Electronic Supplementary Information (ESI)

Bifunctional TiO_2 underlayer for α–Fe_2O_3 Nanorod based PEC cell: Enhanced interface and Ti^{4+} doping

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1. Supporting figures and captions.

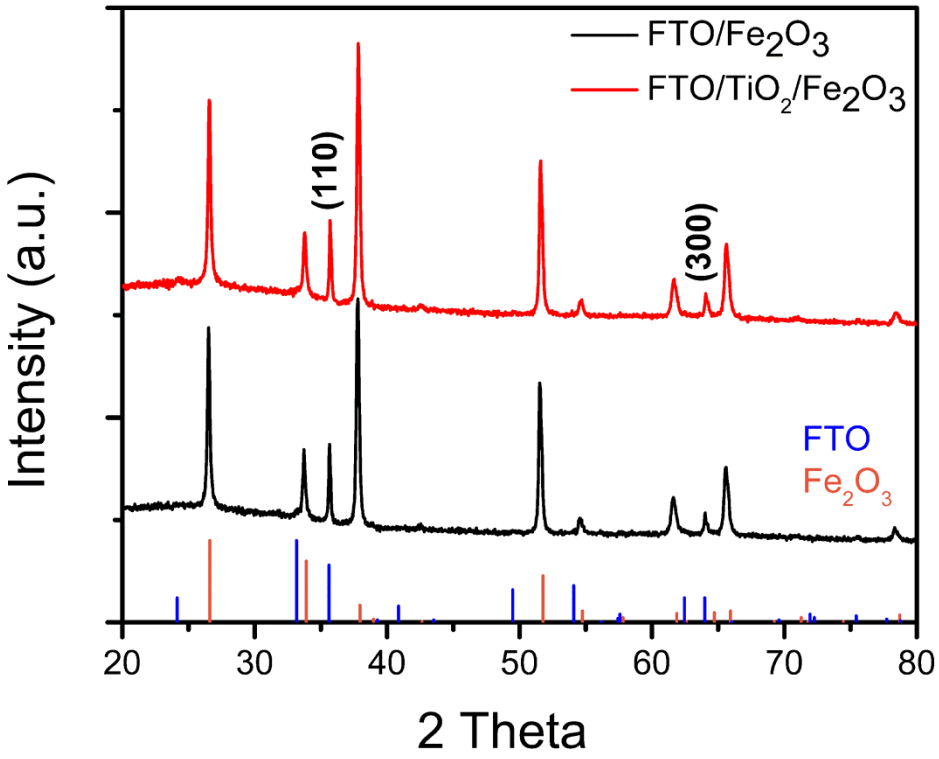


Fig. S1.X-ray diffraction patterns of FTO/α–Fe_2O_3 and FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800°C. With the exception of FTO substrate peaks, all other peaks can be indexed to α–Fe_2O_3 (JCPDS card # 33–0664). Both FTO/α–Fe_2O_3 and FTO/TiO_2/α–Fe_2O_3 samples display similar XRD patterns with a predominant (110) diffraction peak, which has been suggested as preferential direction for electron transport in hematite photoanodes.[1]

