

# Synthesis of Cadmium Sulfide Quantum Dots with Simultaneous Desulfurization of Kerosene Oil

Shyamalima Sharma, Pronob Gogoi, Bhaskar Jyoti Saikia, and Swapan K. Dolui\*

Department of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam, India, 784028

Received November 27, 2015; Accepted November 13, 2015

**ABSTRACT:** Cadmium sulfide (CdS) quantum dots (QDs) were synthesized by a standard hydrothermal method with simultaneous desulfurization of kerosene oil. Sulfur containing kerosene oil was treated with cadmium chloride (CdCl<sub>2</sub>) in the presence of sodium hydroxide (NaOH) at 120 °C for 1.5 to 5 h. CdS was formed and sulfur content of oil gradually decreased. Thus, desulfurization of the oil occurred with the formation of the CdS QDs. The concentration of sulfur decreased to a minimum of 0.055% after 5 h of the reaction. In addition, the particle size of QDs increased from 5.4 nm to 8.1 nm as the reaction time was increased from 1.5 to 5 h. Transmission electron microscopy (TEM) study revealed the formation of CdS QDs of particle size 5.4–8.1 nm.

**KEYWORDS:** Desulfurization, CdS, quantum dots, TEM, XRD

## 1 INTRODUCTION

Natural crude oil distillates, such as kerosene oil, contain a significant amount of sulfur components such as thiols, sulfides, disulfides, thiophenes, etc., which are converted to sulfur oxy acids (SO<sub>x</sub>) on combustion. These sulfur compounds blow out to the environment and cause serious environmental hazards [1, 2]. The sulfur emission can also cause asthma, aggravates heart disease, promotes respiratory illnesses and contributes to the formation of atmospheric particulates [3]. Therefore, desulfurization of such oils is very necessary to avoid environmental hazards. So far, various efficient techniques such as hydrodesulfurization (HDS), oxidative desulfurization (ODS), etc., have been employed for sulfur removal. In the year 1992, HDS method was employed for desulfurization of low sulfur distillates which included straight-run gas oil (GO), coker gas oil (CGO), and FCC light cycle oil (LCO) [4]. In 1922, refining of gasoline and kerosene was carried out by a hypochlorite process and sulfur content of kerosene was found to be 0.06–0.1% [5]. The ODS method was used for desulfurization of model sulfur compounds such as thiophene derivatives, benzothiophene derivatives and dibenzothiophene derivatives, straight run-light gas oil (S: 1.35 wt%),

and vacuum gas oil (S: 2.17 wt%) [6]. However, it is observed that sulfur removal by extraction becomes more effective for the oxidized samples than the untreated samples. In addition, lighter sulfur compounds are preferentially extracted. Tam and coworkers used an ODS process to remove sulfur from diesel oils and improved the extraction efficiency for atmospheric gas oil (AGO) by preceding the extraction with oxidation [7]. In general, the sulfur removal from fossil fuels is carried out by oxidation, distillation, extraction and adsorption.

Although various desulfurization techniques are available in the literature [8–11], these techniques are very specific to some specific sulfur-containing compounds that require severe high energy conditions. In addition, the sulfur extracted from such desulfurization may cause environmental hazards or sulfur poisoning, including health problems like lung disease, severe corneal damage, etc. [12]. In addition, oxide of sulfur promotes many environmental issues and reduces buffer capacity of the leaves; consequently the leaves become chlorotic and cease to function. The excess sulfur dioxide causes injury to the cells of a plant [12]. Therefore, a suitable *green* methodology is required for desulfurization of such oils so that the extracted sulfur cannot cause such harmful effects. In this regard, a desulfurization process with simultaneous formation of sulfide nanoparticle not only minimizes the possibility of sulfur poisoning, but also

\*Corresponding author: dolui@tezu.ernet.in

diminishes the requirement for an additional sulfide source for nanoparticle synthesis.

