Research Article Adv. Mat. Lett. 2014, **5**(9), 538-542 ADVANCED MATERIALS *Letters*

www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2014.4561

Bio- polymer assisted solvothermal growth and optical characterization of CdS nanostructures

J. S. Roy, K. Pal, T. Pal Majumder

Department of Physics, University of Kalyani, Kalyani 741235, West Bengal, India

*Corresponding author. Tel: (+91) 03325820184; E-mail: tpm@klyuniv.ac.in, tpmajumder1966@gmail.com

Received: 01 April 2014, Revised: 22 June 2014 and Accepted: 28 June 2014

ABSTRACT

Various nanostructured CdS samples have been synthesized with assistance of starch (bio-polymer) by solvothermal method. We have synthesized nano-regime, nanorods and nanoparticles by simply changing the starch-solvent combinations. The highly polymeric (branched) structure of starch capped the CdS samples to modify the surfaces and hence tune the optical properties. The optical band gaps for three samples are 2.34, 2.37 and 2.38 eV. The photoluminescence emission peak also changes with surface modification of the nanomaterials. The sensitivity of the optical properties of CdS nanomaterials with structural modification by means of polymer may be used for practical application like solid state lighting. Copyright © 2014 VBRI press.

Keywords: CdS nanostructure; starch; morphology; optical property.

Joy Sankar Roy is a research scholar in the Department of Physics of the University of Kalyani, West Bengal, India. He completed his M.Sc. in Physics from University of Calcutta, Kolkata, India, in 2010. His research interests are TiO_2 and II-VI semiconductor nanomaterials, core-shell nanostructures and nanomaterials doped liquid crystalline materials.

Kaushik Pal obtained his B.Sc. from University of Calcutta (India) and M.Sc. in Physics from Utkal University, Bhubaneswar (India). He submitted his Ph.D. thesis on ‘Spectroscopic and dielectric properties of nano-rods doped liquid crystalline optical materials’ and is awaiting degree from Kalyani University. During his PhD, he published 9 scientific papers in reputed journals and 5 conference proceedings papers. He performed scientific contribution in 13 National and International conferences.

Tapas Pal Majumder was born in India on February 1965. He completed his B.Sc. in 1988 from Calcutta University, India and he received his M.Sc. in Physics in 1991 from Calcutta University, India. He obtained his Ph. D. Degree in Science from Jadavpur University, India in 1997. He worked as UNESCO fellow in Tokyo Institute of Technology, Japan from 1997 to 1998 and he also received diploma from there. He worked as ITIT fellow in Nanotechnology Research Institute, Japan from 1999 to 2000. He worked as a BAT fellow in Rostock University, Germany for six months in 2001. He worked as an Assistant Professor in Krishnagar Government College, India from 2002 to 2005. At present, he is an Assistant Professor in Physics in the University of Kalyani, India since 2005. He has published more than 50 research papers in international journals.

Introduction

Nanostructured materials exhibit distinct properties that are different from those of bulk materials due to their small size and large surface to volume ratios. Experimentally, many research efforts have been done to investigate the physical properties of nanostructures such as nanowires, nanorods, nanobelts and nanotubes **[1-4]**, any of whose laterial dimension falls into the range from 1 to 100 nm. Furthermore, semiconductor nanostructures have drawn considerable attention due to their wide-ranging applications in optoelectronics, biotechnology and so on. Among these semiconductors, CdS, one of the best direct band-gap semiconductors of II-VI group, has drawn intense interest due to their wide application in solar cell, light-emitting diodes for flat panel display and photocatalyst for chemical reaction **[5-6]**. Over the last decade, various routes have been developed to synthesize 1D CdS nanostructures including template-assisted synthesis, laser ablation, photochemical method, solvothermal methods etc **[7-10]**. Out of those methods, solvothermal method is an effective and easiest way to synthesize CdS nanostructures. In recent years, various surfactants or polymers like PEG, CTAB, and PVA etc have been used to synthesize uniform CdS nanomaterials **[11-14]**. However, further studies on controlling the length, aspect ratios and crystallization of nanomaterials are still necessary for widespread application.

In this research work, we have prepared different CdS nanostructures by changing starch-solvent combinations.

