

Supporting Information

**A Versatile Kinetics-Controlled Coating Method to Construct
Uniform Porous TiO₂ Shells for Multifunctional Core-Shell
Structures**

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Experimental Section

Chemicals. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, potassium dihydrogen phosphate (KH_2PO_4), trisodium citrate, ethylene glycol, sodium acetate, tetraethyl orthosilicate (TEOS), tetrabutyl titanate (TBOT), glucose, ethanol and concentrated ammonia solution (28 wt%) were of analytical grade and purchased from Shanghai Chemical Corp. All chemicals were used as received without further purification. Deionized water was used for all experiments.

Synthesis of $\alpha\text{-Fe}_2\text{O}_3$ Ellipsoids. The $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals were prepared by aging a solution of FeCl_3 (0.02 M) and KH_2PO_4 (0.45 mM) at 105 °C for 48 h.¹ The obtained ellipsoids were separated and collected by centrifugation, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of Fe_3O_4 Nanoparticles. The water-dispersible Fe_3O_4 nanoparticles were synthesized according to the method reported previously.² Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.25 g), trisodium citrate (1.3 g), and sodium acetate (NaAc, 6.0 g) were dissolved in ethylene glycol (100 mL) with magnetic stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave (200 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with deionized water and ethanol for 3 times, respectively.

Synthesis of SiO_2 Spheres. The SiO_2 spheres were prepared according to Stöber's method.³ For a typical process, TEOS (3.8 mL), concentrated ammonia solution (28 wt%, 7.5 mL) and deionized water (18 mL) were mixed into ethanol (120 mL). The mixture was allowed to react for 24 h at 25 °C. The resultant product was separated and collected by centrifugation, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of Graphite Oxide (GO). Graphite oxide (GO) was synthesized from graphite purchased from Sigma–Aldrich, using the Staudenmaier method and developed by other authors.⁴ Briefly, graphite (5.0 g) was added into a mixture solution of concentrated H_2SO_4 (87.5 mL) and fuming HNO_3 (45 mL) cooled in an ice-water bath. KClO_3 (55 g) was added very slowly (with a period more than 15 min) into the mixture. All the operations were carried out very slowly in a fume hood to reduce the risk of explosion due to the release of chlorine dioxide gas. After 96 h stirring at room temperature, the mixture was poured into water (4.0 L), and filtered to obtain the graphite oxide.

Synthesis of Carbon Nanospheres. Glucose (3.5 g) was dissolved in deionized water (35 mL) to form a clear solution and then transferred into a Teflon-lined stainless-steel autoclave (40 mL in capacity). The autoclave was maintained at 180 °C for 3 h, and then allowed to cool to room temperature. The products were separated

by centrifugation, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of SiO₂ Shell Core-Shell Microspheres. The SiO₂ shell core-shell microspheres were prepared through a versatile sol-gel method as follows. An ethanol dispersion of the core particles (3.0 mL, 0.05 g/mL) was added to a three-neck round-bottom flask charged with absolute ethanol (280 mL), deionized water (70 mL) and concentrated ammonia solution (28 wt%, 5.0 mL) under ultrasound for 15 min. Afterward, 4.0 mL of TEOS was added dropwise in 10 min, and the reaction was allowed to proceed for 10 h at room temperature under continuous mechanical stirring. The resultant product was separated, followed by washing with deionized water and ethanol for 3 times, respectively.

Synthesis of Uniform Porous TiO₂ Shell Core-Shell Nanostructures. The uniform porous TiO₂ shell core-shell structures were prepared via the versatile kinetics-controlled coating method. The core nanoparticles were dispersed in absolute ethanol (100 mL), and mixed with concentrated ammonia solution (0.30 mL, 28 wt%) under ultrasound for 15 min. Afterward, 0.75 mL of TBOT was added dropwise in 5 min, and the reaction was allowed to proceed for 24 h at 45 °C under continuous mechanical stirring. The resultant products were separated and collected, followed by washing with deionized water and ethanol for 3 times, respectively. Then, the obtained powders were dried at 100 °C overnight. Finally, the resulting samples were calcined at 500 °C in air for 2 h to remove the organic species and improve crystallinity.

Synthesis of Magnetic Photocatalysts. The magnetic photocatalysts (Fe₃O₄@TiO₂) were prepared via a reduction and crystallization process with the as-made α -Fe₂O₃@TiO₂ micro-ellipsoids as the starting materials. The α -Fe₂O₃@TiO₂ micro-ellipsoids were annealed in a furnace at 450 °C under a continuous H₂/Ar gas flow (5 % H₂) for 2 h. Then the furnace was allowed to cool to room temperature while still under a continuous H₂/Ar gas flow.

