Electronic supplementary Information

α-Fe_2O_3 hollow structures: formation of single crystalline thin shells

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Experimental Section

Preparation of α-Fe_2O_3 hollow polyhedron: In the experiment, all the reagents were analytical grade and were used without further purification. The α-Fe_2O_3 hollow polyhedron structures were synthesized by a facile hydrothermal approach. In a typical synthesis, 3 mmol of $FeCl_3{\cdot}6H_2O$ was dissolved in 80 ml of ultra-pure water, followed by addition of 0.1 ml of C_4MimBF_4 (1-Butyl-3-methylimidazolium tetrafluoroborate) to form a clear solution at room temperature. After stirring for three hours, the solution was transferred into a 100 ml Teflon-lined stainless steel autoclave, maintained at 200 °C for 2.0, 2.75, 7.0, 15.0 hours, respectively. After the reaction, the precipitates were washed with distilled water and ethanol several times and then dried at 60 °C for 6 h in air.

Characterization: XRD measurements were carried out on a Bruker D8-Avance X-ray powder diffractometer with a Cu-Kα X-ray tube (λ = 0.154056 nm, the accelerating voltage and the applied current were 40 kV and 35 mA). The morphologies of the samples were observed by SEM (Hitachi S-4800 microscope, acceleration voltage = 7 kV, working distance = 4 mm).The TEM images and SAED patterns were performed by a JEOL JEM-2100 instrument. UV/vis diffuse reflectance spectra (DRS) were recorded on a Shi-madzu UV2550 recording spectrophotometer equipped with anintegrating sphere from 300 to 700 nm with a step size of 0.5 nm. $BaSO_4$ was used as a reference. The Brunauer-Emmett-Teller method with a Builder 4200 instrument at liquid nitrogen temperature was used to measure the surface area.

Photodegradation evaluation: The photodegradation activity of the as-prepare samples was characterized by the degradation of rhodamine B (RhB) under visible light irradiation in the presence of H_2O_2 at the room temperature. In a typical procedure, 0.05 g catalyst was suspended in 60 ml of RhB (20 mg/L) aqueous solution, followed by addition of 1 mL of H_2O_2 (30 wt%). Before irradiation, the suspensions were stirred in dark for 1 h to reach an adsorption/desorption equilibrium. The visible light was provided by a 300 W Xe arc lamp equipped with UV cutoff filter. The concentration of RhB dye was determined by a UV/Vis spectrophotometer (Xinmao UV-7502PC, Shanghai).

