Supplementary Information

Highly efficient and recyclable triple-shelled Ag@Fe₃O₄@SiO₂@TiO₂ photocatalysts for degradation of organic pollutants and reduction of hexavalent chromium ions

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Synthesis of TiO₂ microspheres
The TiO₂ microspheres were prepared via a typical solvothermal method reported previously.¹ Briefly, DETA (0.03 mL) was added to IPA (42 mL) under gently stirred, followed with the addition of TIP (1.5 mL). The obtained solution was then transferred into a 70 mL Teflon-lined stainless steel autoclave and kept at 200 °C for 24 h. The autoclave was left to cool down to room temperature naturally. The white products was collected by centrifugation, washed with ethanol, and dried at 60 °C overnight. The products were calcined at 400 °C for 2 h with a heating rate of 1°C·min⁻¹ to obtain a highly crystalline anatase phase.

Synthesis of Fe₃O₄@SiO₂@TiO₂ nanospheres
The Fe₃O₄ nanospheres were synthesized following a modified method reported previously.² Briefly, Fe(NO₃)₃·9H₂O (4 mmol) and NaAc (35 mmol) were dissolved in EG (40 mL), followed by the transfer of the mixture into a 70 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 8 h. For SiO₂ coating, 0.05 g of the as-prepared Fe₃O₄ NPs were dispersed in the mixture of ethanol (19 mL), deionized water (3 mL), ammonia solution (1 mL, 25~28%) and the solution of TEOS (0.01 mL) in ethanol (1 mL). After proceeding for 3 h, the black precipitate was harvested. The amorphous TiO₂ coating is the same as described above, leading to the formation of triplex Fe₃O₄@SiO₂@TiO₂ nanospheres.

Synthesis of Ag@Fe₃O₄@TiO₂ nanospheres:
The synthesis of Ag@Fe₃O₄@TiO₂ nanospheres without the SiO₂ interlayers was similar to the procedures above. Briefly, the as-prepared Ag@Fe₃O₄ (30 mg) was dispersed in IPA (27.97 mL), followed by the addition of DETA

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†Electronic supplementary information (ESI) available: Synthesis of TiO₂ microspheres; Synthesis of Fe₃O₄@SiO₂@TiO₂ nanospheres; Synthesis of Ag@Fe₃O₄@TiO₂ nanospheres; SEM images of the as-prepared products: (a) Ag@Fe₃O₄, (b) Ag@Fe₃O₄@SiO₂ and (c) Ag@Fe₃O₄@SiO₂@TiO₂ (Fig.S1); TEM images of the Ag@Fe₃O₄@SiO₂ synthesized with adding different amount of TEOS (Fig.S2); SEM, TEM and EDS spectrum of Fe₃O₄@SiO₂@TiO₂ NPs (Fig.S3); SEM and TEM images of as-prepared TiO₂ microspheres (Fig.S4); Nitrogen adsorption-desorption isotherm and pore size distribution plot for as-prepared Fe₃O₄@SiO₂@TiO₂ and TiO₂ microspheres (Fig.S5); Adsorption rate curve of MB in dark for Ag@Fe₃O₄@SiO₂@TiO₂ and P25 (10 mg) under Xe lamp illumination (Fig.S7).
(0.02 mL) and TIP (1.33 mL) under mechanical stirring. Afterward, the mixture was transferred to a 50mL Teflon-lined stainless-steel autoclave and kept at 200°C for 24 h. After being collected, washed and dried, the brown powder was obtained.

**Fig. S1** SEM images of the as-prepared products: (a) Ag@Fe₃O₄, (b) Ag@Fe₃O₄@SiO₂ and (c) Ag@Fe₃O₄@SiO₂@TiO₂.
Fig. S2 TEM images of the Ag@Fe₃O₄@SiO₂ synthesized with adding amount of TEOS of 10 μL (a), 15 μL (b), 25 μL (c).
Fig. S3 (a) TEM images of Fe$_3$O$_4$@SiO$_2$@TiO$_2$ nanoparticles; (b) SEM images of Fe$_3$O$_4$@SiO$_2$@TiO$_2$ nanoparticles; (c) EDS spectrum of Fe$_3$O$_4$@SiO$_2$@TiO$_2$ nanoparticles.
Fig. S4 (a) TEM image of as-prepared TiO$_2$ microspheres; (b) SEM images of as-prepared TiO$_2$ microspheres.
**Fig. S5** Nitrogen adsorption-desorption isotherm and pore size distribution plot for as-prepared (a) amorphous Fe₃O₄@SiO₂@TiO₂, (b) TiO₂ microspheres.

**Fig. S6** Adsorption rate curve of MB in dark for Ag@Fe₃O₄@SiO₂@TiO₂ samples.
Fig. S7 Photocatalytic degradation of MB over unannealed Ag@Fe₃O₄@SiO₂@TiO₂ (3 mg) and P25 (10 mg) under Xe lamp illumination.

References
