

Supplementary Material

“Enhanced water splitting on thin-film hematite photoanodes functionalized with lithographically fabricated Au nanoparticles”

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Experimental details

Fe films were deposited by electron-beam evaporation on top of ITO coated glass pieces (20mm x 15mm, $\leq 15 \Omega/\text{sq}$, PGO GmbH) and subsequently oxidized in a furnace for 6 hours at 350 °C in a mixed N_2/O_2 atmosphere. Then, Au nanodisks (50 or 100 nm diameter, 25 nm height, ca. 5% surface coverage) were deposited on top of the Fe_2O_3 films by Hole Mask Colloidal Lithography. The technique is described in detail in Reference [17] of the main body of the paper and we therefore report only the main parameters here. The sacrificial layer consisted of a 240 nm thick resist (MCC 950k PMMA A4, Microlithography Chemicals Corp.). 0.1% by weight aqueous solutions of 58 or 110 nm PS beads (Interfacial Dynamics Corporation) were pipetted onto the resist layer. The adsorption time was 1 minute in all cases. A 10 nm thick electron beam evaporated Cr layer was used as hole mask (Lesker evaporator, model PVD 225, evaporation rate of $2 \text{ \AA}/\text{s}$). The resist under the holes in the Cr mask was etched by O_2 plasma (Plasmatherm Batchtop m/95, 250 mTorr, 50W, 2min 30s). Before electron-beam evaporating the Au disks, 5 nm of Ti were deposited in order to improve adhesion to the Fe_2O_3 films (Lesker evaporator, model PVD 225, evaporation rate of $2 \text{ \AA}/\text{s}$). After fabrication, the samples were examined in a high-vacuum scanning electron microscope (Zeiss Supra 60 VP). The thickness of the Fe_2O_3 films was measured in a surface profiler (Dektak D150, Veeco). Optical extinction measurements in the wavelength range between 300 and 900 nm were performed in a Cary 5000 spectrophotometer (Varian), by measuring the

optical transmission in the forward direction. Photoelectrochemical measurements were carried out in a standard three-electrode configuration, with the fabricated samples as working electrode, a Pt wire as counter electrode, and a saturated calomel electrode (saturated KCl, Radiometer Analytical) as reference electrode. A 1M KOH solution (pH=13.5) was used as electrolyte. The light source used in all measurements was an ozone-free arc Xe lamp (75 W, model 6263, Newport). A water filter was used to eliminate IR light. The distance between the lamp and the cell was adjusted so that the total light intensity was 100 mW/cm^2 . The light intensity was measured with a laser power meter (Molelectron Detector Incorporated). Given the lamp irradiance (from product specification) and by comparison with the AM 1.5 spectrum, it is reasonable to consider the photocurrent obtained under these illumination conditions to be a factor between 3 and 4 larger than what would have been obtained under AM 1.5 illumination conditions. For the IPCE measurements, a high pass filter (Schott) was used to eliminate UV light that might pass the monochromator (Photon Technology International).

