

FACILE SYNTHESIS OF ZnS/CdS AND CdS/ZnS CORE-SHELL NANOPARTICLES USING MICROWAVE IRRADIATION AND THEIR OPTICAL PROPERTIES

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ZnS/CdS and CdS/ZnS core shell nanoparticles with tunable shell thickness were synthesized via a two steps route under microwave irradiation. In the first step core nanoparticles were prepared using polyol method, and in the second step capping process of shells were performed at moderate temperature by choosing ethanol as a solvent. The thickness of the shells was controlled by adjusting the concentration of core nanoparticles and shell precursors. The structural and chemical characterizations were performed using X-ray diffraction, energy dispersive X-ray spectroscopy and transmission electron microscopy which provide direct evidence for shell growth. The structures of ZnS/CdS and CdS/ZnS core shell nanoparticles were similar to the cubic and hexagonal core structures, respectively. The optical properties of obtained core shell nanoparticles were characterized using UV-Visible and photoluminescence spectroscopy. The absorption edge of ZnS/CdS core shells shows a red shift compared to ZnS (core) while for CdS/ZnS, the absorption edge shows a blue shift compare to CdS (core) owing to the size effect and the potential-well effect. The emission peaks of ZnS/CdS and CdS/ZnS core shell nanoparticles in the range of 400–650 nm are from sulfur, zinc and cadmium vacancy defects and created surface states at ZnS/CdS and CdS/ZnS interfaces.

(Received June 18, 2012; Accepted September 18, 2012)

Keywords: ZnS, CdS, Core shell nanoparticles, Shell thickness, microwave, Optical properties

1. Introduction

Semiconductor nanomaterials have drawn much research attention due to their useful functionalities that can differ considerably from their bulk counterparts. Generally, they exhibit strong size-dependent optical properties, an increase in band gap energy with the decreasing particle sizes which leads to a blue shift in the absorption edge [1-2]. As a large portion of atoms in nanocrystals is located at the surface, the modification of the surface has been recognized as one of the most advanced methods to improve the reactivity of surface and enhance the thermal, mechanical, and chemical stability of the material [3-5]. The growth of a shell of a second material on a core of another material to form a heterostructure has been a successful route in the surface modification of nanostructured particles [6-7]. Especially, useful are the core-shell type nanoparticles composed of two kinds of II–VI semiconductors, both core and shell, with a short

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lattice mismatch between them to achieve a better passivation and minimize the structure defects [8-9]. As compared with the single core nanoparticles, core-shell nanoparticles have shown improvement in photoluminescence quantum yields and photo-oxidative stability [10]. Surface coatings can alter the charge and reactivity of the materials and consequently enhance the functional properties due to localization of the electron-hole pairs [3]. Core-shell semiconductor nanoparticles are typically classified as type-I or type-II, depending on the relative alignment of conduction and valence band edges. In the type-I, both the conduction and the valence band edges of one semiconductor are located within the energy gap of the other semiconductor. In this case, an electron-hole pair tends to localize in semiconductor with lower band gap, which provides the lowest energy states for both electrons and holes. In the type-II, the lowest energy states for electrons and holes are in different semiconductors [11-12]. These nanocomposite materials have desired widespread application for solar photovoltaic devices, chemical and biological sensors, and optoelectronics such as light-emitting devices and optical switches [4, 13].