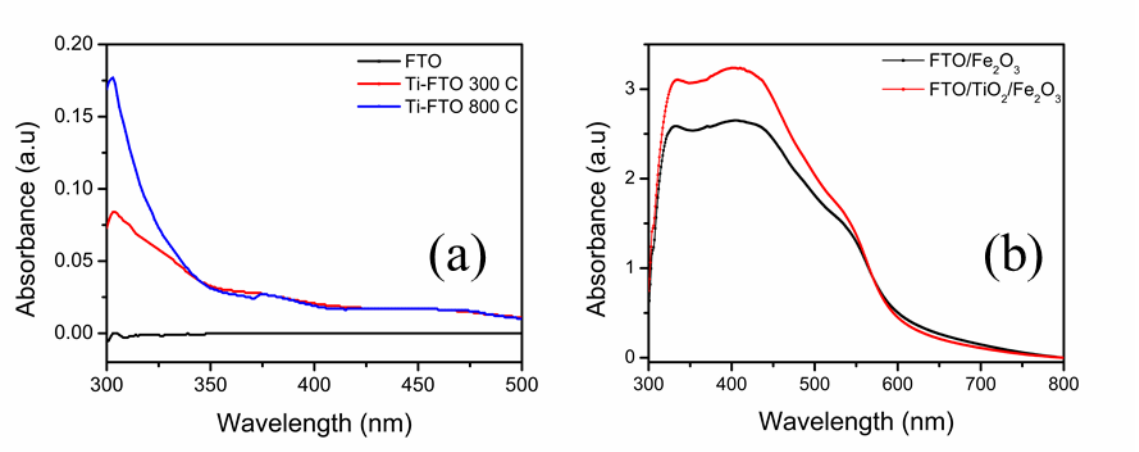
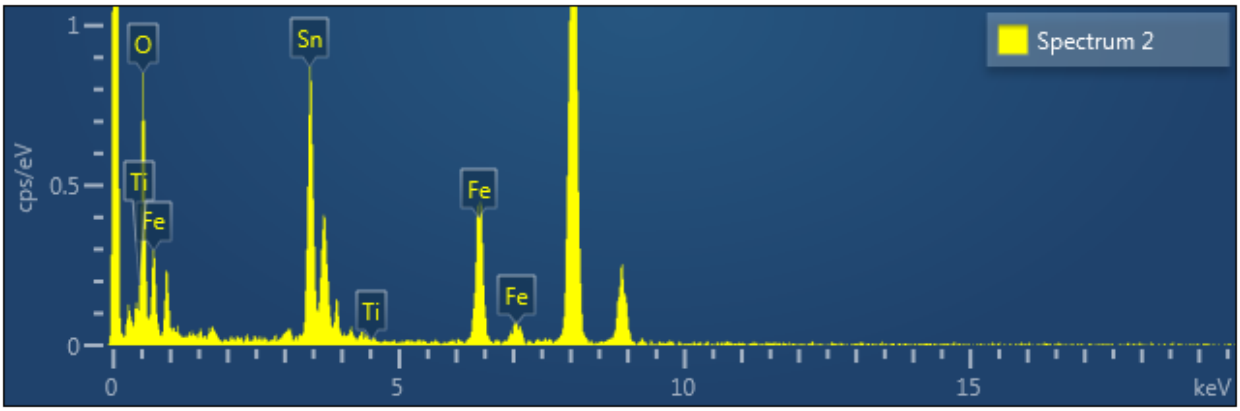


Fig. S2. (a) Optical property of FTO/TiO_2 samples sintered at various temperatures, which shows the absorption coefficient as a function of wavelength. The absorption edges near 350 nm are characteristic of TiO_2 thin films,[2] suggesting that the FTO substrates are successfully modified with TiO_2 layers after spin coating. Although 800°C sintered FTO/TiO_2 sample shows the highest value of absorption coefficient, this can result from the difference in film thickness. (b) FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800 °C showed higher absorption when compared to FTO/α–Fe_2O_3 photoanodes. Higher absorption can be interpreted as an implication of clustered α–Fe_2O_3 density, which probably resulted from different nucleation mechanism during the hydrothermal synthesis or probably due to light scattering induced by the TiO_2 underlayers at the FTO/α–Fe_2O_3 interface.



	Weight %	Atomic %
O	29.58	70
Ti	0.17	0.14
Fe	20.54	14.01
Sn	49.71	15.85
Total	100	100

Fig. S3. TEM-EDS mapping results conducted on FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800°C.

