Electronic Supporting Information

Solar water splitting: preserving the beneficial smaller feature size in porous α-Fe_2O_3 photoelectrodes during annealing

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Experimental Details

In order to fabricate FeOOH layers, anodic electrodeposition was carried out using an aqueous acidic solution (pH 4.1) containing 0.02 M $FeSO_4 \cdot 7H_2O$ (99%, Sigma-Aldrich) according to literature.[1,2] In our case anodic deposition was carried out potentiostatically at 1.2 V for 8 min at 70~80 °C using a power supply (Voltcraft VSP 2653) – this resulted in a FeOOH layer thickness of ~200 nm. As substrate we used Fluorine-doped tin oxide (FTO-15 Ω, Solaronix, Switzerland). Before deposition, the FTO glass was washed with acetone, ethanol, and then deionized water. After each deposition, the film on the FTO was thoroughly rinsed with deionized water, and dried with a gentle stream of nitrogen gas. DI water purified with a Barnstead purification system (resistivity $\geq$ 18.2 MΩ) was used to prepare all the solutions used in this study. The as-deposited films were subsequently annealed in furnace (Heraeus, ZEW 1450-4, Germany) at 500 °C and 600 °C for 2 h, respectively, and then further annealed at 750 °C for additional 20 min in air and argon atmospheres, respectively. For the argon atmosphere, the furnace was purged with argon (99.9%, Linde Gas, Germany) at least for 20 min in a flux of 250 ml min^{-1} before the annealing treatment.

The photoelectrochemical experiments were carried out under simulated AM 1.5 (100 mW cm^{-2}) illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight; RT) in 1 M KOH solution. A three-electrode configuration was used in the measurements, where the α-Fe_2O_3 electrode served as the working electrode (photoanode), a saturated Ag/AgCl as the reference electrode and a platinum foil as the counter electrode. Photocurrent vs. voltage (*I*-*V*) characteristics were recorded by scanning the potential from − 0.5 V to 0.8 V (vs. Ag/AgCl) with a scan rate of 2 mV s^{-1} using a Jaissle IMP 88 PC potentiostat. The measured potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.059\ \mathrm{pH} + E^{\mathrm{o}}_{\mathrm{Ag/AgCl}} \qquad (1)$$

where E_{RHE} is the converted potential vs. RHE, $E^{\mathrm{o}}_{\mathrm{Ag/AgCl}} = 0.1976$ at 25 °C, and $E_{\mathrm{Ag/AgCl}}$ is the experimentally measured potential against Ag/AgCl reference. Photocurrent spectra were acquired at an applied potential of 0.5 V (vs. Ag/AgCl) in 1 M KOH recorded with 10 nm steps in the range of 300-700 nm using an Oriel 6365 150 W Xe-lamp equipped with a Oriel Cornerstone 7400 1/8 m monochromator. Incident photocurrent conversion efficiencies (IPCE) were calculated by IPCE = $(1240 i_{\mathrm{ph}})/(\lambda I_{\mathrm{light}})$, where i_{ph} is the photocurrent density (mA cm^{-2}), λ is the incident light wavelength (nm), and I_{light} (mW cm^{-2}) is the intensity of light source at each wavelength. The Mott-Schottky curves were performed via the use of Zahner IM6 (Zahner Elektrik, Kronach, Germany). Measurements were obtained under dark conditions at a frequency of 500 Hz in 1 M KOH solution.

In order to evaluate the main factors for the different performance of the different geometrics, dye loading was measured for the surface area, The samples annealed at 600 °C/750 °C in air and Ar were immersed in a 300 μm Ru-based dye (cis-bis(isothiocyanato) bis (2,2-bipyridyl4,4-dicarboxylato) ruthenium (II) bis-tetrabutylammonium (D-719, Ecersolar, Taiwan)) solution in a mixture of acetonitrile and tertbutyl alcohol (volume ratio:1:1) for 1 days at 50 °C. After dye-sensitization, the samples were rinsed with ethnoal to remove non-chemisorbed dye. Dye desorption measurements of the dye sensitized Fe_2O_3 layers were carried out by immersing the samples in 5 ml of 0.1 M KOH for 0.5 h. The concentration of fully desorbed dye was measured spectroscopy (Lambda XLS UV/VIS spectrophotometer, PerkinElmer) at 520 nm following a procedure descried in Ref **3**.

