

# **Facile Synthesis of Iron Oxide Coupled and Doped Titania Nanocomposites: Tuning of Physicochemical and Photocatalytic Properties**

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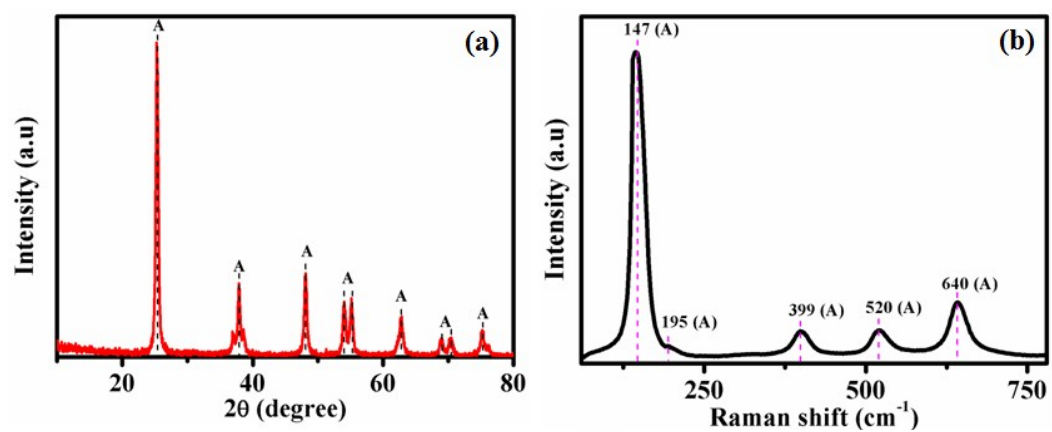
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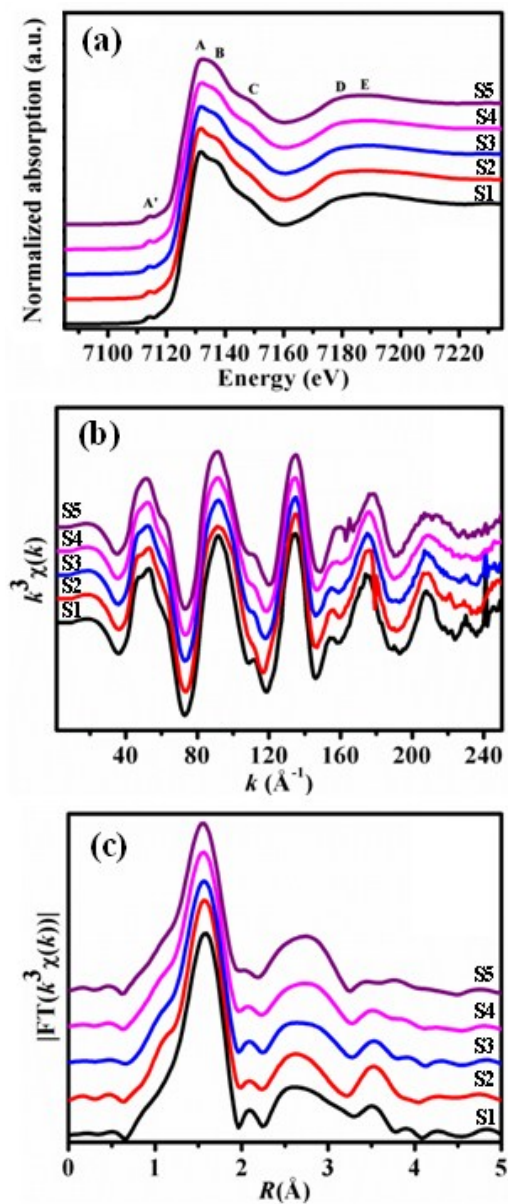
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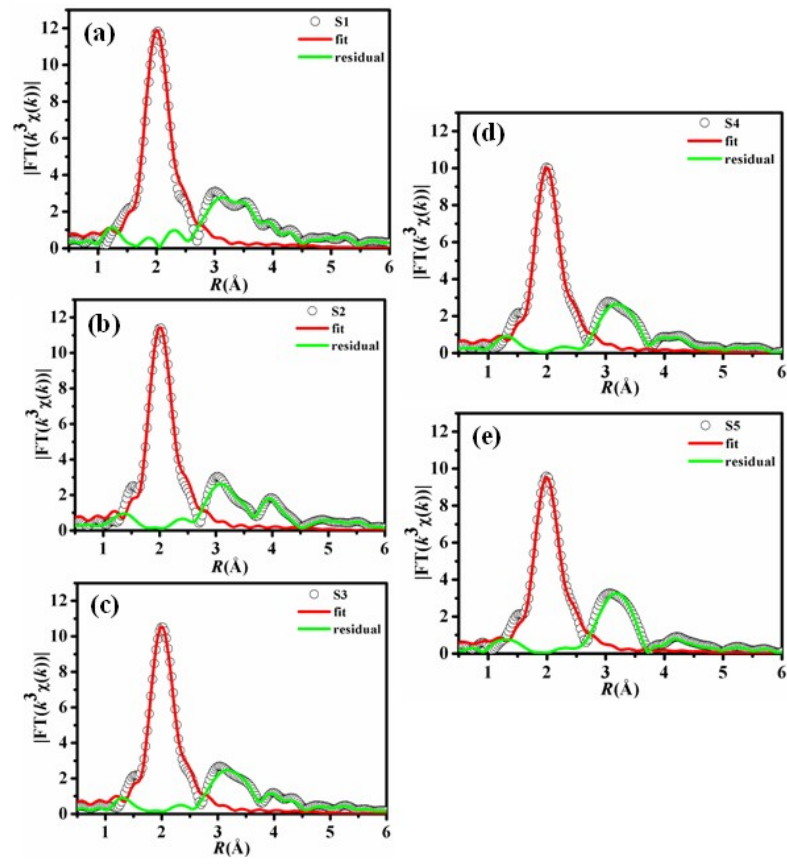
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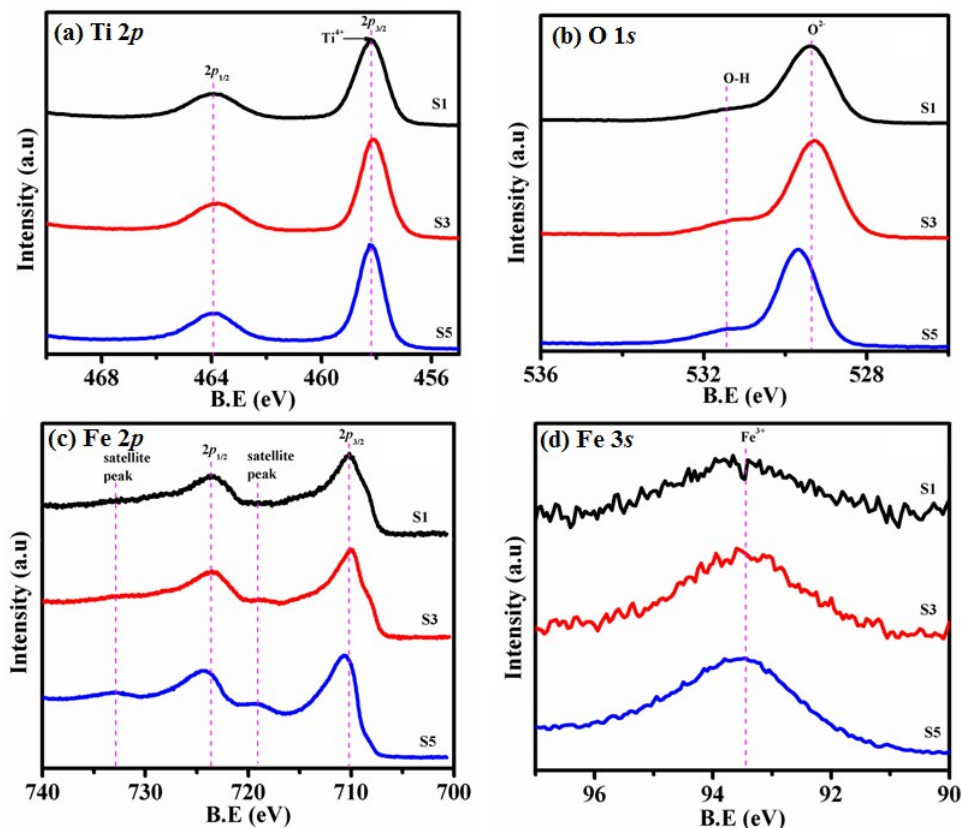
**Fig. S1** (a) XRD and (b) Raman spectra of undoped TiO<sub>2</sub> as same preparation method at room temperature.



