A general and rapid synthesis of metal sulphides hollow spheres that have properties enhanced by salt-assisted aerosol decomposition: A case of ZnS and other multicomponent solid solutions

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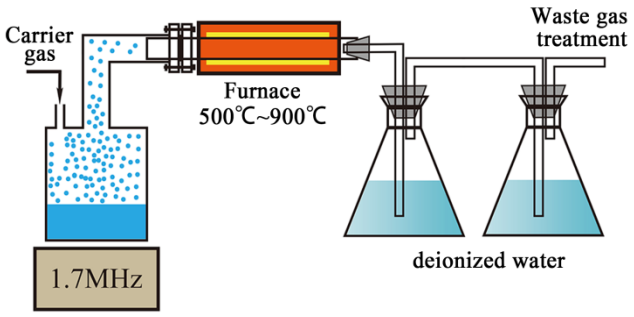
Supporting Information

Experimental Section

Experimental apparatus:



The aerosol droplets are generated by an ultrasonic atomizer and then carried by air or nitrogen into a furnace operated at 500-900℃. The products are collected by two bubblers and NaCl is washed away by deionized water.

Materials: $Zn(NO_3)_2 \cdot 6H_2O$, $In(NO_3)_3 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Mn(NO_3)_2$, $SC(NH_2)_2$ and NaCl were purchased from Sinopharm Chemical Reagent Beijing Co.,Ltd. Deionized water was used in all synthesis. All chemicals were used as received.

Synthesis of ZnS particles: Prepared 100ml mixed aqueous solution of 0.2M $Zn(NO_3)_2$, 0.5M $SC(NH_2)_2$ and 0~1M NaCl under stirring. Then poured into an atomization cell and nebulized by a 1.7MHz household ultrasonic humidifier (YADU YC-X101W). Droplets produced by the nebulization were carried into the furnace by N_2 gas flow at a rate of 1.0mL

per minute. The furnace temperature was 500-900℃ for microspheres synthesis. The particles were collected by the bubblers, and centrifuged, washed several times with deionized water, finally dried at 80℃ in the air.

Synthesis of $ZnIn_2S_4$ particles: Prepared 150ml mixed aqueous solution of 0.01M $Zn(NO_3)_2$, 0.02M $In(NO_3)_3$, 0.3M $SC(NH_2)_2$ and 0~0.1M NaCl under stirring. The furnace temperature sets to 600℃. Other reaction conditions are the same with above.

Synthesis of $CuInS_2$ particles: Prepared 150ml mixed aqueous solution of 0.01M $Cu(NO_3)_2$, 0.01M $In(NO_3)_3$, 0.2M $SC(NH_2)_2$ and 0~0.1M NaCl under stirring. The furnace temperature sets to 500℃. Other reaction conditions were the same with above.

Synthesis of ZnS-$CuInS_2$ solid solution particles: Prepared 150ml mixed aqueous solution of 0.0045M $Cu(NO_3)_2$, 0.0045M $In(NO_3)_3$, 0.091M $Zn(NO_3)_2$, 0.3M $SC(NH_2)_2$ and 0.1M NaCl under stirring. The furnace temperature sets to 500 °C. Other reaction conditions were the same with above.

Characterization: The structure and morphology of products were characterized by x-ray diffraction patterns (XRD, Rigaku D/Max 2200PC diffractometer; Rigaku Corp., Tokyo, Japan), a scanning electron microscope (Supra 55; Zeiss, Oberkochen, Germany), and high-resolution transmission electron microscope (HRTEM, JEM-2010; JEOL, Ltd., Tokyo, Japan). The excitation and emission spectra were taken on an F-4500 spectrophotometer equipped with a 150W xenon lamp as the excitation source. A PERSEE TU-1901 double monochromator UV-vis spectrophotometer was used to record the UV/Vis spectra of various sample.

