

Large-scale synthesis of tube-like ZnS and cable-like ZnS–ZnO arrays: Preparation through the sulfuration conversion from ZnO arrays via a simple chemical solution route

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Abstract

Arrayed structures are desirable for many applications, but the fabrication of many material arrays remains a significant challenge. As a prominent II–VI semiconductor, large-scale arrayed ZnS structure has not been easily fabricated. Here, we introduce a simple structure conversion route for the synthesis of novel arrayed structures, and large-scale tube-like ZnS structure arrays and cable-like ZnS–ZnO composite arrays were successfully prepared through sulfuration conversion from arrayed rod-like ZnO structure based on a hydrothermal method at low temperature. XRD, EDS, SEM, TEM and PL are used to confirm the formation of the novel arrayed structure and trace the conversion process. The results show that the conversion ratio can be conveniently tailored by the reaction time, and the PL properties of the obtained materials can be adjusted through the conversion ratio. Especially, the cable-like structure holds the PL properties of both ZnO and ZnS structures. This simple solution method can be further extended to the preparation of other semiconductor sulfide and selenide, and can amplify the application field of large-scale arrays of semiconductors.

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Keywords: ZnS; Structure conversion; ZnO; Array; Tube-like; Cable-like

1. Introduction

One-dimensional (1D) structures such as wires, rods, belts and tubes have become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices [1]. The creation of these structures in large arrays with a low-cost and clean method is essential challenge that scientists have to assemble these outstanding structures into functional devices. Previously, large-scale arrays of many functional materials such as carbon nanotubes [2], titanic oxide nanowires [3], iron oxide nanorods [4], bismuth tellurium nanowires [5], antimony trisulfide [6],

and other nanostructures [7] have been successful synthesized by various methods. However, lots of prominent materials have not been fabricated in arrayed structures. As an important II–VI semiconductor, zinc sulfide (ZnS) has wide bandgap energy of 3.66 eV at room temperature [7]. It is a well-known luminescent material having prominent applications in displays, sensors, and lasers [8], and also has been applied in photocatalyst [9], pigment [10], and non-linear optical devices [11]. The nanoscale ZnS has a broader energy band gap than its bulk material, which extends its application range [12]. Recently, 1D ZnS nanomaterials have attracted much attention because of their potential applications in nanoscale electronics, optics and other novel devices. Nanowires, nanorods, and nanobelts of ZnS have been obtained by physical evaporation [13], liquid-crystal template [14], irradiation [12], and

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solvothermal [15] approach. In addition to these methods, solution chemical route has become a promising option for large-scale production of 1D nano-/microscale materials due to its simple, fast, and less expensive virtues. But, up to now, the fabrication of large-scale arrayed structures of 1D ZnS material through solution chemical route has not yet been reported. It implies that direct synthesis of arrayed ZnS structures on substrates has some difficulties. Recently, chemical conversion route [16,17] and atmospheric press chemical vapor deposition method (APCVD) [18] have been successfully developed to prepare 1D nano-/microscale II–VI semiconductor arrays, but all of them must be carried out in high temperature with S or H₂S as sulfur source. More recently, a mild conversion route [19] was introduced to synthesize 1D ZnS and ZnS–ZnO materials with ZnO nanobelts as template, but only mixtures of ZnS nanoparticles, ZnS nanobelts, ZnS nanocables and ZnS nanotubes were obtained through the method. Furthermore, the large-scale arrays of 1D ZnS cable-like or tube-like structures cannot be obtained. Inspired by the above method, we present a novel chemical conversion route to synthesize large-scale arrayed ZnS structures via hydrothermal process in low temperature. By this chemical conversion method, large scale arrayed ZnO columns can be partially or fully converted to ZnS–ZnO cable-like or ZnS tube-like arrays. As a similar semiconductor, ZnO has been fully investigated [20], and large-scale ZnO arrays with various crystal size, morphology, and length/width ratio have been successfully synthesized onto substrates [21,22]. So this chemical conversion route can be widely applied in ZnO and other oxide structure arrays to obtain novel sulfide structure arrays.

