

Supporting Information

Magnetically separable Fe₃O₄-Ag₃PO₄ sub-micrometer composite: facile synthesis, high visible light-driven photocatalytic efficiency, and good recyclability

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Experimental section

Materials: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, poly(N-vinyl-2-pyrrolidone) (PVP, K30), NaAc, ethylene glycol (EG), AgNO_3 , Na_2HPO_4 and ethanol were purchased from Beijing Chemical Factory (Beijing, China) and used as received without further purification. Water used throughout all experiments was purified with the Millipore system.

Synthesis of Fe_3O_4 nanospheres: Porous Fe_3O_4 nanospheres were prepared by a solvothermal method. In a typical synthesis, 0.5 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.5 g PVP and 1.0 g NaAc were added to 30 mL ethylene glycol (EG). The mixture was stirred vigorously until all reagents were completely dissolved. Then, the mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 200 °C for 8 h. The black products were collected with an external magnet and washed with water and ethanol, each for three times, and finally dried at 60 °C in a vacuum oven for 24 h.

Synthesis of Ag_3PO_4 sub-micrometer particles and $\text{Ag}_3\text{PO}_4\text{-Fe}_3\text{O}_4$ sub-micrometer composites (AF MCs): Ag_3PO_4 particles were obtained by a simple precipitation process. In a typical synthesis, 100 μL aqueous solution of Na_2HPO_4 (0.15 M) was added to 2 mL water, to which 300 μL aqueous solution of AgNO_3 (0.15 M) was added drop-by-drop under sonication to form yellow milk solution.

The AF MCs were prepared by a similar precipitation process at room temperature. In a typical synthesis, 100 μL aqueous solution of Na_2HPO_4 (0.15 M) was added into the aqueous dispersion of the Fe_3O_4 nanospheres (0.25 mg/mL, 2 mL). After being sonicated for 1 min, 300 μL aqueous solution of AgNO_3 (0.15 M) was added drop-by-drop to the above dispersion under while sonication, and the resulting mixture was then sonicated for another 1 min. The product was separated by an external magnet and re-dispersed in water.

The sub-micrometer composites with different contents of Ag_3PO_4 were prepared by adding different volumes of Na_2HPO_4 (0.15 M) and Ag_3PO_4 (0.15 M) into the aqueous dispersion of Fe_3O_4 nanospheres. In this case, three sets of samples were prepared with addition of 50 μL Na_2HPO_4 and 150 μL AgNO_3 (0.15 M) (Sample 1), 100 μL Na_2HPO_4 and 300 μL AgNO_3 (Sample 2), and 200 μL Na_2HPO_4 and 600 μL AgNO_3 (Sample 3), into the aqueous dispersion of Fe_3O_4 nanospheres.

Characterization: Scanning Electron Microscopy (SEM) images were taken using an S-4800 (Hitachi, Japan). The crystal structures were determined by using a Japan Rigaku D/max 2500 X-Ray diffractometer with Cu-K α radiation (18 kW). Photographs were taken

with a Nikon CoolPix S60 digital camera. The ultraviolet-visible diffuse reflectance spectra were measured using the diffuse reflection method with a UVPC-1601 spectrophotometer. The UV-vis absorption spectra were recorded on a TU 1900 spectrometer. The magnetic hysteresis loops were measured on powder samples by using vibrating sample magnetometer (VSM, LakeShore 7410) at room temperature.

Evaluation of photocatalytic activity: The photocatalytic performance of the synthetic magnetic photocatalyst was evaluated by degradation of methylene blue (MB) dye in water. The experiments were carried out at room temperature in air with mechanical stirring. In a typical photocatalytic reaction, 20 mg AF MCs powder was added to the aqueous solution of MB (5 mg/L, 20 mL) at room temperature and the mixture was kept in dark for 30 min to achieve an equilibrium adsorption of MB on the surface of AF MCs. The suspension was then exposed to a 500W xenon arc lamp equipped with an ultraviolet cutoff filter to provide visible light with $\lambda \geq 400$ nm, and 1 mL of the solution containing AF MCs and MB dye was taken out from the reaction system at different time interval. The AF MCs were separated by an external magnet and the concentration of the MB dye was determined by monitoring the absorbance at 664 nm in UV-vis spectra.

