

Absorption Enhancement of CdS Nanoparticles using Poly Vinyl Alcohol (PVA)

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Abstract—We report synthesis of PVA capped CdS nanoparticles following chemical route. A series of CdS nanoparticles were synthesized by varying the concentration of the polymer and sulfur source to enhance stability of the colloids at higher concentration of Cd ions and to achieve non uniform particle size distribution respectively. At an optimal PVA concentration a very stable colloidal sample was obtained. Non uniform particle size distribution shows wider absorption of visible light which can be attractive for use in solar cells as higher photo conversion efficiency can be obtained using those nanoparticles as sensitizers.

1. INTRODUCTION

CdS nanoparticles due to their interesting size dependent optical and electronic properties and potential applications in Photonics and Electronics have been the subject for several studies for a long time [1, 2, 3]. Due to their size dependent electronic and optical properties, CdS quantum dots and thin films have been extensively studied [4, 5, 6, 7] for last few decades. The dependence of physical properties on size mainly arises from two factors, (a) changes of the surface-to-volume ratio with size, and (b) quantum confinement effects. At nanoscale, most phenomena and processes are dominated by quantum physics and hence they exhibit extraordinary behavior and quantum dots (QD)s are attractive for optoelectronic and solar cell application because of their band gap tunability and higher stability. In order to absorb photons with a wide range of energies, it becomes necessary to tailor the band gaps of the sensitizer. This is possible through size control of QDs and inclusion of quasi stable energy states within the band gap. The absorption of quantum dots can be tuned from UV through the visible into the NIR, and can be possible band-edge absorption which is favorable for effective light harvesting [8].

Plasmonic nanoparticles have an unprecedented control over NIR region. Metal nanoshell used on colloidal quantum dots (CQDs) is a very recent trend to improve absorption at near IR region. Embedding gold nano shell in PbS CQD film, a resultant of 35% enhancement in photo current in the near infrared spectral region is achieved [9]. Particle size distribution is another important issue for enhancement of absorption. Particle size distribution can be tuned by varying

the concentration of the precursor. Non uniform particle size distribution is attractive for solar cell application because it can absorb a wide spectrum.

2. EXPERIMENTAL

Synthesis of CdS nanoparticle:

Chemical route one-pot synthesis methods is followed to synthesis CdS nanoparticle. In one pot process we added the following reagents: 4wt% solution of poly-vinyl alcohol is taken as matrix as capping agent. It is prepared by stirring 4 gm of poly-vinyl alcohol powder in 100 ml of distilled water at 60°C and 700 rpm for 2 hrs in a magnetic stirrer. Poly-vinyl alcohol and CdCl₂ of 0.01M concentration are then mixed in 2:1 volume ratio. Two different concentration of Na₂S, viz [Na₂S] = 0.001M and [Na₂S] = 0.01M respectively mixed in the above solution to achieve two different particle size distribution of CdS nanoparticles [Fig 1].

Synthesis of Ag nanoparticle:

Aqueous solution of AgNO₃ (5mM) is prepared with 10 mL de-ionized water and stirred at 80°C and 700 rpm in magnetic stirrer until the boiling point has achieved. When AgNO₃ solution reach boiling point, the solution of 5mM Trisodium citrate and 10 mL de-ionized water is then mixed in the former solution. The formation of silver particles was manifested by the gradual appearance of a yellowish coloration in the solution.

Synthesis of CdS@Ag Core-Shell nanoparticle:

Freshly prepared AgNO₃ solution with concentration of 0.88 mM is added dropwise into the already prepared CdS QD solution with gentle stirring. Then the colour of the resulting solution quickly changes from kelly to dark yellow. The whole synthesis process is shown diagrammatically in fig 1.

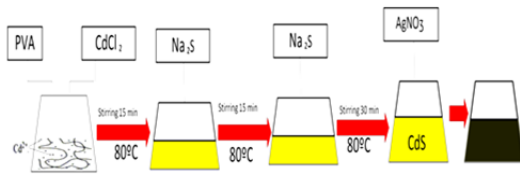
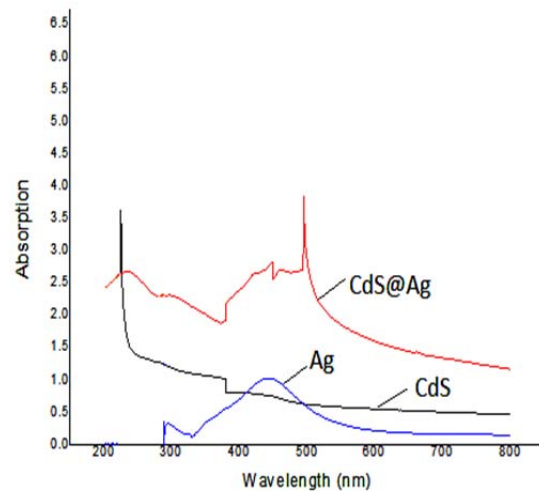


Fig1. Pictorial representation of CdS@Ag Core-Shell synthesis process.

