ISSN 2229-5518

Cadmium Selenide Quantum Dots Synthesized by HVPC Growth Technique for Sensing Copper ion Concentrations

Arra C. Quitaneg, Gil Nonato C. Santos

Abstract— Cadmium selenide quantum dots of different radii were synthesized using Horizontal Vapor Phase Crystal (HVPC) Growth Technique. Fluorescence quenching is the sensing mechanism utilized in the study. The synthesized CdSe quantum dots were used effectively in the optical sensing of copper ion concentrations.

Index Terms— Energy gap, Fluorescence quenching, Optical sensing, Photoluminescence, Quantum confinement, Quantum dots, Solid support

1 Introduction

SYNTHESIZING quantum dots have gained enormous attention due to their potential applications such as solar cells optical sensing in vivo molecular and cellular imaging ,etc. [1], [2], [3].

Quantum dots also known as semiconductor nanocrystals or nanocrystallites are nanostructured materials. These semiconductor nanocrystallites, usually composed of II-VI, III-V or IV-VI, are roughly spherical and with sizes typically ranging from 1-12 nanometer (nm) in diameter. Quantum dots have remarkable attractive optoelectronic properties including their high emission quantum yields, size tunable emission profiles and narrow spectral bands. These properties were much different from those of the bulk systems, due to quantum confinement effects [2].

Quantum dots have been used in fabricating solar cells. Quantum dot has widespread biological applications e.g. nanoimaging, cell labeling, nanosensing, drug delivery. Fluorescent nanoparticles such as quantum dots, exhibiting size and composition tunable fluorescence properties, have been used to demonstrate their applicability for imaging and sensing [4],[5],[6].

Fluorescent semiconductor quantum dots have been used for optical nanosensing. Researchers have been developing optical sensors for detecting toxins, heavy metals and other environmental pollutants [2],[7].

Cadmium selenide semiconductor has often been investigated due to its well-known physical properties and potentially controllable band-gap energy in full visible spectral range [8]. Cadmium selenide has a direct band gap of 1.74 eV that can be tuned across the visible spectrum, making it an interesting material for application such as light emitting diodes, in solar scells, non-linear optical material for X-ray detectors and in bio-labeling [9]. When compared to CdS and ZnS, the semiconductor CdSe has a larger bulk exciton radius, hence, any quantum size effects due to the presence of CdSe nanocrystals will be more pronounced and clearly noticeable by optical measurements [10].

Various methods, such as hydrothermal and solvothermal routes, surfactant assisted approach, had been used for the synthesis of nanomaterials [11], [12], [13].Some studies tried to prepare the CdSe quantum dots at mild condition around room temperature [8].

Quantum dot applications were restricted to solution sensing assays and further development in optical sensing is consists of immobilizing quantum dots in suitable supports to fabricate active solid phases for working in flowing solutions. Challenge on integrating quantum dots into appropriate solid supports to develop reliable optosensors was posted by Costa-Fernandez group [2].

Because of the remarkable applications of quantum dots especially in biological labeling, imaging and sensing, this study was conducted. This study answered the challenge of integrating the quantum dots into solid support. The applicability of the synthesized Cadmium selenide

- *Arra C. Quitaneg, Master of Science in Physics, Lecturer, De La Salle – College of St. Benilde-Manila, Philippines. E-mail: arra1028@yahoo.com*
- *Gil Nonato C. Santos, Doctor of Philosophy in Materials Science, Professor, De La Salle University-Manila, Philippines. E-mail: santosg@dlsu.edu.ph*

ISSN 2229-5518

quantum dots in optical sensing of copper ion concentrations was investigated.

2 Experimental Section

2.1 Synthesis and Characterization Cadmium selenide Quantum Dots

Cadmium selenide quantum dots were synthesized using the Horizontal Vapor Phase Crystal Growth (HVPCG) Technique. CdSe quantum dots were synthesized according to the method reported in the literature [14]. Thirty-five (35) mg of CdSe powder with 99.99% purity, ordered from Aldrich Corporation, was used in the study. The fully sealed amorphous silica tube was inserted halfway in the Horizontal Thermolyne furnace, growth time and temperature were set to 4 hrs, 6 hrs, 8 hrs and 600⁰C, 800⁰C, 1000⁰C, 1200⁰C respectively. The tube was retrieved after cooling down to room temperature. The

synthesized nanomat
scanning electron r

dispersive x-ray analysis (Oxford with Link Isis) and photoluminescence spectra (Applied Spectral Imaging SD-300). Brus equation (1) was used in the quantitative description of the grown CdSe quantum dots' radii.

