Fabrication of Au(Ag)/AgCl/Fe₃O₄@PDA@Au nanocomposites with enhanced visible-light-driven photocatalytic activity

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Experimental Section

Materials

AgNO₃ was purchased from Shanghai Reagent Factory. PVP (Mn=40000) was purchased from Yonghua Chemical Technology co., Ltd. (Jiangsu, China). Iron(III) acetylacetonate (Fe(acac)₃, 99%) was from energy chemical. Triethylene glycol (TREG, 99%), glycerol and HAuCl₄ were purchased from SCRC. Dopamine hydrochloride was purchased from Alfa Aesar co., Ltd (shanghai China). All other reagents used were analytical grade.

Characterization

The morphology of the nanocomposites was observed using a scanning electron microscope (SEM, Hitachi S-8000, Japan) in a secondary electron scattering mode at 5 kV and a transmission electron microscope (TEM). X-Ray powder diffraction (XRD) patterns of the products were recorded with a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Kα source (λ = 0.154 nm). X-Ray photoemission spectroscopy (XPS) data were obtained with an ESCALAB 250Xi instrument equipped with a monochromatic Al anode X-ray gun. The magnetic characterization of the nanocomposites were carried out using a vibrating specimen magnetometer.

Preparation of Fe₃O₄-coated AgNWs

Fe₃O₄-coated AgNWs were synthesized according to our previously work. Briefly, 10 mL Ag NWs (10 mg/mL) ethanol solution and 30 mL triethylene glycol were added to the flask, and the above mixture was then heated to 95°C to remove ethanol. After the ethanol was removed completely, 150 mg of the iron precursor Fe(acac)₃ and 30 mL triethylene glycol were added to the flask. The solution was sonicated for 5 min. Finally, the resulting mixture was then heated to 278 °C under vigorous stirring and N₂ protection and kept at reflux for 30 min. After cooling to room temperature, 60 mL ethanol was added to dilute the solution. Then, the solution was centrifuged at 4300 rpm for several times until the centrifugal supernatant fluid was colorless transparent and dried in vacuum.
**Pdop coated Magnetic silver nanowires**

Pdop coated Magnetic silver nanowires were prepared as follows. Briefly, 2 mL of the Ag NWs/Fe$_3$O$_4$ (10 mg/mL) ethanol solution and 20 mg dopamine hydrochloride were dispersed in 22 ml tris-HCl buffer (PH=8.5) solution, and allowed to proceed for 12 h at room temperature under stirring. The resulting product was washed with deionized water and ethanol for several times to remove by-products. And finally the composites was dried in a vacuum at 60°C for 24 h.

**Preparation of Au(Ag)/AgCl/Fe$_3$O$_4$@PDA@Au Nanotubes**

The hybrids were prepared as follows: Briefly, 10 mg of the Pdop coated magnetic silver nanowires were dispersed in 35 ml deionized water, and the mixture was ultrasonicated for 10 min. Then a certain amount of HAuCl$_4$ aqueous solution (1 mg/mL) was added to the above mixture under vigorous mechanical stirring and reacted for 10 h. The Ag NWs/Fe$_3$O$_4$@PDA with different mass ratios of HAuCl$_4$=7:1, 8:5, 1:3, 1:7. Note: The details of the amount of the HAuCl$_4$ aqueous solution was 1.43 mL for 7:1; 6.25 mL for 8:5; 30 mL for 1:3, 70 mL for 1:7 respectively. The final product in the mass ratio of 7:1 is defined as Ag(Au)/AgCl/Fe$_3$O$_4$@PDA@Au; the product in the mass ratio of 1:7 is defined as Au(Ag)/AgCl/Fe$_3$O$_4$@PDA@Au. The products were separated with a magnet and washed with water for several times. And finally the hybrids was dried in a vacuum at 60°C for 24 h.

**Photocatalytic activity measurement**

Photocatalytic activity of the as-prepared sample nantubes were evaluated with a decomposition reaction of methylene blue under xenon lamp (500 W, Model PLSSXE300) with a cut-off filter that emits visible light (λ> 400 nm). The obtained composites (4 mg) were dispersed in 50 mL MB aqueous solution (5 mg/L) uniformly and the mixture was stored in the dark for 60 min to reach an adsorption-desorption equilibrium of MB molecules on the novel nantubes. The solution was then exposed to the Xe lamp to trigger decomposition of the MB molecules. During the decomposition reaction, aliquots of 3.5 mL of the solution was taken out from the reaction system at a certain time interval. The magnetic nanotubes were separated from aqueous solution by using a magnet. The top solution was moved to a quartz cuvette with optical length of 10 mm for the absorbance measurement. The reaction was performed under constant magnetic stirring at room temperature.
**Scheme S1** Schematic illustration for the galvanic replacement reaction between AgNW and AuCl\(_4^-\) as a function of the concentration of AuCl\(_4^-\). Step (I): deposition of Au and formation of AgCl, step (II): deposition of Au and dissolution of AgCl.

**Fig. S1** SEM images of Ag NWs(a,b), Ag NWs/Fe\(_3\)O\(_4\) composites(c,d) and Ag NWs/Fe\(_3\)O\(_4\)@PDA(e,f)
Fig. S2 (a, b) TEM images of Fe₃O₄/Au-AgCl nanotubes

Fig. S3 The XPS spectra wide scan of the Au 4f½ and Au 4f½, A: Ag(Au)/AgCl/Fe₃O₄@PDA@Au (7:1); B: Au(Ag)/AgCl / Fe₃O₄@PDA@Au(1:7) .
**Fig. S4** The XPS spectra wide scan of the Cl 2p$_{1/2}$: A: Ag(Au)/AgCl/Fe$_3$O$_4$@PDA@Au(7:1); B: Au(Ag)/AgCl/Fe$_3$O$_4$@PDA@Au(1:7).

**Fig. S5** The comparison graph of Au, Cl content for A: Ag(Au)/AgCl/Fe$_3$O$_4$@PDA@Au (7:1) ; B: Au(Ag)/AgCl/Fe$_3$O$_4$@PDA@Au(1:7).
Fig. S6 UV-Vis absorption spectra of MB during the reduction catalyzed by Ag(Au)/AgCl/Fe$_3$O$_4$@PDA@Au (7:1).

Fig. S7 UV-Vis absorption spectra of MB during the reduction catalyzed by Au(Ag)/AgCl/Fe$_3$O$_4$@PDA@Au (1:7) composites in the five-cycle tests.
Fig. S8 Magnetic hysteresis curves of Fe₃O₄ (without the addition of Ag NWs) measured at room temperature