Adsorption and Photocatalytic Degradation of Dyes: The photocatalytic degradation of RhB and CR was proceeded in an aqueous solution at 10 °C. 20mg of ZnIn2S4 was suspended in an 80mL aqueous solution containing 20 ppm RhB and 20 ppm CR respectively. The system was cooled by circulating water to keep the given temperature. Before irradiation, the suspension was magnetically stirred for half hour in the dark to reach the absorption-

desorption equilibrium. The visible light source was 300W Xe lamp (CEL-HXF300). A cutoff filter was placed outside the Pyrex jacket to completely remove the wavelengths under 420nm and ensure the irradiation with visible light only.

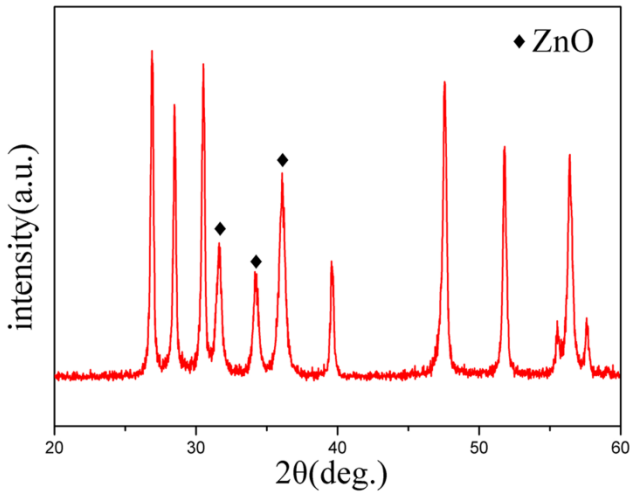


Fig. S1 X-ray diffraction patterns of ZnS hollow spheres prepared by salt-assisted aerosol decomposition at 800 °C with salt of NaCl in mole ratio of Zn:S:Na=1:1:1.

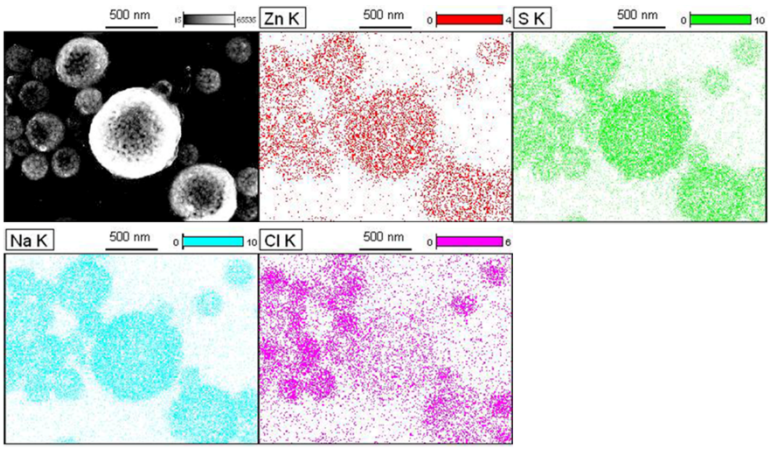


Fig. S2 SEM-EDS elemental mapping analysis of ZnS hollow spheres with residual NaCl.