We have got nanoparticles, nanorod and nanoregime like structures of CdS for different starch-solvent combinations. We have observed the significant tuning in optical properties of those synthesized CdS nanostructures as a function of shape and size of the nanostructures.

Experimental

Chemicals

The cadmium acetate, sulfur powder, Isopropyl amine and ethylenediamine were purchased from Merck Limited. The starch (maize) powder was provided by Fluka analytical. All the chemicals were of analytical grades and used without further purification.

Synthesis of CdS nanostructures

Different nanocrystalline cadmium sulphide (CdS) samples were grown by solvothermal method. Cadmium Acetate [$Cd(CH_3COO)_2.2H_2O$] and sulfur powder were used as reactant and starch as the capping reagent. Three CdS samples S1, S2 and S3 were synthesized by using different starch and solvent.

Preparation of sample S1: 0.6 g Cadmium Acetate, 0.08 g sulfur powder and 0.5 g maize powder were dissolved in 40 ml ethylenediamine under vigorous magnetic stirring and then transferred into a 50 ml Teflon-lined autoclave. The autoclave was heated at 150 °C for 2 hr and then cooled to the room temperature. Finally, the resultant sample was filtered off and then dried at 65 °C.

Preparation of sample S2: We repeated the above experiment taking 0.1 g starch powder instead of 0.5g starch powder to get the sample S2.

Preparation of sample S3: We repeated the S2 synthesis procedure using 40 ml Isopropyl amine instead of ethylenediamine to get the sample S3.

Characterizations

The morphology of the CdS nanomaterials was evaluated by ESEM (FEI Quanta 200). The samples were coated with gold-palladium to prevent the charging during ESEM analysis. XRD analysis was performed on X'Pert PRO PANalytical with CuKα radiation (λ=1.5418Å). An ultraviolet-visible spectrometer (UV-2401PC, TCC-240A, Shimadzu) was used to identify the absorption band of the sample and Photoluminescence (PL) spectra were recorded on LS55 PerkinElmer fluorescence spectrometer.

Results and discussion

Structural properties

The CdS nanostructures synthesized by solvothermal method are shown in **Fig. 1**. The sample S1 (Fig. 1a & 1b) is prepared as nano regime like structures whose edges' are like nanorods. Basically, the nanorods are accumulated to form nano regime by maize starch. But, we have obtained nanorods in case of S2, shown in **Fig. 1c** & **d**. The nanomaterials have high surface to volume ratio that maximizes the interfacial contact between the nanostructures' surfaces and polymer matrix. Due to the increased surface area at the interface, there is a good adhesion between the nanomaterials and starch matrix. So, it is clear that the CdS nanorods are accumulated to form nano regime like structure due to higher concentration of maize starch. The sample S3 have nano-sphere like structure as shown in **Fig. 1e** and **f**.

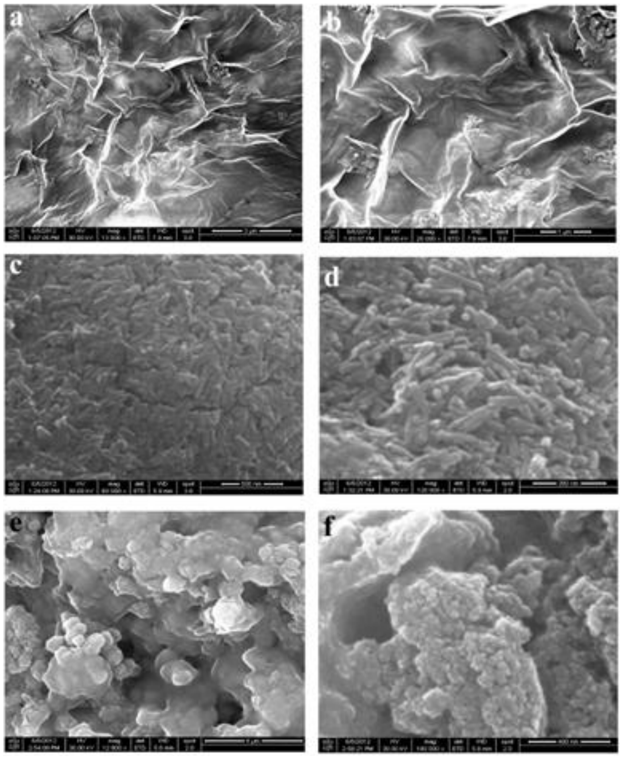

Fig. 1. SEM images of sample S1 i.e. nano-regime (**a** and **b**), sample S2 i.e. nanorods (**c** and **d**), sample S3 i.e. nanoparticles (**e** and **f**).