Modern techniques are allowed to fabricate different kinds of core shell nanoparticles with well-defined structural properties such as mean size, morphology and crystallography including solvothermal synthesis [3, 14], micro-emulsion [15], chemical precipitation [16-18], microwave irradiation [19], and so on. Among the methods microwave assisted synthesis requires short reaction time and produces small particles with a narrow size distribution and high purity [20]. Microwave irradiation induces interaction of the dipole moment and ions with alternating electronic and magnetic fields causing molecular-level heating, which leads to a homogenous and quick thermal reaction [21]. To fabricate core-shell nanomaterials two critical issues must be considered during the growth of shell materials, the elimination of the nucleation of the shell materials and homogeneous growth of shell precursors onto all core nanocrystals in solution. In principle, the reactivity of the precursors should be weak enough to prevent independent nucleation, but sufficiently strong to promote the epitaxial growth around the existing core nanocrystals [22]. Moreover, the control of the shell thickness is a delicate point in the fabrication of core shell nanoparticles. If the shell is too thin, the passivation of the core particles is inefficient, resulting in reduced stability. In the opposite case, the strain and defect states may deteriorate the properties of the resulting core shell nanoparticles [23]. In order to calculate the required amount of shell precursor to obtain the desired shell thickness, it is necessary to know the size and concentration of the nanoparticles. Assuming all the shell material is used for deposition on the existing core nanoparticles, the amount of precursor for the growth of a shell with the desired thickness of δ can be calculated as follows [15, 23]:

$$V_{shell} = \frac{nM}{N_{core}\rho_{shell}} = \frac{\pi}{6}((d_{core} + 2\delta)^3 - d_{core}^3) \quad (1)$$

where V_{shell} is the shell volume, d_{core} is the core diameter, n is the number of moles of shell material that can form by reaction, M and ρ_{shell} are the molecular weight and density of shell material, respectively, and N_{core} is the number of core nanoparticles.

In this work, ZnS/CdS and CdS/ZnS core-shell structure quantum dots were synthesized using microwave irradiation in a two-step route. In the first step, the core nanoparticles were synthesized using microwave polyol (M-P) method and in the second step the homogeneous layers of shell material grew onto core nanocrystals. To control the shell thickness and obtain epitaxial growth of shell on core materials, the concentration of shell precursors were varied during synthesis process. The obtained nanoparticles were characterized using X-ray diffraction, energy dispersive X-ray spectroscopy, transmission electron microscopy, ultraviolet-visible and photoluminescence spectroscopy.

2. Experimental

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and cadmium chloride ($\text{CdCl}_2 \cdot 9\text{H}_2\text{O}$) were used as zinc and cadmium sources, respectively. Thioacetamide (CH_3CSNH_2) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) were used as sulfur source and solvent, respectively. Zinc acetate was purchased from R

& M Chemical, cadmium chloride from Acros Organics, thioacetamide from Sigma–Aldrich and ethylene glycol from ALFA Chemical Co. All chemicals are analytical grade products and used without further purification.

The core shell nanoparticles were fabricated in a two-step route: initial synthesis of core nanoparticles, followed by a purification step, and the subsequent shell growth reaction. In the first step the desired core material, ZnS or CdS nanoparticles, was synthesized using microwave-polyol method by reaction of zinc and cadmium sources with sulfur source in ethylene glycol. The domestic microwave oven with high power (1100W) was used for synthesis by a pulse regime of 20% power for 25 min. The precipitates were centrifuged (3500 rpm, 5 min) and washed several times with distilled water and ethanol before drying in air at 60°C for 24 h under control environment. In the next step of shell growth reaction, in order to prevent nucleation of the shell material and uncontrolled ripening of the core nanoparticles, the reaction temperature must be lower than the temperature used for the core nanoparticles synthesis. Therefore ethanol with lower boiling point than ethylene glycol was used as a solvent. The appropriate amount of shell precursors were dissolved in 40 ml ethanol and subsequently the proper amount of core nanoparticles was added to the ethanol solution and dispersed using sonication for 60 min at 40°C. Then the solution was put in microwave oven for 25 min with power of 20%. During this step, a small number of monolayers of the shell material are deposited on the cores. The precipitates were centrifuged (3500 rpm, 5 min) and washed several times with distilled water and ethanol and dried in air at 60°C for 24 h under control environment.

