Supplementary Information for

Improved Photoelectrochemical Performance of Ti-doped α-Fe_2O_3 Thin Films by Surface Modification with Fluoride

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Experimental details:

Synthesis of the undoped and Ti-doped iron oxide thin films:

A modified method as described in literature[1-4] was used to synthesize the undoped and Ti-doped iron oxide thin films. Electrodeposition was performed with a three-electrode configuration where a graphite rod, Ag/AgCl saturated by KCl and Pt (150 nm)/Ti (50 nm) coated quartz or Fluorine-doped Tin Oxide (TEC 15, Pilkington glass, FTO) were used as counter, reference and working electrodes, respectively. The electrodeposition bath contained an aqueous solution of 5 mM $FeCl_3$ + 5mM KF + 0.1 M KCl + 1 M H_2O_2. KF was added to the solution to shift the reduction potential from Fe^{3+} to Fe^{2+}, making it more negative. For the Ti-doped sample, titanium isopropoxide was used as the Ti-precursor and was complexed in H_2O_2 under stirring to form a clear yellow solution (0.05 M/L). The molar ratio (Ti/(Ti+Fe)) in the electrodeposited solution was fixed at 6%. The final concentration of all the compounds in the electrodeposition solution is 5 mM $FeCl_3$ + 5mM KF + 0.1 M KCl + 1 M H_2O_2 + 0.32 mM Ti-precursor. An EG&G 273A potentiostat controlled by custom software written in LabView (National Instruments) was used to obtain the cyclic voltammograms. The applied voltage was between -0.49 and 0.41V vs. Ag/AgCl. The scan rate was 0.2 V/sec. For the Pt/Ti coated quartz substrate, five cycles were enough to deposit an appreciable amount of iron oxide with a thickness of ~600±90 nm. The FTO substrate required 50 cycles to create a uniformly thick film. After electrodeposition, the films were washed by DI water three times to remove the residual electrolyte followed by calcination at 700 ^oC for the Pt/Ti substrate and 600 ^oC for the FTO substrate. The heating rate was 2 ^oC/min with a dwell time of 4 hours for all samples.

In the case of CoF_3 aqueous solution treated sample, firstly, a 0.1 M CoF_3 aqueous solution was prepared in hood (Note that when dissolve CoF_3 in water, the following reaction happens:

$$4CoF_3 + 2H_2O \rightarrow 4CoF_2 + 4HF + O_2$$

resulting in a pH of ~ 3.0 of the solution with red brown color. We called this solution as CoF_3 aqueous solution in the whole text.). Secondly, the Ti-doped iron oxide thin films were placed in a capped plastic container and dipped in the CoF_3 solution overnight. Finally, the sample was removed from the solution and then rinsed with DI water and dried under a stream of N_2 gas.

Structural characterizations:

X-ray diffraction (XRD) was obtained from samples deposited on FTO rather than on the platinum electrodes. The instrument was a Phillips PANalytical X'PERT powder diffractometer using Cu-Kα radiation with a CNRS position sensitive detector. A Kratos "Axis Ultra" spectrometer using a monochromated Al-Kα source (1486.6 eV) for excitation and an eight-channel detector was used for X-ray Photoelectron Spectroscopy (XPS). The base pressure was 5 x 10^{-10} Torr, and the spectra were calibrated to C_1s at 285.0 eV and processed with Casa XPS. The Ti/(Fe + Ti) ratio was determined from the XPS survey scan from the Fe_2p and Ti_2p photoelectron emission, after fitting a Shirley background and normalizing with Scofield sensitivity factors. Ion etching was conducted at an Ar partial pressure of 10^{-7} Torr at 4 kV and 10 mA/cm^2 resulting in ~20 nm/min etching rate. The thickness of the samples was obtained with a Dektak 5 surface profilometer. Micro-Raman spectra were recorded on a Jobin Yvon LabRam spectrometer using a 632.8 nm excitation laser line. UV-vis spectroscopy was conducted on a Shimadzu UV3600 UV-Nir-NIR Spectrometer with an integrating sphere under reflection mode.

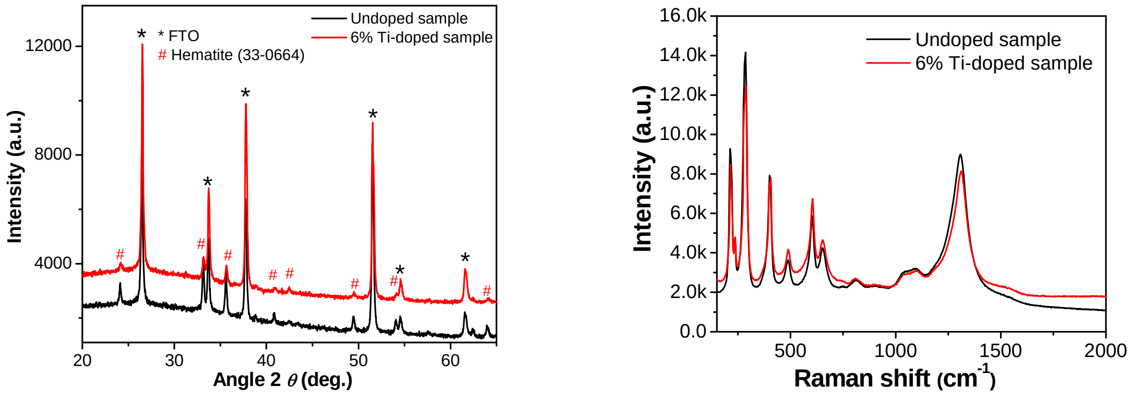
PEC characterizations:

