Research Article

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Chemical Synthesis of CdSe Nanoparticles by using Hydrazine Monohydrate as A Reducing Agent

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ABSTRACT

Cadmium selenide (CdSe) nanoparticles (NPs) is a low band gap material (Eg = 1.75 eV, at room temperature). II-VI semiconductor nanoparticles are currently of great interest for their practical applications in zero-dimensional quantum confined materials and for their applications in optoelectronics and photonics. In the present work, we have synthesized nanoparticles of CdSe by using chemical method. The synthesized CdSe NPs were well characterized by powder X- ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FE-SEM). It is investigated that as synthesized powder has a hexagonal structure of CdSe with diameters of the particles in the range of 74.68 nm. The FTIR spectra were used to identify the possible chemical-molecules responsible for the reduction of cadmium, selenide ions and reducing of hydrazine monohydrate formed CdSe NPs. Synthesized CdSe NPs were investigated at room temperature photoluminescence for excitation wavelengths 422 nm.

Keywords: Chemical synthesis, nanoparticles, optical studies, CdSe, hydrazine monohydrate.

1. INTRODUCTION

Nanoscience is a rapidly emerging field of science. The synthesis and control of materials in nanometer dimensions can lead to access to new material properties and device characteristics in unprecedented ways. Semiconductor nanoparticles, which exhibit properties different from bulk materials, are a new class of materials that hold considerable promise for numerous applications in the field of electronics and photonics (Archana *et al.* 2010). Nanoscale modification of molecular design and morphology of such particles provides a powerful approach to control their electronic and optical properties as well as their process ability (Changlong *et al.* 2005). Among the colloidal nanocrystals, CdSe (generally Gr-II to Gr-VI) is studied because of the efficiency of its synthesis, the high quality of the resulting sample, and the fact that the optical gap lies in the visible range (Colvin *et al.* 1994). Also it is an important semiconducting material with unique electrical properties, which makes it a promising material in the field of such as optoelectronic devices (Duck Jong Suh *et al.* 2002), solar cells (Encai Hao *et al.* 1999), photocatalytic activity (Fabien Pinaud *et al.* 2004), light emitting diodes (LEDs) (Jennifer Zemke *et al.* 2015), photoluminescence (PL) devices (Julian Eastoe *et al.* 2006) and other biological labels (Kikuo Okuyama *et al.* 2003). There are variety of methods has been developed to control the size and morphology of nanoparticles such as the spray method (Lianhua Qu *et al.* 2002), vapor-phase (Lifei Xi *et al.* 2008), thin films (Lihui Zhang *et al.* 2009), hydrothermal method (Manna *et al.* 2011), reverse miscell method (Mark Swihart *et al.* 2003), wet chemical method (Parvaneh Iranmanesha *et al.* 2015) and co-precipitation method (Preeti Gupta *et al.* 2009) and chemical method (Punita Srivastava *et al.* 2012). Among these methods, the chemical method is of particular interest since it is relatively simple, inexpensive and convenient.

In this work, CdSe nanoparticles were synthesized by using polyvinyl pyrrolidone (PVP) and hydrazine monohydrate in aqueous medium under the room temperature conditions. The particles were characterized by different experimental techniques and studied their optical properties. This work is mainly focused on synthesis of monodispersed CdSe nanoparticles.

2. MATERIALS

The chemicals mainly used are cadmium chloride ($CdCl_2$), sodium selenide (Na_2SeO_3), ethylene glycol ($HO\text{-}CH_2\text{-}CH_2\text{-}OH$), hydrazine monohydrate ($N_2H_4 .H_2O$), polyvinyl pyrrolidone (PVP) and ethanol. All chemicals were used without further purification or treatment. Deionized water was used in all experiments.

3. SYNTHESIS OF CdSe NANOPARTICLES

0.2 M solution of cadmium chloride and sodium selenide was prepared in 70 mL of distilled water and the solutions were transferred in a 250 mL round bottom flask. After that, equal ratio (1:1) of hydrazine

monohydrate, ethylene glycol solution was added to the above solution at a room temperature. Then polyvinyl pyrrolidone (PVP) solution was added dropwise to the above solution with constant stirring for 2 hours. It is reflected under vigorously at 70 °C for 5 hours. Finally, a brown precipitate were collected and washed with anhydrous ethanol for several times, then dried under vacuum at 70 °C for 2 hours.