The products were characterized by X-ray diffraction (XRD) at a scanning rate of 5°/min in the 2θ range 20–70° using a Philips X-ray diffractometer (7602 EA Almelo) with Cu K α radiation ($\lambda = 0.1542$ nm). Energy dispersive X-ray (EDX) measurements were performed under a variable pressure scanning electron microscope (VPSEM, LEO 1455) with an Oxford INCA EDX 300 microanalysis attachment. The particle size and size distribution were determined from the transmission electron microscopy (TEM) micrographs (HTACHI H-7100 TEM). The TEM characterization was carried out at 100 keV. The optical properties of core shell nanoparticles were characterized using UV–visible absorption spectroscopy (UV-1650PC SHIMADZU).

3. Result and discussion

The XRD pattern of bare ZnS nanoparticle (core material) and ZnS/CdS core shell nanoparticles with different shell thickness are shown in Fig.1. The main peaks observed in the XRD patterns of ZnS/CdS core shell nanoparticles at 2θ values of 28.5, 47.6 and 56.3° matching well with both crystalline planes of the cubic structure of ZnS and CdS reported in ICDD PDF 65-1691 and 21-0829 with the crystal lattice parameters of 5.41 and 5.45 Å, respectively.

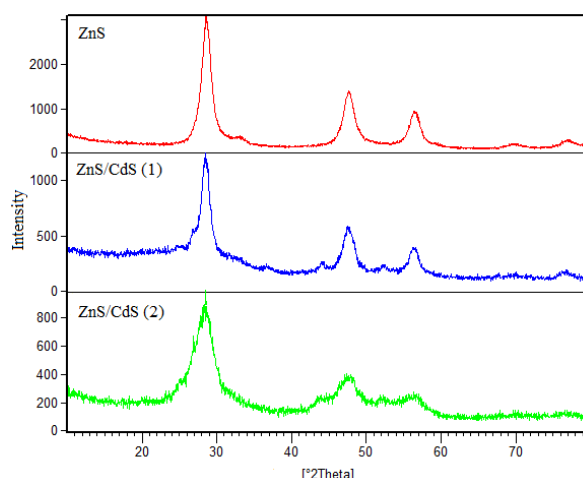


Fig. 1. XRD pattern of the ZnS nanoparticles and ZnS/CdS core shell nanoparticles with (1) low and (2) high shell thickness.

The XRD pattern of bare CdS nanoparticle (core material) and CdS/ZnS core shell nanoparticles with different shell thickness are shown in Fig. 2. The peaks observed in the XRD patterns of CdS/ZnS core shell nanoparticles at 2θ values of 26.6° , 28.3° and 52.0° matching with both crystalline planes of the hexagonal structure of ZnS and CdS reported in ICDD PDF 77-2306 and 02-1310, respectively. The crystal lattice parameters for hexagonal CdS pattern are 4.1, 4.1 and $6.7 \text{ \AA}$ and for hexagonal ZnS are 3.8, 3.8 and $6.2 \text{ \AA}$.

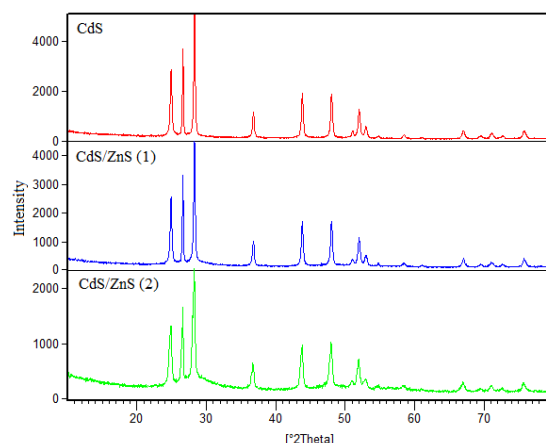


Fig. 2. **Error! No text of specified style in document.** XRD pattern of the CdS nanoparticles and CdS/ZnS core shell nanoparticles with (1) low and (2) high shell thickness

