Video Article

Synthesis of Ligand-free CdS Nanoparticles within a Sulfur Copolymer Matrix

Trevor R. Martin^{1,2,3}, Katherine A. Mazzio⁴, Hugh W. Hillhouse^{2,3,5}, Christine K. Luscombe^{1,2,3,6}

¹Department of Materials Science and Engineering, University of Washington

²Molecular Engineering and Sciences Institute, University of Washington

³Clean Energy Institute, University of Washington

⁴Institut für Nanospektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH

⁵Department of Chemical Engineering, University of Washington

⁶Department of Chemistry, University of Washington

Correspondence to: Christine K. Luscombe at luscombe@uw.edu

URL: <http://www.jove.com/video/54047>

DOI: [doi:10.3791/54047](https://doi.org/10.3791/54047)

Keywords: Chemistry, Issue 111, nanoparticles, nanocrystals, synthesis, cadmium sulfide, sulfur polymer, elemental sulfur, ligands

Date Published: 5/1/2016

Citation: Martin, T.R., Mazzio, K.A., Hillhouse, H.W., Luscombe, C.K. Synthesis of Ligand-free CdS Nanoparticles within a Sulfur Copolymer Matrix. *J. Vis. Exp.* (111), e54047, doi:10.3791/54047 (2016).

Abstract

Aliphatic ligands are typically used during the synthesis of nanoparticles to help mediate their growth in addition to operating as high-temperature solvents. These coordinating ligands help solubilize and stabilize the nanoparticles while in solution, and can influence the resulting size and reactivity of the nanoparticles during their formation. Despite the ubiquity of using ligands during synthesis, the presence of aliphatic ligands on the nanoparticle surface can result in a number of problems during the end use of the nanoparticles, necessitating further ligand stripping or ligand exchange procedures. We have developed a way to synthesize cadmium sulfide (CdS) nanoparticles using a unique sulfur copolymer. This sulfur copolymer is primarily composed of elemental sulfur, which is a cheap and abundant material. The sulfur copolymer has the advantages of operating both as a high temperature solvent and as a sulfur source, which can react with a cadmium precursor during nanoparticle synthesis, resulting in the generation of ligand free CdS. During the reaction, only some of the copolymer is consumed to produce CdS, while the rest remains in the polymeric state, thereby producing a nanocomposite material. Once the reaction is finished, the copolymer stabilizes the nanoparticles within a solid polymeric matrix. The copolymer can then be removed before the nanoparticles are used, which produces nanoparticles that do not have organic coordinating ligands. This nascent synthesis technique presents a method to produce metal-sulfide nanoparticles for a wide variety of applications where the presence of organic ligands is not desired.

Video Link

The video component of this article can be found at <http://www.jove.com/video/54047/>

Introduction

Although proven useful for synthesis, conventional aliphatic ligands present a number of challenges for the implementation of nanoparticles in photonic and electrochemical devices. Aliphatic ligands are highly insulating, hydrophobic, and constitute a significant barrier to electrochemical surface reactions.¹ Accordingly, several studies have developed ligand exchange and ligand stripping protocols that replace these aliphatic ligands with functional moieties or that strip away the ligands to reveal a bare nanoparticle surface.¹⁻³ These reactions, however, pose several intrinsic problems. They significantly add to the complexity of the synthetic process, do not always go to completion, and can deteriorate the surface of the nanoparticles, which can in turn impose significant problems during device fabrication when using these techniques.⁴

We have developed a sulfur copolymer that can be used as both a high temperature solvent and sulfur source during the synthesis of CdS nanoparticles.⁵ This copolymer is based on a network copolymer developed by Chung *et al.* that uses elemental sulfur and 1,3-diisopropenylbenzene (DIB).⁶ In our case, a methylstyrene monomer is implemented instead of DIB. The methylstyrene monomer limits cross-linking reactions, which would otherwise produce a high molecular weight network copolymer.^{5,6} The presence of only one vinylic functional group on the methylstyrene monomer promotes the formation of oligomeric radicals once heated, which allows the sulfur copolymer to operate as a liquid solvent and sulfur source in parallel during the nanoparticle synthesis.⁵ Specifically, the sulfur polymer is produced by heating elemental sulfur to 150 °C, which causes the S₈ rings to transition into a linearly structured liquid sulfur diradical form. Next, methylstyrene is injected into the liquid sulfur in a 1:50 molar ratio of methylstyrene molecules to sulfur atoms.⁵ The methylstyrene double bond reacts with the sulfur chains to produce the copolymer, as presented in **Figure 1**.⁵ The sulfur copolymer is then cooled and the cadmium precursor is added. This mixture is then reheated to 200 °C, during which, the sulfur copolymer melts and the nanoparticle nucleation and growth processes are initiated within the solution.⁵ A 20:1 molar ratio of sulfur to cadmium precursor is used, so that only some of the sulfur is consumed during the reaction.⁵ This copolymer stabilizes the nanoparticles by suspending them within a solid polymer matrix once the reaction has been terminated.⁵ The copolymer can be removed after the synthesis, resulting in the production of CdS nanoparticles that do not have organic coordinating ligands, as depicted in **Figure 2**.⁵