Electrochemical Tests: The working electrodes were prepared by mixing the calcined α -Fe₂O₃@TiO₂ samples with 10 % acetylene black as a conductive material, and 5 % polyvinylidene difluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidinone (NMP). Then, the slurries of the mixture were cast onto a copper foil current collector. After coating, the electrodes were dried at 80 °C for 1 h to remove the solvent before pressing. The electrodes were punched in the form of disks typically with a diameter of 12 mm and weight of ~ 8 mg and then vacuum-dried at 80 °C for 24 h. The cell assembly was operated in a glove box (model 100G, MBraun, Germany) filled with high purity argon. The electrolyte solution was 1 M LiPF₆/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1: 1: 1 by volume). The cells were assembled with the as-prepared positive electrode, lithium metal, and separators made of a Celgard 2300 film. The electrochemical tests of the samples

were evaluated using an automatic battery testing system (LAND CT2001A model).

Photocatalytic Activity. The photodegradation of Rhodamine B (RhB) was carried out in an aqueous solution at room temperature under UV light irradiation. A 20 W tube-like UV lamp ($\lambda = 365$ nm) was used as a light source. The reactor was open to air in order to reach the air-equilibrated condition. In a typical experiment, 40 mg of the photocatalyst powders were dispersed in 40 mL of RhB solution (1×10^{-5} M) with stirring. The suspension was stirred for 1 h in the dark to reach an adsorption equilibrium. The mixture was subsequently illuminated with the UV lamp for different time intervals under continuous stirring. Prior to determining the concentration of RhB, the solution was separated from the catalyst by applying an external magnetic field. To investigate the reusability, we reused $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids by exposing them in UV light for 1 h. Then, they were washed with distilled water three times and dried in an oven overnight to remove the residual reactants. The concentration of residual RhB was monitored by using a UV-vis spectrometer (Jasco V-550) at the characteristic absorption wavelength of 553 nm.

Characterization.

Wide-angle XRD patterns were recorded on a Bruker D8 diffractometer (Germany) with Ni-filtered Cu $K\alpha$ radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer. All of the samples were degassed under vacuum at 180 °C for at least 8 h prior to measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions (PSD) were derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volume V_t was estimated from the adsorbed amount at a relative pressure P/P_0 of 0.995. Thermogravimetric analysis was conducted on a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 40 to 900 °C under air with a heating rate of 5 °C/min. Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100 F microscope (Japan) operated at 200 kV. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Field-emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4800 microscope.

References.

- (1) Ozaki, M.; Kratochvil, S.; Matijevic, E.; *J. Colloid Interface Sci.* **1984**, 102, 146.
- (2) Liu, J.; Sun, Z. K.; Deng, Y. H.; Zou, Y.; Li, C. Y.; Guo, X. H.; Xiong, L. Q.; Gao, Y.; Li, F. Y.; Zhao, D. Y. *Angew. Chem. Int. Ed.* **2009**, 48, 5875.
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- (4) Huang, X. D.; Zhou, X. F.; Zhou, L.; Qian, K.; Wang, Y. H.; Liu, Z. P.; Yu, C. Z.; *ChemPhysChem* **2011**, 12, 278.

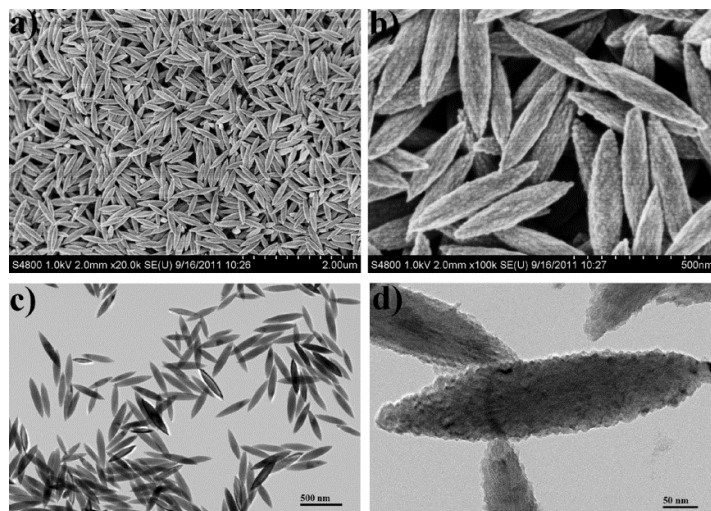


Figure S1. FESEM images (a, b) and TEM images (c, d) of the α -Fe₂O₃ ellipsoids prepared by aging a solution of FeCl₃ (0.02 M) and KH₂PO₄ (0.45 mM) at 105 °C for 48 h.

