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From ZnO Microrods to ZnS Microspheres by a Hydrothermal Treatment: The Case of Thiourea

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Zinc oxide microrods (MRs) were successfully prepared without the addition of template and additive by a simple hydrothermal route using only $Zn(CH_3COO)_2 \cdot 2H_2O$ as a precursor at 160 °C for 3 h. Interestingly, the ZnO MRs can be transformed to ZnS microspheres (MSs) with the sulfur source of thiourea under the same conditions. The products were characterized by X-ray diffraction (XRD), energy-dispersive spectrum (EDS), and scanning electron microscopy (SEM). Results show that the obtained ZnO MRs and ZnS MSs belonged to hexagonal phase and cubic phase, respectively. A possible reaction mechanism is proposed and discussed.

Zinc oxide (ZnO) and zinc sulfide (ZnS), as two kinds of n-type semiconductive materials from II–VI families, have caused great attention due to wide applications in different fields. Owing to wide band gaps of 3.3 (ZnO) and 3.7 eV (ZnS), they can be used to fabricate optoelectric devices such as blue light-emitting diodes,[1] optical coating,[2] electroluminescent devices,[3] photovoltaic devices,[4] heterojunction solar cells,[5] n-window layers,[6] and photoconductors.[7] To date, considerable efforts have been devoted to fabricating various ZnO and ZnS nanostructures including wires, rods, belts, tubes, sheets, spheres, and so on due to their strong size- and morphology-dependent properties or device performance. Among these nanostructures, one-dimensional (1D) and sphere structures have received the most attention. This is partly because these 1D nanostructures possess unique electron-transport properties, which are favorable for electronic devices.[8] Also, ZnO is known to readily and intrinsically grow into 1D morphology in a solution environment due to its unique hexagonal crystal structure.[9] On the other hand, hollow spheres possess low density, large surface area, and a special hollow core.[10] Various techniques have been developed to prepare ZnO rods and ZnS hollow spheres.[11–16] Unfortunately, most previous preparations require template, organic reagents, multiple steps, or a long time (more than 10 h). It is still promising to find a template-free, green, simple, and time-saving approach to fabricate ZnO rods and ZnS hollow spheres. Furthermore, it will be meaningful to find a precursor to realize the transformation from ZnO rods to ZnS hollow spheres.

In this paper, we use a simple hydrothermal method to fabricate ZnO MRs using only $Zn(CH_3COO)_2 \cdot 2H_2O$ as a precursor at 160 °C for 3 h. Further, after introducing a certain amount of thiourea as sulfur source, ZnS MSs can be obtained. To the best of our knowledge, this is likely to be the first report on the transformation from ZnO MRs to ZnS MSs.

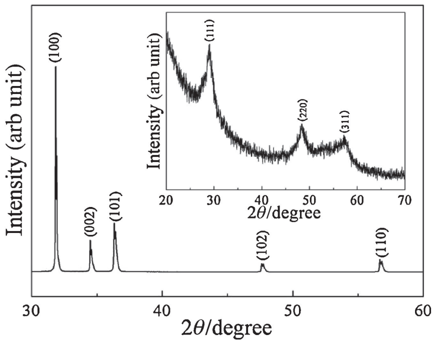

Figure 1. XRD patterns of ZnO MRs and ZnS MSs (inset).

The syntheses of ZnO MRs and ZnS MSs were carried out by a hydrothermal method. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Typically, 3.0 g of zinc acetate was dissolved in 70 mL of deionized water at room temperature under fierce stirring. Then the solution was transferred into a Teflon-lined autoclave (100 mL capacity), which was put in an oven at 160 °C for 3 h. After the autoclave was cooled to room temperature, the precipitate was collected, washed with deionized water and absolute ethanol several times, and then dried in a vacuum oven at 80 °C for 4 h. So the products of sample "a" were obtained. In addition, adding 1.0 g of $CS(NH_2)_2$ to the $Zn(OAc)_2$ solution, followed the same procedure as ZnS, sample "b" can be obtained.

The samples were characterized by XRD (Bruker D8 Advance diffractometer) using Cu Kα radiation source, EDS (Bruker), and SEM (Zeiss EVO LS-15).

The typical XRD patterns of the resultant ZnO MRs and ZnS MSs (inset) are shown in Figure 1. The diffraction peaks of sample "a," corresponding to (100), (002), and (101) of standard ZnO powder in the 2θ range of 30–40°, indicating that the sample has polycrystalline hexagonal structure (zincite, JCPDS card 36-1451, $a = b = 3.250$ Å, $c = 5.207$ Å). The intensity of (100) diffraction peak at 31.78° was much stronger than that of other peaks. This indicates that the ZnO MRs had a high preferential growth along [100] direction. The diffraction peaks at 29.06, 48.24, and 57.35°, as shown in Figure 1 (inset), were assigned to the (111), (220), and (311) planes of the cubic phase ZnS (JCPDS card 80-20). No diffraction peaks from other crystalline form were detected, indicating high purity and well-crystalline ZnS polycrystals. Our previous work has reported that the fabricated ZnS MSs were hexagonal phase ($a = b = 3.777$ Å, $c = 6.188$ Å) using $ZnCl_2$ as precursor under the same conditions,[17] demonstrating that the pH value plays a significant role during the formation the ZnS MSs. For the sample "b," the XRD peaks were quite broad, indicating the ZnS MSs were composed of nanosized particles. The size of the nanocrystals (NCs) (D) was calculated on the basis of the Schemer formula, $D = k\lambda/\beta\cos\theta$,[18] where $k = 0.9$ is the shape factor, λ is the X-ray wavelength of Cu Kα radiation (1.5418 Å), θ is the Bragg diffraction angle, and β (0.048) is the full width at half maximum (FWHM) of the (111) peak. The average NCs size in ZnS MSs is 2.35 nm, which is nearly equal to the Bohr radius (2.4 nm).