4. CHARACTERISATION TECHNIQUES

The CdSe NPs were characterized by Powder X-ray Diffraction (XRD) by using X-ray diffracto meter - Cu Kα radiation (Rigaku, Miniflex-600, Japan). UV-Visible spectrophotometer (Perkin Elmer -Lambda 35) was used for studying the spectral response of CdSe NPs. Fourier-Transform Infrared Spectroscopy (FTIR) results were acquired from Jasco 6300 spectrometer (Perkin Elmer mode) in the range of 400-4000 cm^{-1}. The surface morphology of CdSe NPs and binding energy of the element was inspected using SEM (Hitachi SU6600, Japan) and EDAX (EMAX, Horiba 8121-H, Japan). The photoluminescence (PL) spectra of the collected powders were recorded using Perkin-Elmer LS-55 spectrofluorometer.

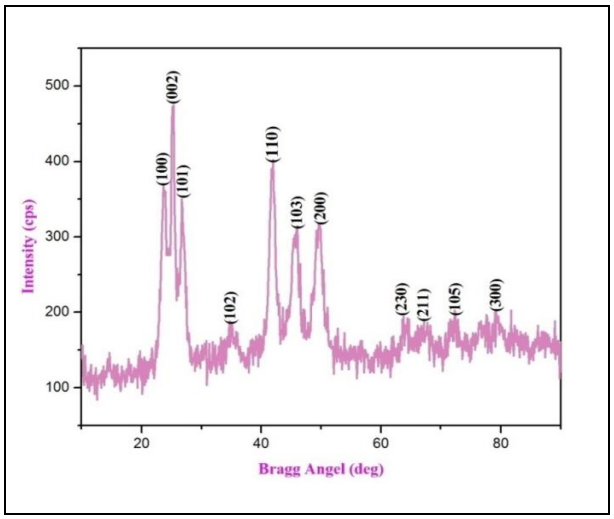

Fig. 1: XRD pattern of synthesized CdSe NPs

5. RESULTS & DISCUSSION

5.1 X-ray Diffraction (XRD) Studies

The X-ray diffraction pattern of synthesized CdSe NPs is as shown in figure 1. The XRD peaks are obtained at angles (2θ) of 23.70, 25.17, 26.72, 34.90, 41.79, 45.66, 49.55, 56.50, 64.53, 72.33, and 79.30 corresponding to the indices of (100), (002), (101), (102), (110), (103) (200), (202), (203), (105) and (300) planes respectively. In order to confirm all the diffraction peaks are indexed as the typical hexagonal structure (JCPDS 08-0459) of CdSe NPs (Qing Peng *et al.* 2002; Sachin Pawar *et al.* 2013).

The size of the nanoparticles was estimated by using the Debye Scherrer's formula

$$d = (0.9\lambda)/\beta\cos\theta \quad (1)$$

Where, λ is the wavelength of X-ray used (0.15418 nm in the present case), β is the full width in radiation at half-maximum of the peak, and θ is the Bragg angle of X-ray diffraction peak. Calculation made on the (002) peak at $2\theta = 25.17^{\circ}$ gave a value of 45 nm for the average crystalline diameter of the synthesized CdSe nanoparticles.