Fig. S1 – L. Mao *et al.*

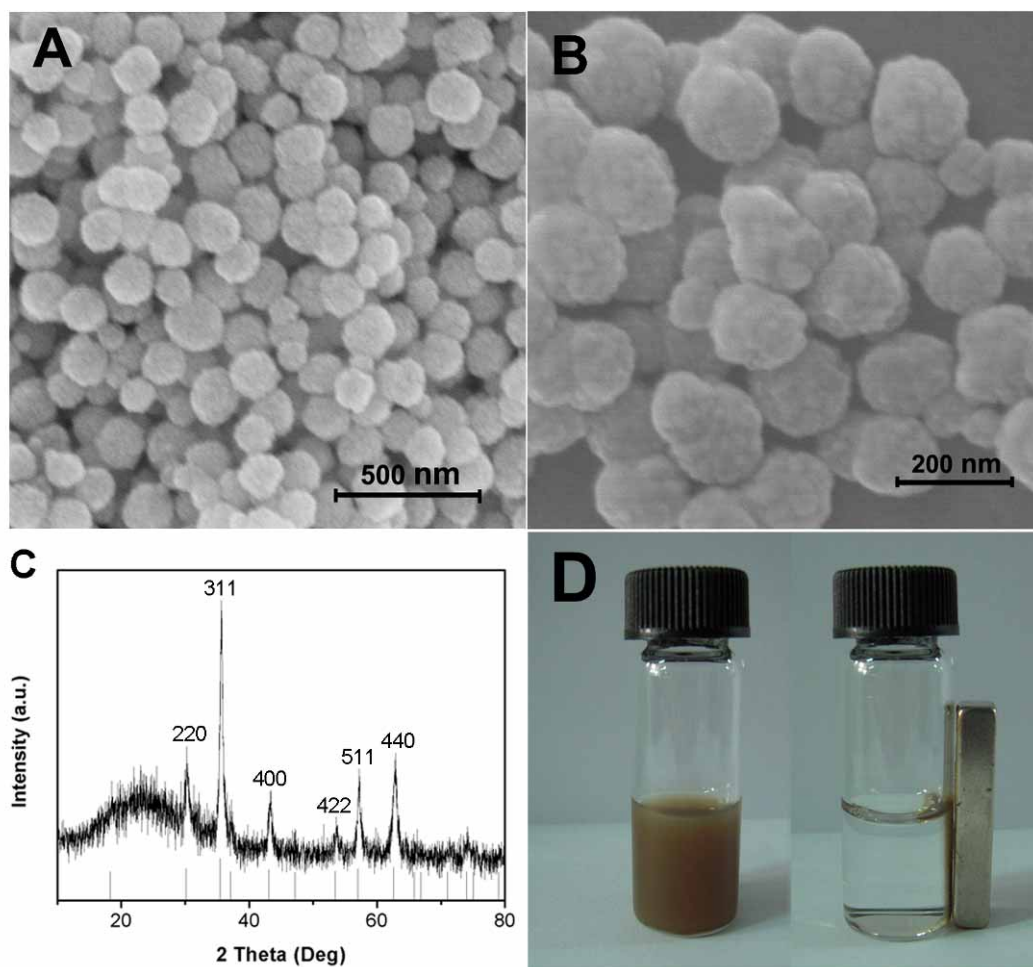


Fig. S1 SEM images (A and B) of as-synthesized Fe₃O₄ nanospheres at different magnification (as indicated in figure). XRD patterns (C) of the Fe₃O₄ nanospheres and the standard Fe₃O₄. Photographs (D) of the aqueous dispersion of Fe₃O₄ nanospheres (left), of which Fe₃O₄ nanospheres could be simply separated from the dispersion by an external magnet (right).

