Effect of shell thickness on heterostructure of CdSe/CdS core/shell nanocrystals

Anh Thi Le[1,3], Minh Tan Man[2,3], Minh Hoa Nguyen[4*]

[1] Institute of Research and Development, Duy Tan University, 3 Quang Trung St., Da Nang, Vietnam
[2] Institute of Theoretical and Applied Research, Duy Tan University, Hanoi, Vietnam
[3] Faculty of Natural Sciences, Duy Tan University, 3 Quang Trung St., Da Nang, Vietnam
[4] Faculty of Fundamental Sciences, University of Medicine and Pharmacy, Hue University, 6 Ngo Quyen St., Hue, Vietnam

* Correspondence to Minh Hoa Nguyen <nmhoa@huemed-univ.edu.vn>

Abstract. Core/shell hetero-nanostructures are promising materials for fabricating optoelectronic devices, photodetectors, bioimaging, and biosensing. The CdSe/CdS core/shell nanocrystals (NCs) were synthesized in a wet chemical reaction. The shell thickness was modified by varying reaction times. The structure and optical properties as a function of the CdS shell thickness were investigated. A systematic redshift of the first exciton absorption peaks and photoluminescent (PL) spectra occurred after coating with CdS confirmed the shell growth over the CdSe core. The PL's intensity increased compared with that of bare NCs. The formation of high-quality NCs with uniform size distribution was shown in the transmission electron microscopy (TEM) image and confirmed by the narrow PL band and small FWHM.

Keywords: core/shell, nanocrystal, heterostructure, wet chemical reaction, optical properties, CdSe, CdS

1   Introduction

Colloidal nanocrystals are attractive for light emission because their size/shape/composition-dependent electronic and optical properties are based on the quantum confinement effect [1-3]. Therefore, these nanocrystals (NCs) are favourable materials for optoelectronic devices, such as solar cells, LEDs, photodetectors [4, 5], chemical sensing [6], biosensing, and bioimaging [7]. However, the photoluminescence quantum yield (PLQY) of the NCs fabricated from a single semiconductor is relatively tiny. Their optical properties deteriorate with lifetime, thus limiting their applications.

The heterostructures of a core/shell type have been proposed to improve the PLQY and stability of NCs. Their cover shells are made of a wide-bandgap semiconductor. The synthesis methods of the core/shell [8], core/crown [9, 10], and core/crown/shell structures [11] have been reported. By altering the thickness and composition of the cover material, the researchers can tune the first exciton absorption and luminescence bands of the NCs in a wide spectral range [12].

One widely studied system is NCs with the CdSe/CdS heterojunction. In the past decades, the CdSe-based colloidal hetero-nanostructures have been attractive because of their optical and

electrical properties. Different materials are conveniently designed to cover the CdSe core, including CdS. Because of a minor lattice mismatch between CdSe and CdS (~4%) [13], CdS can provide high flexibility to the shell growth. Tetrapod-shaped [14], plate-shaped [15], and rod-shaped [16] CdS shells surrounding a CdSe spherical core have been manufactured. The core/shell CdSe/CdS heterostructures allow for electron-hole wave function overlap engineering owing to their small conduction band offset between CdSe and CdS [17, 18]. The literature reported the CdS shell on the CdSe core helps remove the surface states [19, 20]. With differences in the CdS shell thickness and the partial spatial separation of the exciton wave function, these NCs efficiently inhibit Auger recombination and photoluminescence blinking [21, 22]. A relatively long reaction time for the CdS shell could contribute to forming an alloyed interfacial layer that smooths the confinement potential. These results can reduce Auger decay rates compared with those samples with a sharp core/shell interface [23, 24].

In this article, we report a wet chemical technique to obtain the colloidal heterostructured CdSe/CdS core/shell NCs to engineer the electronic band alignment and tune the electron transfer efficiency by varying the CdS shell thickness. We investigated changes in the crystal structure and optical properties of the core/shell NCs with tunable shell thickness. The results indicated that the first exciton absorption peaks and PL efficiency of core/shell NCs increased when a CdSe core was first coated with a CdS layer. The results and conclusions will be helpful for the development of sensors adopting NCs as fluorescence labels.