**Fig. S2** Experimental XANES (a),  $k^3$  weighted EXAFS spectra (b) and Fourier transforms of  $k^3$  weighted EXAFS (c) and (c) at Fe *K*-edge for all species.



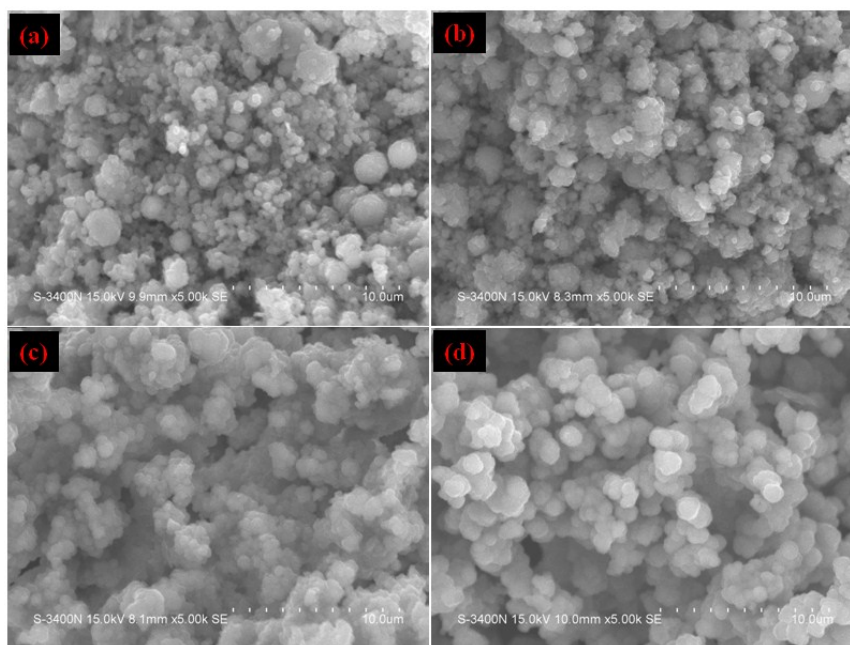
**Fig. S3** EXAFS fitting of S1-S5 samples.



