Electronic Supplementary Information (ESI) for:

**Ellipsoidal hollow nanostructures assembled from anatase TiO$_2$ nanosheets for magnetically separable photocatalyst**

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**Experimental Section**

**Materials preparation**

*Synthesis of $\alpha$-Fe$_2$O$_3$@SiO$_2$@SnO$_2$ core-shell templates.* The ellipsoidal $\alpha$-Fe$_2$O$_3$@SiO$_2$@SnO$_2$ core-shell templates are synthesized following our previously reported method (Adv. Mater. 2007, **19**, 3328). Briefly, $\alpha$-Fe$_2$O$_3$ nanospindles were first synthesized via aging 0.02 M FeCl$_3$ with 0.45 mM NaH$_2$PO$_4$ at 105 °C for 50 h (J. Colloid Interface Sci., 1984, **192**, 146). For SiO$_2$ coating, 0.15 g of the as-prepared $\alpha$-Fe$_2$O$_3$ nanospindles was dispersed in 650 ml isopropanol and 65 ml of H$_2$O, followed by the addition of 60 ml of ammonia (28%). 0.5 ml of tetraethylorthosilicate was then added under magnetic stirring, and the reaction was continued for 18 – 22 h before the product was collected via centrifugation, followed by washing and drying at 60 °C overnight. For the final SnO$_2$ deposition, 0.3 g of the as-obtained $\alpha$-Fe$_2$O$_3$@SiO$_2$ was dispersed in a 50 ml of ethanol/H$_2$O mixture (37.5 vol % ethanol) with the addition of 1.5 g of urea and 0.2 g of K$_2$SnO$_3$$\cdot$3H$_2$O. After that, the solution was hydrothermally treated at 170 °C for 36 h, before the product was
collected, washed and dried.

*Synthesis of cocoon-like SnO$_2$@TiO$_2$-NS double-shells.* Typically, 0.04 g of as-synthesized ellipsoidal $\alpha$-Fe$_2$O$_3$@SiO$_2$@SnO$_2$ templates was dispersed in 41.5 ml of isopropanol (IPA) followed by the addition of 0.03 ml of diethylenetriamine (DETA; 99%, Sigma-Aldrich). After stirring gently by hand, 2 ml of titanium isopropoxide (TIP; 97%, Sigma-Aldrich) was added into the solution. The reaction mixture was transferred into a 60 ml Teflon-lined stainless steel autoclave and kept at 200 °C for 24 h. After that, the product was collected and washed via centrifugation, before drying at 60 °C overnight. The powder was then calcined at 400 °C in air for 2 h with a ramping rate of 1 °C min$^{-1}$ to obtain highly crystalline anatase phase. For removal of the intermediate silica layer, calcined $\alpha$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$-NS was dispersed into 0.6 wt% hydrofluoric acid (HF) solution and shaken under room temperature for 1 h before washing with water.

*Synthesis of cocoon-like rattle-type Fe$_3$O$_4$@TiO$_2$ and hollow TiO$_2$.* The synthesized $\alpha$-Fe$_2$O$_3$@SiO$_2$ templates were synthesized similar to the above procedures, without the final deposition of the SnO$_2$ layer. The templates were first calcined at 300 °C for 2 h in static air. Then 0.04 g of template was dispersed in 41.47 ml of IPA, followed by the addition of 0.03 ml of DETA and 2 ml of TIP. The subsequent calcination and removal of SiO$_2$ is the same as described above, leading to the rattle-type $\alpha$-Fe$_2$O$_3$@TiO$_2$-NS structures. Fe$_3$O$_4$@TiO$_2$-NS nanorattles with magnetic functionality are simply obtained by reducing $\alpha$-Fe$_2$O$_3$@TiO$_2$-NS under the dynamic flow of a mixture of 5% H$_2$ with 95% N$_2$ at 300 °C for 9 h. Further treating
α-Fe₂O₃@TiO₂-NS nanorattles with 0.5 M oxalic acid overnight will dissolve the α-Fe₂O₃ nanospindle core, giving the hollow cocoon-like TiO₂ nanostructure.

**Materials characterization**

The morphology of products was examined by transmission electron microscope (TEM; JEOL, JEM-2100F, 200 kV), field-emission scanning electron microscope (FESEM; JEOL, JSM-6700F, 5 kV). The elemental compositions of the samples were analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to FESEM. Crystallographic information of the samples was investigated with X-ray powder diffraction (XRD; Bruker, D8 - Advance X-Ray Diffractometer, Cu Kα, \( λ = 1.5406 \) Å). The surface area of the sample was measured using Quantachrome Instruments, Autosorb AS-6B. For the uncalcined sample, the thermogravimetric analysis (TGA) was carried out in a flow of air with a temperature ramp of 5 °C min⁻¹.

**Photocatalytic degradation of Methylene Blue**

30 mg of TiO₂ sample (e.g., Fe₃O₄@TiO₂, or commercialized Degussa P25 nanoparticles) was dispersed in an aqueous solution containing 0.01 M NaOH and 25 ppm Methylene Blue (MB). The mixture was first stirred in dark for 1 h to assure that the adsorption/desorption equilibrium between the TiO₂ catalysts and MB can be reached. UV radiation was then introduced with ~0.5 mW cm⁻² (with a wavelength peak at 365 nm) under continuous stirring. 1 ml of solution was taken out every 30 min and the catalyst was separated. The concentration of MB was determined from the absorbance at the wavelength of 665 nm.
Figure S1. (A) FESEM image of $\alpha$-Fe$_2$O$_3$@SiO$_2$@SnO$_2$@TiO$_2$ composite spindle-like nanostructure; (B) EDX analysis of the sample shown in A; (C) FESEM image of sample A in Figure 1; (D) EDX analysis of sample A.
Figure S2. (A) FESEM image of $\alpha$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ spindle-like nanostructure; (B) EDX analysis of the sample shown in A; (C) FESEM image of sample B in Figure 1; (D) EDX analysis of sample B; (E) FESEM image of sample C; (F) EDX analysis of sample C.
Figure S3. XRD patterns of the sample shown in S1A (A) and S2A (B) after (I) and before (II) calcination at 400 °C. The peaks marked by asterisks in A and B are attributed to $\alpha$-Fe$_2$O$_3$ (JCPDS card no. 33-0664). TGA results of the samples shown in S1A (C) and S2A (D) before calcination.
Figure S4. N₂ adsorption-desorption isotherm of sample A, B and C shown in Fig. 1. The hysteresis loop indicates a mesoporous structure. The insets show the pore size distribution by Barrett-Joyner-Halenda (BJH) method from both branches of the isotherm of the corresponding sample.