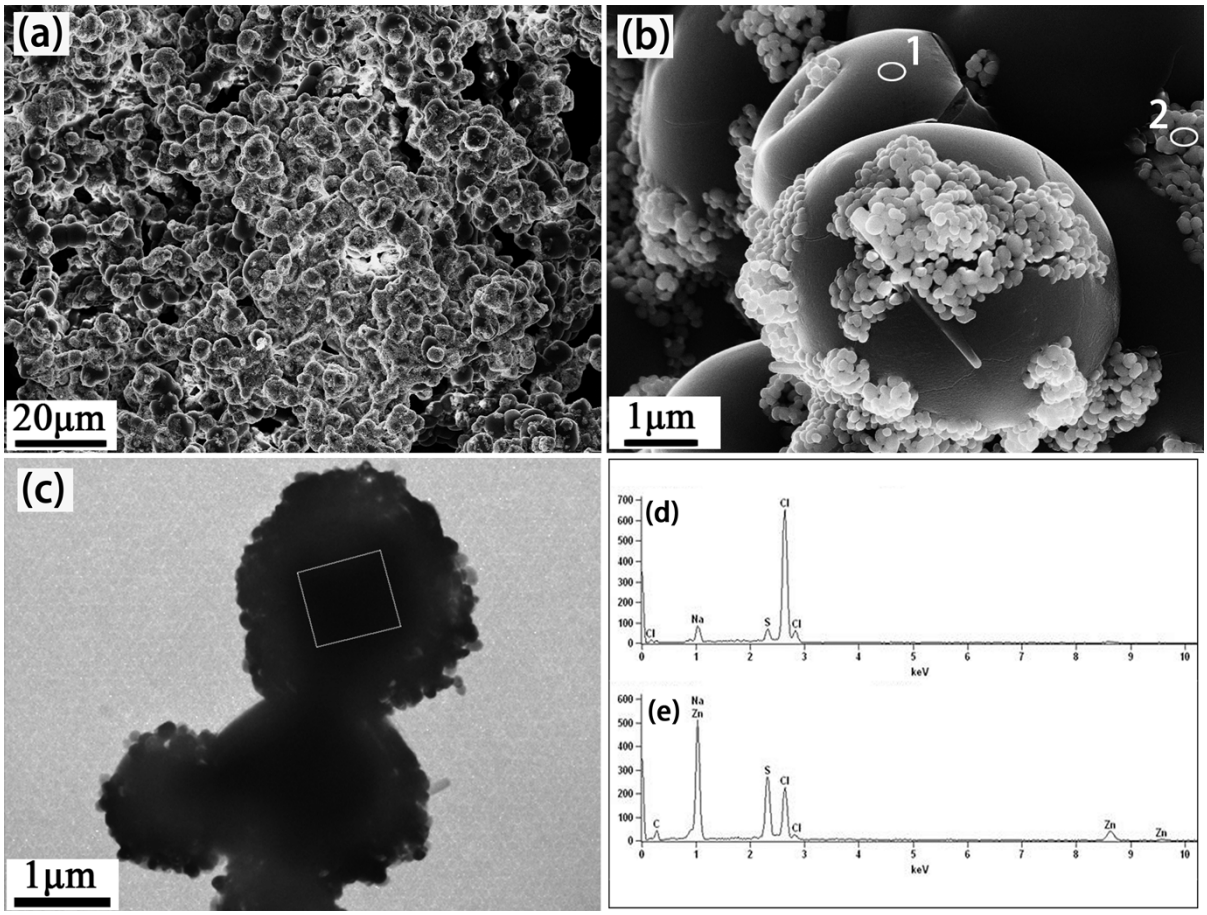


Fig. S3 ZnS particles without exposure to water prepared at 800 °C with the mole ratio of Zn:S:Na=2:5:10. (a) SEM lower magnification image; (b) SEM higher magnification image; (c) TEM; (d) and (e) are EDS analysis of the point of 1 and 2 in figure (b), respectively.

