VNU Journal of Science, Mathematics - Physics 29 (2013) 40-47

Synthesis and optical properties of $CdSe/CdSe_{1-x}S_x$ heterostructure nanorods using Oleylamine

Nguyen Thi Luyen[1,3,*], Nguyen Xuan Nghia[2]
Nguyen Kien Cuong[3], Nguyen Thi Thuy Lieu[4]

[1]*University of Sciences, Thai Nguyen University, Quyet Thang, Thai Nguyen, Vietnam*
[2]*Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi*
[3]*VNU University of Engineering and Technology, 144 Xuan Thuy, Hanoi*
[4]*Posts and Telecommunications Institute of Technology, Vietnam Posts and Telecommunications Group, Km 10, Nguyen Trai, Hanoi*

Received 15 January 2013
Revised 20 February 2013; Accepted 21 March 2013

Abstract: Colloidal $CdSe/CdSe_{1-x}S_x$ heterostructure nanorods were synthesized by the seeded growth method. By changing the temperature, type of ligand, we synthesized the Wz-CdSe nanocrystals as seeds for growth of $CdSe/CdSe_{1-x}S_x$ heterostructure nanorods. The yield of heterostructure nanorods depend on the amount of oleylamine in the reaction mixture. Their morphology, crystalline structure and optical properties were investigated by transmission electron microscopy, X-ray diffraction, optical absorption and photoluminescence spectroscopy.

Keywords: heterostructure nanorods, oleylamine, photoluminescence.

1. Introduction

Fundamental and applicable research on type I and type II of nanoheterostructures (NHS) have attracted enormous attention in recent years. Regarding the type I of the NHS, geometrically a CdSe/CdS nanorod consists of a rod-like Wurtzite arm CdS grown from the {002} facet of the dot-like Wurtzite core CdSe [1-2]. So far, most of papers reported on syntheses and optical characteristics of CdSe/CdS nanorods, have been mainly focused on a TOPO-HDA-ODPA reaction system in which phosphonic acids ligand of too expensive Cd^{2+} precursors have been usually used [3-4]. For this reason, exploring and using materials having less expensive, safe and friendship to environment are one of solutions applied to the synthesis of CdSe/CdS nanorods, at present. Therefore, we have tried to synthesis CdSe/CdS nanorods using additional TOPO and Oleylamine ligands to the reaction system

* Corresponding author. Tel.: 84- 986360679
E-mail: luyen0803@gmail.com

of ODE–OA–TOP. Moreover, effects of processing parameters such as reaction temperature, ligand types on phase transfer of CdSe nanoparticles's structure are still misunderstood and unsolved.

In this paper, we have been studied the synthesis of CdSe/$CdSe_{1-x}S_x$ nanorods by using Oleylamine-primary amine (NH_2) value. By changes in the processing parameters like the reaction temperature and ligand types, we have successfully synthesized Wz-CdSe nanocrystals that were used as seeds for growing CdSe/$CdSe_{1-x}S_x$ nanorods.

2. Experimental

Materials: Initial materials and chemicals including cadmium oxide (CdO, 99.99%), selenium powder (Se, 99.999%), sunfur power (S, 99.99%), octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OLA, 98%), trioctylphosphine (TOP, 90%) and trioctylphosphine oxide (TOPO, 99.90%) were purchased from Aldrich and used as received without further purification.

Synthesis of Wz-CdSe nanocrystals: We synthesized CdSe spherical nanoparticles having Wz-structure by changing the reaction temperature and ligand types, based on the process producing CdSe nanoparticles in ODE-OA-TOP reaction systems.

Synthesis of CdSe/$CdS_{1-x}S_x$ nanorods: CdSe/$CdSe_{1-x}S_x$ nanorods were synthesized by quickly injected simultaneously two solvent precursors of Cd^{2+} và S^{2-} into mixed solvents of Wz-CdSe nanoparticles**.**

Measurements: Absorption spectra of the samples was measured in a range of 300 nm to 800 nm on a spectrometer with the model of V-570 (Varian) while their photoluminescent spectra were determined on LABRAM – 1B (Horriba, Jobin Yvon) spectrometer, using an excited wavelength of 488 nm generated by laser Ar. Also, TEM images of CdSe/$CdSe_{1-x}S_x$ NHS were performed on a Joel-JEM 1010 microscope with a high voltage of 80 kV. The samples were mounted on a carbon-coated cooper-mesh grid. X-ray diffractometer (XRD) analysis was performed on D5005 using a Cu Kα current.

