



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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ABSTRACT

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 overlayers [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-Ga₂O₅ [20], Nb₂O₅ [21] or Al₂O₅ [22–24] under- or overlayers 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 (Δ 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 (10¹⁰ 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].

* Corresponding author. Fax: +1 530 752 8995.

E-mail address: fosterloh@ucdavis.edu (F.E. Osterloh).

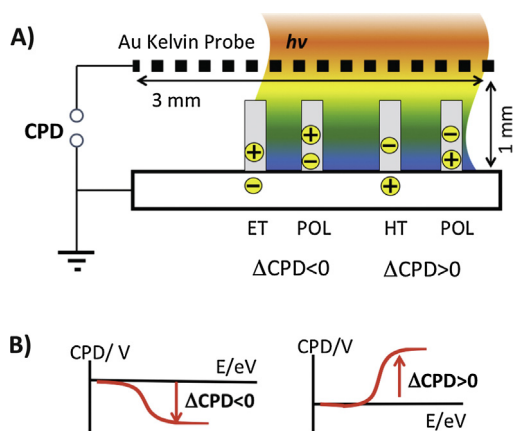


Fig. 1. (A) Measurement configuration of SPS. The sample film is illuminated through the semi-transparent Kelvin probe. Photovoltage signals are due to polarization of electron-hole pairs (POL) or due to electron or hole injection (ET or HT). (B) Spectra show a negative voltage when electrons move away from the Kelvin probe and a positive voltage when electrons move towards the Kelvin Probe.

Here we apply the technique to thin films of Fe_2O_3 nanorods grown onto FTO. We find that the photovoltage of the material is very sensitive to the ambient environment in the chamber and to any surface treatment of the films. This provides support for the earlier observation of the importance of surface states in hematite for hole trapping and water oxidation [37–39]. The data shows that Fe_2O_3 can oxidize a variety of compounds under zero applied electrochemical bias, and that oxygen promotes the oxidative ability.

These findings are relevant to the understanding of the photochemistry of hematite and to its optimization as a photoanode.

2. Results and discussion

Fe_2O_3 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 Fe_2O_3 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 Fe_2O_3 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. BiVO_4 [35] and $\text{HfCa}_2\text{Nb}_3\text{O}_{10}$ [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

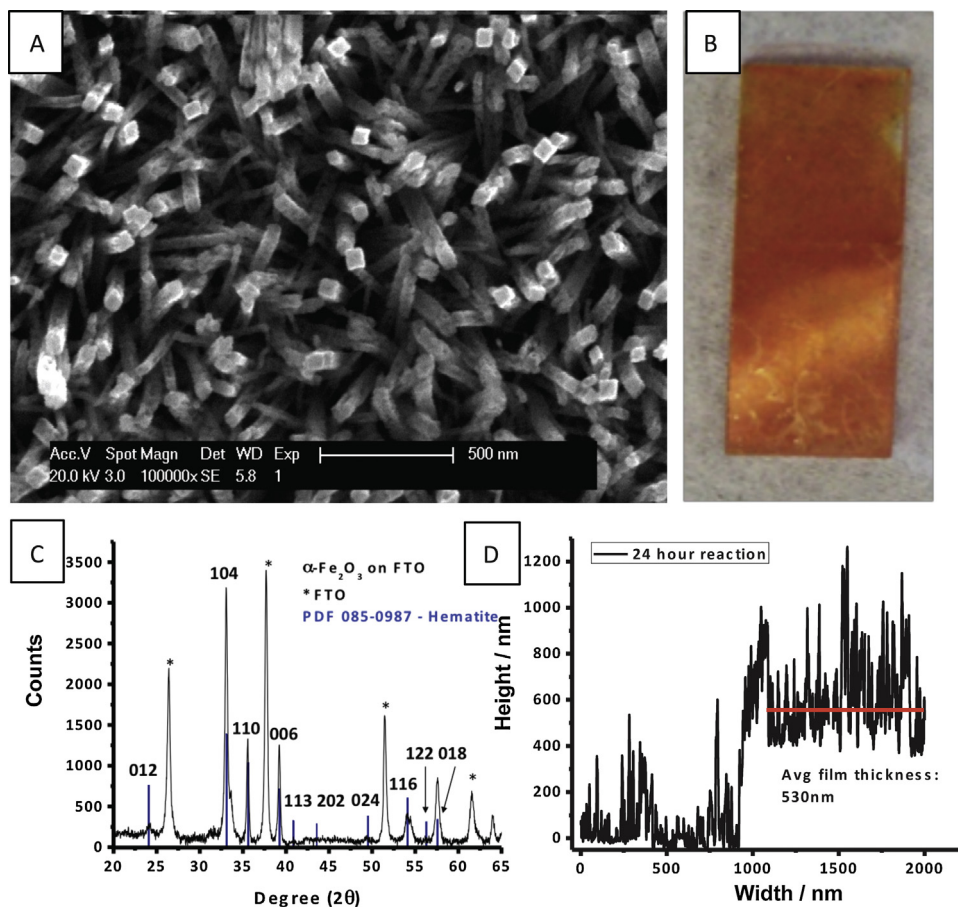


Fig. 2. (A) SEM and (B) photograph of 550 °C annealed Fe_2O_3 nanorod array, showing the characteristic red color of hematite. (C) XRD of annealed Fe_2O_3 film with reference pattern. (D) Profilometer scan of hematite film on FTO after 24 h hydrothermal synthesis.

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