2. Experimental

2.1. Materials

Thioacetamine (TAA, analytical purity, Shanghai Chemical Reagent Corporation) was used as sulfuration agent and deionized water was used as solvent.

2.2. Growth procedures

In a typical synthesis, arrayed tube-like ZnS structures were obtained according to the following procedures. First, ZnO column arrays were synthesized onto crystalline quartz substrates according to Ref. [23]. Then, the as-synthesized ZnO arrays were vertically immersed in a 40 mL Teflon autoclave containing 30 mL 0.2 M TAA aqueous solution. The reaction system was heated to 130 °C and kept for 48 h. Finally, the reaction system was cooled to room temperature naturally, and

then the final material was washed in deionized water and dried in vacuum oven. The cable-like ZnS–ZnO arrays can be prepared by the same chemical solution method with less sulfuration reaction time (12–15 h).

2.3. Characterization

The crystal structure of the as-prepared material was analyzed using XRD (SHIMADZU XRD-6000) with a Cu K α radiation. The morphology and dimension of the as-synthesized ZnO arrays were observed by scanning electron microscopy (SEM, JEOL JSM-6360LV) equipped with EDS (EDAX, FALCON) and transmission electron microscopy (TEM, JEM-100 CX). Room-temperature photoluminescence spectra (PL) were recorded by a PL spectrometer (Perkin Elmer LS50B).

3. Results and discussion

Large-scale arrayed tube-like ZnS and cable-like ZnS–ZnO structures are obtained from ZnO column arrays by the conversion reaction of thioacetamine and ZnO in aqueous solution. The structure of obtained materials including the pure ZnS and the ZnS–ZnO composite with various ratios can be conveniently controlled by the reaction time.

After the reaction at 130 °C for 48 h, arrayed tube-like ZnS structures are obtained by full conversion from ZnO arrays. Fig. 1 shows a scanning electron microscope (SEM) image of the as-synthesized ZnO column arrays. The whole quartz substrates are covered with arrayed ZnO crystals. Curve a in Fig. 3a shows the typical XRD pattern of ZnO arrays. All the obtained ZnO crystals are of wurtzite structure and the diffraction peaks can be indexed to a hexagonal structure with cell constants of $a = 3.24 \text{ \AA}$ and $b = 5.19 \text{ \AA}$ (JCPDS card No. 36–1451). XRD studies also indicate strong

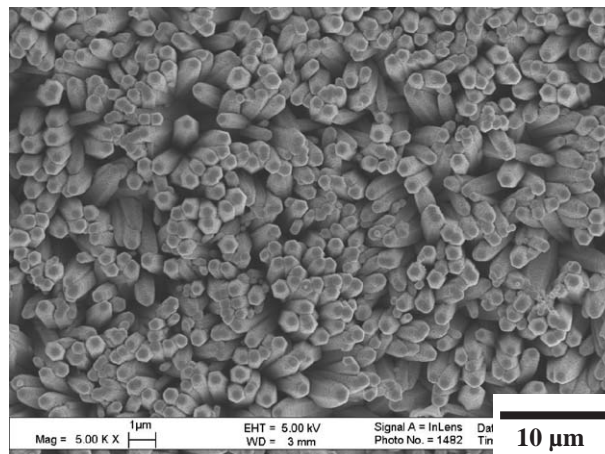


Fig. 1. SEM images of arrayed ZnO columns.

preferred orientation along the c -axis because the [002] reflection is greatly enhanced relative to the usual [101] maximum reflection. Fig. 2a shows the morphology of the as-synthesized ZnS thin film. From it we can see that the arrayed column-like structure has been converted into arrayed tube-like structure over a large area. These tubes have a diameter of $1\ \mu\text{m}$ with an average wall thickness of $350\ \text{nm}$. Compared with arrayed ZnO columns, the diameters of these columns increase from 600 to $1\ \mu\text{m}$ due to the low atom density and large unit axis of ZnS crystals [18]. From the amplified images in Fig. 2b, we also can clearly find that the surface of tube-like structure is considerable roughness, and these arrayed tubes are composed of smaller short-rod-like crystals with an average length of $250\ \text{nm}$ and diameter of $80\ \text{nm}$. The considerable surface roughness of tube-like structure indicated that the growth process of ZnS is nonepitaxial, and this finding is also compatible with the ideal that the growth of ZnS is via ion exchange and the diffusion of zinc and sulfide ions [16]. The structure of these crystals is examined by XRD (curve b in Fig. 3a), which shows that the obtained materials are composed

of pure ZnS crystals with cubic structures (JCPDS No. 05-0566).