3. Results and Discussion

3.1. Synthesis of Wz-CdSe nanocrystals

3.1.1. Effects of reaction temperature

CdSe nanocrystals (NCs) were synthesized at different temperature of 290^{o}C, 300^{o}C and 310^{o}C with the OA concentration of 0,05M in ODE-OA-TOP reaction system are shown in figure 1. The TEM images reveal CdSe spherical nanoparticles that are regular sizes.

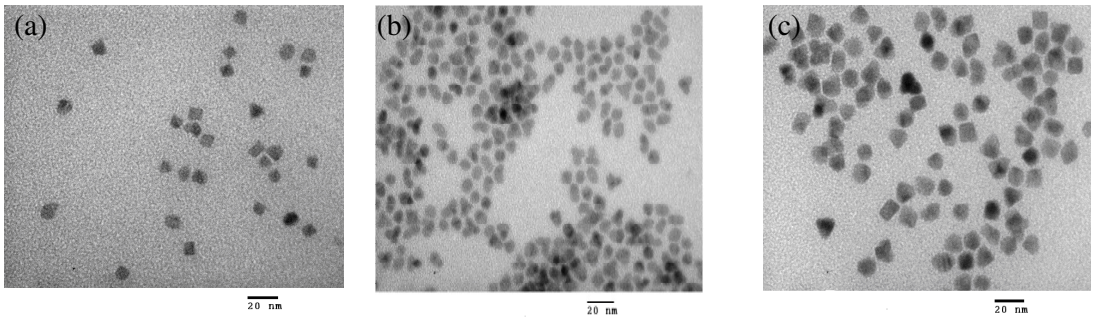

Figure 1. TEM images of CdSe NCs were synthesized at different reaction temperature of a) 290°C , b) 300°C, c) 310°C in the ODE-OA-TOP reaction system.

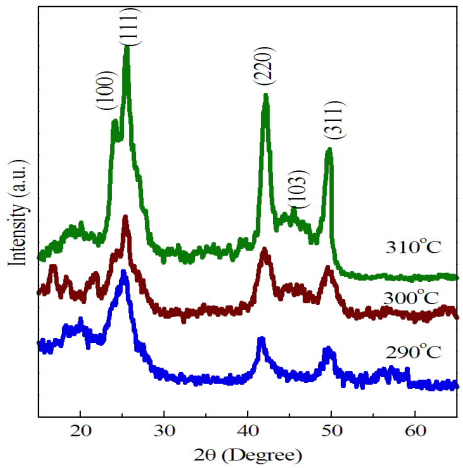

Figure 2. XRD patterns of CdSe NCs were synthesized at reaction temperature of 290° to 310°C in the ODE-OA-TOP reaction system.

Figure 2 shows XRD patterns of CdSe NCs were synthesized at different reaction temperature of 290°C, 300°C, 310°C. These patterns show that CdSe NCs synthesized at 290°C, possess Zincblend structure phase and diffraction patterns at 2θ of 25,3 °, 42,1 ° and 49,5° corresponding to the Miller indices (111), (220), (311), respectively. When increasing the reaction temperature up to 300°C and 310°C, XRD patterns of CdSe NCs demonstrate an appearance of two new diffraction peaks at 2θ of 23,9° and 46° which correspond to the Miller indices (100) and (103), respectively. This may be attributed to the simultaneous existence of both Zincblend and Wurtzite phases.

3.1.2. Effect of ligands

As we know, ligands play an important role affecting structural phase transition and the configuration of nanoparticles [5-8].

Figure 3(a) shows a TEM images of CdSe NCs were synthesized in the mixed solutions of ODE-OA-TOP at the temperature of 250°C using the ratio of OLA/TOPO solutions equal to 3:1, respectively. It can be seen that CdSe NCs have a spherical shape with a size of about 6 nm.

