Electronic Supplementary Information

Copper sulfide cages wholly exposed with nanotwinned building blocks

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Experimental Section

Synthesis of cubic Cu_2O templates

All chemicals used in our experiment were of analytical grade and used without further purification. In a typical synthesis, 0.9982 g of $Cu(CH_3COO)_2$ powder was dissolved in deionized water (100 mL) using a beaker under a constant stirring at 70 °C for 2 min. A dark precipitate was produced when a sodium hydroxide solution (6 M, 5 mL) was added dropwise to the above solution. After being stirred for 5 min, D-(+)-glucose powder (0.2 g) was added into the dark precursor with a constant stirring for another 60 min at 70 °C, and then was allowed to cool to room temperature naturally. Afterward, the obtained products were centrifuged at 5000 rpm for 1min (XIANYI TG16-WS centrifuge). The precipitates were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 70 °C for 12 hours in a vacuum oven.

Synthesis of Cu_2O/CuS core/shell architectures

In a typical synthesis, the obtained Cu_2O templates (0.6 g) were added to a mixed anhydrous ethanol solution (150 mL) composed of Na_2S (0.36 g) and NaOH (0.006 g) at room temperature and ambient pressure for 10 min under magnetic stirring. The precipitates were separated by centrifugation, washed with deionized water and anhydrous ethanol.

Synthesis of CuS hollow cages with nanotwinned building blocks

In a typical synthesis, the above Cu_2O/CuS core/shell particles were immersed in ammonia solution (25%) for 120 hours to remove the inner Cu_2O cores. The particles were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 60 °C for 12 hours in a vacuum oven.

Synthesis of CuS hollow cages without nanotwinned building blocks

In a typical synthesis, the as-obtained Cu_2O templates (0.6 g) were added to a mixed pure water solution (150 mL) composed of Na_2S (0.36 g) and NaOH (0.006 g) at room temperature and ambient pressure for 10 min under magnetic stirring. The precipitates were separated by centrifugation, washed with deionized water and anhydrous ethanol. The above Cu_2O/CuS core/shell particles were immersed in ammonia solution (25%) for 120 hours to remove the inner Cu_2O cores. The particles were centrifuged twice more in deionized water and anhydrous ethanol, respectively. And finally were dried at 60 °C for 12 hours in a vacuum oven.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker-AXS D8 ADVANCE diffractometer operated at 40 kV voltage and 40 mA current using Cu Kα radiation (λ = 1.5406 Å) in the range (20 ~ 80 °). The morphology of the products was investigated by field-emission scanning electron microscopy (FE-SEM) using JEOL (JSM-7000F) at an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) analysis images as well as selected-area electron diffraction (SAED) pattern analysis were performed on a JEOL JEM-2100 transmission electron microscopy operating at an accelerating voltage of 200 kV. Sample for the TEM analysis was prepared by ultrasonic dispersion for 30 s with anhydrous ethanol (1.5 mL) in a 2 mL centrifuge tube. Then, the products were dropped onto a carbon-coated copper grid and dried in air before TEM analysis.

Photocatalytic property

The catalytic activity experiments of the different kinds of CuS powders for the oxidation and decoloration of the methylene blue (MB) dye with the assistance of hydrogen peroxide (H_2O_2) were carried out at ambient temperature. The original solution was prepared by adding 1.25 mL H_2O_2 (30%, w/w) and 1.25 mL MB solution (400 mg/L) to 50 mL deionized water, then 1.5 mg CuS powder was added into the solution to form the aqueous dispersion, and was magnetically stirred in the dark for 20 min to ensure establishing an adsorption–desorption equilibrium. Afterwards, the dispersion was irradiated by a 300 W xenon lamp equipped with a filter cutoff ($\lambda \geqslant 420$ nm) under magnetic stirring. At given time intervals, the dispersions were sampled and centrifuged to separate the catalyst. They centrifuged at 10000 rpm for 2 min (XIANYI TG16-WS centrifuge). UV-vis absorption spectra were recorded at different intervals to monitor the reaction using a UV/vis/NIR spectrophotometer (Hitachi U-4100).

