Electronic supplementary information

Microwave-assisted synthesis of porous CdO/CdS core-shell nanoboxes with enhanced visible-light-driven photocatalytic reduction of Cr(VI)

Wenlong Yang, Yu Liu, Yong Hu,* Mojiao Zhou and Haisheng Qian

Experimental Section

1. Materials and Methods

All reagents were of analytical grade, purchased from the Shanghai Chemical Reagent Factory, and used as received without further purification.

1.1 Synthesis of $CdCO_3$ nanocubes

The $CdCO_3$ nanocubes were prepared by a simple precipitation process. In a typical procedure, 0.5 mmol of $CdCl_2·2.5H_2O$ and 1 g of polyvinylpyrrolidone (PVP) were dissolved in 20 mL of deionized water forming a clear solution followed by a dropwise addition of 20 mL of as-prepared $NaHCO_3$ aqueous solution (0.05 M). Minutes later, when the solution turned milky white, the mixture was continuously stirred for 1 h at room temperature and collected by centrifugation. After washed with deionized water and ethanol for three times, the as-prpared $CdCO_3$ nanocubes were dried at 60ºC for 6 h.

1.2 Synthesis of $CdCO_3$/CdS core-shell nanocubes and porous CdO/CdS nanoboxes

In a typical procedure, 50 mg of as-prepared $CdCO_3$ microcubes and 10 mg portion of thioacetamide (TAA) were added into a round-bottom flask and dispersed in 20 mL of deionized water with the assistance of ultrasonication for 10 min. Then, the above mixture was placed in a microwave refluxing system irradiated at 400 W for 15 min to prepare the $CdCO_3$/CdS core-shell nanocubes. After collection by centrifugation, the final products were washed with ethanol and deionized water three times before drying at 60ºC for 6 h. The porous CdO/CdS core-shell nanoboxes were obtained by thermal decomposition of the $CdCO_3$/CdS core-shell nanocubes at 450ºC in static air for 2 h, the temperature was raised at a heating rate of 2ºC/min. The sulfidation reactions are similar to what we reported previously (see Ref. 23 in the manuscript). The formation of $CdCO_3$/CdS core-shell nanocubes may be ascribed to the following reactions. First, TAA reacts with H_2O to form $CH_3(NH_2)C(OH)SH$ via microwave irradiation (eqn (1)), which further hydrolyzes releasing H_2S (eqn (2)).

$$CH_3CSNH_2 + H_2O \rightarrow CH_3(NH_2)C(OH) - SH \qquad (1)$$

$$CH_3(NH_2)C(OH)SH + H_2O \rightarrow CH_3(NH_2)C(OH)_2 + H_2S \qquad (2)$$

Then, H_2S readily reacts with $CdCO_3$ at the surface of the $CdCO_3$ nanocubes to produce CdS nuclei (eqn (3)).

$$H_2S + CdCO_3 \rightarrow CdS + H_2O + CO_2 \qquad (3)$$

2. Characterization

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer using Cu Kα radiation at a scanning rate of 0.06 deg s^{-1}. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron micro-analyzer with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted at 200 kV with a JEM-2100F field emission TEM. Energy dispersive X-ray spectrometry (EDS) was performed with a spectroscope attached to HRTEM, which was used for elemental analysis. Samples for TEM measurements were prepared for TEM by dispersing the products in ethanol and placing several drops of the suspension on holey carbon films supported by copper grids. UV-vis diffuse reflectance spectra (UV-vis DRS) of the as-prepared samples were recorded over the range of 200-800 nm in the absorption mode using a Thermo Nicolet Evolution 500 UV-vis spectrophotometer equipped with an integrating sphere attachment. The absorption spectra were measured using a PerkinElmer Lambda 900 UV-vis spectrophotometer at room temperature.

3. Photocatalytic reduction of Cr(VI)

The photocatalytic activities of the as-prepared porous CdO/CdS core-shell nanoboxes and pure CdS were evaluated by photocatalytic reduction of Cr(VI) under visible light irradiation of a 500 W Xe lamp with a 420 nm cutoff filter. The reaction cell was placed in a sealed black box with the top opened, and the cutoff filter was placed to provide visible-light irradiation. In a typical process, 7 mg of as-prepared CdO/CdS core-shell porous nanoboxes and pure CdS as photocatalysts were added into 20 mL Cr(VI) solution (10 mg/L) which were prepared by dissolving $K_2Cr_2O_7$ into deionized water, respectively. After being dispersed in an ultrasonic bath for 5 min, the solution was stirred for 2 h in the dark to reach adsorption equilibrium between the catalyst and the solution and then was exposed to visible light irradiation. The samples were collected by centrifugation at given time intervals and the Cr(VI) concentration was determined colorimetrically at 540 nm using the UV–vis spectroscopy.

Cr(VI) reduction was determined colorimetrically at 540 nm using the diphenylcarbazide (DPC) method and was followed as previously reported paper.[1] 1 mL of solution after photocatalytic reduction of Cr(VI) was mixed with 9 mL of 0.2 M H_2SO_4 in a 10 mL volumetric flask. Subsequently, 0.2 mL of freshly prepared 0.25% (w/v) DPC in acetone was added to the volumetric flask. After vortexing the mixture for about 15-30 s, it was allowed to stand for 10-15 min so as to ensure full color development. Using deionized water as reference the red-violet to purple color formed was then measured at 540 nm.

