

Electronic Supporting Information

Enhanced Photoelectrochemical Oxidation of Water over Undoped and Ti-doped α -Fe₂O₃ Electrodes by Electrochemical Reduction Pretreatment

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Total 6 pages and Figures S1~S6.

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Experimental Details

The undoped and Ti-Fe₂O₃ films were prepared on indium-doped tin oxide (ITO) conducting glass by a slightly modified method described in ref ¹. Briefly, the ethanol based 60 mM FeCl₃ solution was dispersed onto the ITO glass by spin-coating, and subsequently heated in air at 350 °C for 5 min. This procedure was repeated 8 times and then the film was annealed in air at 550 °C for 4 h. Ti-doped samples were prepared under similar conditions as for undoped Fe₂O₃, adding 5 mM titanium butoxide (99%, Aldrich) as the Ti precursor. The film thickness was estimated to be ~100 ± 10 nm (profilometer, Veeco Dektak 150). The method of making film photoelectrodes is the same as that described previously ². The illuminated surface area of films was 0.28 cm² (Φ 0.6 cm).

(Photo)electrochemical experiments were the same as that reported previously,³ using the film electrode as a working electrode, saturated calomel electrode (SCE) as a reference electrode and a large surface area of Pt mesh as a counter electrode. For visible light illumination, a glass filter (FGL 420, Thorlabs Inc.) was used to remove light at $\lambda < 420$ nm. The average incident white light and visible light intensity into the reactor cell was ~180 and ~130 mW cm⁻², respectively, detected by a photodiode (S370, UDT Instruments) unless otherwise specified. A layer of FeOOH was photoelectrochemically deposited on the Ti-Fe₂O₃ surface in 0.1 M FeCl₂ (pH 4.1) by the same method described in the literature⁴. The amount of FeOOH is in terms of the passed charge (by integrating photocurrent) and its thickness is not optimized. As explained in the literature,⁴ since O₂ evolution occurs simultaneously during the photodeposition of FeOOH, the value reported corresponds to the upper limit of the amount of FeOOH deposited. Electrochemical impedance spectroscopy (EIS) measurements were the same as that described previously ³ under a simulated sunlight illumination (AM 1.5 G; 100 mW cm⁻²) obtained by a 150 W xenon lamp (Newport 6255) coupled with an AM 1.5 global filter (Newport 81094). The Mott-Schottky experiments were performed in the dark by applying the starting potential for 1 min and then performing a potential scan from negative to positive with a potential step of 50 mV and equilibrium time for 30 s at each potential. The magnitude amplitude of the ac modulation was set at 10 mV and other experimental conditions are the same as those for the EIS measurements. Scanning

electron microscopy images (SEM) and energy dispersion spectra (EDS) were collected with a field emission microscopy (Zeiss ULTRA 55). X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALab220i-XL) was performed with Al K α as radiation source. The binding energy was referenced to the C1s level (284.5 eV) due to surface contaminants. The transmittance (T) and reflectance (R) measurements for the samples were made with a spectrophotometer (Shimadzu UV-2550) equipped with an integrating sphere using BaSO₄ as the background.

An aqueous solution of 1.0 M NaOH, deaerated with nitrogen flow, was used as an electrolyte in all experiments. All experiments were performed at room temperature and normally repeated twice. Comparison experiments (before and after ER pretreatment) were performed over an identical electrode. All other chemicals and solvents were at least of analytical grade and used as received. Milli-Q-Water (Millipore Corp, 18.2 M Ω cm at 25 °C) was used. All potentials in the paper are vs. SCE.

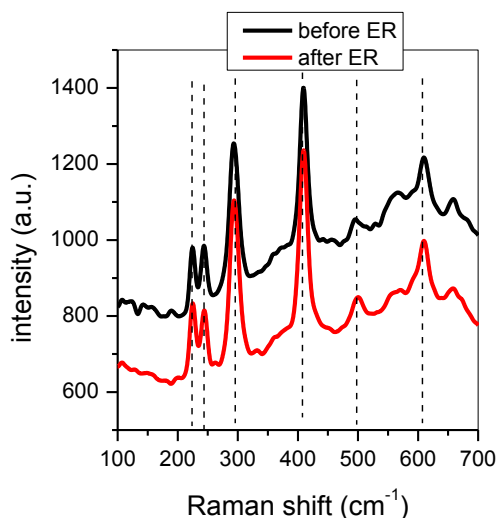


Figure S1. Raman spectra of Ti-Fe₂O₃ thin films before and after electrochemical reduction at -1.0 V_{SCE} for 20 min. The dashed lines highlight the characteristic Raman peaks of α -Fe₂O₃.