Nowadays, some green methodologies using ionic liquids (ILs) are part of an emerging area of research for desulfurization of fuel oils [13–15]. In such techniques, efficiency of sulfur removal can be achieved to a level of 85% [15]. Still, there is not much literature to be found on simultaneous synthesis of sulfide nanoparticles using the elemental sulfur during desulfurization. As water is regarded as green solvent with its many attributes, an attempt has been made to use it as the reaction medium for the synthesis of cadmium sulfide (CdS) nanoparticles with simultaneous desulfurization of kerosene oil by a one-pot hydrothermal process. Desulfurization yield was achieved to a level of 87% with simultaneous formation of CdS QDs. The obtained CdS nanoparticles and the desulfurized kerosene oil were well characterized by various analytical techniques. The process used here avoids chemical poisoning and other hazardous effects of sulfur. Here, sulfur is eliminated in the form of CdS QDs, which is an important optical material.

## 2 EXPERIMENTAL

### 2.1 Materials

Raw commercial kerosene oil (contains 0.41% sulfur) was purchased from a local market.  $\text{CdCl}_2$  was purchased from Sigma Aldrich. Thioglycolic acid (TGA) and NaOH were purchased from Merck India. All the chemicals were used as received without any further purification.

### 2.2 Synthesis of CdS Nanoparticles and Desulfurization of Kerosene Oil

Simultaneous synthesis of CdS nanoparticles and desulfurization of kerosene oil was carried out by one-pot hydrothermal process. Briefly,  $4 \times 10^{-4}$  mol  $\text{CdCl}_2$  solution was prepared in 40 mL doubled distilled water and 0.1 mL of TGA, 2.4 mL kerosene, and 20 mL 1M NaOH were added to the mixture with continuous stirring for 2 h at room temperature (27 °C). The mixture was then transferred to a teflon-sealed autoclave of 100 mL capacity and kept in a hot-air oven at 120 °C. After a defined time period, the autoclave was removed from the oven and allowed to cool to room temperature. The treated kerosene was separated for sulfur analysis and the yellow precipitate was washed thoroughly with distilled water followed by acetone and finally dried in a vacuum oven at 50 °C. In a similar way, three sets of reactions were carried out for different reaction times.

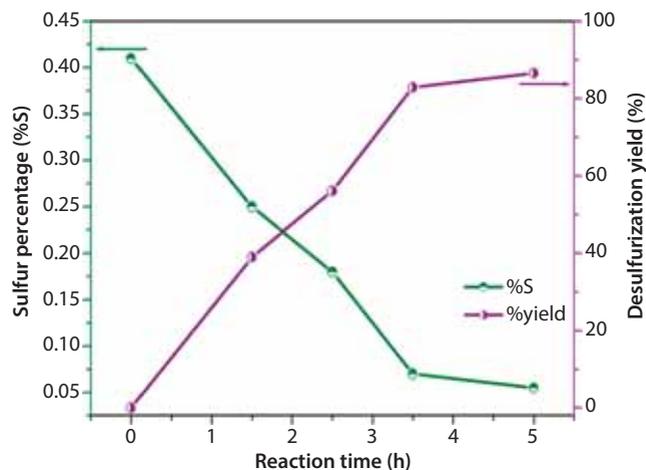
## 2.3 Characterization

The percentage of sulfur content in both untreated and treated kerosene was determined by the S-144DR-Leco sulfur analyzer (model no. 606-000-300). The morphology as well as size of the CdS nanoparticles were investigated by transmission electron microscopy (TEM) (model JEM 2100) with an acceleration voltage of 200 kV. Elemental analysis of the samples was done by energy dispersive X-ray spectroscopy (EDX) (model JSM6390LV). To study the structural characteristics of the synthesized CdS nanoparticles, X-ray diffraction (XRD) spectra was recorded in a Rigaku X-ray diffractometer (Miniflex, UK) under 24  $\text{CuK}\alpha$  ( $\lambda = 0.154$  nm) radiation at a scan rate of  $2^\circ \text{min}^{-1}$  in the range of  $10^\circ$ – $80^\circ$ . The ultraviolet-visible (UV-visible) absorption spectra of the nanoparticles was recorded in the range of 200–800 nm using a Shimadzu UV-2550 UV-visible spectrophotometer taking water as solvent. The photoluminescence (PL) analysis of the synthesized QDs was done using a Perkin Elmer LS55 fluorescence spectrometer in the range of 250–800 nm (excitation wavelength of 350 nm).