The synthetic method presented in this work is relatively simple in comparison with other methods presented in the literature.^{1-3,7} It is applicable for a diverse range of applications where traditional ligated nanoparticles have proven problematic or undesirable. This technique can open doors to higher throughput testing, where one batch of nanoparticles can be used to examine a complete spectrum of subsequent functionalizations without the need for complex and time consuming ligand stripping or exchange procedures.^{2,4,8,9} These unligated nanoparticles also offer opportunities to reduce the number of carbon defects commonly observed in printed nanoparticle devices, by eliminating the carbon source.¹⁰⁻¹⁶ This detailed protocol is intended to help others implement this new method and to help spur its active use in a variety of fields that will find it of particular significance.

Protocol

Caution: Cadmium precursors are highly toxic and must be handled with great care. Wear proper protective equipment, use appropriate engineering controls and consult relevant materials safety data sheets (MSDS). In addition, the formation of nanoparticles may present additional hazards. The reactions described herein are conducted with a standard vacuum gas manifold, in order to conduct the experiments within an inert atmosphere. All chemicals were purchased commercially and used as received. This protocol is based upon a previously developed synthetic method, which we recently described elsewhere.⁵

1. Sulfur Copolymer Synthesis

1. Preparation of Molten Elemental Sulfur

1. Place elemental sulfur (4 g, 124.8 mmol, S₈, 99.5%) in a 50 ml three neck flask with an attached condenser and temperature probe. Perform pump and purge cycles with vacuum and nitrogen several times.
2. Heat under nitrogen to 150 °C with stirring, which will cause the sulfur to become a yellow colored liquid.

2. Preparation of Sulfur Copolymer

1. Once all of the sulfur has dissolved into the liquid, immediately inject α -methylstyrene (330 μ l, 2.5 mmol, 99%) into the solution.
2. Heat solution to 185 °C with stirring at 500 rpm for 10 min. As the copolymer forms, the solution will change color from yellow to orange, finally producing a deep red color.
3. Remove the solution from heat and cool to room temperature. As it cools, the copolymer will slowly crystallize to form an orange rubbery solid. At this stage, the copolymer can be stored at room temperature for a subsequent synthesis or it can be used immediately.

2. CdS Nanoparticle Synthesis

1. Add cadmium acetylacetonate (Cd(acac), 900 mg, 2.9 mmol 99.9%) to the three neck flask from the previous step, so that the powder is placed evenly on top of the solid sulfur copolymer (4.0 g, 116 mmol).
2. Perform pump and purge cycles on the flask with nitrogen and vacuum several times.
3. Heat the solution to 200 °C under nitrogen with stirring. The sulfur copolymer will melt and mix with the cadmium precursor, and the nanoparticle nucleation and growth processes will begin.
4. Allow the nanoparticles to grow for 30 min.
Note: Varying the reaction time will influence the growth of the nanoparticles, so it is possible to tune the final size of the nanoparticles.⁵ A 30 min reaction time will with a size range of 7-10 nm.⁵
5. Remove the solution from heat and allow to cool to room temperature.
6. Once cooled, remove the solid nanocomposite from the flask and store at room temperature.

3. Remove the Sulfur Copolymer and Isolate the Nanoparticles

1. Removal of the Sulfur Copolymer

1. Place the nanocomposite (200 mg) in a 20 ml glass vial and add chloroform (20 ml).
2. Place the vial in an ultrasonicator and sonicate for 1 hr, to break up the nanocomposite and suspend the nanoparticles within the solution.
3. Separate the solution into two 30 ml centrifuge tubes and add another 20 ml of chloroform to each.
4. Centrifuge the solution at 8,736 x g (relative centrifugal force) for 15 min.
5. Decant the sulfur copolymer from the centrifuge tubes, making sure to not disturb the settled nanoparticles.

