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Supporting information

Tailoring charge recombination in photoelectrodes using oxide nanostructures

*Beniamino Iandolo^{1,2}, Björn Wickman¹, Elin Svensson¹, Daniel Paulsson¹ and Anders
Hellman^{1,*}*

¹ Department of Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

² Center for Electron Nanoscopy, Technical University of Denmark, 2800, Kongens Lyngby,
Denmark

*Correspondence to: anders.hellman@chalmers.se.

Electrodes fabrication

Fe films were deposited on top of ITO coated glass (PGO GmbH, sheet resistance $\leq 20 \Omega/\text{square}$) by physical vapor deposition (PVD 225, Kurt. J. Lesker, base pressure $< 5 \times 10^{-7}$ mbar), and their thickness was measured *in situ* using a quartz-crystal microbalance monitor. The Fe films were converted into Fe_2O_3 by thermal oxidation in a tube furnace in a 3:1 $\text{N}_2:\text{O}_2$ atmosphere. The temperature was ramped from room temperature up to 350°C at a rate of $15^\circ\text{C min}^{-1}$, after which the temperature was kept constant at 350°C for a certain time t_{ox} . Then, the furnace was allowed to cool down to room temperature naturally. t_{ox} was set to 12 h for the $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ disks, $\text{Fe}_2\text{O}_3 + \text{SiO}_2$ disks and $\text{Fe}_2\text{O}_3 + \text{Cu}_2\text{O}$ disks samples, and to 6 h for the $\text{Fe}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ disks samples. Reference Fe_2O_3 samples were fabricated with $t_{ox} = 6$ h, as well as to 6 + 6 h (i.e. two runs each with $t_{ox} = 6$ h). The reference sample shown in all figures in the main manuscript is the 6 + 6 h oxidized sample, which showed slightly better j_{photo} than the 12 h sample (see Figure S4).

Hole-mask colloidal lithography was employed to deposit Ti, Cu, Fe or SiO_2 nanodisks on top of the Fe_2O_3 films (average disk diameter 40 nm, disk thickness 5 nm, surface coverage ranging from 0.01 to 0.21). First, the films were cleaned in ultrasonic bath in acetone and isopropanol for 10 minutes each, then under ozone flow (FHR UVOH 150) for 10 min. Then, a 240 nm thick layer of polymethyl metacrylate (PMMA) was spun on top of Fe_2O_3 , followed by soft baking (170°C , 10 min on hotplate). The PMMA layer was ashed for 5 s in directional O_2 plasma (Plasma Therm BatchTop, 5 s, 50 W, 250 mTorr) in order to increase its hydrophilicity. A 5% weight solution of aluminum chloride hydrate (ACH) was pipetted and adsorbed on the surface for 60 s, followed by rinsing with high resistance (Milli-Q) water and blow-drying with a N_2 stream. Then, a 0.1% weight solution of polystyrene (PS) nanospheres was pipetted and adsorbed, also for 60 s, prior to rinsing and drying as above. As the PS nanospheres are negatively charged, they are attracted to the positively charged surface (due to the ACH), while they repel other nanospheres. This results in a short range ordered array of PS nanospheres. The distance between first nanoparticle neighbors was controlled by adding an appropriate amount of NaCl to the nanosphere solution. Afterwards, a 10 nm thick Cr film was evaporated by physical vapor deposition (PVD 225, Kurt. J. Lesker). The PS nanospheres were then removed from the sample surface by tape stripping (Nitto Scandinavia AB), which left an array of nanoholes into the Cr film. The latter was used as etching mask in the subsequent directional oxygen plasma etch (Plasma Therm BatchTop, 2.5 min, 50 W, 250 mTorr). At this point 5 nm of Ti, Fe or Cu were evaporated using the same PVD system as above. Finally, the mask was removed by lift-off in acetone, followed by rinsing in isopropanol and Milli-Q water and N_2 blow-dry. The Ti disks were converted into TiO_2 by overnight exposure to air. The Fe disks were converted into Fe_2O_3 by thermal oxidation using the same procedure as for the Fe film and t_{ox} of 6 h. The Cu disks were converted into Cu_2O by exposure to isotropic oxygen plasma (TePla 300PC, 2 kW, 120 s).

XPS measurements

In order to analyze the chemical state of the elements present in the nanodisks, XPS characterization on $\text{Fe}_2\text{O}_3 + \text{TiO}_2$, $\text{Fe}_2\text{O}_3 + \text{Cu}_2\text{O}$ and Fe_2O_3 samples was carried out. The results are summarized in Figure S2. As seen panel (a), the Fe(2p) peaks are almost identical for the three samples, with the Fe(2p_{3/2}) peak located between 710.74 and 710.79 eV, in excellent agreement with Fe in the Fe_2O_3 state.¹ As the samples were subjected to atmosphere after fabrication, carbon impurities from the air adsorbed on the surface give rise to the C(1s) peak shown in panel b. The size and shape of the C(1s) peak is very similar for all samples with a binding energy between 285.72 and 285.82 eV, indicating that there was no individual charging of the samples with respect to each other, nor differences in the types of impurities. Panel c shows the Ti(2p) region and as expected, only the sample with TiO_2 disks show peaks here. The Ti(2p_{3/2}) peak is located at 458.93 eV, in good agreement with Ti in the TiO_2 form.¹ The $\text{Fe}_2\text{O}_3 + \text{Cu}_2\text{O}$ sample in panel d clearly shows Cu in an oxidized state with the presence of shake-up peaks. The location of Cu(2p_{3/2}) peak is 932.82 eV, in good agreement with Cu in the Cu_2O form.¹