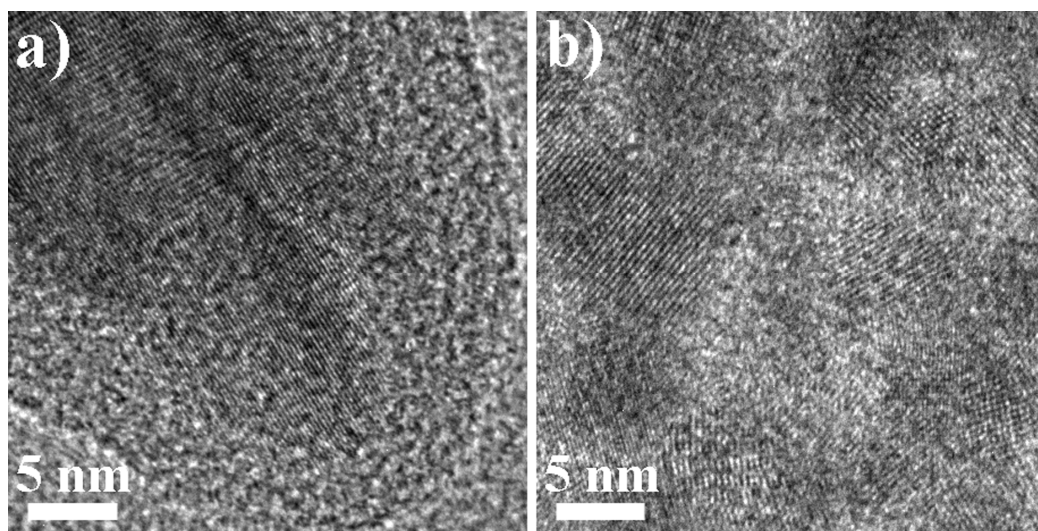


Figure S2. The corresponding magnified HRTEM images of the core-shell $\alpha\text{-Fe}_2\text{O}_3\text{@TiO}_2$ micro-ellipsoids (a) before calcinations and (b) after calcinations at 500 °C in air.

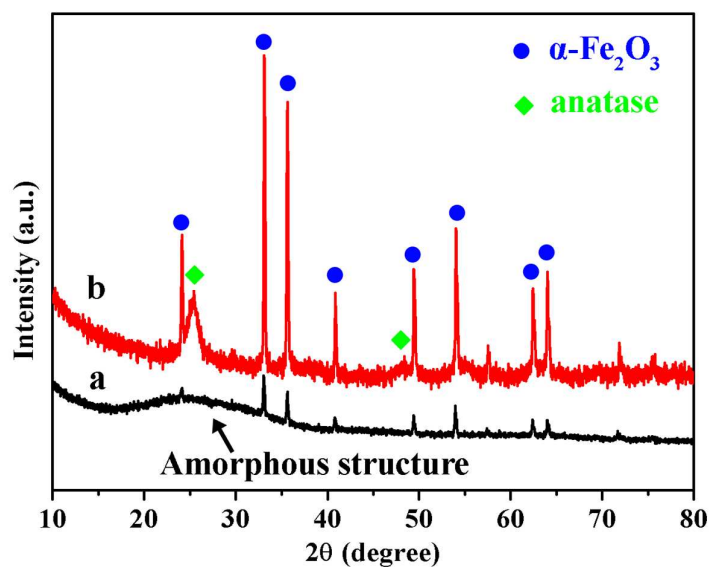


Figure S3. XRD patterns of the uniform core-shell $\alpha\text{-Fe}_2\text{O}_3\text{@TiO}_2$ micro-ellipsoids prepared by the versatile kinetics-controlled coating method before (a) and after (b) calcination at 500 °C in air for 2 h. For the typical synthesis, $\alpha\text{-Fe}_2\text{O}_3$ ellipsoids (75 mg), ethanol (100 mL), and TBOT (0.75 mL) were mixed with concentrated ammonia (0.3 mL), and then the mixture was heated at 45 °C for 24 h. The blue spheres (●) and green rhombuses (◆) indicate the typical diffraction peaks of $\alpha\text{-Fe}_2\text{O}_3$ and anatase TiO_2 , respectively.