Since the Zn^{2+} and Cd^{2+} ions have the same total ionic charge and their radii are not too dissimilar, they could substitute with each other in ZnS or CdS crystal lattices so that no alteration takes place in the form of crystal structures. As seen in both figures, core and shell materials crystallize in the same structure but the intensity of XRD peaks of core shell nanoparticles is lower than the bare nanoparticle (core material) which is attributed to lower degree of crystallinity. Moreover, the degree of crystallinity of ZnS/CdS core shells nanoparticle decreases with increasing of shell thickness. In contrast, the broadening of peaks increases after coating with shell nanoparticles which is more pronounced for high thickness shell. Since it is expected that the size of nanoparticles increases after coating, such an increase in boardening is could only due to existence of stress and strains which are induced by the lattice mismatch of ZnS and CdS across their interface. In a critical layer thickness of shell material the minimum dislocation could be obtain in the interface of core and shell.

To investigate the chemical composition of ZnS and CdS in the ZnS/CdS and CdS/ZnS core shell nanoparticles the elemental analysis of samples was performed using Energy-dispersive X-ray spectroscopy. The EDX patterns of ZnS/CdS and CdS/ZnS core shell nanoparticles with low shell thickness are shown in Fig. 3. The results show that the weight percentage of Cd in the ZnS/CdS is 16% and the weight percentage of Zn in the CdS/ZnS is about 12%.

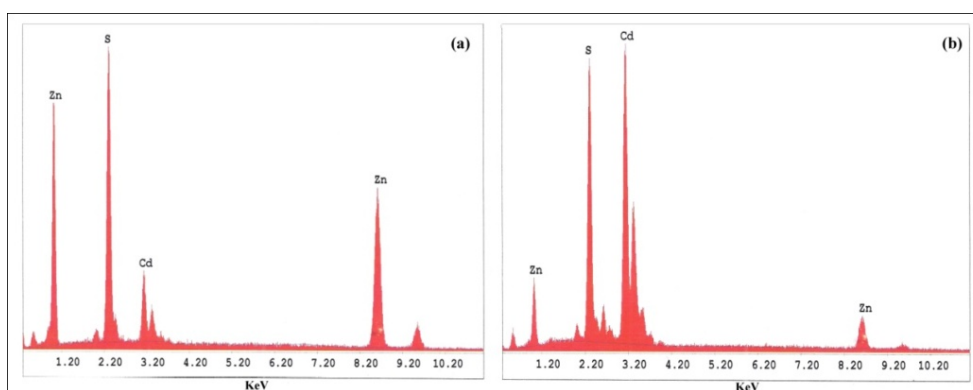


Fig. 3. EDX pattern of (a) ZnS/CdS and (b) CdS/ZnS core shell nanoparticles

The TEM images and related size distribution histogram of ZnS/CdS core shell nanoparticles with different shell thickness are shown in Fig. 4. From these figures it can be clearly observed that ZnS/CdS core shell nanoparticles are spherical in shape which looks aggregated. The average size and size distribution of core shell nanoparticles were evaluated in TEM images using UTHSCA Image Tool considering at least 200 nanoparticles for each sample. The calculated average sizes are 11.2 and 14.6 nm for ZnS/CdS core shell nanoparticles with low and high thickness shell, respectively. Since the average size of core ZnS nanoparticles was about 4.3 nm, the estimated average shells thickness are 3.4 and 5.1 nm, respectively.

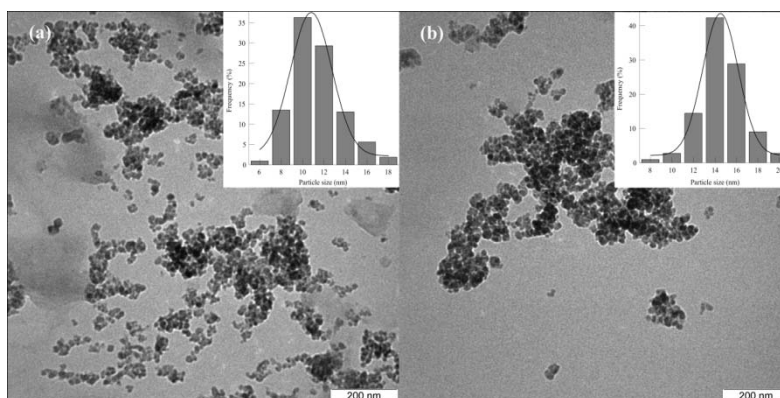


Fig. 4. TEM images and particle size distribution histogram of ZnS/CdS core shell nanoparticles with (a) low and (b) high thickness shell