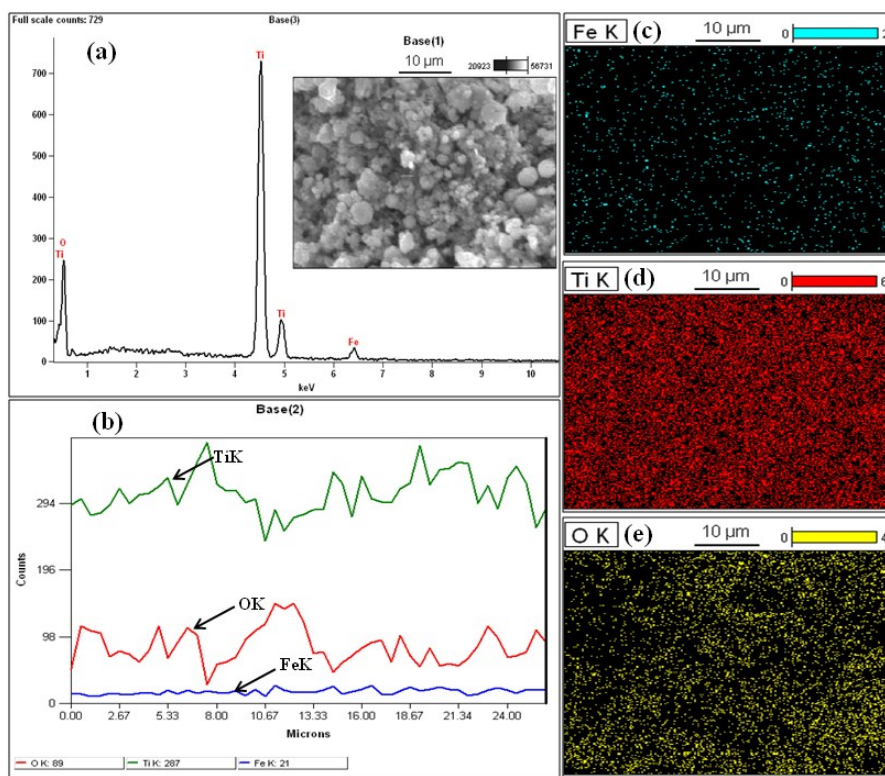
**Fig. S4** Ti 2*p* (a), O 1*s* (b), Fe 2*p* (c) and Fe 3*s* (d) XPS core level spectra of typical S1, S3 and S5 samples.

The Ti 2*p*<sub>1/2</sub> and Ti 2*p*<sub>3/2</sub> spin-orbital splitting photoelectrons are located at B.E. of 464.6 and 458.9 eV, respectively (Figure S4a). It seems that these energies are not affected by iron content. No Ti<sup>3+</sup> species were observed in XPS. The absence of peak broadening of Ti 2*p*<sub>3/2</sub> signals may also indicate the presence of Ti<sup>4+</sup> species only, and good crystallization. The peaks at 530.1 and 531.45 eV are due to O<sup>2-</sup> ion in the TiO<sub>2</sub> lattice and surface hydroxyl groups, respectively (Figure S4b).<sup>1,2</sup> In the Fe 2*p* core level spectra as shown in Figure S4c, the spectrum can be successfully fit to three main peaks and two satellite peaks in 2*p*<sub>3/2</sub> region, with a repeated pattern, anticipated to be at half the intensity for the 2*p*<sub>1/2</sub> component but with no restrictions placed upon B.E., intensities or peak widths. The lowest binding energy peak at 710.2 eV is attributed to Fe<sup>2+</sup>, with a

