

Studies on ternary zinc blend based semiconducting quantum dots for hybrid solar cell applications

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Abstract: A systematic study is presented in the present work on the fabrication of hybrid solar cell using doped zinc blend based semiconductor quantum dots (QDs) prepared by a simple wet chemical precipitation method. Formation of quantum dot has been ascertained by X-ray Diffraction (XRD), UV-visible Spectroscopy and Impedance Spectroscopy measurements. XRD studies established the zinc-blende phase in quantum dot regime. UV-visible studies reveal decrement in optical bandgap of the QDs with co-doping of Cd ion in ZnS lattice. Mott-Schottky analysis revealed n- type conductivity with increase in band bending from binary to ternary configuration respectively. Bulk heterojunction hybrid solar cells fabricated in 1cm X 1cm size in conjunction with p type Polypyrrole under AM 1.5 illumination resulted in highest conversion efficiency of 1.6 %.

1. Introduction

One of the major concerns for solar cell technology is to find novel materials that have appropriate properties for solar energy conversion. In this perspective synthesis and characterization of semiconductor nanoparticles have attracted much interest in recent times due to their novel size dependent properties as a consequence of the large number of surface atoms and the three dimensional confinement of electrons [1-2]. Among the different semiconductor materials, binary metal chalcogenides of group II-VI have been extensively investigated in recent times [2]. In the case of ZnS chalcogenides, the band gap varies in the range of 3.7 to 5.5 eV depending upon the particle size and finds application in variety of opto-electronic applications [2-4]. It has been well recognized in recent years that optical absorption and photoluminescence properties of semiconductor nanoparticles are strongly modified due to size quantization [3-5]. Alternatively, ternary semiconducting nanoparticles formed by two binary semiconductors can also be used to tailor these optical properties. Such semiconducting particles are expected to improve the performance of thin film solar cells and photo electrochemical energy conversion cells. In recent report energy band gap has been found to vary from 5.5 to 2.5 eV at room temperature in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution semiconductors [5] which favours their candidature for solar cell applications. Bearing these aspects in mind, an attempt has been made in the present work to dope ZnS with Cd^{2+} ions leading to formation of ternary system $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ and characterize them for hybrid solar cell application.



2. Experimental details

Zinc blend based semiconductor quantum dots have been synthesized at room temperature using co-precipitation method. The chemical reaction involved in the synthesis of ZnS, $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles has been described elsewhere [5]. The resulting precipitates were filtered several times with methanol to remove impurities and dried at room temperature. X-ray studies were conducted on Shimadzu make X-ray diffractometer (model 6100) in 2θ range 20° to 70°C having $\text{CuK}\alpha$ radiation wavelength 1.5406\AA . Band gap of all the samples were estimated from UV-Vis data obtained with the help of Systronics make UV-visible spectrophotometer (model 2203) in 200nm-1100nm wavelength range. Mott-schottky analysis was carried out with the help of LCR meter (Hioki Japan, model 3520). With these nanopowders and as synthesized p type polypyrrole a bulk heterojunction solar cell was fabricated employing doctor blade technique. Electrical characterization was performed using a computer-controlled Keithley 2400 Source Meter in the dark and under illumination to assess the performance of solar cell. The photovoltaic devices were illuminated using a metal-halide lamp calibrated to an intensity of 1 kW/m^2 (in accordance with standard testing conditions AM 1.5G). All measurements were performed at a temperature of 295 K (room temperature) and the temperature of the device was kept constant.

3. Results and discussions

3.1 X-ray diffraction studies

Figure 1 depicts the XRD pattern of wet-chemical derived $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ nanoparticles for different mole percentages of cadmium (x). Polycrystalline nature of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ QDs is apparent from these X-ray diffraction patterns. Further, these patterns exhibit three prominent peaks around 2θ values 28.54° , 47.62° , and 56.28° corresponding to (111), (220), and (311) planes of the cubic phase of ZnS with the lattice constant $a = 5.4\text{\AA}$ (JCPDS card no. 05-0566). These results reflect zinc blend structure of as synthesised powders. The gradual shift of diffraction peak positions towards lower diffraction angles with increase of Cd concentration (from 0 to 0.5) indicates that the synthesised crystals are not a simple mixture of pure ZnS and CdS rather a solid solution of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ [5-6]. The small difference in the bond length of ZnS and CdS and the very close electronegativity value of Cd and Zn allow the formation of such a solid-solution.