Cable-like ZnS–ZnO composite arrays are obtained by the partial conversion reaction at $130\ ^\circ\text{C}$ for less than $48\ \text{h}$. Fig. 2c,d shows the SEM images of cable-like ZnS–ZnO arrays, which are obtained by the reaction for $12\ \text{h}$. It can be seen that all the ZnO columns are covered with a dense layer of particles with an average diameter of $80\ \text{nm}$. Fig. 3a shows the XRD patterns of the as-prepared arrayed structures, in which curves a , b and c are the diffraction patterns of ZnO, ZnS–ZnO and ZnS arrays accordingly. The XRD results (curve c in Fig. 3a) show that the cable-like materials are composed of two types of crystals, i.e., hexagonal ZnO structure and cubic ZnS structure. In order to investigate the detailed construction of the ZnS–ZnO composite columns, EDS test was conducted on the surface of the composite arrays. Fig. 3b shows the typical EDS spectra. It is found that zinc and sulfide were the primary detected elements with tiny oxygen element, implying that the surface of the obtained composite columns is composed of zinc sulfide, and the inner core of the composite

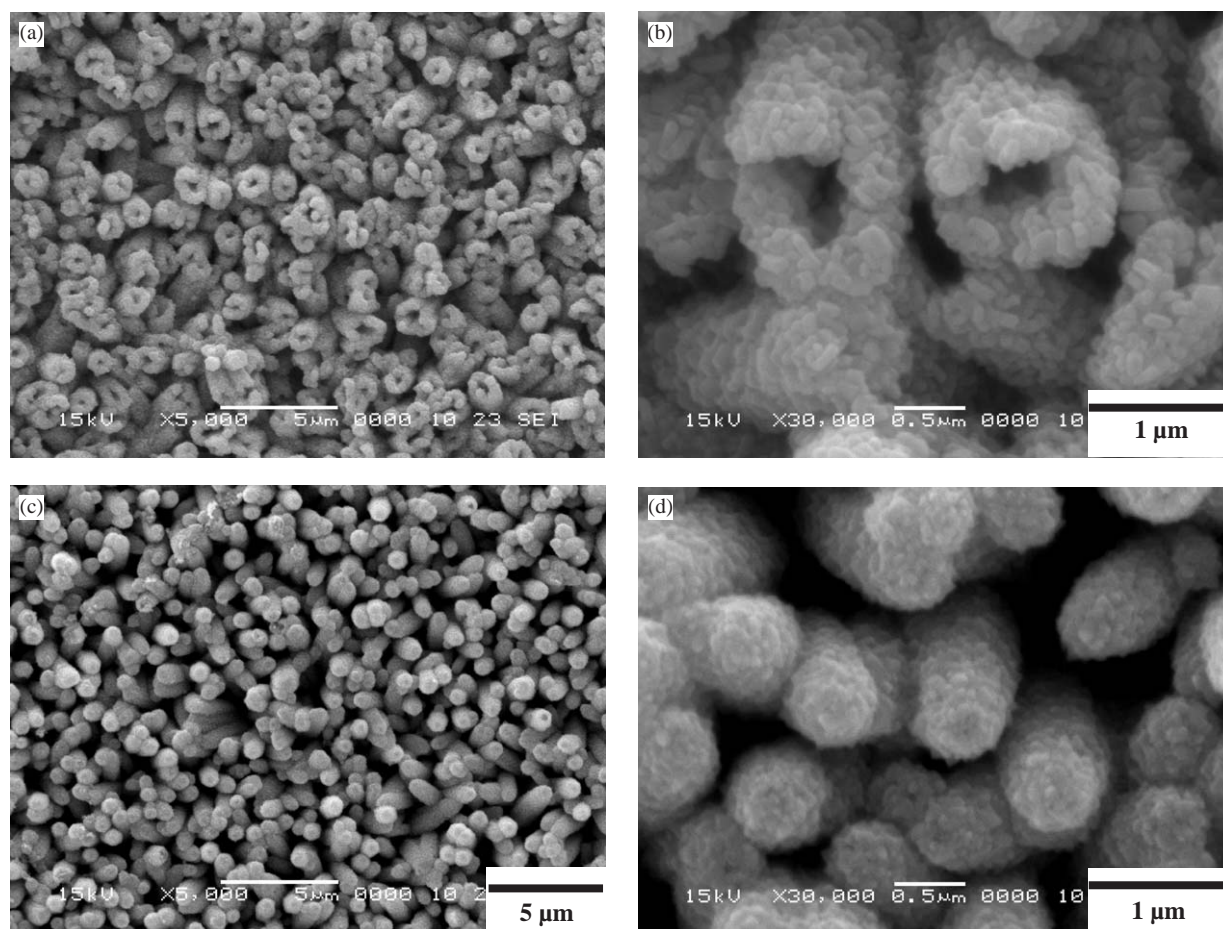


Fig. 2. SEM images of arrayed (a,b) tube-like ZnS structure and (c,d) cable-like ZnS–ZnO composite structure.

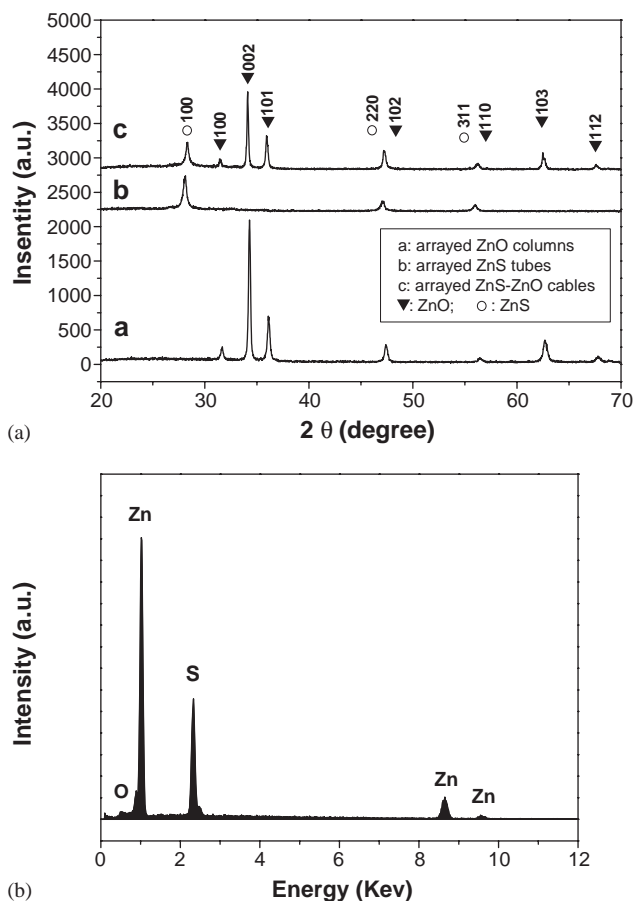


Fig. 3. (a) XRD patterns of the as-prepared arrayed structure, in which curve a, b and c are the patterns of ZnO, ZnS–ZnO and ZnS arrays accordingly. (b) EDS patterns of the as-prepared ZnS–ZnO composite arrays.