X-ray diffraction (X'pert Philips MPD with a Panalytical X'celerator detector, Germany) was carried out using graphite monochromized Cu K*α* radiation (Wavelength 1.54056 Å). Chemical characterization was carried out by X-ray photoelectron spectroscopy (PHI 5600, spectrometer, USA) using AlKα monochromatized radiation. A field-emission scanning electrode microscope (Hitachi FE-SEM S4800, Japan) was used for the morphological characterization of the electrodes.

1. R. L. Spray and K. S. Choi, *Chem. Mat.* 2009, **21**, 3709.
2. L. Wang, C. Y. Lee and P. Schmuki, *Electrochim. Acta* submitted.
3. D. S. Tsoukleris, I. M. Arabatzis, E. Chatzivasiloglou, A. I. Kontos, V. Belessi, M. C. Bernard and P. Falaras, Solar Energy 2005, **79**, 422.

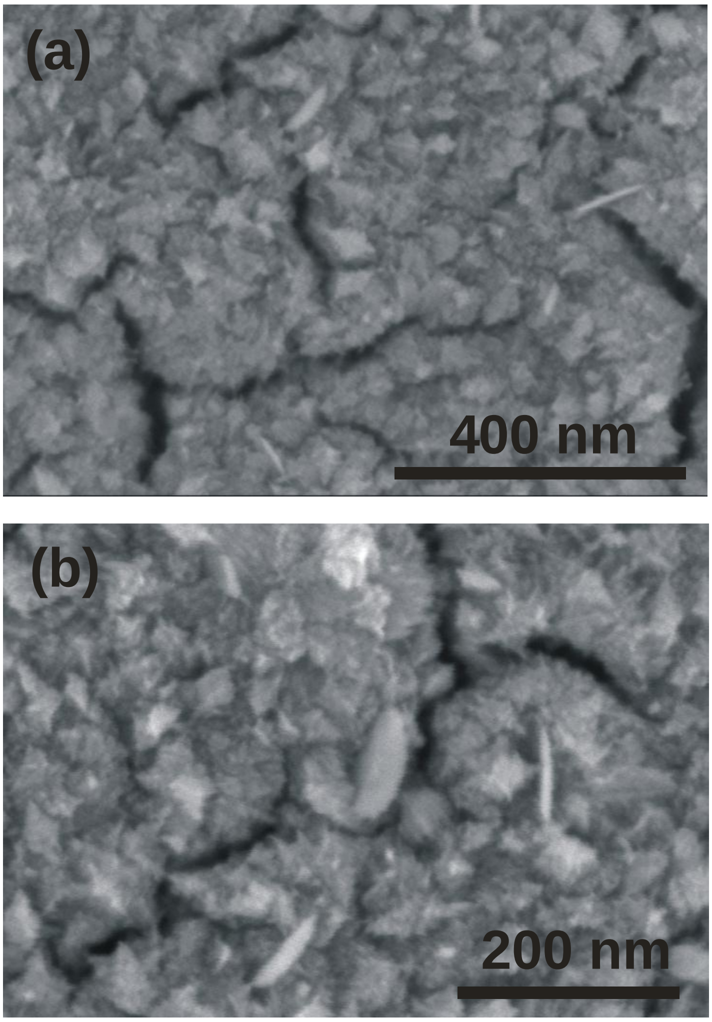

Fig. S1: SEM top view image of as-prepared FeOOH/FTO electrode at (a) lower and (b) higher magnification.

