

Full Length Research Paper

Enhanced photoluminescence from ZnO/ZnS core-shell structure

Sarmila Dutta^{1*}, Shibabrata Basak² and Pijus Kanti Samanta³

¹Department of Physics, IMPS College of Engineering and Technology Malda, India.

²School of Applied Sciences, Haldia Institute of Technology, Haldia, India.

³Department of Physics, Ghatal Rabindra Satabarsiki Mahavidyalaya, Ghatal, Paschim Medinipur, India.

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The effect of ZnS coating over ZnO core is discussed in this present report. Very simple two step wet chemical method was used for the fabrication of this core-shell structure. XRD and HRTEM data reveal the formation of good shell coating over the ZnO core. Photoluminescence spectra shows that emission intensity is at least four times higher when coated with ZnS compare to bare ZnO. Band gap is also calculated using UV-vis spectroscopy. This study will be very useful towards tuning the emission properties and developing intense violet light-emitting and nanophotonic devices.

Key words: Core-shell, photoluminescence, violet emission, green emission.

INTRODUCTION

Semiconductor nanostructures have gained considerable interest during the past decade. These materials offer advanced applications in the various optoelectronic (Chengyao et al., 2009), biological (Manish et al., 2010) areas due to their size dependant physical and optical properties. ZnO being a wide direct band gap (~3.37 eV) material with very stable emission properties (exciton binding energy 60 meV) at near UV to visible region (Jadwisieniczak et al., 2002; Xiaosheng et al., 2010; Mingsong et al., 2010) is one of the most investigated nanomaterials. Different synthesis routes (Ye et al., 2008; Hong et al., 2006; Nause and Nemeth, 2005; Kaidashev et al., 2003; Lim et al., 2008; Pai-Chun et al., 2004; Walter and Sheng-Yuan, 2002; Pijus et al., 2011; Hua et al., 2011) with variation of synthesis parameters (that is, precursor concentration, reaction time, pH level, temperature, doping) (Bin et al., 2006; Rai et al., 2011; Vernardou et al., 2007) has been employed to tune the luminescent property of the fabricated structures. In this context surface coating with different band-gap materials also leads to dramatic change of the luminescence properties (Iqbal et al., 2009; Tang et al., 2010) of the host material.

ZnS with wide band-gap energy of ~3.66 eV at room temperature is a well-known luminescent material, having prominent applications in flat-panel displays, electroluminescent devices, sensors and lasers (Peng et al., 2006; Murugadoss and Arun, 2008; Zengxing et al., 2005). In this paper we analyze the coating effect of higher band gap ZnS over ZnO prepared using simple, low cost two step chemical route synthesis of ZnO/ZnS with high quantum yield.

METHODOLOGY

Material preparation

In the typical preparation of ZnO/ZnS core-shell nanostructure, 1 M 50 ml of zinc acetate stirred vigorously for 25-30 min over a magnetic stirrer. Oxide particles were precipitated by slowly addition of 50 ml of 1 M NaOH, after 4 h 50 ml of 1 M Na₂S solution was added to the above mixture and stirring was continued for an hour. The same procedure was used for the synthesis of ZnO, except for the addition of Na₂S solution. The precipitate was filtered and washed several times with ethanol. Finally the precipitate was dried at 40°C for further characterization.

Material characterizations

The grazing incidence X-ray diffraction was carried in Rigaku X-ray diffractometer system over an angular range of 30° < 2θ < 60° using

*Corresponding author. E-mail: sarmila.dutta09@gmail.com.

