

# Aqueous synthesis of thioglycolic acid-capped $\text{Tb}^{3+}$ -doped cadmium sulfur quantum dots

Rongfang Wang<sup>1,2</sup>, Xingming Wei<sup>1,2</sup>, Pingfang Tao<sup>1,2</sup>,  
Qinmin Wei<sup>1</sup>, Pei Zhang<sup>1</sup>, and Yiguang Tan<sup>1</sup>

## Abstract

Cadmium sulfur nanocrystals doped with the rare earth ion  $\text{Tb}^{3+}$  were synthesized using an easy aqueous method. Powder X-ray diffraction was used for the crystallography analysis of the nanocrystals. Results showed that cadmium sulfur:  $\text{Tb}^{3+}$  quantum dots had a cubic crystal structure. Effects of the pH of the original solution and  $\text{Tb}^{3+}$ -dopant amount on luminescence properties of cadmium sulfur quantum dots were also systematically investigated. The luminescence properties of cadmium sulfur quantum dots were further improved using an appropriate  $\text{Tb}^{3+}$ -dopant amount.

## Keywords

Quantum dots,  $\text{CdS}:\text{Tb}^{3+}$ , semiconductors, luminescence

Date received: 20 April 2016; accepted: 27 October 2016

Topic: Synthesis of Nanostructured and Nanoscale Materials

Topic Editor: Di Gao

Associate Editor: Ewa Rogalska

## Introduction

Semiconductor nanocrystals (NCs), also referred as quantum dots (QDs), demonstrate a great potential for future applications, such as in biotechnology, photovoltaic devices, and solar cell devices, owing to their unique optical properties.<sup>1–5</sup> Cadmium sulfur (CdS) is one of the most important groups II–VI NC semiconductors and displays a wide direct band gap (2.42 eV) and small Bohr exciton radius (about 2.5 nm).<sup>6</sup> Various methods were developed to prepare CdS NCs. These methods can be broadly divided into two groups: one is organic synthetic methods and the other is aqueous synthesis methods, which involve the use of different thiols as stabilizing agents in aqueous solution. Compared with the organic synthetic methods, the aqueous synthesis methods are advantageous owing to its being simple, green, and highly reproducible, and its products exhibit good water solubility, stability, and biological compatibility.<sup>7–9</sup> The properties of QDs can be further adjusted, for instance, by doping impurity atoms in the NCs, the range of tunable fluorescence can be

expanded, the stability of QDs can be improved, and magnetic properties can be introduced.<sup>10–12</sup> Daocheng's group synthesized  $\text{Cu}^{+}$ - and  $\text{Ag}^{+}$ -doped  $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{ZnS}$  QDs through an

<sup>1</sup> Guangxi Key Laboratory of Agricultural Products Processing (Cultivating Base), Colleges and Universities Key Laboratory for Efficient Use of Agricultural Resources in the Southeast of Guangxi, College of Chemistry and Food Science, Yulin Normal University, Yulin, Guangxi, People's Republic of China

<sup>2</sup> Guangxi Experiment Center of Information Science, Guilin University of Electronic Technology, Guilin, Guangxi, People's Republic of China