$$\Delta E_g\ (R) = \frac{h^2}{8m_0R^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\ \varepsilon_0\varepsilon_r R} \quad (1)$$

2.2 Optical Sensing of Copper ion Concentrations using the grown CdSe quantum dots

Fluorescence quenching mechanism was the optical sensing mechanism utilized in the study. Copper sulphate solution was used as a source of copper ions. Different concentrations of copper ions were prepared (1.253 x 10^{-4} M, 2.506 x 10^{-4} M,3.759 x 10^{-4} M, 5.012 x 10^{-4} M and 6.260 x 10^{-4} M). Fluorescence quenching was analysed using the change in the photoluminescence spectra as the quencher is introduced to the CdSe quantum dots.

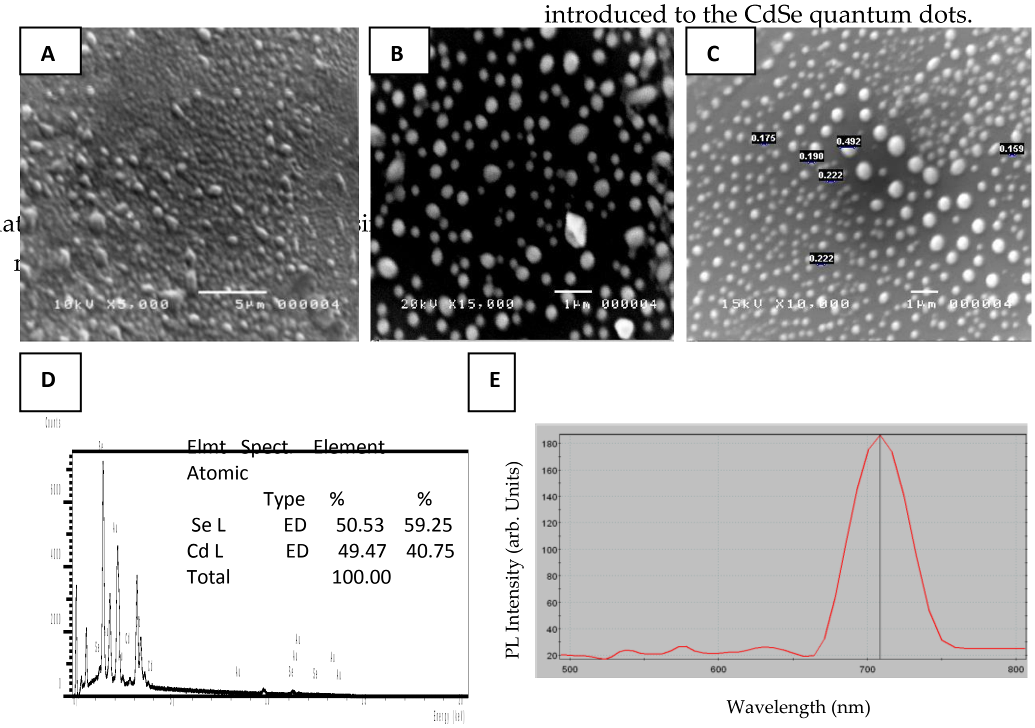

Fig.1. (a-c) SEM images of the synthesized CdSe nanosphere, (d) EDX spectrum of a nanosphere, (e) photoluminescence spectra of CdSe nanosphere

3 Results And Discussion

Cadmium selenide quantum dots were successfully synthesized using HVPC growth technique. Fig 1 presents the SEM images of the synthesized nanospheres. Fig 1 A demonstrated the island growth mechanism or Stranski-Krastanov growth mode of the self-assembled quantum dots. Findings showed that an increased growth temperature favors the growth of larger structures because particle growth and aggregation was enhanced by anything that reinforces atomic or molecular motion [15]. The photoluminescence spectra in Fig 1 has a peak at 708.7 nm and the computed energy gap is 1.749 eV, this value is close to the reported energy gap of 1.74 eV [16].

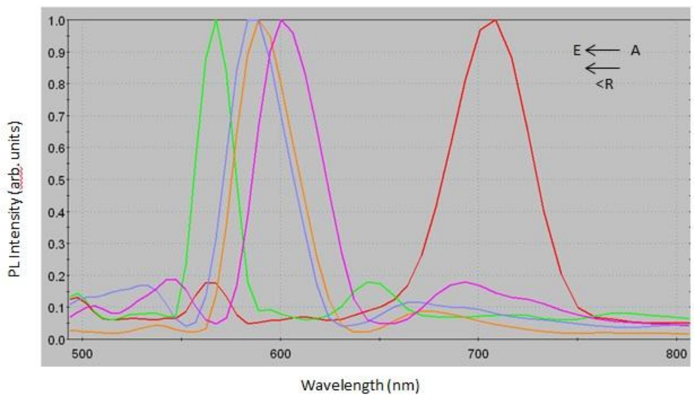

Fig 2. Normalized Photoluminescence spectra of synthesized CdSe quantum dots

This study did not employ high resolution microscope to see the images of quantum dots. Therefore, to investigate quantum confinement effects Photoluminescence study was used.