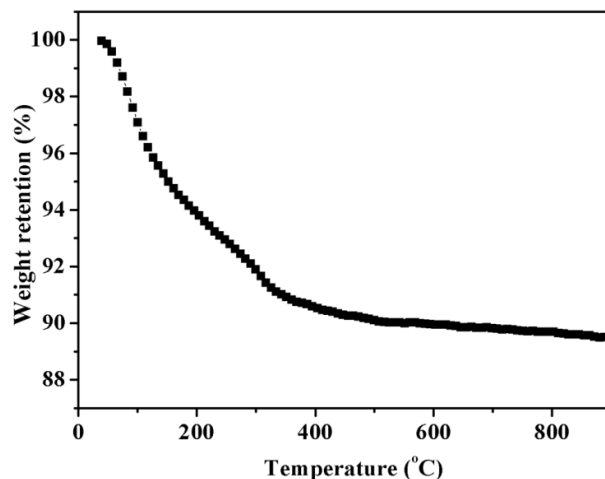


Figure S4. TGA curve of the uniform core-shell $\alpha\text{-Fe}_2\text{O}_3\text{@TiO}_2$ micro-ellipsoids prepared by the versatile kinetics-controlled coating method. For the typical synthesis, $\alpha\text{-Fe}_2\text{O}_3$ cores (75 mg), ethanol (100 mL), and TBOT (0.75 mL) were mixed with concentrated ammonia (0.3 mL), and then the mixture was heated at 45 °C for 24 h. Approximately 10 % weight loss was observed at a temperature before 400 °C, which is attributed to the desorption of adsorbed water and further condensation of the TiO_2 network process.

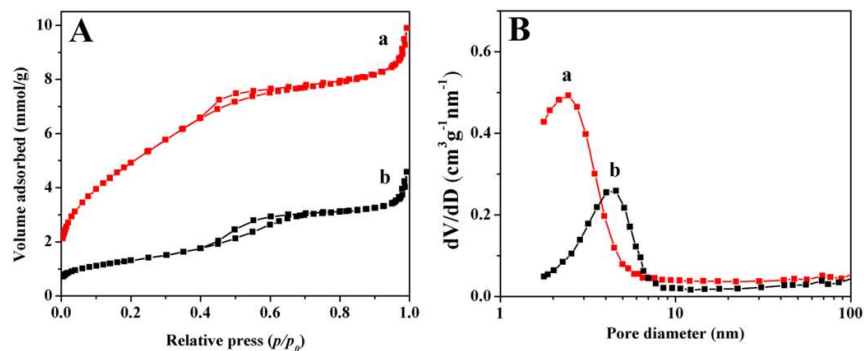


Figure S5. N₂ sorption isotherms (A) and the corresponding pore size distribution curves (B) of the uniform core-shell $\alpha\text{-Fe}_2\text{O}_3@\text{TiO}_2$ micro-ellipsoids prepared by the versatile kinetics-controlled coating method before (a, —■—) and after (b, —■—) calcination at 500 °C in air for 2 h. For the typical synthesis, $\alpha\text{-Fe}_2\text{O}_3$ cores (75 mg), ethanol (100 mL), and TBOT (0.75 mL) were mixed with concentrated ammonia (0.3 mL) and heated at 45 °C for 24 h.