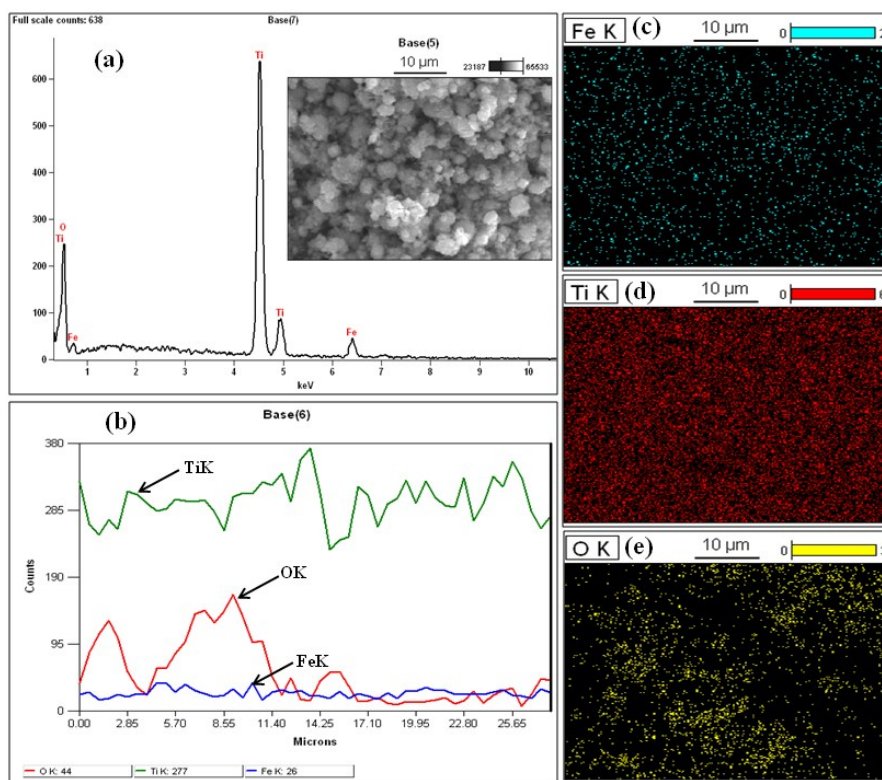
corresponding satellite at 716.0 eV, the presence of  $\text{Fe}^{2+}$  ions or Fe metal may be plausible considering that the XPS measurement was performed under high vacuum conditions ( $10^{-10}$ - $10^{-9}$  Torr). Upon introduction of the photocatalyst into the high vacuum XPS chamber, the surface  $\text{Fe}^{3+}$  ion may have been reduced to  $\text{Fe}^{2+}$  ion.<sup>3</sup> The B.E. 710.8 eV and 723.6 eV should be assigned to  $2p_{3/2}$  and  $2p_{1/2}$  of  $\text{Fe}^{3+}$ , respectively, and the  $\text{Fe}^{3+}$  tetrahedral species has a B.E. of 713.3 eV. These values are comparable to others found in the literature.<sup>4,5</sup> The Fe 3s peak is observed at  $\sim 93.4$  eV, although the peak with considerable intensity (Figure S4d). Therefore, it can be concluded that Fe is not only doped into  $\text{TiO}_2$ , but to be iron oxide particles coupled with titania.



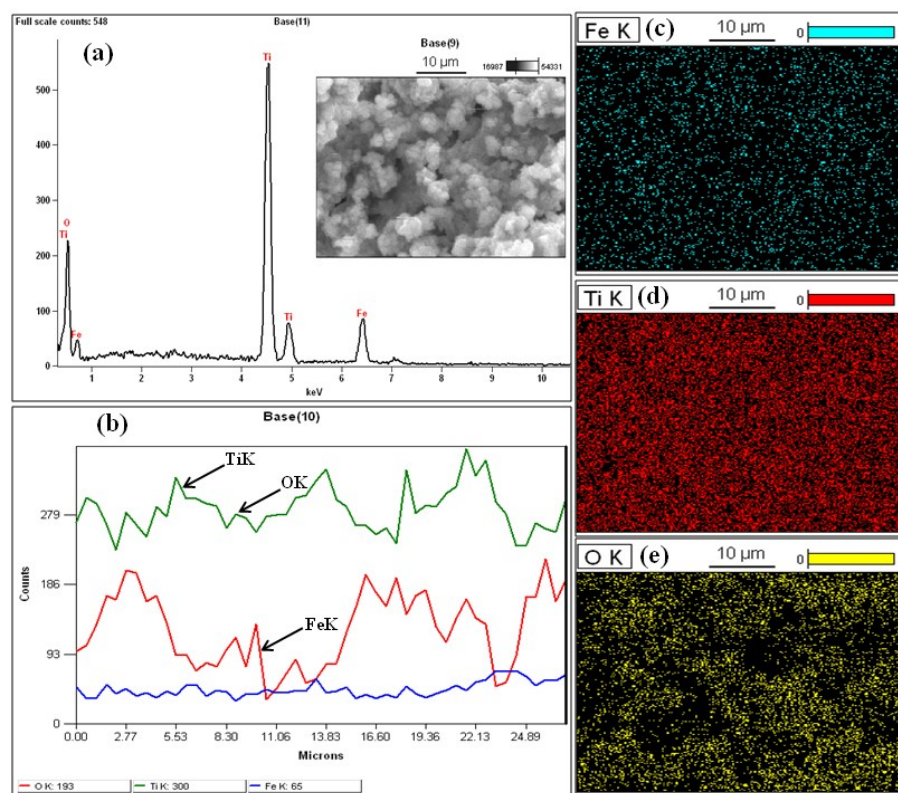
**Fig. S5** SEM images of S1 (a), S2 (b), S4 (c) and S5 (d) samples.



