Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

New insight into the roles of oxygen vacancy in hematite for solar water splitting

Xin Zhao, Jianyong Feng, Shi Chen, Yizhong Huang, Tze Chien Sum and Zhong Chen*

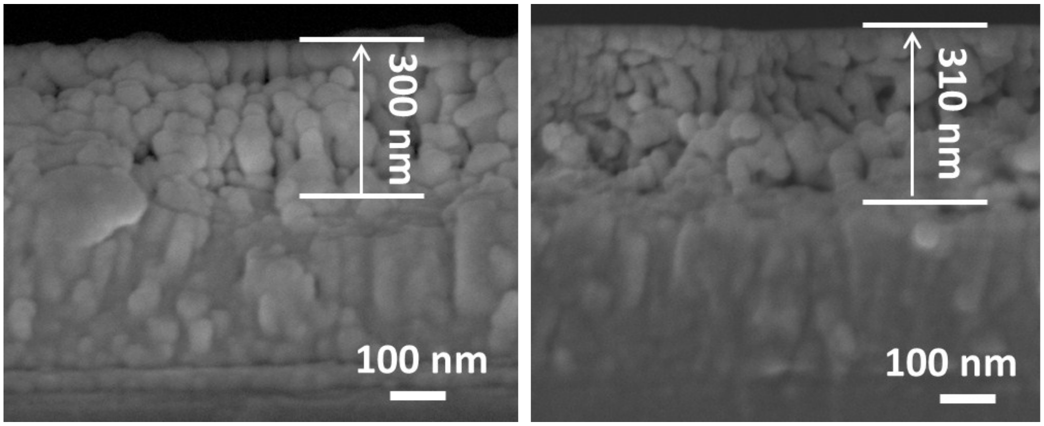

Fig. S1. Cross-section SEM images of (a) pristine and (b) Ti-doped hematite films.

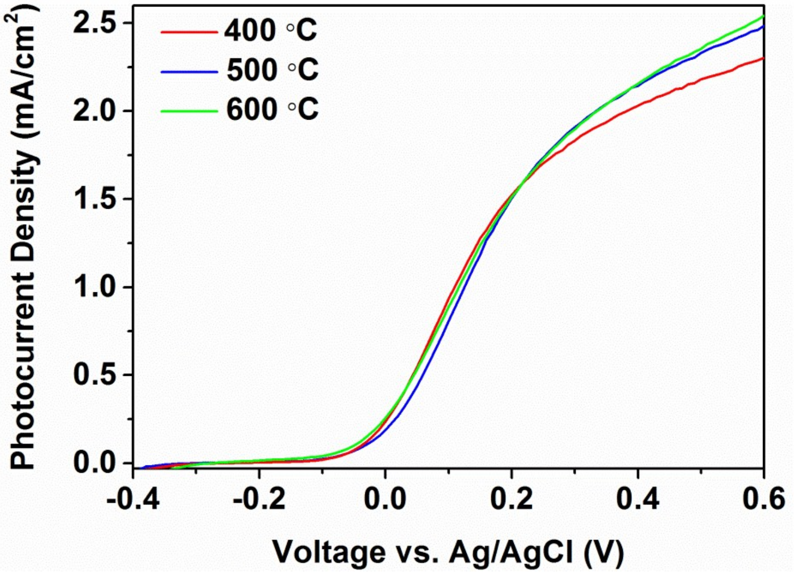

Fig. S2. The photocurrents of Ti doped hematite after annealing in nitrogen gas at different temperature measured under AM 1.5 solar simulator illumination.

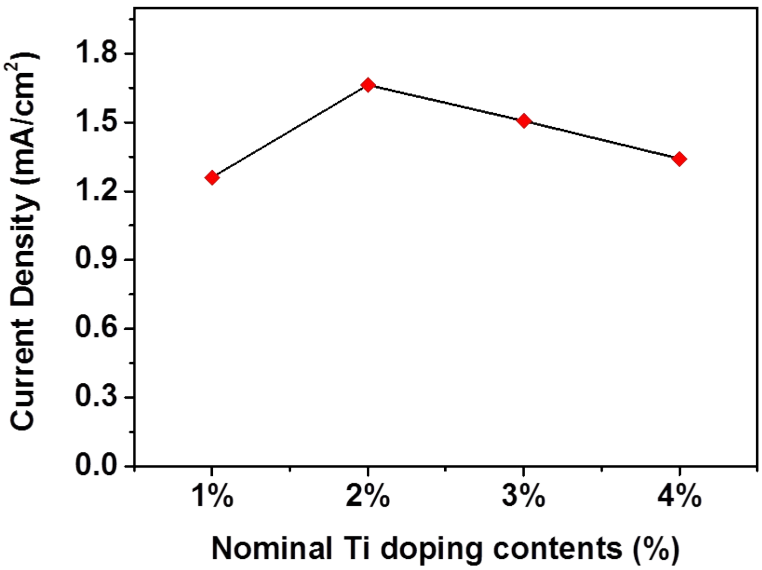

Fig. S3. The photocurrents at 1.23 V vs. RHE of Ti doped hematite versus nominal Ti doping concentration after annealing in nitrogen gas measured under AM 1.5 solar simulator illumination.