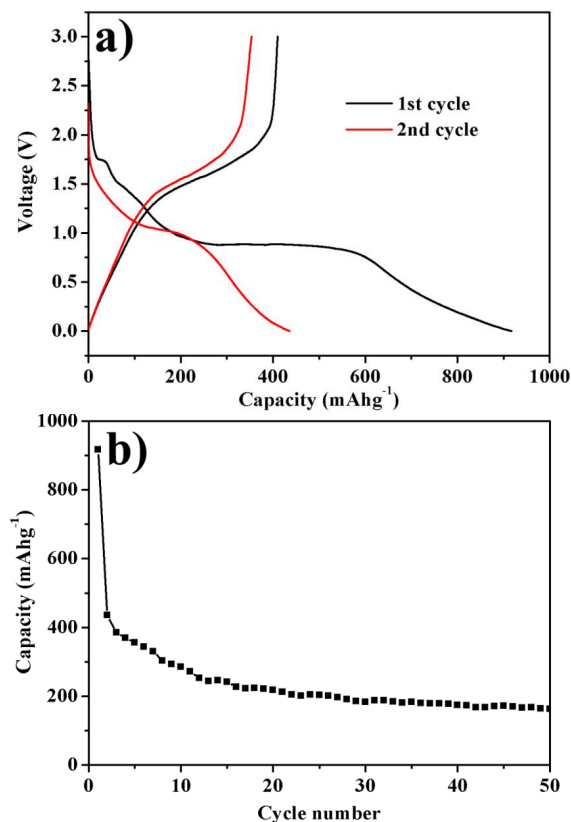


Figure S6. The first and second charge-discharge curves (a) and cycling performance (b) of the electrode made from the uniform core-shell α -Fe₂O₃@anatase TiO₂ micro-ellipsoids in the voltage range of 0.0 – 3.0 V at 0.5 C. The initial discharge and charge capacities are 917 and 410 mAhg⁻¹, respectively. In the second cycle, the discharge capacity decreases to 435 mAhg⁻¹ with a corresponding charge capacity of 354 mAhg⁻¹, leading to a high Coulombic efficiency of 81.4%. After 50 cycles at 0.5 C, a high discharge capacity of 162.7 mAhg⁻¹ is still retained, corresponding to 37.5 % of the second one.

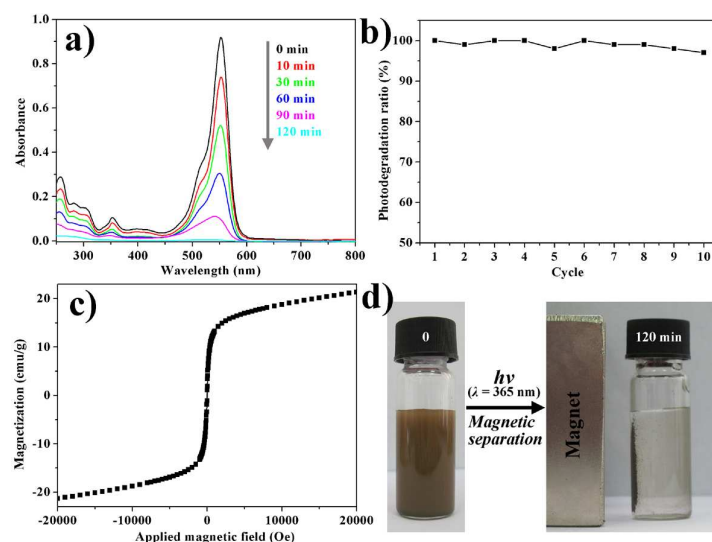


Figure S7. a) UV-Vis absorption spectra of a solution of RhB in the presence of the $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids after irradiation by UV light for different time intervals. The typical absorption peak at 553 nm gradually diminishes as the UV exposure time increases, and completely disappears after 120 min, suggesting the complete photodegradation of RhB by the $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids. b) The cyclic stability of the $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids for photodegradation of RhB. It clearly shows that the performance of the magnetic catalyst for photocatalytic degradation of RhB remains approximately constant even after ten cycles. c) The magnetic hysteresis loops at 300 K of the $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids. It clearly shows the typical hysteresis loops with no detectable remanence or coercivity, reflecting a superparamagnetic property with a high magnetization saturation value of ~ 21 emu/g. d) The magnetic separation process of the $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids from the RhB solution after the photodegradation treatment. It clearly shows the $\text{Fe}_3\text{O}_4@\text{TiO}_2$ micro-ellipsoids can be conveniently separated upon application of an extend magnetic field.