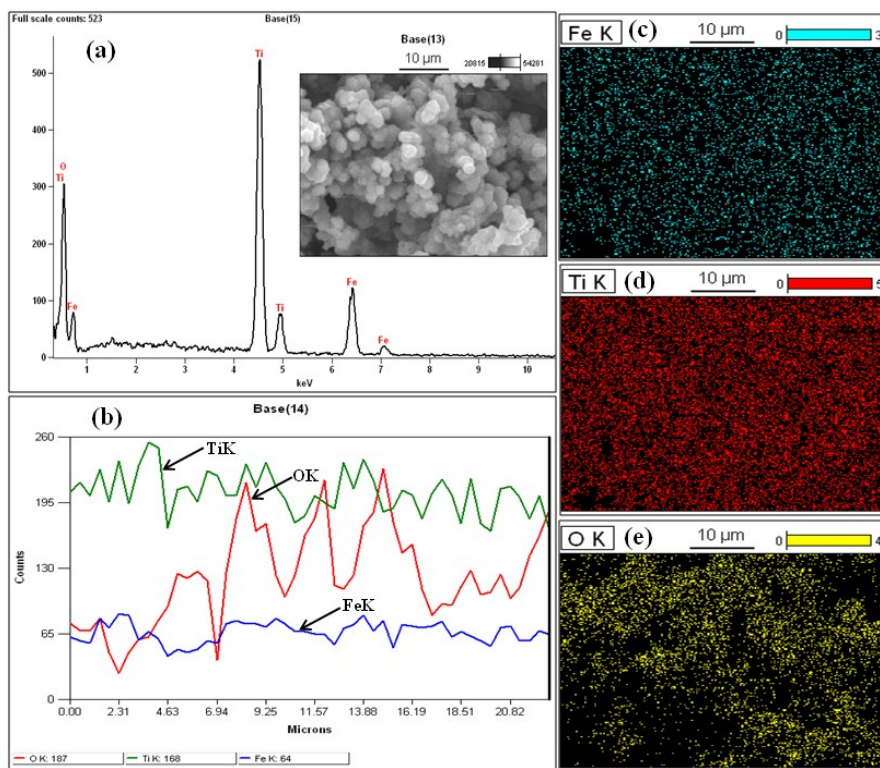
**Fig. S6** EDX spectrum (a), line spectra (b) and elemental mapping (c) (d) and (e) of S1 sample.