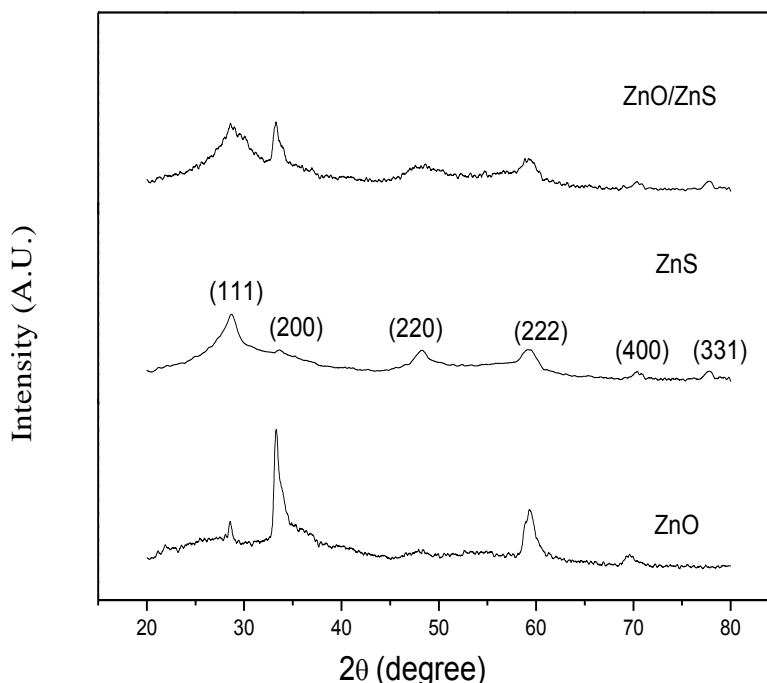


Figure 1. XRD pattern of the ZnO, ZnS and ZnO/ZnS core-shell structures.

Cu- k_{α} radiation of wavelength $\lambda = 1.54\text{\AA}$. For further structural characterization transmission electron microscopy images were taken in a JEOL transmission electron microscope. Room temperature photoluminescence data were recorded using a PERKIN ELMER LS-55 with a xenon lamp with excitation of 325 nm. UV-visible spectroscopy was used to calculate the band gap.

RESULTS AND DISCUSSION

X-ray diffraction

Figure 1 shows the XRD patterns of the ZnO nanocrystals, ZnS nanoparticles and the ZnO/ZnS core-shell structures. All the peaks of ZnO were consistent with the literature data of JCPDS 21-1486. After the introduction of Na_2S , both ZnO and cubic ZnS (JCPDS card no.80-0020) were found to coexist in the synthesized products. Because the peaks of ZnS were almost at same position of ZnO, the peaks were overlapped together in ZnO/ZnS core-shell structures.

HRTEM analysis

To study the structural information in details, HRTEM was done. Figure 2a shows the structures are of 50 nm in diameter with almost uniform shell coating. Figure 2b shows the SAED pattern of the core-shell structures. The SAED of an individual ZnO/ZnS core/shell structures displays a spotted pattern that corresponded to the single

crystal of ZnO and a set of diffraction rings that fitted to the polycrystalline ZnS nanoparticles.

Photoluminescence study

Figure 3 shows the PL spectra of as grown ZnO/ZnS core-shell structures. To compare the luminescence intensity of the ZnO/ZnS core-shell PL spectra of bare ZnO is use as a reference. Two emitting bands, including a strong violet emission centered at around 422 nm and a weak green band centered at around 530 nm, were observed in ZnO nanocrystals. The origin of the violet and green emission could be attributed to the defect-related emissions between Zn_i and VB; O_i and VB respectively. The PL spectra of ZnO/ZnS core-shell structures show an enhanced broad violet emission and a disappearing green emission compared to that of ZnO nanocrystals. The enhancement in violet emission was because ZnS nanoparticles has higher band gap than ZnO and it suppressed the tunneling of the charge carriers from the core to the ZnS nanoshell. As a result, more photo generated electrons and holes are confined inside the ZnO core, giving rise to a high quantum yield about 4 times more that of nano ZnO alone. However, the green emission is weakened to a great extent.

As we know, the green emissions originate from oxygen interstitials. During the process of the formation of ZnO/ZnS core-structures, the hydrolysis of Na_2S can produce H_2S and Sulphur atom can replace and squeeze