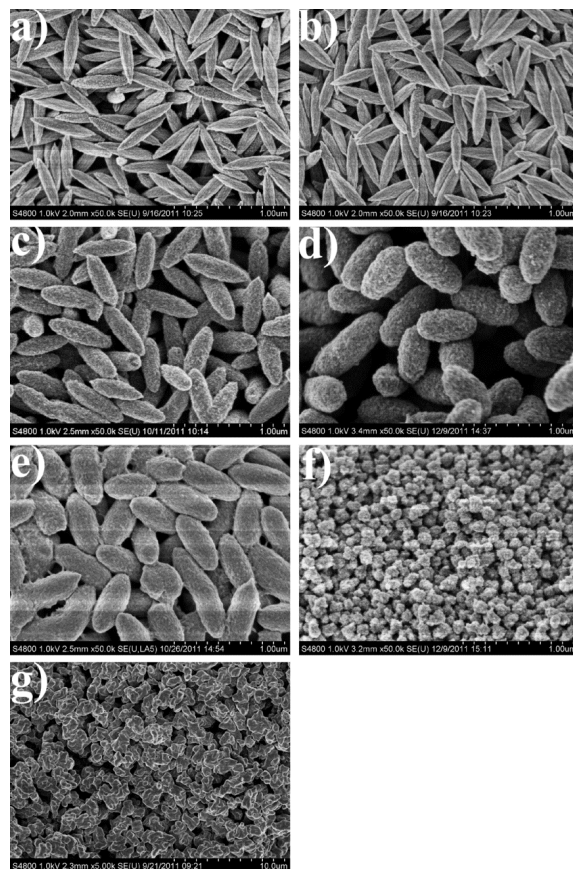


Figure S8. FESEM images of the α -Fe₂O₃/TiO₂ composites prepared in a typical mixture of α -Fe₂O₃ cores (75 mg), ethanol (100 mL), and TBOT (0.75 mL) with different content of concentrated ammonia and reaction time, (a) 0 mL, for 24 h, (b) 0.2 mL, for 24 h, (c) 0.25 mL, for 24 h, (d) 0.4 mL, for 24 h and (e) 0.4 mL, for 12 h. (f) the FESEM image of the isolated TiO₂ nanoparticles obtained with 0.4 mL of concentrated ammonia for 24 h after removing the core-shell α -Fe₂O₃@TiO₂ micro-ellipsoids in the resulted mixtures through centrifugation. (g) the FESEM image of the α -Fe₂O₃/TiO₂ composites synthesized by the versatile kinetics-controlled coating method. For the typical synthesis, α -Fe₂O₃ cores (75 mg), ethanol (100 mL), deionized water (1.0 mL) and TBOT (0.75 mL) were mixed with concentrated ammonia (0.4 mL) and heated at 45 °C for 24 h.

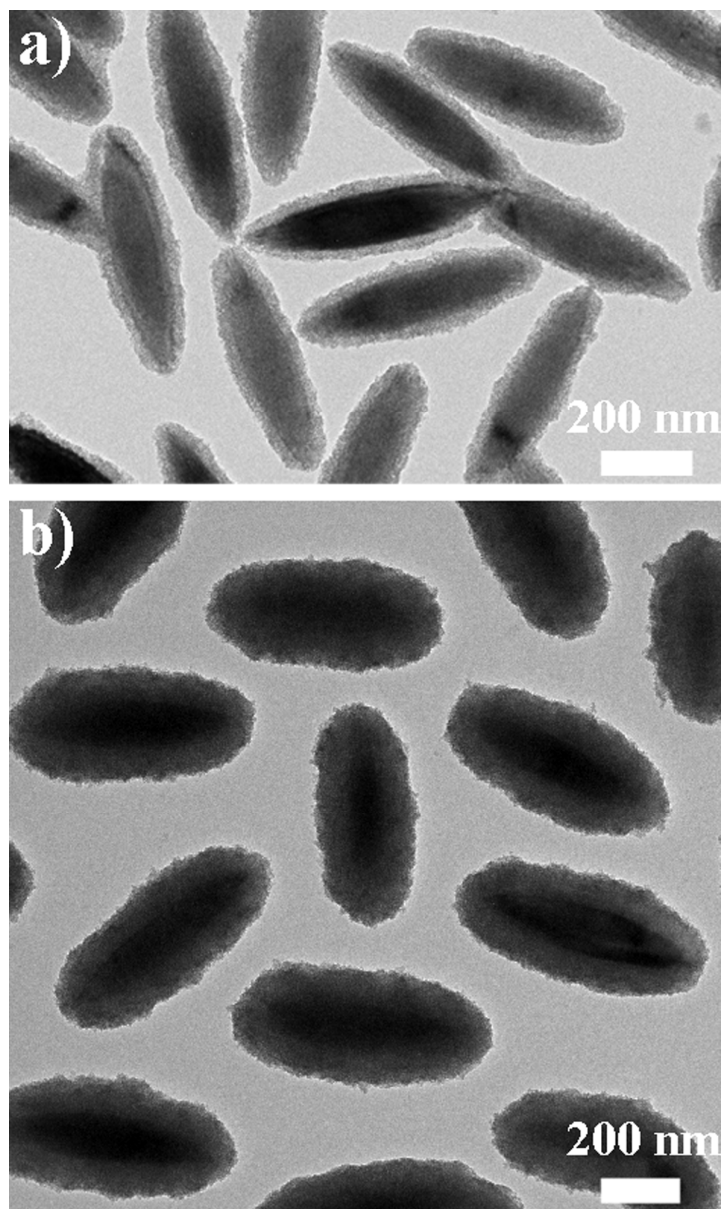


Figure S9. TEM images of the α -Fe₂O₃/TiO₂ composites prepared in a typical mixture of α -Fe₂O₃ cores (75 mg), ethanol (100 mL), and TBOT (0.75 mL) with different content of concentrated ammonia and reaction time, (a) 0.25 mL, for 24 h and (b) 0.4 mL, for 24 h.