## 3 RESULTS AND DISCUSSION

### 3.1 Determination of Sulfur Content in Kerosene

Figure 1 shows the variation of sulfur percentage in kerosene oil as a function of reaction time. The sulfur content decreases to 0.055% for a reaction period of 5 h. The more the reaction time, the more pronounced is the effect, i.e., most of the elemental sulfur has been converted to CdS nanoparticle. Finally, the efficiency

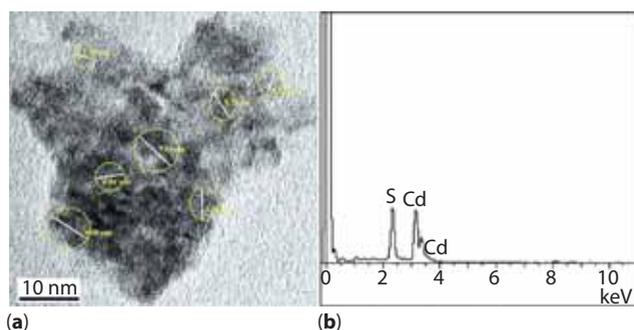


**Figure 1** Sulfur content (%) in kerosene and the desulfurization yield (%) with reaction time.

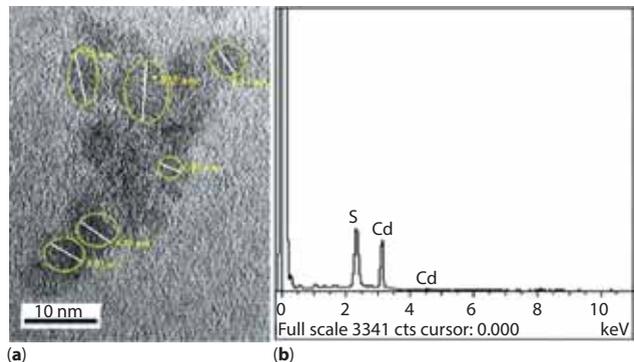
of sulfur removal is achieved to a level of 87% for the 5 h reaction time.

### 3.2 TEM-EDX Analysis

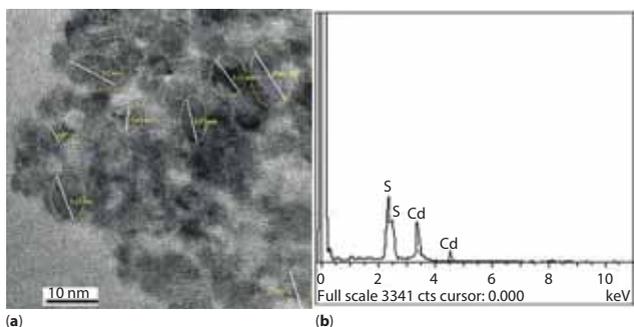
A detailed morphological study of the synthesized CdS nanocrystals is revealed by TEM analysis. Figures 2–4 show the representative TEM micrographs of a set of three CdS nanoparticles prepared at different reaction times. In each micrograph the individual nanoparticles are labeled by green circles. The formation of well-defined and irregular shaped QD nanostructures