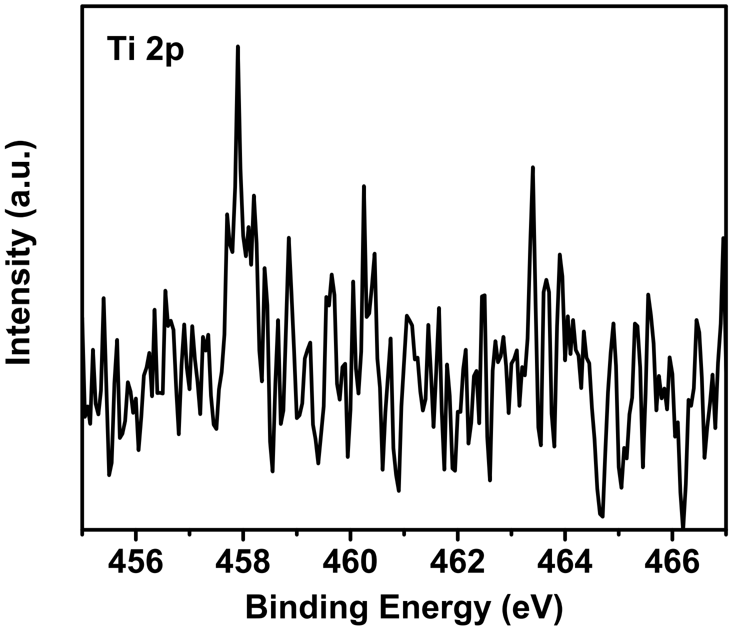

Fig. S4. Ti 2p core-level X-ray photoelectron spectroscopy (XPS) spectra of Ti-doped hematite

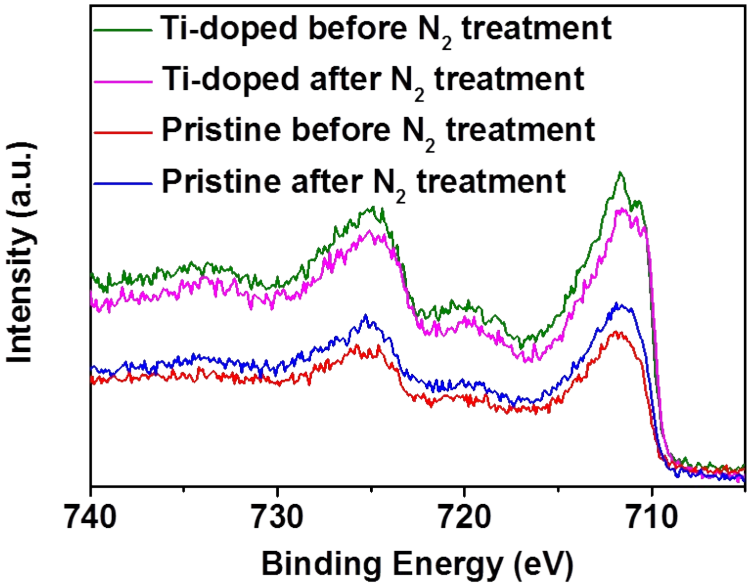

Fig. S5. Fe 2p core-level X-ray photoelectron spectroscopy (XPS) spectra of pristine and Ti-doped hematite before and after N_2 treatment.

Fe 2p core-level X-ray photoelectron spectroscopy (XPS) spectra reveal two strong peaks centered at binding energies of 711.4 eV and 725.0 eV, which are attributed to Fe^{3+} following previous reports on hematite.[1-3] The satellite peak at about 720.0 eV also indicates the presence of Fe^{3+} species.[4] Previous works showed that the creation of Fe^{2+} indicates the presence of oxygen vacancy.[1] However, no obvios changes were found between the samples before and after nitrogen treatment for both pristine and Ti-doped hematite. This is mainly attributed to the less amout of oxygen vacancies generated using this method, which is supported by the Mott-Schottky results that carrier density is not too high. The carrier density is only 5.9×10^{19} cm^{-3} for the nitrogen treated pristine hematite. In the pristine hematite, the carrier is contributed by the oxygen vacancy, 2 electrons generated by 1 oxygen vacancy. Thus, the oxygen vacancy density in pristine hematite is about 3×10^{19} cm^{-3}. For hematite, the density is 5.26 g cm^{-3}, corresponding to a density of 1×10^{23} cm^{-3} in the atom. Hence the oxygen vacancy density is about 0.01% in hematite, which is still below the XPS detection limit (about 0.1% for our equipment). Therefore, no obvious changes were observed in Fe 2p spectra.