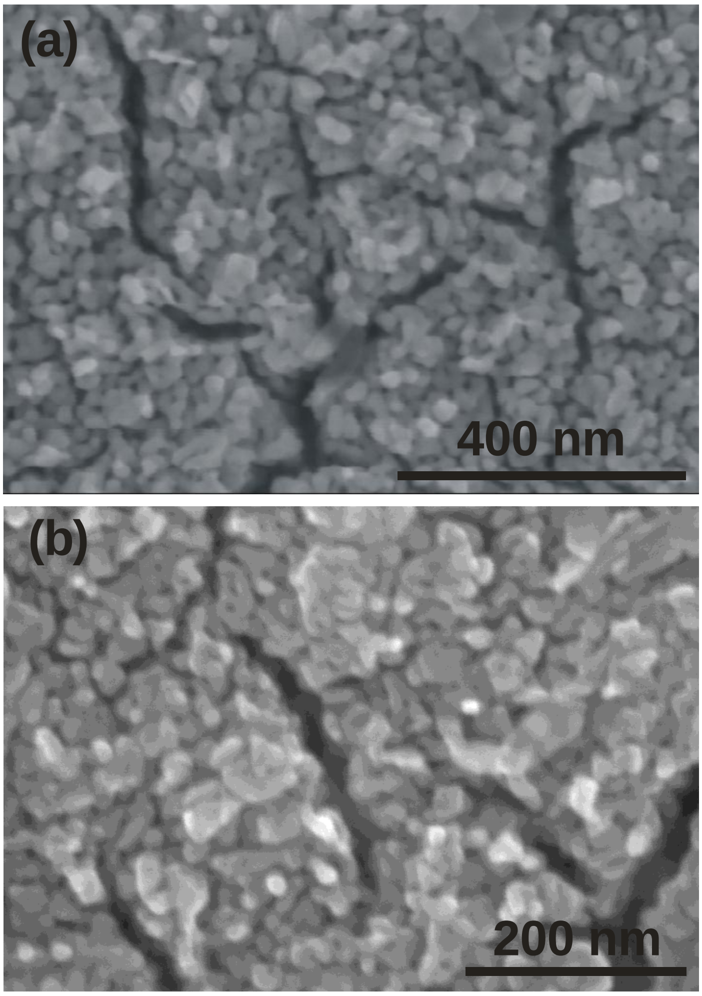

Fig. S2: SEM top view image of FeOOH/FTO electrode annealed at 500 °C in air at (a) lower and (b) higher magnification.

