Electronic Supplementary Information

Synthesis of novel ZnS nanocage utilizing ZIF-8 polyhedral template

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Synthesis

All reagents were of analytical grade and used without further purification.

ZIF-8 nanocrystals: Typically, 330 mg (1.5 mmol) of zinc acetate dihydrate and 985 mg (12 mmol) of 2-methylimidazole were each dissolved in 90.0 mL anhydrous ethanol. The latter clear solution was poured into the former clear solution under stirring with a magnetic bar. Stirring was stopped after combining the component solutions. After 24 h, the solid was separated from the milky colloidal dispersion by centrifugation. After washed with anhydrous ethanol and centrifugation three times, the product was dried at room-temperature.

ZnS nanocages: The as-prepared template was transferred into a round bottomed flask containing 0.1 M thioacetamide and 25.0 mL ethanol and 25.0 μL water. Then the mixture was refluxed for 1 h under stirring. At last the product was collected by centrifugation, washed with anhydrous ethanol and dried at 60 °C overnight.

ZnS individual nanoparticles: The dried ZnS nanocages were dispersed in 20.0 mL ethanol and under ultrasonic response for 2 h. Then the product was collected by centrifugation, washed with anhydrous ethanol and dried at 90 °C. The procedure was repeated three times.

Characterization

The morphology and microstructure of the products were characterized by a transmission electron microscope (TEM, JEOL JEM-1230) with an accelerating voltage of 100 kV, high resolution transmission electron microscope (HR-TEM, JEOL JEM-2100) with an accelerating voltage of 200 kV, and field emission-scanning electron microscope (FE-SEM, JEOL JSM-6700F). X-ray energy dispersive spectrometry (EDS) in a JSM-6700F field emission-scanning electron microscope. X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2200PC diffractometer with a graphite monochromator and CuKα radiation (λ=0.15418 nm). The X-ray photoelectron spectrum (XPS) was recorded on a PHI-5300 ESCA spectrometer (Perkin Elmer) with its energy analyzer working in the pass energy mode at 35.75 eV, and the AlKα line was used as the excitation source. The binding energy reference was taken at 284.7 eV for the C1s peak arising from surface hydrocarbons. UV-vis absorption spectra of the products dispersed in ethanol were collected on a UV-vis spectrophotometer (Lambda-35, Perkin-Elmer).
**Fig. S1** SEM images of single ZIF-8 nanocrystal (a, b, c) and corresponding schematic models (d, e, f).

**Fig. S2** ZIF-8 nanocrystals prepared with the same Zn and Hmim molar ratio 1:8 while different Zn precursor-(a) zinc nitrate hexahydrate, (b) zinc acetate dihydrate.

**Fig. S3** HR-TEM images (a, b), SEAD pattern (b), and TEM image (c) of ZnS nanocages.
**Fig. S4** TEM images of ca. 200nm ZIF-8 nanocrystals (a) and ZnS nanocages (b).

**Fig. S5** TEM images of ZnS nanocages formed after reaction for 20 min (a) and 40 min (b).

**Fig. S6** TEM images of ZnS formed with the volume ratio of water and ethanol of 1:100 (a) and the molar ratio of ZIF-8 and ethanol of 1:8000 (b).

**Fig. S7** TEM image of individual ZnS nanoparticle.
**Fig. S8** EDS pattern of ZnS nanocages and individual ZnS nanoparticles.

<table>
<thead>
<tr>
<th>sample</th>
<th>Zn/S atom ratio</th>
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<tr>
<td>individual NPs</td>
<td>1:1.036</td>
</tr>
<tr>
<td>nanocages</td>
<td>1:1.178</td>
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**Fig. S9** XPS pattern of ZnS nanocages and individual ZnS nanoparticles.

**Fig. S10** N₂ adsorption/desorption isotherm of ZnS nanocages.
**Fig. S11** SEM (a) and HR-TEM (b) images of ZnS nanocages.

![SEM and HR-TEM images of ZnS nanocages](image)

**Fig. S12** FTIR spectra of ZnS nanocages and individual particles.

The absorption band at 3424 cm\(^{-1}\) is ascribed to hydroxyl group at the particle surface, those at 3122 and 1622 cm\(^{-1}\) are respectively ascribed to N-H stretching and N-H rocking in acetamide, and those at 1568 and 1421 cm\(^{-1}\) are ascribed to C=O stretching vibration in acetate.

![FTIR spectra](image)