XRD patterns of the synthesized CdS samples are shown in **Fig. 2**. From the **Fig. 2** it is clear that all the samples are of well crystalline. The samples S1 (**Fig. 2a**) and S2 (**Fig. 2b**) have hexagonal phase (JCPDS 41-1049). The sample S3 (**Fig. 2c**) is a mixture of cubical (JCPDS 80-0019) and hexagonal phases in which hexagonal phase has very low percentage. For sample S1 the XRD peaks found at 2θ values 19° and 23.2° (denoted by S) are due to maize starch. These peaks arise due to crystalline nature of starch which contains 70-80% amylopectin (crystalline nature) and 20-30% amylose (amorphous nature). In case of samples S1 and S2 we don't find any such peak due to starch. It may be due to their low intensity we are unable to detect them in obtained XRD patterns. The crystallite size can be calculated using Debye Scherrer's formula;

$$D= 0.9\lambda / \beta\cos\theta$$

where, D is the crystallite size, λ is the wavelength of X-rays, β is the full-width at half-maxima (FWHM) in radians and θ is the diffraction angle. In single-crystal sample, crystallite size corresponds to nano size while in polycrystalline sample they differ, but the average crystallite size are well approximated to the average nano size. The calculated average nano size for samples S1, S2 and S3 are 11.32 nm, 15.62 nm and 6 nm respectively. Nano size distribution histogram for three samples is shown in **Fig. 3**. From histograms obtained from XRD pattern, nanomaterials are largely distributed with a range of dimensions having uniformity.

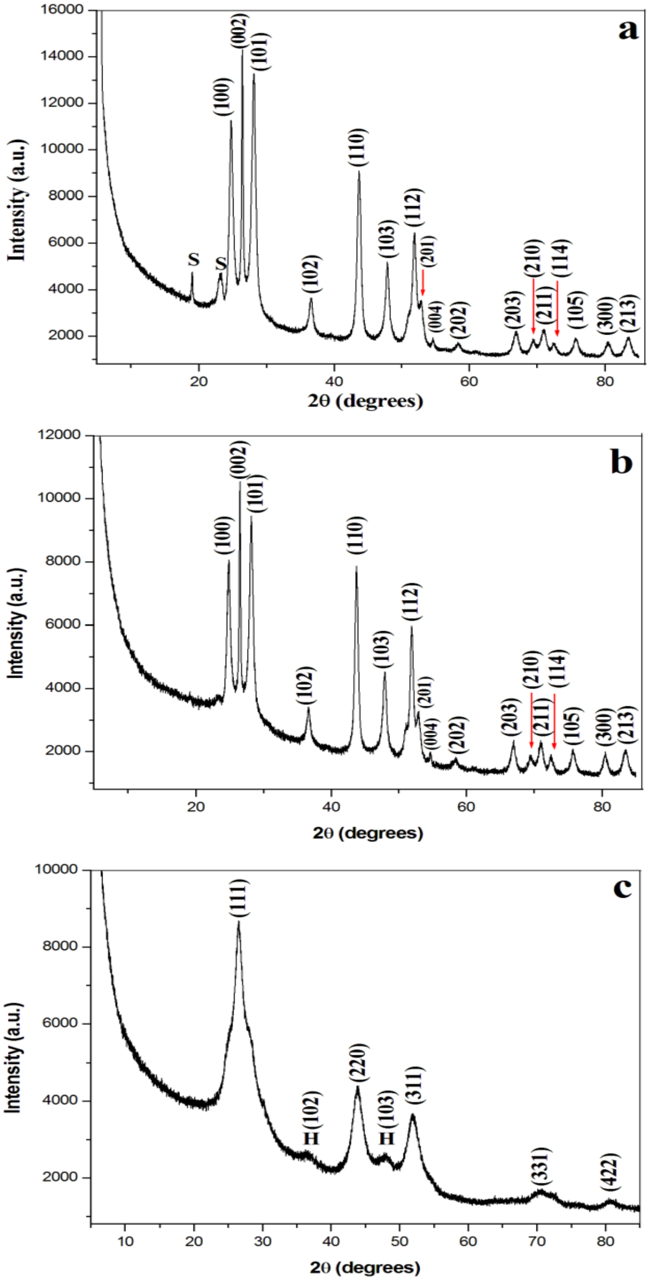

Fig. 2. XRD patterns of synthesized samples **(a)** S1, **(b)** S2 and **(c)** S3.