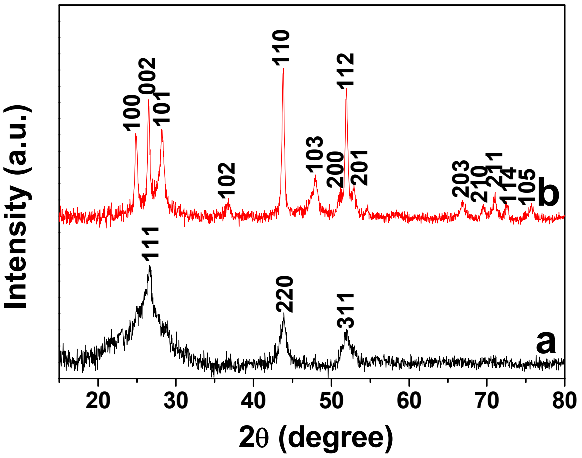

Fig. S1. XRD patterns of the as-prepared pure CdS obtained via microwave-assisted method before (a) and after calcinations at 450ºC for 2 h (b).

The XRD patterns of the as-prepared pure CdS obtained via microwave-assisted method before and after calcinations at 450ºC for 2 h are shown in Fig. S1. The peaks (Fig. S1a) at 2θ values of 26.4°, 43.9°, and 51.9° are correspond to the crystal planes of the (111), (220), and (311) of face-centered cubic (fcc) CdS (JCPDS standard card no. 89-0440) with a cell constant of a=5.811Å, respectively. The XRD pattern of pure CdS after calcinations at 450ºC for 2h is shown in Fig. S1b. All the peaks can be indexed as hexagonal CdS structure.

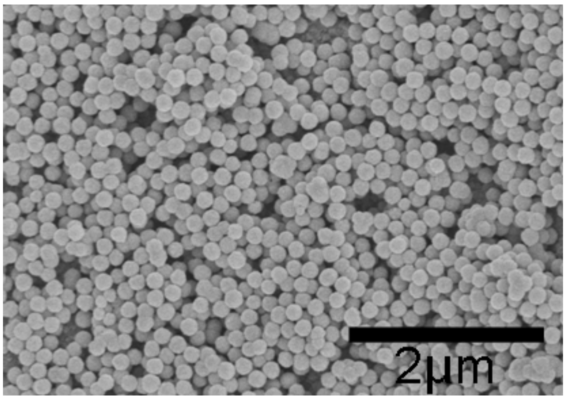

Fig. S2. SEM image of as-prepared pure CdS via a microwave-assisted method.

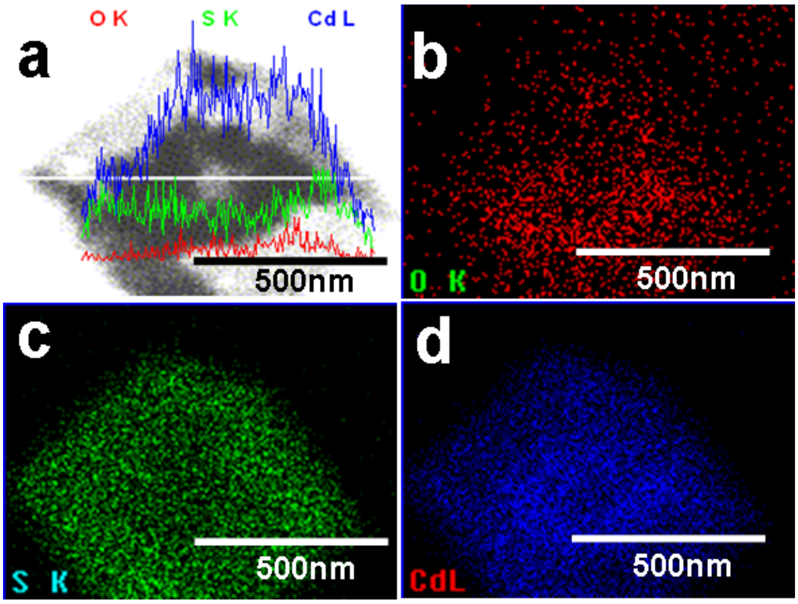

Fig. S3. (a) EDS line scan profile along the axis of a porous nanobox indicated by a white line and the corresponding EDS elemental mappings of (b) O, (C) S, and (d) Cd elements.

Fig. S3a demonstrates the EDS line scan profile along the axis of a porous nanobox indicated by a white line. It can be seen that element Cd exists dominantly in the whole region. The corresponding EDS elemental mapping of O, S, and Cd elements is shown in Figure S3b, c and d, indicating that both CdO and CdS co-exist in the nanohybrids.

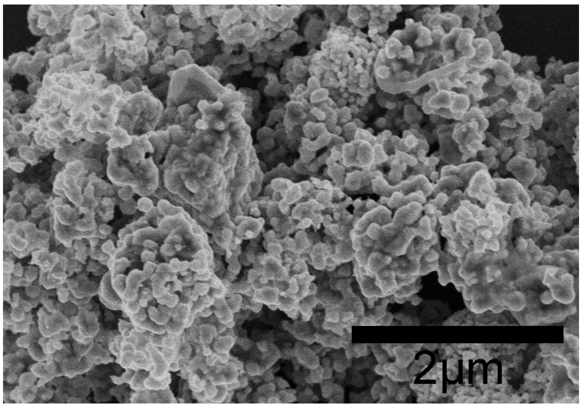

Fig. S4. SEM image of the as-prepared CdO obtained directly annealed $CdCO_3$ templates at 450 ºC for 2 h.

References:

(1) Idris, A.; Hassan, N.; Rashid, R.; Ngomsik A. F. *J. Hazard. Mater*. **2011,** *186*, 629.