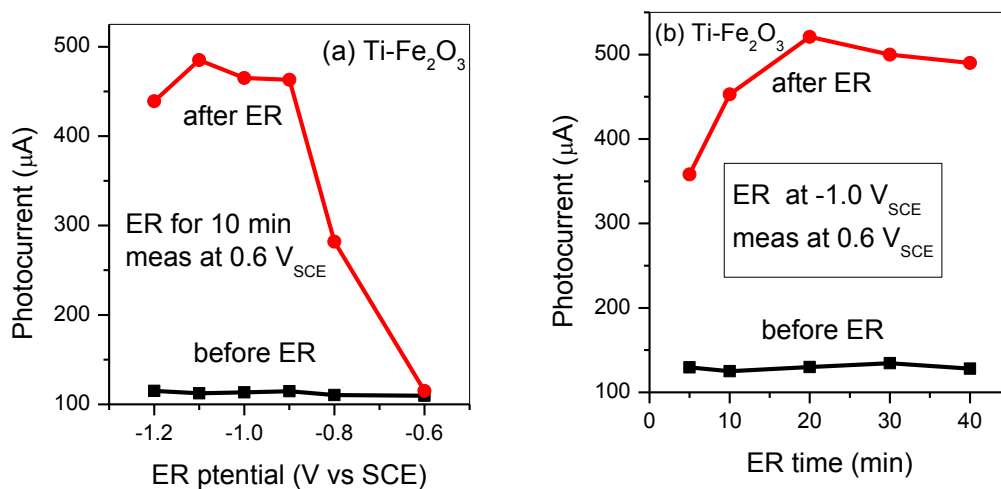


Figure S2. Photocurrent of Ti-Fe₂O₃ electrode under visible light versus ER potential (a) and ER time (b).

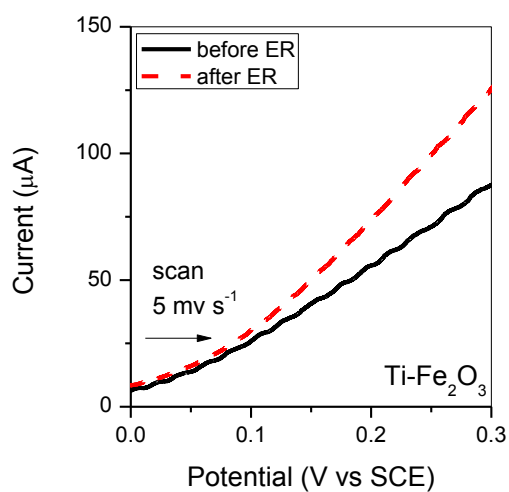


Figure S3. *I-V* curves of Ti-Fe₂O₃ electrodes under white light illumination before and after ER at -1.1 V_{SCE} for 20 min. Other experimental conditions are the same as that in Figure 2 in the text.

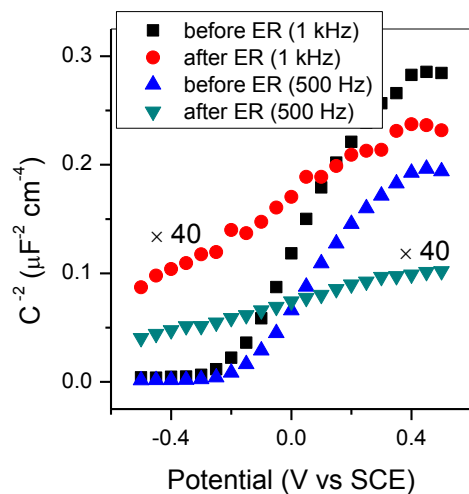


Figure S4. Mott-Schottky plots of Ti-Fe₂O₃ electrodes before and after ER at -1.1 V_{SCE} for 20 min. Note that the data shown for the ER treated electrode were multiplied by a factor of 40.

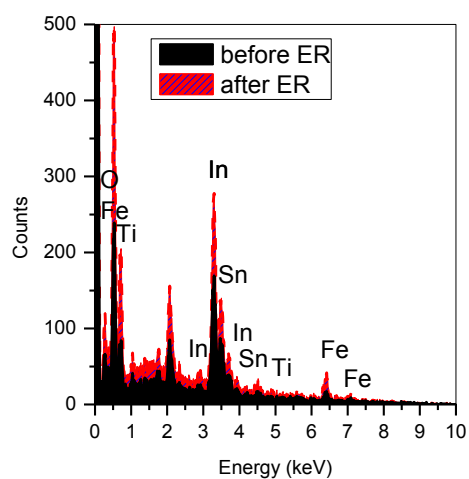


Figure S5. Typical EDX patterns of Ti-doped iron oxide thin films before and after electrochemical reduction at -1.0 V_{SCE} for 20 min.

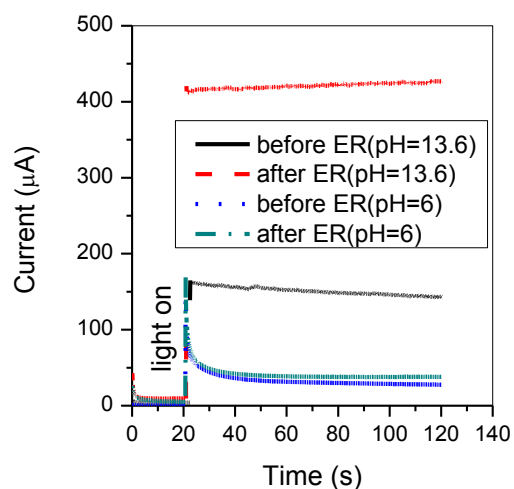


Figure S6. $I-t$ curves of Ti-Fe₂O₃ electrodes under visible light illumination before and after ER at -1.1 V_{SCE} for 20 min. pH 13.6: 1 M NaOH; pH 6: 1 M NaClO₄.

Notes and references

1. G. Wang, Y. Ling, D. A. Wheeler, K. E. N. George, K. Horsley, C. Heske, J. Z. Zhang and Y. Li, *Nano Lett.*, 2011, **11**, 3503-3509.
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3. X. F. Cheng, W. H. Leng, D. P. Liu, Y. M. Xu, J. Q. Zhang and C. N. Cao, *J. Phys. Chem. C*, 2008, **112**, 8725-8734.
4. J. A. Seabold and K.-S. Choi, *J. Am. Chem. Soc.*, 2012, **134**, 2186-2192.