2. Isolation of the Nanoparticles

1. Re-disperse the settled nanoparticles by adding chloroform to each centrifuge tube (30 ml) and sonicate for 15 min.
2. Repeat the steps described in sections 3.1.4, 3.1.5 and 3.2.1 three more times to ensure that all of the sulfur copolymer has been removed. Once all of the sulfur copolymer is removed, the decanted solution will no longer have an orange color.
3. Collect the final nanoparticles by adding chloroform (2 ml) to each centrifuge tube.
4. Combine the collected nanoparticles in one 20 ml glass vial (4 ml solution total) and place the glass vial under vacuum to remove all of the chloroform and to dry the nanoparticles. At this stage, the mass of the resulting nanoparticles can be determined and compared to the starting mass of the precursors in order to determine the yield of the reaction using molar ratios of the starting material and product.

4. Characterize the CdS Nanoparticles

1. Transmission Electron Microscopy

1. Dilute the isolated nanoparticles (20 mg) in chloroform (20 ml) and ultrasonicate for 1 hr.
2. Dilute this solution in chloroform (5 drops/5 ml) and sonicate for 15 min.
3. Drop the final solution onto an ultrathin carbon film substrate with holey carbon support films on a 400 mesh copper Transmission Electron Microscopy (TEM) grid.
4. Place the TEM grid in a glass vial and hold under vacuum overnight, to remove any residual solvent from the sample.
5. Once the drying is completed, acquire TEM images using a 200 kV accelerating voltage, a spot size of 3 and an attached Energy Dispersive X-ray Spectroscopy (EDS) detector.

2. X-ray Diffraction

1. Dilute the isolated nanoparticles in chloroform (10 mg/ml).
2. Clean molybdenum coated soda lime glass substrates (1 cm^2) by sonicating in detergent, deionized water, acetone and isopropyl alcohol, each for 10 min. Finally, clean the substrates in an air plasma cleaner for 10 min prior to drop casting.
3. Drop cast the solution from 4.2.1 onto the substrates from 4.2.2 in 7 μl increments.
4. Once the films have dried, acquire X-ray Diffraction (XRD) data. Collect data using 7,000 data points at a scan rate of 1 data point per second with a Cu-K α X-ray source and an incident wavelength of 1.54059 Å.

3. Solution Spectroscopy

1. Disperse the isolated nanoparticles (0.1 mg/ml) in chloroform and sonicate for 30 min and place samples in a sealed quartz cuvette.
 2. Disperse the nanocomposite from section 2.6 and the sulfur copolymer from section 1.2.3 in formamide (1 mg/ml), stir at 700 rpm, and heat to 70 °C to facilitate suspension of the material.
 3. Acquire photoluminescence (PL) and absorbance spectra for all three samples. Conduct optical absorbance measurements using a spectrometer with a triple detector that extends across the ultraviolet, visible and near infrared ranges (UV-Vis-NIR). Conduct PL measurements using a fluorescence spectrophotometer with an excitation wavelength of 330 nm.
- NOTE: The specific protocol for characterizing nanoparticles using the techniques discussed in sections 4.1.5, 4.2.4, and 4.3.2 varies widely depending on the nature of the specific equipment used, so we present only general characterization parameters here. The interested reader is directed to several review papers for more information regarding using these analysis techniques for CdS nanoparticles.¹⁷⁻¹⁹

Representative Results

The TEM image in **Figure 3a** shows small CdS nanoparticles (3–4 nm) that have nucleated within the sulfur copolymer before the sulfur copolymer has been completely removed. The image in **Figure 3a** was acquired by taking an aliquot of the nanoparticle solution immediately after the solution reached 200 °C. **Figure 3b** shows larger nanoparticles (7–10 nm) that have grown in solution for 30 min before the sulfur copolymer has been completely removed. **Figure 3c** shows a higher magnification image of the highlighted area in **Figure 3b**. One nanoparticle in **Figure 3c** has a particularly clear atomic plane spacing that was measured to be 3.3 Å. The 3.3 Å atomic plane spacing is consistent with the (111) plane spacing of zinc-blende CdS or the (002) plane spacing of wurtzite CdS. **Figure 3d** shows that once the sulfur copolymer is completely removed and dissolved in chloroform, the nanoparticles will aggregate together. The EDS data presented in **Figure 3d** confirms the stoichiometry of CdS (nearly 1:1) and confirms that the sulfur copolymer has been effectively removed.