**Fig. S7** EDX spectrum (a), line spectra (b) and elemental mapping (c) (d) and (e) of S2 sample.



**Fig. S8** EDX spectrum (a), line spectra (b) and elemental mapping (c) (d) and (e) of S4 sample.

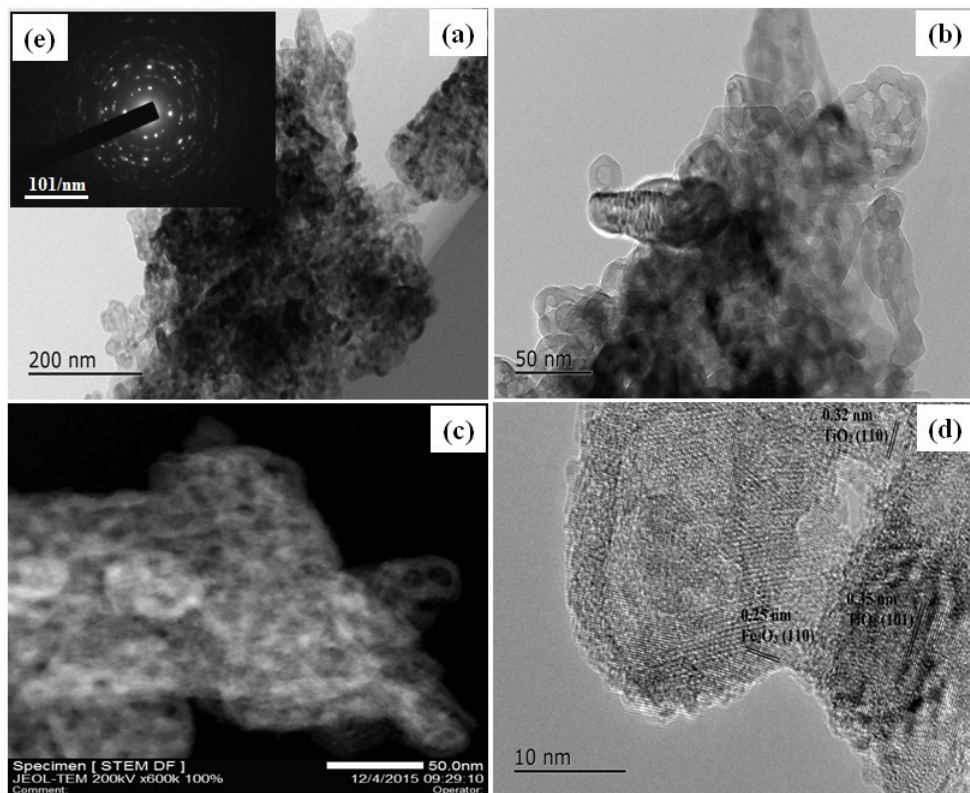


**Fig. S9** EDX spectrum (a), line spectra (b) and elemental mapping (c) (d) and (e) of S5 sample.

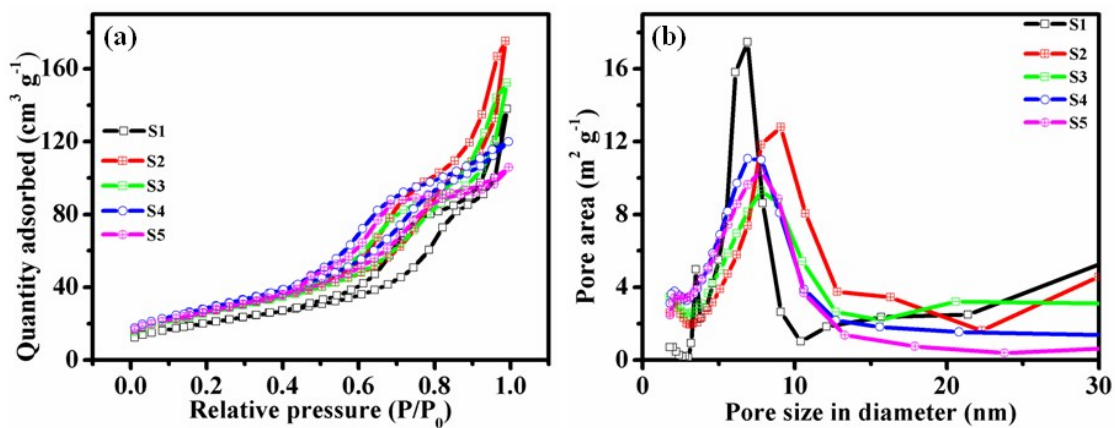
**Table S1** EDX and ICP (in 100 mL phosphoric acid (90%) solution) data of S1-S5 samples.

	EDX			ICP		
sample	Ti, (at. %)	Fe, (at. %)	O, (at. %)	Ti, ppm	Fe, ppm	Fe/Ti, (at. %)
S1	28.86	1.50	69.64	25.29	3.87	0.13
S2	26.55	2.89	70.56	9.89	2.94	0.26
S3	NA	NA	NA	11.06	3.83	0.30
S4	25.76	6.46	67.78	8.89	4.25	0.41

S5	22.33	9.57	68.10	7.61	5.20	0.59
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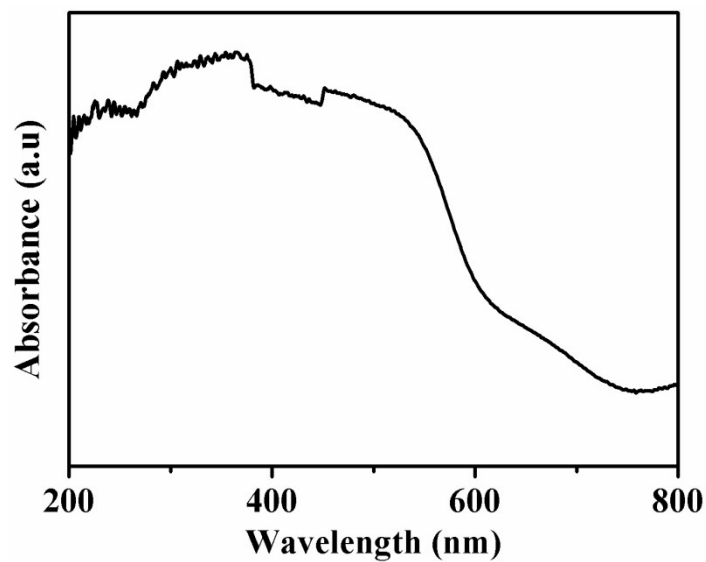