The TEM images and related size distribution histogram of CdS/ZnS core shell nanoparticles with different shell thickness are shown in Fig. 5. From these figures it can be clearly observed that with increasing the shell thickness the shape of CdS/ZnS core shell nanoparticles changes from monodispersed spherical to nearly spherical which looks aggregated. Creating spherical core shell nanoparticles requires epitaxial shell growth which may affected with concentration of shell precursors. The average size and size distribution of core shell nanoparticles were evaluated in TEM images using UTHSCA Image Tool considering at least 200 nanoparticles for each sample. The calculated average sizes are 17.0 and 20.7 nm for ZnS/CdS core shell nanoparticles with low and high thickness shell, respectively. Since the average size of core CdS nanoparticles was about 10.1 nm, the estimated average shells thickness are 3.4 and 5.3 nm, respectively.

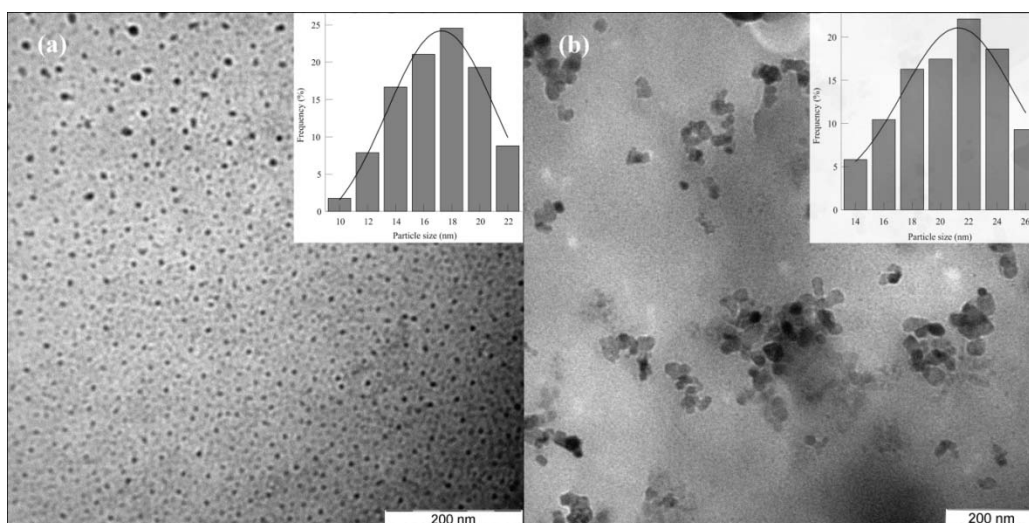


Fig. 5. TEM images and particle size distribution histogram of CdS/ZnS core shell nanoparticles with (a) low and (b) high thickness shell