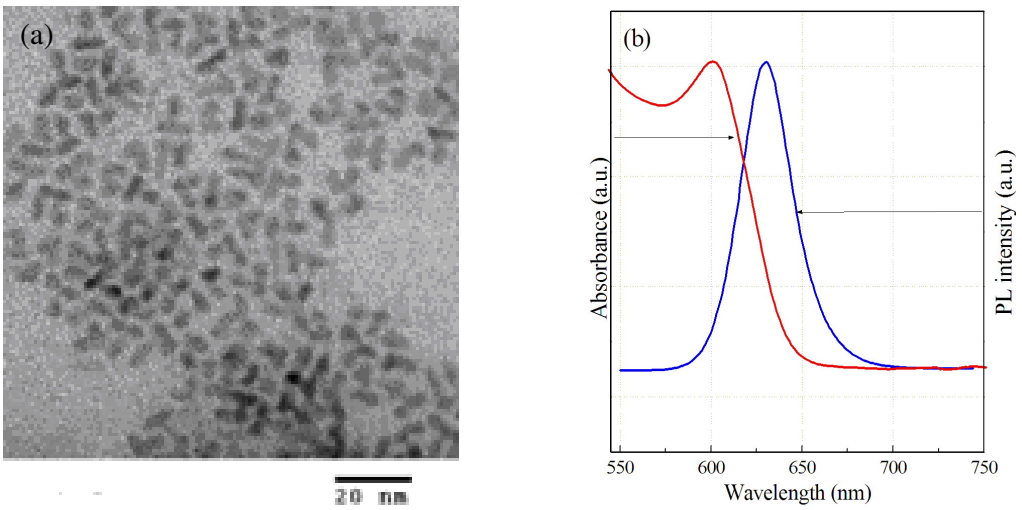

Figure 3. TEM images (a), and absorption and PL of CdSe NCs (b), were synthesized in the mixed solutions of ODE-OA-TOP using TOPO and OLA at temperature of 250°C.

Figure 4 shows XRD patterns of CdSe NCs synthesized, at temperatures of 200°C and 290°C, in the ODE-OA-TOP reaction system coupled with the OLA/TOPO solution having the ratio of 3:1, respectively.

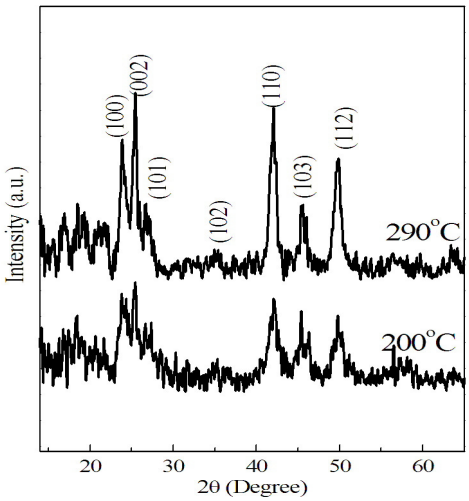

Figure 4. XRD patterns of CdSe NCs formed in the ODE-OA-TOP reaction system coupled with OLA/TOPO solution having the ratio of 3:1 and at reaction temperatures of 200°C and 290°C.

XRD patterns of CdSe NCs demonstrate structural phase of Wz-crytals. This can be ascribed to the change in crystal structure of CdSe NCs due to controlling the concentrations of two additional ligands such as TOPO and OLA. First, precursors reacted with TOPO ligand to form CdSe seeded having eclipsed structure. And then, dynamic interaction between ligand molecules and the seeded of CdSe has lead to a chance for OLA molecules absorbed on these seeded. This process has an effect on the growth of CdSe NCs [9]. Therefore, employing OLA and TOPO in the ODE-OA-TOP reaction solution has the considerably effect on the structural phase and shapes of CdSe NCs.

3.2. Synthesis of CdSe/CdSe$_{1-x}$S$_x$ nanorods

Not similar to the synthesis process of core/shell CdSe/CdS spherical nanoparticles, we synthesized CdSe/CdSe$_{1-x}$S$_x$ nanorods by quickly injecting Cd^{2+} và S^{2-} precursor solution into the solution in which spherical CdSe cores had been shaped to form and grow arms. This process formed CdSe/CdSe$_{1-x}$S$_x$ nanorods by keeping unchanged parameters for the synthesis of CdSe/CdS spherical nanoparticles, however, by changing an amount of OLA in the precursor solution.