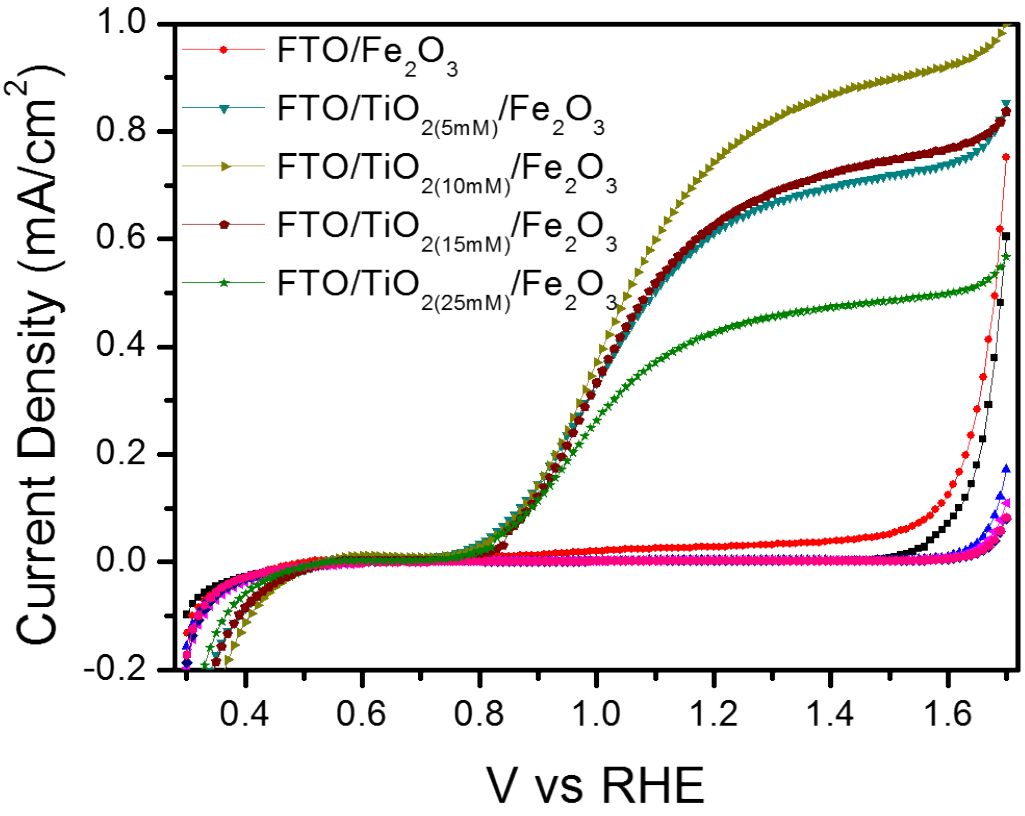


Fig. S4. Photocurrent-potential (*J-V*) curves for PEC water oxidation reaction of FTO/α–Fe_2O_3 and FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 550°C under standard illumination conditions. Photocurrent was sensitive to the thickness of TiO_2 underlayers. There was a decrease in photocurrent increasing the TiO_2 sol concentration more than 10mM.