2 Experimental

Materials

Cadmium oxide (CdO, 99.999%), selenium (Se, 99.99%), sulfur (S, 99.99%), oleic acid (OA, 90%), and 1-octadecene (ODE, 90%) were purchased from Aldrich. Toluene, isopropanol, and ethanol were purchased from J&K Scientific Ltd., China. The solvents were of technical grade, and the chemicals were used without further purification. All syntheses were performed under nitrogen purchased from Singapore Oxygen Air Liquide Pte Ltd.

Synthesis of CdSe core and CdSe/CdS core-shell NCs

For a typical preparation of Se precursor (0.1 M), 3 mmol of Se was transferred to a three-necked round-bottom flask, and 20 mL of ODE was added. This mixture was heated at 180 °C and stirred for 30 min under nitrogen. The 0.1 M sulfur precursor was prepared by dissolving 0.1 mmol of sulfur in 5 mL of ODE at 140 °C and stirred for 30 min under nitrogen.

A mixture of cadmium oxide (0.6 mmol), 10 mL of ODE, and 1.2 mmol of oleic acid was loaded into a three-necked flask, heated up to 250 °C, and set under nitrogen gas until the mixture turned clear. Further, the Se precursor was quickly injected into the cadmium solution and stirred at 260 °C. The reaction was allowed for 5 min to occur and then cooled to 240 °C; the S precursor was quickly injected. The amounts of the added precursors were calculated to obtain the desired shell thickness. The reaction mixture was kept at 240 °C and allowed for growth for 180 min at this temperature. An aliquot of CdSe/CdS was withdrawn at different times from 1 min to 180 min. The samples were precipitated with a mixture of isopropanol and chloroform (1:2 and

1:1, v/v), separated by centrifugation, and redissolved in toluene.

Characterization

Transmission electron microscopy (TEM) images were collected by using a JoelJEM1010 operating at 80 kV. UV-vis absorption spectra were recorded on a Varian-Cary-5000 Ultraviolet-visible (UV-Vis) spectrometer. A JobinYvonFlurolog FL3-22 fluorescence spectrometer performed luminescence measurements with the wavelength of the exciting radiation of 400 nm. X-ray powder diffraction (XRD) diagrams were obtained on a Siemens D5005 X-ray diffractometer with Cu-Kα_1 radiation and a wavelength of 0.15406 nm. For XRD measurements, the samples were deposited on glass slides. All measurements were performed at ambient temperature.

3 Results and discussion

The morphology of the as-obtained samples has been studied by using TEM. The images of CdSe bare core and CdSe/CdS core/shell NCs after 120 min of reaction are shown in Figure 1. The additional TEM images related to the aliquots extracted at interim stages during the coating process and TEM images with different magnifications are not shown here. The average particle diameter increases from 4.2 to 6.0 nm, corresponding to a shell thickness of 2.2 nm (~6 monolayers). Furthermore, the shape is quasi-spherical with high homogeneity and small size distribution.

The crystallographic properties have been investigated to identify core/shell structures. Figure 2 shows the XRD patterns of the CdSe core and CdSe/CdS core/shell NCs prepared at 120 min of reaction. The CdSe core and core/shell materials display a cubic zinc blende (ZB) crystal structure with three peaks corresponding to the

