

# Development of PBS/CdS Core-Shell Nanocomposites Through Ligand Etching for Optoelectronic Application



K. C. Handique, B. Barman, P.K. Kalita

**Abstract:** Core-shell nanocomposites are of immense interest among the research community for its potential applicabilities in various optoelectronic devices. In this work cadmium sulphide (CdS), lead sulphide (PbS) and their core shell PbS/CdS nanostructures have been synthesized through chemical bath deposition method. Their structural and optical properties are studied accordingly through diffractometric and spectrometric techniques. The phase of the core PbS is cubic zinc blende and of the shell CdS is hexagonal wurtzite confirmed from the XRD data. The optical bandgaps are calculated from the absorption spectra and are found to be 2.2eV for PbS and 2.7eV for CdS whereas for core shell PbS/CdS it reduces to 2.1 eV. The photoluminescence spectroscopy has been done on the samples and the spectra shows a blue shift of its near band gap emission for core PbS when it is coated with shell CdS which is not according to the usual behavior of core shell nanostructures. These optical properties are clearly carrying evidences of cationic ligand exchange between the cadmium and lead ion complexes. The conductivity of the prepared samples are measured at room temperature and it is found to be higher in case of PbS/CdS than the core PbS and shell CdS. The increase of bandgap and conductivity of PbS/CdS is a suitable nature for the application of this material in photovoltaic devices. The quantum yield of the core shell nanocomposites is also greatly enhanced that makes the synthesized nanostructures one of the potential candidates for the application in various optoelectronic devices.

**Keywords:** Ligand etching, cation exchange, photoluminescence, core shell

## I. INTRODUCTION

Semiconductor nanostructures especially the core shell quantum dots have been attracting a tremendous attention in recent years for its exciting tunable optoelectronic properties [1-3]. For a long time PbS is also attracting the attention of research community due to its size tunable structural and optoelectronic properties [4-5]. CdS is also one of the most important and commercially viable wide band gap semiconductors with its size and shape tunable optoelectronic applicabilities [6-8].

In the meantime development of core shell, a new hybrid structure is also emerging as a potential technique to produce high quality quantum dots and other nanostructures. Cation exchange especially in the synthesis of core shell nanostructures has also recently been explored as an important phenomena which sometime can bring some promisingly newer properties to the parent materials [9-10]. In this work the phenomenon and effect of cation exchange through ligand etching is explored and studied briefly with the simple and cost effective chemical bath deposition technique.

## II. EXPERIMENTAL

### A. Materials used

All the required chemicals needed for our synthesis are used as received from Merck without going through any further purification. The chemicals and reagents used in the synthesis are cadmium acetate, thiourea, lead acetate, polyvinyl pyrrolidone (PVP), ammonia solution and distilled water. The pH and molar concentration of the sample are taken as 10 and 0.5 respectively.

### B. Synthesis of PbS, CdS and PbS/CdS

The core PbS, shell CdS and core shell PbS/CdS are prepared simultaneously with same growth conditions. Firstly 1.88 gm of lead acetate is dissolved in 3% PVP solution. 3 to 4 drops ammonia solution is added to it to get the lead complex. 25 ml of thiourea solution is prepared in the same manner in another beaker and 25 ml of lead complex is added to it. The whole system is kept under constant magnetic stirring at 50<sup>o</sup>c for 4 hours which yield blackish PbS nanocrystals. Similarly 50 ml of cadmium complex is prepared of which 25 ml is taken for the preparation of core CdS by mixing it with 25 ml of thiourea. For the preparation of core shell CdS/PbS initially 25 ml of PbS is taken on a reaction flask and 25 ml each of cadmium complex and thiourea solution is injected dropwise slowly on the PbS under constant magnetic stirring at 60<sup>o</sup>c for 3 hour. In the preparation of the core shell a volumetric ratio 1:2 of core to shell is maintained.