Table 1. XRD data of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ nanocrystallites

Sample description	Angle (2θ)	d-spacing (\AA)	Peak width (2θ in $^\circ$)	Identified possible h k l	Crystalline size (nm)	Lattice constant (\AA)
ZnS	28.54	3.1250	4.39	1 1 1	1.75	5.406
	47.62	1.9080	2.63	2 2 0	2.76	
	56.28	1.6332	2.58	3 1 1	2.71	
$\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$	27.57	3.2318	2.97	1 1 1	2.59	5.613
	45.67	1.9849	2.74	2 2 0	2.67	
	53.84	1.7012	2.57	3 1 1	2.75	
$\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$	26.50	3.3608	1.36	1 1 1	5.68	5.716
	43.95	2.0582	1.56	2 2 0	4.72	
	52.15	1.7523	1.81	3 1 1	3.94	

The crystallite size corresponding to the observed $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ peaks have been calculated from the Debye-Scherrer relation [7]. It is apparent from these calculations (table 1) that crystallites size of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ Nanocrystallites increases with increasing Cd concentration.

3.2 Optical studies (UV-visible absorption study)

Band gap of synthesized nano-powder is estimated using the well-known Tauc's relation.

$$(\alpha h\nu) = K(h\nu - E_g)^n(1)$$

where K is the edge width parameter, n is a parameter which depends on the type of transition, i.e. allowed direct, allowed indirect, forbidden direct and forbidden indirect and can have values $\frac{1}{2}$, 2, $\frac{3}{2}$, and 3 respectively. The direct band gap value of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ nanoparticles was evaluated from the plot of a graph between $(\alpha h\nu)^2$ versus $h\nu$ as shown in figure 2.

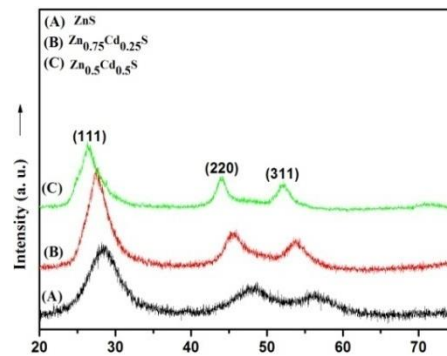


Figure 1. X-ray diffraction pattern of $\text{Zn}_{(1-x)}\text{Cd}_x\text{S}$ ($0 \leq x \leq 0.5$) semiconductor quantum dots

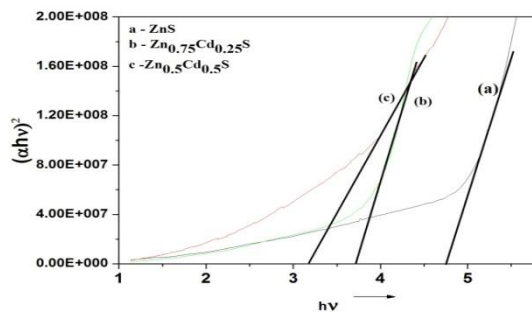


Figure 2. Shows optical band gap graph of $\text{Zn}_{(1-x)}\text{Cd}_x\text{S}$ ($0 \leq x \leq 0.5$) semiconductor

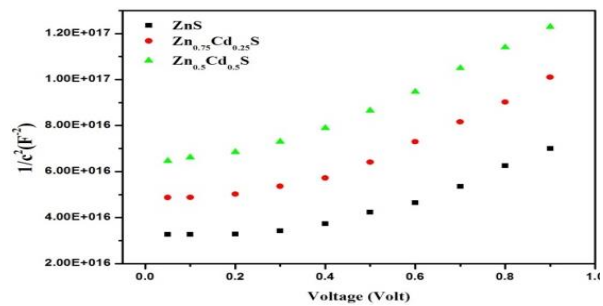


Figure 3. Mott-schottky study of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$: Agsystem samples

The obtained experimental band gap energy 4.7 eV, 3.7 eV and 3.2 eV for ZnS , $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ respectively reveal decrement of optical band gap with increasing Cd^{+2} concentrations in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ QD's. This red shift of band gap can be attributed to quantum confinement effect which takes place essentially due to growth of grain size and decrease in defect states near the band edges.