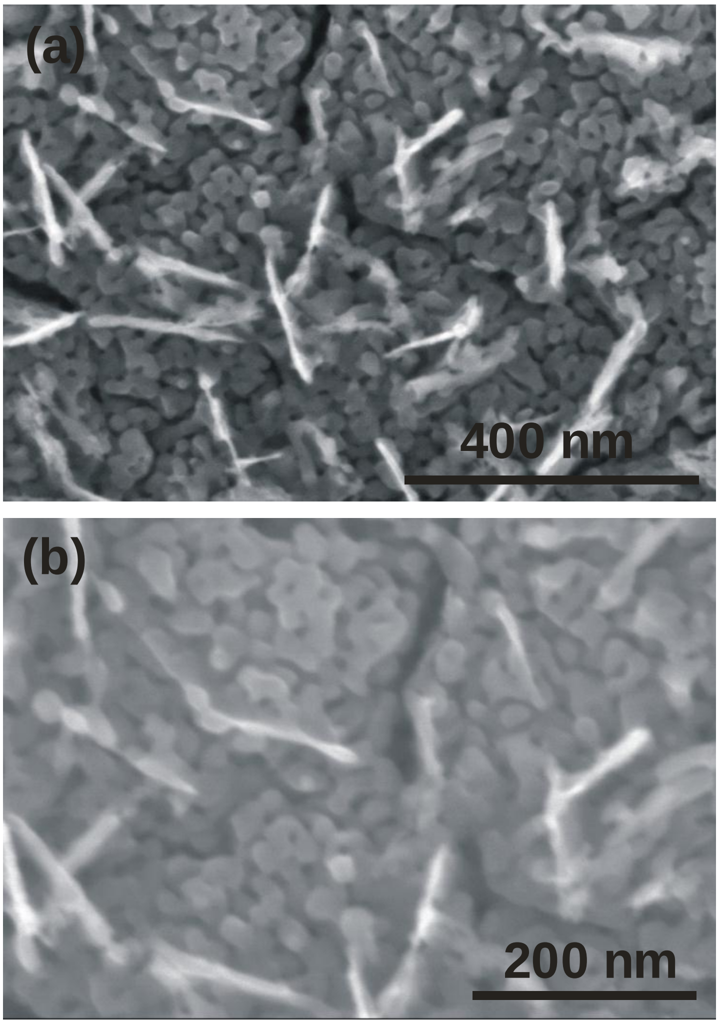

Fig. S3: SEM top view image of FeOOH/FTO electrode annealed at 500 °C in Ar at (a) lower and (b) higher magnification.

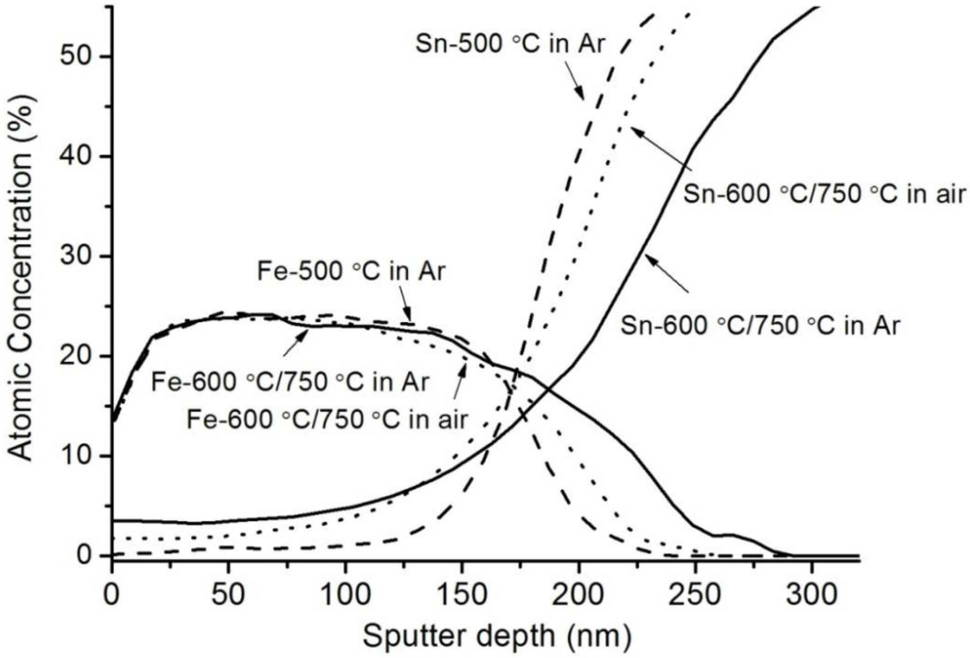

Fig. S4: Fe and Sn depth profiles of the α-Fe_2O_3 electrodes annealed at 500 °C in Ar, and at 600 °C/750 °C in Ar and air, respectively. Measured were the Fe 2p peak and the Sn 3d peak.

Please note that for the comparison air with Ar after the 750 °C treatment a clearly higher Sn concentration tail extends throughout the sample than for air annealing. This may be ascribed to a different diffusion geometry provided in these samples. The Sn concentrations in the outer part are found to the in the range of 3-4% for Ar and ≈2% for air.