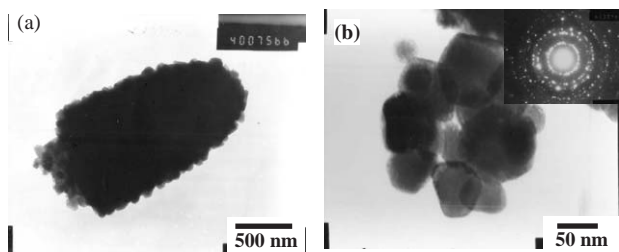


Fig. 4. TEM images of as-synthesized cable-like ZnS–ZnO composites: (a) integrated cable-like composite; (b) dispersive particles.

columns is composed of ZnO crystals, and the tiny oxygen element may be come from the absorbed oxygen. In addition, the typical XRD peaks show that the ZnO core keeps the oriented structure along its *c*-axis because the crystal facet [002] reflection is still much higher than [100] and [101] reflection. Further structural characterization of the ZnO crystals was performed by TEM. The samples for TEM tests were prepared by separating the powders from substrate via ultrasonic treatment. As a

result, cable-like composites are found, as shown in Fig. 4a. In addition, large amount of tiny particles with average diameter of 80 nm are found, which are identified as ZnS by electron diffraction analysis [24], as shown in Fig. 4b. These tiny particles were obtained from the surface of cable-like particles by strong ultrasonic spoilt. Combining XRD, EDS and TEM results, we can make a conclusion that the obtained composite columns are of cable-like structures with a coat of ZnS on ZnO core. So the arrayed cable-like ZnS–ZnO structures can be obtained by the sulfuration conversion from arrayed ZnO structures. In previous reports, the cable-like composite structures such as ZnS–ZnO [16,17,19], Zn–ZnO [25], ZnS–Zn [26], and so on, have also been successfully fabricated by various methods including solid–vapor decomposition, thermal reduction, and ion exchange in vapor. In most cases, these reactions are carried out at high reaction temperature. In our case, the sulfuration reaction is conducted at low temperature (100–130 °C). Especially, the conversion ratio of ZnS/ZnO can be easily controlled by the reaction time. So, this chemical solution method is simple and controllable (Fig. 5).

In previous reports, the formation of tube-like ZnS crystals is attributed to the ion exchange reaction and the diffusion between zinc and sulfide ions [16,18]. In order to further understand the formation mechanism, different conversion stages controlled by reaction time were examined by XRD (Fig. 6) and SEM (Fig. 7). Fig. 6 shows XRD patterns of samples at different conversion period (0–48 h). XRD results show that the conversion from ZnO crystals to ZnS is continuous with increased reaction time. So, the ratio of ZnS/ZnO can be conveniently controlled by the reaction time. Moreover, the preferred orientation of ZnO [002] crystal facet through all conversion stages implies that the conversion from ZnO to ZnS takes place on the surface of ZnO columns and continues across the side wall of the

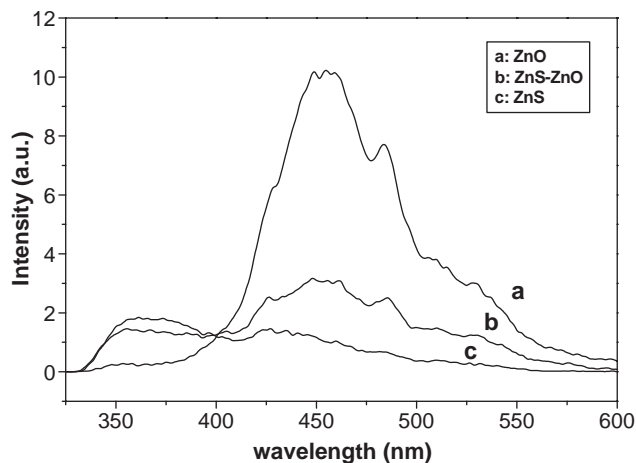


Fig. 5. PL spectra of the as-prepared arrayed structure: (a) ZnO; (b) ZnS–ZnO composite; (c) ZnS.