The photoelectrochemical measurements of the samples were measured using a high-throughput photoelectrochemical setup. In brief, the setup consists of a probe in which a Pt counter electrode, an Ag/AgCl reference electrode, a gas diffuser and an optical Fiber which is isolated from the electrolyte via a flat wall borosilicate tube (Chemglass) are housed. The contact to the photoelectrode (which are the working electrode) is made via an O-ring exposing a geometric area of 0.24 cm^2 to the electrolyte and the illumination source; during the experiments no stirring was performed; however, nitrogen gas was bubbled slowly through the electrolyte. The electrolyte consisted of a 1 M NaOH dissolved in Milli-Q water without and with 10 mM glucose which was degassed with N_2 before and during the photoelectrochemical testing (to minimize any Oxygen Reduction reaction at the counter electrode). In the presence of glucose experiment, a glass frit was used between counter and working electrode. The counter electrode side was kept with 1 M NaOH solution as electrolyte whereas the working electrode side used 10 mM glucose in 1 M NaOH solution as electrolyte, which results in a small chemical bias. The purpose of this is to ensure that photogenerated electrons are used to reduce water not others to hydrogen. Note that in this case little current was also observed at zero applied bias in the dark after adding glucose into the electrolyte, which might be due to the direct exposure of Pt substrate into electrolyte solution due to the existence of pin-holes in the thin films. The illumination source consists on a 1000 W Ozone Free Xenon Lamp (Newport Corporation #6271), which was filtered through a water filter, a monochromator (Newport Corporation CS 260 ¼m), and focused to a fiber optic. For the IPCE measurements, a diffraction grating was used to give a ~20 nm bandpass (FWHM) from 400 to 600 nm and diverse cut-off filters to eliminate second-harmonics for IPCE experiments. For full spectrum visible light photoelectrochemical measurements experiments the diffraction grating was switched to a mirror in the monochromator housing and a 300 nm cut-off filter was used to remove the excess UV from the lamp source. The power density of the collimated beam of white light was controlled precisely by tilting the mirror inside the monochromator. The light intensity existing in the fiber optic was measured with a radiometer (Thorlabs, S120UV/S121B detectors) with power densities from 410 mW/cm^2 for white light experiments and ~10 mW/cm^2 for monochromatic light. The IPCE of the samples was calculated as follows:

$$\text{IPCE (\%)} = (1240 \times i_{\text{photocurrent}}\ \mu\text{A/cm}^2 \times 100) / (\lambda\ \text{nm} \times j_{\text{photons}}\ \mu\text{W/cm}^2)$$

The zero applied bias photocurrent from the experiments was measured with an HP multimeter (HP 4210) while the applied potential photocurrent in a three-electrode configuration was performed with an EG&G 273A potentiostat and the current was measured by the HP multimeter. For the IV or chopped IV curves, the experiments were performed at 100 mV/sec by the potentiostat in a range from -0.5 to 0.8 V vs. Ag/AgCl. The high-throughput screening system is computer controlled by custom software written in LabView (National Instruments).

The AC impedance of iron oxide thin films was measured using a BIO-Logic SP-150 with potentiostat with an impedance analyzer. The iron oxide thin films before and after CoF_3 treatment were used as working electrode while Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The AC amplitude of 10 mV was used for all the measurements. The AC impedance measurements were carried out in the dark at 1 M NaOH solution at a fixed frequency of 100 Hz.



(a) (b)

Figure S1 XRD patterns (a) and Raman spectra (b) of undoped and Ti-doped iron oxide thin films.

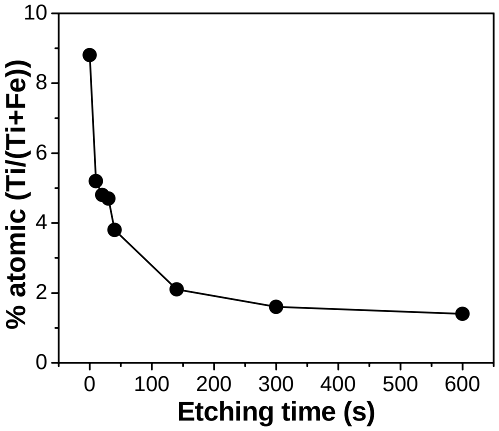


Figure S2 XPS etching (depth) profile for the 6% Ti-doped sample obtained from Ar^+ etching.