### C. Characterization techniques

X-Ray Diffraction on the samples are performed in a Rigaku Ultima IV. Phase and crystal structures are determined from the XRD peaks.  $CuK\alpha$  radiation is used in all the slits. The current and generator tension has been kept at 40 mA and 40 kV respectively. XRD for all the samples are done in continuous scan mode for the purpose of comparison. The scanning has been done in the range of  $2\theta = 10^{\circ}$  to  $70^{\circ}$ .

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\* Correspondence Author

**K C Handique\***, Ph.D. Scholar, Department of Physics, Rjiv Gandhi University, India.

**Barnali Barman**, PhD, Department of Physics, Rajiv Gandhi University, India.

**P K Kalita**, Professor, Department of Physics, Rajiv Gandhi University, India.

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Optical absorption of the samples were done using an Agilent Technologies Cary 60 UV-Vis spectrometer with the range from 800nm to 350 nm. All the spectra were corrected for baseline. Photoluminescence measurement were performed with a Cary Eclipse fluorescence Spectrometer with the scanning range 380nm to 900nm.

## III. RESULT AND DISCUSSION

### A. X-Ray diffraction

The XRD spectra of core PbS, shell CdS and core/shell PbS/CdS is shown in Fig.1. The diffraction peaks for PbS can be seen at  $2\theta=24.9^\circ, 26.6^\circ, 28.3^\circ, 36.8^\circ, 43.9^\circ, 48.10^\circ$  and  $52.1^\circ$  corresponding to the diffraction planes (100), (002), (101), (102), (110), (103) and (112) of the cubic zinc blende structure compared with the standard JCPDS data (JCPDS 05-592)[11]. An additional diffraction peak is seen at  $2\theta=31.63^\circ$  that may be assigned to CdO. For CdS the peaks are obtained at  $2\theta=24.9^\circ, 26.6^\circ, 28.3^\circ, 36.8^\circ, 43.9^\circ, 48.10^\circ$  and  $52.1^\circ$  which corresponds to the diffraction planes (100), (002), (101), (102), (110), (103) and (112) that reflects the hexagonal wurtzite structure after comparing it with the standard JCPDS data (card no. 41-1049)[12]. In the Fig. 1 (a) the presence of diffraction peaks of both the core and shell confirms the formation of core shell type nanostructure. The lattice constant for PbS estimated from its cubic structure is found to be  $a = 0.595$  nm using (1) which matches well with the standard one [13]. For hexagonal phase of CdS the lattice parameters are found to be  $a = 0.409$  nm and  $c = 0.692$  nm by using (2) [12, 14].

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (1)$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \frac{h^2 + hk + kl}{a^2} + \frac{l^2}{c^2} \quad (2)$$

The crystallite size is calculated from the well-known Scherer formula as in (3) [15] and found as 15.59 nm for PbS and 6.66 nm for CdS respectively.

$$D = \frac{k\lambda}{\beta_d \cos\theta} \quad (3)$$

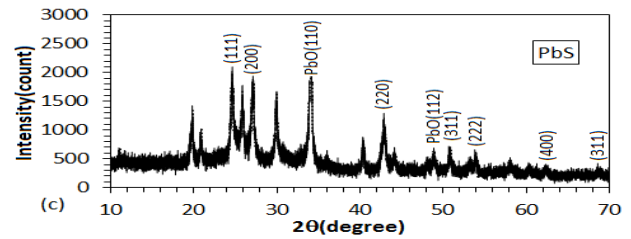
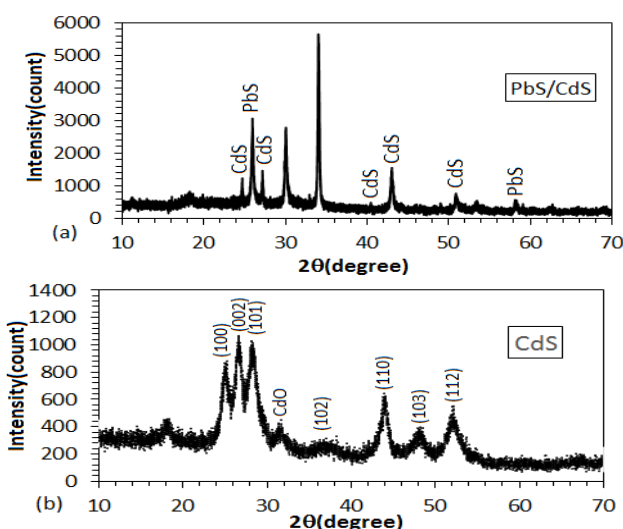


