the cross-sectional view of the hematite/$NiFeO_x$ combination. A simple drop-casting preparation method (see the Experimental Section) produced a relatively uniform $NiFeO_x$ layer with a height of approximately 100 nm. High-resolution TEM analysis (Figure 3b) revealed that $NiFeO_x$ is amorphous in nature, in agreement with the description of this material by Smith et al.[26] Although voids between hematite and $NiFeO_x$ are present, good contact between the two layers is ensured (Figure 3a). The $NiFeO_x$ overlayer absorbs light in the region in which hematite absorbs, but the absorbed light by $NiFeO_x$ does not produce any photocurrent (see Figure S3 in the Supporting Information). This issue was not a concern in our experiments, because we conducted PEC measurements by illumination from the FTO side (see Figure S4).

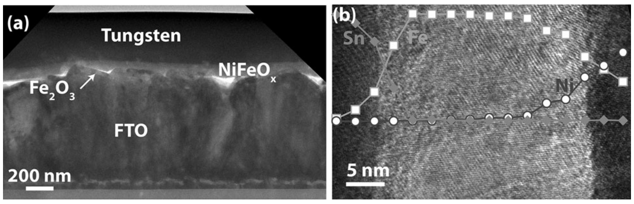

Figure 3. Microstructure of a $NiFeO_x$-decorated hematite photoelectrode. a) Mid-magnification TEM image showing the cross-sectional view of the electrode. The sample was prepared by a focused ion beam (FIB) method, and W was deposited prior to FIB to protect the top layer. b) High-resolution TEM image revealing the crystalline nature of hematite and FTO. $NiFeO_x$ is amorphous. The results of elemental analysis in the form of line scans are superimposed on the TEM image.

We used three methods to quantitatively analyze the PEC performance of the decorated hematite photoelectrode. Our first treatment of the PEC data (Figure 1b) followed the report by Le Formal et al.,[27] in which V_{on} is defined as the potential at which the change in photocurrent as a function of potential first exceeds $0.2\,mA\,cm^{-2}\,V^{-1}$. By plotting the first-order derivative of the photocurrent density against the voltage for both bare hematite and hematite with $NiFeO_x$ (Figure 4a), we obtained a V_{on} value for $NiFeO_x$-decorated hematite of 0.62 V; the V_{on} value for bare hematite was 1.00 V. A cathodic shift of 0.38 V was measured. We emphasize that the result was highly reproducible. It was consistently observed on more than 30 electrodes from 10 batches of samples.

Alternatively, the PEC data can be analyzed by the method introduced by Butler.[28] By assuming that charge transfer is not a limiting factor in a PEC process, Butler derived the relationship $(V - V_{fb}) \propto (J/\alpha W_0 q \phi_0)$, in which α is the optical absorption coefficient, W_0 is the depletion width, and ϕ_0 is the light intensity. Because this treatment simply deals with semiconductor behavior, it provides a measure of the light-to-charge energy-conversion performance of the photoelectrode. Even under conditions under which charge transfer across the semiconductor/electrolyte interface is indeed slow (such as in the hematite system under consideration herein), the Butler equation is of value if we treat V_{fb} as the apparent flat-band potential, which carries information about the overpotentials (both the kinetic overpotential, η, and the potential drop across the Helmholtz layer, η_H, as shown in Figure 2a,c).[22] Within this context, V_{fb} values of 1.05 V for bare hematite and 0.69 V for hematite with $NiFeO_x$ were obtained; these values correspond to a 0.36 V cathodic shift caused by $NiFeO_x$ decoration. The difference is explained by the schematic illustrations in Figure 2 and is in good agreement with that found by the method developed by Le Formal et al. (0.38 V). The magnitude of the cathodic shift is among the highest that has been reported for hematite-based water-splitting reactions without the application of additional absorbers. Finally, the V_{fb} value of bare hematite as measured by the Mott–Schottky method (0.67 V)[9] was consistent with that derived by the Butler method. The 1.05 V measured on bare hematite by the Butler method is a result of a severe Fermi level pinning effect, which is a key reason for the low photovoltages observed (Figure 2).

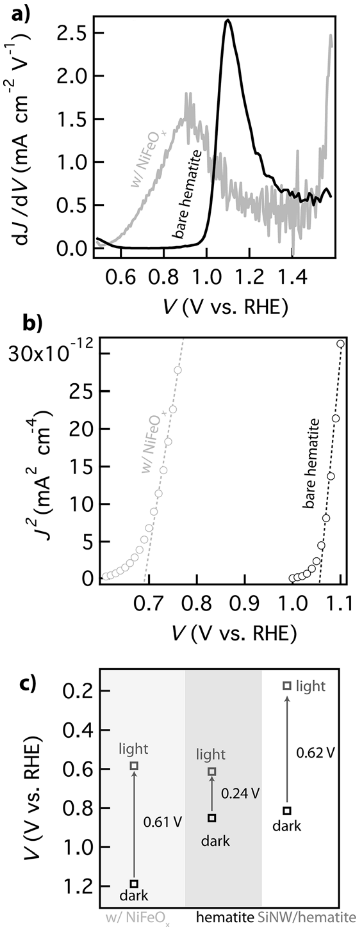

Figure 4. Comparison of the PEC performance of hematite with and without NiFeO$_x$ decoration. a) First-order derivative of the photocurrent density as a function of voltage. V_{on} is defined as the voltage at which $dJ/dV \geq 0.2$ mA cm^{-2}V^{-1}. b) Butler plots, in which V_{fb} is defined as the value at which the extrapolation of the linear relationship between J^2 and V intercepts with $J^2 = 0$. c) Graph showing the significant difference observed between the measured photovoltages generated by bare hematite and hematite decorated with NiFeO$_x$. For comparison, the voltages measured for the SiNW/hematite system are also shown.