Optical properties

The UV-visible absorption spectroscopy and photoluminescence spectroscopy have been used to monitor the optical properties of synthesized CdS nanostructures. The absorption spectra are shown in **Fig. 4**. The **Fig. 4** shows three distinct spectra with little shift in absorption bands for samples S1, S2 and S3 respectively. All the peaks are considerably blue-shifted relative to the absorption peak of bulk CdS (522 nm) indicating quantum size effect. The obtained peaks are assigned to the optical transition of the first excitonic state. Generally, this wavelength of the maximum exciton absorption decreases as the particle size decreases as a result of quantum confinement of the photo generated electron-hole pairs. Moreover, the sharp edges of the absorption spectra can be ascribed to size uniformity on nanostructures. These conclusions are consistent with the above statistical results shown in **Fig. 3**. The optical band gap of CdS nanostructures are determined by the following equation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where α is the absorption coefficient, E_g is the optical band gap, A is constant and depends on type of transition.

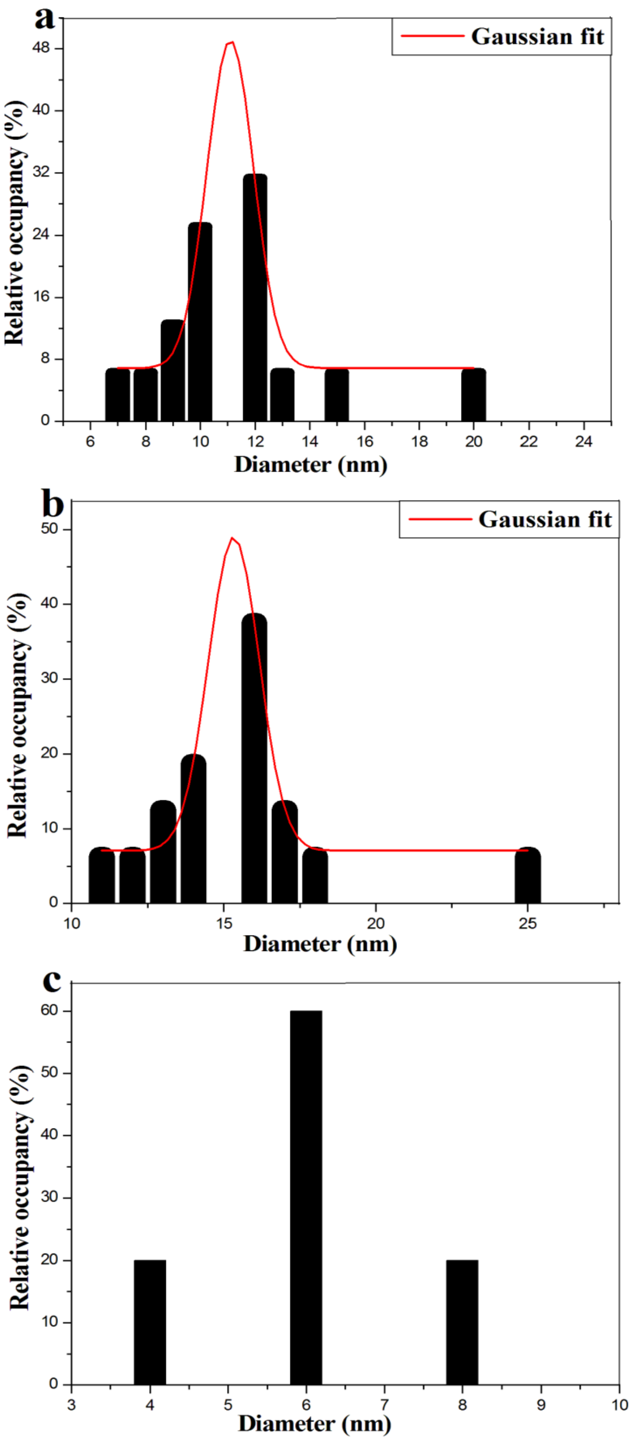

Fig. 3. Nano size distribution histogram and corresponding Gaussian curve fitting of (a) S1, (b) S2 and (c) S3.