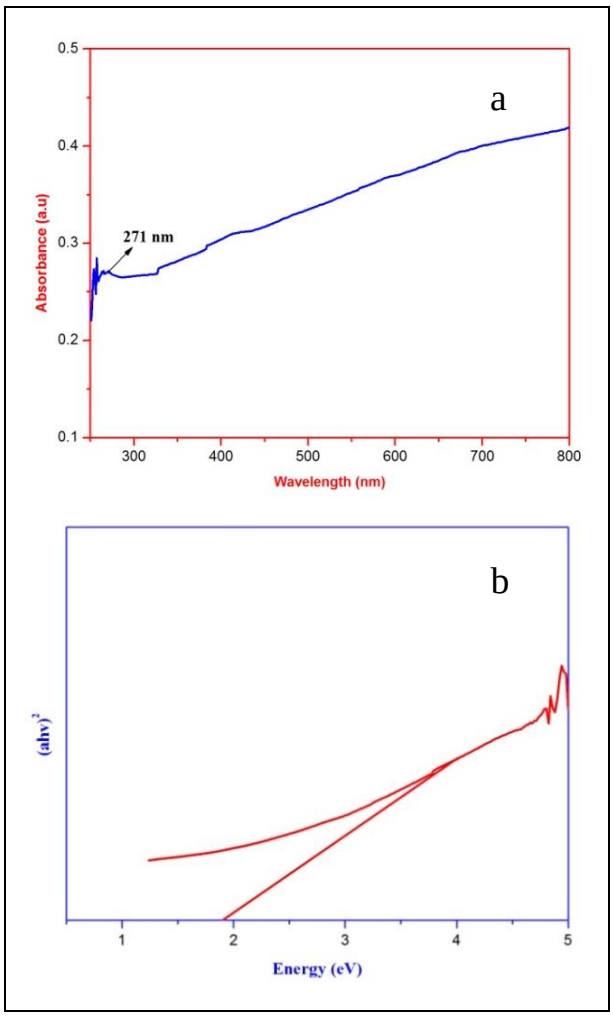

Fig. 2: (a) UV–visible absorption spectrum, (b) Band gap spectrum

5.2. UV-Visible Spectroscopy

The optical properties of CdSe NPs are dependent on the size and the shape. The optical properties of CdSe NPs were characterized by UV–Vis absorption and the result is as shown in fig. 2a. The UV–visible absorption spectra exhibited strong surface plasmon resonance peak at 271 nm which is characteristic of CdSe NPs. The optical band gap of CdSe nanoparticles is determined by plotting $(\alpha h\nu)^2$ versus $h\nu$

shown in fig. 2b. The band gap energy of CdSe NPs, was found to be 2.9 eV that showed the 'blue shift' of the standard bulk band gap at room temperature (Eg = 1.74 eV). It is familiar that the reaction situation such as heating time, temperature, and amount of reagents has an effect on the morphology, structure and size of the products in the processes (Saravanan *et al.* 2011).

5.3 Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectrum of the synthesized CdSe NPs is shown in fig. 3. The characteristic major peaks appearing at 493, 511,536, 651, 671 cm^{-1} belong to CdSe vibrations. The broad peak at 3431cm^{-1} is assigned to –OH stretching intra molecular hydrogen bonds due to the small quantity of H_2O molecule on the sample. N-H stretching vibration peak is observed at 3282 cm^{-1} due to the presence of hydrazine hydrate in our sample. The peak observed at 1598 cm^{-1} is assigned to OH of water absorbed from the molecular precursors. C-N stretching vibration peak is positioned at 1145 cm^{-1} is due to the interaction of ethylene glycol with the hydrazine hydrate and regular periodic structure of molecular precursors. The PVP characteristic vibrations such as C=O and C–N appeared at 1658 cm^{-1} and 1348 cm^{-1}, respectively (Vidyalakshmi *et al.* 2009; Xi L.F *et al.* 2007).

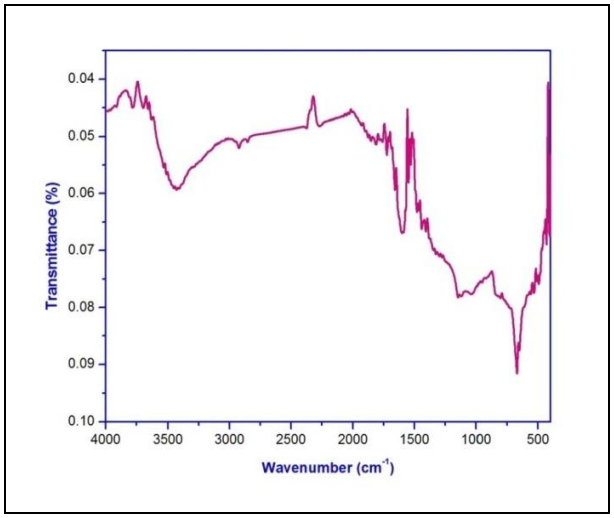

Fig. 3: FTIR spectrum formation of CdSe NPs

5.4. Morphological and Elemental Analysis

Fig. 4. displays the FE-SEM analysis of synthesized CdSe NPs. The images showed that the shape of the synthesized CdSe NPs were polydispersed spherical. The average particle size was found to be 74.68 nm. It is in close agreement with XRD value. EDAX analysis [fig.4 (inset)] confirmed the presence of expected elements such as, cadmium (64.50 weight %) and selenide (35.50 weight %) are present in the synthesized sample.