Nevertheless, the above analyses shed little light on the true cause of the cathodic shift. Although greater photovoltage generation can be used to explain the observation, the reduction in the kinetic overpotential is equally able to account for the difference. In other words, both kinetic and thermodynamic factors can lead to a cathodic shift in PEC characterizations.[25] To understand whether the thermodynamic contribution (increase in V_{ph}) or the kinetic contribution (reduction in η) plays a more important role in the observed cathodic shift, we next performed experiments under open-circuit conditions. By having a zero net exchange current across the semiconductor/water interface, we aimed to collect thermodynamic information with minimum influence by kinetic factors.

The proposed working mechanism of the experiment can be understood with the help of the schematic illustration in Figure 2a,b. In the absence of illumination, the equilibrium between the photoelectrode and the electrolyte dictates that the measured open-circuit potential reports on the position of the Fermi level. Under illumination, the equilibrium between the electrolyte and the photoelectrode is maintained by the quasi-Fermi level of holes; the Fermi level of electrons shifts negatively. The difference between the newly measured potential (quasi-equilibrium) and that in dark (equilibrium) reports on the photovoltage. From Figure 2, we see that, under illumination, the quasi-equilibrium potentials measured on hematite with and without decoration should be comparable because this value is determined by the nature of the hematite (grown by atomic layer deposition without intentional doping). Indeed, the experimentally obtained values are 0.61 ± 0.01 V for bare hematite and 0.58 ± 0.04 V for hematite with NiFeO$_x$. The key difference between the measured open-circuit potentials would be seen in the dark, as was again confirmed by our experiments: 0.85 ± 0.01 V for bare hematite and 1.19 ± 0.05 V for hematite with NiFeO$_x$. The corresponding photovoltages for hematite with and without NiFeO$_x$ were 0.24 and 0.61 V, respectively (Figure 4c). The difference of 0.37 V accounts for the 0.36–0.38 V cathodic shift, as discussed above. We therefore understand the cathodic shift as a result of greater photovoltage generation.

The equilibrium open-circuit potentials in the dark require further comment. Under ideal conditions, in the complete absence of an overpotential η_H, an equilibrium open-circuit potential of 1.23 V would be expected. The measurement of only 0.85 V on bare hematite strongly suggests that a significant potential drop, up to 0.38 V, takes place within the Helmholtz layer; this potential drop is detrimental to the photovoltage-generation capabilities of hematite. NiFeO$_x$ decoration corrects the deficiency by bringing the equilibrium potential close to 1.23 V. Whereas surface catalytic modifications may help reduce the kinetic overpotential, it is important that such surface treatments do not compromise the performance of the photoelectrode, for example, through Fermi level pinning, as was recently observed in another system involving MnO$_x$ catalysts.[23]

A control system to further test our understanding of these processes is the dual-absorber system composed of Si nanowires (SiNWs) and hematite,[7] which also yielded a significant cathodic shift. We understood that shift as a result of additional photovoltage generation by the SiNWs. In other words, the nature of the hematite/water interface should be identical to that of the interface between water and bare hematite; thus, the open-circuit potential in the dark should be comparable for bare hematite and SiNW/hematite. The main difference in the open-circuit potentials would be observed in light. This prediction was confirmed by our experimental data (0.81 ± 0.02 V in the dark and 0.19 ± 0.01 V in light; Figure 4c). We are therefore confident that the explanations presented herein provide new insight into the photoelectrode properties of PEC systems.

In principle, the two approaches (dual-absorber and surface modification) used to increase photovoltage are based on distinct principles and may be combined to yield even greater cathodic shifts. To test this idea, we applied NiFeO$_x$ decorations on hematite-coated SiNWs and measured a record-low V_{on} value of 0.32 V (see Figure S6), which corresponds to a 0.24 V cathodic shift, as compared to the

V_{on} value of 0.56 V for the SiNW/hematite dual-absorber system without $NiFeO_x$.

In conclusion, we have demonstrated that $NiFeO_x$ decoration by the PMOD method induced a significant cathodic shift in hematite-based photoelectrochemical water splitting reactions. A V_{on} value of 0.62 V (versus RHE) was measured. Significantly, the effect was understood as an increase in photovoltage generation owing to minimization of the surface Fermi level pinning effect. When applied to the SiNW/hematite dual-absorber system, a record-low V_{on} value of 0.32 V (versus RHE) was observed. As the establishment of a high V_{on} value, and hence a low V_{ph} value, is a major challenge that prevents the full potential of hematite, an earth-abundant anode material for water splitting, from being realized, the results are new and significant.