UV-Vis absorption spectra and Tauc plots of ZnS/CdS and CdS/ZnS core shell nanoparticles with different shell thickness are shown in Fig. 6 and Fig. 7, respectively. The absorption edge of ZnS/CdS core shells shows a red shift compared to ZnS (core) while for CdS/ZnS core shells, the absorption edge shows a blue shift compare to CdS (core). This could be explained as the overall result of the size effect and the potential-well effect. When a shell is formed on the surface of the core, the total size is larger than that of the core. This allows a further delocalization of the electronic wavefunction and creates a red-shift of the band edge transition (size effect). On the other hand, because both the conduction and the valence band of CdS are located within the energy gap of the ZnS, type I, electron-hole pairs tend to localize in semiconductor with lower band gap, i.e., CdS, which provide the lowest energy states for both electrons and holes. However the potential well of ZnS/CdS and CdS/ZnS become deeper than that of the pure CdS nanoparticles. As a result for ZnS/CdS core shell nanoparticles that potential well decreased with respect to ZnS core and the absorption spectra shows a red-shift while for CdS/ZnS core shell nanoparticles the increased potential well can lead to an increase of the transition energies with respect to CdS core and blue-shifts of the absorption spectra (potential well effect). Moreover, the stress induced by the lattice mismatch of ZnS and CdS results in an asymmetric internal electric field across the interface, which affects the electronic states and absorption properties of core shell nanoparticles.

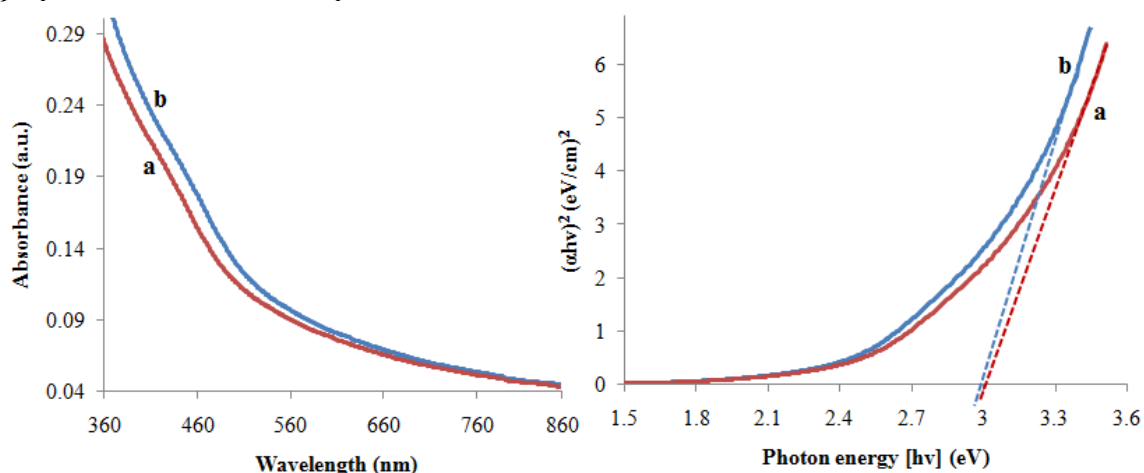


Fig. 6. UV-Vis spectra and Tauc plots of the ZnS/CdS core shell nanoparticles with (a) low and (b) high thickness shell

