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Supporting Information



Figure S1. Side views of some thicker layered structure for the typical α-Fe₂O₃ nanosaucers.



Figure S2. Morphology evolution (SEM images) of α -Fe₂O₃ nanosaucers synthesized at different stages, (a) 1.5 h (primary nanoparticles), (b) 2.5 h, (c) 3.0 h, and (d) 5.0 h (pure nanosaucers).



Figure S3. Typical TEM image and structure of Fe₂O₃ primary nanoparticles, (a) low magnification bight-field TEM image and diameter distribution (inset) of the sample, (b) HRTEM images and geometrical configuration (inset) of the isolated primary nanoparticles.



Figure S4. Low magnification TEM image of the nanosheets with thickness of about 10 nm and diameter of \sim 45 nm synthesized by the same mechanism as typical hematite nanosaucers.



Figure S5. Several control photodegradation experiments performed under similar conditions, including (1) dye + H_2O_2 (without Fe₂O₃ catalyst), (2) dye + Fe₂O₃ catalyst, (3) dye + H_2O_2 + Fe₂O₃



Figure S6. Degradation curves of phenol (a) and MO (b) in the presence of Fe_2O_3 nanoparticles and H_2O_2 .

The degradations of other two organic dyes such as phenol and methyl orange (MO) have also been investigated (Fig. S6). After irradiation for some definite time, the MO and phenol molecules could also degrade. And the saucer-like products (Sample B) also show the better photodegradation performance than the other two samples.



Figure S7. (a) Absorption spectra for α-Fe₂O₃ nanoparticles with various shapes (A for Fe₂O₃ primary ultra small nanoparticle, B for Fe₂O₃ nanosaucers and C is typical Fe₂O₃ single crystal polyhedron), the inset above shows linear fits (dashed lines) of the (αhv)²-hv curves calculated from the absorption

spectra; (b) EIS spectra of samples from A to C.

Figure S7a shows the absorption spectra of α -Fe₂O₃ primary nanoparticles (Sample A), final saucer products (Sample B) and typical Fe₂O₃ single crystal polyhedrons (Sample C, with diameter of 146±15 nm and height of 120±8 nm) in deionized water. The absorption features of the three typical Fe₂O₃ nanoparticles are different from each other, with the morphology and size changed small, the absorption band blue-shifts from 546 nm to about 205 nm. ^[1] According to the interband transition formula in semiconductor near the absorption edge, the absorption coefficient (α) and optical gap (E_g) obey the following equation: ^[2,3]

$$(\alpha h v)^2 = A(h v - E_{\sigma})$$

where A is restricted by the valence and conduction band of material and hv represents the photon energy. Thus by linearly fitting on the absorption edge of the corresponding curve, the band gaps of the single crystal Fe_2O_3 nanopaticles were calculated to be 3.14, 2.31 and 1.92 eV (from Sample A to C, upper inset of Fig. S7a), respectively.

The EIS measurement results illustrate a typical capacitor behavior of the three typical Fe₂O₃ nanopaticles (Fig. S7b). The equivalent series resistance (*Rs*) of the Fe₂O₃ nanopaticles shows the sequence as: Sample C > Sample B > Sample A, inverse to the specific surface area (SSA) order of the materials. The lower '*Rs*' value of Sample A is deduced attributing to the large SSA of the sample, which could enhance the diffusivity of the ionic at the interface between electrode and electrolyte, lowering the contact resistance. ^[4, 5] In addition, a more vertical feature of the impedance curve for Sample B may representing the fast ion diffusion in electrolyte and the adsorption onto the nanosaucer electrode.

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- [2] W. Liu, R. M. Wang, N. Wang, Appl. Phys. Lett., 2010, 97, 041916.
- [3] N. R. Pawaskar, S. D. Sathaye, et al., Mater. Res. Bull., 2002, 37, 1539.
- [4] C. R. Zheng, C. B. Cao, Z. Alia, J. H. Hou, J. Mater. Chem. A, 2014, 2, 16467.
- [5] S. Vijayakumar, S. Nagamuthu, et al., ACS Appl. Mater. Inter., 2013, 5, 2188.