Experimental Section

Preparation of the $NiFeO_x$ amorphous catalyst: Iron(III) 2-ethylhexanoate (50% w/w in mineral spirits, Strem Chemicals) and nickel(II) 2-ethylhexanoate (78% w/w in 2-ethylhexanoic acid, Strem Chemicals) were mixed in a 1:1 ratio, and an appropriate amount of hexane was added as a solvent to produce a solution of the metal complex with a total concentration of 15% (w/w). A quantity of 5 µL of this mixture was then dropped directly on a FTO–hematite electrode surface with a transfer liquid gun. The electrodes used in PEC and photovoltage measurements had typical surface areas of around 0.05 cm^2. The thin film was left in air for 5 min and then irradiated with UV light for 3 h. The electrode with the $NiFeO_x$ coating was then annealed in an oven at 100°C for 1 h. Similar procedures were used to prepare the $SiNW/Fe_2O_3/NiFeO_x$ and $FTO/NiFeO_x$ samples.

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[1] M. Graetzel, *Acc. Chem. Res.* **1981**, *14*, 376.
[2] J. R. Bolton, *Solar Energy* **1996**, *57*, 37.
[3] W. J. Youngblood, S.-H. A. Lee, K. Maeda, T. E. Mallouk, *Acc. Chem. Res.* **2009**, *42*, 1966.
[4] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, *110*, 6446.
[5] T. Bak, J. Nowotny, M. Rekas, C. Sorrell, *Int. J. Hydrogen Energy* **2002**, *27*, 991.
[6] F. E. Osterloh, *Chem. Soc. Rev.* **2013**, *42*, 2294.
[7] M. T. Mayer, Y. Lin, G. Yuan, D. Wang, *Acc. Chem. Res.* **2013**, *46*, 1558.
[8] K. Sivula, F. Le Formal, M. Grätzel, *Chem. Mater.* **2009**, *21*, 2862.
[9] Y. Lin, S. Zhou, S. W. Sheehan, D. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 2398.
[10] Y. Lin, Y. Xu, M. T. Mayer, Z. I. Simpson, G. McMahon, S. Zhou, D. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 5508.
[11] M. T. Mayer, C. Du, D. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 12406.
[12] D. K. Zhong, J. Sun, H. Inumaru, D. R. Gamelin, *J. Am. Chem. Soc.* **2009**, *131*, 6086.
[13] D. K. Zhong, M. Cornuz, K. Sivula, M. Grätzel, D. R. Gamelin, *Energy Environ. Sci.* **2011**, *4*, 1759.
[14] B. Klahr, S. Gimenez, F. Fabregat-Santiago, J. Bisquert, T. W. Hamann, *J. Am. Chem. Soc.* **2012**, *134*, 16693.
[15] L. Badia-Bou, E. Mas-Marza, P. Rodenas, E. M. Barea, F. Fabregat-Santiago, S. Gimenez, E. Peris, J. Bisquert, *J. Phys. Chem. C* **2013**, *117*, 3826.
[16] K. Sivula, F. Le Formal, M. Grätzel, *ChemSusChem* **2011**, *4*, 432.
[17] M. J. Katz, S. C. Riha, N. C. Jeong, A. B. F. Martinson, O. K. Farha, J. T. Hupp, *Coord. Chem. Rev.* **2012**, *256*, 2521.
[18] J. R. Bolton, S. J. Strickler, J. S. Connolly, *Nature* **1985**, *316*, 495.
[19] A. Braun, K. Sivula, D. K. Bora, J. Zhu, L. Zhang, M. Grätzel, J. Guo, E. C. Constable, *J. Phys. Chem. C* **2012**, *116*, 16870.
[20] D. K. Bora, A. Braun, E. C. Constable, *Energy Environ. Sci.* **2013**, *6*, 407.
[21] R. A. Fredlein, A. Bard, *J. Electrochem. Soc.* **1979**, *126*, 1892.
[22] Y. V. Pleskov, *Solar Energy Conversion: A Photoelectrochemical Approach*, Springer, New York, **1990**.
[23] X. Yang, C. Du, R. Liu, J. Xie, D. Wang, *J. Catal.* **2013**, *304*, 86.
[24] S. D. Tilley, M. Cornuz, K. Sivula, M. Grätzel, *Angew. Chem.* **2010**, *122*, 6549; *Angew. Chem. Int. Ed.* **2010**, *49*, 6405.
[25] D. R. Gamelin, *Nat. Chem.* **2012**, *4*, 965.
[26] R. D. Smith, M. S. Prevot, R. D. Fagan, Z. Zhang, P. A. Sedach, M. K. Siu, S. Trudel, C. P. Berlinguette, *Science* **2013**, *340*, 60.
[27] F. Le Formal, M. Grätzel, K. Sivula, *Adv. Funct. Mater.* **2010**, *20*, 1099.
[28] M. Butler, *J. Appl. Phys.* **1977**, *48*, 1914.