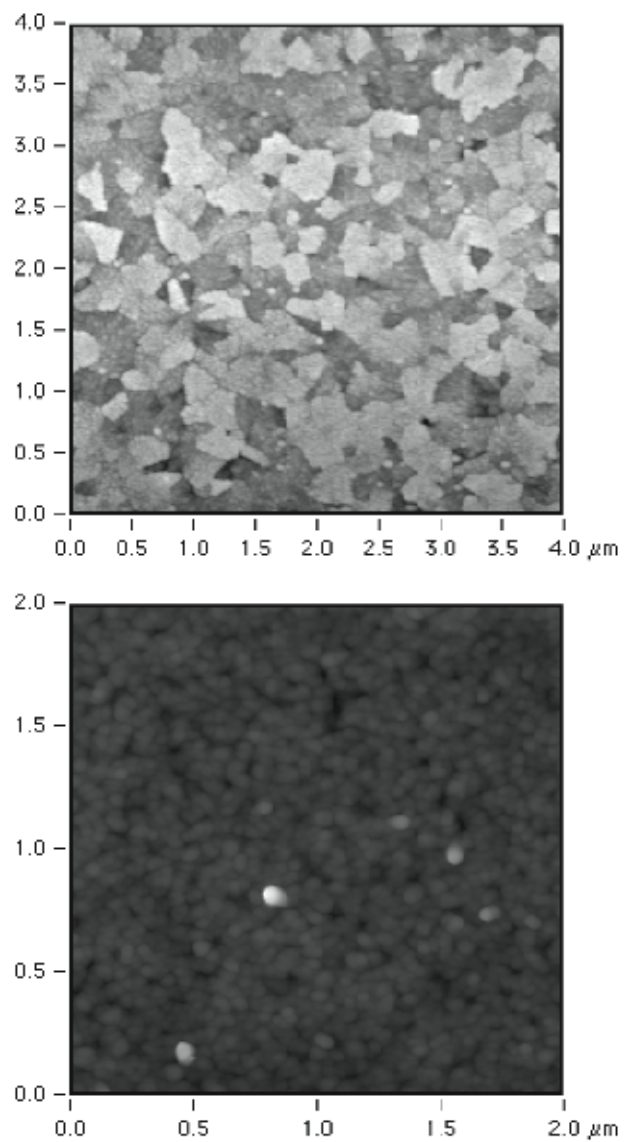


Figure S1. Top: AFM scan height image of an ITO- covered glass substrate. Bottom: AFM height image of a 55 nm Fe_2O_3 film on ITO. Note the different scale between the two scans. The height range is 23 and 121 nm respectively. The RMS roughness was measured to be of 2.8 and 4.0 nm for the ITO and the Fe_2O_3 , respectively.

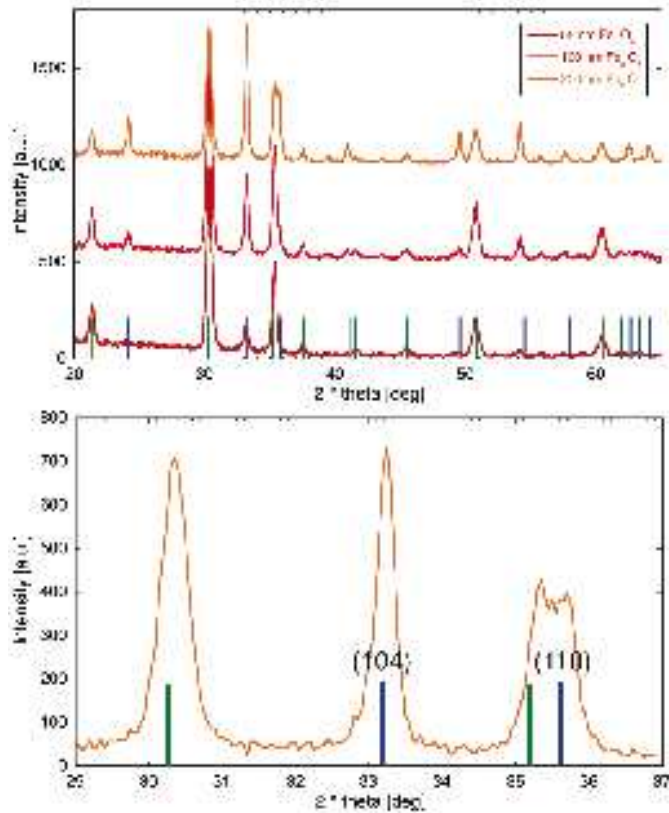


Figure S2. Top: XRD scan of iron oxide films of different thickness. The peaks corresponding to Fe₂O₃ and ITO are indicated by blue and green segments, respectively. The Fe₂O₃ peaks are more easily detectable in the scan of the thickest film. Bottom: XRD scan of the 200 nm thick iron oxide film between diffraction angles of 29 and 37 degrees. The presence of the (110) Fe₂O₃ peak is here clearly distinguishable.