**Figure 2** (a) HRTEM image and (b) EDX spectrum of CdS nanoparticles prepared at 1.5 h.



**Figure 3** (a) HRTEM image and (b) EDX spectrum of CdS nanoparticles prepared at 2.5 h.

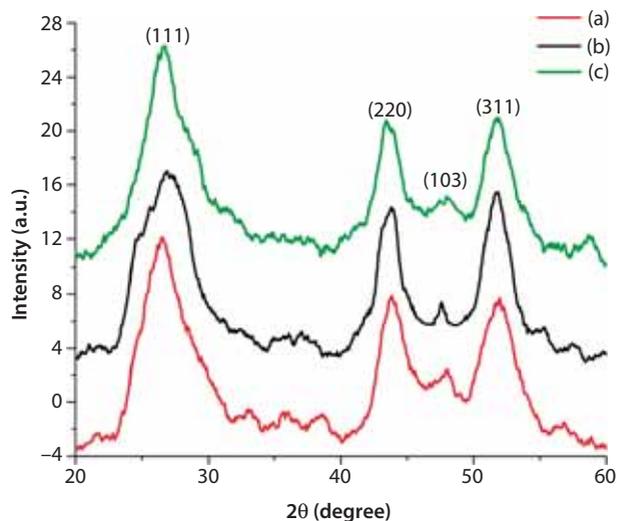


**Figure 4** (a) HRTEM image and (b) EDX spectrum of CdS nanoparticles prepared at 5 h.

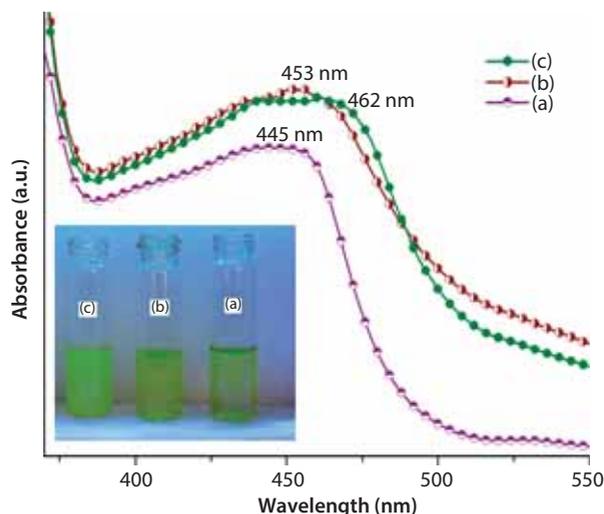
is evident from the TEM micrographs. A wide distribution of size is observed for particles formed at a reaction time of 1.5 h, with an average size of  $\sim 5.4$  nm. With an increase in reaction time from 2.5 to 5 h, the particle size increases from 5.6 to 8.1 nm. The elemental sulfur present in the oil is consumed to form sulfide nanoparticles. Therefore, with an increase in reaction time more elemental sulfur is consumed in the nanoparticle synthesis, thereby gradually increasing the particle size with reaction time. EDX analysis confirms the presence of Cd and S in the nanostructures.

### 3.3 XRD Analysis

To investigate the crystal structure of the prepared QDs XRD analysis was performed. Figure 5 shows the XRD pattern of CdS QDs prepared at different reaction times. The presence of broad peaks indicates the formation of very small size QDs. The peaks at  $26.45^\circ$ ,  $43.85^\circ$  and  $52.0^\circ$  correspond respectively to the reflections from (111), (220) and (311) planes of the simple cubic phase of CdS nanoparticles having zinc blende structure [16]. In addition, there is one additional peak located at  $48.05^\circ$  which corresponds to the (103) reflection of the hexagonal phase of CdS. In bulk form, CdS generally crystallizes in hexagonal (wurtzite) structure; as it approaches towards the range of QDs, the cubic phase of CdS becomes dominant in XRD spectra. Since the size of QDs are somewhat larger (5–8 nm), some sort of hexagonal properties, apart from the cubic phase, appear in the structure as a consequence of which the small intensity peak for (103) reflection appears in the XRD spectra [16]. With an increase in reaction time the FWHM of (220) peak decreases, which shows better crystalline



**Figure 5** XRD pattern of CdS quantum dots prepared at different times: (a) 1.5 h, (b) 2.5 h and (c) 5 h.



**Figure 6** UV-visible spectra of CdS nanoparticles prepared at different reaction times: (a) 1.5 h, (b) 2.5 h and (c) 5 h. Inset shows photographs taken under UV light of CdS QDs prepared at different times: (a) 1.5 h, (b) 2.5 h and (c) 5 h.

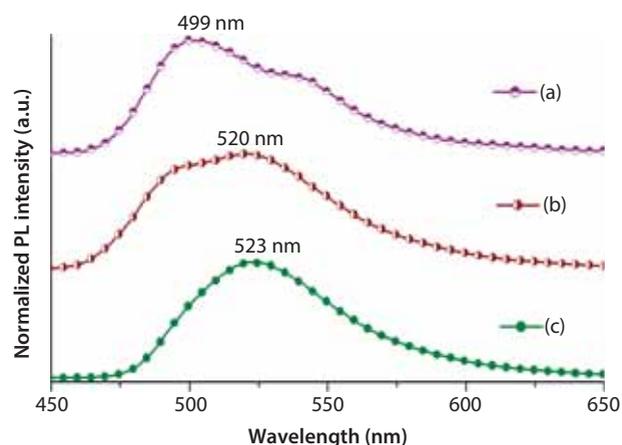
structure with increased size [17]. Average crystallite size can be determined from Scherrer's equation and it is observed that with an increase in reaction time the crystallite size increases from 3.61 nm to 4.63 nm.

