

Enhanced Ultraviolet Emission from ZnS-Coated ZnO Nanowires Fabricated by Self-Assembling Method

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A simple chemical route for ZnS-coated ZnO nanowires with preferential (002) orientation is reported. Sodium sulfide and zinc nitrate were employed to supply S and Zn atoms at 60 °C to form ZnS-coated ZnO nanowires structures. Electron diffraction measurement shows that the ZnO/ZnS core-shell nanostructure is single crystalline. Interesting features are found in the photoluminescence (PL) spectra of ZnS-coated ZnO nanostructures. After coating, the UV emission of nanorods is dramatically enhanced at the expense of the green emission. The core/shell structure with higher band gap shell material and reduced surface states should be responsible for this PL enhancement.

Introduction

Zinc oxide (ZnO), a unique material for its semiconducting and piezoelectric properties, has been widely investigated for applications in wave filters, UV detectors, transparent conductive films, gas sensing, etc.^{1,2} Recently, one-dimensional (1D) and quasi-one-dimensional ZnO nanostructures have attracted a great deal of attention due to their unique nanoscale electronic and optoelectronic properties and novel applications.^{1–3} Modification of ZnO properties by impurity incorporation and surface coating are currently another important issue for possible applications in ultraviolet optoelectronics and spintronics.^{1,4–9} For semiconductor materials, doping with different elements can adjust their electrical, optical, and magnetic properties effectively.^{1,6–11} Surface modification has been recognized as one of the most advanced and intriguing methods to build tailored nanostructure materials effectively and reliably.¹² ZnO quantum dots capped with poly(vinylpyrrolidone) (PVP) molecules have obtained enhanced ultraviolet emission.¹³ Gao and Z. L. Wang's group reported ZnO nanorod/CdS nanoparticle composites and rectangular porous ZnO–ZnS nanocables, respectively.¹⁴ However, ZnS-coated ZnO nanorod has not been reported. Because the band gap of ZnS is larger than that of ZnO, we think the luminescence from ZnO could be improved by ZnS coating. In this paper, ZnO/ZnS core shell nanostructures were fabricated by a self-assembling method. In the photoluminescence spectra an enhanced ultraviolet emission was observed for the ZnS-modified sample, and the visible emission was quenched after S and ZnS coating on ZnO.

Experimental Section

Synthesis of the ZnO/ZnS core shell structure included two processes. ZnO nanowires growth was carried out in a traditional horizontal furnace by a simple vapor-phase transport process at 520 °C. The detailed process was described in another work

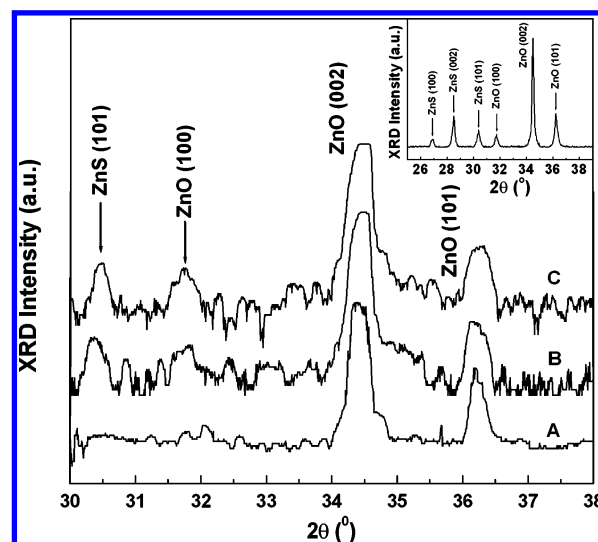


Figure 1. XRD spectra of samples A, B, and C, showing ZnS forming on the surface of ZnO nanowires after immersing in the Na₂S solution. (inset) XRD pattern of sample B measured from 25° to 40°, showing the (002) diffraction of ZnS.

of our group.¹⁵ Then a simple two-step chemical solution reaction was employed to build ZnS-coated ZnO nanowire with a self-assembling method. First, the fabricated ZnO nanowires (labeled A) were immersed in 0.16 mol/L sodium sulfide (Na₂S) solution at a temperature of 60 °C for 2 h. After being taken out, the sample was washed with deionized water (labeled B). The second step was performed by immersing B into zinc nitrate (Zn(NO₃)₂) solution with the same solution concentration as the Na₂S solution at 60 °C for 2 h. Then the sample was dried at 40 °C in air (labeled C).

