Growth and Optical Properties of ZnO/CdS Heterostructures

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Abstract—In order to realize the growth of ZnO/CdS nanorod with high quality, ZnO nanorods were firstly fabricated on glass substrates,and then the synthesis of ZnO/ZnS and ZnO/CdS heterostructures were realized by a chemical conversion method.the field-emission scanning electron microscopy (SEM), X-ray diffraction (XRD) pattern and Raman spectra were used to analyze the morphologies and structure properties of the prepared samples. The prepared ZnO nanorods display perfectly hexagonal surface, which suggests that ZnO nanorods grow along (002) direction. SEM image and XRD pattern indicate the ZnO/CdS core shell structure can be prepared by anion-exchange method. Raman spectra further testify the translation process from ZnO nanorod to ZnO/CdS heterostructures. Photoluminescence (PL) spectra shows that the coverage of CdS leads to the decreasing ultraviolet peak intensity due to the lowing free exciton recombination. The present results prove a effective means in the synthesis of ZnO/CdS heterostructures, which can be used as the preparation of photoelectrode in solar cells.

Keywords-ZnO nanorods; Heterostructures; CdS; SEM image; Raman

I. INTRODUCTION

In recent years, scientists have paid great attention to the study of solar cells with high efficiency because of the increasing demand for clean energy. In the researches of solar cell, it is found that its efficiency can be improved by the quantum dot (QD). So far, many QD have been extensively used as lightharvesters, such as CdS [1, 2], PbS [3], PbSe [4], CdSe [5], and CdTe [6]. In spite of a lot of advantages with the use of QD, effective loading of QDs on the surface of metal oxide nanostructure electrodes is still a huge challenge. Core/ shell structures often exhibit upgraded physical and chemical properties.

Zinc oxide (ZnO) has great potential in the application of solar cell due to the high chemical stability, wide band gap and large exciton binding energy at room temperature. Especially, one-dimensional (1D) or quasi-1D ZnO nanostructures have attracted much attention owing to their unique and fascinating properties. It has been testified that ZnO/CdS core shell heterostructures can be used in the solar cell. Rawal *et al.* had reported the preparation of ZnO/CdS nanostructure by the immergence of ZnO nanowires into the $Cd(NO_3)$ and Na_2S methanol solution [7]. However, The experimental process is very complex and time-consuming. It is necessary for us to further develop the growth of ZnO/CdS core shell heterostructures.

Here, we are to report a general chemical conversion route and use inexpensive and commercially available reagents to prepare high quality ZnO-based core/CdS shell nanorod. The successful premise of present method depends on the use of reactive templates to make the synthesis of various ZnO-based core/shell structures possible, which can be potentially applied in solar cells. The field-emission scanning electron microscope testify that the ZnO-based nanorod was prepared, and Raman further shows that ZnO/CdS core shell heterostructures was fabricated by chemical reaction. Photoluminescence (PL) spectra also investigate the optical properties of ZnO nanorods and ZnO/CdS heterostructures. The current way of chemical conversion will be likely to a large area of applications to fabricate innovative semiconductor core/shell structures with different compositions and shapes for unique properties.

II. Experimental set-up

The FTO glasses cleared by sonication in ethanol and acetone were used as substrate. It is an established route for the formation of ZnO colloids and nanocrystals when zinc salts are decomposed or hydrolyzed in aqueous solution. We employ this approach to form layers of ZnO nanocrystals directly on a substrate by thermally decomposing zinc acetate at 350 ^{o}C. A substrate is wet with a droplet of 0.005 M zinc acetate dihydrate in ethanol, rinsed with clean ethanol after 10 s, and then blown dry with a stream of argon. This coating step is repeated three to five times. The substrate, now covered with a film of zinc acetate crystallites, is heated to 350 ^{o}C in air for 20 min. The zinc acetate deposition and decomposition procedure are executed twice to ensure a complete and uniform coverage of ZnO nanocrystals. ZnO nanorod were prepared via the typical synthetic procedure: the synthesis of ZnO nanorod was realized by immersing the substrate

with ZnO nanocrystals in an aqueous solution containing 10 mM zinc nitrate hexahy-drate ($Zn(NO_3)_2 \cdot 6H_2O$) and 10 mM hexamethylenetetramine($C_6H_{12}N_4$) at 90 ^oC for 2.5 h. This synthetic process was repeated several times to obtain ZnO nanorod with the desired length. Then, the ZnO/ZnS nanostructures was prepared by transferring the substrates with ZnO nanorod into a glass bottle containing 0.2 M thioacetamide at 90 ^oC for 1 h. In the end, the obtained ZnO/ZnS core/shell products were treated in a 40 mM aqueous cadmium chloride solution for 1 h at 90 ^oC, and fabricated ZnO/CdS core shell heterostructures.