The EDS spectra of the obtained ZnO MRs and ZnS MSs are shown in Figure 2, which reveals the atomic ratio 1:0.96 of Zn and O and 1:0.92 of Zn and S in the samples of "a" and "b,"

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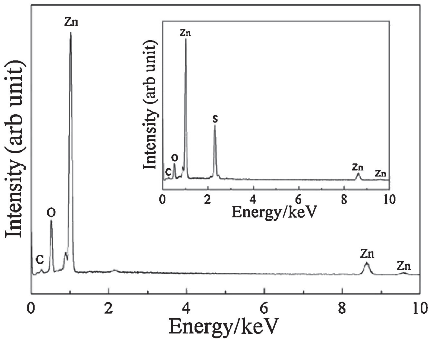

Figure 2. EDS spectra of ZnO MRs and ZnS MSs (inset).

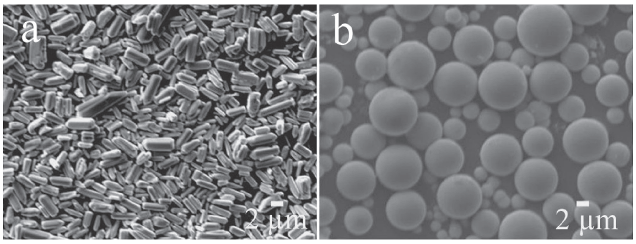

Figure 3. SEM images of (a) ZnO MRs and (b) ZnS MSs.

respectively. The relatively weak carbon peaks in the spectra probably originate from unavoidable surface contaminative carbon on the samples from exposure to air during sample preparation. In sample "a," the atomic ratio is a little less than the stoichiometric ratio (1:1) probably originating from the formation of oxygen vacancies. In sample "b," the relatively weak oxygen peaks may come from the surface absorption of oxygen.[19]

Figure 3 shows the SEM images of the as-prepared ZnO MRs and ZnS MSs. The surfaces of the samples are smooth. No cavities and deficiencies are found in the samples. In our synthesis route, Zn^{2+} ions will hydrolyze to form the transition complex of $Zn(OH)_2$, which will decompose to form the final products of ZnO rods. The reaction is as follow: $Zn(OAc)_2 + 2H_2O \rightarrow Zn(OH)_2(s) + 2HOAc$, $Zn(OH)_2(s) \rightarrow ZnO(s) + H_2O$. The small ZnO NCs have a tendency to form crystal nucleus through oriented attachment (OA) mechanism[20] leading to the formation of ZnO MRs. Huang et al.[21] also fabricated peanut-like ZnO MRs using a certain amount of cetyltrimethylammonium bromide (CTAB) as surfactant in the precursor of $Zn(OAc)_2 \cdot 2H_2O$ followed by a hydrothermal treatment. After introducing the $CS(NH_2)_2$, Zn^{2+} ions react with S^{2-} ions to form ZnS NCs. At 160 °C, the thiourea can hydrolyze to form H_2S, NH_3, and CO_2. The reaction is as follows: $NH_2CSNH_2 + 2H_2O \rightarrow 2NH_3(g) + H_2S(g) + CO_2(g)$. The gas bubbles in situ generated in the reaction may serve as a soft template for the final formation of ZnS hollow MSs. Around the bubbles, nucleation, growth, and mineralization of ZnS occurred. In the aqueous medium, H_2S disassociates to form S^{2-} as follows: $H_2S + H_2O \rightarrow HS^- + H_3O^+$, $HS^- + H_2O \rightarrow S^{2-} + H_3O^+$. Then the ZnS NCs are gradually absorbed on H_2S, NH_3, or CO_2 bubbles through oriented aggregation leading to the formation of ZnS hollow MSs.

During the formation of ZnS hollow MSs, there was no hard template for the hollow structure. The main driving force leading to the formation of ZnS hollow MSs was probably due to Ostwald ripening, which has been applied in fabrication of hierarchical structures such as In_2O_3,[22] CuO,[23] ZnO,[24] MnO_2,[25] and Fe_2O_3.[26] The Ostwald ripening process was associated with a progressive redistribution of ZnS NCs from the interior to the exterior of the MSs. The amorphous remains out of equilibrium with the surrounding solution due to its high solubility dissolves and undergoes diffusion. Compared to the template-assisted methods employing glucose,[27] polystyrene (PS),[28] silica,[29] amino acid,[30] and so forth, this self-template method is very simple and convenient and avoids the introduction of impurities and the removal of the template, therefore, it is suitable for modern chemical fabrication.

In conclusion, ZnO MRs and ZnS MSs were successfully prepared by a hydrothermal route using $Zn(OAc)_2 \cdot 2H_2O$ as a precursor at 160 °C for 3 h without and with the sulfur source of thiourea, respectively. The obtained ZnO MRs and ZnS MSs were hexagonal phase and cubic phase, respectively. The produced bubbles played a soft template role in the transformation from ZnO MRs to ZnS MSs. The formations of ZnO MRs and ZnS MSs were probably due to oriented attachment (OA) and Ostwald ripening mechanisms.

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