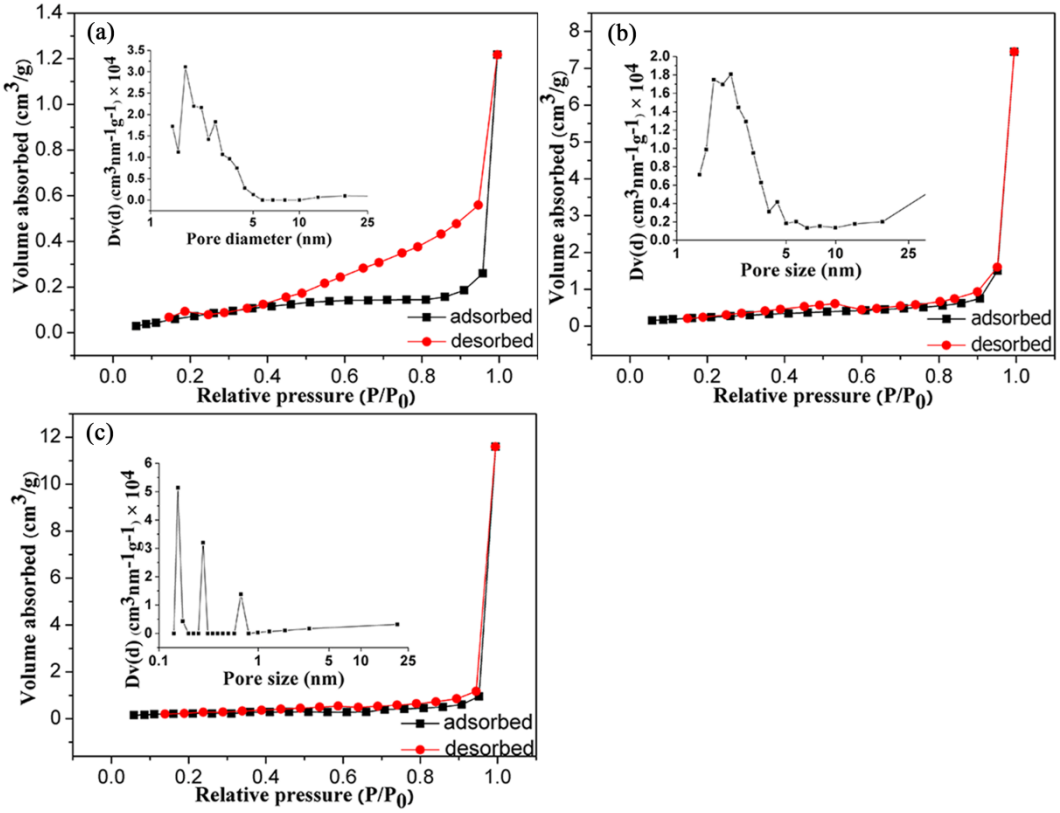


Fig. S4 Nitrogen adsorption/desorption isotherm and Pore-size distribution (insets) of ZnS particles prepared at 800 °C: (a) solid spheres ; (b) hollow spheres ; (c) dispersed particles.

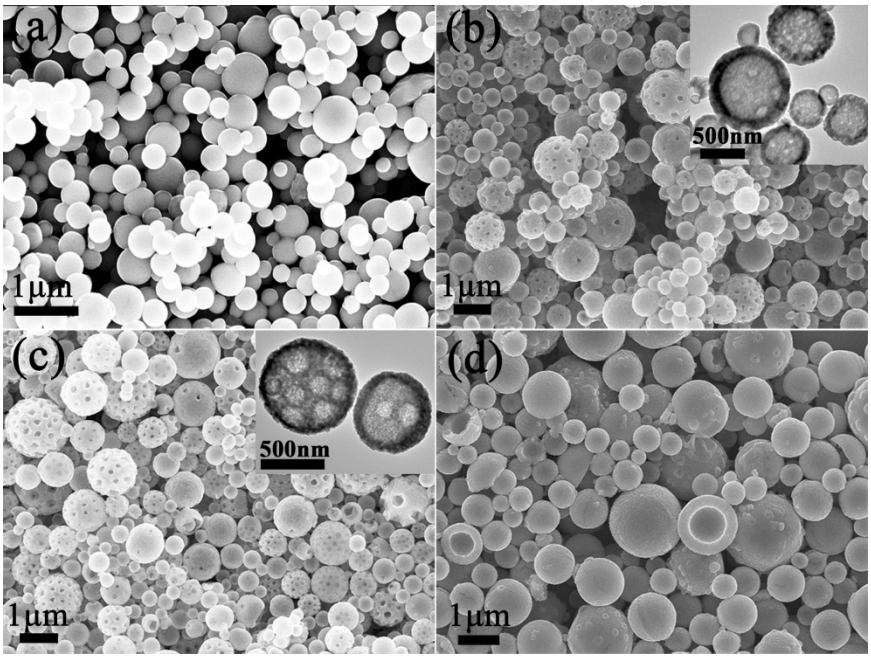


Fig. S5 SEM images of ternary chalcogenide and solid solution synthesized by SAD method: (a) $ZnIn_2S_4$ solid spheres synthesized at 600°C; (b) $ZnIn_2S_4$ hollow spheres synthesized at 600°C. The inset is the TEM image of $ZnIn_2S_4$ hollow spheres; (c) $CuInS_2$ hollow spheres synthesized at 500°C. The inset is the TEM image of $CuInS_2$ hollow spheres; (d) ZnS-$CuInS_2$ solid solution synthesized at 500°C.