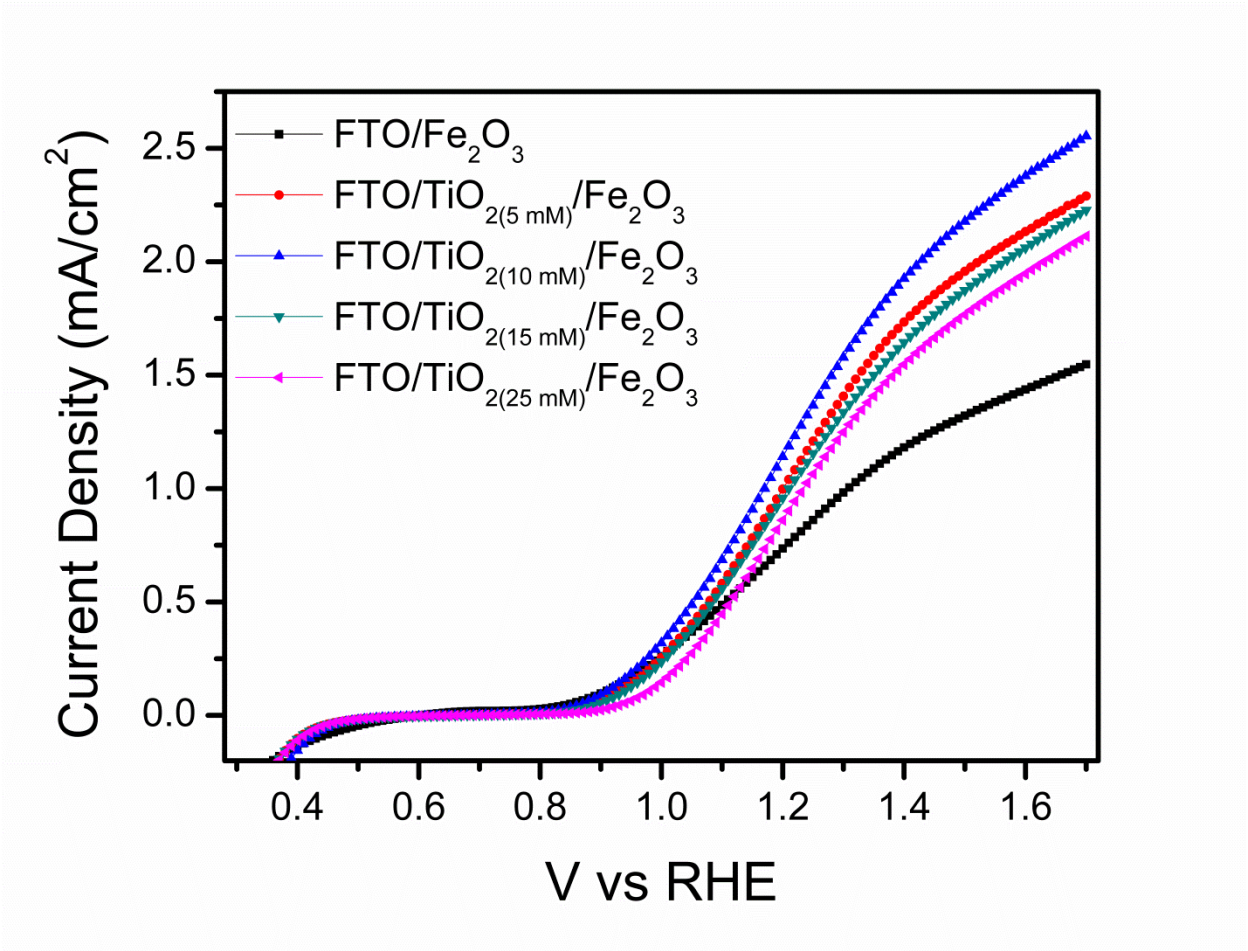


Fig. S5. Photocurrent-potential (*J-V*) curves for PEC water oxidation reaction of FTO/α–Fe_2O_3 and FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800°C under standard illumination conditions. Photocurrent was sensitive to the thickness of TiO_2 underlayers. There was a decrease in photocurrent and an anodic shift for photoanodes increasing the TiO_2 sol concentration more than 10mM.

