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Morphological control of ZnS nanopowders by different capping molecules

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Abstract

Complex 3D architectures of ZnS microflowers have been successfully synthesized via a quick water-based precipitation synthesis method at moderate temperature (<100°C) using an inorganic capping agent $K_2S_2O_7$. The synthesized samples were characterized by SEM, XRD, FTIR and BET analysis. The as-synthesized ZnS microflowers are composed of numerous nanowires and has a cubic structure. Surface area is $42 \text{ m}^2 \cdot \text{g}^{-1}$ and the pore diameter is 3.7 nm. Comparison with equivalent synthesis with an organic capping agent (PVP) was performed.

Keywords

Semiconductors, Zinc sulfide, Inorganic capping agent, Nanoparticles

1. Introduction

ZnS is a wide bandgap (3.6-3.9 eV) II-VI semiconductor compound with versatile properties in the fields of optics, photocatalysis, electronics... Hence there has been an extensive amount of work done on the synthesis of a wide range of nanostructured morphologies of ZnS (from 1D nanomaterials (nanowires, nanobelts...) to 3D microspheres [1]) as the properties of the latter can be tuned with their size, structure and morphology. Various 3D structures of ZnS (hierarchical or solid microspheres, cauliflower-like structure...) were obtained by different synthesis processes (hydrothermal, precipitation) with or without using a template or a capping agent [2-5]. Among those, there are relatively few reports on synthesis of 3D ZnS nanostructures by a precipitation method at low temperature using an inorganic capping agent. Although organic molecules such as polyvinylpyrrolidone (PVP) are frequently used for the synthesis of ZnS nanomaterials [3], they proved to be quite difficult to remove from the surface once the reaction was completed [6]. Inorganic small species offer an interesting alternative as they occupy less surface of the particles and can possibly lead to innovative morphologies [7].

In the present work, we have synthesized ZnS mesoporous microspheres by combining a water-based precipitation method under 100 °C and an inorganic capping agent ($K_2S_2O_7$). Synthesis of ZnS in similar conditions was also realized without any capping agent and with a standard organic one (PVP).

2. Experimental

Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) (Sigma-Aldrich, $\geq 98\%$), thioacetamide (TAA) (Sigma-Aldrich, $\geq 99\%$), polyvinylpyrrolidone (PVP, $M_w=40000$ g/mol) (Sigma-Aldrich) and potassium pyrosulfate ($K_2S_2O_7$) (Sigma-Aldrich, $\geq 99\%$) were commercially purchased

and used as received. Zinc precursors ($[Zn]=0.06$ M) and the capping agent ($K_2S_2O_7$, PVP) were weighed and dissolved in 25 ml of double distilled water. The mixture was stirred for 1 hour at RT. TAA ($[TAA]=0.4$ M) was added to the mixture which was then heated at 80 °C for 3 hours. Precipitate was centrifuged and washed several times with distilled water and ethanol and dried under air overnight. Resulting powders were white-yellow. Samples were characterized by scanning electron microscopy (Hitachi S-3400N), X-Ray powder diffraction (D8-Bruker, Cu $K\alpha_{1,2}$ radiation), Fourier transform infrared spectrometry (Perkin Elmer 400 FTIR) and N_2 adsorption–desorption method (Belsorp-Max, BET and BJH methods).

3. Results and discussion

The morphology and the size of the obtained ZnS microspheres are observed from the SEM pictures (Figure 1 (a, b)). The samples are composed of numerous nanorods ($200 - 500$ nm \times 20 nm) structured in soft full micron-sized spheres (between 3 and 5 μ m). Sample crystallizes in the cubic phase of ZnS, (Figure 2 (a)). The shoulder at 27° could be characteristic of the (100) peak of the hexagonal wurtzite phase of ZnS or be attributed to stacking defects [10]. Calculation using the Debye-Scherrer formula for the strongest peak (111) leads to a crystalline domain size of about 6.5 nm.

