Photochemistry of hematite photoanodes under zero applied bias

Timothy L. Shelton, Nicholas Harvey, Jiarui Wang, Frank E. Osterloh

Department of Chemistry, University of CA, One Shields Avenue, Davis, CA 95616, United States

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Surface photovoltage spectroscopy (SPS) was used to observe photochemical charge separation and oxidation reactions on Fe2O3 nanorod arrays under zero applied bias. Nanorod films were grown from FeCl3 under hydrothermal conditions followed by calcination at 550 °C. A negative photovoltage of up to 130 mV is observed under 2.0–4.5 eV (0.1 mW cm−2) illumination, confirming 2.0 eV as the effective bandgap of the material, and electrons as majority carriers. SPS in the presence of air, nitrogen, water, oxygen, and under vacuum suggest that the photovoltage is associated with the oxidation of surface water and with reversible surface hole trapping on the 1 min time scale and de-trapping on the 1 h time scale. O2 promotes water oxidation by increasing the concentration of surface holes. Sacrificial donors KI, H2O2 or potassium hydroxide increase the voltage to ~240 and ~400 mV, due to improved hole transfer. Cobalt oxide and Co–Pi cocatalysts quench the voltage, which is tentatively attributed to the removal of surface states and enhanced e/h recombination. An energy diagram is used to relate the experimental photovoltage to the built-in potentials at the respective interfaces.

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1. Introduction

Hematite photoelectrodes are among the best examples for the successful implementation of the nanoscaling strategy to improve performance for solar water splitting [1–10]. By making the dimensions of the light absorber equal to the minority carrier diffusion length, short-lived holes can be extracted and used for water oxidation. As the concentration and mobility of charge carriers for metal oxides is several orders of magnitude below that of doped II–VI, III–V, or group V semiconductors, the space charge layers/electric fields that form at the interface are much weaker, and do not strongly affect charge separation. Also, the electric field in nanostructured photoelectrodes is strongly screened by electrolytes. Charge separation in nanoscale absorbers can be improved through surface modifications with electrocatalysts, charge selective contacts, and recombination resistant materials [11]. For example, Dunwei Wang’s group has shown that the photovoltage of Fe2O3 can be raised by surface recrystallization [12] or by the addition of NiO overlays [13]. Higher photovoltage can be also be achieved with Co–Pi, [14] RuO2 [15] or cobalt oxide coatings [16–18] whereas n-SnO2 [19], n-Ga2O3 [20], Nb2O5 [21] or Al2O3 [22–24] under- or overlays increase the photocurrent of Fe2O3. However, the reason for the improvement is often not clear. For example, Co–Pi and NiO speed up the water oxidation kinetics and they are also thought to aid e/h separation at the interface [13,14,25,26]. Similarly, diamagnetic metal oxide coatings are believed to simultaneously eliminate recombination sites and promote selective charge transfer [19–24]. Photoelectrochemistry is not able to resolve the kinetic and thermodynamic contributions because the measured photocurrent and photopotential are the result of coupled charge transfer at solid–solid and solid–liquid interfaces [27]. Thus any changes in the photopotential across an absorber film could be the result of a change in majority carrier transport through the film (affects Ohmic drop), due to a change of the electrochemical overpotentials, formation of a junction, or changes in the electrochemical double layer in front of the electrode.