### 3.4 UV-Visible Analysis

Figure 6 depicts the UV-visible spectra of CdS nanoparticles prepared at three different time periods. The spectra show an absorption maximum at  $\sim 445$  nm which is due to the formation of wide band gap CdS nanoparticles [18]. It is observed that with an increase in reaction time, the UV-visible spectra remarkably shift towards a higher wavelength, up to 462 nm. This arises due to the increased size of quantum dots with time that reduces the energy gap between conduction band and valence band of semiconductor quantum dots as a result of quantum confinement effect [18]. These results can be correlated with the TEM analysis. The inset of Figure 6 shows the photographs taken under UV light of QD solutions synthesized at different reaction times. The images also indicate the difference in color of the solutions that signifies change in particle diameter with reaction time.

### 3.5 PL Analysis

Figure 7 presents the normalized PL spectra of CdS QDs synthesized at three different reaction times. A broad and intense peak is observed at around 523 nm of the PL spectra, which can be described by the band edge emission of CdS QDs [19]. With a decrease in



**Figure 7** PL spectra of CdS nanoparticles prepared at different reaction times: (a) 1.5 h, (b) 2.5 h and (c) 5 h.

diameter of the QDs the band shows a blue-shift, from 523 nm to a minimum wavelength of 499 nm, i.e., band edge emission energy increases with the decrease in size of the QDs from 8.1 nm to 5.4 nm. The PL quantum yield ( $\phi$ ) for all the QD samples are determined using the following formula [20,21]:

$$\phi = \phi' \times (I/I') \times (A'/A) \times (n/n')^2 \quad (i)$$

Here,  $\phi$  (sample),  $\phi'$  (standard): quantum yield

$I$  (sample),  $I'$  (standard): integrated emission peak area at a given wavelength

$A$  (sample),  $A'$  (standard): absorption intensities at the same wavelength used for PL excitation

$n$  (sample),  $n'$  (standard): refractive index of the solvent

Taking anthracene in ethanol media as the standard ( $\phi'$ : 27%), the quantum yield for the QDs are found to be 5.43%, 2.5% and 1.58% respectively for the CdS QDs synthesized at 1.5 h, 2.5 h and 5 h. The increased value of quantum yield with decrease in size of the QDs indicates an increase in surface states which facilitate the radiative emission enormously [20].

## 4 CONCLUSION

The method used here avoids chemical poisoning and other hazardous effects of sulfur. We have successfully prepared CdS QDs with simultaneous desulfurization of kerosene oil. The desulfurization yield gradually increases with reaction time and it reaches a maximum value of 87% for a reaction time of 5 h. The percentage of sulfur content can be decreased to as low as 0.055% for a reaction period of 5 h. TEM images confirmed the formation of CdS QDs with particle size 5.4–8.1 nm. XRD analysis revealed that with an increase in reaction time the crystallite size increases from 3.61 to 4.63 nm.

The particle size of synthesized QDs increased from 5.4 to 8.1 nm when the reaction time was increased from 1.5 to 5 h. As an overall conclusion we can say that this simple hydrothermal method seems to be a promising route to synthesize CdS QDs with simultaneous desulfurization of kerosene oil. In addition, the eliminated sulfur in the form of CdS QDs can contribute to decorate an important class of nanomaterials to be used in diverse fields of application like biological labels, biosensors, light-emitting diodes, lasers, electronic devices and many more.

## ACKNOWLEDGMENT

This work was financially supported by the Department of Electronics and Information Technology, New Delhi, India (Sanction No. 1(11)/2012-EMCD dated 5.3.2013). The authors also acknowledge SAIF, NEHU, Meghalaya, India, NEIST, Assam, India and SAIC, Tezpur University, India, for analytical support.