Figure S8. PL and photocurrent spectra of the three typical Fe_2O_3 nanoparticles: A for Fe_2O_3 primary ultra small nanoparticle, B for Fe_2O_3 nanosaucers and C is typical Fe_2O_3 single crystal polyhedron.

The PL spectra have been performed with a FluoroMax-4 (Horiba) fluorescence spectrophotometer at the excitation wavelength around 360 nm (Fig. S8a). The PL bands of the α -Fe₂O₃ nanoparticles mainly appear at 411, 467 and 571 nm, there is almost no difference in the band position. The strong peak around 411 nm of all the three samples can be attributed to the band-band PL phenomenon. The other two broad peaks at around 467 and 571 nm are attributed to the excitonic PL spectra. ^[6] In addition, the intensity of these peaks increases from sample A to C, which may be attributed to the larger crystallite size and better crystalline of sample B and C. ^[7]

The photoelectrochemistry test was conducted with a typical three-electrode system (containing the as-prepared working electrode, ^[8, 9] a Pt wire as the counter electrode and AgCl electrode as the reference electrode) and performed by an electrochemical workstation (IM6, Zahner GER) under a 500 W Xe lamp (100 mW/cm⁻²). Figure 8b displays the chopping photocurrent responses test of the three typical α -Fe₂O₃ nanoparticles at const 1.0 V. The photocurrent of Fe₂O₃ nanosaucers (Sample B) is

about 2.6 and 1.7 times than sample A and C, respectively, which serving as the possible origin for the comparative visible-light photocatalytic activities of the typical Fe_2O_3 nanosaucers (Sample B).

[6] L. Jing, Y. Qu, et al., Sol. Energ. Mat. Sol. C., 2006, 90, 1773.

[7] T. Adinaveen, J. J. Vijaya, et al., J. Supercond. Nov. Magn., 2014, 27, 1721.

[8] J. Liu, S. L. Yang, W. Wu, et al., Acs Sustainable Chem. Eng., 2015, 3, 2975.

[9] S. Liu, L. Zheng, P. Yu, S. Han and X. Fang, Adv. Funct. Mater., 2016, 26, 3331.

TOC tests have been performed on a Ps61-E (Elementar) total organic carbon (TOC) analyzer (Table S1). The tests show the similar results as the photodegradation experiment. Although couldn't completely rule out the influence of the dye sensitization, TOC analysis further confirms the photocatalytic properties of the Fe2O3 catalyst. The difference between the TOC test and experiment value is ascribed to the incomplete degradation (eg. Some organic intermediates produced) of the organic dyes. ^[10]

[10] S. J. A. Moniz, S. A. Sneviin, et al., Chem. Eur. J., 2014, 2
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Table S1. Toc analysis of the samples before and after the photocatalytic reaction.						
Sample	Characteristics	C/C ₀ ^a	TOC content test (mg/L, %)			
S			Initial	Light on ^b	Light off ^b	
Α	Ultra small primary nanoparticles	59%	6.72, 100%	6.11, 91%	4.51, 67%	
В	Saucer-like products	14%	6.72, 100%	5.78, 86%	1.81, 27%	
С	Single crystal polyhedrons	53%	6.72, 100%	6.25, 93%	4.10, 61%	

Notes: (a), C/C_0 refers to the experiment value of the RhB relative concentrations after photocatalytic degradation;

(b), 'Light on' means the beginning of the photodegradation; and 'Light off' refers to the finish of the photodegradation.



Figure S9. Recycling capability of Fe₂O₃ primary nanopartiles (Sample A) and typical single crystals (Sample C).



Figure S10. SEM images of the three typical Fe₂O₃ nanoparticles before and after reused over 10 times on the degradation of RhB, (a-c) before used; (d-f) after reused over 10 times.



Figure S11. The original TEM picture of Fig. 2c.