As we show here, some of these shortcomings can be overcome with Surface Photovoltage Spectroscopy (SPS). SPS is a contactless technique that probes Contact Potential Difference changes (∆CPD) in light absorbing films in response to excitation with spectrally resolved light (Fig. 1) [28,29]. For example, migration of negative charge towards the Kelvin probe leads to a positive voltage. Because even small displacements (10 nm) of charge carrier concentrations (1016 per cm2) can yield potentials on the mV scale, the sensitivity of the method is much higher than that of photoelectrochemistry [30]. Due to the low current, losses from overpotentials and ohmic potential drops are insignificant, and since no electrolyte is used, electrochemical double layer effects can be excluded. This makes SPS particularly useful to probe intrinsic charge transfer processes in nanostructured light absorbing materials [31–36].
Fe₂O₃ nanorod arrays (Fig. 2) were fabricated by hydrothermal synthesis followed by calcination, according to the method by Vayssieres [9]. The films exhibit the characteristic rod morphology reported previously in the literature [3,9,10]. X-ray diffraction of the annealed film confirms that the rods crystallize in the hematite structure type (Fig. 2C). A profilometry scan for a film synthesized over a 24 h period is shown in Fig. 2D. The average thickness of the film is 520 nm, which can be taken as the approximate nanorod length. Fig. 3 shows SPV and diffuse reflectance optical spectra of a Fe₂O₃ nanorod array film exposed to air atmosphere. The onset of the photovoltage coincides with the indirect band gap absorption at 2.0 eV, close to the reported band gap of the material [3]. The absence of sub-gap signals indicates that the material is free of mid-gap defect states [40]. Also, no significant signal variation is observed at 2.5 eV, even though an earlier resonant inelastic X-ray scattering study had postulated a quantum size confinement effect in the Fe₂O₃ nanorod arrays [41]. The measured photovoltage is negative, indicating that it is due to majority (electron) carrier movement towards the substrate, as shown in Fig. 1, and as previously observed for other n-type nanocrystals, incl. BiVO₄ [35] and HCa₂Nb₃O₁₀ [40].

The photovoltage reaches its most negative value of ~140 mV at a photon energy 2.75 eV, in a region of strong visible absorbance. To determine the extent to which the photovoltage is limited by

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2. Results and discussion

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the film thickness, SPV spectra were recorded for Fe$_2$O$_3$ arrays synthesized over 1, 3, 6, and 24 hour periods. In these samples, the film thickness varies between 67 and 520 nm, as determined with profilometry (data not shown). From Fig. 4, it can be seen that the photovoltage increases with film thickness (the lower voltage for the 200 nm film is due to statistical variation). Also, it can be seen that the photovoltage maximum shifts from 3.75 eV for the thinnest film to 2.75 eV for the thicker films, close to the optical absorbance maximum in Fig. 3. This suggests that the photovoltage is limited by light absorption in the films. Indeed, based on the published absorption coefficient $\alpha=8 \times 10^8$ m$^{-1}$ at 2.75 eV for a hematite nanorod film [3], absorption of 99% of all 2.75 eV photons requires a 575 nm thick film, close to the thickest films observed here. This confirms that light absorption is a limiting factor for the photovoltage of the films.

To investigate the effect of surface chemistry on the photovoltage, SPV scans were recorded for Fe$_2$O$_3$ films exposed to vacuum, air, nitrogen, and water saturated nitrogen atmosphere, as shown in Fig. 5. Interestingly, the strong SPV signal in air disappears almost completely when the Fe$_2$O$_3$ film is exposed to vacuum (10$^{-4}$ mbar) for an hour. Admission of 99% pure N$_2$ gas to a vacuum-dried film restores 18–21% of the original photovoltage, depending on the photon energy (2.7 and 3.6 eV respectively), while the addition of saturated water vapor in nitrogen or of pure oxygen leads to 70% recovery of the signal. When pure O$_2$ is introduced to a Fe$_2$O$_3$ film without the vacuum drying step, the photovoltage increases to 115% of the value in air and to 1750% of the vacuum value. This demonstrates the strong effect of water and oxygen on the ability of the Fe$_2$O$_3$ nanorod film to separate charge.