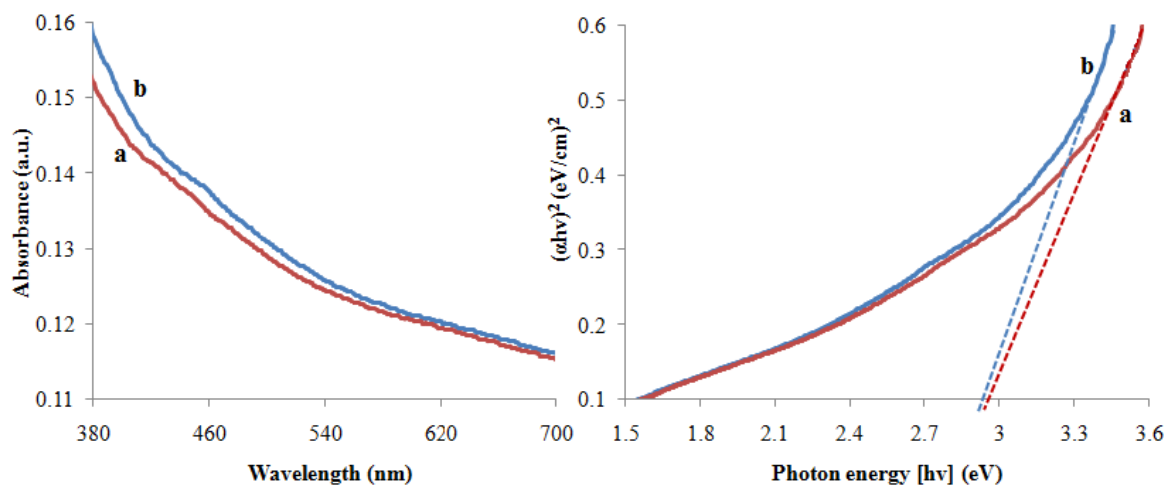


Fig. 7. UV-Vis spectra Tauc plots of the CdS/ZnS core shell nanoparticles with (a) low and (b) high thickness shell

The energy of band gap (E_g) of ZnS/CdS and CdS/ZnS core shell nanoparticles were evaluated from the Tauc plot according to [24-25]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap energy, and B is a constant. The estimated optical band gaps for ZnS/CdS core shells are about 3.02 and 2.98 eV for low and high shell thickness, respectively which show around 1.22 and 1.26 eV red-shift compared to ZnS core nanoparticles ($E_g \sim 4.24$ eV). The estimated optical band gaps for CdS/ZnS core shells are about 2.97 and 2.94 eV for low and high shell thickness, respectively which show around 0.25 and 0.22 eV blue-shift compared to CdS core nanoparticles ($E_g \sim 2.72$ eV).

The room temperature PL spectra of ZnS/CdS core shell nanoparticles under 350-nm excitation were shown in Fig. 8. The figure shows a broad blue-green emission spreading up to 600 nm which is due to emergence of multiple emission bands along with the blue emission features of ZnS core. Gaussian curve fitting is applied to de-convolute the multiple bands that constitute the envelope spectrum. The PL spectra of samples have been deconvoluted into four different bands with peak maxima at ~ 424 , 470, 530 and 573 nm. The first and second peaks are attributed to the recombination of electron-hole pairs in sulfur and zinc vacancies of ZnS nanocrystals. The third and fourth peaks are assumed to originate from the radiative recombination of carrier at surface trap states resulted from the compounded effect of CdS at ZnS/CdS interface. The relative intensities of bands vary with change in the shell thickness so that in ZnS/CdS core shell nanoparticles with low thickness shell the first and second peaks show higher intensity compared to high thickness shell nanoparticles while the third and fourth peaks show lower intensity. With increasing thickness of the shell material, all the coherency stress will be relieved which leads to trapped charge carriers, so the thickness of the shell layer is critical for the optical response.

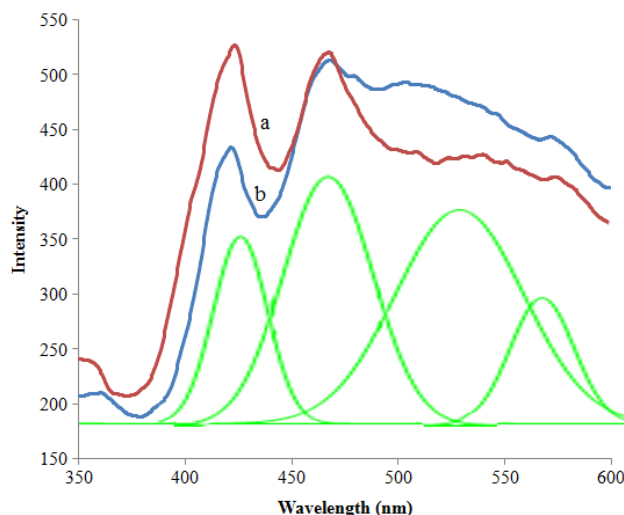


Fig. 8. PL spectra of the ZnS/CdS core shell nanoparticles with (a) low and (b) high thickness shell