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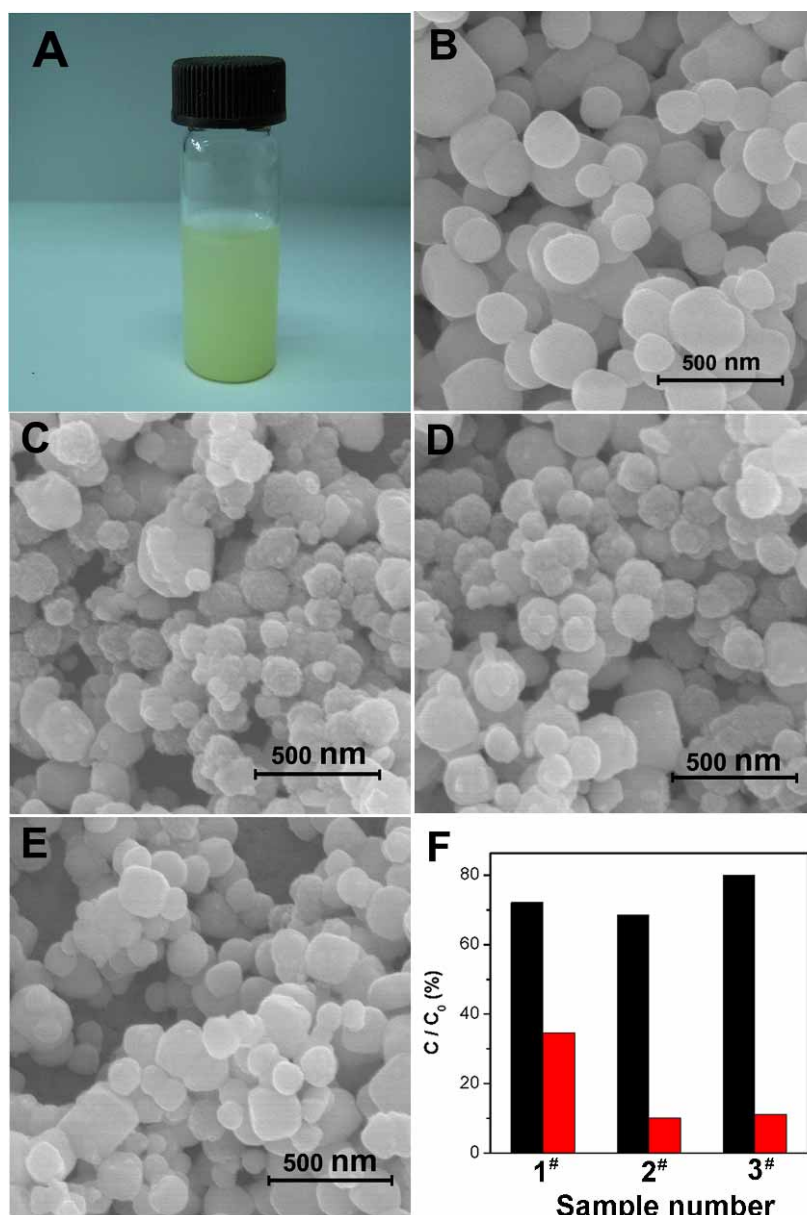


Fig. S2 (A) Photograph of the aqueous dispersion of Ag_3PO_4 sub-micrometer particles in sunlight. SEM images of Ag_3PO_4 particles (B) and AF MCs prepared by adding different volumes of Na_2HPO_4 (0.15 M) and AgNO_3 (0.15 M) into the aqueous dispersion of Fe_3O_4 nanospheres (C, D and E). (C) 50 μL Na_2HPO_4 + 150 μL AgNO_3 (Sample 1), (D) 100 μL Na_2HPO_4 + 300 μL AgNO_3 (Sample 2), and (E) 200 μL Na_2HPO_4 + 600 μL AgNO_3 (Sample 3). (F) Results on the adsorption ability (black) and photocatalytic activity (red) of samples 1, 2 and 3 under the identical conditions.

