

## Supporting Information

Typical morphology and structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons synthesized at the [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> concentration of about 0.1 mM have been discussed systemically by SEM and TEM (Fig. S1). SEM and bright field TEM images at low magnification clearly reveals the truncated hexagonal bipyramidal structure of the as-synthesized Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The crystallographic orientation of each exposed surface was determined through the analysis of diffraction and high resolution TEM (HRTEM) images (Fig. S1c-o). To assign the surface facets, the nanoparticles were tilted in TEM until the surface was parallel to the beam. When the Fe<sub>2</sub>O<sub>3</sub> icositetrahedron was tilted along the [006] direction, six side facets were parallel to the electron beam (Fig. S1c-f). The SAED pattern and HRTEM image indicated the exposed surfaces of the single crystal were six equivalent {110} facets. When the crystal was tilted along the [2-10] direction, there were also six side facets parallel to the electron beam (Fig. S1g-k). From the SAED pattern and HRTEM images of the selected areas (region '2' and '3' in Fig. S1g), the exposed side planes could be indexed to four equivalent {113} facets and two {110} planes, respectively. In addition, when the particle was tilted anticlockwise 30° from [2-10] to [100] zone axis (Fig. S1i-o), two top surfaces have become parallel to the electron beam and can be indexed as the {104} planes according to the SAED pattern and HRTEM image.

Figure S2 shows the SEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons with the increasing of [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> concentration, 0.5 mM and 0.8 mM. It could be found that the imperfections of the Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons, especially the end of the crystals, becomes more evident with the [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> concentration excessive. When the concentration of [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> greater than 0.8 mM, the end of the crystals vanished and the samples tended to be hollow spindles.

The typical temporal evolutions of the spectra during the RhB photodecomposition over the as-prepared Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons catalyst (Sample A to D) were shown in Fig. S3. During the 4 h photodegradation process of RhB dyes, the characteristic absorption of RhB at about 554 nm decreases gradually over time for all the four

samples. After 4 h irradiation, the absorption values of RhB are all below 0.5, particularly, the absorption values decline to about 0.2 (corresponding to the degradation rate 80%) with the sample's axial length decreased to 120 nm (Sample A), which means that the synthesized Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons have good photocatalytic performance.

Figure S4 shows the typical temporal evolutions of MO photodecomposition over the as-prepared Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons catalyst (Sample A to D). During the 4 h photodegradation process of MO dyes (Fig. S4a-d), the characteristic absorption of MO at about 462 nm (the absorption band red shift to 468 nm, when H<sub>2</sub>O<sub>2</sub> was added) decreases gradually over time for all the four samples. After 4 h irradiation, the lowest absorption value of MO reached to about 0.7 (Sample A), which means that all of these four samples have certain photocatalytic performance. However, comparing with the RhB degradation, the photocatalytic activity toward the MO was so limited. Maybe the electronegative Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons (Fig. 5b) interact more strongly with cationic dye RhB.<sup>1-4</sup>

The changes of the MO relative concentrations ( $C/C_0$ ) as a function of irradiation time were shown in Fig. S4e. Comparing with the photodegradation of MO only with H<sub>2</sub>O<sub>2</sub>, the photodegradation rates of MO with Fe<sub>2</sub>O<sub>3</sub> catalyst have a certain degree of growth. The sequence of the adsorption capacity and photocatalytic activities of different Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons is as follows: Sample A > Sample B > Sample C > Sample D, the same order with that of RhB degradation. This verifies again that larger SSA the sample with, higher photocatalytic activities the sample is. Simultaneously, photodegradation rate constants of MO degradation on iron oxides normalized to BET specific surface area have also been calculated (Fig. S4f, Tab. 1), which shows that 'k<sub>s</sub>' increased with the reduction of the sample size. This testified the deduction in the text, that is, the exposed crystal facets, mainly the corrugated, unsaturated {104} planes directly affect the photodegradation process.

## References

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- 2 X. Zhou, Q. Xu, W. Lei, T. Zhang, X. Qi, G. Liu, K. Deng and J. Yu, *Small*, 2014, **10**, 674-679.
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### Figure and Table Captions

Figure S1. Typical morphology and structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons synthesized at the [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> concentration of about 0.01 mM (Sample A). (a, b) SEM and bright field TEM images; (c-f) TEM image, corresponding SAED pattern, HRTEM images and geometrical configuration pattern showing the [006] zone axis parallel to the electron beam; (g-k) TEM image, corresponding SAED pattern, HRTEM images and geometrical configuration pattern showing the {113} and {110} surfaces parallel to the electron beam; (l-o) TEM image, corresponding diffraction pattern, HRTEM images and geometrical configuration pattern showing the {104} surfaces parallel to the electron beam when the same particle was tilted anticlockwise 30°.

Figure S2. SEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> icositetrahedrons with the increasing of [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> concentration: (a) 0.5 mM, (b) 0.8 mM.

Figure S3. UV-vis spectral changes of RhB aqueous solutions as a function of irradiation time in the presence of iron oxides (Sample A to D) and H<sub>2</sub>O<sub>2</sub> additive.

Figure S4. (a-d) UV-vis spectral changes of MO aqueous solutions as a function of irradiation time in the presence of iron oxides (Sample A to D) and H<sub>2</sub>O<sub>2</sub> additive; (e,f)

Degradation conditions of MO solution, with (e) and without (f) the factor of BET surface area is considered.