In a previous publication, we used Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance spectroscopy (^1H NMR) to show that once the sulfur copolymer is completely removed, these nanoparticles do not have conventional organic ligands.⁵ One study by Nag *et al.* showed that metal-sulfide nanoparticles can be effectively ligated with anionic sulfur species.⁷ We posit that the nanoparticles made using this method have similarly structured sulfur species on the nanoparticle surface. The EDS data presented in **Figure 3d** shows a slight stoichiometric excess of sulfur, which is in accordance with the presence of sulfur species on the nanoparticle surface.

The XRD pattern for the drop cast nanoparticle thin films is presented in **Figure 4** and is consistent with the formation of wurtzite and possibly also zinc blende structured CdS. The peak located at 26.6 degrees corresponds to an atomic plane spacing of 3.3 Å, which is consistent with the (111) plane spacing of zinc-blende CdS or the (002) plane spacing of wurtzite CdS and corroborates the planar spacing seen in the TEM image of **Figure 3c**.

The sulfur copolymer and the nanocomposite were analyzed using UV-Vis spectroscopy as shown in **Figure 5**. Since the concentrations of each dispersion are equal, the data show that the nanocomposite exhibits a significantly enhanced absorbance in comparison to only the sulfur copolymer. The photoluminescence data presented in **Figure 6** show that the nanocomposite exhibits a peak that is blue-shifted from the bulk bandgap of CdS (510 nm, 2.4 eV), while the sulfur copolymer peak is comparatively small.

The isolated nanoparticles were also examined using UV-Vis-NIR and PL spectroscopy once the sulfur copolymer was removed. **Figure 7** shows both the UV-Vis-NIR and PL data. In **Figure 6**, the nanoparticles have a broad PL peak that is centered at the bulk bandgap of CdS and a correspondingly broad absorption spectrum with a small absorption edge that is in the range of 450–550 nm. Once the sulfur polymer is removed, the nanoparticle surface is no longer passivated and contains surface defects due to the presence of dangling bonds. This leads to the presence of new surface-mediated energy states that subsequently broaden and red-shift the PL and absorbance spectra in comparison to the spectra presented in **Figures 5** and **6** for the nanocomposite material.^{18,20-22} In addition, the polydispersity of the nanoparticles results in a population of nanoparticles that exhibit quantum confinement effects, which also broadens the spectra.²³ Therefore, in conjunction with our previous work, this data supports the claim that these nanoparticles do not have conventional defect passivating organic ligands once the sulfur copolymer is removed.⁵ Furthermore, this data shows that the sulfur copolymer passivates the surface defects of the CdS nanoparticles prior to its removal.

Figure 1. Synthesis and structure of sulfur copolymer. Elemental sulfur is heated to produce a linearly structured liquid sulfur diradical, which reacts with methylstyrene to produce the sulfur copolymer. [Please click here to view a larger version of this figure.](#)

Figure 2. Nanoparticle growth and isolation. The CdS nanoparticles nucleate and grow within the sulfur copolymer. Once the reaction is complete, the sulfur copolymer is removed to produce ligand-free CdS nanoparticles. [Please click here to view a larger version of this figure.](#)

Figure 3. TEM images of isolated CdS nanoparticles. **a)** 3-4 nm CdS nanoparticles beginning to grow within the copolymer. **b)** 7-10 nm nanoparticles once the reaction is terminated. S copolymer is still present at this stage. **c)** Magnified image of highlighted region in **b**. **d)** TEM image after removal of S copolymer. Inset shows EDS data. [Please click here to view a larger version of this figure.](#)

Figure 4. XRD pattern for CdS nanoparticle films. XRD pattern is consistent with the formation of wurtzite or zinc-blende CdS. The molybdenum peak is due to the substrate. [Please click here to view a larger version of this figure.](#)

Figure 5. Absorbance spectroscopy for sulfur copolymer and nanocomposite. The nanocomposite exhibits a significantly enhanced absorption peak in comparison to the sulfur copolymer alone. Both materials have equal concentrations while in dispersion. [Please click here to view a larger version of this figure.](#)

