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Supporting Information

Direct electron transfer from photosystem II to hematite in a hybrid photoelectrochemical cell

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1 Experimental section

1.1 Preparation of PSII core complex

PSII core complexes were isolated from the thermophilic cyanobacterium *T. vulcanus* as described previously[1]. Steady-state O_2 evolution activity was measured with a Clark-type electrode fitted with a circulating water jacket at 30°C. The assay medium contained 30 mM Mes (pH 6.0), 20 mM NaCl, 3 mM $CaCl_2$ with 0.5 mM phenyl-p-benzoquinone and 0.5 mM potassium ferricyanide as electron acceptors. Under saturated illumination, the O_2 evolution rate exceeded 3000 μmol O_2 (mg of Chl)$^{-1}$h^{-1}. The chlorophyll (Chl) a concentration was employed for calculating the quantity of the PSII centers by using 35 Chl a/PSII as a reference[2]. The Chl a concentration was determined by recording the absorbance at 665 nm in methanol according to the equation [Chl a] = A_{665}×13.4 × dilution factor[3].

1.2 Preparation of Manganese-depleted PSII core complex

Mn-depleted PSII core sample was made as described previously[4]. PSII core samples were treated with 5 mM NH_2OH in a buffer containing 20 mM Mes(pH 6.0), 20 mM NaCl, and 3 mM $CaCl_2$ at a chlorophyll concentration of 0.5 mg/mL for 60 min in the dark on ice. After NH_2OH treatment, the samples were precipitated at 4 ^{o}C by adding polyethylene glycol (PEG 1450) to a final concentration of 15% (w/v) followed by centrifugation.

1.3 Preparation of the hematite film

The surface Ti doped hematite films (Ti/Fe_2O_3) on an F-doped SnO_2 (FTO) substrate electrode were prepared using a modified chemical bath deposition method and annealing treatment[5]. For the synthesis of the FeOOH nanorod arrays, typically,

the freshly washed FTO substrate (2.0 cm × 2.0 cm) was immersed in 50 mL aqueous solution containing 0.1 M $FeCl_3 \cdot 6H_2O$ and 0.15 M urea. The sheets are vertically placed in the reactor, which were then was sealed and heated in an oven at 100°C for 4 h. After the reaction, the films were thoroughly rinsed and put in a 0.1 M tetrabutyl titanate solution for 10 min and then dried by sweeping under compressed air. The titanium modified samples were calcinated at 500°C for 3 h. Finally, the as-prepared samples were further annealed at 750°C for 10 min, and noted as Ti/Fe_2O_3.

1.4 Preparation of PS II/α-hematite hybrid photoanode

The PS II/α-hematite hybrid photoanodes were prepared by self-assembling of PSII dimers on the mesopopous surface of the Ti/Fe_2O_3 film. 40 microliters of the PSII solution (0.06 mg Chl mL^{-1}) were placed on the freshly washed Ti/Fe_2O_3 surface (0.25 cm^2) for 60 min in the dark condition. The Ti/Fe_2O_3 electrode with adsorbed PSII was washed with the buffer solution for several times to remove the redundant PSII samples before characterization and photoelectrochemical measurements.

1.5 Photoelectrochemical measurement

Photocurrent measurements were made in a three electrodes system with a potentiostat (Iviumstat, Ivium Technologies) under simulated AM 1.5G solar light irradiation (100 mW cm^{-2}, Newport Sol 3A, Class AAA solar simulator). A hybrid electrode was used as working electrode and a Pt electrode and saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The phosphate sodium buffer solution containing 50 mM phosphate sodium and 15 mM NaCl, (pH 6.0) was used as the electrolyte for all the experiments.

For linear sweep voltammertry (LSV) measurement, the current was recorded in

the range of 0.2~0.8 V vs. SCE at a scan rate of 50 mV/s. For the Chronoamperometry measurements, the current was recorded with every 10 s chopping of light under the test potential.

