

Morphology control and characteristics of ZnO/ZnS nanorod arrays synthesised by microwave-assisted heating

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Published in *Micro & Nano Letters*; Received on 5th November 2015; Revised on 6th January 2016; Accepted on 7th January 2016

The morphology control investigations on ZnO/ZnS core/shell nanorod fabricated by microwave-assisted in-situ surface sulphidation of ZnO nanorod arrays is presented. First, the ZnO nanorod arrays are grown on ZnO/Si substrate by microwave heating of a mixed zinc nitrate hexahydrate and hexamethylenetetramine precursors in deionised water. Then, the grown ZnO nanorod arrays on ZnO/Si substrate are immersed in thioacetamide (TAA) aqueous solution to undergo sulphidation process to form ZnS shell on ZnO core. The morphological, structural, and optical characteristics of the as-prepared ZnO nanorods and ZnO/ZnS core/shell nanorods are investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and photoluminescence (PL) measurements, respectively. The SEM images and XRD patterns show that the ZnS shell becomes thicker due to more and more ZnS nanoparticles formed with increasing the concentration of TAA solution. The PL spectra demonstrate that the thicker ZnS shell results in more oxygen vacancies occupied by S atom, and would decrease the intensity ratio of the deep-level emission to the ultra-violet emission for the ZnO/ZnS core/shell nanorods synthesised with the higher concentration of TAA solution.

1. Introduction: Recently, core/shell structured materials have attracted much attention in the improved physical and chemical properties for electronics, optics, catalysis, and electrochemistry applications because of their specific structures [1–3]. For the application in the ultra-violet (UV) region, the II–VI semiconductors, ZnO and ZnS have been considered to be the candidates for the core/shell structured materials because of the wide bandgap of 3.37 and 3.67 eV for ZnO and ZnS, respectively [4, 5]. It indicates that higher bandgap of ZnS can prevent tunnelling of the excited electrons from the ZnO core to the ZnS shell.

Up to now, several methods have been reported for fabricating the ZnO/ZnS core/shell structure such as chemical conversion route [2, 6], thermal evaporation method [4], hydrothermal process [5, 7], and microwave-assisted heating [8]. Among different techniques, microwave irradiation has been known as an attractive method for rapid synthesis of nanostructure with uniform particle size distribution. Microwave energy can transform into heat inside material to reduce the energy consumption and provide rapid and controllable volumetric heating with a particular temperature distribution, thus the high-performance nanostructure can be achieved. Although the ZnO/ZnS core/shell nanorods can be synthesised surely by microwave-assisted heating [8], the useful nanostructure of nanorod arrays applied to novel optoelectronic devices have to be further prepared using this technique.

In this Letter, we present a microwave-assisted rapid route to synthesise ZnO/ZnS core/shell nanorod arrays and investigate the feasibility of controlling morphologies of the as-synthesised ZnO nanorods and fabricated ZnO/ZnS core/shell nanorods under various conditions by scanning electron microscopy (SEM). Additionally, the crystalline quality and optical property of the synthesised ZnO/ZnS core/shell nanorod arrays are discussed by X-ray diffraction (XRD) and photoluminescence (PL) measurements, respectively.

2. Experimental details

2.1. Synthesis of ZnO nanorod arrays: The ZnO nanorod arrays were prepared by a two-step method including substrate

pretreatment and microwave heating process. First, the ZnO seed layer with a thickness of about 300 nm was deposited on Si substrate by sputtering technology. Then, the prepared substrate was suspended in the mixed aqueous solution of 0.005 M zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.005 M hexamethylenetetramine. Then, the well-mixed precursor solution was placed into the microwave oven and heated at a constant temperature of 95°C with magnetic stirring for 2 h at the atmospheric environment. During the reaction process, the Zn (NO_3)₂ solution provided Zn²⁺ ions to react with OH⁻ ions dissociated from the C₆H₁₂N₄ solution to form ZnO nanorod arrays [9, 10]. Finally, the prepared sample named S1 was rinsed with deionised water and dried at room temperature in the atmosphere.