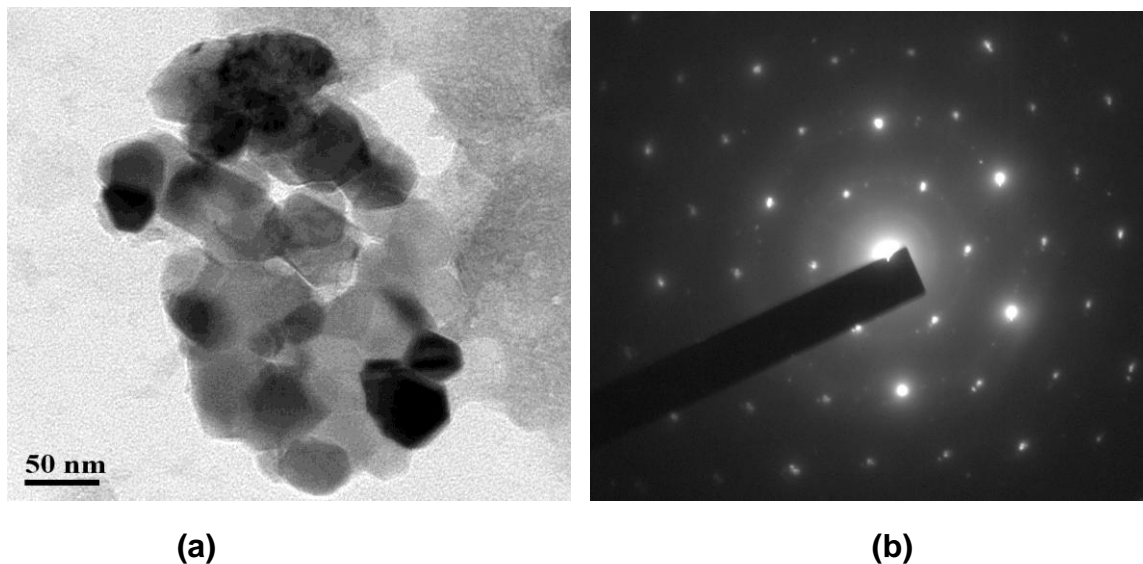


Figure 2. (a) HRTEM image of ZnO/ZnS core-shell structure and (b) its SAED pattern.

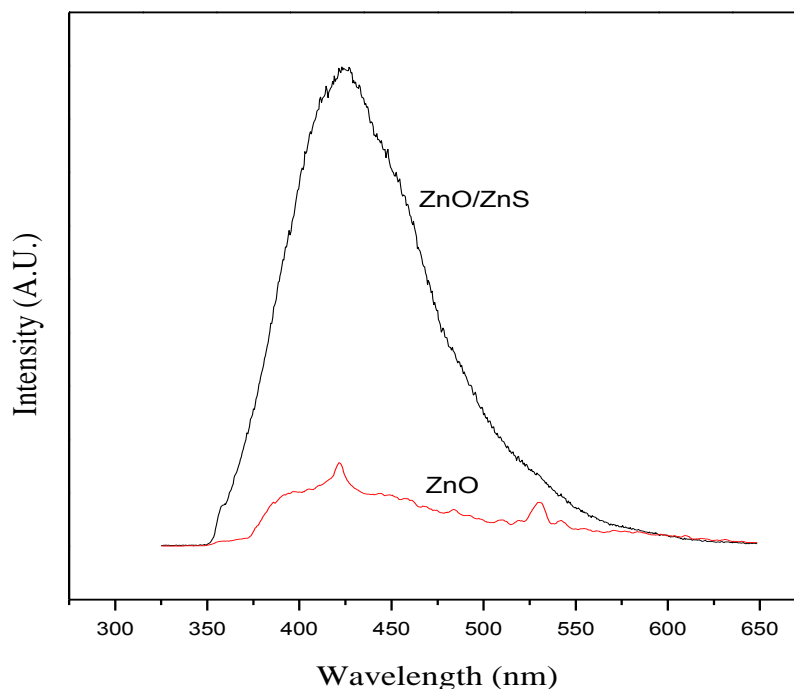


Figure 3. Room temperature PL spectra of ZnO and ZnO/ZnS core-shell structure.

out the oxygen interstitials from the surface of ZnO nanocrystals. As a result, the concentration of oxygen interstitials is reduced greatly and the green emission is weakened. The above results indicated that the sulfidation process has a great effect on the relative intensity and position of typical PL properties of ZnO nanocrystals. Therefore, the PL properties of ZnO nanocrystals could be tuned by this approach.

