Highly Active Zinc Sulfide Composite Microspheres: A Versatile Templates for Synthesis of a Family of Hollow Nanostructures of Sulfides

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1. Supporting Methods

1.1 Scalable synthesis of AA-[Zn(OH)₄]²⁻ complex microspheres

In a typical synthesis route, 7.2 mmol of CTAB and 0.72 mmol of AA were added into a 250 mL round-bottom flask and dissolved using 150 mL deionized water. Subsequently, 2.7 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 2.7 mmol of HMTA were introduced into the solution with vigorously stirred for 30 min before being heated and maintained at 85 °C for 10 h. The resulting milky white suspension was washed three times with deionized water and absolute ethanol, and then dried at 50 °C for 24 h. Finally, the AA-[Zn(OH)₄]²⁻ complex was obtained.

1.2 Hyperthermic effect of the as-prepared samples under NIR irradiation

To evaluate the photothermal conversion performance, 2.0 mL of the as-prepared CuS hollow nanosphere aqueous dispersions (150 μ g mL⁻¹) were irradiated by an 808 nm laser, and the temperature change of the aqueous dispersions was recorded every 10 s by a digital thermometer.

2. Supporting Figures

Table S1. The reaction parameters of $SS-M_xS_y$ (M = Cu, Ag, Bi) hollow microspheres.

Hollow nanosphere	Amount of thiourea	Solvent	Reaction temperature
CuS	0 mmol	Deionized water	25, 45, 65, 85 °C
Ag ₂ S	0 mmol	Ethylene glycol	130 °C
Bi ₂ S ₃	0.81 mmol	Ethylene glycol	130 °C

Table S2. The reaction parameters of $SS-Zn_xM_{1-x}S$ (M = Co, Cd, Ni) and $DS-Zn_xM_{1-x}S$ (M = Mn, Cd) hollow nanosphere.

Hollow nanosphere	Amount of thiourea	Solvent	Reaction temperature
SS-Zn _x Co _{1-x} S	16.2 mmol	Deionized water	150 °C
SS-Zn _x Cd _{1-x} S	16.2 mmol	Ethylene glycol	140 °C
SS-Zn _x Ni _{1-x} S	16.2 mmol	Deionized water	150 °C
DS-Zn _x Mn _{1-x} S	16.2 mmol	Glycerinum + water	160 °C
DS-Zn _x Cd _{1-x} S	40.5 mmol	Deionized water	140 °C

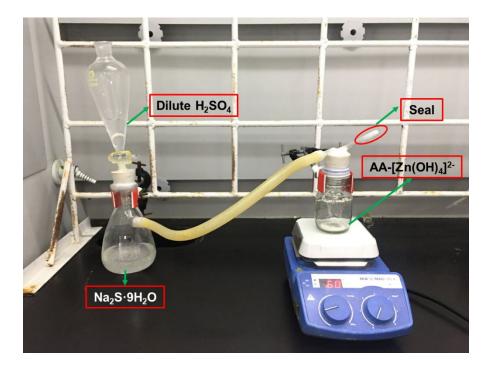


Figure S1. Photograph of the self-regulating gas sulfidation installation.

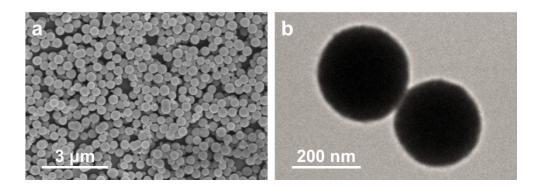


Figure S2. SEM (a) and TEM (b) images of as-prepared monodisperse $AA-[Zn(OH)_4]^{2-}$ composite microspheres.

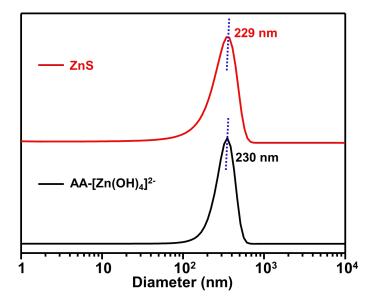


Figure S3. Particle size distribution of the as-prepared $AA-[Zn(OH)_4]^{2-}$ complex microspheres and ZnS composite microspheres.

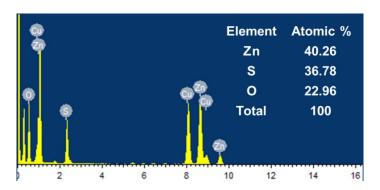


Figure S4. Energy dispersive X-ray spectra of the as-prepared ZnS composite microspheres.