## REFERENCES

1. F.M. Collins, A.R. Lucy, and C. Sharp. Oxidative desulphurisation of oils via hydrogen peroxide and heteropolyanion catalysis. *J. Mol. Catal. A: Chem.* **117**, 397–403 (1997).
2. W.L. Fang. Inventory of U. S. Greenhouse Gas Emissions and Sinks, (1990-2003).
3. G.A. Emison. United States Environmental Protection Agency, Office of Air Quality Planning and Standards, (2000).
4. S.S. Shih, S.M.L.A. Green, and M.S. Sarli. Deep desulfurization of distillates. *Ind. Eng. Chem. Res.* **31**, 1232–1235 (1992).
5. A.E. Dunstan and B.T. Brooks, Refining of Gasoline and Kerosene by Hypochlorites. *J. Ind. Eng. Chem.* **14**(12), 1112–1114 (1922).
6. S. Otsuki, T. Nonaka, N. Takashima, W. Qian, A. Ishihara, T. Imai, and T. Kabe, Oxidative desulfurization of light gas oil and vacuum gas oil by oxidation and solvent extraction. *Energy Fuels* **14**, 1232-1239 (2000).
7. P.S. Tam, J.R. Kittrell, and J.W. Eldridge, Desulfurization of fuel oil by oxidation and extraction. 1. enhancement of extraction oil yield. *Ind. Eng. Chem. Res.* **29**, 321–324 (1990).
8. F.A. Duarte, P. de A. Mello, C.A. Bizzi, M.A.G. Nunes, E.M. Moreira, M.S. Alencar, H.N. Motta, V.L. Dressler, and E.M.M. Flores, Sulfur removal from hydrotreated petroleum fractions using ultrasound-assisted oxidative desulfurization process. *Fuel* **90**(6), 2158–2164 (2011).
9. M. Shakirullah, I. Ahmad, W. Ahmad, and M. Ishaq, Desulphurization study of petroleum products through extraction with aqueous ionic liquids. *J. Chil. Chem. Soc.* **55**(2), 179–183 (2010).
10. A.G. Akhmadullina and R.M. Akhmadullin, Desulphurization of petroleum products and sewage decontamination using new advantages of heterogeneous catalyst. *Rio Oil & Gas Expo and Conference* 1–9 (2012).
11. V.C. Srivastava, An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances* **2**, 759–783 (2012).
12. M.D. Thomas, R.H. Hendricks, and G.R. Hill, Sulfur metabolism of plants: Effect of sulfur dioxide on vegetation. *Ind. Eng. Chem.* **42**(11), 2231–2235 (1950).
13. S. Zhang and Z.C. Zhang, Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature. *Green Chem.* **4**, 376–379 (2002).
14. A. Bosmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, and P. Wasserscheid, Deep desulfurization of diesel fuel by extraction with ionic liquids. *Chem. Commun.* **23**, 2494–2495 (2001).
15. W.H. Lo, H.Y. Yang, and G.T. Wei, One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids. *Green Chem.* **5**(5), 639–642 (2003).
16. P. Nandakumar, C. Vijayan, K. Dhanalakshmi, G. Sundararajan, P.K. Nair, and Y.V.G.S. Murti, Synthesis and characterization of CdS nanocrystals in a perfluorinated ionomer (Nafion). *Mater. Sci. Eng. B.* **83**, 61–65 (2001).
17. M. Tanveer, A. Habib, and M.B. Khan, Structural and optical properties of electrospun ZnO nanofibres applied to P3HT:PCBM organic photovoltaic devices. *J. Exp. Nanosci.* **10**(8), 640–650 (2015).
18. K.M. Mullaugh and G.W. Luther III, Spectroscopic determination of the size of cadmium sulfide nanoparticles formed under environmentally relevant conditions. *J. Environ. Monit.* **12**(4), 890–897 (2010).
19. P. Nandakumar, C. Vijayan, and Y.V.G.S. Murti, Optical absorption and photoluminescence studies on CdS quantum dots in Nafion. *J. Appl. Phys.* **91**(3), 1509–1514 (2002).
20. N. Paul, A. Deka, and D. Mohanta, Augmented photocatalytic activity and luminescence response of Tb<sup>3+</sup> doped nanoscale titania systems. *J. Appl. Phys.* **116**(14), 144902 (2014).
21. Z. Deng, F.L. Lie, S. Shen, I. Ghosh, M. Mansuripurand, and A.J. Muscat, Water-based route to ligand-selective synthesis of ZnSe and Cd-doped ZnSe quantum dots with tunable ultraviolet A to blue photoluminescence. *Langmuir* **25**, 434–442 (2009).