## Corresponding author:

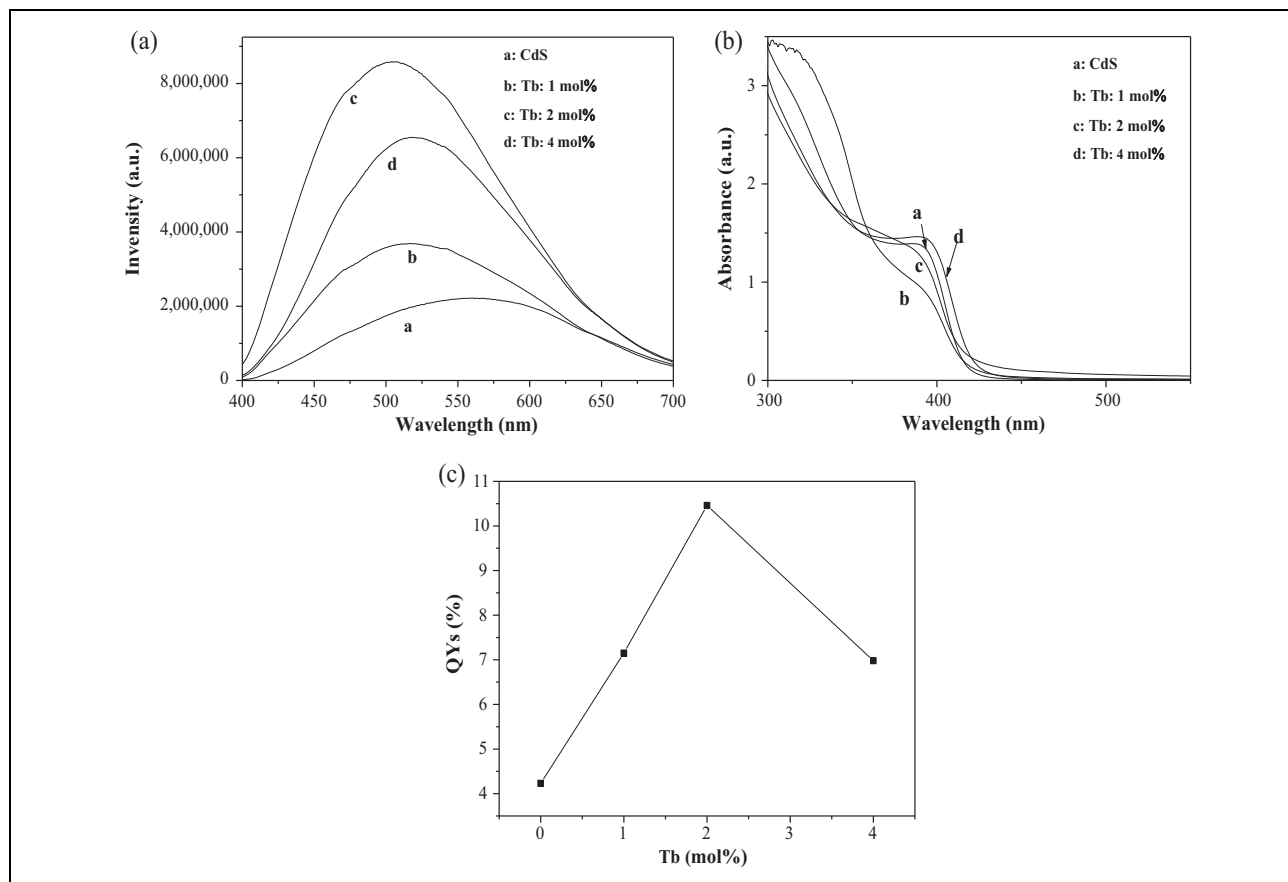
Rongfang Wang, Guangxi Key Laboratory of Agricultural Products Processing (Cultivating Base), Colleges and Universities Key Laboratory for Efficient Use of Agricultural Resources in the Southeast of Guangxi, College of Chemistry and Food Science, Yulin Normal University, Yulin, Guangxi 537000, People's Republic of China; Guangxi Experiment Center of Information Science, Guilin University of Electronic Technology, Guilin, Guangxi 541000, People's Republic of China.

Email: fangfang393@163.com



Creative Commons CC-BY: This article is distributed under the terms of the Creative Commons Attribution 3.0 License

(<http://www.creativecommons.org/licenses/by/3.0/>) which permits any use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (<https://us.sagepub.com/en-us/nam/open-access-at-sage>).



**Figure 1.** Effect of  $\text{Tb}^{3+}$  ion dopant amount on the PL (a) and absorption spectra (b), the corresponding QYs, and (c) of  $\text{CdS:Tb}^{3+}$  QDs. PL: photoluminescence; QYs: quantum yields; QDs: quantum dots; CdS: cadmium sulfur.

easy and green method using hydrophilic glutathione as capping agent. The as-prepared  $\text{Cu}^{+}$ - and  $\text{Ag}^{+}$ -doped  $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{ZnS}$  core-shell QDs exhibit tunable emission covering the entire visible light region, expanding the range of tunable fluorescence.<sup>13</sup> To date, a variety of transition-metal and lanthanide ions, including  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^{+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Er}^{3+}$ , have been doped into groups II–VI QDs.<sup>14–20</sup>

In this study, we proposed a simple method for the synthesis of  $\text{CdS:Tb}^{3+}$  QDs by simply mixing a Cd precursor, Tb precursor, thioglycolic acid (TGA), and an S precursor prior to refluxing. All of the synthetic procedures were conducted in the open air at  $100^\circ\text{C}$ .  $\text{CdS:Tb}^{3+}$  QDs exhibiting different compositions were obtained by tuning the  $\text{Tb}^{3+}$ -dopant amount in the precursor solution. In addition, the effects of pH on the luminescence properties were systematically investigated.