Fig.1. XRD spectra of (a) PbS/CdS (b) CdS (c) PbS

### B. UV-Vis spectra

UV-Vis spectroscopy has been done on all the three samples in the scanning range 350 nm to 800 nm as shown in Fig.2. Both the PbS and CdS are showing a blue shift of their absorption edges which indicates the quantum confinement of the particles and this is due to the effect of the polyvinyl pyrrolidone used as capping agent. The functional group of PVP attached immediately to the as grown particles and thereby it prevents the incoming particles from further agglomeration. The absorption spectra of the core shell PbS/CdS is showing a slight blue shift than the core PbS which is an unusual nature of core shell nanostructure and the same type of observations are also found and justified in photoluminescence spectra also. Approximate bandgaps and the particle size of all the samples are calculated from the Tauc relation and Brus equation respectively as shown in (4) and (5).

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

Where  $E_g$  is the optical bandgap of the materials and  $A$  is a constant. We are taking the value of  $n$  as  $\frac{1}{2}$  assuming the direct allowed transition in all the samples. The optical bandgaps are found to be 2.7 eV, 2.2 eV and 2.1 eV for PbS, CdS and PbS/CdS respectively. In (5)  $R$  is the particle size,  $E_g$  is the optical bandgap of nanoparticles and  $E_g^{bulk}$  is the bandgap of all the composites in their bulk form. The particle size calculated from the following equation are 2.34 nm for PbS and 4.55 nm for CdS which are smaller than the exciton bohr radius and it clearly signify a strong quantum confinement in the synthesized samples.

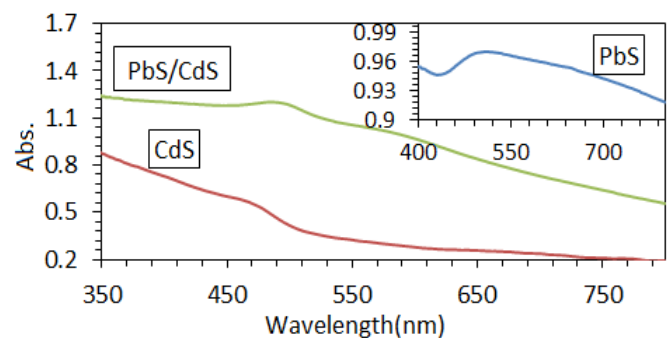


Fig.2. Absorption spectra of PbS, CdS and PbS/CdS.

The calculated grain size using Brus equation agrees with the XRD data for CdS but for PbS it is deviating slightly which may be due to the oxide phase present in the sample. The lead oxide is likely to influence the growth of the host particle PbS.

$$E_g = E_g^{bulk} + \frac{h^2}{8R^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi \epsilon_0 \epsilon_r R} \quad (5)$$