In principle, the gas-dependence of the photovoltage could be due to changes of the band bending in Fe$_2$O$_3$ in response to the formation of new surface states, as observed with a silicon photoelectrode, for example [33]. However, time dependent measurements (below) show that the photovoltage signal recovery with Fe$_2$O$_3$ is slow (0.5 h) and therefore more likely associated with chemical reactions of photoholes. Reactions 2 and 4 are possibilities, although complete water oxidation according to Eq. (4) normally requires applied bias of >0.6 V RHE with Fe$_2$O$_3$ [13]. Because of that reaction 2 is more likely. The positive effect of oxygen on the photovoltage size could be related to its ability to accept photoelectrons from Fe$_2$O$_3$ according to Eq. (3), forming superoxide [42]. The resulting increase in surface hole concentration would then facilitate water oxidation according to Eq. (2).

\[ \text{hv} \rightarrow \text{e}^- + h^+ \]  
\[ \text{h}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H}^+ \]  
\[ \text{e}^- + \text{O}_2 \rightarrow \text{O}_2^{2-} \]  
\[ 4\text{h}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{O}_2 + 4\text{H}^+ \]  

A synergistic interaction between oxygen and H$_2$O oxidation has been previously hypothesized in nano-TiO$_2$ photoelectrodes, on the basis of time resolved absorption measurements [43]. Furthermore, for Fe$_2$O$_3$, oxygen plays a role in acetaldehyde degradation [44]. To further investigate the role of surface-adsorbed water on the photovoltage, a Fe$_2$O$_3$ film sample was scanned repeatedly every 24 h under 1.0 atm of air in a sealed chamber (Fig. 6A). It can be seen that the measured photovoltage is reduced with each scan from initially ~85 mV to ~70 mV and then to ~65 mV. When the sample was removed from the chamber, rinsed thoroughly with water, dried in air and retested, the photovoltage increased to ~100 mV, 118% of the initial value. These observations support the conclusion that slow water oxidation occurs according to Eq. (2). The gradual decay of the photovoltage in subsequent scans would then be due to build-up of protons and hydroxyl groups on the Fe$_2$O$_3$ surface. Interestingly, there is a slow reversible component to the photovoltage (Fig. 6B): When the light is turned off after an initial 0.6 h illumination period, about 20% of the initial photovoltage (~0.225 V) decays over the course of 30 min. Additional on/off cycles (Fig. 6C) performed over a 6 h period, show that the reversible portion amounts to about 75–125 mV, or 50% of the initial value in Fig. 6B. The slow time scale of the signal recovery rules out photocatalytic charge separation inside a space charge layer, which should occur much faster. Instead we assign this reversible voltage
component to deep hole trapping at surface Fe-OH sites, according to equation 2. Reversible hole trapping in surface states has been previously observed with impedance spectroscopy by Klahr et al. [37,38] and independently by Cummings et al. [39]. These surface states are involved in water oxidation and are believed to consist of either hydroxyl radicals or Fe(3+) species. These states are also likely responsible for the Fermi pinning effect in Fe2O3, as discussed by Thorne et al. in a recent paper [27]. As expected, the oxidizing surface states generated in illuminated Fe2O3 films have the ability to oxidize a variety of electron donors. SPV spectra of Fe2O3 films treated with 0.01 M KI solution and 1%/wt. hydrogen peroxide solution in water are shown in Fig. 7A. It can be seen that while KI treatment has little effect on spectral shape, it increases the maximum photovoltage to ∼240 mV, 185% of the untreated film in air. Similarly, H2O2 treatment induces a photovoltage of ∼400 mV, a 307% increase over the untreated film. These effects can be explained with photochemical oxidation of iodide and hydrogen peroxide, according to Eqs. (5) and (6) [45,46].

\[
\begin{align*}
    & h^+ + I^- \rightarrow \frac{1}{2}I_2 & (5) \\
    & 2h^+ + H_2O_2 \rightarrow O_2 + 2H^+ & (6) \\
    & h^+ + OH^- \rightarrow OH^+ & (7)
\end{align*}
\]