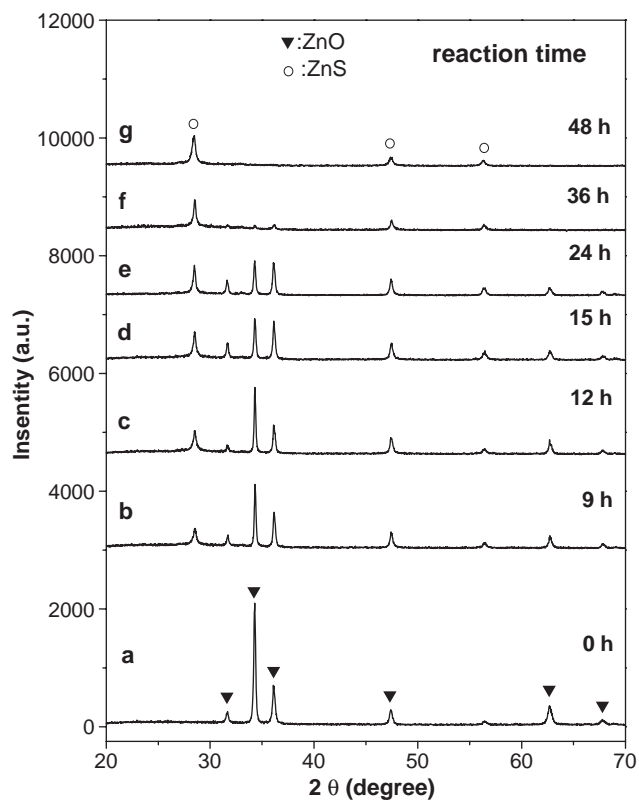


Fig. 6. XRD patterns of different conversion period from arrayed ZnO columns to arrayed ZnS tubes: (a) ZnO; (b–g) ZnS–ZnO composite at reaction time of (b) 9 h; (c) 12 h; (d) 15 h; (e) 24 h; (f) 36 h; (g) 48 h.

crystals. Fig. 7 shows SEM images of samples at different conversion period (15 and 24 h). SEM results show that the conversion process undergoes three stages. First, the outer surface of ZnO crystals is converted to ZnS crystals by the in situ reaction of sulfide ion and the soluble zinc ion. Then, after the sulfuration reaction for about 15 h, the top surface of arrayed columns was broken, which may be due to the fragile structure of ZnS crystals capped on the top of the arrayed crystals. The exposed ZnO is apt to dissolve into the reaction solution and reacts with TAA inside the surface of the arrayed columns and outside the arrayed structures, which is confirmed by the fact that some tiny powders of zinc sulfide are found suspended in the solution. Moreover, hollow structure forms in the arrayed columns due to the fast outgoing speed of zinc ions. After that, the newly formed zinc sulfide inside the surface of arrayed columns prevents the diffusion of zinc ions, and the remained zinc oxide crystals are sulfurated in situ into zinc sulfide. As a result, tube-like zinc sulfide arrays formed on the substrates by the full conversion from zinc oxide. The conversion process is clearly illustrated in Fig. 8.

The PL property of the obtained ZnO, ZnS and ZnS–ZnO composite arrays was measured (Fig. 5). Compared with arrayed ZnO columns, the arrayed zinc sulfide exhibits different emission bands centered at 370 and 425 nm ($\lambda_{\text{ex}} = 315$ nm). A blue shift (~ 70 nm) of the emission band relative to that of the bulk ZnS