TABLE 1

QUANTUM COFINEMENT EFFECTS

Sample	Emission Peak (nm)	FWHM (nm)	Energy gap (eV)	Radius (nm)
A	708.70	49.74	1.749	6.84
B	600.60	37.68	2.065	2.19
C	589.21	37.17	2.105	2.08
D	583.66	35.73	2.125	2.04
E	567.58	26.96	2.185	1.91

Table 1 presents the summary of the wavelength, full width at half maximum, energy gap and radius for each sample of CdSe quantum dot. Brus equation was employed in the calculation of the quantum dot's radius. Sample A has an energy gap close to the reported energy gap of bulk CdSe. CdSe has a Bohr radius of approximately 6nm and a CdSe particle smaller than this will exhibit quantum confinement [16]. It was also reported that CdSe quantum dots with FWHM≤40nm exhibit quantum confinement. [17]. In table 1, it can be observed that samples B to E exhibit quantum confinement. In Fig 2, blue-shift in the emission spectra of CdSe quantum dots, as the radius decreases, is also evident. CdSe quantum dots were therefore synthesized through HVPC growth technique.

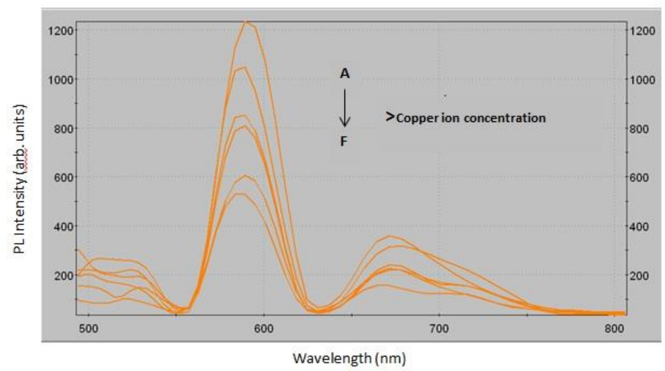

Fig 3. Fluorescence emission spectra of CdSe quantum dots after exposure to different copper ion concentration (10^{-4} M) (a) blank solution, (b) 1.253, (c) 2.506, (d) 3.759, (e) 5.012, and (f) 6.265.

Fig 3 shows the effects of copper ion concentration on the fluorescence intensity of CdSe quantum dots. The fluorescence intensity is of CdSe quantum dots was reduced continuously with an increased concentration of copper ions. Because of its sensitivity to different concentration of copper ions, it can be developed to a sensitive Copper ion sensor.

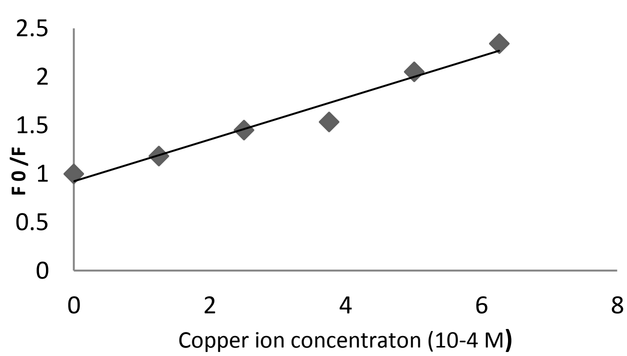

Fig 4. Stern-Volmer plot for the interaction between CdSe quantum dots and copper ions.

The linearity of the plot of F_0/F against copper ion concentration validate the Stern-volmer description of fluorescence quenching. Static and dynamic fluorescence quenching explains the quenching of the intensity of CdSe quantum dots as they are exposed to higher concentration of copper ion. In dynamic quenching, exposing CdSe quantum dot to concentration of copper ions resulted to non-radiative recombination. In static quenching, non-

ISSN 2229-5518

fluorescent CdSe-Cu (II) complex can be formed between Cu (II) and CdSe quantum dots [2].