The morphology of the as-synthesized samples were characterized using the field-emission scanning electron microscopy (FESEM) (NoVaTM Nano SEM 430) and X-ray diffraction (XRD, X' Pert Pro with Cu Ka of 1.5406 Å). Raman spectra were recorded by a Jobin Yvon LabRAM HR UV-NIR micro-Raman system under 488 nm laser excitation. The photoluminescence (PL) spectra were recorded at room temperature by Spectro-fluorophotometer (Hitachif-4010) with excitation wavelength of 275 nm and wavelength ranges from 350 to 700 nm.

III. Results and discussion

The FESEM images in Fig .1 (a) show the general morphologies of the products deposited on the FTO glass substrate. The diameter of single nanorod is non-uniform and its length is up to several micrometers. During the experiment, the samples was prepared by immersing the glass substrates in an aqueous solution containing $Zn(NO_3)_2$ and $C_6H_{12}N_4$, in which ZnO nanorods can be synthesized. The energy dispersive X-ray (EDX) spectrum also further confirms that the prepared samples are pure ZnO nanostructures with the atomic ratio of Zn and O = 1.01:1. the corresponding EDS spectra can not be given at present. In order to clearly observe morphology, the inset in Fig .1(a) displays a top view of single nanorod, which exhibits that the prepared nanorod has perfectly hexagonal surface. The each nanorod has a hexagonal shape, suggesting that the prepared nanorods preferentially grow along c-axis direction.

In order to realize the synthesis of ZnO/CdS core/shell heterostructures, we also prepared ZnO/ZnS core shell by chemical conversion method. During the present experiment, the prepared ZnO nanorods at the first step immerse into thioacetamide solution for a desired time period. Fig .1(b) shows morphology of the prepared ZnO/ZnS structure. Compared with Fig .1(a), the morphology of sample has a slight change. The reactions for the formation of ZnO/ZnS nanostructures are following [4, 8]:

$$CH_3CSNH_2 + H_2O \leftrightarrow CH_3CONH_2 + H_2S \quad (1)$$

$$ZnO(s) + H_2S \leftrightarrow ZnS(s) + H_2O \quad (2)$$

In the end, ZnO/CdS core shell heterostructures can be prepared by anion-exchange method. The driving force for the ion exchange is provided by the large difference in solubility, i.e. the solubility product constant of ZnS and CdS are $2.93*10^{-25}$ and $1.40*10^{-29}$, respectively [9]. Fig .1(c) shows the prepared morphology of ZnO/CdS heterostructures. It is obviously different from that in Fig .1(a), which suggests that ZnO/CdS structures have been prepared. In addition, many small nanoparticles can be observed, which should be related with reaction of $CdCl_2$ and rudimental thioacetamide.

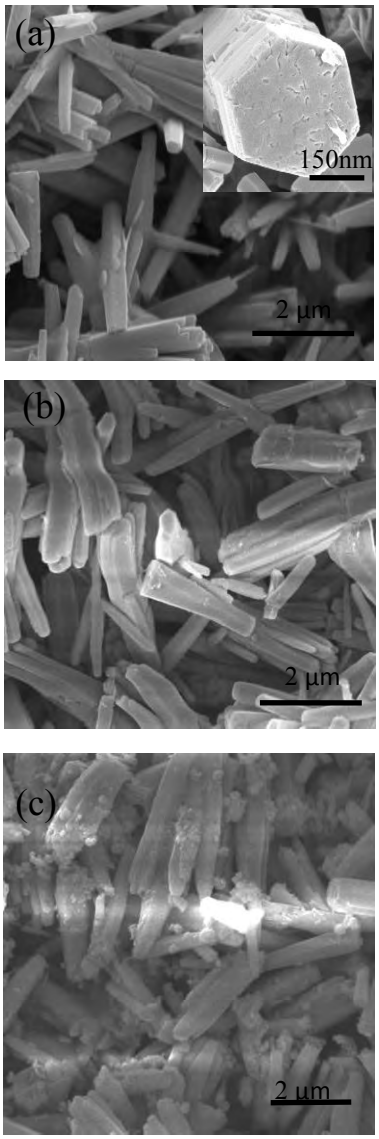

Figure 1 SEM image of the prepared samples, (a) ZnO nanorod, the inset shows top view of single nanorod; (b) ZnO/ZnS nanorods; (c) ZnO/CdS core shell heterostructures