(1 1 1), (2 2 0), and (3 1 1) lattice planes. Diffraction peak broadening confirms the formation of nano-sized particles in the samples. XRD techniques have verified the uniform growth of the shell. The peaks in the diffraction patterns of CdSe/CdS core/shell NCs shift towards higher angles for the zincblende CdS phase with the increasing volume of the CdS in the shell, indicating dilation of the crystal lattice.
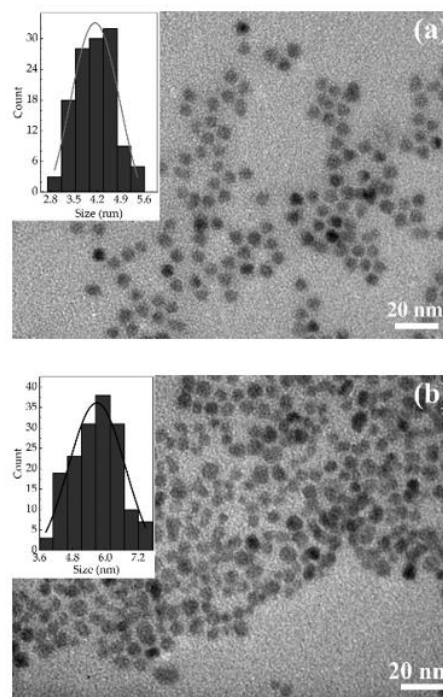

Fig. 1. TEM images and the size histograms (inset) of CdSe core (a) and CdSe/CdS core/shell (b)
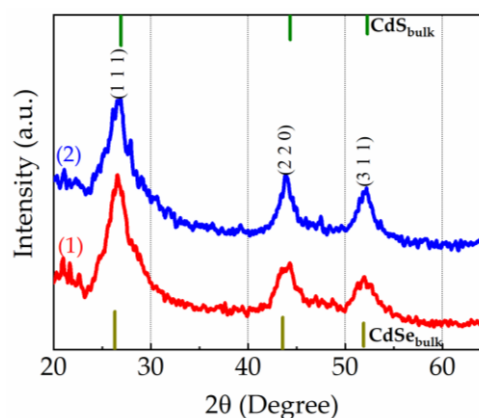

Fig. 2. The XRD patterns of CdSe core (1) and CdSe/CdS core/shell (2) NCs

The optical properties of the obtained samples have been studied by using absorption and PL spectroscopy. Figure 3 presents the absorption and photoluminescence (PL) spectra of CdSe cores and CdSe/CdS core/shell NCs. The injection was carried out at 240 °C, whereas the coating continued at this temperature for 180 min. The first exciton absorption and PL maximum peaks were redshifted during the growth of CdS monolayers. This redshift indicates the formation of the CdS shell that covers the core CdSe as a result of the increase in the size of quantum dots. It has been considered that the excitons leakage has more effects on the confinement energy of the charge carriers from the growth of the shell. After 30 min of reaction, a small shift of the emission maximum was observed in the core-shell spectrum, indicating no further shell growth. Figure 4a shows the temporal evolution of the Stokes shift of the NCs, attributed to the energy difference between the first exciton absorption and emission peaks. In general, the Stokes shifts are small (20–30 meV). These Stokes shift values decrease as the shell thickness increases.
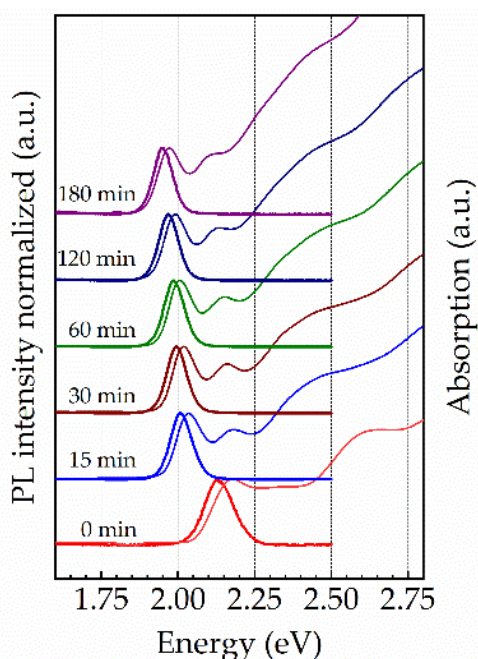

Fig. 3. Temporal evolution of photoluminescence (PL) and UV-vis absorption of CdSe core and CdSe/CdS core/shell