Fig. S3 – L . Mao *et al.*

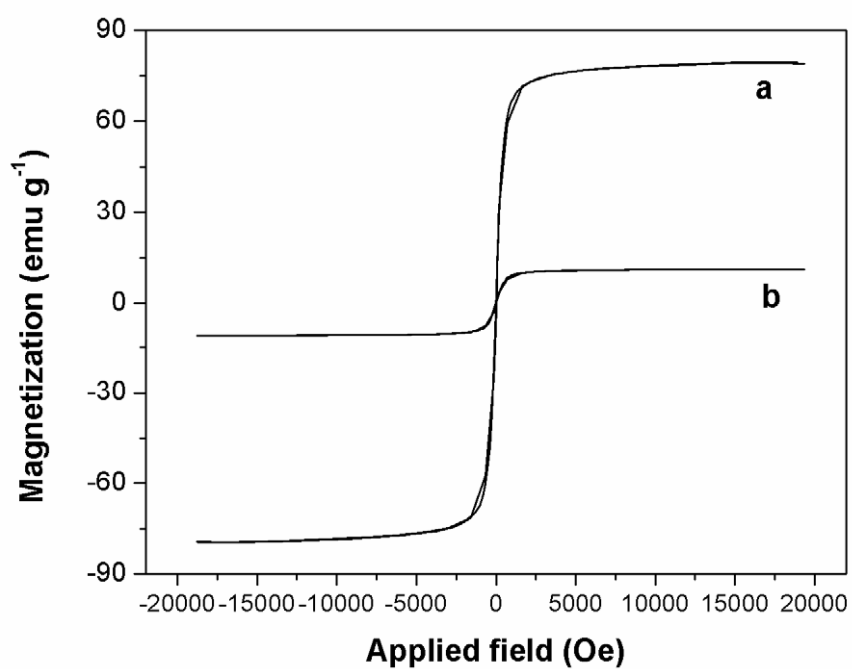


Fig. S3 Magnetization curves of Fe₃O₄ nanospheres (a) and the AF MCs (b).

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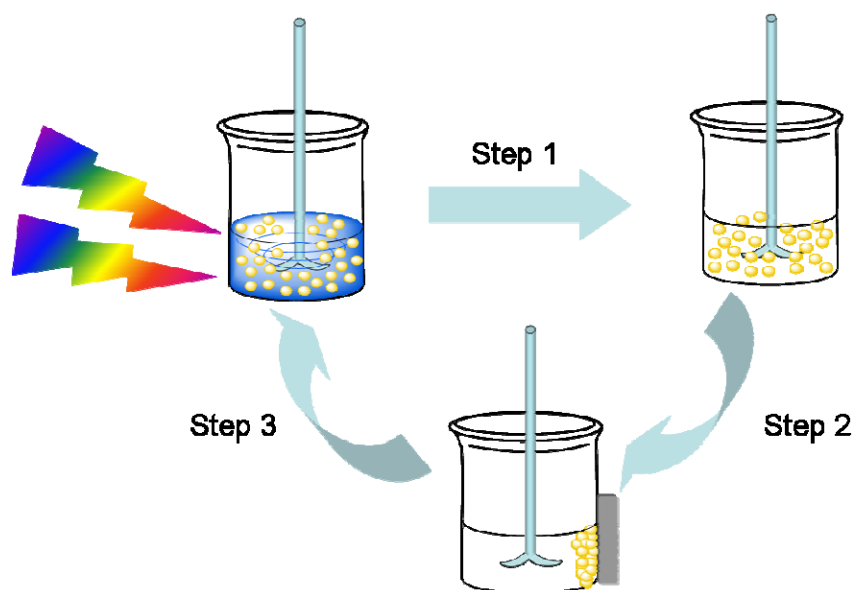