The products were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), X-ray energy-dispersive spectroscopy (EDX) attached to SEM, transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Photoluminescence (PL) spectra were also measured using a wavelength of 325 nm as the excitation source.

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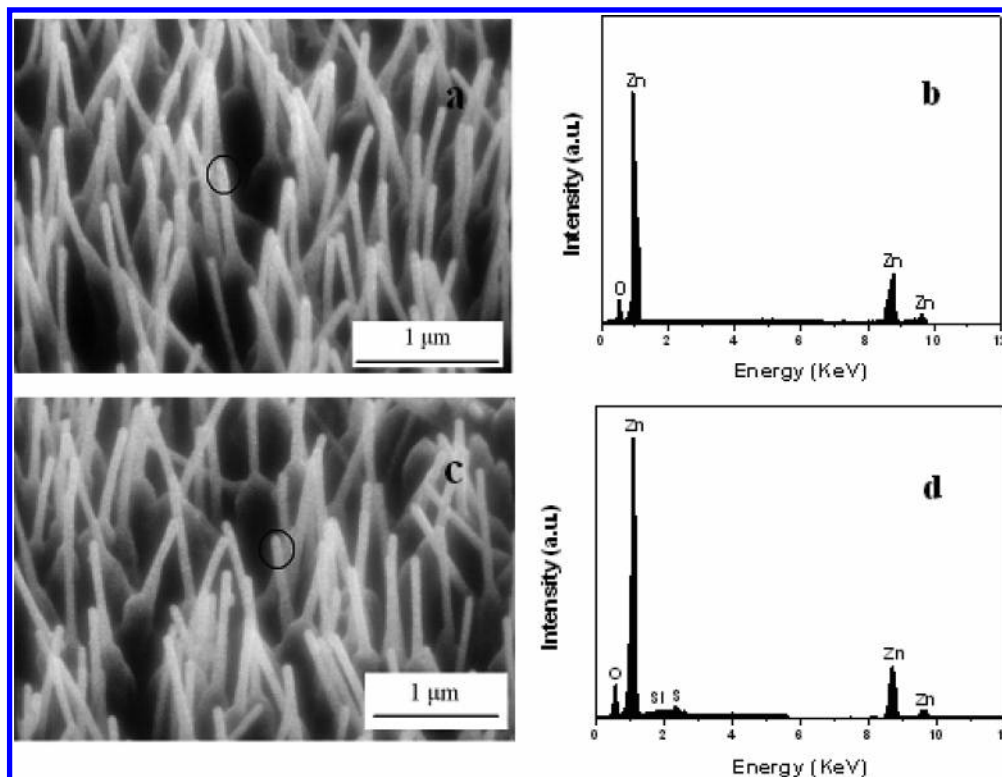


Figure 2. (a and c) SEM images of samples A and C. (b and d) EDX of samples A and C, respectively. S element exists on the surface of the ZnO nanowires induced from these figures.

Results and Discussion

Figure 1 shows the θ - 2θ XRD spectra of samples A, B, and C. Every pattern was shown in a log scale instead of a linear scale. In this way the ZnS-related diffraction peak is observed more clearly. For the as-grown sample A there are a predominant peak centered at 34.5° and a weak peak located at 36.4° , which belongs to the (002) and (101) diffraction peaks of ZnO wurtzite structure. The strong (002) diffraction peak indicates that nanowire growth is with a *c*-axis orientation. The full width at half-maximum (FWHM) of the sharp (002) diffraction peak is only 0.17° , which indicates the nanowire has a narrow size distribution. For samples B and C a new diffraction peak centered at about 30.3° can be observed which corresponds to the (101) planes of ZnS wurtzite structure, which indicates that a thin ZnS layer was formed. To further confirm the structure of ZnS, the XRD pattern of sample B was measured from 25° to 40° , saved as electronic data again, and shown in the inset. A stronger diffraction peak corresponding to the (002) diffraction of ZnS is observed, which further indicates formation of a ZnS layer.