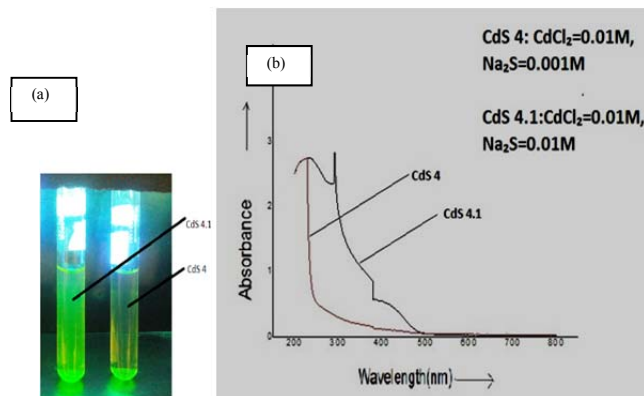
3. RESULTS & DISCUSSION:

UV-Visible Spectra:

The optical absorption of the samples is carried observed using double beam automated spectrometer (HITACHI-U3210). The band gap estimated from Tauc’s formula for the CdS samples are found to be higher than that of bulk band gap of CdS [Fig 2(c)]. From the Fig. 2(a) & Fig. 2(b) it is clear that with increase in the concentration of S source the particle size distribution of the samples also increased. From Fig1(d) the enhancement of absorption in case of CdS@Ag Core-Shell is confirmed.



(b) Fig 2:(a) CdS NPs illuminated by UV light (b) UV-Vis absorption spectra of CdS samples (c) Band Gap from Tauc Method (d) UV-Vis absorption spectra.



XRD Study:

The as prepared samples were characterized by X-ray powder diffraction (Philips X’ pert) operating at 40kV-30ma. The radiation source used was CuK α ($\lambda = 1.542 \text{ \AA}$) and a Nickel filter was used to block K β radiation. Fig. 3 shows the XRD patterns of PVA capped CdS . The XRD peaks can be indexed to the hexagonal structure of CdS [10]. As shown in the Fig.3, the main peaks are obtained at (111), (220) and (202) plans. The peaks are broad compared to the bulk peaks of CdS which confirms nanoformation of the samples. The average crystallite size (D) from X-ray line broadening has been calculated using the Scherrer equation $D = 0.9\lambda / \beta \cos \theta$.

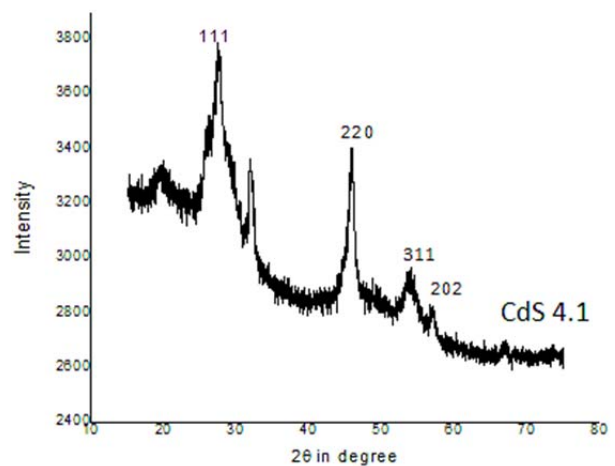
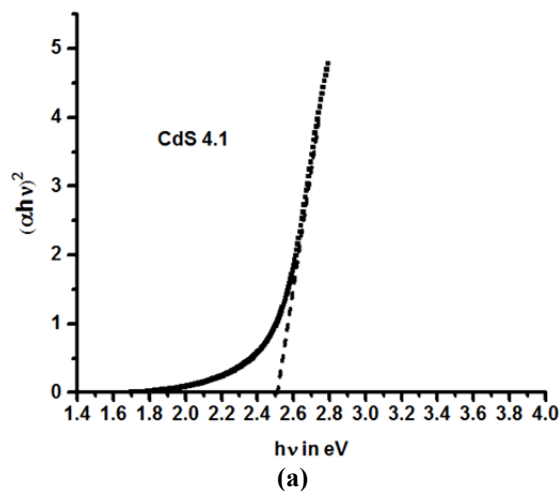


Fig 3: XRD pattern of CdS Nanoparticles.

Where λ is the wavelength of the X-ray beam, β is the full width at half maximum (FWHM) in radian and θ is the Bragg angle. The average crystallite size of CdS calculated is about 5.2 nm.