UV-Vis Spectroscopy

UV-Visible spectroscopy is frequently employed for band gap calculation (Samanta and Roy, 2011). For this purpose, dilute solution of the sample is prepared mixing deionized water in ultrasonic bath and in UV spectrometer transmittance (T) with respect to wavelength (λ) is measured. Absorbance (α) at the

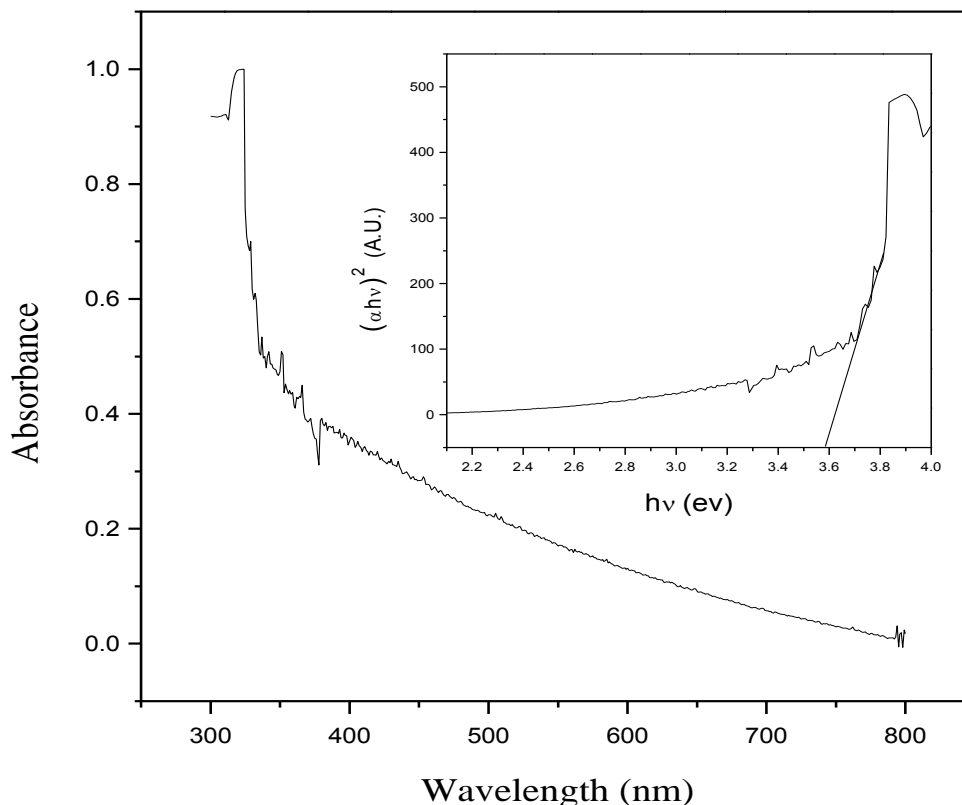


Figure 4. Absorbance spectra of ZnO/ZnS and inset show the band gap.

corresponding wavelengths λ obtained using Beer-Lambert's relation, $\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right)$, where, d is the path traversed by the light inside the solution. For direct band gap ZnO, $(\alpha hv) \propto \frac{\sqrt{hv-E_g}}{hv}$, where E_g is the band gap and $h\nu$ is the incident energy of the photon. Thus band gap energy (E_g) obtained from the intercept of the straight plot of $(\alpha hv)^2$ vs. $h\nu$. Figure 4 shows the UV absorbance spectra of ZnO/ZnS core-shell structures which reveal the highest absorbance at ~ 325 nm. Band gap of 3.58 eV is calculated from the $\alpha(h\nu) \propto \frac{\sqrt{h\nu-E_g}}{h\nu}$ as discussed above, inset of Figure 4.

Conclusion

This simple two-step, solution-based route to synthesize ZnO/ZnS core-shell structures have a wide potential application in large-scale conversion from metal oxides to metal sulfide. The study on the PL spectra of ZnO/ZnS core-shell nanostructures reveals enhanced violet emissions by a factor of four and also passivated green emission. Thus the present study shows a way to tune the visible emission of the ZnO by the formation of ZnO/ZnS core-shell structure. Also high intensity violet

emission leads to potential fabrication of nanoscale optical devices.

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