Figure 2a and 2c shows the FESEM images of samples A and C. The SEM picture indicates that both ZnO- and ZnS-coated ZnO nanowires are quasialigned on substrates about 100 nm in diameter and about 1–3 μm in length. There is no obvious size change of the nanowires before and after S and ZnS modification. EDX patterns of a single nanowire for these two samples are also shown in Figure 2b and 2d to get the composition of the samples. The EDX pattern of the ZnO nanowire precursors shows only the presence of O and Zn elements. S element was found to be present after sample A was immersed in Na_2S and $\text{Zn}(\text{NO}_3)_2$ solutions, which provides powerful evidence for successful incorporation of S elements into ZnO nanowires. The S content in sample C is about 5 atom %, which is consistent with the XRD result of a ZnS phase existing in the surface of the nanowire.

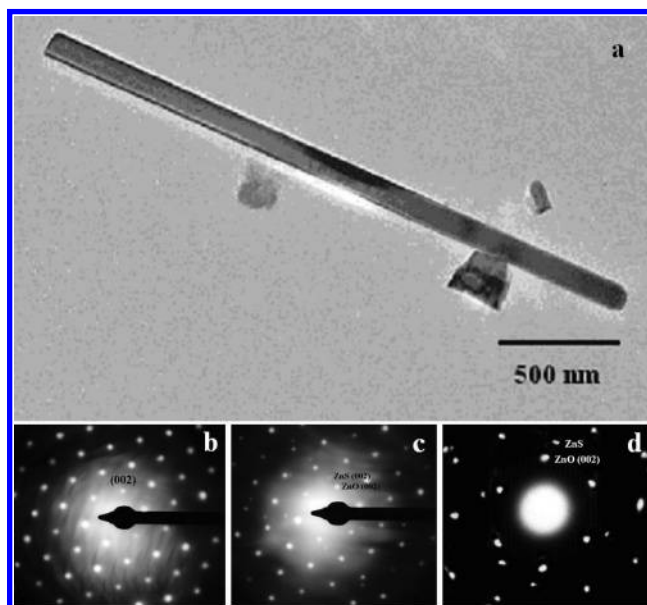


Figure 3. (a) TEM image of sample C without significant change in diameter of the nanowire. SAED images of samples A (b), B (c), and C (d). The double diffraction in the SAED clearly shows that ZnS shells form on the ZnO nanowires.

To observe the ZnS-coated ZnO nanostructure clearly, TEM measurements were performed on a single nanowire. The zone axis is [0110]. First, we selected one ZnO nanowire on a Cu grid. The diameter of this nanowire is 100 nm with a length of 3 μm . Then a ZnS layer was coated on the ZnO nanowire by the self-assembling method mentioned above. After treatment the diameter of the nanowire was almost kept unchanged, which is possibly because the thickness of the ZnS layer was too thin to induce an obvious size change (Figure 3a). Figure 3b shows the selected-area electron diffractive pattern of a single ZnO nanowire, which indicates that ZnO nanowire is single crystal-

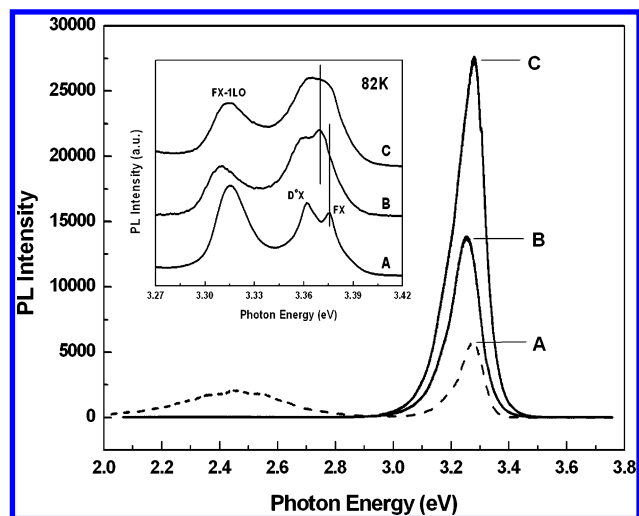


Figure 4. Photoluminescence spectra for samples A, B, and C at room temperature. (inset) Low-temperature PL of the three samples. After coated, UV emission of nanowires is dramatically enhanced at the expense of the green emission. The core/shell structure with higher band gap shell material should be responsible for this PL enhancement.