During synthesis, the initial pH is 5. Then, as H_2S is produced *in situ* during the precipitation of ZnS, pH decreases to a final value of around 2. Since isoelectric point (IEP) of ZnS is around 3 [8], it is not obvious to state if it is K^+ , $S_2O_7^{2-}$ or both ions that act as capping agents. Nevertheless, considering that initial pH is above IEP of ZnS, primary seeds of ZnS may be firstly capped by a compact layer of K^+ cations. $S_2O_7^{2-}$ anion form a second diffuse layer around those particles, as suggested by Kumar and

Upadhyay [7]. Kumar *et al* obtained 3 nm-sized ZnS nanoparticles by using Na₂S as the sulfur source in the precipitation process and the same inorganic capping agent K₂S₂O₇ [7], suggesting that the nature of the sulfur source controls the final morphology of the product [9].

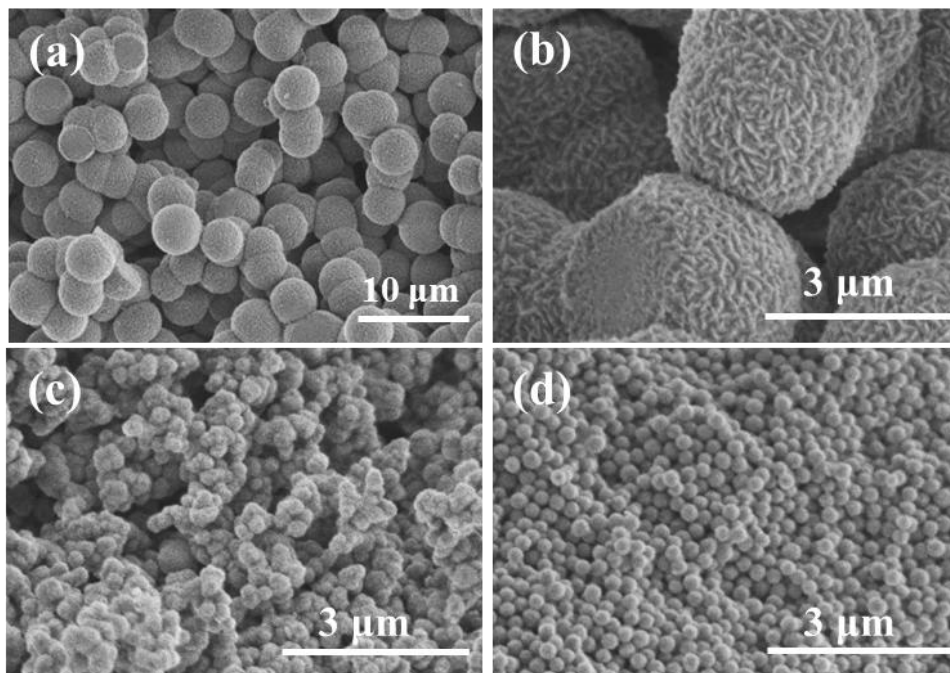


Figure 1: SEM pictures of the synthesized ZnS. (a, b) Microspheres of ZnS with an inorganic capping agent (K₂S₂O₇ 0.1% w/v), (c) Nanoparticles of ZnS (no capping agent), (d) Nanospheres of ZnS with an organic capping agent (PVP, 2% w/v).

In order to understand the influence of the capping agent on the morphology of ZnS, syntheses were performed with (i) no capping agent then (ii) an organic capping agent (PVP) while keeping the other conditions unchanged. Instead of the nanostructured microspheres (Figure 1 (a, b)), agglomerated nanoparticles (size between 100 and 300 nm) and monodispersed dense nanospheres (size of 250 nm) are obtained, respectively (Figure 1 (c) and (d)). It proves the essential role of the capping agent on the

morphology of the synthesized products. With no capping agent, the nucleation step occurs to form ZnS nuclei in the solution which assemble randomly to form agglomerated particles with irregular morphology. In the presence of a capping agent, this latter will adsorb on the surface of the nuclei and then control the further growth of the particle and its final morphology.

The amount of the used capping agent also determines the morphology of the obtained products (see Additional Data). Microflowers can be obtained with an amount of potassium pyrosulfate equal or superior to 0.1% w/v, against 2% w/v when PVP is used. For higher amount of $K_2S_2O_7$, bigger microflowers are obtained. The subsequent analyses are performed on the structures obtained with 0.1% w/v for $K_2S_2O_7$ or 2% w/v for PVP.