HRTEM of CdS Nanoparticles:

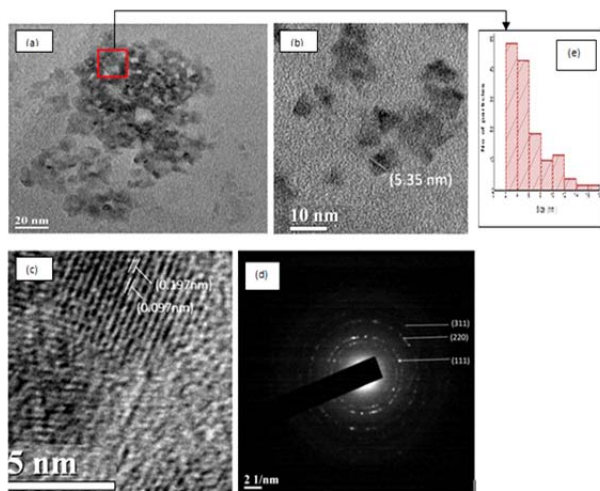


Fig4: HRTEM images of (a) CdS NPs, (b) Single CdS NP, (c) Lattice pattern of CdS NPs (d) SAED pattern of CdS NPs (e) Particle size distribution.

High Resolution Transmission Electron Microscopy (HRTEM, JEM-2100, 200 kV, JEOL microscope) results for CdS samples are given in Fig.4. The particle size of the samples is calculated by measuring an average of 50 nanoparticles per micrograph. The average particle size estimated for CdS is about 5 nm.

4. CONCLUSION

Analysis of the as-synthesized nanomaterials showed that the amount of the sulfur source can be varied to control the size of the CdS quantum dots which can fulfill an important aspect of solar cell design i.e. to achieve wider absorption of the solar spectrum. Stability of the as-synthesized nanomaterials is also an important issue. PVA concentration of 5wt% is found to be the optimum for synthesis of CdS quantum dots with various size distributions.

UV-Visible spectra confirm that absorption is enhanced in case of CdS@Ag Core-Shell structure. It is found that particle size obtained from XRD and HRTEM are in good agreement. As size of the samples are less than 5 nm (exciton Bohr radius for CdS = 2.8 nm), strong confinement is achieved for CdS samples which are therefore Quantum Dots.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge Head, SAIF, Gauhati University for providing XRD facilities. We would also like to acknowledge Department of ECE, Don Bosco University for providing UV-Vis observation and SAIF, NEHU Shillong for HRTEM facility.

REFERENCES

- [1] Morales-Acevedo, A., "Can we improve the record efficiency of CdS/CdTe Solar Cells", *Solar Energy Materials and Solar Cells* 90, 2006, pp. 2213-2220.
- [2] Cao, H., Wang, G., Zhang, S., Zhang, X. and Rabinovich, D., "Growth and optical properties of Wurtzite-type CdS nanocrystals", *Inorganic Chemistry*, Volume -45, Issue 13, 2006, pp 5103-5108.
- [3] Das, H., Boruah, P.K. and Datta, P., "Microwave Assisted Synthesis of CdS & CdS/ZnS Core-Shell Nanoparticles and Their Characterization", *International Journal of Advanced Research in Physical Science (IJARPS)*, Volume 2, Issue 12, December 2015, PP 18-23.
- [4] Dwivedi, D.K., "Synthesis, Structural and Optical Characterization of CdS Nanoparticles", *Journal of Ovonic Research*, Vol. 6, Issue 1, 2010, pp 57-62.
- [5] Das, H. and Datta, P., "Semiconductor quantum dots as nanoelectronics circuit components", *Journal of Experimental Nanoscience*, 11:11, pp. 901-915.
- [6] Shalom, M., Ruhle, S., Hod, I., Yahav, S. and Zaban, A., "Energy level Alignment in CdS Quantum Dot Sensitized Solar Cells Using Molecular Dipoles", *J. AM. CHEM. SOC.* 2009, vol.131, pp 9876-9877.
- [7] Prabakar, S., Suryanarayanan, N. and Kathirvel, D., "Electrical and photoconduction Studies on Chemical Bath Deposited Cadmium Sulphide Thin Films", *Chalcogenide Letters*, Vol. 6, No. 11, 2009, pp 577-581.
- [8] Vogel, R.; Hoyer, P.; Weller, H., "Quantum-sized PbS, CdS, Ag₂S, Sb₂S₃, and Bi₂S₃ particles as sensitizers for various nanoporous wide-bandgap semiconductors", *J. Phys. Chem.* 1994, vol. 98, pp. 3183-3188.
- [9] Michael, M., Adachi, Haopeng Dong, Pouya Maraghechi, Mingjian Yuan, André J. Labelle, Sjoerd Hoogland, KunLiu, Eugenia Kumacheva, and Edward H. Sargent, "Jointly Tuned Plasmonic Excitonic Photovoltaics Using Nanoshells" *Nano Lett.* 2013.
- [10] Wang, S., Yang, S., Yang, C. and Li, Z., "Poly (N-vinylcarbazole) (PKV) Photoconductivity Enhancement induced by doping with CdS nanocrystals through chemical hybridization", *J. Phy. Chem. B*, vol. 104, 2000, pp. 11853-11858.