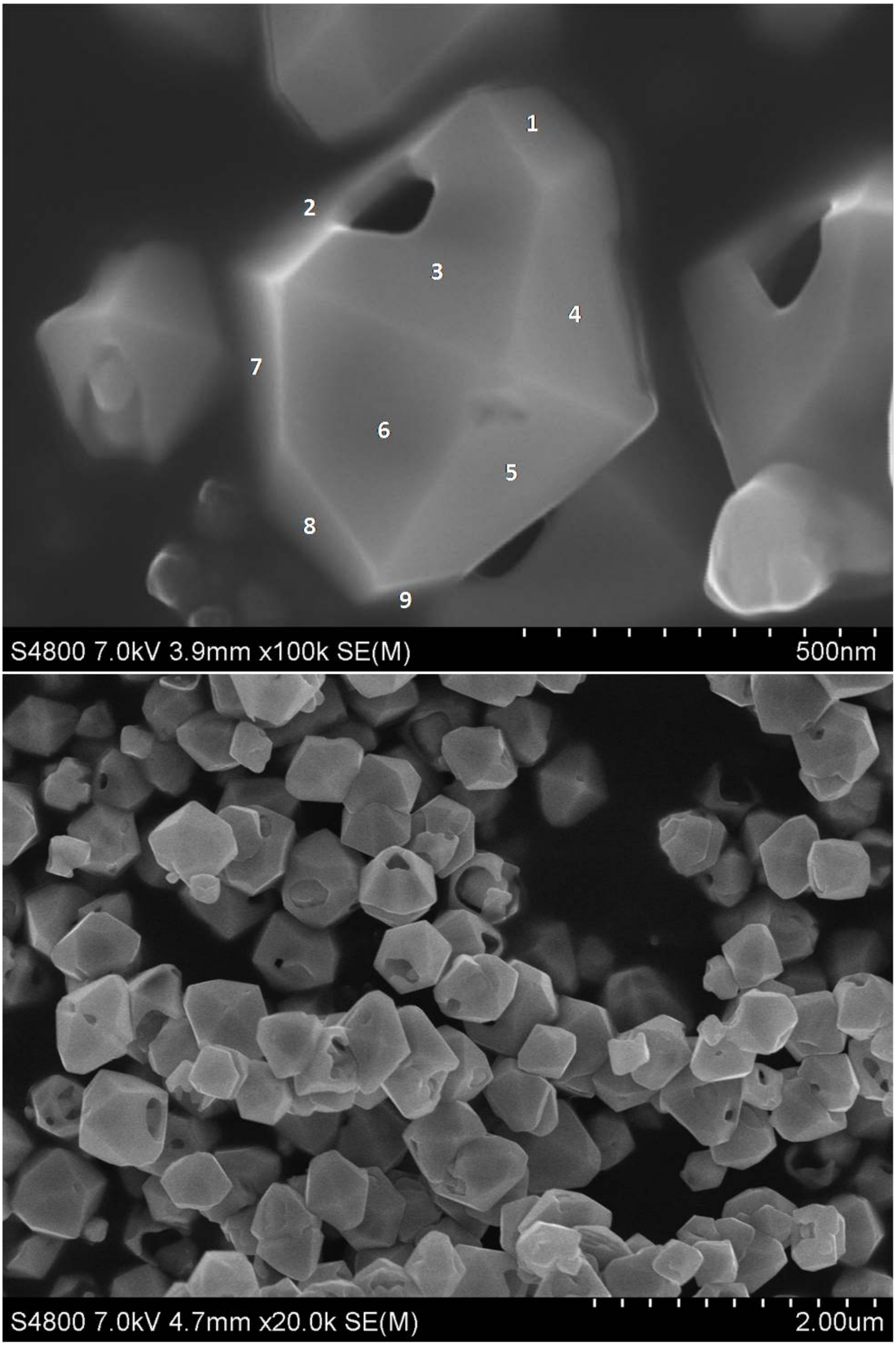

Fig. S1 SEM images of hollow polyhedrons

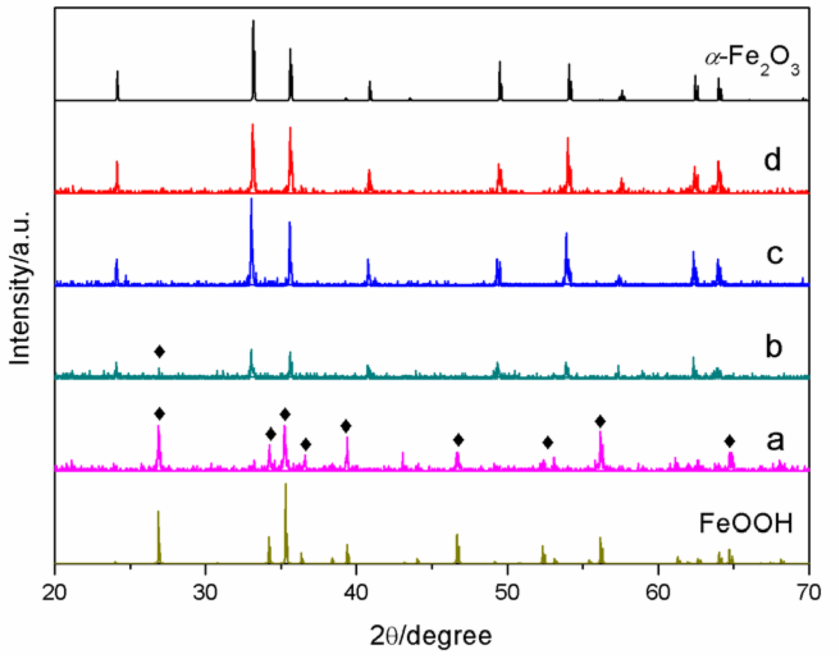

Fig. 2S XRD patterns of the samples prepared for different hydrothermal times: (a) 2, (b) 2.75, (c) 7, (d) 15 h. For comparison, the XRD patterns of FeOOH and α-Fe_2O_3 are also shown. Symbol: ◆ = FeOOH.