line with a Wurtzite structure. The SAED pattern of sample B (Figure 3c) has two sets of spots, weak spots and bright spots, corresponding to ZnS and ZnO Wurtzite structures, respectively. This evidence also means that a core-shell nanostructure was formed and the coated ZnS shell is single crystalline. The diffractive spots of ZnS are much weaker than those of ZnO, which indicates the quantity of ZnS is quite little. The insert of Figure 3d shows the SAED with two sets of spots of sample C. The diffraction spots of ZnS become much clearer as shown in Figure 3d, indicating more ZnS formed on the outer surface of the nanowires.

To investigate the optical properties of these core/shell nanowires structures, PL was performed at both room temperature and low temperature. PL studies are powerful tools to investigate the optical properties of novel semiconductor compared to pure semiconductor nanostructures.^{1,6–15} To our knowledge, most of the work on S doping and sulfide coating has reported a blue-shifted ultraviolet (UV) emission and enhanced visible emission related to oxygen vacancy.^{1,9,11,12} The Burstein–Moss effect generally interpreted these PL changes.¹⁶ They think the probability of forming a new band structure deformation increases with carrier concentration. This will give rise to some new defects, such as oxygen vacancies, which should result in the changes of the PL intensity of green light emission. However, Yoo et al. observed another result. With increasing induced S content, the E_g of S-doped ZnO films was observed to shift to low energy. They attributed this red shift to an E_g bowing mechanism due to the orbital energy and size difference of elements, respectively.^{10,17}

Figure 4 shows the room-temperature PL spectra of A, B, and C. Completely unlike earlier reports, the room-temperature PL spectra exhibit distinct enhanced UV emission accompanied with almost outright quenched green emission after S incorporation. In addition, the UV emission intensity of sample B slightly shifts to low energy compared to A. To identify the origin for these PL changes, low-temperature PL spectra were measured at 82 K, as shown in the inset of Figure 4. Free exciton emission (FX), bound exciton emission ($D^{\circ}X$), and phonon replica of free exciton (FX-ILO) for three samples without any other emission are observed in the low-temperature PL spectra. For sample B, the FX emission shifts about 5 meV to lower energy compared to that of sample A. According to Yoo's report, the

E_g bowing due to charge exchange and structural relaxation should be responsible for the UV emission red shift from A to B rather than band gap deformation and lattice distortion. The red shift of the free exciton emission supports that there must be some S atoms which diffuse into ZnO very near the surface to form isoelectronic centers besides the S layer on the surface. After S atoms fill up the oxygen vacancies on the surface of the ZnO nanowire, they significantly modify the visible emission, which can be seen in Figure 4, with strong improvement in the luminescence efficiency. The increased PL quantum yield (YQ) was also reported in CdSe/CdS/ZnCdS/ZnS multishell structure.¹⁸ The above-mentioned mechanisms are also suitable for the enhanced UV emission from A to B. For sample C, ZnO/ZnS core/shell structure with a very thin ZnOS between layer was formed between core and shell. According to the above-mentioned effect, more photogenerated electrons and holes were confined inside the ZnO nanowire since a much higher band gap of shell material suppresses tunneling of the charge carriers from the core to the shell.

In summary, ZnS-coated ZnO nanowires have been formed by low-temperature reaction in Na_2S solution. XRD and EDX spectra show S existing on the surface of ZnO nanowires. SAED patterns show that ZnO/ZnS core-shell structures are single crystalline. The study on the PL spectra of nanowires at room temperature reveals enhanced UV emission and passivated green emission. The results indicate that the ZnS shell with a higher band gap confines the photogenerated carriers inside the ZnO core.

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