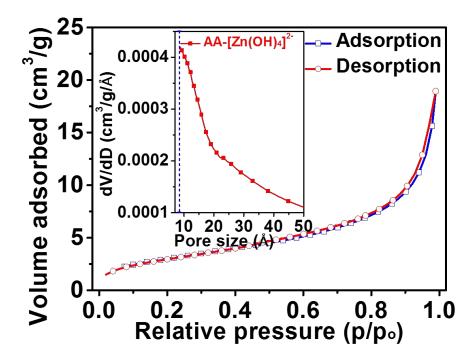


Figure S5. Nitrogen adsorption-desorption isotherms and pore-size distribution curves of the as-synthesized $AA-[Zn(OH)_4]^2$ - complex microspheres.

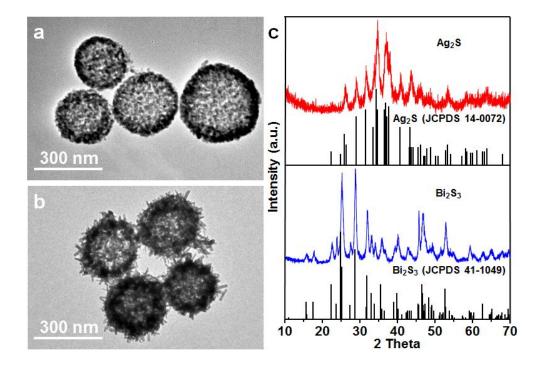


Figure S6. TEM images of as-obtained Ag₂S (a) and Bi₂S₃ (b) hollow microspheres; (c) XRD patterns of as-obtained samples.

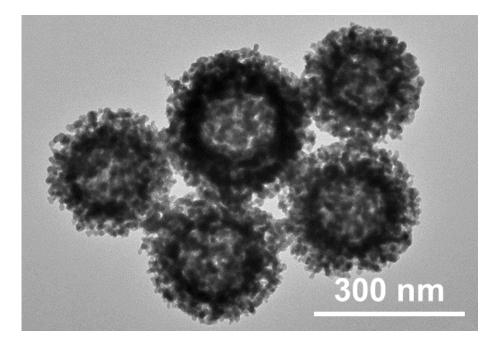


Figure S7. TEM image of as-prepared $Cu_xBi_{1-x}S$ hollow microspheres.

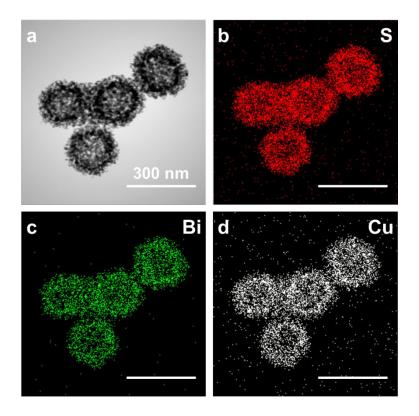


Figure S8. (a-d) STEM image and elemental mappings of S, Bi and Cu elements.

Scale bars are 300 nm.

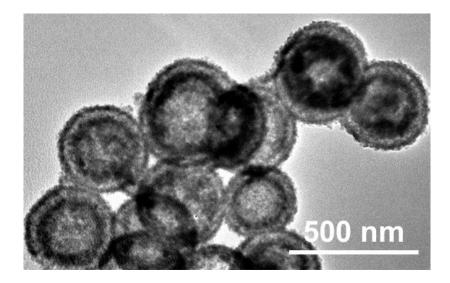


Figure S9. TEM image of DS- $Zn_xCd_{1-x}S$ hollow microspheres.

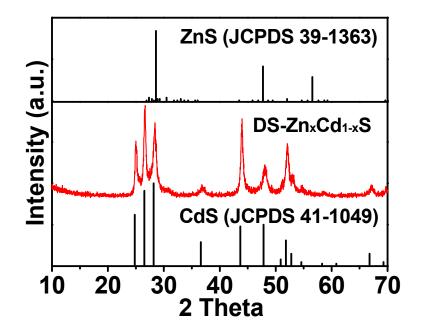


Figure S10. XRD patterns of the as-obtained DS-Zn_xCd_{1-x}S hollow microspheres.