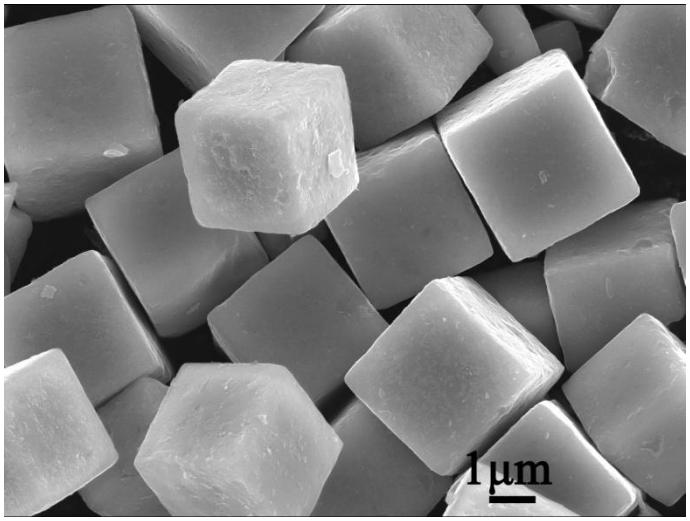

Fig. S1 FESEM image of the cubic Cu_2O templates.

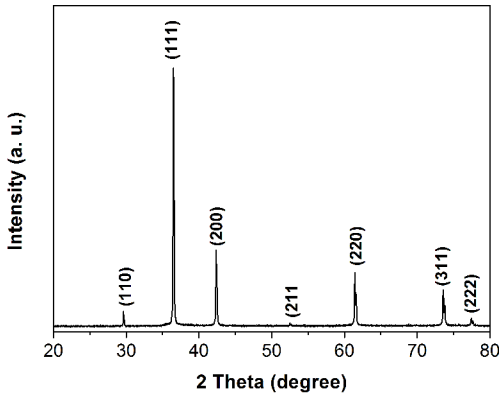

Fig. S2 XRD pattern of the cubic Cu_2O templates.

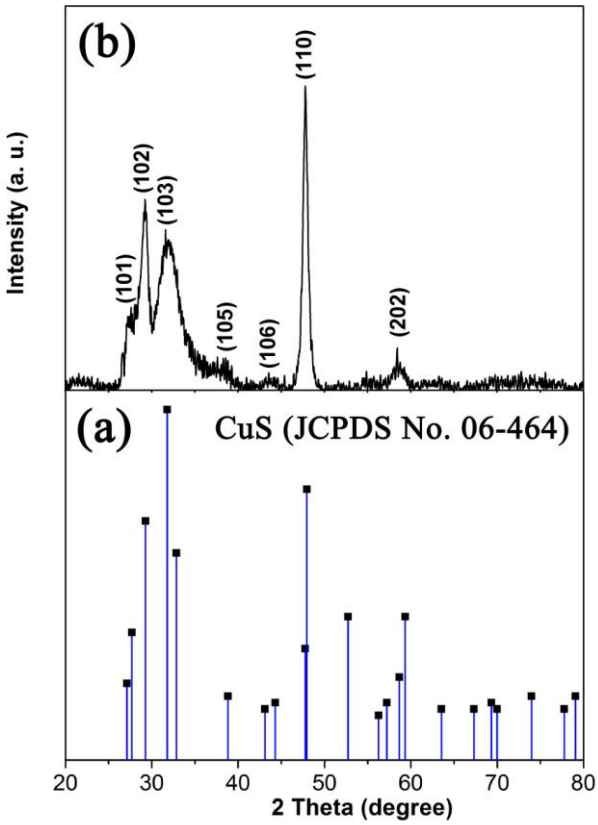

Fig. S3 XRD pattern of the as-prepared cubic CuS cages with nanotwinned building blocks: (a) CuS with JCPDS No. 06-0464; (b) the corresponding XRD pattern of CuS cages.