**Fig. S10** TEM (a), (b), STEM (c), HRTEM (d) images and SAED pattern (e) of S1 sample.

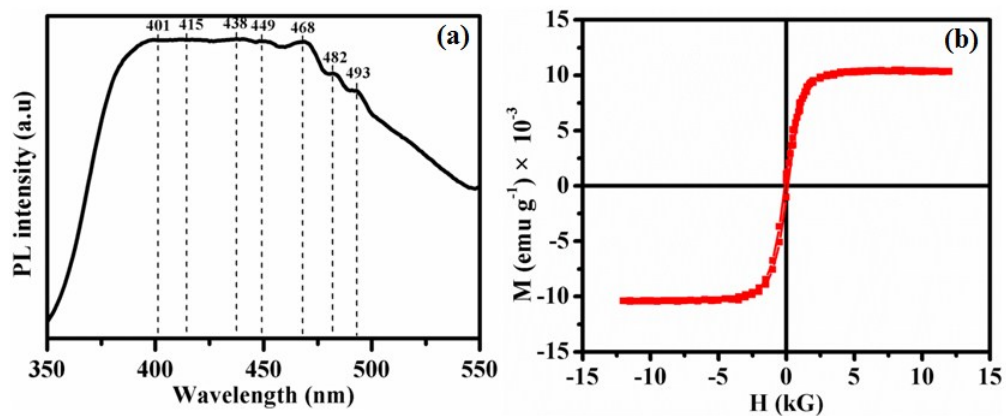


**Fig. S11** Nitrogen adsorption-desorption isotherms (a) and pore-size distribution curves

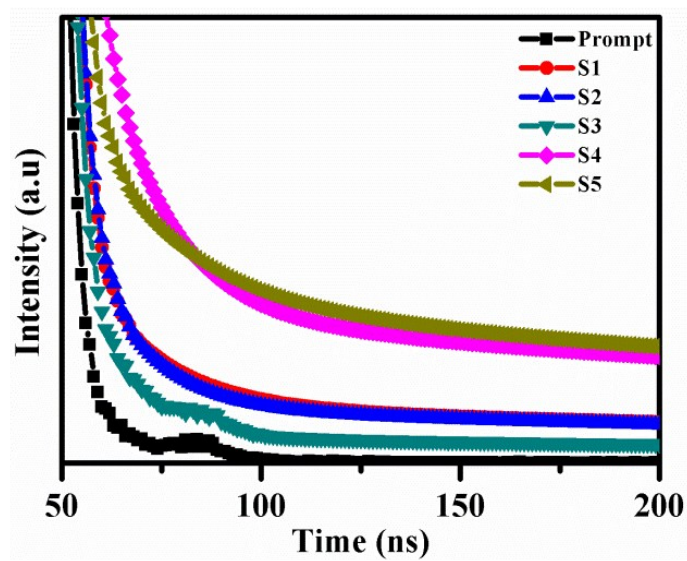
(b) for S1-S5 samples.



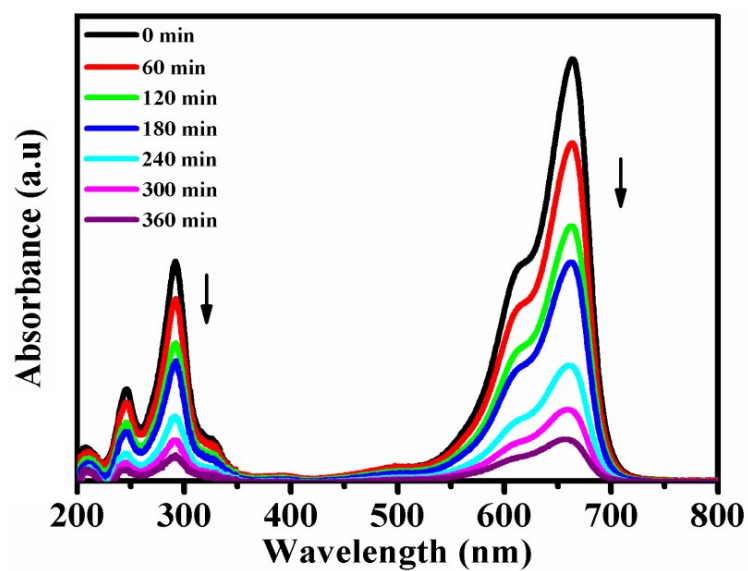
**Fig. S12** UV-vis DRS of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at room temperature.



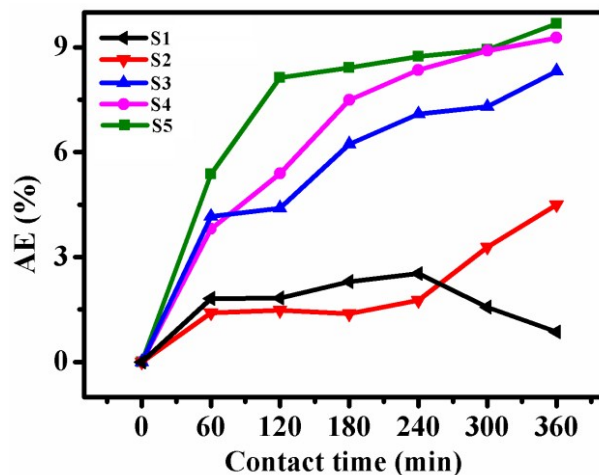
**Fig. S13** (a) Emission spectra and (b) magnetic hysteresis loop of undoped TiO<sub>2</sub> as same preparation method at room temperature.



**Fig. S14** Lifetime profiles of S1-S5 samples at room temperature.

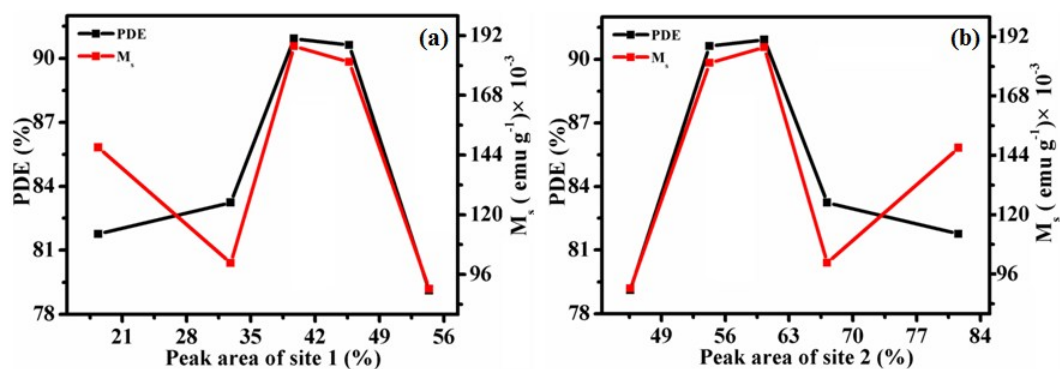


**Fig. S15** Repetitive scan spectra of photodegradation of MB with S5 sample under visible light ( $\lambda > 480$  nm) irradiation at various times in water.