The incident photo-to-current conversion efficiency (IPCE) was measured in the same three-electrodes setup and the same electrolyte used in the photocurrent measurement above. Monochromatic light from a tungsten lamp equipped with monochromator (CROWNTECH QEM24-D 1/4 m Double) was used as the light source, and the light intensity was calibrated with a silicon photodiode. The IPCE was calculated according to the equation:

$$\text{IPCE}(\lambda) = [N_A j(\lambda)/F]/[P_i(\lambda)/E(\lambda)]$$

Where $j(\lambda)$ is the measured photocurrent (A), $P_i(\lambda)$ is the incident light intensity (W) for each wavelength, N_A is the Avogadro's constant, F is the Faraday constant and $E(\lambda)$ is the photon energy, respectively.

1.6 Quantification of PSII on Ti/Fe_2O_3 film

The content of PSII on the electrode was analyzed by absorption spectra. The chlorophyll of PSII on the electrode is desorbed by methanol. The amount of chlorophyll is measured by UV-visible absorption spectra (Varian Cary 50, USA) according to the equation [Chl a] = A665×13.4×dilution factor. The quantity of the PSII centers on the electrode is calculated to be 2.224±0.093pmol by using 35 Chl a/PSII as a reference. The PSII coverage on the surface of electrode is calculated by assuming that the PSII is an ideal two-dimensional size (20.5×11.0 nm^2)[6].

1.7 Fluorescence imaging characterizations

Fluorescence imaging characterizations were carried out by a combined instrument

which consists of a microscope (IX81, Olympus, Japan) and a laser confocal scanning fluorescence imaging microscopy system (LCS-FLIM; DCS120, B&H, Germany). For fluorescence measurement of the electrode films, a laser (500 nm in wavelength) was used as excitation source. The transient fluorescence signal in the range 670 ± 20 nm was collected as data for the fluorescence intensity imaging of the samples.

2 results and characterizations

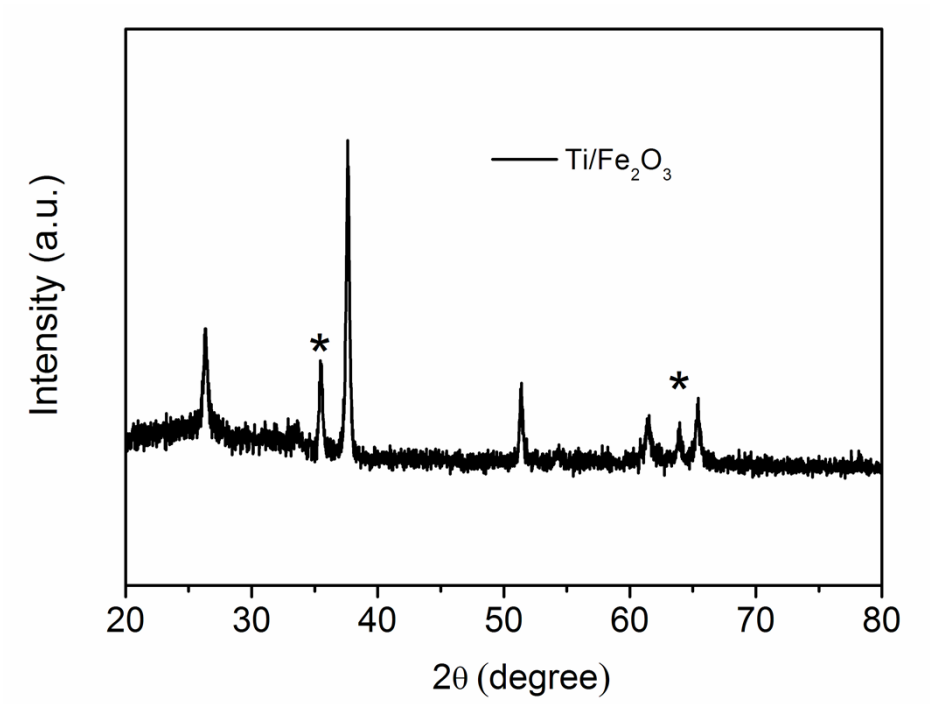

Fig. S1 XRD patterns of Ti/Fe_2O_3 film on a FTO substrate (* is characteristic peak of hematite phase)