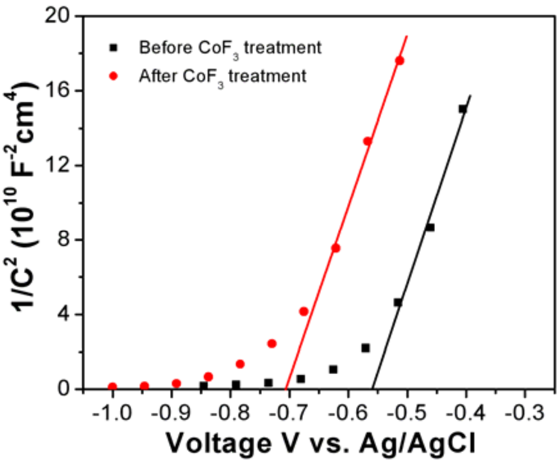


Figure S3 Mott-Schottky plots for iron oxide thin films before and after CoF_3 treatment in the 1 M NaOH electrolyte.

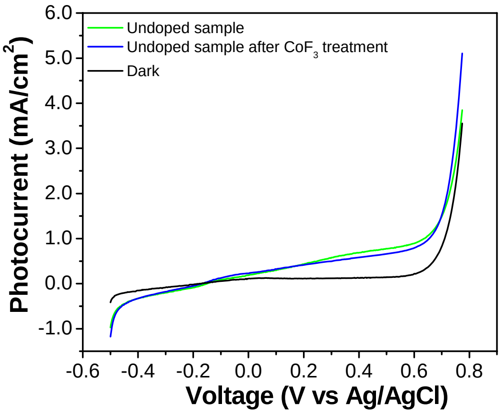
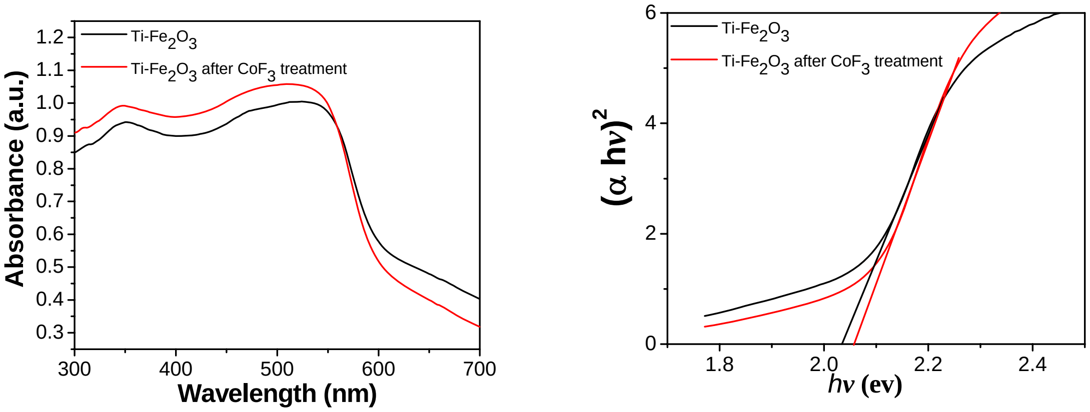


Figure S4 IV curves for the undoped iron oxide thin film photoanodes before and after CoF_3 aqueous solution treatment under 410 mW/cm^2.



(a) (b)

Figure S5 UV-Visible spectra (a) and Tauc plots (b) of 6% Ti-doped sample before and after CoF_3 aqueous solution treatment.

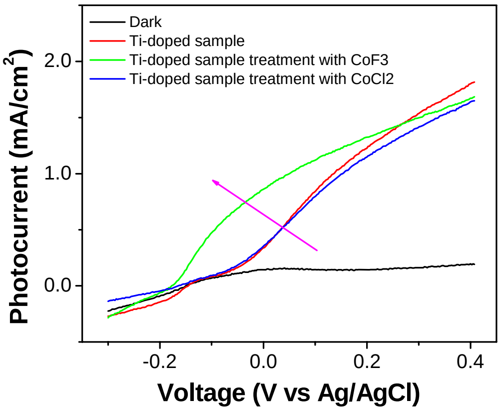


Figure S6 Comparison in PEC performance of untreated and treated samples in CoF_3 and $CoCl_2$ aqueous solutions with the same pH, respectively.

References:

1. Schrebler, R.; Bello, K.; Vera, F.; Cury, P.; Munoz, E.; deRio, R.; Meier, H. G.; Cordova, R.; Dalchiele, E. A. Electrochem. Solid State Lett. 2006, 9, C110.
2. Schrebler, R.; Bello, K.; Vera, F.; Cury, P.; Munoz, E.; Rio, R. D.; Meier, H. G.; Cordova, R.; Dalchiele, E. A. Electrochem. Solid State Lett. 2007, 10, D95.
3. Hu, Y. -S.; Kleiman-Shwarsctein, A.; Forman, A. J.; Hazen, D.; Park, J. N.; McFarland, E. W. Chem. Mater. 2008, 20, 3803.
4. Kleiman-Shwarsctein, A.; Hu, Y. -S.; Forman, A. J.; Stucky G. D.; McFarland, E. W. J. Phys. Chem. C 2008, 112, 15900.