Figure 6. Photoluminescence spectroscopy for sulfur copolymer and nanocomposite. The nanocomposite exhibits a peak that is blue-shifted from the bulk bandgap of CdS (510 nm, 2.4 eV), while the sulfur copolymer exhibits comparatively little photoluminescence. [Please click here to view a larger version of this figure.](#)

Figure 7. Absorbance and Photoluminescence spectroscopy of ligand-free CdS nanoparticles. The PL data show a broad peak centered at 510 nm. The UV-Vis-NIR data show a broad absorption curve with a weak absorption shoulder in the range of 450-550 nm. [Please click here to view a larger version of this figure.](#)

Discussion

We have developed a method to synthesize CdS nanoparticles within a sulfur copolymer matrix. This sulfur copolymer is composed of elemental sulfur and methylstyrene.⁵ An important feature of this method is that the copolymer can be used as both a high-temperature solvent and a sulfur source that reacts with a cadmium precursor to produce CdS nanoparticles in solution.⁵ The critical step in the procedure is the synthesis of the sulfur copolymer with a suitable ratio of methylstyrene and sulfur. The use of methylstyrene and in the appropriate concentration is important to form the copolymer that can be stored as a powder at room temperature, and then be heated to produce a liquid to allow the nanoparticle synthesis to occur. During the synthesis, only some of the sulfur reacts with the cadmium precursor, while the remainder stays within the sulfur copolymer.⁵ Once the reaction solution is cooled and solidified, this procedure produces CdS nanoparticles suspended within a sulfur copolymer matrix.⁵ The copolymer can subsequently be removed, producing nanoparticles that do not have conventional organic ligands.⁵ A limitation of our method however, is that once the copolymer is removed, the nanoparticles are prone to aggregation, which can be prevented when conventional organic ligands are present. This makes it difficult to control the self-assembly of our nanoparticles during film formation. The nanoparticle size can be tuned by varying the reaction time, although another limitation is that this method produces nanoparticles with a higher level of polydispersity in size than conventional techniques,^{5,18} which broadens the absorption and emission spectra of our nanoparticles.

This nascent synthesis method can be useful in a range of fields where the presence of conventional aliphatic ligands diminishes the charge transfer or surface reaction properties of the nanoparticles. Furthermore, this synthesis method is relatively simple in comparison to other methods that require multistep ligand exchange or ligand stripping procedures to remove conventional aliphatic ligands.^{1,4} For example, one set of nanoparticles could be functionalized with a range of ligands to produce nanoparticles with a spectrum of different properties.⁹ In addition, this method could be used to produce nanoparticle based devices where the presence of organic ligands would otherwise introduce unwanted carbon impurities.^{10,12}

Disclosures

The authors disclose no competing financial interests.

Acknowledgements

The authors would like to acknowledge the State of Washington for supporting this research through the University of Washington Clean Energy Institute Exploratory Fellowship Program, and National Science Foundation (NSF) Sustainable Energy Pathway (SEP) Award CHE-1230615.