## Materials and methods

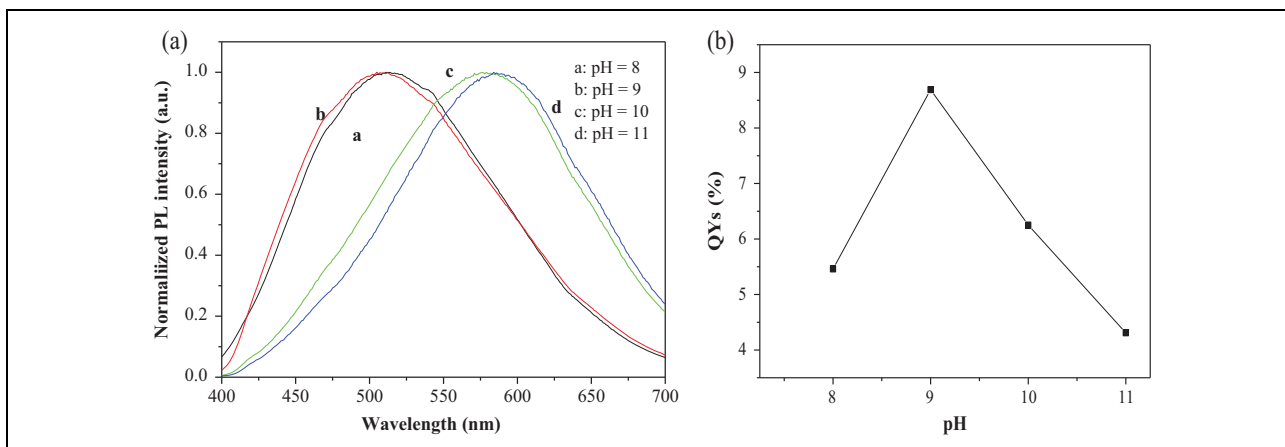
### Synthesis of $\text{CdS:Tb}^{3+}$ QDs

CdS QDs doped with the rare earth (RE) ion  $\text{Tb}^{3+}$  were synthesized through a one-step process in aqueous solution containing sodium sulfide ( $\text{Na}_2\text{S}$ ),  $\text{Tb}(\text{NO}_3)_3$ , and  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  as

precursors. TGA (0.3 mL) was added into the mixture (100 mL) of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  solution (0.02 M, 96–100 mL) and  $\text{Tb}(\text{NO}_3)_3$  (0.02 M, 0–4 mL) under stirring. The solution was subsequently adjusted to pH 9 by dropwise addition of 1 mol/L sodium hydroxide solution.  $\text{Na}_2\text{S}$  was added into the original solution, stirred, and then heated to  $100^\circ\text{C}$ .  $\text{CdS:Tb}^{3+}$  QDs of varying compositions were synthesized by controlling the  $\text{Tb}^{3+}$ -dopant amount. The CdS QDs without RE were synthesized using the methods described earlier; however, the  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  precursor was increased to 100 mL.

### Characterization

Ultraviolet–visible absorption and photoluminescence (PL) spectra were measured using an Agilent Technologies Cary 5000 spectrophotometer (Santa Clara, California, USA) and a HORIBA JY FluoroMax-4 fluorescence spectrophotometer (France) with an xenon lamp as the excitation source, respectively. The PL quantum yield (QY) was determined using rhodamine 6G as reference. X-ray diffraction (XRD) analysis was performed using Rigaku/Dmax-2500 (Japan;  $\text{Cu } K_\alpha = 1.5406 \text{ \AA}$ ). The morphologies of the samples were observed under a JEOL-2010 high-resolution transmission electron microscope (HRTEM; JEOL, Philips, the Netherlands).