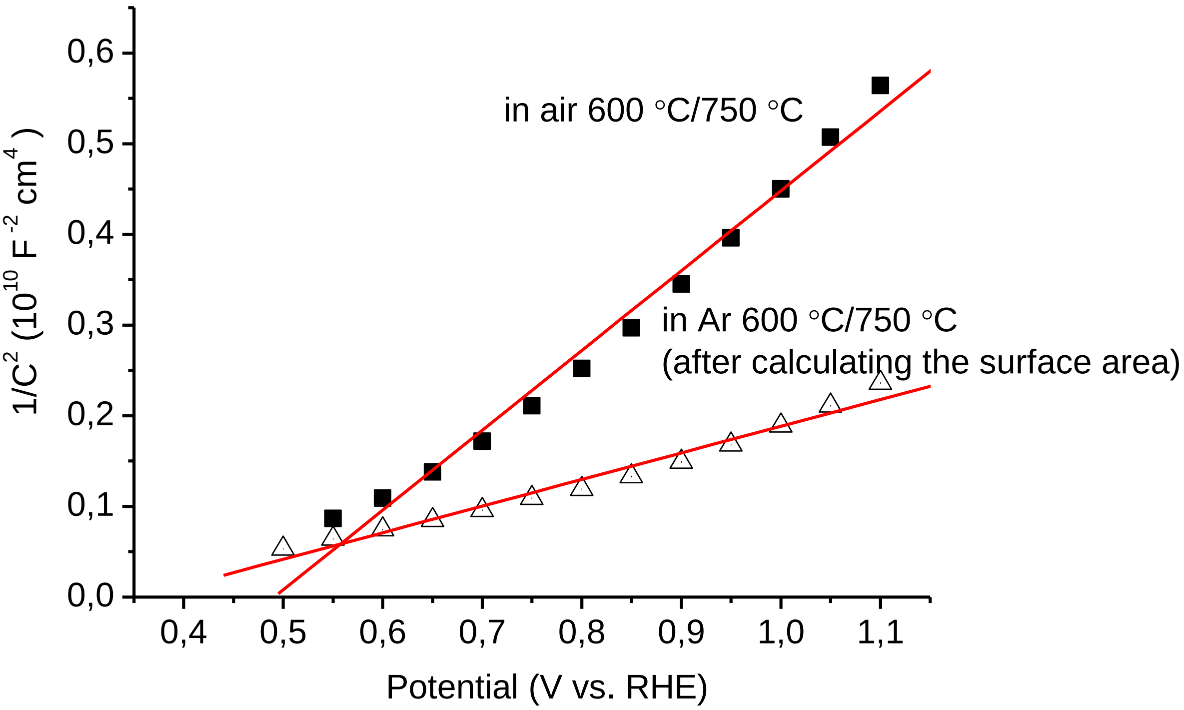

Fig. S5: Mott-Schottky plot for the α-Fe_2O_3 electrodes annealed at 600 °C/750 °C in air and Ar in 1 M KOH under dark recorded at a frequency of 500 Hz.

To understand the role of Sn doping on the electronic properties of α-Fe_2O_3, the Mott-Schottky measurements were performed in the dark to determine the capacitance of the α-Fe_2O_3 electrodes annealed in air and Ar. The carrier density and flatband potential at α-Fe_2O_3/electrolyte interface can be estimated by the Mott-Schottky equation:

$$1/C=(2/e_0\varepsilon\varepsilon_0 N_d)[(V-V_{FB})-kT/e_0] \qquad (2)$$

where C is the specific capacitance (F cm^{-2}), e_0 is the electron charge, ε the dielectric constant of hematite, ε_0 the permittivity of vacuum, N_d the carrier density, V the electrode applied potential, V_{FB} the flatband potential, and kT/e_0 is a temperature-dependent correction term.

Mott-Schottky plots collected from the α-Fe_2O_3 electrodes annealed in air and Ar are present in Fig. S5. The slope determined from the analysis of Mott-Schottky were used to estimate the donor densities, and the electron densities of α-Fe_2O_3 annealed in air and Ar are calculated to be $2.26*10^{20}$ and $7.15*10^{20}$ cm^{-3}, respectively. The surface areas were corrected (normalized to results from dye absorption measurements resulting, in 311 mM for Ar, and 182 mM for air per 0.9 cm^2 projected area).

The amount of Sn doping on the top surface from depth profiles (Fig. S4) shows the values of ≈2% and 3-4% for the electrodes annealed in air and Ar, respectively. In other words the Ar-effect is two-fold i) it maintains a high surface area, and ii) aids Sn diffusion.