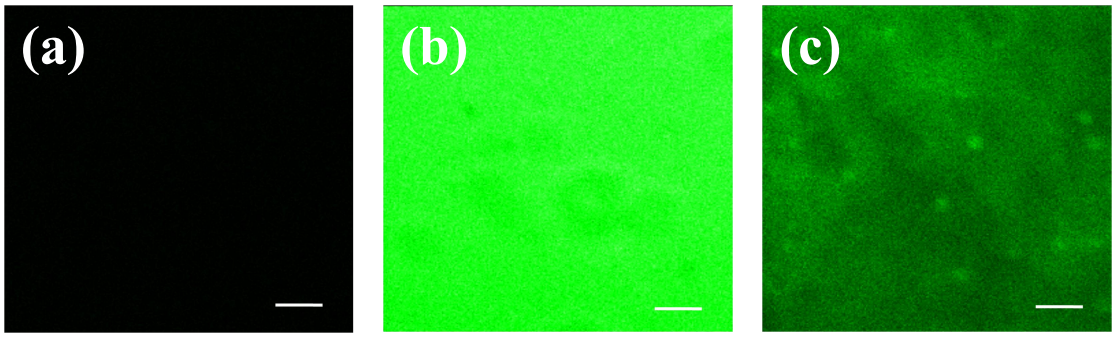

Fig. S2 The fluorescence intensity images of the Ti/Fe_2O_3 electrode (a), PSII on a glass slide (b) and the PSII-Ti/Fe_2O_3 hybrid electrode after photoelectrochemical test (c), scale bars, 5 μm

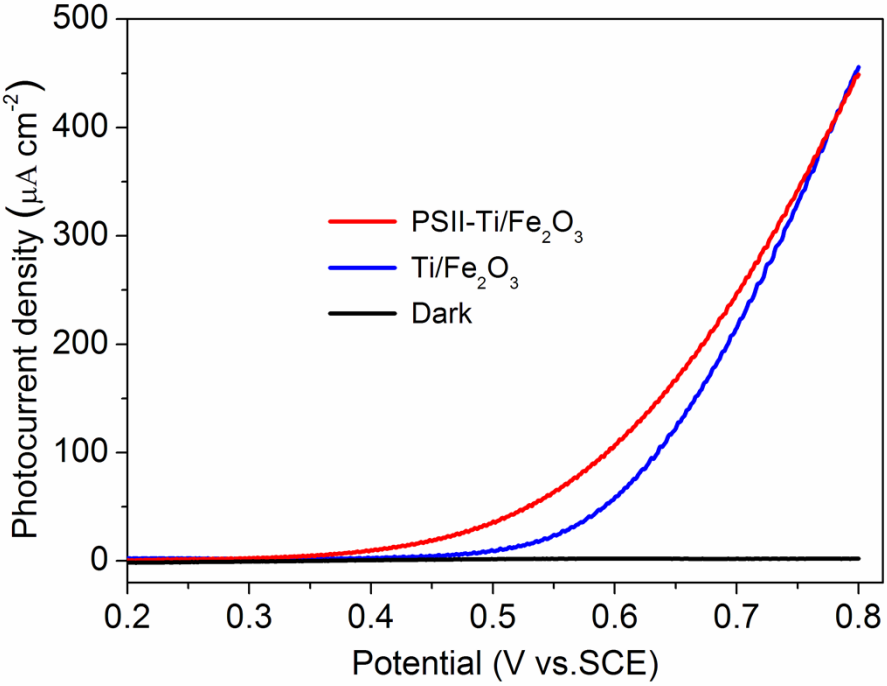

Fig. S3 Linear sweep voltammetric curves of Ti/Fe_2O_3 and PSII-Ti/Fe_2O_3 electrodes in 50 mM phosphate sodium buffer solution (pH=6.0) under AM 1.5G simulated solar light (100 mW cm^{-2}); Scan rate: 50 mV s^{-1}.