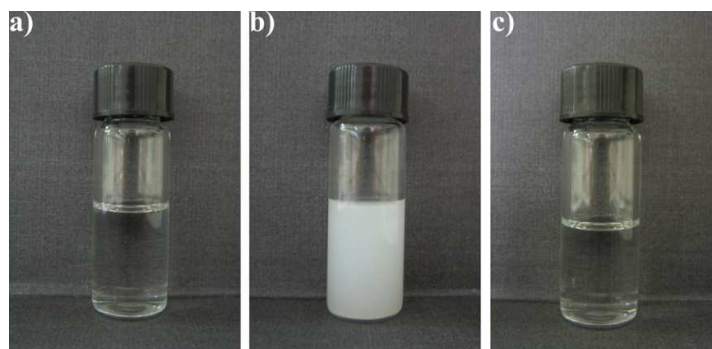


Figure S10. The optical photographs of the solutions obtained after removing the core-shell $\alpha\text{-Fe}_2\text{O}_3\text{@TiO}_2$ micro-ellipsoids in the resulted mixtures through centrifugation with different content of concentrated ammonia and reaction time, a) 0.25 mL, for 24 h, b) 0.4 mL, for 24 h, and c) 0.4 mL, for 12 h.

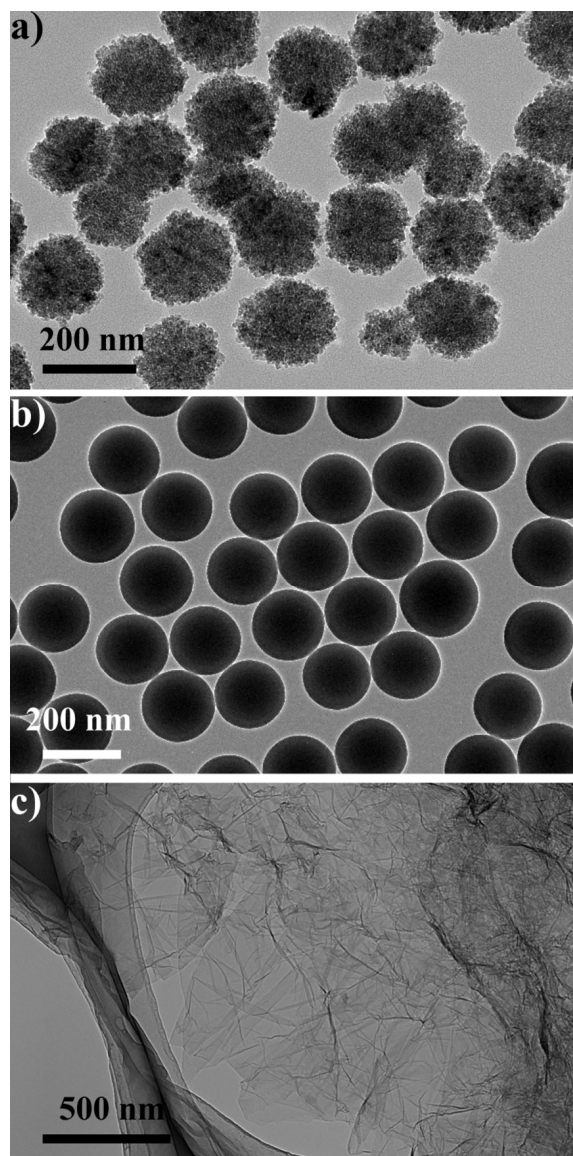


Figure S11. TEM images of (a) the Fe_3O_4 spheres capped with citrate groups prepared by aging a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.25 g), trisodium citrate (1.3 g), and sodium acetate (NaAc, 6.0 g) and ethylene glycol (100 mL) at 200 °C for 10 h. (b) SiO_2 spheres prepared in a typical sol-gel coating process. In the preparation, TEOS (3.8 mL), concentrated ammonia solution (28 wt%, 7.5 mL) and deionized water (18 mL) were mixed into ethanol (120 mL), and stirred at 25 °C for 24 h. and (c) graphene oxide (GO) nanosheets synthesized from graphite using the classical Staudenmaier method.