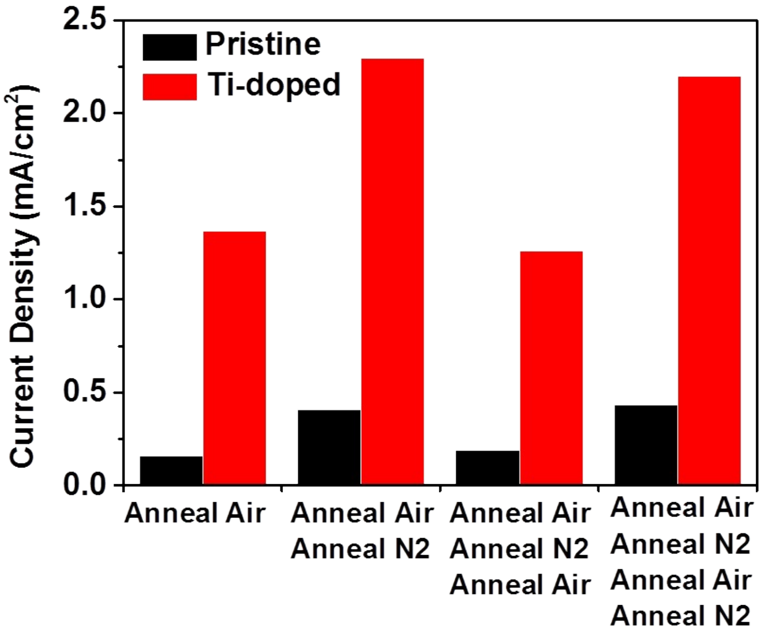

Fig. S6. The photocurrents of pristine and Ti doped hematite at 0.6 V vs. Ag/AgCl with multiple treatments as follows.

Anneal Air represents the synthesized films calcined in air 700 °C for 20 min.

Anneal Air Anneal N2 represents the synthesized films calcined in air 700 for 20 min, then reannealed in N_2 at 600 °C for 2h.

Anneal Air Anneal N2 Anneal Air represents the synthesized films calcined in air 700 for 20 min, then reannealed in N_2 at 600 °C for 2h, then reannealed in air at 600 °C for 2h.

Anneal Air Anneal N2 Anneal Air Anneal N2 represents the synthesized films calcined in air 700 for 20 min, then reannealed in N_2 at 600 °C for 2h, then reannealed in air at 600 °C for 2h, then reannealed in N_2 at 600 °C for 2h.

Calculation of J_{abs}

J_{abs} is the photocurrent density determined by the photon absorption that will be used to generate photocurrent, which can be calculated by:

$$J_{abs} = \int_{300}^{620} \frac{P_\lambda\left(\mu W / cm^2\right) \cdot \eta_{abs} \cdot \lambda\left(nm\right)}{1240\left(V \cdot nm\right)} d\lambda \qquad \text{(S1)}$$

where λ (nm) is the wavelength, P_λ (μW·cm^{-2}) the light intensity at λ from AG 1.5 data, η_{abs} is the light absorption efficiency of the hematite thin film. From Equation S1 the calculated J_{abs} is about 6.85 mA·cm^{-2} for the Ti-doped hematite in this study according to the AM 1.5 data and light absorption efficiency (Fig. 4 in the main text).

[1] Y. Ling, G. Wang, J. Reddy, C. Wang, J. Z. Zhang and Y. Li, Angew. Chem. 124 (2012) 4150.
[2] T.-Y. Yang, H.-Y. Kang, U. Sim, Y.-J. Lee, J.-H. Lee, B. Koo, K. T. Nam and Y.-C. Joo, Phys. Chem. Chem. Phys. 15 (2013) 2117.
[3] D. Cao, W. Luo, J. Feng, X. Zhao, Z. Li and Z. Zou, Energy Environ. Sci. 7 (2014) 752.
[4] R. Morrish, M. Rahman, J. MacElroy and C. A. Wolden, ChemSusChem 4 (2011) 474.