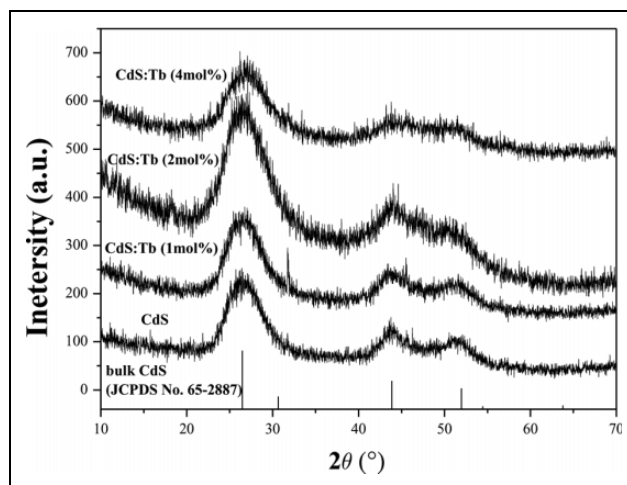
**Figure 2.** Effect of pH on the PL (a) and the corresponding QYs (b) of CdS:Tb<sup>3+</sup> QDs. PL: photoluminescence; QYs: quantum yields; QDs: quantum dots; CdS: cadmium sulfur.

## Results and discussion

The composition of CdS:Tb<sup>3+</sup> QDs mainly depends on Tb<sup>3+</sup>-dopant amount in the precursor solution. Hence, the effect of Tb<sup>3+</sup>-dopant amount on the optical properties of CdS:Tb<sup>3+</sup> QDs was investigated. Figure 1(a) and (b) shows the PL emission and absorption spectra of a series of CdS:Tb<sup>3+</sup> QDs with different doping amount and prepared in aqueous phase. Moreover, the corresponding PL QYs were determined with rhodamine 6G as reference (QYs = 0.95; Figure 1(c)). The reflux time is 3 h and the temperature of the system is maintained at 100°C. An evident blueshift was observed in the maximum emission peak as the Tb<sup>3+</sup> ions complexed with the CdS QDs. In addition, with increased Tb<sup>3+</sup>-dopant amount from 1 mol% to 2 mol%, the PL intensity of CdS:Tb<sup>3+</sup> QDs gradually increased. When Tb<sup>3+</sup>-dopant amount was higher than 4 mol%, PL intensity decreased. The absorption spectra indicate that CdS and CdS:Tb<sup>3+</sup> QDs have a wide absorption range. Compared with CdS QDs, an small redshift was observed in the absorption spectra. The QYs of CdS:Tb<sup>3+</sup> QDs initially increased and then decreased with increasing Tb ion amount. The maximum QY of 10.46% was obtained when the amount of Tb ions reached 2 mol%.

In the aqueous method, the formation of Cd-thiol complexes strongly depends on the pH of solution.<sup>21</sup> Hence, the pH of the original solution was adjusted to 8, 9, 10, and 11 in our experiment. The effect of pH of the original solution on the optical properties of CdS:Tb<sup>3+</sup> QDs was subsequently investigated. The maximum emission peak of CdS:Tb<sup>3+</sup> exhibited an evident redshift from 511 nm to 584 nm with the increase in pH from 8.0 to 11.0 (Figure 2(a)). Figure 2(b) shows the corresponding PL QYs. Compared with the CdS:Tb<sup>3+</sup> QDs obtained under the aforementioned pH, the CdS:Tb<sup>3+</sup> QDs prepared at pH 9 demonstrated a high PL QY.

The crystalline structure of CdS and a series of CdS:Tb<sup>3+</sup> QDs was examined by XRD, as shown in Figure 3. The XRD patterns show that the position of the XRD peaks