Fig. S4 Schematic illustration of experimental procedures for photocatalysis of MB degradation. **Step 1:** visible light catalyzed MB degradation with AF MCs as the photocatalyst. **Step 2:** separation of the AF MCs photocatalyst from the photocatalytic system by an external magnet. **Step 3:** repeated uses of the recycled AF MCs photocatalyst for next photocatalytic degradation reaction of MB.

Fig. S5 – L . Mao *et al.*

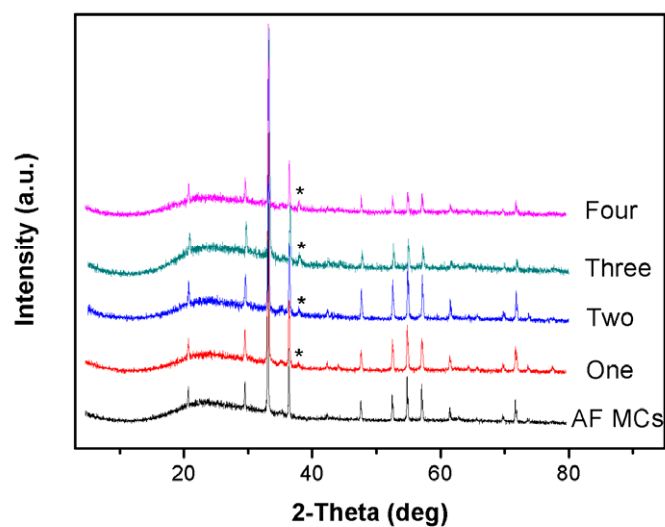


Fig. S5 XRD patterns of the AF MCs before (black curve) and after each cycling photocatalytic reaction under visible light irradiation. The stars indicate the Ag⁰ peak.

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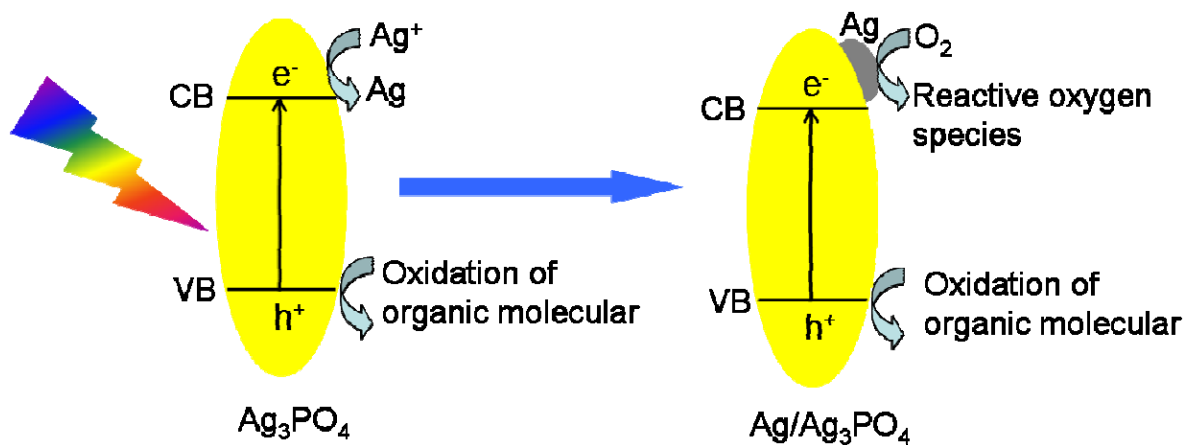


Fig. S6 Schematic illustration of the photocatalytic processes under visible light irradiation (h^+ : holes, e^- : electrons).