

Electronic Supplementary Information

A novel synthetic route for magnetically retrievable Bi_2WO_6 hierarchical microspheres with enhanced visible photocatalytic performance

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Experimental Section

1. Chemicals

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, sodium acetate, polyethylene glycol, ethylene glycol, ethanol, concentrated ammonia solution (28 wt%), tetraethyl orthosilicate (TEOS), isopropyl alcohol, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ are of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. The 3-amino-propyltriethoxysilane (APTES) was purchased from WD Silicon Co. Ltd (Wuhan, China). All chemicals were used as received. Distilled water was used for all experiments.

2. Synthesis of Fe_3O_4 magnetic spheres

The Fe_3O_4 magnetic spheres were prepared via a solvothermal method reported elsewhere.¹ First, 2.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved into 80.0 mL of ethylene glycol and stirred for 0.5 h to form solution. After that, sodium acetate (7.2 g) and polyethylene glycol (2.0 g) were added into the solution and further vigorously stirred for 2.0 h. The mixture was then transferred to a Teflon-lined stainless-steel autoclave

(100.0 mL capacity) and heated at 200 °C for 8 h, and allowed to cool to room temperature, the black Fe₃O₄ powders were obtained after washed several times with ethanol and dried at 60 °C overnight.

3. Preparation of Fe₃O₄@SiO₂ and APTES modified Fe₃O₄@SiO₂ magnetic spheres

The Fe₃O₄@SiO₂ core-shell microspheres were prepared through a commonly used sol-gel method. Briefly, 0.1 g of Fe₃O₄ powders were added into a mixture solution containing absolute ethanol (80.0 mL), deionized water (20.0 mL), and concentrated ammonia solution (1.0 mL, 28 wt %). After mechanical stirred for 0.5 h at room temperature, 0.3 g of TEOS was slowly added, and the reaction was proceed for 8.0 h under continuous stirring. Then the black products were separated and washed with ethanol. Finally, the Fe₃O₄@SiO₂ microspheres were obtained after dried at 60°C overnight.

The APTES modified Fe₃O₄@SiO₂ microspheres were prepared according to a reported method.² Typically, 0.1 g of previous obtained Fe₃O₄@SiO₂ powders were added to isopropyl alcohol (100 mL) in a beaker, and 1.0 mL of APTES was then added. After bubbled with nitrogen gas for 30 min, the resultant dispersion was then mechanical stirring for 6 h at 70 °C. At last, the APTES-modified Fe₃O₄@SiO₂ microspheres were separated by a magnet and repeatedly washed with ethanol for several times for further use.

4. Synthesis of Fe₃O₄@SiO₂@Bi₂WO₆ hierarchical spheres

The newly prepared APTES-modified Fe₃O₄@SiO₂ microspheres was firstly underwent a rapid protonated process and forming a layer of positive charges at the surface.³ Briefly, 2.0 mL of diluted HNO₃ solution (prepared by mixing 0.1 mL of 6 M HNO₃ with 40 mL of ethanol) was introduced into the mixing of ethanol (100 mL) and APTES-modified Fe₃O₄@SiO₂ microspheres (0.1 g) and then stirred for 4 h. After separation by a magnet and washed by deionized water, the positive charged Fe₃O₄@SiO₂ formed. These microspheres and Na₂WO₄·2H₂O (0.15 g) were then sonicated in 100 mL deionized water. The obtained suspension was aged for 1 h,

followed by magnetic separation and redispersion in 65 mL aqueous solution containing 5 mL of 6 M HNO₃. Na₂WO₄·2H₂O (0.165 g) and Bi(NO₃)₃·5H₂O (0.485 g) were added into the solution sequentially under vigorously stirring. After this, the mixed solution was sealed into a Teflon-lined autoclave and maintained at 180 °C for 24 h. When the autoclave had cooled to room temperature, the products were separated magnetically, washed with deionized water, and dried under vacuum at 60 °C for 12 h. Finally, the Fe₃O₄@SiO₂@Bi₂WO₆ hierarchical microspheres were obtained.

Besides, the composites photocatalyst without SiO₂ layer (termed as Fe₃O₄/Bi₂WO₆) and the pure Bi₂WO₆ powders were also prepared in same conditions.

5. Characterization

Powders X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with Cu K α radiation and the accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Scanning electron microscopy images were collected on field-emission scanning electron microscope (SEM, SIRION, The Netherlands). Transmission electron microscopy (TEM) images were obtained by JEM-2010-FEF instrument at the accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) and the porous structure of the catalysts were determined by nitrogen adsorption isothermals measurements at 77 K on a JW-BK nitrogen adsorption apparatus (China). The chemical structures of samples were studied by an attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR, Nicolet iS10). UV-Vis diffuse reflectance spectrum was recorded using a UV-Vis spectrophotometer (SHIMADZU UV-2550) in the spectral range 200–800 nm. BaSO₄ was used as a reflectance standard in the experiment. The magnetic behavior was analyzed using a vibrating sample magnetometer on a physical property measurement system (PPMS-9, Quantum Design) with the applied field from -20000 to 20000 Oe.