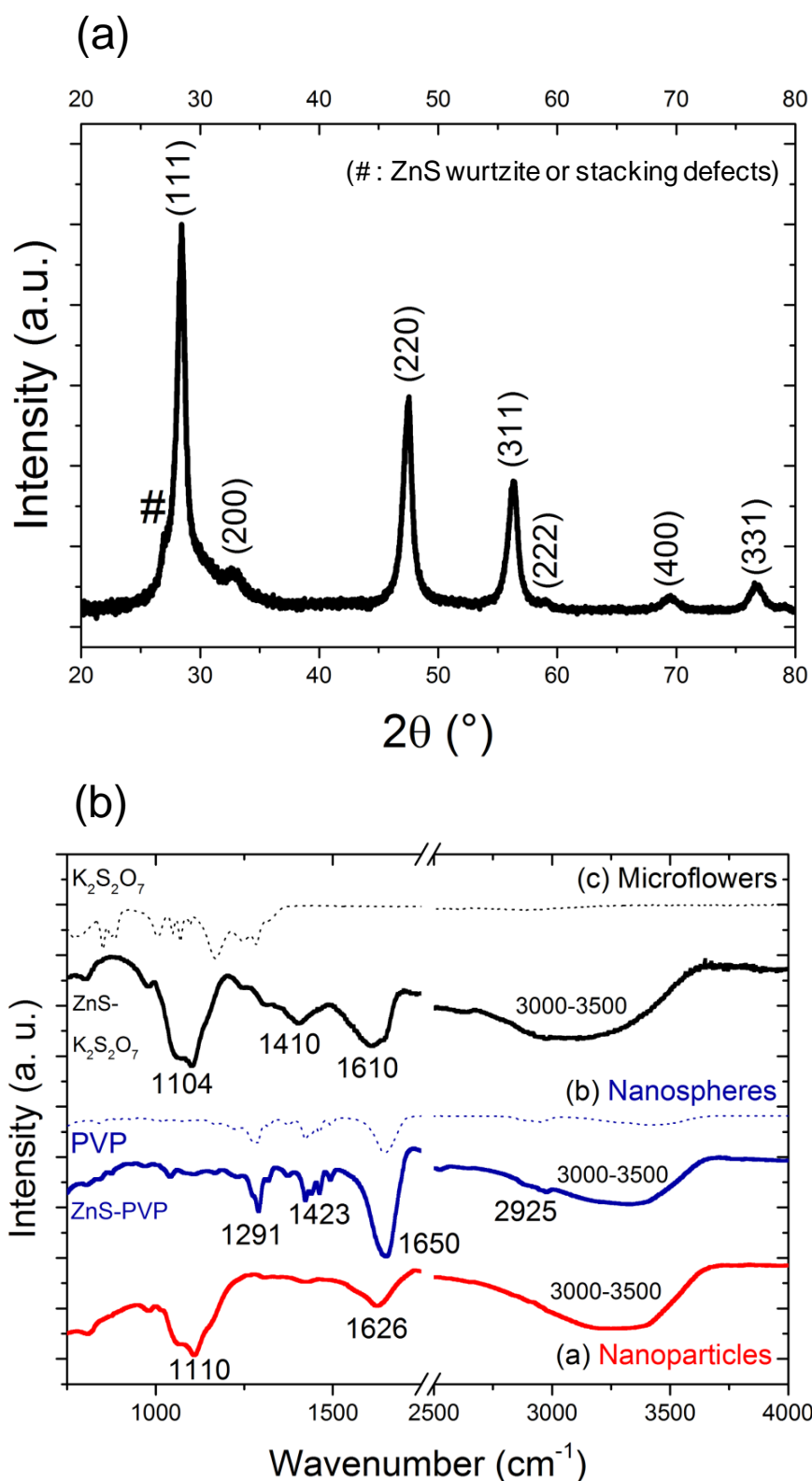


Figure 2: (a) XRD pattern of the synthesized microflowers of ZnS. (b) FTIR spectra of the synthesized ZnS