TEM images, absorption and photoluminescent (PL) spectra of CdSe/CdSe$_{1-x}$S$_x$ nanorods were synthesized with amount OLA 5% mixed in the reaction solution, are shown in figure 5(a) and 5(b), respectively. The TEM images revealed that formation capability of CdSe/CdSe$_{1-x}$S$_x$ nanorods is very low, it is about 8%, when the amount of the OLA component in the mixed reaction solution is low.

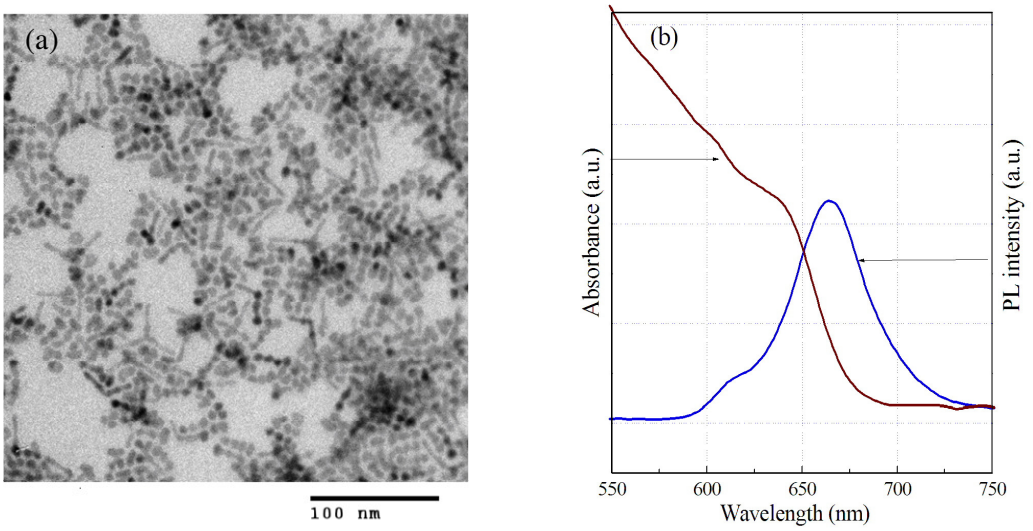

Figure 5. TEM images (a) and absorption, PL spectra (b) of CdSe/CdSe$_{1-x}$S$_x$ nanorods were synthesized with OLA 5% mixed in the reaction solution.

This is attributed to dynamic bonding of OLA molecules that is not enough strong to be absorbed onto CdSe seeds having eclipsed structure, and this might prevent CdSe/CdSe$_{1-x}$S$_x$ nanorods to be grow up from dots to rods. When the amount of OLA mixed in the reaction solution increased up to 30%, the formation capability of CdSe/CdSe$_{1-x}$S$_x$ nanorods is about 55% (see Fig. 6 (a)). We also kept

$CdSe/CdSe_{1-x}S_x$ nanorods sample (figure 6(a)) in the OLA solution at temperature of 80°C for 12 hours in order to examine growth mechanism of $CdSe/CdSe_{1-x}S_x$ nanorods.

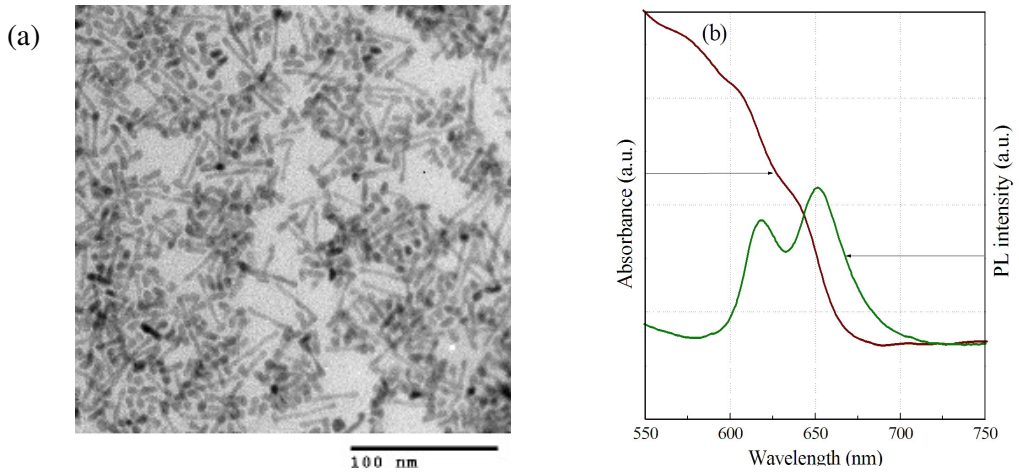

Figure 6. TEM images (a) and absorption, PL spectra (b) of $CdSe/CdSe_{1-x}S_x$ nanorods were synthesized with OLA 30 % mixed in the reaction solution.