6. Measurement of photocatalytic activity

The photocatalytic activities of the prepared catalysts were evaluated by the photocatalytic decomposition of Rhodamine B (RhB). In the experiment, 0.1 g of the

photocatalyst was dispersed in 100 mL of RhB solution (10^{-5} mol/L). A 160 W high-pressure mercury lamp with a filter cut off the wavelength below 400 nm was used to irradiate the solution. Before illumination, the suspension was mechanically stirred in dark for 1.0 h to ensure an adsorption-desorption equilibrium between the photocatalysts and RhB. After irradiation for some time (20 min), 1.60 mL of solutions was withdrawn. The catalysts were separated from the suspension by centrifugation, and the clear solution after diluted four times were analyzed by recording variations of the maximum absorption band (553 nm) using a Shimadzu UV-2550 spectrophotometer.

When each photocatalytic experiment ended, the catalysts were separated from the solution by a magnet. The recycled magnetic catalysts were then washed with ethanol and deionized water for several times. After that, the obtained magnetic microspheres were redispersed in 100 mL of RhB solution (10^{-5} mol/L), and the new photocatalytic cycle began.

References

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2. Y. Deng, Y. Cai, Z. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang and D. Zhao, *J. Am. Chem. Soc.*, 2010, **132**, 8466.
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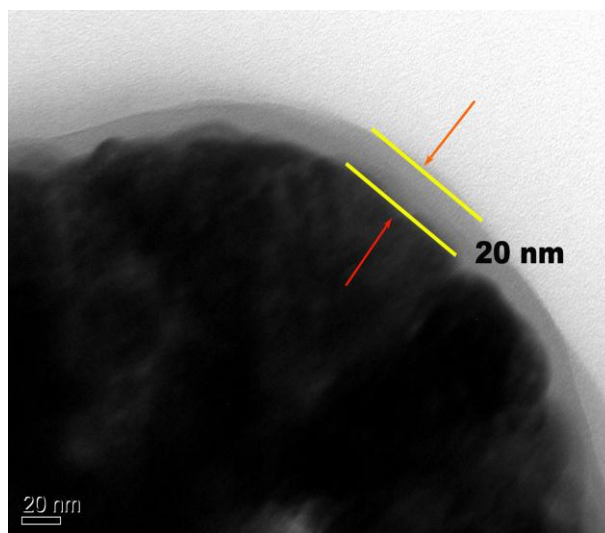


Figure S1 TEM image of enlarged part of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and the average thickness of the silica shell is about 20 nm.

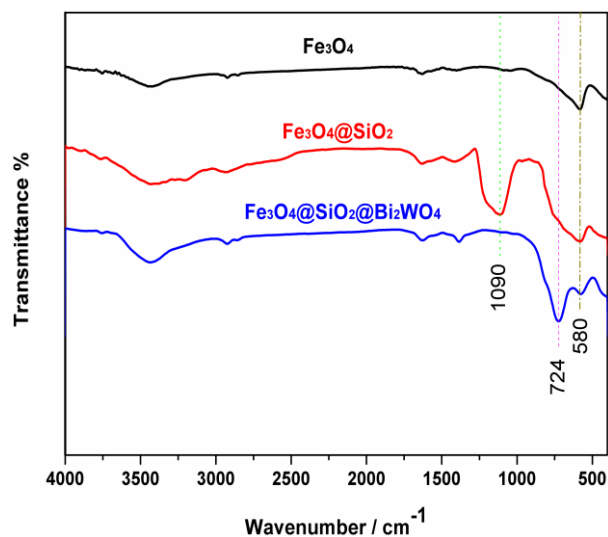


Figure S2 FT-IR spectrum of different catalysts. Typical band assigned to the Fe-O stretching are visible at around 580 cm^{-1} . The new peak at 1090 cm^{-1} corresponds to Si-O-Si vibration from $\text{Fe}_3\text{O}_4@\text{SiO}_2$, which implies a shell of SiO_2 formed after the sol-gel process.