The XRD analysis was employed to determine the structure and crystallinity of the prepared samples. The curves 1 and 2 in Fig .2 shows the XRD pattern of the prepared ZnO (sample 1) and ZnO/CdS core shell heterostructures (sample 2), respectively. Curve 1 displays the relatively strong diffraction peaks of ZnO (002), (100) and (101) and weak other ones, further confirming that the prepared sample at the first step is composed of pure ZnO phase. Apart from the ZnO diffraction peaks, sample 2 also displays the weak CdS (101) diffraction peak, which indicates that ZnO/CdS core shell heterostructures has

been prepared. Those observation is consistent with the SEM analysis.

Raman spectra, as a useful means, can provide valuable structural information on the prepared samples. The curves 1 and 2 in Fig .3 show Raman spectra of the prepared of ZnO and ZnO/CdS nanostructures, respectively. The curve 1 in Fig .3(a) shows photon modes at 330, 381, 438 and 586 cm^{-1}, respectively. In an ideal ZnO crystal, only the optical phonons at the center of the Brillouin zone are involved in the first order Raman spectra. However, the phonons near the zone center must be considered in the nanomaterials because the phonon scattering will not be limited to the center of Brillouin zone [10]. Therefore, the Raman peak at 330, 381, 438 and 586 cm^{-1} can be assigned to ZnO multiple-phonon scattering process, A_1 (TO), E_2 (high), and E_1 (LO), respectively [10, 11]. There is a strong Raman peaks at 438 cm^{-1}, suggesting that the prepared ZnO nanorods grow along (001) direction. This observation is consistent with SEM results.

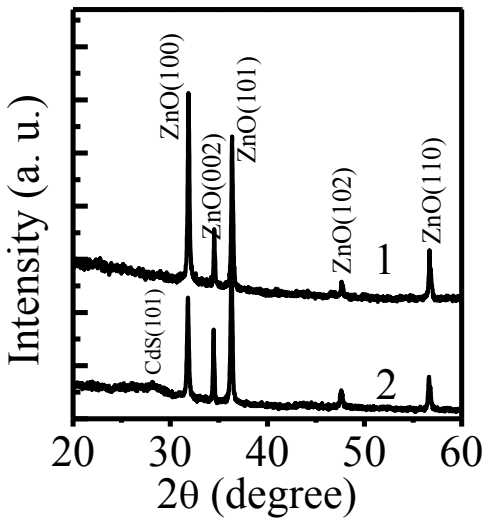

Figure 2 XRD pattern of the prepared samples: (1) ZnO nanorod, (2) ZnO/CdS core shell nanostructures.

In addition, it is generally accepted that E_1 (LO) mode is associated with the oxygen vacancies [9]. It is reported that the oxygen vacancies can increase the electrical conductivity remarkably by inducing defect states in the band gap [12]. Therefore, the appearance of E_1 (LO) mode suggest that the prepared ZnO nanorod are suitable for fabricating solar cells. The curve 2 in Fig .3 shows the Raman spectra of the treated ZnO nanorod by chemical conversion. Compared with the curve 1 in Fig.3, Raman spectra have obvious change, suggesting that ZnO/CdS structures has been successfully prepared. Apart from the vibration mode at 437 cm^{-1} related with ZnO, there are two peaks located at 301 and 604 cm^{-1}. Those peaks should be be ascribed to the E_1 and $2E_1$ vibrational modes (first- and second-order longitudinal optical phonon modes) of CdS, respectively [13]. The appearance of optical phonon peak suggests that CdS in the present samples exists in cubic phase [9].