Interestingly, the photoonset with peroxide is shifted to ∼1.9 eV, indicating the formation of a new Fe(3+)((O2)) surface state that can be directly excited with light (see discussion below). Considering Reactions (2),(3),(6) and (7), the charge separation dynamics in Fe2O3 are expected to depend strongly on the surface pH. The effect of pH on the photoelectrochemistry of Fe2O3 was noted in 1974 by Allen Bard’s group [47]. Below pH 4, Fe2O3 is found to dissolve, while above this pH the water oxidation photoonset potential shifts negatively with pH, due to variation of the flatband potential (Fermi energy) in Fe2O3 [47,48]. Indeed, SPV spectra in Fig. 7B are also found to have a strong pH-dependence. Reduced photovoltage values are seen for films treated with dilute acid solutions of pH 5, 4 and a fully quenched signal is observed at pH 1. This is attributed to etching of the Fe2O3 surface and introduction of electron/hole recombination centers at the hematite surface. Raising the pH to 9 and 11 does not bring about notable change, but at pH 13 the voltage at 2.75 eV is increased to −166 mV, i.e., 128% of the value for the as-prepared Fe2O3 film. This agrees with the fact that hydroxide is a better hole acceptor than water, based on
thermodynamic and mechanistic considerations [49], and in agreement with improved photocurrents at high pH [3]. Lastly, we probe photovoltage spectra of cobalt oxide modified Fe2O3 films. Cobalt oxide coatings on Fe2O3 had been previously shown to increase the photovoltage by up to 80 mV [18,50]. Interestingly, we find that for Co(NO3)2 treated and annealed films the photovoltage is completely quenched (Fig. 8). The same is found for Fe2O3 films that were modified by electrodeposition of Co-Pi [51,52]. The finding of photovoltage quenching contrasts with our previous observation that Co3O4 coatings on BiVO4 lead to a photovoltage boost [53]. We hypothesize that the added cocatalyst layer interferes with the hole trap sites in untreated Fe2O3 films [37–39], thus quenching the photovoltage. Also, the Co2O3 conduction band edge [53] is positive of that of Fe2O3, making hole transfer difficult based on thermodynamic reasons.

To further analyze the thermodynamics of the FTO/Fe2O3/L system at pH 7 (L = air, water, KI, H2O2, vacuum, nitrogen) we construct the energy scheme in Fig. 9. As can be seen from the diagram, the built in voltage at the FTO/Fe2O3 interface (Eg0–E0) is very small. This explains the lack of a photovoltage of a dried Fe2O3 film in vacuum environment. Most of the photovoltage signal is generated by electron hole separation at the Fe2O3 surface. This occurs by either injection of holes into sacrificial electron donors (KI, H2O2, H2O) or by reversible trapping into Fe2O3 surface states. The addition of Co-Pi or CoOx cocatalysts completely quenches the photovoltage, either via removal of the surface traps or by reducing the hole lifetime. Overall, observed photovoltages for Fe2O3 represent one forth of the theoretical (thermodynamic) values. For example, the built-in potential of the Fe2O3–H2O2 contact is Vbe = +0.27 V − 2.40 V = −2.13 V, while the observed photovoltage for H2O2 oxidation is −0.4 V based on Fig. 7A. The difference between the observed and expected signals is due to the low amount of H2O2 on the Fe2O3 film and due to the low hole concentration in the Fe 3d band, under the 0.1 mW cm−2 illumination conditions. Assuming the observed signal for hole trapping (75–125 mV, i.e., reversible photovoltage component in Fig. 5) is also four times lower than the built-in potential, the position of the surface trap sites can be estimated 0.3–0.5 V above the Fe 3d band, as shown in Fig. 9. This position is close to the hydroxyl reduction potential of +0.02 V vs NHE in alkaline solution [54], suggesting trapping of holes is associated with the conversion of surface bound water/hydroxide into hydroxyl according to Eq. (7).