References

- Rosen, E. L., Buonsanti, R., Llordes, A., Sawvel, A. M., Milliron, D. J., & Helms, B. A. Exceptionally Mild Reactive Stripping of Native Ligands from Nanocrystal Surfaces by Using Meerwein's Salt. *Angew. Chemie Int. Ed.* **51** (3), 684-689, (2012).
- Anderson, N. C., Hendricks, M. P., Choi, J. J., & Owen, J. S. Ligand exchange and the stoichiometry of metal chalcogenide nanocrystals: spectroscopic observation of facile metal-carboxylate displacement and binding. *J. Am. Chem. Soc.* **135** (49), 18536-18548, (2013).
- Owen, J. S., Park, J., Trudeau, P. E., & Alivisatos, A. P. Reaction chemistry and ligand exchange at cadmium-selenide nanocrystal surfaces. *J. Am. Chem. Soc.* **130** (37), 12279-12281, (2008).
- Lokteva, I., Radychev, N., Witt, F., Borchert, H., Parisi, J., & Kolny-Olesiak, J. Surface Treatment of CdSe Nanoparticles for Application in Hybrid Solar Cells: The Effect of Multiple Ligand Exchange with Pyridine. *J. Phys. Chem. C* **114** (29), 12784-12791, (2010).
- Martin, T. R., Mazzi, K. A., Hillhouse, H. W., & Luscombe, C. K. Sulfur copolymer for the direct synthesis of ligand-free CdS nanoparticles. *Chem. Commun.* **51** (56), 11244-11247, (2015).
- Chung, W. J. *et al.* The use of elemental sulfur as an alternative feedstock for polymeric materials. *Nat. Chem.* **5** (6), 518-524, (2013).
- Nag, A., Kovalenko, M. V., Lee, J.-S., Liu, W., Spokoyny, B., & Talapin, D. V Metal-free Inorganic Ligands for Colloidal Nanocrystals: S²⁻, HS⁻, Se²⁻, HSe⁻, Te²⁻, HTe⁻, TeS³⁻, OH⁻, and NH₂⁻ as Surface Ligands. *J. Am. Chem. Soc.* **133** (27), 10612-10620, (2011).
- Dong, A. *et al.* A generalized ligand-exchange strategy enabling sequential surface functionalization of colloidal nanocrystals. *J. Am. Chem. Soc.* **133** (4), 998-1006, (2011).
- Cossairt, B. M., Juhas, P., Billinge, S., & Owen, J. S. Tuning the Surface Structure and Optical Properties of CdSe Clusters Using Coordination Chemistry. *J. Phys. Chem. Lett.* **2** (4), 3075-3080, (2011).
- Lee, E., Park, S. J., Cho, J. W., Gwak, J., Oh, M.-K., & Min, B. K. Nearly carbon-free printable CIGS thin films for solar cell applications. *Sol. Energy Mater. Sol. Cells* **95** (10), 2928-2932, (2011).
- Buchert, C. N., Oleson, K. R., & Hillhouse, H. W. Thin film solar cells from sintered nanocrystals. *Curr. Opin. Chem. Eng.* **2** (2), 168-177, (2013).
- Cai, Y. *et al.* Nanoparticle-induced grain growth of carbon-free solution-processed CuIn(S,Se)₂ solar cell with 6% efficiency. *ACS Appl. Mater. Inter.* **5** (5), 1533-1537, (2013).
- Zhou, H. *et al.* CZTS nanocrystals: a promising approach for next generation thin film photovoltaics. *Energy Environ. Sci.* **6** (10), 2822-2838, (2013).
- Polizzotti, A., Repins, I. L., Noufi, R., Wei, S.-H., & Mitzi, D. B. The state and future prospects of kesterite photovoltaics. *Energy Environ. Sci.* **6** (11), 3171-3182, (2013).
- Suehiro, S. *et al.* Solution-Processed Cu₂ZnSnS₄ Nanocrystal Solar Cells: Efficient Stripping of Surface Insulating Layers using Alkylating Agents. *J. Phys. Chem. C* **118** (2), 804-810, (2013).
- Graessner, B. K. *et al.* Synthesis of (CuInS₂)_{0.5}(ZnS)_{0.5} Alloy Nanocrystals and Their Use for the Fabrication of Solar Cells via Selenization. *Chem. Mater.* **26** (14), 4060-4063, (2014).
- Yin, Y., & Alivisatos, A. P. Colloidal nanocrystal synthesis and the organic-inorganic interface. *Nature* **437** (7059), 664-670, (2005).

18. Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science*. **271** (5251), 933-937, (1996).
19. Alivisatos, A. P. Perspectives on the Physical Chemistry of Semiconductor Nanocrystals. *J. Phys. Chem.* **100** (95), 13226 - 13239, (1996).
20. Xiao, Q., & Xiao, C. Surface-defect-states photoluminescence in CdS nanocrystals prepared by one-step aqueous synthesis method. *Appl. Surf. Sci.* **255** (16), 7111-7114, (2009).
21. Zhang, J. Z. Interfacial Charge Carrier Dynamics of Colloidal Semiconductor Nanoparticles. *J. Phys. Chem. B.* **104** (31), 7239-7253, (2000).
22. Joswig, J.-O., Springborg, M., & Seifert, G. Structural and Electronic Properties of Cadmium Sulfide Clusters. *J. Phys. Chem. B.* **104** (12), 2617-2622, (2000).
23. Unni, C., Philip, D., & Gopchandran, K. G. Studies on optical absorption and photoluminescence of thioglycerol-stabilized CdS quantum dots. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **71** (4), 1402-1407, (2008).