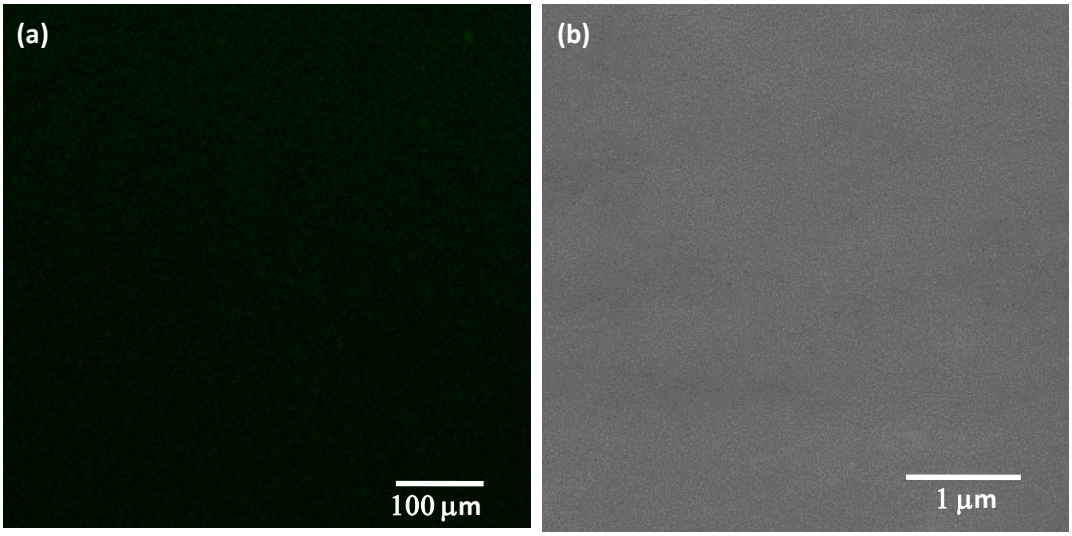

Fig. S4 The fluorescence intensity image of the PSII-FTO electrode and SEM of the FTO glass