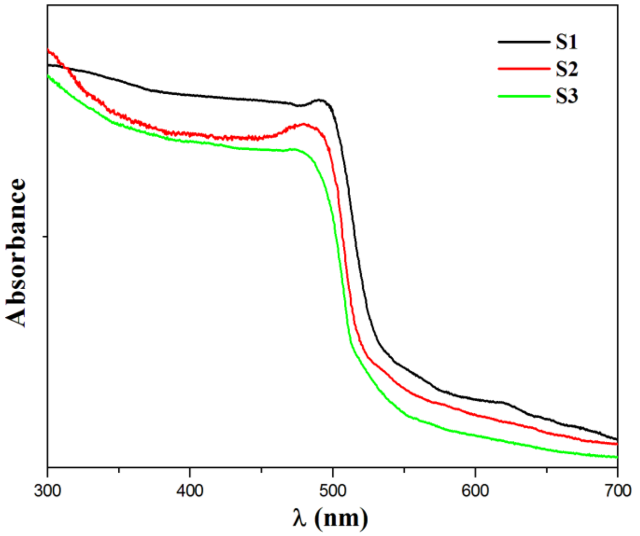

Fig. 4. UV-vis absorption spectra, recorded at room temperature (300K), of CdS nanostructures.

The band gap are determined by extrapolating the linear portion of $(\alpha h\upsilon)^2$ vs hυ plot to the energy axis as shown in **Fig. 5**. The obtained band gaps from **Fig. 5** are 2.34, 2.37 and 2.38 eV for samples S1, S2 and S3 respectively. Therefore, with the structural modification of the CdS nanomaterials by starch – solvent combinations, optical band gap of the samples have been tuned.

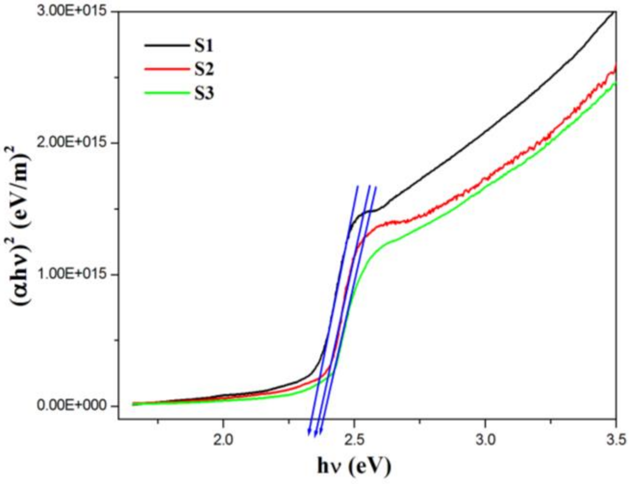

Fig. 5. Plot of $(\alpha h\upsilon)^2$ vs hυ of synthesized CdS nanostructures.

The PL spectra of the CdS samples are shown in **Fig. 6**. The PL spectra are recorded at 450 nm excitation under room temperature. Each spectrum displays two distinct emission peaks. The first emission band is associated with the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the second emission band is due to the recombination via surface localized states, a transition from interstitial cadmium to valence band **[4]**. The first PL emission peak have been observed at 525.5nm, 521 nm and at 520 nm while the second PL emission peaks have detected at 626.5 nm, 619.5 nm and at 622 nm respectively for the samples S1, S2 and S3. The variations in emission bands for three samples reveal that the shape and nano size of those samples are different. This conclusion is consistent with our obtained results shown in **Fig. 3.**