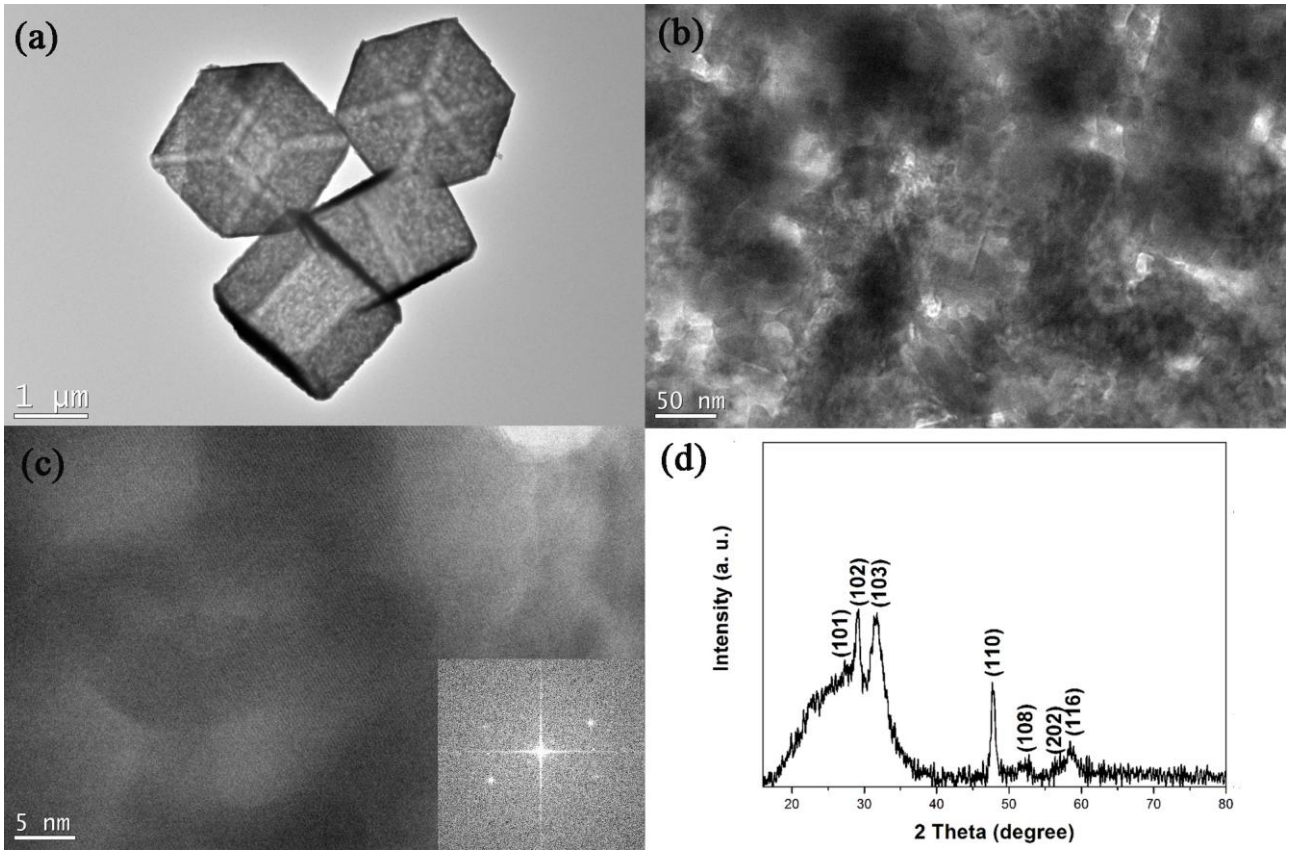

Fig. S4 TEM images, HRTEM image and XRD pattern of the cubic CuS cages without nanotwinned building blocks.

Fig. S4 shows the corresponding TEM images, HRTEM image and XRD pattern of the cubic CuS cages without nanotwinned building blocks. Fig. S4a shows the TEM image of CuS particles, and the high-magnification TEM image is shown in Fig. S4b. It cannot be seen the nanotwinned building blocks as shown in Fig. 2, suggesting the formation of CuS cubic cages without nanotwinned building blocks. The HRTEM image and corresponding FFT image (insert of Fig. S4c) as show in Fig. 4c can demonstrate the formation of single crystals. Fig. S4d displays the pure primitive hexagonal phase of CuS hollow architectures, and all the diffraction peaks of the products are indexed according to the standard hexagonal structure of CuS. No peaks of impurities such as copper oxide or other copper sulfide were detected, suggesting the high purity of the as-prepared CuS hollow cages.