4 CONCLUSION

The HVPC growth technique was found to be effective in synthesizing CdSe quantum dots in solid support. The synthesized CdSe quantum dot can be applied in optical sensing of copper ions. These quantum dots were found to be sensitive to copper ion concentration, thus , these quantum dots can be used in the development of a sensitive copper ion sensor. Fluorescence quenching of the emission spectra of the CdSe quantum dots can be explained by the presence of both static and dynamic quenching.

ACKNOWLEDGMENT

The work described in this paper was supported by Department of Science and Technology-Science Education Institute, Philippines and De La Salle University Manila.

REFERENCES

[1] S.H. Choi, H. Song, I.K. Park, J.H. Yum, S.S. Kim, S. Lee, Y.E. Sung "Synthesis of size-controlled CdSe quantum dots and characterization of CdSe-conjugated polymer blends for hybrid solar cells," *Journal of Photochemistry and Photobiology A: Chemistry* ,179,pp. 135-141,2006.

[2] J.M Costa- Fernandez, R. Pereiro, A. Sanz-Medel, "The use of luminescent quantum dots for optical sensing," *Trends in Analytical Chemistry*, vol. 25,(3), pp. 207-218,2006.

[3] A.M. Smith, H. Duan, A.M Mhs, S. Nie, "Bioconjugated quantum dots for in vivo molecular and cellular imaging.,"*Advanced Drug Delivery Reviews*, 60, pp. 1226-1240, 2008.

[4] P. Tallury, A. Malhorta, L.M. Byrne, S. Santra, "Nanobioimaging and sensing infectious diseases.,"*Advanced Drug Delivery Reviews, 2008,* doi:10.1016/j.addr.2009.11.014.

[5] H.M.E Azzazy, M.M.H. Mansour, S.C. Kazmierczak, "From diagnostics to therapy: Prospects of quantum dots," *Clinical Biochemistry*, 40, pp. 917-927, 2007.

[6] T. Vo-Dinh, " Nanosensing at the single cell level,"*Spectrochimica Acta Part B*,63, pp. 95-103, 2007.

[7] C. Wang, J. Zhao, Y. Wang, N. Lou, Q. Ma, X. Su, " Sensitive Hg (II) ion detection by fluorescent multilayer films fabricated with quantum dots,"*Sensors and Actuators B* 139, pp. 476-482, 2009.

[8] J.H. Yoon, W.S. Chae, S.J. Im, Y.R. Kim, "Mild synthesis of ultra-small CdSe quantum dots in ethylediamine Solution," *Materials Letters*, 59, pp. 1430-1433. 2005.

[9] P.K. Khanna, P. More, B.G. Bharate, A.K. Vishwanath, " Studies of light emitting CdSe quantum dots in commercial polymethylmethacrylate," *Journal of Luminescence*, 130,pp. 18-23, 2010.

[10] M.C. Neves, J. Soares, R. Hempelmann, T. Monteiro, T. Trindade, "Growth of Cadmium selenide nanocrystals on submicron silica," *Journal of Crystal Growth* ,279, pp. 433-438, 2005.

[11] R. Seoudi, M.M Elokr, A.A. Shabaka, A. Sobhi, "Synthesis and characterization and electrical properties studies of cadmium selenide nanoparticle," *Physica B.*,403, pp.152-158,2007.

[12] Y. Gao, Q. Zhang, Q. Gao, Y. Tian, W. Zhou, L. Zheng, S. Zhang , "Synthesis of high quality CdSe quantum dots through a mild solution-phase synthetic route," *Materials Chemistry and Physics* 115,pp. 724-727,2009.

[13] G.G Yordanov. H. Yoshimura, C.D. Dushkin, " Fine control of the growth and optical properties of CdSe quantum dots by varying the amount of stearic acid in a liquid paraffin matrix" *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, 322, pp. 177-182, 2008.

[14] W. Espulgar, "Characterization of Silver nanomaterials synthesized by Horizontal Vapor Phase Crystal Growth Technique for Antimicrobial purposes,"M.S. Physics thesis, De La Salle University-Manila, Philippines, 2010.

[15] A. Edelstein, R. Cammarata, R. , *Nanomaterials: Synthesis, Properties and Applications.* Philadelphia, USA: Institute of Physics Publishing pp. 316-395,1998.

[16] J. V. Williams, J.V., "Hydrothermal Synthesis and Characterization of Cadmium selenide nanocrystals,"PhD dissertation, Dept. of Eng., University of Michigan, USA, 2008.

[17] B. Dabbousi, B.,"Fabrication and Characterization of Hybrid Organic/Inorganic Electroluminescent Devices Based on Cadmium Selenide Nanocrystallites (Quantum Dots),"PhD dissertation, Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge , 1997.