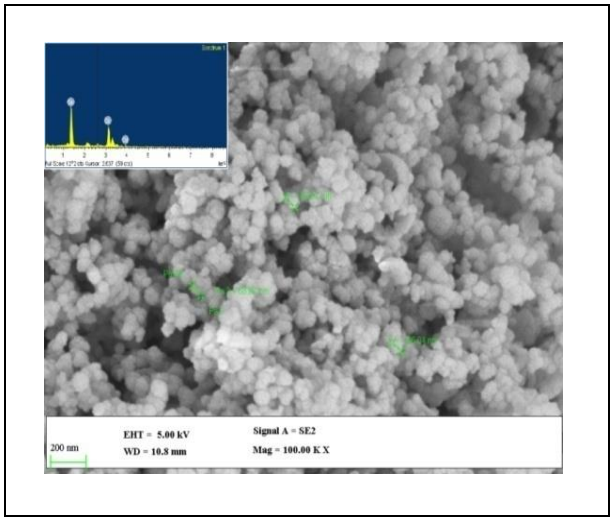

Fig. 4: FESEM & EDAX analysis of CdSe NPs

5.5 Photoluminescence Analysis of CdSe NPs

Fig. 5 shows the photoluminescence emission spectra of the synthesized CdSe nanoparticles obtained excitation wavelengths single broad peak at 422 nm are attributed to the red emission resulting from the recombination of a photon generated hole with a charge state of the specific defect. The absorption and PL peak of the CdSe were shifted towards a shorter wavelength in comparison to bulk CdSe due to the nanosized effect (Yanli Liu *et al.* 2013; Ying Wang *et al.* 2004).

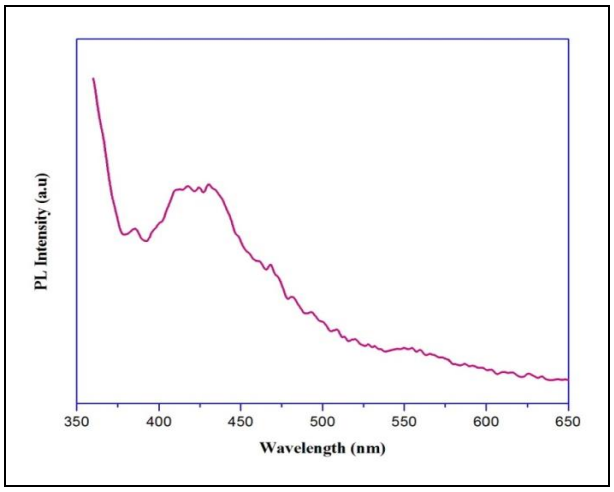

Fig. 5: Photoluminescence spectra of the CdSe NPs at room temperature

6. CONCLUSIONS

The CdSe nanoparticles were successfully synthesized via simple chemical method at 70˚C. The SEM data indicated that, nanoparticles were formed with polydispersed spherical shape. The XRD analysis confirmed that CdSe nanoparticle has hexagonal structure. The average particle size of the synthesized

CdSe NPs is in 74.68 nm range. UV–Visible and photoluminescence spectra indicated that the presence of surfactants could influence the optical properties of the CdSe nanoparticles. The monodispersed CdSe NPs would have potential applications as photocatalyst, luminescence and photoelectron transfer devices.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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REFERENCES

Archana, J., Navaneethan, M., Ponnusamy, S., Hayakawa, Y., Muthamizhchelvan, C., Synthesis of organic ligand passivated zinc selenide nanorods via wet chemical route, *Mater. Lett., 64(19), 2094–2097(2010).* https://doi.org/10.1016/j.matlet.2010.06.001

Changlong Jiang., Wangqun Zhang, Guifu Zou., Weicao Yu. and Yitai Qian., Synthesis and characterization of ZnSe hollow nanospheres via a hydrothermal route, *Nanotechnology., 16(4), 551–554(2005).* https://doi.org/10.1088/0957-4484/16/4/036

Colvin, Schlamp, V. L., Alivisatos, M. C., Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer, *Nature.*, 370, 354- 357(1994).

Duck Jong Suh., O Ok Park., Hee-Tae Jung., and Moo Hyun Kwon., Optical properties and characteristics of the CdSe nanoparticles synthesized at room temperature, *Korean J. Chem. Eng.*, 19(3), 529-533(2002).

Encai Hao., Haiping Sun., Zheng Zhou., Junqiu Liu., Bai Yang., and Jiacong Shen., Synthesis and Optical Properties of CdSe and CdSe/CdS Nanoparticles. *Chem. Mater.*, 11(11), 3097-3102(1999).

Fabien Pinaud., David King., Hsiao-Ping Moore and Shimon Weiss., Bioactivation and Cell Targeting of Semiconductor CdSe/ZnS Nanocrystals with Phytochelatin-Related Peptides. *J. Am. Chem. Soc.*, 126(19), 6115-6123(2004).