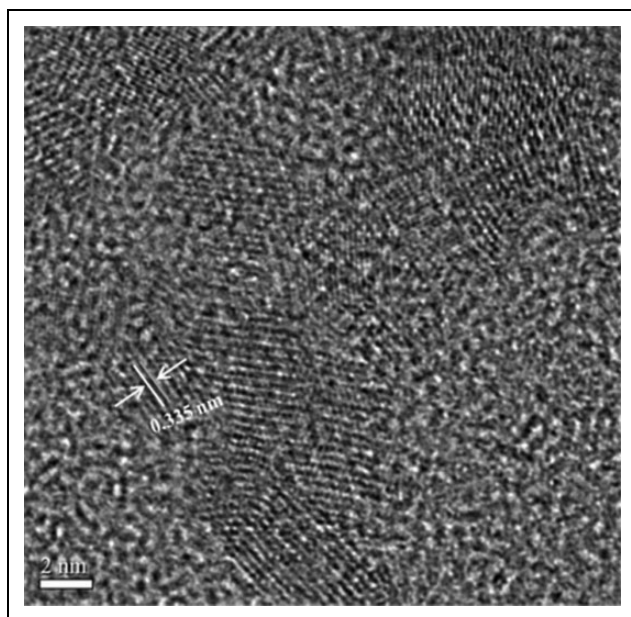
**Figure 3.** XRD pattern of CdS:Tb<sup>3+</sup> QDs. XRD: X-ray diffraction; CdS: cadmium sulfur; QDs: quantum dots.

matches well with those of the cubic crystal structure of bulk CdS Joint Committee on Powder Diffraction Standards (JCPDS, No. 65-2887), and the doped Tb<sup>3+</sup> ion have no obvious influence on the host structure. The three typical distinct peaks can be readily assigned to the (111), (220), and (311) planes, respectively. These peaks are broadened because of finite crystalline size. The particle size was estimated using the full width at half maximum (FWHM) of the characteristic peak (111) via the Debye–Scherrer formula<sup>22</sup>

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where  $D$  is the grain size,  $k$  is a constant (0.89),  $\beta$  is the FWHM of the respective diffraction peak, and  $\theta$  is the angle of diffraction for the (111) plane, respectively. The estimated diameter of the CdS:Tb<sup>3+</sup> QDs (Tb<sup>3+</sup>: 2 mol%) is about 2.33 nm.

The HRTEM images of the as-prepared CdS:Tb<sup>3+</sup> QDs were also measured, and the results are shown in Figure 4.



**Figure 4.** HRTEM images of CdS:Tb<sup>3+</sup> QDs. HRTEM: high-resolution transmission electron microscope; CdS: cadmium sulfide; QDs: quantum dots.

It can be seen that the CdS:Tb<sup>3+</sup> QDs appeared as spherical morphology with an average diameter of approximately 2.5 nm, which is basically in agreement with that calculated from the XRD. In addition, the lattice fringes of an individual particle indicate a well-ordered crystal structure of the CdS:Tb<sup>3+</sup> QDs. The lattice spacing was 0.335 nm corresponding to atomic planes along the [1 1 1] lattice plane direction of the cubic CdS.

## Conclusion

We successfully doped CdS QDs with the RE ion Tb<sup>3+</sup> through a green and easy method using TGA as capping agent. The QY of the cubic crystal structure CdS:Tb<sup>3+</sup> QDs reached 10.46% at a Tb<sup>3+</sup>-dopant amount of 2 mol% and pH 9. The luminescence properties of CdS QDs can be improved using the appropriate Tb<sup>3+</sup>-dopant amount.

## Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

## Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by grants from the Guangxi Natural Science Foundation (2015GXNSFBA139043); Yulin Normal University Research Grant (2016YJKY15); the PhD research startup foundation of Yulin Normal University (G20140011).