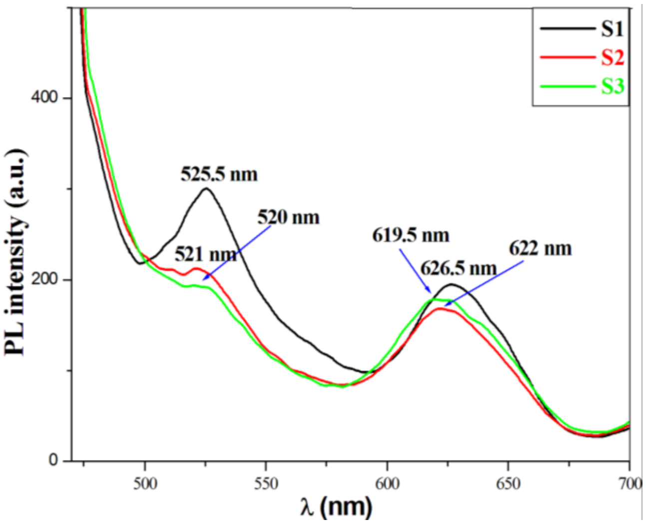

Fig. 6. PL emission spectra recorded at excitation 450 nm.

Conclusion

We have synthesized CdS nanostructures by solvothermal method. We have got different structures like nano-regime, nanorods and nanoparticles by simply changing starch-solvent combination. The obtained UV-visible and PL spectra reveal that the samples have good optical properties. We have observed the significant shift in absorbance and emission band of those samples. This simply synthesis method together with good optical properties make these materials scientifically and technologically interesting.

Acknowledgements
We thank Department of chemistry, University of Kalyani for providing UV-vis and PL facility.

Reference

1. Chand P.; Gaur, A.; Kumar, A.; Adv. Mat. Lett. **2013**, 4, 220.
DOI: 10.5185/amlett.2012.7391
2. Park, S.; Jin, C.; Kim, H.; Hong, C,; Lee, C.; J. Lumin. **2012**, 132, 231.
DOI: 10.1016/j.jlumin.2011.08.029
3. Gao, F.; Lu, Q.; Nanoscale Res. Lett. **2009**, 4, 371.
DOI: 10.1007/s11671-009-9256-3
4. Roy, J.S.; Pal Majumder, T.; Dabrowski, R.; J. Lumin. **2014**, 148, 330.
DOI: 10.1016/j.jlumin.2013.12.045
5. Murai, H.; Abe, T.; Matsuda, J.; Sato, H.; Chiba, S.; Kashiwaba, Y.; Appl. Surf. Sc. **2005**, 244, 351.
DOI: 10.1016/j.apsusc.2004.10.125
6. Grover, R.; Srivastava,R.; Rana, O.; Srivastava, A.K.; Maurya,K.K.; Sood,K.N.; Mehta,D.S.; Kamalasanan, M.N.; J. Lumin. **2012**, 132,330.
DOI:10.1016/j.jlumin.2011.08.021
7. Reddy, M.P.; Jamalaiah, B.C.; Kim, I.G.; Yoo, D.S.; Siva Kumar, K.V.; Reddy, R.R.; Adv. Mat. Lett. **2013**, 4, 621.
DOI: 10.5185/amlett.2012.12483
8. Shen, G.; Cho, J.H.; Yoo, J.K.; Yi, G.C.; Lee, C.J.; J. Phys. Chem. B **2005**, 109, 9294.
DOI: 10.1021/jp044888f
9. Zhang, P.; Gao,L.; Langmuir **2003**, *19,* 208.
DOI: 10.1021/la0206458

10. Zhou, S.M.; Feng, Y.S.; Zhang, L.D.; Mater. Lett. **2003**, 57, 2936.
DOI: 10.1016/S0167-577X(02)01400-3
11. Kotkata, M.F.; Masoud, A.E.; Mohamed, M.B.; Mahmoud, E.A.; Physica E **2009**, 41, 1457.
DOI: 10.1016/j.physe.2009.04.020
12. Zou, L.; Fang, Z.; Gu, Z.; Zhong, X.; J. Lumin. **2009**, 129, 536.
DOI: 10.1016/j.jlumin.2008.12.009
13. Jun, Y.W.; Lee, S.M.; Kang, N.J.; Cheon, J.; J. Am. Chem. Soc. **2001**, 123, 5150.
DOI: 10.1021/ja0157595
14. Pal, K.; Maiti, U.N.; Pal Majumder, T.; Debnath. S.C.; Appl. Surf. Sc. **2011**, 258, 163.
DOI: 10.1016/j.apsusc.2011.08.024