3. Conclusion

In conclusion we present the first quantitative SPV study on hematite films. A negative photovoltage of up −130 mV is observed under 2.0–4.5 eV (0.1 mW cm−2) illumination, confirming 2.0 eV as the effective bandgap of the material and no detectable mid gap states. For thin Fe2O3 films, the photovoltage is limited by light absorption and for thick films it is determined by the Fe2O3 surface chemistry. Under zero applied bias, the photochemistry of Fe2O3 nanorod arrays on FTO is dominated by hole injection into added sacrificial donors (iodide, water, and hydrogen peroxide) and by reversible hole trapping in surface states, likely involving hydroxyl groups. Quenching of the photovoltage by added Co-Pi and CoOx cocatalysts is attributed to removal of surface bound water and/or shortened hole lifetimes. The quenching of the photovoltage under vacuum is due to removal of surface bound water. Oxygen is found to boost the photovoltage, which is attributed to its ability to stabilize photoholes at the Fe2O3 surface. High pH promotes the photovoltage because hydroxide oxidation is thermodynamically preferred over water oxidation. These findings confirm that photochemical charge separation at nanostructured Fe2O3 is mostly determined by the kinetics and thermodynamics at the surface.

4. Experimental

4.1. Chemicals

FeCl3·6H2O (Sigma–Aldrich, 99+%), Na3HPO4·7H2O (Sigma–Aldrich, 99.5%), NaI04 (Fischer Scientific, 99%, recrystallized), cobalt(II) nitrate hexahydrate (98% Aldrich), NaOH (Fischer Scientific, 99.9+%), NaNO3 (Sigma–Aldrich, 99%), conc. (16N) HNO3 (aq) and HCl (aq) were obtained from Fischer Scientific and diluted as necessary. Water was purified to 18 MΩ cm resistivity using a Nano-pure Infinity system. FTO coated glass slides used were Corning brand TEC-15.

4.2. Synthesis of electrodes

Fe2O3 films on FTO were prepared according to the method by Vayssieres. A FTO-coated glass slide 1 × 2 cm2 was cleaned by subsequent sonication in acetone, methanol, and isopropanol followed by thorough rinsing in water. All but a 1 cm2 area was masked with Scotch tape placed in a Teflon-lined steel autoclave that contained 25 ml of a solution that was 0.15 M in FeCl3·6H2O and 0.1 M in NaNO3. The container was sealed and heated to 100 °C for 1 h. The
FTO slide was removed, sonicated for 10 s in water, rinsed twice with water, and then calcined at 550 °C for 1 h. Thicker Fe2O3 films were grown by increasing the hydrothermal heating time to 3, 6, and 24 h. For pH modification, 0.01 mL of HNO3 or NaOH adjusted to the desired pH by dilution from a 1 M stock solution was dropped onto the electrodes, allowed to soak in for two minutes and then dried in a stream of nitrogen gas. CO2−-modified Fe2O3 films were obtained by dropping 0.1 mL of 0.1 M and 0.01 M CO2− solutions on the Fe2O3 with followed by annealing at 550 °C for two hours before SPV analysis. Diffuse reflectance UV/vis spectra were taken on as-prepared hematite films using a Thermo Scientific Evolution 220 Spectrometer. Surface photovoltage (SPS) measurements were performed under air atmosphere using a vibrating gold Kelvin probe (3 mm diameter, Delta Phi Besocoe) mounted inside a home-built vacuum chamber and a Kelvin control 07 (Delta Phi Besocoe) with a sensitivity of 1 mV. The sample-probe distance was kept consistent (ca. 1 mm). Hematite films were illuminated through the probe with monochromatic light from a 300 W Xe lamp filtered through an Oriel Cornerstone 130 monochromator (light intensity range: 0.1−0.3 mW/cm2). For excitation spectrum see Wang et al. [31]. SPV spectra were corrected for drift by subtracting a dark background. Vacuum measurements were performed under 10−4 mbar. Controlled gas conditions were established by evacuating the chamber to 10−1 mbar and backfilling with either N2, O2, or water vapor in N2. This cycle was repeated twice. Water saturated N2 was prepared by storing nitrogen over water for one hour.

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