### C. PL spectra

Fig. 3 shows the PL spectra of all the samples with the excitation wavelength 320 nm and the scanning range is from 380 nm to 880 nm. The PL spectra of PbS and CdS are showing their prime emission peaks at 422 nm and 528 nm but surprisingly the core PbS shows a blue shift of 5 nm from 422 nm to 417 nm after coating the core by the shell. Usually the PL spectra of core shell shows a red shift with respect to the core of their emission wavelength due to the incorporation of impurities by the shell. But in the present case the observation of blue shift is a matter of importance in the context of synthesizing core-shell nanostructures. A blue shift implies the lowering of particle size which is contrary to the usual behavior of core shell nanostructures that shows red shift and in our case some of the cadmium ion replaces the lead ions on the surface of lead sulphide complex through ligand etching. Due to this reason the overall particle size of PbS/CdS is decreasing than the core PbS. Haiguang Zhao *et al* [9] also found the same type of results and they termed it as cation exchange that play a crucial role in the variation of the size of core and shell while synthesizing core shell nanoparticles. This process of ligand etching is important now a days because we can design a new hybrid particle without changing the size and other structural parameters. The surface of the nanoparticles thus gets modified through this technique of ligand etching with another high or low bandgap material that directly enhances the optoelectronic properties of the final composite. In almost all types of core shell nanostructures we can tailor the properties of the materials but only at the expense of increased size of the particles. But through cationic ligand exchange we can get an efficient material with highly modified properties without changing the sizes. The role of ligand etching in various types of core shell nanostructures is being studied in our nano synthesis laboratory. The PL intensity of the core is getting tremendously enhanced after coating with the shell which makes this particular core shell nanomaterial a potential candidate for optoelectronic device applications.

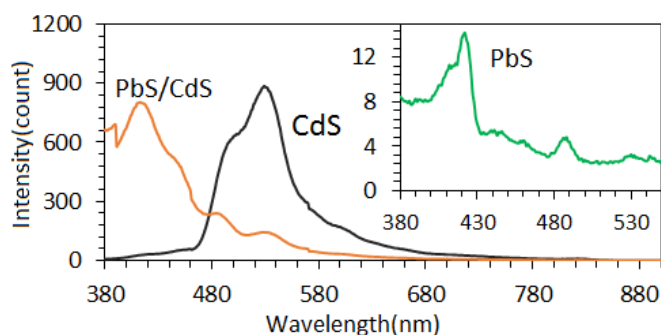


Fig. 3. PL spectra of PbS, CdS and PbS/CdS

### D. Electrical conductivity

The DC electrical conductivity of the samples have been measured at room temperature. Thin films of the as prepared samples have been prepared on ITO coated glass substrates for measuring the conductivity. The conductivity of PbS is found to be slightly increased after coating it with shell CdS. This may be due to the charge separation takes place between the core and shell. Due to the ligand etching effect of cadmium ions on the surface of PbS the band discontinuity becomes smaller and as a result one of the charge carrier of

the exciton pair may escape from the core PbS to the shell CdS whereas another carrier is trapped within the core. The separated charge carriers are assumed to contribute towards the conductivity mechanism in case of PbS/CdS core shell nanostructures.

### IV. CONCLUSION

The observation of cationic exchange through ligand etching is an important aspect of the present work. Here we have synthesized and studied the structural and optical properties of PbS, CdS quantum dots along with their core shell PbS/CdS nanocomposites. The XRD shows cubic zinc blende structure for PbS and hexagonal wurtzite structure for CdS. The blue shift in the absorption spectra of both PbS and CdS clearly signifies the quantum confinement on the particles. In both UV-Vis and PL spectra, a blue shift is observed in the core shell which establishes smoothly the effect of ligand etching and it is broadly discussed in the PL part. The increase of DC electrical conductivity for core/shell nanostructure clearly indicates its potential possibilities in the fabrication of optoelectronic devices.

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## AUTHORS PROFILE



and study of optoelectronic devices.

**K C Handique**, is currently doing his reseach as a Ph.D. scholar in the Department of Physics, Rjiv Gandhi University, India. He has got his B.Sc. degree from Dibrugarh University, Assam, India and M.Sc. degree from Rajiv Gandhi University, Arunachal Pradesh, India. His current area of research lies in material science and nanotechnology



both theoretically and experimentally.

**Barnali Barman**, is presently doing her PhD in the Department of Physics, Rajiv Gandhi University. She has done her M.Sc. from Dibrugarh University, Assam, India. She is interested in material science and study of photovoltaic devices. Her research work involves the application of various computer tools in characterisation of thin film devices



conference proceedings.

**P K Kalita**, is currently working as a Professor in the Department of Physics, Rajiv Gandhi University. He has done his Ph.D. from Gauhati University. His area of research is material science, nanotechnology and thin film photovoltaics. He has already published around 65 numbers of research papers in various national and international journals including