Fig. 2S shows the powder X-ray diffraction (XRD) patterns of the as-prepared samples which were synthesized at 200 °C for different hydrothermal times. From this figure, we can find that the sample prepared under 2 h reaction time are tetragonal FeOOH (space group: I4/m; a=10.480, c=3.023Å; JCPDS No. 75 -1594). As the reaction time increased to 2.75 h, FeOOH gradually transformed to α-Fe_2O_3 (space group: R-3c; a=5.0356, c=13.7489 Å, JCPDS No. 33 -664), and only small amount of FeOOH remained. The weak intensity of the α-Fe_2O_3 indicates that the sample is poor crystallinity which could be ascribed to the short reaction time. When the reaction time increased further, pure phase of α-Fe_2O_3 can be obtained with improved crystallinity.

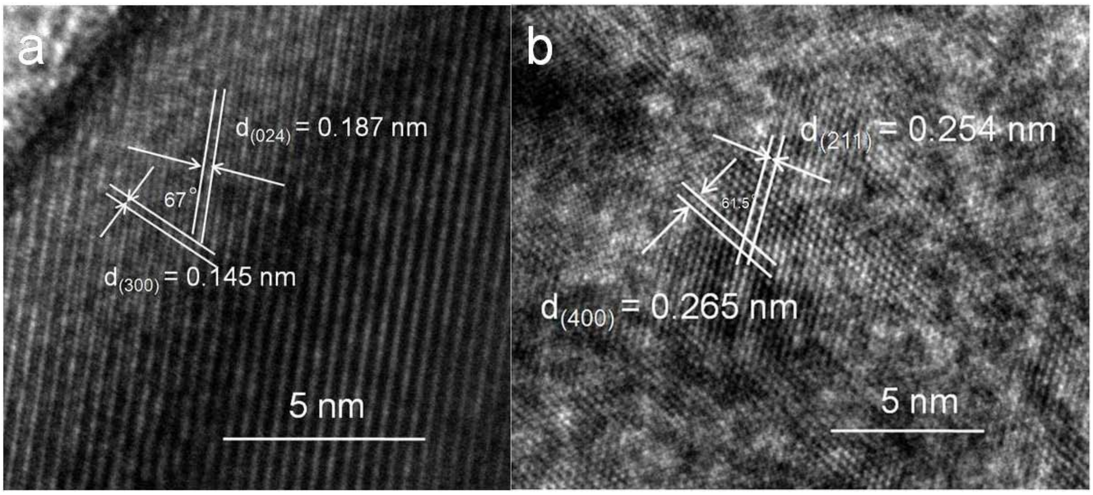

Fig. S3 HRTEM images of (a) near-spherical solid particle, (b) debris.

As shown in Fig. S3a, the lattice spacings of 0.145 nm and 0.187 nm correspond to the (300) and (024) plane of the α-Fe_2O_3, respectively. According to the crystal system of α-Fe_2O_3 and its lattice constants, the angle between (300) plane and (024) plane was calculated to be 65°, which nearly matched the measured angle 67°. In Fig. S3b, the lattice spacings of 0.265 nm and 0.254 nm correspond to the (400) and (211) plane of the FeOOH, respectively. According to the crystal system of FeOOH and its lattice constants, the angle between (400) plane and (211) plane was calculated to be 61°, which nearly matched the measured angle 61.5°. Thus, the near-spherical solid particles can be identified as α-Fe_2O_3 and the debris are confirmed to FeOOH.