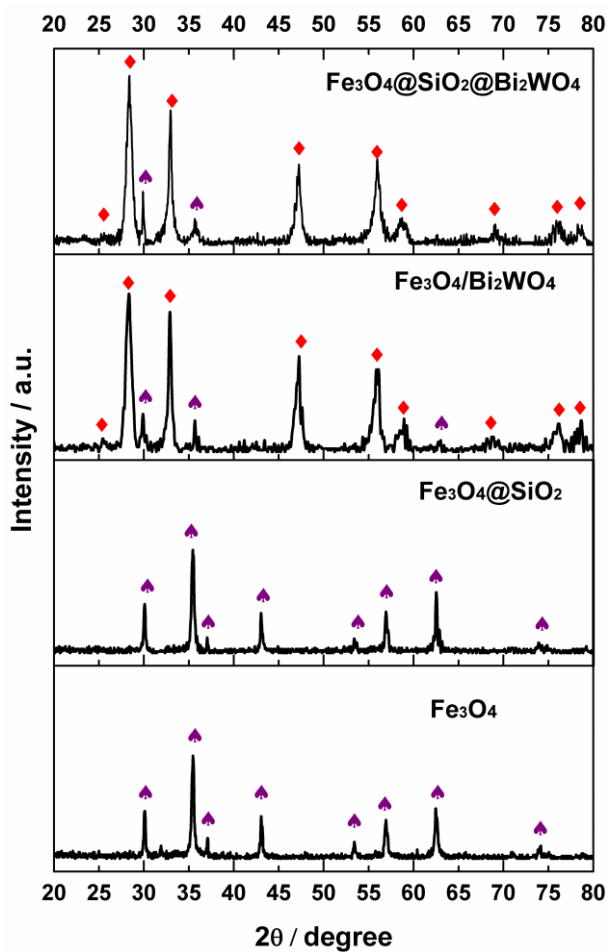


Figure S3 XRD patterns of different catalysts.

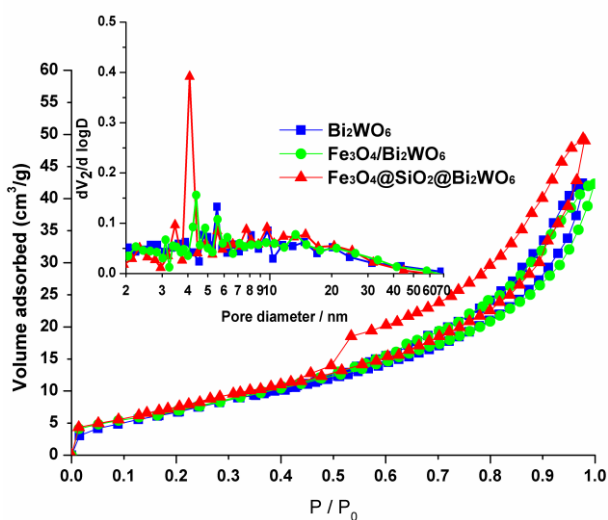


Figure S4 Adsorption/desorption isotherms and pore size distribution curves of Bi_2WO_6 , $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{Bi}_2\text{WO}_6$.

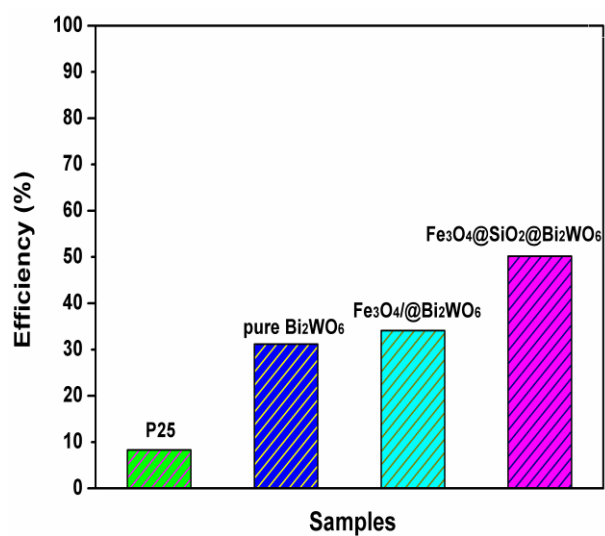


Figure S5 The dark adsorption of RhB over different samples.

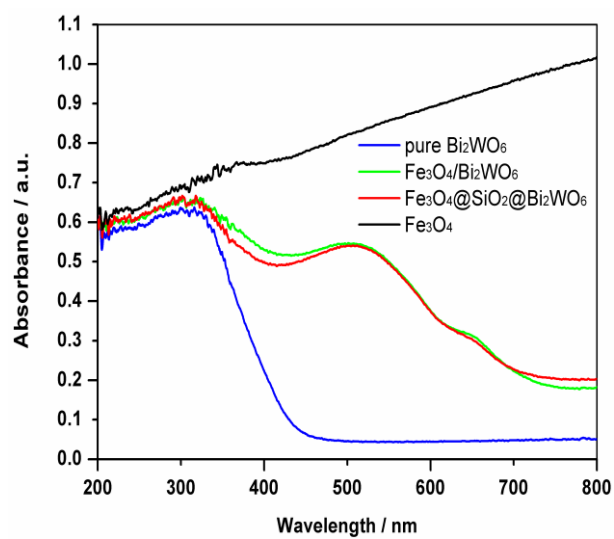


Figure S6 UV-Vis diffuse reflectance absorption spectra of different samples.