Figure 4b shows the dependence of the full width half maximum (FWHM) and the integrated intensity of the PL on reaction time. The integrated intensity of the PL increases as the shell thickness increases after 30 min of reaction and then decreases. This increased intensity could be attributed to the increased radiative recombination resulting from the combined effect of reduced defect states and energy transfer, caused by QD surface passivation. The decreased PL intensity as the shell layers increase results in the lattice mismatch between the CdSe core and CdS shell that induces more defects with more layers in the CdS shell. The small FWHM value (78–114 meV) indicates a good size monodispersity of the materials. This finding is also consistent with that from the morphology study. The PL peak FWHM decreases significantly from 114 meV for bare CdSe NCs to 78 meV for final CdSe/CdS core/shell NCs.
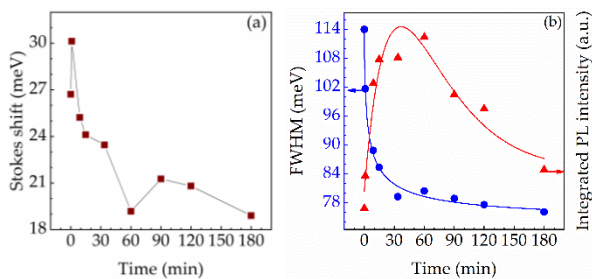

Fig. 4. (a) Temporal evolution of Stokes shift; (b) Integrated PL maximum and FWHM as a function of reaction time for CdSe and CdSe/CdS core/shell NCs

4   Conclusions

We successfully synthesized CdSe core and CdSe/CdS core/shell heterostructures. The XRD data confirm the growth of CdS shell coating to the CdSe ZB core. The TEM images of CdSe and CdSe/CdS NCs demonstrated their crystalline structure and approximately spherical shape. Temporal evolution of the first excitonic absorption and PL bands of the heterostructure tuned in a range of 1.96–2.16 eV and 1.95–2.13 eV

with a small Stokes shift. The PL's intensity of the CdSe/CdS NCs was higher than that of the bare CdSe NCs. Meanwhile, the PL FWHM of the CdSe/CdS NCs decreased with the CdS shell thickness. The results indicate a promising application of CdSe/CdS NCs where optical properties, such as lasing or bio labeling, need to be stable.

References

1. Gaponik N, Hickey SG, Dorfs D, Rogach AL, Eychmüller A. Progress in the light emission of colloidal semiconductor nanocrystals. Small. 2010; 6:1364-78.

2. Talapin DV, Lee JS, Kovalenko M V, Shevchenko E V. Prospects of colloidal nanocrystals for electronic and optoelectronic applications. Chem Rev. 2010; 110:389-458.

3. Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP. Semiconductor Nanocrystals as Fluorescent Biological Labels. Science. 1998;281(5385):2013-6.

4. Litvin AP, Martynenko IV, Purcell-Milton F, Baranov AV, Fedorov AV, Gun'Ko YK. Colloidal quantum dots for optoelectronics. J Mater Chem A. 2017;5:13252-75.

5. [5]Melnikov AA, Fedichkin LE. Quantum walks of interacting fermions on a cycle graph. Sci Rep 2016;6. https://doi.org/10.1038/srep34226.

6. Chaniotakis N, Buiculescu R. 11 - Semiconductor quantum dots in chemical sensors and biosensors. In: Honeychurch KC, editor. Nanosensors for Chemical and Biological Applications: Woodhead Publishing; 2014. p. 267-94.

7. Martynenko IV, Litvin AP, Purcell-Milton F, Baranov AV, Fedorov AV, Gun'Ko YK. Application of semiconductor quantum dots in bioimaging and biosensing. J Mater Chem B. 2017;5:6701-27.

8. Mahler B, Nadal B, Bouet C, Patriarche G, Dubertret B. Core/shell colloidal semiconductor nanoplatelets. J Am Chem Soc. 2012;134:18591-8.

9. Prudnikau A, Chuvilin A, Artemyev M. CdSe-CdS nanoheteroplatelets with efficient photoexcitation of central CdSe region through epitaxially grown CdS wings. J Am Chem Soc. 2013;135:14476-9.