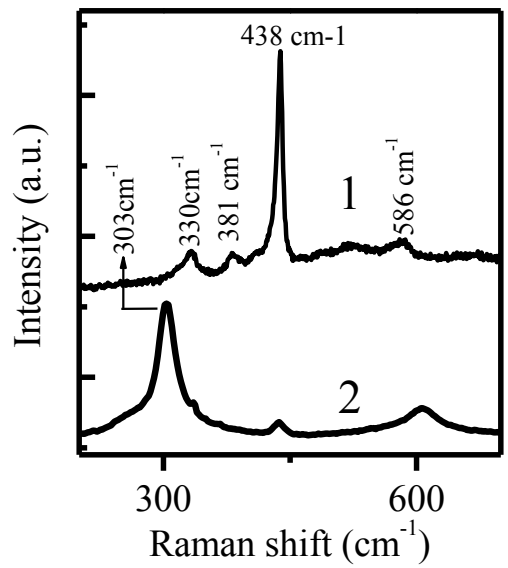

Figure 3 Raman spectra of the prepared samples: (1) the prepared ZnO nanorods, (2) ZnO/CdS core shell structure

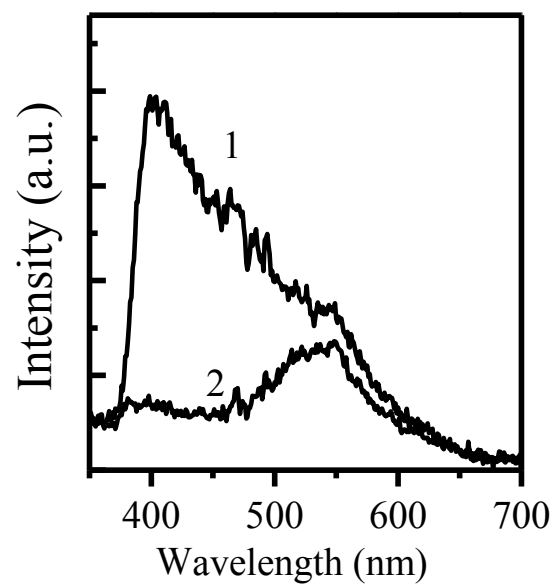

Figure 4 PL spectra of the prepared samples: (1) the prepared ZnO nanorods, (2) ZnO/CdS core shell structure

PL emission is one of the most important properties for semiconductor materials. The curve 1 and 2 in Fig .4 shows the PL spectra of the prepared ZnO nanorods and ZnO/CdS core shell heterostructures, respectively. For the deposited ZnO nanorods, there is a strong ultraviolet peak at ~ 395 nm and a relatively weak green emission at ~ 550

nm, as shown in the curve 1 of Fig .5. It is generally accepted that the ultraviolet emission in ZnO films is related with the recombination of free exciton and the green peak at ~ 500 nm comes from the singly ionized oxygen vacancies. The curve 2 in Fig .4 shows the PL spectra of ZnO/Cds core shell heterostructures, which is obvious different from the curve 1. The intensity of ultraviolet peak decreases obviously, and that of green emission increases sharply. In fact, there is no ultraviolet emission in CdS materials due to the relatively narrow band gap. The decrease of ultraviolet emission intensity indicates that CdS should cover on the surface of ZnO nanorods. The coverage of CdS is harmful to the emission of free exciton recombination, which leads to the decreasing ultraviolet emission intensity. In addition, there is the relatively strong green emission in ZnO/CdS structure. We presume that the relatively strong green emission could be related with oxygen vacancies or CdS materials.

IV. CONCLUSION

In this paper, we successfully prepared ZnO/CdS nanorod with high quality by a chemical conversion method. ZnO nanorods were firstly fabricated on glass substrates by the reaction between $Zn(NO_3)_2$ and $C_6H_{12}N_4$ at 90 ^oC for 2.5 h, then ZnO/ZnS core shell structure was synthesized when ZnO nanorod immerges into thioacetamide solution, and finally we realized the preparation of ZnO/CdS heterostructures by anion-exchange method. The morphologies and structural properties of the prepared samples can be analyzed by SEM, XRD and Raman spectra. The prepared ZnO nanorods display perfectly hexagonal surface, which suggests that ZnO nanorods grow along (002) direction. The translation process from ZnO nanorod to ZnO/CdS heterostructures has been testified by Raman spectra. PL spectra shows that the coverage of CdS can lead to the decreasing ultraviolet peak intensity due to the lowing free exciton recombination. The present results prove a effective means in the synthesis ZnO/CdS heterostructures.

V. ACKNOWLEDGMENTS

This work is partly supported by the Natural Science Foundation of Guangdong Province, China (Grant No. S2012010010017) and the (key) Project of DEGP (No. 2013KJCX0181).

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