2.2. Synthesis of ZnO/ZnS core/shell nanorod arrays: The prepared ZnO nanorod arrays on ZnO/Si substrate were immersed in thioacetamide (TAA) aqueous solution with different concentration of 0.05 and 0.10 M, named as S2 and S3, respectively. Then, the mixture was placed in the microwave system for heating at 60°C for 30 min to form the ZnO/ZnS core/shell nanorod arrays. The produced samples were washed with ethanol and deionised water three times and then put in a vacuum oven to dry at 60°C for 30 min.

2.3. Characterisation of the samples: The morphologies of the synthesised ZnO/ZnS core/shell samples were characterised by field-emission scanning electron microscope (JEOL JSM-6701F). The XRD (Shimadzu XRD-6000) with a CuK α line of 1.5405 Å was carried out to study the crystalline characterisation of the prepared samples. The PL measurements were carried out at room temperature (RT) using a He–Cd laser which has an excitation wavelength of 325 nm. The luminescence was collected using a spectrometer (Zolix omni- λ 500) with a 1200 grooves/mm grating and detected using a photomultiplier (PMT). The PL signal

obtained from the PMT was analysed using lock-in technique and recorded in a computer.

3. Results and discussion: The SEM images of the as-synthesised ZnO nanorods and formed ZnO/ZnS core/shell nanorods are displayed in Figs. 1a–c, and the scale bar is shown for each picture. It is noted that the magnifications of the as-synthesised ZnO nanorods and ZnO/ZnS core/shell nanorods are not the same because the SEM images have been selected to be clearly presented. Fig. 1a shows the well-aligned ZnO nanorods arrays with smooth surface. After the sulphidation with the TAA solution concentration of 0.05 M, shown in Fig. 1b, the surface morphology of the ZnO nanorods would become coarse due to the dense distribution of nanoparticles. The inset of Fig. 1b presents the transmission electron microscope (TEM) image of the S2 sample, clearly showing the ZnO nanorod covered ZnS nanoparticles with a thickness of ~10 nm to form ZnO/ZnS core/shell structure. By sulphidising with the TAA concentration of 0.10 M, the diameter and surface of the ZnO nanorods covered

more ZnS nanoparticles becoming narrower and rougher, respectively, are clearly presented in Fig. 1c.

The sulphidation process for forming ZnS shell on ZnO core is described by the following reactions [11, 12]



During the reaction (1), TAA reacting with H₂O via microwave irradiation is hydrolysed and releases H₂S. Then the ions exchange occurs between H₂S and ZnO by reaction (2) as the S²⁻ reacts with the Zn²⁺ slowly dissolved from the surface of ZnO nanorods to form ZnS nanoparticles. The low reaction temperature of 60°C is controlled by microwave irradiation to stabilise the sulphidation process for producing optimised crystallinity of ZnS nanoparticles. With increasing the concentration of TAA, the more and more ZnS nanoparticles were produced during the reaction processes, which result in the formation of ZnO/ZnS core/shell nanorods.