Mott-Schottky analysis

The Mott-Schottky equation used in this work reads:

$$\frac{A_{\text{contact}}}{C_{\text{bulk}}^2} = \frac{2}{\varepsilon_0 \varepsilon_r N_D} \left(E - E_{fb} - \frac{k_B T}{e} \right)$$

where: A_{contact} is the semiconductor/electrolyte contact area, k_B is the Boltzmann constant, T is the absolute temperature, e is the elementary charge, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the semiconductor (estimated to be 19 from a previous work on photoanodes fabricated according to the same procedure used here²), N_D is the density of charge donors in the semiconductor (typically replaced by N_A in case of a majority of charge acceptors), and E_{fb} is the flat band potential in the semiconductor.³

Figure S1. Extension of Figure 1b explaining the origin of the direction of charge transfer, and therefore of the associated dipole-like field, in the case of weakly doped Fe_2O_3 . We determined Fe_2O_3 to be n-doped from the Mott-Schottky, and using the value of the donor density extracted from the Mott-Schottky plot we determined that the Fermi level lies ~ 0.25 eV below the bottom of the conduction band. This allows the relative Fermi level of TiO_2 to be 0.85 eV above the undoped case without changing the charge transfer picture described in the main body of the manuscript. Given that the formation energy of TiO_2 is much larger as compared to hematite there should be a thermodynamic driving force to oxidize the TiO_2 more as compared to the Fe_2O_3 , hence, we expect the n-doping should be less pronounced on the TiO_2 disks as compared to Fe_2O_3 . These arguments support the same charge transfer direction as in the case of undoped Fe_2O_3 . Also, the Fermi energy of the doped Fe_2O_3 is lower than that of Cu_2O , which leads to the opposite direction of charge transfer direction and therefore of dipole-like field.

Figure S2. XPS measurements on Fe_2O_3 reference sample (black), $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ disks (green) and $\text{Fe}_2\text{O}_3 + \text{Cu}_2\text{O}$ disks (red). (a) Fe(2p) peak. (b) C(1s) peak. (c) Ti(2p) peak. (d) Cu(2p) peak. The traces have been shifted vertically to ease comparison.

Figure S3. Steady state photocurrent density as a function of applied electrochemical potential and under AM 1.5 solar simulated illumination, on $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ disks (green diamonds) and $\text{Fe}_2\text{O}_3 + \text{SiO}_2$ disks (blue squares). Fe_2O_3 thickness: 25 nm thick, nanodisks average diameter: 41 nm, thickness: 5 nm, surface coverage: 0.1. The solid lines are a guide to the eye.

Figure S4. j - E curves for Fe_2O_3 samples: reference Fe_2O_3 film with $t_{\text{ox}} = 6+6$ h (two oxidation runs, circles), reference Fe_2O_3 film with $t_{\text{ox}} = 6+6$ h and Fe_2O_3 disks on top (squares), reference Fe_2O_3 film with $t_{\text{ox}} = 12$ h (one oxidation run, downward triangles) and reference Fe_2O_3 film with $t_{\text{ox}} = 12$ h after the same 2 minutes O_2 plasma treatment to oxidize Cu disks into Cu_2O (upward triangles).

Figure S5. Photocurrent density from cyclic voltammetry under AM 1.5 solar simulated illumination, in 0.1 M KOH + 0.3 M H₂O₂, for bare Fe₂O₃ film (circles), Fe₂O₃ + Fe₂O₃ disks (squares), Fe₂O₃ + TiO₂ disks (diamonds) and Fe₂O₃ + Cu₂O disks (triangles).

Figure S6. Comparison of photocurrent density from cyclic voltammetry under AM 1.5 solar simulated illumination, with and without additional H₂O₂, for Fe₂O₃ + Fe₂O₃ disks (circles and squares respectively), and for Fe₂O₃ + TiO₂ disks (triangles and diamonds, respectively).

Figure S7. Nyquist plots (real component vs. negative imaginary component of the total impedance Z) for $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ nanodisks at different values of potential E .

Figure S8. Equivalent circuits used to fit the Nyquist plots. (a) Hamann's circuit with surface states, used for $E < 1.6 \text{ V}_{\text{RHE}}$ under illumination. (b) Randle's circuit without surface states used for $E \geq 1.6 \text{ V}_{\text{RHE}}$ under illumination and at all potentials in the dark.

Figure S9. Top-view SEM micrographs of $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ nanodisks, with increasing surface coverage of the nanodisks, θ , from 0 (corresponding to a bare Fe_2O_3 film) to 0.21. The nanodisks are not obvious to identify due to their small thickness and to the poor atomic contrast between Fe and Ti.

Figure S10. (a) Charge transport efficiency η_{tr} within the photoanode as function of E for different surface coverage θ of TiO_2 nanodisks: $\theta = 0$ (circles), $\theta = 0.01$ (squares), $\theta = 0.05$ (upward triangles), $\theta = 0.1$ (diamonds), $\theta = 0.14$ (downward triangles) $\theta = 0.21$ (rectangular triangles). (b) Semiconductor/electrolyte charge transfer efficiency η_{ct} as function of E .

Supplementary References

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