It proved that $CdSe/CdSe_{1-x}S_x$ nanorods (figure 7(a)) obtained is the as same as that of the previous sample that had not been kept in the OLA solution for 12 hours. Therefore, it could be considered that $CdSe/CdSe_{1-x}S_x$ nanorods are formed by CdSe seeds with Wz-structure. This growth mechanism we have found is rather different from adhesion mechanism reported by Yu *et Al.* [10].

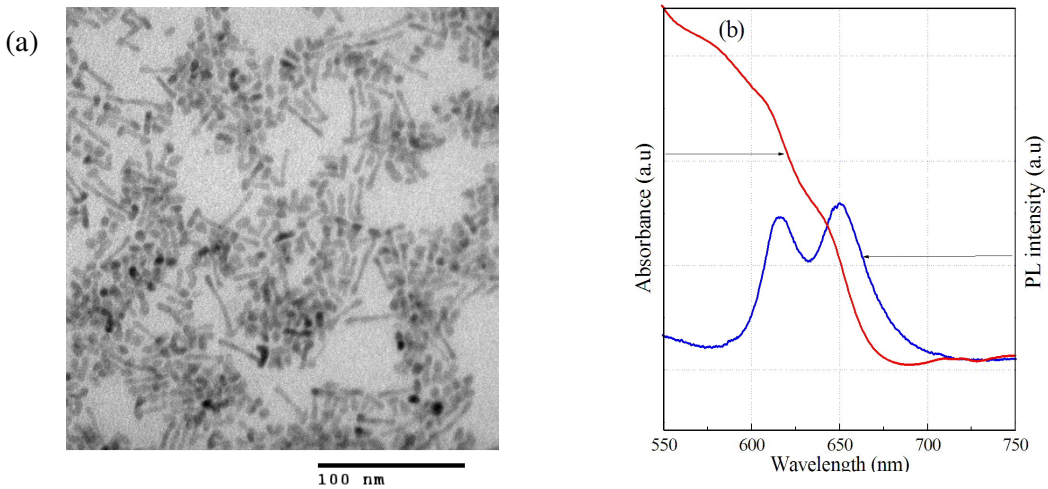

Figure 7. TEM images (a) and absorption, PL (b) of $CdSe/CdSe_{1-x}S_x$ nanorods samples kept in the OLA solution at 80°C for 12 hours.

Moreover, observing PL spectra of Fig.5 (b), Fig.6 (b) and Fig.7 (b), we can realize that all PL spectra have two peaks located at around 620 nm and 650 nm. However, the peak at 620nm of sample synthesized with OLA 5% mixed in the reaction solution has low intensity compared to the rest spectra. This might be ascribed to growth CdSe/$CdSe_{1-x}S_x$ nanorods increased; it leads to PL peak intensity at the shorter wavelength being increased (higher emission energy). Also, PL-peak at longer wavelength (lower emission energy) might be related to the emission of CdSe quantum dots while PLpeak at shorter wavelength (higher emission energy) might be considered as the photoluminescent emission of branched rods (arm shaped) that are composed of the composition of three components like $CdSe_{1-x}S_x$

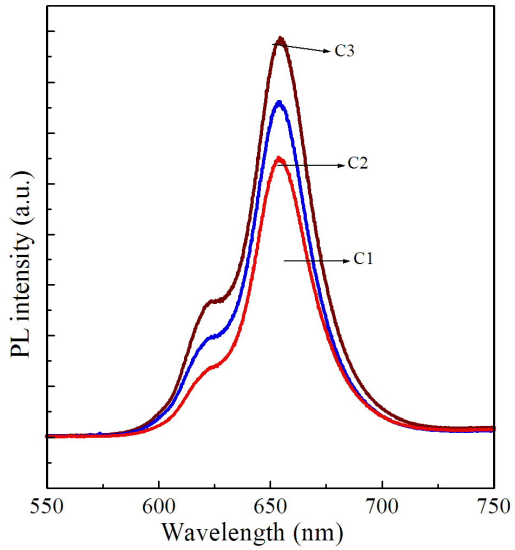

Figure 8. PL peak intensity of NHS CdSe/$CdSe_{1-x}S_x$ nanorods obtained by size- selective centrifugation.