The FTIR spectra of the synthesized products are shown in Figure 2 (b). The characteristic ZnS vibration bands can be observed at 1104 and 1110 cm^{-1} for the microflowers and the nanoparticles respectively [3]. These latter spectra displayed broad absorption bands around 1610-1650 cm^{-1} and 3000-3500 cm^{-1} , attributed to the stretching vibration of OH and to the bending vibration of H-O-H from water molecules on the surface as observed elsewhere [11]. No clear evidence of infrared bands attributed to the capping agent $\text{K}_2\text{S}_2\text{O}_7$ was found on the microflower's FTIR spectrum [12], showing that the potassium pyrosulfate is largely removed by washing of the synthesized products. On the other hand, the bands at 1291 cm^{-1} , 1423 cm^{-1} , 1650 cm^{-1} and 2925 cm^{-1} observed on the IR spectrum of the nanospheres correspond to the vibrations of C-N, C=O and CH_2 of the residual PVP [13].

Specific surfaces of nanoparticles, nanospheres and microflowers obtained by the BET method are 33 $\text{m}^2 \cdot \text{g}^{-1}$, 33 $\text{m}^2 \cdot \text{g}^{-1}$ and 42 $\text{m}^2 \cdot \text{g}^{-1}$ respectively. The isotherms of the nanoparticles and microflowers present a type IV behavior (Figure 3), typical of mesoporous materials whereas the nanospheres exhibit a type-II isotherm, indicating a non-porous material. Without the capping agent, the ZnS nuclei assemble randomly to form agglomerated particles with irregular morphology, which could explain the observed mesoporosity of nanoparticles.