Jennifer Zemke M., and Justin Franz ., A Biphasic Ligand Exchange Reaction on CdSe Nanoparticles: Introducing Undergraduates to Functionalizing Nanoparticles for Solar Cells. *J. Chem. Educ.*, 93(4), 747-752(2016).

Julian Eastoe., Martin Hollamby J., Laura Hudson., Recent advances in nanoparticle synthesis with reversed micelles. *Adv. Colloid and Interface Sci.*, 128–130, 5–15(2006).

Kikuo Okuyama ., Wuled Lenggoro, I., Preparation of nanoparticles via spray route. *Chem. Eng. Sci., 58(3-6), 537–547(2003).*

Lianhua Qu., and Xiaogang Peng., Control of Photoluminescence Properties of CdSe Nanocrystals in Growth. *J. Am. Chem. Soc.*, 124(9), 2049-2055(2002).

Lifei Xi., Yeng Ming Lam., Yan Ping Xu., Lain-Jong Li., Synthesis and characterization of one-dimensional CdSe by a novel reversemicelle assisted hydrothermal method. *Journal of Colloid and Interface Sci.*, 320(2), 491–500(2008).

Lihui Zhang., Heqing Yang., Jie Yu., Fanghong Shao., Li Li., Fenghua Zhang., and Hua Zhao., Controlled Synthesis and Photocatalytic activity of ZnSe Nanostructured Assemblies with Different Morphologies and Crystalline Phases. *J. Phys. Chem.*, 113(14), 5434–5443(2009).

Manna, A., Bhattacharya, R., Das, T.K., Saha, S., Effect of reducing agent in the formation of CdSe nanoparticles by chemical reduction route. *Phys. B.*, 406(4), 981–984(2011).

Mark Swihart, T., Vapor-phase synthesis of nanoparticles. *Current Opinion in Colloid Interface Sci.*, 8(1), 127–133(2003).

Parvaneh Iranmanesha., Samira Saeedniab., and Mohsen Nourzpoor., Characterization of ZnS nanoparticles synthesized by co-precipitation method. *Chin. Phys. B.*, 4(24), 046-104(2015).

Preeti Gupta., and M. Ramrakhiani., Influence of the Particle Size on the Optical Properties of CdSe Nanoparticles. *The Open Nanoscience Journal.*, 3, 15-19(2009).

Punita Srivastava., and Kedar Singh., Synthesis of CdSe nanoparticles by solvothermal route: Structural, optical and spectroscopic properties. *Adv. Mat. Lett.*, 3(4), 340-344(2012).

Qing Peng., Yajie Dong., Zhaoxiang Deng., and Yadong Li., Selective Synthesis and Characterization of CdSe Nanorods and Fractal Nanocrystals. *Inorganic Chemistry.*, 41 (20), 5249-5254(2002).

Sachin Pawar, A., Rupesh Devan, S., Dipali Patil, S., Annasaheb Moholkar, V., Myeng Gil Gang., Yuan-Ron Ma., Jin Hyeok Kim., Pramod Patil, S., Improved solar cell performance of chemosynthesized cadmium selenide pebbles. *Electrochimica Acta.,* 98, 244–254(2013).

Saravanan, L., Diwakar, S., Mohankumar, R., Pandurangan, A., and Jayavel, R., Synthesis, Structural and Optical Properties of PVP Encapsulated CdS Nanoparticles. *Nanomater. nanotechnol., 1(2), 42-48(2011).*

Vidyalakshmi Rajendran., Manfred Lehnigb., and Christ of Niemeyer, M., Photocatalytic activity of colloidal CdS nanoparticles with different capping ligands. *J. Mater. Chem., 19(35), 6348–6353(2009).*

Xi, L.F., Lam, Y.M., Synthesis and characterization of CdSe nanorods using a novel microemulsion method at moderate temperature. *Journal of Colloid and Interface Sci., 316(2), 771–778(2007).*

Yanli Liu., Yufang Li., and Haibo Zeng., ZnO-Based Transparent Conductive Thin Films:Doping, Performance, and Processing. *J. Nanomaterials.,* 9, 196-521(2013).

Ying Wang., Zhiyong Tang., Miguel Correa-Duarte, A., Isabel Pastoriza-Santos., Michael Giersig., Nicholas Kotov, A., and Luis Liz-Marzan, M., Mechanism of Strong Luminescence Photoactivation of Citrate-Stabilized Water-Soluble Nanoparticles with CdSe Cores. *J. Phys. Chem. B.,* 108(40), 15461-15469(2004).