Fig. 9. shows the PL spectra of CdS/ZnS nanocrystals recorded at room temperature under 410 nm excitation. The PL spectra show two green emission peaks centered at ~ 542 and ~ 597 nm which are attributed to the recombination of electron-hole pairs in sulfur and cadmium vacancies of CdS core nanocrystals. But it seems the second peak consist multiple emission bands. Using Gaussian curve fit the second peak of PL spectra has been deconvoluted into three different bands with peak maxima at ~ 578 , 597 and 621 nm. When core/shell nanoparticles are excited, the photoinduced charge carriers migrate to the interface and trap in the misfit dislocations. Therefore, the emissions observed can be attributed to the radiative recombination of carrier at CdS/ZnS interface. With an increase in shell thickness of the CdS/ZnS core shell nanoparticles the intensity of emission peaks decreases which may due to increase of non-radiative recombination.

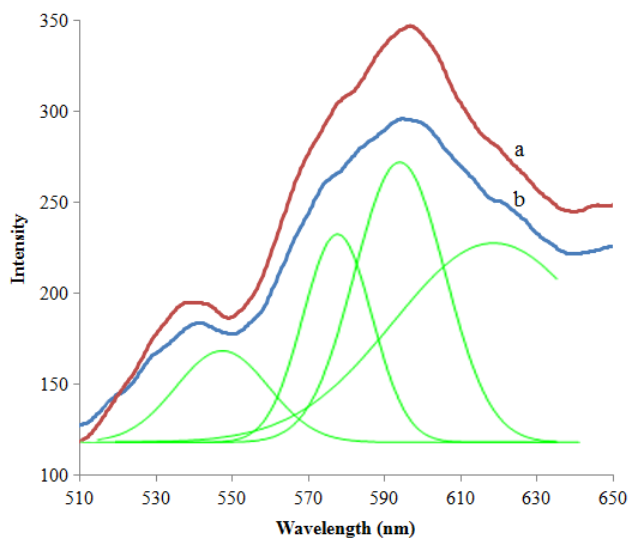


Fig. 9. PL spectra of the CdS/ZnS core shell nanoparticles with (a) low and (b) high thickness shell

4. Conclusions

ZnS/CdS and CdS/ZnS core shells nanoparticles were fabricated by adding the precursors of shell material to ethanol solution consisting of core nanoparticles synthesized using M-P method, and irradiated by microwave for 25 min using pulse regime. The thickness of shell layers was controlled by varying the concentration of shell precursors during synthesis process. The estimated average shell thickness from TEM images was 3.4 and 5.1 nm for ZnS/CdS core shells and 3.4 and 5.3 nm for CdS/ZnS. The XRD spectra of core shell nanoparticles were similar to the XRD pattern of core materials, cubic structure for ZnS/CdS and hexagonal structure for CdS/ZnS, but the intensity of peaks decreases with respect to the core materials attributed to mismatch between core and shell structures. The optical properties of ZnS/CdS and CdS/ZnS core shell nanoparticles in the visible region were dominated by CdS since its band gap is smaller than that of ZnS and both conduction band and valence band of CdS are located within the energy gap of ZnS. The estimated optical band gaps of ZnS/CdS core shells were 3.02 and 2.98 eV for low and high shell thickness, respectively and displayed red-shift compare to ZnS core. For CdS/ZnS, the estimated optical band gaps were 2.97 and 2.94 eV for low and high shell thickness, respectively and displayed blue-shift compare to CdS core. PL spectra of the core shell nanoparticles deconvoluted into four different bands with peak maxima at 424, 470, 530 and 573 nm for ZnS/CdS and 542, 578, 597 and 621 nm for CdS/ZnS attributed to zinc, cadmium and sulfur vacancies, and the radiative recombination of carrier at interfaces.

Acknowledgment

This work was supported by the Ministry of Higher Education of Malaysia under the FRGS and RUGS grants. The authors would also like to thank staff of the Faculty of Science and the Bioscience Institute of University Putra Malaysia, who had contributed to this work.

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