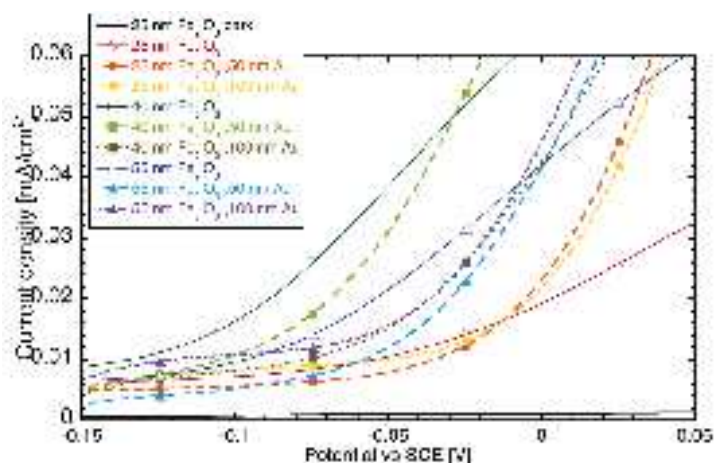


Figure S3. Photocurrent onset potential for functionalized and reference samples. For a given Fe_2O_3 thickness, the presence of Au nanodisks does not shift considerably the onset potential. This points at little – if any – catalytic effect of the Au nanodisks on O_2 evolution.

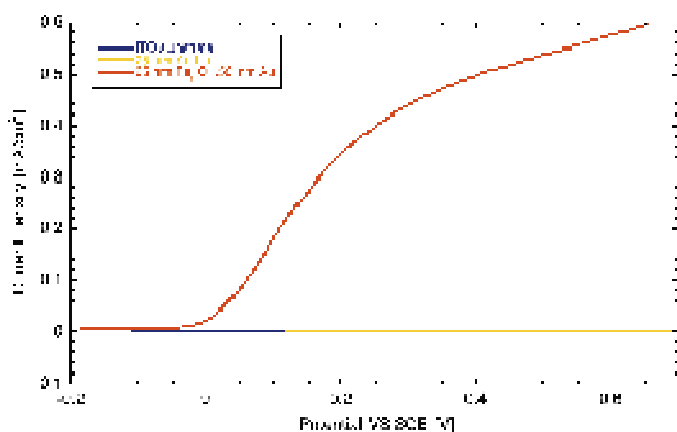


Figure S4. Comparison between the photocurrent of a functionalized Fe_2O_3 sample and the photocurrent of a blank ITO substrate and of an ITO substrate covered with 5 nm Ti (for adhesion) + 25 nm Au. Neither the ITO nor the Au shows any notable photoactivity.

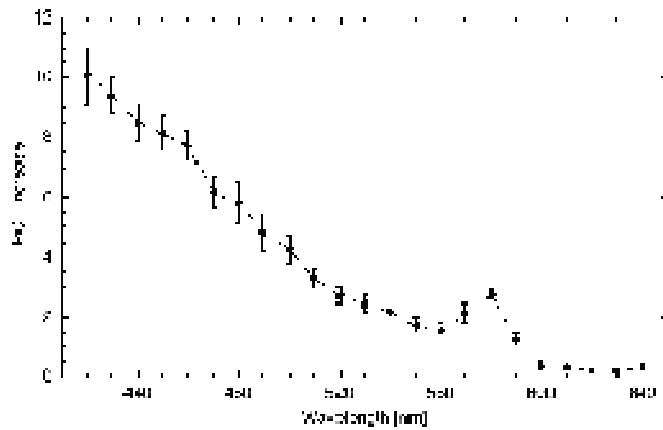


Figure S5. Average IPCE increase measured on four different 25 nm Fe_2O_3 samples functionalized with Au nanodisks of 50 nm diameter and 25 nm height. The behavior of the IPCE increase follows very closely the one shown in Figure 3b. For these four samples, the average IPCE increase is 10.07 at 420 nm, with a standard deviation of 0.95.