To prove our hypothesis, we employed the centrifugal technique to select different sizes of CdSe/$CdSe_{1-x}S_x$ nanorods at 2000 rpm for 2 min., are shown in Fig.8 (C1-first time centrifugation; C2-second time centrifugation (first); C3–second time centrifugation (second)). The PL peak of the sample centrifuged two times at the long wavelength (low emission energy) achieved the highest intensity; this PL peak is emitted one of CdSe quantum dots (QD CdSe). Commonly, nanocrystals or nanoheterostructures synthesized samples are composed of quantum dots having rod, tetrapod or bipod configuration. Moreover, branched structural quantum dots have more heavy weight than that of spherical ones. So the branched structural quantum dot can be separated out of spherical ones by the size-selective centrifugation.

Conclusion

Employing TOPO and primary amine oleylamine ligands in mixed ODE-OA-TOP reaction system, we synthesized CdSe/$CdSe_{1-x}S_x$ nanorods. The effects of the reaction temperature and ligand

types on structural phase transition of CdSe crystal seeds were studied. Nanorod-formable capability of CdSe/$CdSe_{1-x}S_x$ is dependent of primary amine OLA in the mixed reaction solution. It achieves a maximum value of 55% when the amount of OLA reached to 30% in the mixed reaction solution.

Acknowledgement

This work was supported by Vietnamese Ministry of Education and Training, and by the Key Laboratory of Materials and Electronic Devices (Institute of Materials Science, VAST).

References

[1] L. Carbone, K. Kudera, E. Carlino, W. J. Parak, C. Giannini, R. Cingolani and L. Manna, Multiple wurtzite twinning in CdTe nanocrystals induced by methylphosphonic acid, J. Am. Chem. Soc. 128 (2006) 748.

[2] L. Manna, E. C. Scher, L. S. Li and A. P. Alivisatos, Epitaxial growth and photochemical annealing of graded CdS/ZnS shells on colloidal CdSe nanorods, J. Am. Chem. Soc. 124 (2002) 7136.

[3] Y. Jun, J. Lee, J. Choi and J. Cheon, Symmetry-Controlled Colloidal Nanocrystals: Nonhydrolytic Chemical Synthesis and Shape Determining Parameters, J. Phys. Chem. B 109 (2005) 14795.

[4] B. Mahler, N. Lequeux and B. Dubertret, Ligand–controlled polytypism of thick-shell CdSe/CdS nanocrytals, J. Am. Chem. 132 (2010) 953.

[5] S. M. Lee, S. N. Cho and J. W. Cheon, Shape control of II-VI semiconducter nanomaterial, Adv. Mater. 15 (2003) 441.

[6] P. D. Cozzoli, L. Manna, M. L. Curri, S. Kudera, C. Giannini, M. Striccoli and A. Agostiano, Shape and phase control of colloidal ZnSe nanocrytals, Chem. Mater. 17 (2005) 1296.

[7] W. Yu, L. Qu, W. Guo and X. Peng, Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals, Chem. Mater. 15 (2003) 2854.

[8] Y. H. Kim, Y. W. Jun, B. H. Jun, S. M. Lee and J. Cheon, Sterically Induced Shape and Crystalline Phase Control of GaP Nanocrystals, J. Am. Chem.Soc. 124 (2002) 13656.

[9] X. Peng, Mechanisms for the Shape-Control and Shape-Evolution of colloidal Semiconductors Nanocrystals, Adv. Mater. 15 (2003) 459.

[10] J. H. Yu, H. M. Park and S. C. Kim, Synthesis of quantums-sized cubic ZnS nanorods by oriented attachment mechanism J. Am. Chem. 127 (2005) 5662.