Influence of different ions on α-Fe_2O_3 morphology

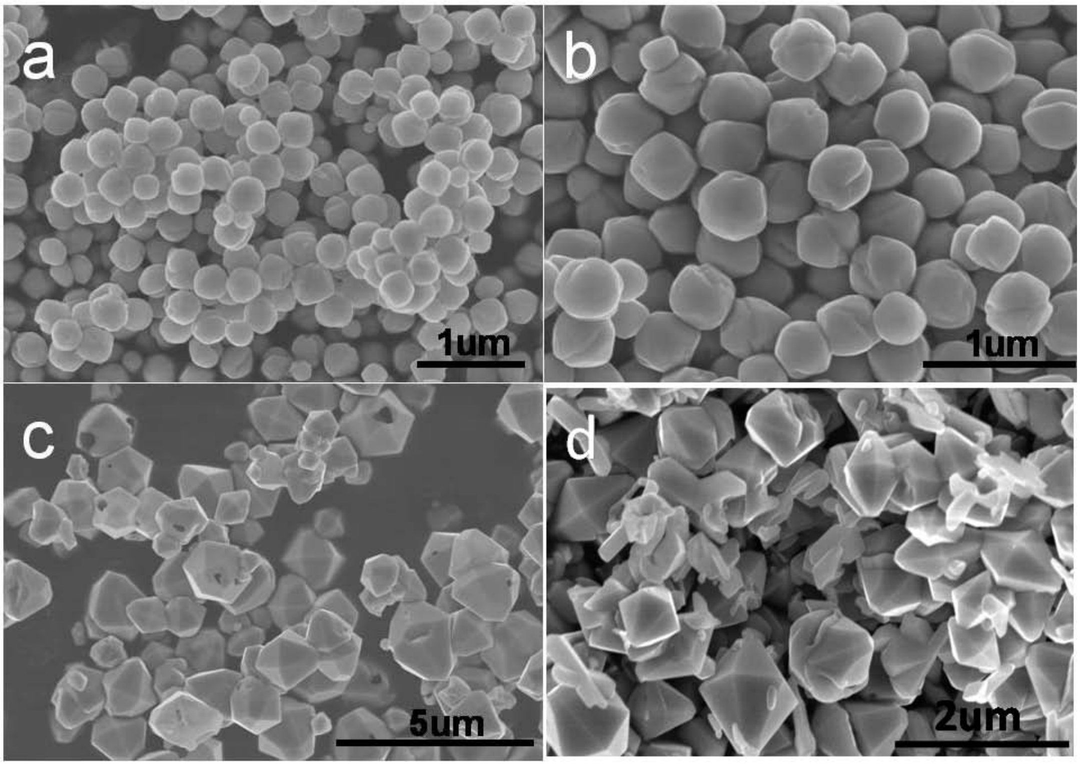

Fig. S4 SEM images of samples prepared with different additives: (a) blank, (b) C_4MimCl, (c) $NaBF_4$, (d) NaF.

As shown in Fig. S4a, the blank sample prepared without any additive exhibits near-spherical shape with particle sizes about 200-450 nm. When C_4MimCl was added during the synthetic procedure, similar morphology, namely near-spherical, can be observed as shown in Fig. S4b. However, the sizes of the α-Fe2O3 particles are much larger (about 450 nm), and the uniformity is also improved. Some cracks can also be observed on the surfaces of the sample, which may be due to the suppressed hydrolysis of ferric ion in presence of C_4Mim^+ leading to slower nucleation rates. And the slower nucleation rate also results in larger particle sizes. Fig. S4c shows the samples synthesized with $NaBF_4$ as additive. The hollow polyhedron structures also can be obtained even without C_4Mim^+, but the polyhedrons are not uniform. As shown in Fig. S4d, the sample was synthesized with NaF as additive. The polyhedron structures can be obtained, but they are not hollow structures.

The photodegradation mechanism

Under visible light irradiation, photogenerated carriers are formed in α-Fe_2O_3 hollow polyhedrons. The holes migrate to surface and oxidize RhB dye. As previously reported[1], the electrons may be consumed by the following ways. They are trapped by H_2O_2 to form OH radicals, which can degrade RhB dyes efficiently. Or the electrons are trapped by Fe^{3+} to form Fe^{2+}. The Fe^{2+}/H_2O_2 is the famous Fenton's reagent[2] and the Fenton reaction is an effective method to oxidize contaminants.

$$Fe_2O_3 \rightarrow Fe_2O_3(e_{cb}^-, h_{vb}^+) \qquad H_2O_2 + e_{cb}^- \rightarrow OH^- + \cdot OH$$

$$Fe^{3+} + e_{cb}^- \rightarrow Fe^{2+} \qquad Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$

Reference

1 J. G. Yu, X. X. Yu, B. B. Huang, X. Y. Zhang and Y. Dai, *Cryst. Growth Des.*, 2009, 9, 1474.

2 H. J. H. Fenton, *J. Chem. Soc., Trans.*, 1894, 65, 899.