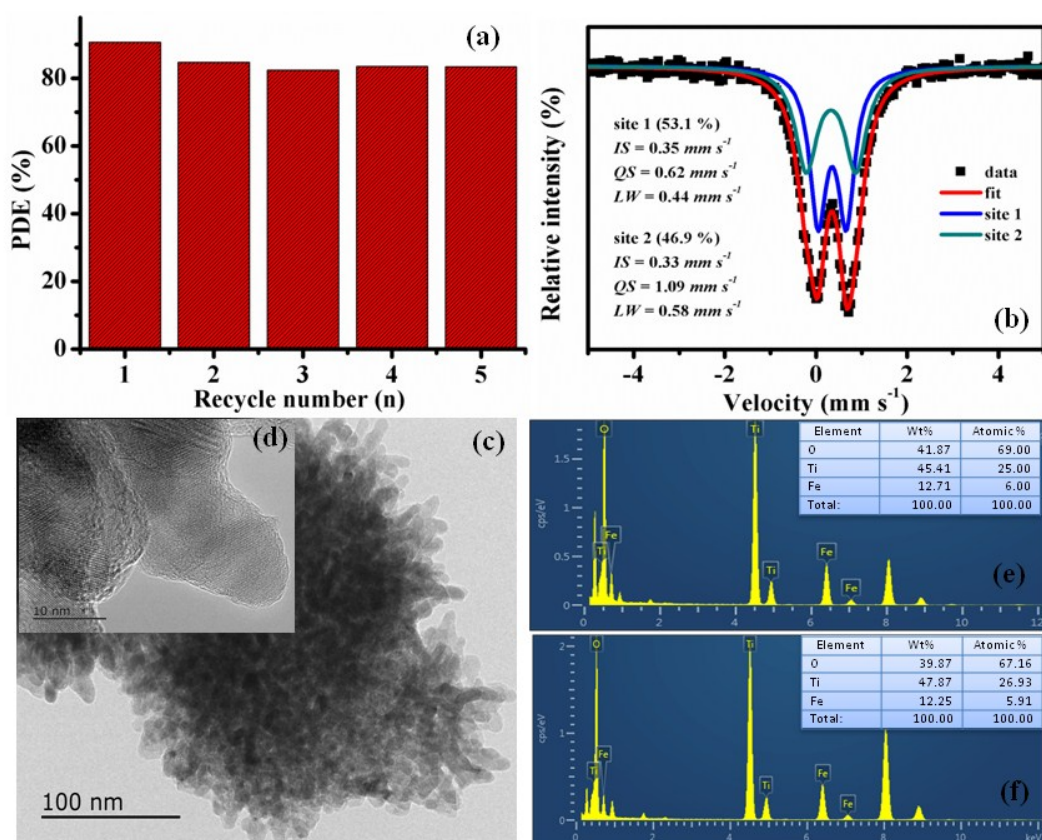


**Fig. S16** MB adsorption efficiency of S1-S5 samples at various contact time in distilled water at room temperature.

In a typical adsorption process, 80 mL of MB aqueous solution with initial concentration  $10^{-5}$  M and 50 mg of S1-S5 samples were separately taken in 100 mL beaker and then the entire solution was stirred at room temperature and at neutral pH conditions (performed in dark place). The filtrate solutions centrifuged after definite time intervals were subjected to electronic absorption spectroscopic analysis at 665 nm. Adsorption efficiency calculated from  $AE = [(A_i - A_t)/A_i] \times 100 \%$ , where,  $A_i$  and  $A_t$  are the absorbance of the adsorption solutions initially and at definite time interval ' $t$ ' respectively.



**Fig. S17** Variation of PDE and magnetization ( $M_s$ ) values of S1-S5 samples with different amount of doped (site 1) (a) and coupled (site 2) (b) iron oxides level obtained from <sup>57</sup>Fe Mössbauer study.



**Fig. S18** Cyclic PDE for MB degradation of S5 sample (a), <sup>57</sup>Fe Mössbauer spectra (b), TEM (c), HRTEM images (d), STEM-EDS (f) of S5 sample obtained from after five

cycle of photocatalytic treatment and STEM-EDS of fresh S5 sample (e).

## References

- 1 K. C. Christoforidis and M. Fernandez-Garcia, *Catal. Sci. Technol.*, doi: 10.1039/C5CY00929D.
- 2 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. St. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717–2730.
- 3 H. Irie, K. Kamiya, T. Shibamura, S. Miura, D. A. Tryk, T. Yokoyama and K. Hashimoto, *J. Phys. Chem. C*, 2009, **113**, 10761–10766.
- 4 T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, **254**, 2441–2449.
- 5 N. S. McIntyre and D. G. Zetaruk, *Anal. Chem.*, 1977, **49**, 1521–1528.