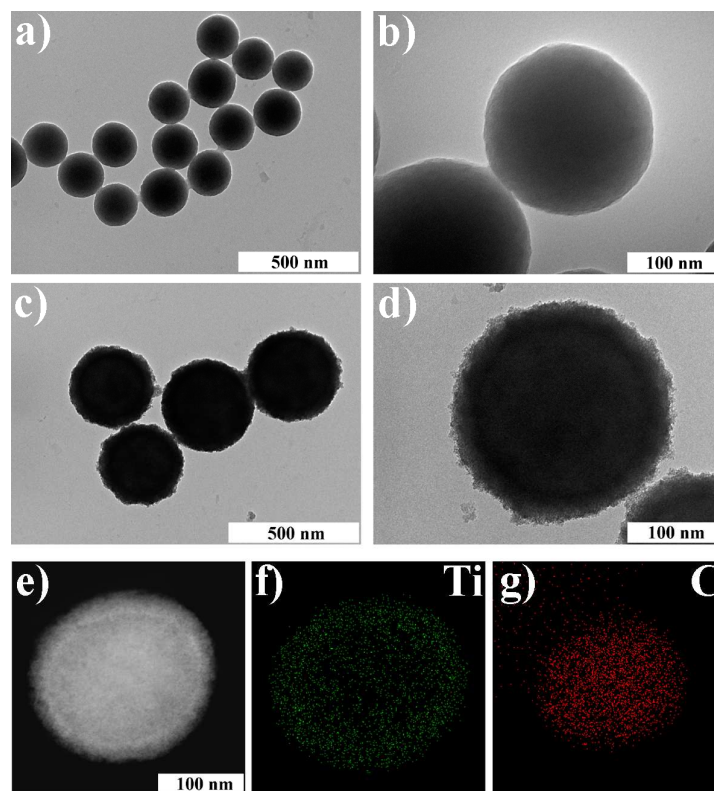


Figure S12. TEM images of (a, b) the carbon nanospheres prepared by aging a solution of glucose (3.5 g) and deionized water (35 mL) at 180 °C for 3 h. The core-shell carbon@TiO₂ nanospheres prepared through the typical kinetics-controlled coating method: (c, d) TEM images, (e) the STEM image and (f, g) EDX elemental maps of Ti and C, respectively. These can clearly show that carbon nanospheres are uniformly coated by the TiO₂ shell.

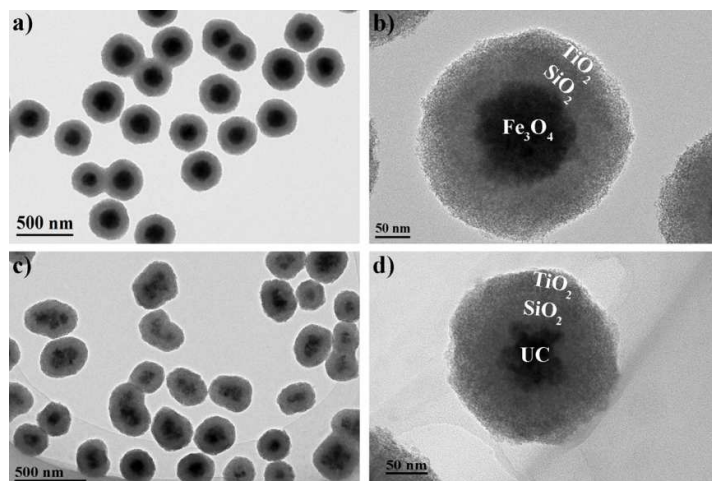


Figure S13. TEM images of (a, b) the sandwich core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ microspheres and (c, d) $\text{NaYF}_4:\text{Yb,Er}@\text{SiO}_2@\text{TiO}_2$ composites prepared through a two-step Stöber sol-gel process with silica as a interlayer, followed by the typical kinetics-controlled coating method for deposition of TiO_2 layer. The $\text{NaYF}_4:\text{Yb,Er}$ upconversion nanoparticles were prepared by aging a solution of NaOH (0.7 g), NaF (0.202 g), malonic acid (2.0 g), $\text{Y}(\text{NO}_3)_3$ (0.80 M, 1.1 mL), $\text{Yb}(\text{NO}_3)_3$ (0.63 M, 0.35 mL), $\text{Er}(\text{NO}_3)_3$ (0.40 M, 0.05 mL) and 20 mL deionized water at 100 °C for 12 h.