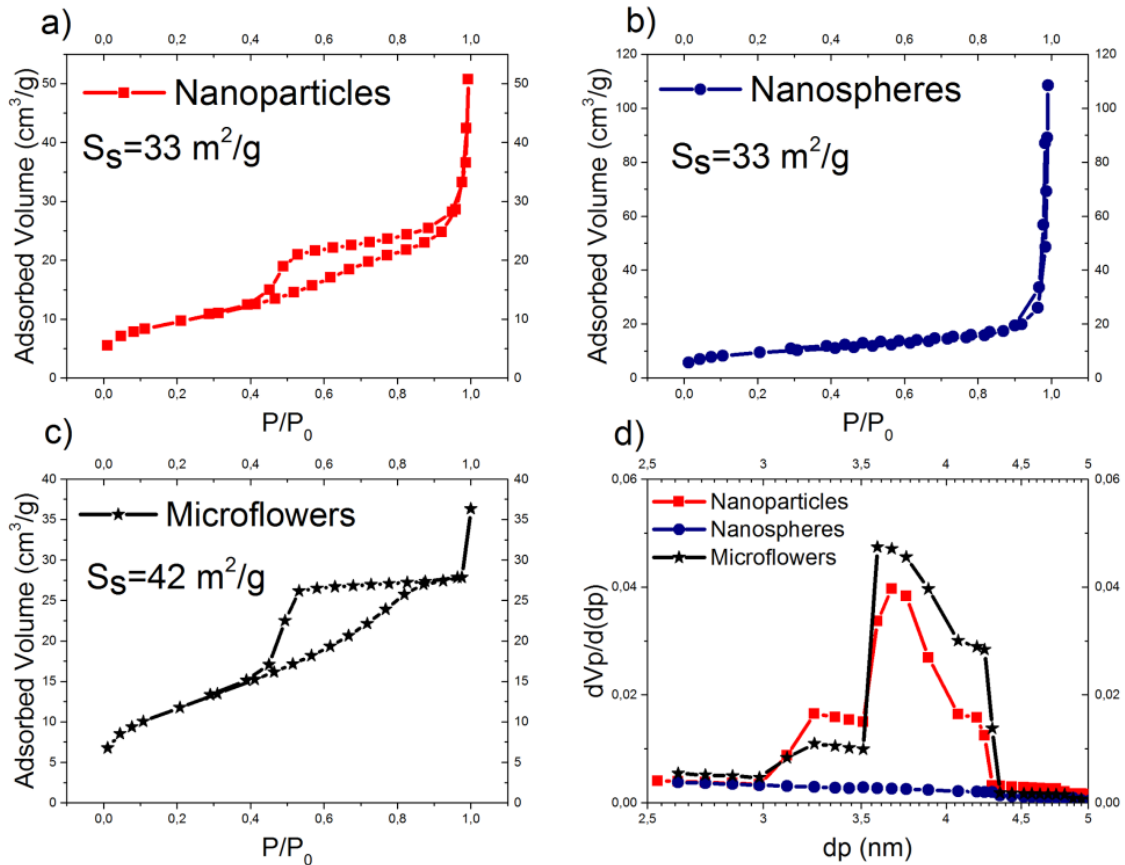


Figure 3: Nitrogen adsorption/desorption isotherms of the synthesized ZnS (a) Nanoparticles (b) Nanospheres (c) Microflowers. (d) Pore-size distribution of each powder.

A possible formation process of the synthesized ZnS can then be proposed, based on the above results: the active S²⁻ released from the hydrolysis of TAA reacts with the cations Zn²⁺ to generate the ZnS nuclei which then aggregate to form irregular nanoparticles. Adding a capping agent at a sufficient concentration (superior to the amount of Zn²⁺ in solution) leads to completely different morphologies: microflowers for K₂S₂O₇ and nanospheres for PVP. Both are the result of the interaction of the capping agent with the Zn²⁺ cations and the ZnS nuclei. Using a “big” molecule (PVP) with numerous

adsorption sites (354 per molecule) leads to equiaxial growth of the ZnS nuclei which further aggregate in nanospheres because of their large surface energy. Because of the specific structure of the capping agent, incomplete removal by post-washing is achieved, leaving a shell of PVP around the nanospheres of ZnS. In the case of $K_2S_2O_7$, the formation of ZnS nanorods proceeds along specific directions due to the small size of the molecule (2 adsorption sites). Finally, these nanorods self-assemble to flower-like structure to decrease their surface energy.

4. Conclusion

Mesoporous cubic ZnS microflowers have been successfully synthesized via a quick water-based precipitation synthesis method at a moderate temperature ($<100^\circ\text{C}$) using an inorganic capping agent $K_2S_2O_7$. The as-synthesized ZnS microspheres are composed of numerous nanowires. FTIR analysis shows that the inorganic capping agent can be easily removed. Hence, the as-synthesized ZnS samples can be used as promising photocatalyst material or may find applications in the field of optics, lighting, LED...

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Additional data

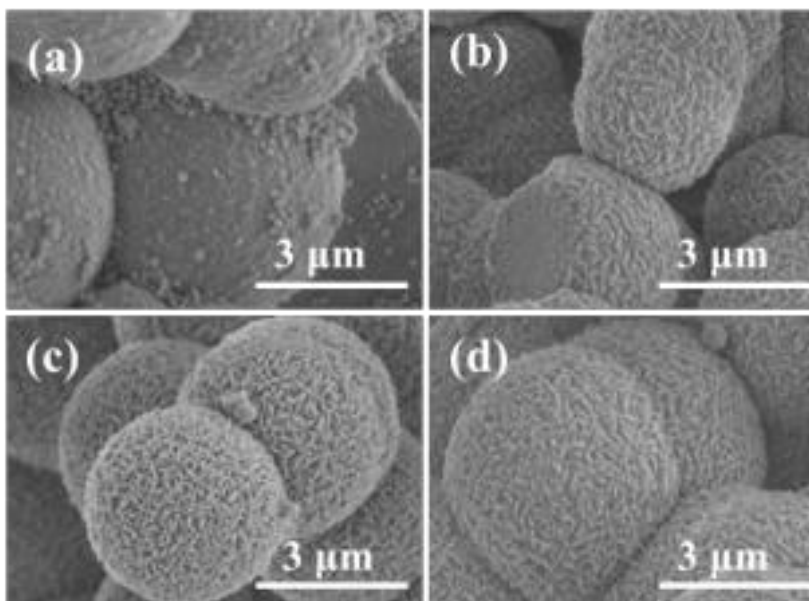


Figure 4 : SEM pictures of the synthesized ZnS microspheres obtained with various amounts of inorganic capping agent $K_2S_2O_7$ (a) 0.02% w/v (b) 0.1% w/v (c) 0.5% w/v (d) 2% w/v.