10. Tessier MD, Spinicelli P, Dupont D, Patriarche G, Ithurria S, Dubertret B. Efficient exciton concentrators built from colloidal core/crown CdSe/CdS semiconductor nanoplatelets. Nano Lett. 2014;14:207-13.

11. Kelestemur Y, Guzelturk B, Erdem O, Olutas M, Gungor K, Demir HV. Platelet-in-Box Colloidal Quantum Wells: CdSe/CdS@CdS Core/Crown@ Shell Heteronanoplatelets. Adv Funct Mater. 2016;26:3570-9.

12. Saidzhonov BM, Kozlovsky VF, Zaytsev VB, Vasiliev RB. Ultrathin CdSe/CdS and CdSe/ZnS core-shell nanoplatelets: The impact of the shell material on the structure and optical properties. J Lumin. 2019;209:170-8.

13. Biadala L, Siebers B, Gomes R, Hens Z, Yakovlev DR, Bayer M. Tuning energy splitting and recombination dynamics of dark and bright excitons in CdSe/CdS dot-in-rod colloidal nanostructures. J Phys Chem C. 2014;118:22309-16.

14. Talapin DV, Nelson JH, Shevchenko EV, Aloni S, Sadtler B, Alivisatos AP. Seeded growth of highly luminescent CdSe/CdS nanoheterostructures with rod and tetrapod morphologies. Nano Lett. 2007;7:2951-9.

15. Cassette E, Mahler B, Guigner JM, Patriarche G, Dubertret B, Pons T. Colloidal CdSe/CdS dot-in-plate nanocrystals with 2D-polarized emission. ACS Nano. 2012;6:6741-50.

16. Carbone L, Nobile C, De Giorgi M, Della Sala F, Morello G, Pompa P, et al. Synthesis and micrometer-scale assembly of colloidal CdSe/CdS nanorods prepared by a seeded growth approach. Nano Lett. 2007;7:2942-50.

17. Rainò G, Stöferle T, Moreels I, Gomes R, Kamal JS, Hens Z, et al. Probing the wave function delocalization in CdSe/CdS dot-in-rod nanocrystals by time-and temperature-resolved spectroscopy. ACS Nano. 2011;5:4031-6.

18. Eshet H, Grünwald M, Rabani E. The electronic structure of CdSe/CdS Core/shell seeded nanorods: Type-I or quasi-type-II? Nano Lett. 2013;13:5880-5.

19. Nan W, Niu Y, Qin H, Cui F, Yang Y, Lai R, et al. Crystal structure control of zinc-blende CdSe/CdS core/shell nanocrystals: Synthesis and structure-dependent optical properties. J Am Chem Soc. 2012;134:19685-93.

20. Peng X, Schlamp MC, Kadavanich A V, Alivisatos AP. Epitaxial growth of highly luminescent

CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility. J Am Chem Soc. 1997;119:7019-29.

21. Christodoulou S, Vaccaro G, Pinchetti V, De Donato F, Grim JQ, Casu A, et al. Synthesis of highly luminescent wurtzite CdSe/CdS giant-shell nanocrystals using a fast continuous injection route. J Mater Chem C. 2014;2:3439-47.

22. Chen O, Zhao J, Chauhan VP, Cui J, Wong C, Harris DK, et al. Compact high-quality CdSe-CdS core-shell nanocrystals with narrow emission linewidths and suppressed blinking. Nat Mater. 2013;12:445-51.

23. Beane GA, Gong K, Kelley DF. Auger and Carrier Trapping Dynamics in Core/Shell Quantum Dots Having Sharp and Alloyed Interfaces. ACS Nano. 2016;10:3755-65.

24. Liao C, Xu R, Xu Y, Zhang C, Xiao M, Zhang L, et al. Ultralow-Threshold Single-Mode Lasing from Phase-Pure CdSe/CdS Core/Shell Quantum Dots. J Phys Chem Lett. 2016;7:4968-76.