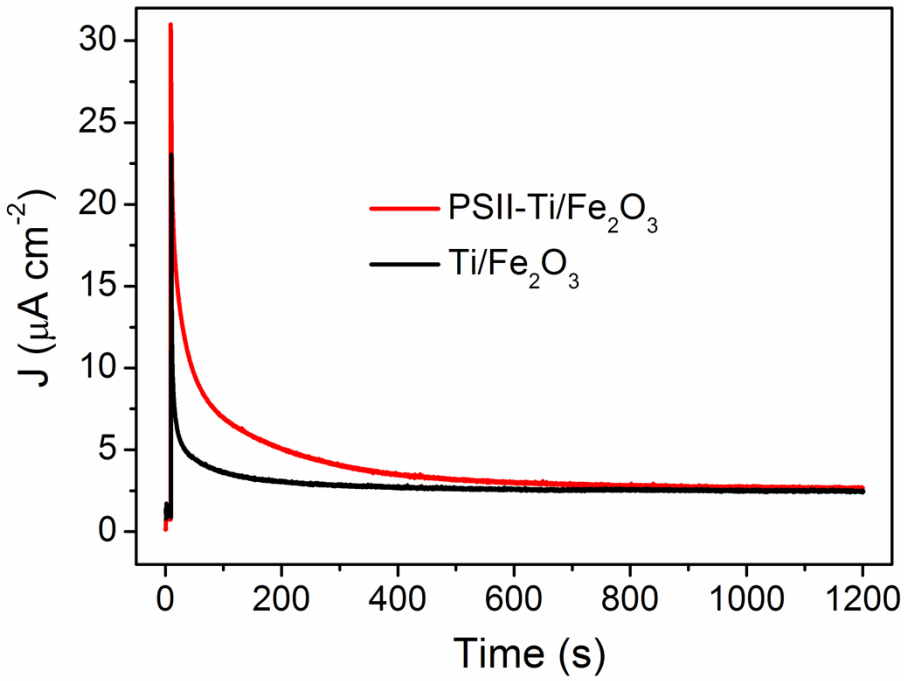

Fig. S5 Photocurrent decay curves of the PSII-Ti/Fe_2O_3 and Ti/Fe_2O_3electrodes at 0.5 V vs SCE under AM 1.5G simulated solar light (100 mW cm^{-2}) in 50 mM phosphate sodium buffer solution (pH 6.0).

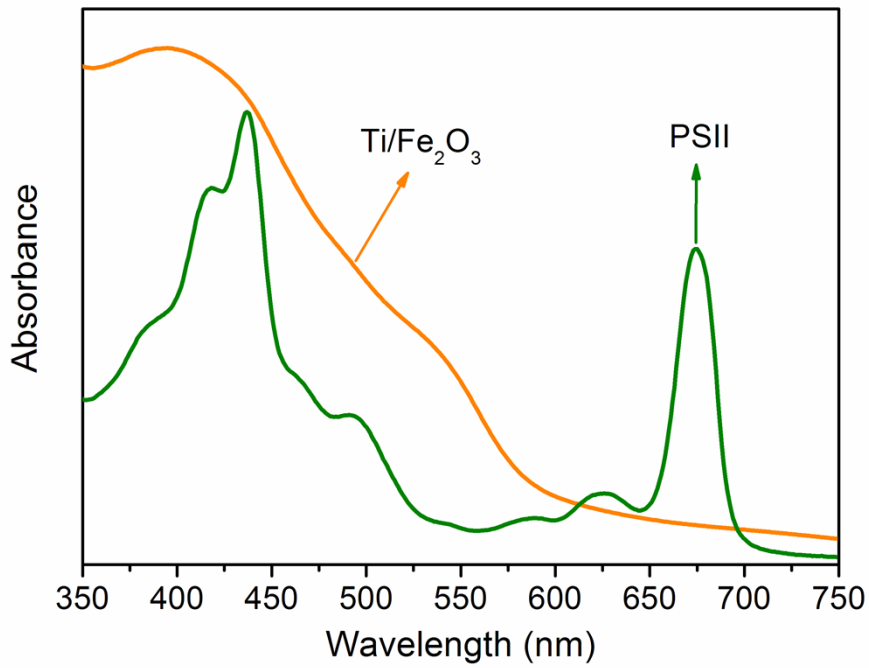

Fig. S6 UV-visible absorption spectra of the PSII (green) and the Ti/Fe_2O_3 film (orange)

Supplementary References

1 J.-R. Shen and N. Kamiya, *Biochemistry*, 2000, **39**, 14739.

2 Y. Umena, K. Kawakami, J.-R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55.

3 R. J. Porra, W. A. Thompson and P. E. Kriedemann, *Biochim. Biophys. Acta*, 1989, **975**, 384.

4 G. Han, Y. Huang, F. H. M. Koua, J.-R. Shen, P.-O. Westlund and J. Messinger, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11924.

5 Z. Wang, G. Liu, C. Ding, Z. Chen, F. Zhang, J. Shi and C. Li, J. Phys. Chem. C, 2015, DOI: 10.1021/acs.jpcc.5b04892 in press

6 M. Vittadello , M. Y. Gorbunov, D. T. Mastrogiovanni, L. S. Wielunski, E. L. Garfunkel , F. Guerrero, D. Kirilovsky, M. Sugiura, A. W. Rutherford, A. Safari and P. G. Falkowski, *ChemSusChem*, 2010, **3**, 471.