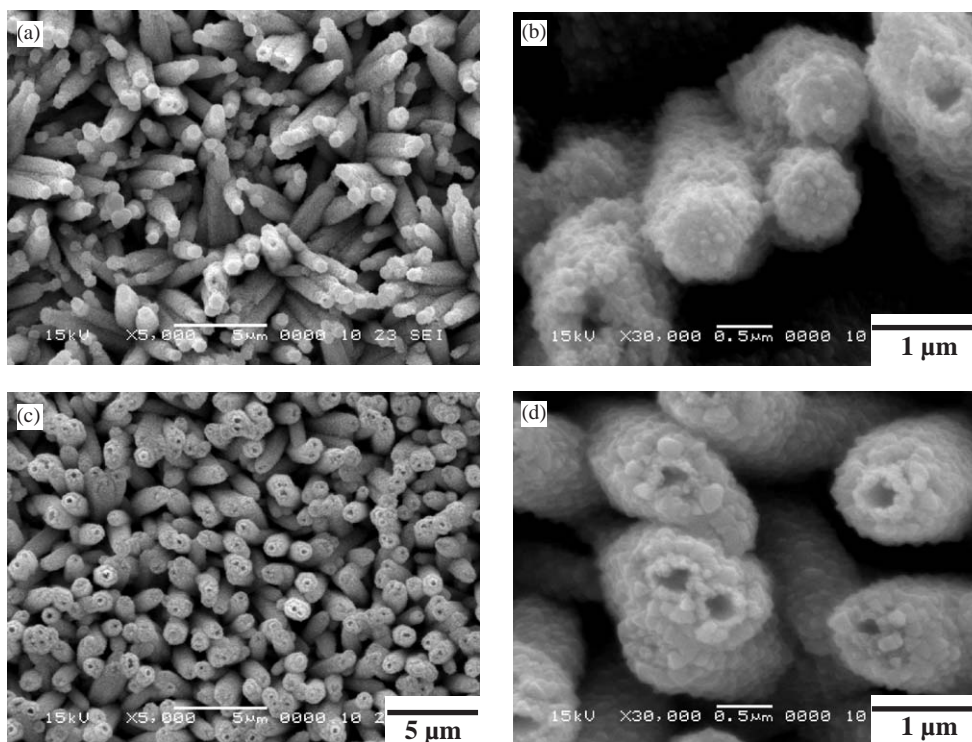


Fig. 7. SEM images of arrayed ZnS–ZnO composite structures for different reaction time (sulfuration conversion time): (a,b) 15 h; (c,d) 24 h.

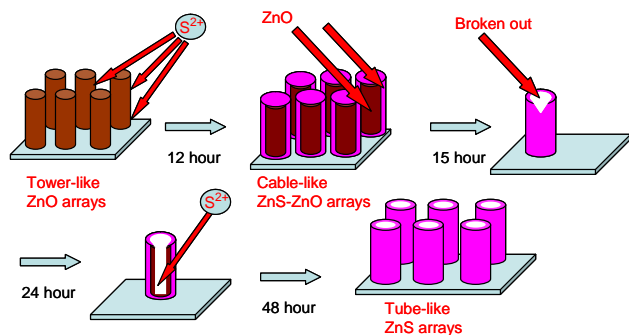


Fig. 8. Illustration of sulfuration conversion from arrayed ZnO columns to arrayed cable-like ZnS–ZnO composite and tube-like ZnS structures.

(440–500 nm) is observed, which may be due to the quantum size effects of the ZnS crystals [12]. As mentioned above, the particle size of ZnS is about 80 nm, which seems difficult to result in the blue shift of PL. But the crystal size calculated from Scherer equation shows these big particles are composed more smaller crystals with diameters of 25 nm, which result in the blue-shift of PL. At the same time, the emission peaks at 450, 485 and 530 nm, which are observed from arrayed ZnO columns, disappeared. The PL spectrum of cable-like ZnS–ZnO arrays shows that this composite structure holds the PL properties of both ZnS and ZnO. Further research finds that the sulfuration ratio has great effects on the relative intensity of typical PL properties of ZnS–ZnO arrays. So the PL properties of cable-like arrays can also be controlled by the reaction time.

The relative intensity of typical PL properties of ZnS and ZnO can be controlled by the sulfuration conversion ratio. So the properties of these semiconductor materials can be controlled conveniently by their different structures via the control of different reaction time.

4. Conclusions

In this report, a simple hydrothermal route was introduced to synthesize large scale arrayed tube-like ZnS and cable-like ZnS–ZnO composite with controlled structures by sulfuration conversion from arrayed ZnO columns. The conversion ratio from ZnO to ZnS can be conveniently controlled by reaction time. The as-synthesized arrayed pure ZnS and ZnS–ZnO composite structures show different PL properties which can be tailored by the structures of these arrayed columns. This simple method has a wide potential application in large-scale conversion from arrayed oxides structure to arrayed sulfide structure. We have also successfully

synthesized zinc selenide and cadmium sulfide by using this chemical solution conversion method. We believe that the present approach can amplify the application field of arrayed sulfides structures.

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