## **Supporting Information**

## **Experimental Section**

**Chemicals:** WCl<sub>6</sub>, glucose, distilled water, absolute ethanol. All reagents used were analytically pure, and were purchased from J&K Scientific (Beijing, China) and were used without further purification.

**Preparation of carbonaceous spheres:** In a typical synthesis, glucose (3 g) was added to distilled water (100 mL) under mild stirring, whereupon a clear solution was formed. The solution was loaded into a Teflon-lined autoclave, which was then sealed, maintained at 180 °C for 24 h, and then allowed to cool to room temperature. The obtained black product was collected and rinsed once with absolute ethanol. It was then dried at 70 °C for 4 h.

Synthesis of Au/WO<sub>3</sub> porous hollow spheres: The as-synthesized carbonaceous spheres (20 g), HAuCl<sub>4</sub>  $\cdot$  4H<sub>2</sub>O (0.3 g), and WCl<sub>6</sub> (6.5 g) were soaked in anhydrous ethanol (200 mL). The obtained mixture was sealed and placed in an ice-water bath for 12 h. Then the ethanol was removed by filtration, and the obtained solid sample was dried in vacuum. Finally, the dry sample was heated from room temperature to 450 °C over a period of 7 h and annealed at 450 °C for a further 1 h in air to obtain the final purple product.

**Photocatalytic property test:** The photocatalytic activities of the Au/WO<sub>3</sub> porous hollow spheres were evaluated by degradation of rhodamine B (RhB) in an aqueous solution under visible light from a 300W Xe lamp (HSX-F300, NBeT) equipped with cutoff filter L42. The photocata-lyst (50 mg) was poured into RhB (100 mL) aqueous

solution (10 mgL<sup>-1</sup>) in a Pyrex reactor at room temperature under air. Before light exposure, the suspension was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption–desorption equilibrium. The concentration of RhB during the degradation was monitored by colorimetry by using a UV/Vis spectrometer (Shimadzu UV-3600).

**Characterization:** XRD patterns of the products were recorded on a Bruker D8 Focus diffractometer by using CuKa radiation (I=1.54178 Å). SEM images and EDS spectrums were obtained on a Hitachi S-4800. TEM and HRTEM characterizations were performed with a JEOL 2100 operated at 200 kV. BET measurements were carried out in Micromeritics Tristar 3020. UV/Vis/NIR absorption spectra were recorded with a Shimadzu UV-3600. FTIR spectra were obtained from THERMO Iz10.



Figure S1. A picture of the product: each time we can produce 465 g of products.



**Figure S2.** FTIR spectrum of the Au/WO<sub>3</sub> porous hollow spheres. The bands in the region of 1000–500 cm<sup>-1</sup> can be attributed to the W-O (827 cm<sup>-1</sup>) units and the stretching vibrations of the bridging oxygen atoms O-W-O (773 cm<sup>-1</sup>). The other two peaks (3450 and 1639 cm<sup>-1</sup>) can be easily identified as the vibrational peaks of water molecules



**Figure S3.** Energy-dispersive X-ray spectroscopy (EDS) of the Au/WO<sub>3</sub> porous hollow spheres..



Figure S4. SEM image of the pure WO<sub>3</sub> hollow spheres with smaller diameter.



Figure S5. The UV-Vis absorption spectrum, XRD pattern, and Raman spectrum of the Au-WO<sub>3</sub> porous hollow spheres after 4 reactions.