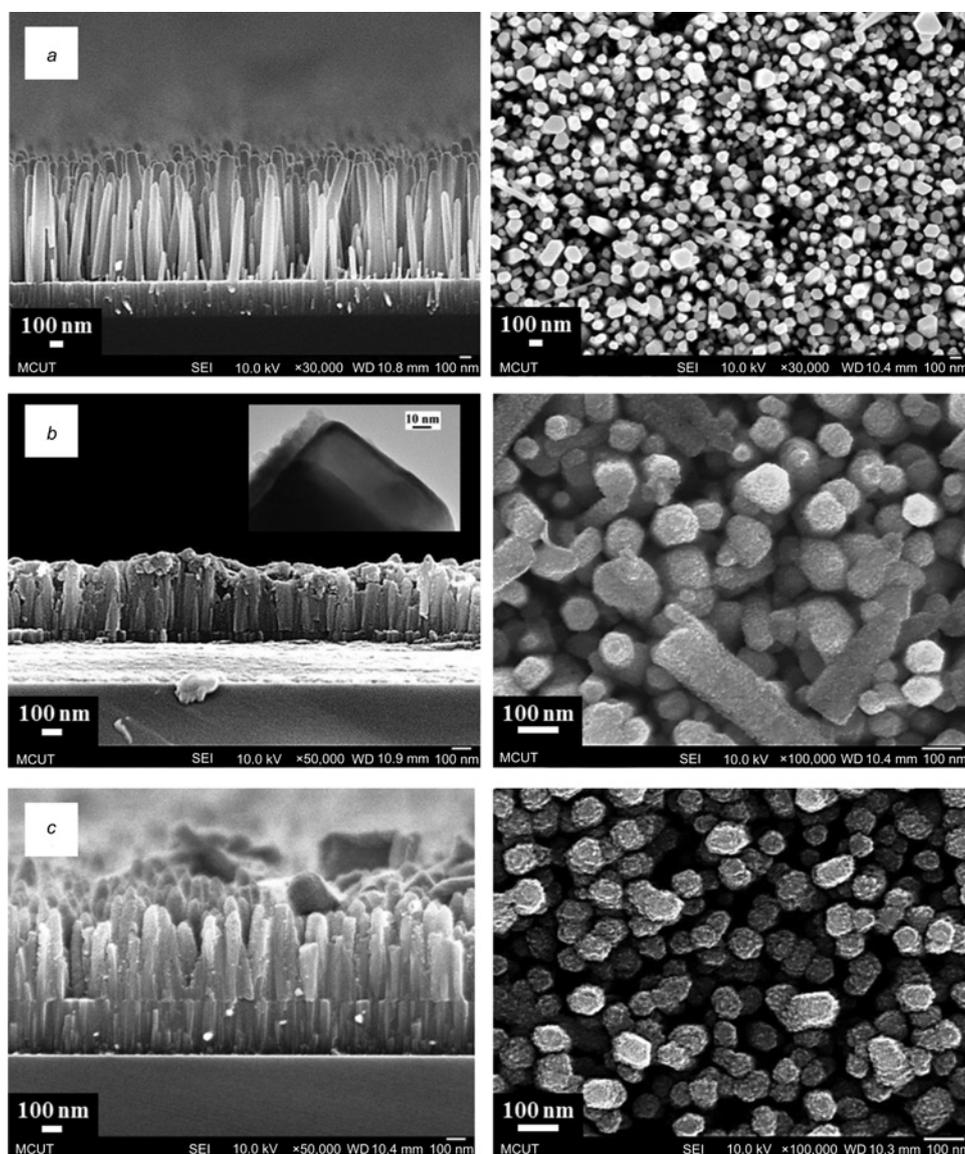


Fig. 1 SEM images of
a As-synthesised ZnO nanorods
b The ZnO/ZnS core/shell nanorods fabricated with the TAA solution concentration of 0.05 M
c The ZnO/ZnS core/shell nanorods fabricated with the TAA solution concentration of 0.10 M

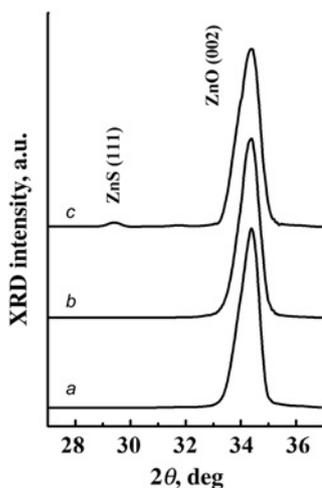


Fig. 2 XRD of
a As-synthesised ZnO nanorods
b The ZnO/ZnS core/shell nanorods fabricated with the TAA solution concentration of 0.05 M
c The ZnO/ZnS core/shell nanorods fabricated with the TAA solution concentration of 0.10 M

The XRD patterns are measured and displayed in Fig. 2 to investigate the phase structure of the products. All synthesised samples exhibit a significant XRD peak at 34.4° , which corresponds to the ZnO (002) plane referred to the JCPDS Card No. 36-1451 [4, 5]. It indicates that the samples have the hexagonal wurtzite structure with preferential orientation along the *c*-axis.