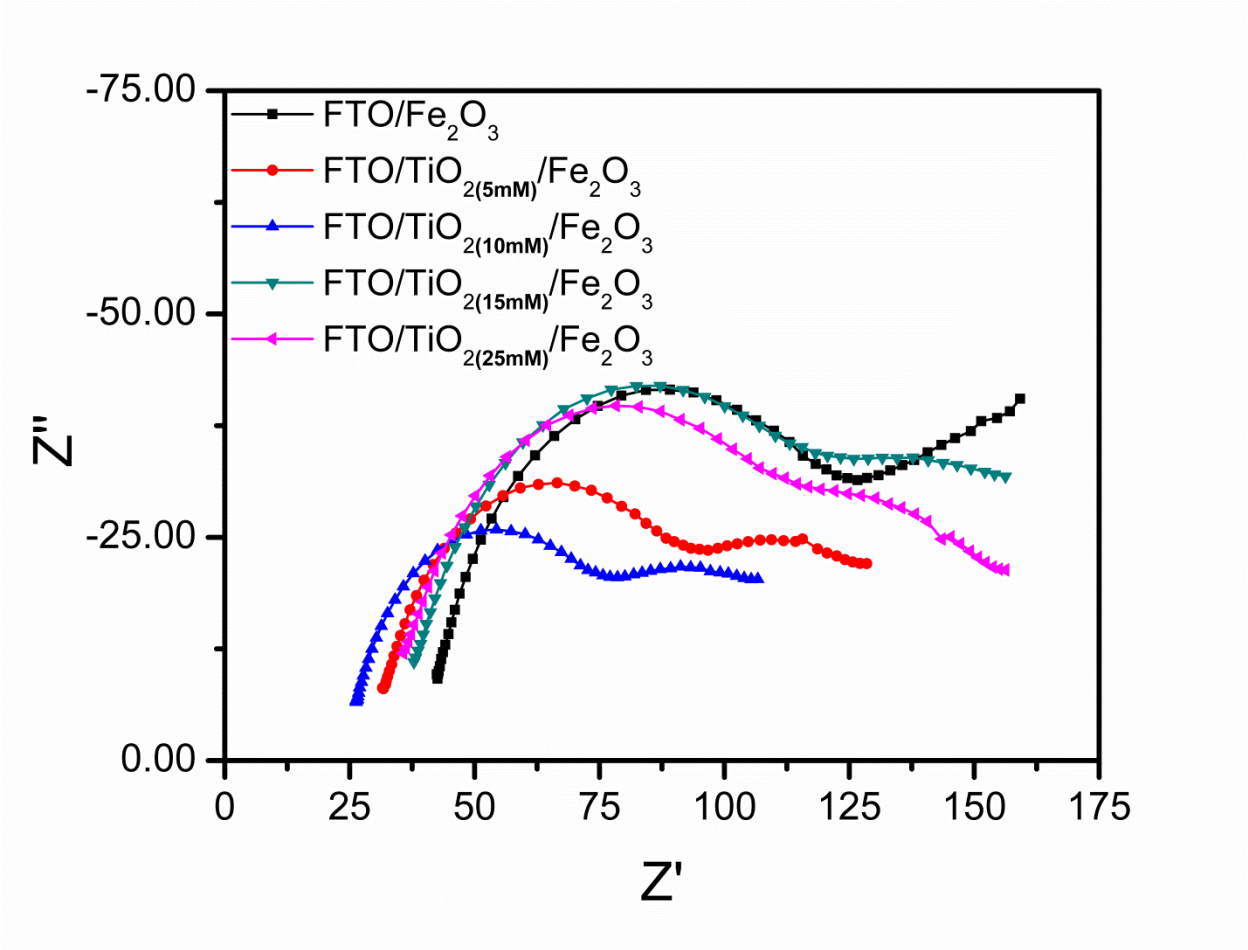


Fig. S6. Electrochemical impedance spectra for PEC water oxidation reaction of FTO/α–Fe_2O_3 and FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800°C under standard illumination conditions. There was a decrease in charge transport resistance with increasing the TiO_2 sol concentration till 10mM. This can be due to reduced charge transport with increasing film thickness of the TiO_2 underlayers.[3]

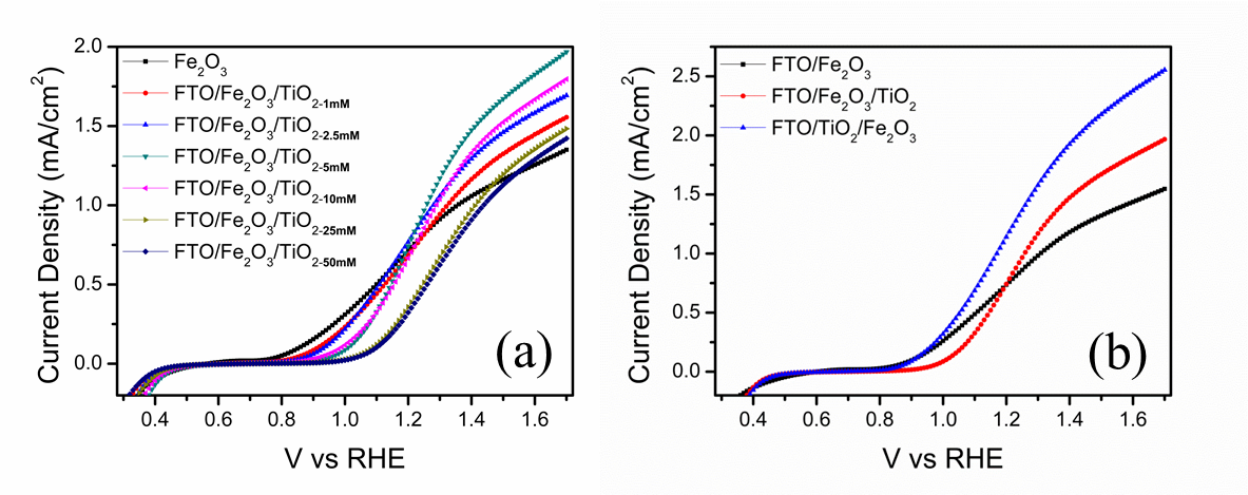


Fig. S7. (a) Photocurrent-potential (*J-V*) curves for PEC water oxidation reaction of various Ti concentration for Ti-doped hematite photoanodes annealed at 800°C under illumination (b) Photocurrent-potential (*J-V*) curves for PEC water oxidation reaction of FTO/α–Fe_2O_3, FTO/α–Fe_2O_3/TiO_2 and FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800°C under standard illumination conditions.

In order to further investigate the intentional Ti doping effect, we performed an ex-situ Ti-doping by dipping the FTO/α–Fe_2O_3 photoanodes in Ti precursor for two minutes and the followed by high temperature sintering to induce Ti^{4+} dopants into hematite lattice.[4] Among various surface treatment conditions, 5 mM of Ti precursor showed highest photocurrent enhancement of 0.87 mA/cm^2 to that of bare Fe_2O_3 photoanodes (0.77 mA/cm^2) at 1.23 V vs RHE. However the observed photocurrent was much lower than FTO/TiO_2/α–Fe_2O_3 photoanodes annealed at 800°C and we observed a positive shift in the onset potential from 0.8 to 1.0 V vs RHE. The obtained shift in onset potential may be due to increased surface states after the surface treatment which limits the water oxidation kinetics.[5]

Reference

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