## References

- Guldi DM, Rahman GMA, Sgobba V, et al. CNT-CdTe versatile donor-acceptor nanohybrids. *J Am Chem Soc* 2006; 128: 2141–2315. DOI: 10.1021/ja0550733.
- Bera S, Singh SB and Ray SK. Green route synthesis of high quality CdSe quantum dots for applications in light emitting devices. *J Solid State Chem* 2012; 189: 75–79. DOI: 10.1016/j.jssc.2011.11.048.
- Liu ZQ, Yin P, Gong H, et al. Determination of rifampicin based on fluorescence quenching of GSH capped CdTe/ZnS QDs. *J Lumin* 2012; 132: 2484–2488. DOI: 10.1016/j.jlumin.2012.03.072.
- Wang R, Wang Y, Xia W, et al. New Cd<sub>1-x</sub>Mn<sub>x</sub>Te quantum dots for application in light-emitting diodes. *Micro Nano Lett* 2012; 7: 978–980. DOI: 10.1049/mnl.2012.0540.
- Landi BJ, Castro SL, Ruf HJ, et al. CdSe quantum dot-single wall carbon nanotube complexes for polymeric solar cells. *Sol Energ Mater Sol Cells* 2005; 87: 733–746. DOI: 10.1016/j.solmat.2004.07.047.
- Green M. Solution routes to III–V semiconductor quantum dots. *Curr Opin Solid State Mater Sci* 2002; 6: 355–363. DOI: 10.1016/S1359-0286(02)00028-1.
- Huang FH and Chen GN. Preparation and application of l-cysteine-modified CdSe/CdS core/shell nanocrystals as a novel fluorescence probe for detection of nucleic acid. *Spectrochim Acta Mol Biomol Spectrosc* 2008; 70: 318–323. DOI: 10.1016/j.saa.2007.08.023.
- Murray CB, Noms DJ, and Bawendi MG. Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites. *J Am Chem Soc* 1993; 115: 8706–8715. DOI: 10.1021/ja00072a025.
- Rogach AL, Katsikas L, Kornowski A, et al. Synthesis and characterization of thiol-stabilized CdTe nanocrystals. *Ber Bunsen Phys Chem* 1996; 100: 1772–1778. DOI: 10.1002/bbpc.1997101123.
- Bryan JD and Gamelin DR. Doped semiconductor nanocrystals: synthesis, characterization, physical properties, and application. *Prog Inorg Chem* 2005; 54: 47–126. DOI: 10.1002/0471725560.ch2.
- Erwin SC, Zu L, Haftel MI, et al. Doping semiconductor nanocrystals. *Nature* 2005; 436: 91–94. DOI: 10.1038/nature03832.
- Norris DJ, Efros AL and Erwin SC. Doped nanocrystals. *Science* 2008; 319: 1776–1779. DOI: 10.1126/science.1143802.
- Chen YY, Huang LJ, Li SJ, et al. Aqueous synthesis of glutathione-capped Cu<sup>+</sup> and Ag<sup>+</sup>-doped Zn<sub>x</sub>Cd<sub>1-x</sub>S quantum dots with full color emission. *J Mater Chem C* 2013; 1: 751–756. DOI: 10.1039/C2TC00107A.
- Nag A, Sapra S, Nagamani C, et al. A study of Mn<sup>2+</sup> doping in CdS nanocrystals. *Chem Mater* 2007; 19: 3252–3259. DOI: 10.1021/cm0702767.
- Zhang W, Zhou X and Zhong X. One-pot noninjection synthesis of Cu-doped Zn(x)Cd(1-x)S nanocrystals with emission color tunable over entire visible spectrum. *Inorg Chem* 2012; 51: 3579–3587. DOI: 10.1021/ic2024023.

16. Shen QH, Liu Y, Xu J, et al. Microwave induced center-doping of silver ions in aqueous CdS nanocrystals with tunable, impurity and visible emission. *Chem Commun* 2010; 46: 5701–5703. DOI: 10.1039/c0cc00237b.
17. Bol AA and Meijerink A. Luminescence of nanocrystalline ZnS: Pb<sup>2+</sup>. *Cheminform* 2001; 32: 173–177. DOI:10.1002/1521-3951(200103).
18. Watekar PR, Kim DH, Yang H, et al. Magnetic field sensitivity of germano-silicate optical fibers doped with CdSe nanoparticles and Eu<sup>2+</sup> ions. *Phys Scr* 2010; 2010: 561–578. DOI: 10.1088/00318949/2010/T139/014054.
19. Li IF and Yeh CS. Synthesis of Gd doped CdSe nanoparticles for potential optical and MR imaging applications. *J Mater Chem* 2010; 20: 2079–2081. DOI: 10.1039/b924089f.
20. Raola OE and Strouse GF. Synthesis and characterization of Eu-doped cadmium selenide nanocrystals. *Nano Lett* 2002; 2: 1443–1447. DOI: 10.1021/nl025805e
21. Swayambunathan V, Hayes D, Schmidt KH, et al. Thiol surface complexation on growing CdS clusters. *J Am Chem Soc* 1990; 112: 3831–3837. DOI:10.1021/ja00166a017
22. Zhou CY, Zhou LY, Xu JH, et al. Controllable synthesis of CdS quantum dots and their photovoltaic application on quantum-dot-sensitized ZnO nanorods. *J Solid State Electrochem* 2016; 20: 533–540. DOI: 10.1007/s10008-015-3075-5.