Furthermore, as shown in Fig. 2*c*, a weak diffraction peak at 29.4° has been observed and can be attributed to the (111) plane of zinc blende ZnS confirmed by JCPDS Card No. 05-0566 [5, 13]. Although the typical ZnS (111) peak cannot be significantly presented in Fig. 2*b* due to its much weaker intensity contrasted to the high intensity of ZnO (002) peak, the TEM image shown in Fig. 1*b* evidences the formation of ZnS nanoparticles. In addition, the appearance of the diffraction peak related to the ZnS (111) plane can indicate the more and more ZnS nanoparticles formed with the higher TAA concentration. By using the Sherrer's relation taken account of the full width at half-maximum

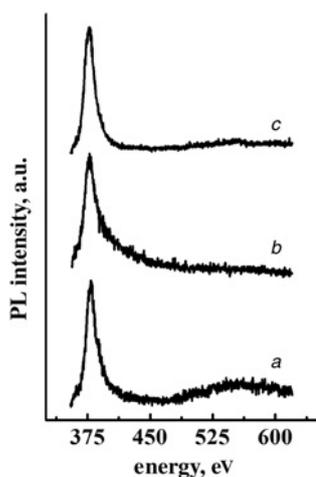


Fig. 3 RT PL spectra of
a As-synthesised ZnO nanorods
b The ZnO/ZnS core/shell nanorods fabricated with the TAA solution concentration of 0.05 M
c The ZnO/ZnS core/shell nanorods fabricated with the TAA solution concentration of 0.10 M

of the (002) diffraction peak of ZnO in Figs. 2*a–c*, the average grain size of the ZnO nanorods can be estimated to be about 9.89, 9.45, and 8.66 nm, respectively. The obvious reduction in the grain size of the ZnO nanorods implies the increases in the surface sulphidation to converse from ZnO to ZnO/ZnS with increasing TAA concentration, which results in the narrower diameter of the ZnO nanorods covered with more ZnS nanoparticles. The investigation of the XRD patterns is quite consistent with the SEM images.

Fig. 3 shows the PL spectra of the as-prepared ZnO nanorods and ZnO/ZnS core/shell nanorods. It can be observed that the PL spectrum of the as-prepared ZnO nanorods (Fig. 3*a*) consists of two types of emission peaks. One is a significant UV emission located at 377 nm, which has been well known as the excitonic recombination at the near band edge emission of ZnO [5, 14]. The other one is a broad green emission centred at 550 nm, which can be corresponded to the deep-level (DL) emission formed by the oxygen vacancies of the surface [14]. As shown in Figs. 3*b* and *c*, it can be observed that the intensity ratio of the DL emission to the UV emission for the fabricated ZnO/ZnS core/shell nanorods would be decreased. The origin can be considered to be the core-shell structure, which forms the S atom filling up the oxygen vacancies on the surface of the ZnO nanorods during sulphidising process [14]. Thus, the increased ZnS thickness results in more oxygen vacancies occupied by S atom to decrease the DL emission intensity.

4. Conclusion: In summary, we have synthesised successfully ZnO/ZnS core/shell nanorods by microwave-assisted heating. The SEM images and XRD results indicate that the particle size and deposited thickness of the ZnS shell could be controlled by the concentration of TAA solution during the microwave irradiation. The PL spectra exhibit the decreased intensity ratio of the DL emission to the UV emission for the ZnO/ZnS core/shell nanorods synthesised with the higher concentration of TAA solution.

5. Acknowledgment: The authors acknowledge the support of the Ministry of Science and Technology Project No. MOST 103-2633-E-236-001.

6 References

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