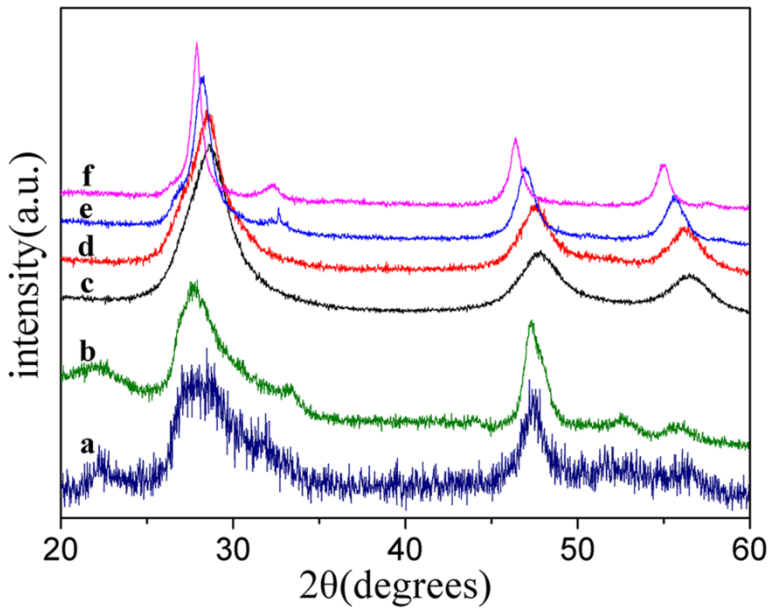


Fig. S6 X-ray diffraction patterns of ternary chalcogenide and solid solutions prepared by SAD: (a) $ZnIn_2S_4$ solid spheres synthesized without salt of NaCl at 600 °C; (b) $ZnIn_2S_4$ hollow spheres synthesized with salt of NaCl at 600 °C; (c-f) Hollow spheres of $(CuIn)_xZn_{2(1-}$

$_{x)}S_2$ solid solutions synthesized at 500°C with the value of x respectively are (c)0, (d)0.09, (e)0.5 and (f)1.

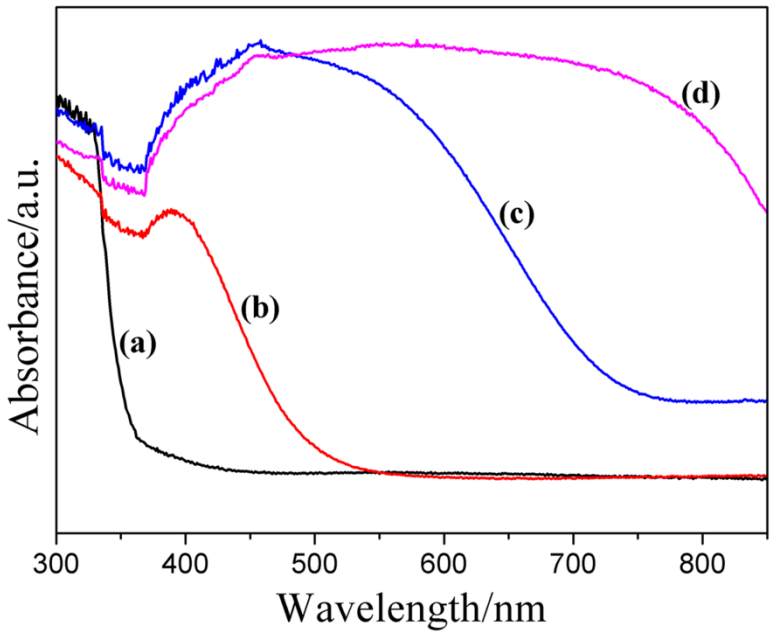


Fig. S7 Diffuse reflectance UV-vis spectra of $(CuIn)_xZn_{2(1-x)}S_2$ solid solutions. The values of x are (a) 0, (b) 0.09, (c) 0.5 and (d) 1, respectively.