3.3 Mott-Schottky study

Mott-schottky plots have been drawn (in dark conditions) to evaluate the semiconductor parameters as shown in figure 3. The value of flatband potential (V_{fb}) was calculated using the relation [8]. the positive slope of the Mott-Schottky plot indicates n-type conductivity and decrement of flat band potential 0.29, 0.21 & 0.15 as for increasing Cd ions in ZnS lattice results increase in doping density of as prepared $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples.

3.4 Solar cell characteristics study

Figure 4 shows the photo response curve of as prepared Polypyrrole/ ZnS and Polypyrrole/ $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ solar cells with respect to variation in voltage. The obtained efficiency of ZnS/Ppy structure is 0.01% while for $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}/\text{Ppy}$ structure it is 1.6%. Such poor efficiency for ZnS/Ppy structure can be attributed to the fact that ZnS being wide band gap semiconductor there is improper band alignment

between polypyrrole and ZnS which in turn causes inefficient excitation dissociation and thus less efficient device formation. On the other hand, the devices with Polypyrrole/ $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ are efficient.

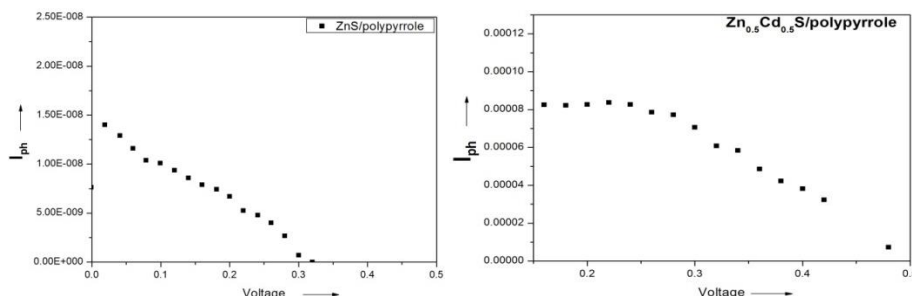


Figure 4. Photocurrent versus voltage graph of ZnS/Ppy and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ hybrid heterojunction solar cell

It can be expected that cell efficiency of Polypyrrole/ $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ results from the good charge balance of hole and electron at the interface and forming of a well-ordered morphology. The reason of the dramatic increase in efficiency could be attributed to the possibility that energy transfer rather than charge transfer could occur from the donor (polypyrrole) to acceptor (using ternary and quaternary QD's) in polypyrrole/ $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ resulting in a sufficient generation of free charge carriers.

4. Conclusions

$\text{Zn}_{1-x}\text{Cd}_x\text{S}$ QD's ($0 \leq x \leq 0.5$) have been prepared by simple wet chemical precipitation method without using any capping agent or surfactant. X-ray diffraction study confirmed cubic phase formation and nanometric size of particles around 2 to 5 nm. Due to the increasing of Cd content, all the XRD peaks shifted towards lower diffraction angles which show alloy formation of nanoparticles of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ samples. Optical study revealed that the optical band gap of materials decreased with the increase of Cd content which shows quantum confinement effect of QDs. Mott-Schottky plot of prepared samples shows n-type of conductivity with decreasing flat band potential for their binary to ternary conversion. Doctor blade technique has been deployed for deposition of active layer onto commercially available SnO_2 coated glass substrate for the preparation of hybrid solar cell structure. The characterization and findings on hybrid solar cell designed around inorganic semiconducting QD's and polymeric semiconductor shows better photoresponse with ternary quantum dots with highest conversion efficiency of 1.6%. Present studies reveal importance of II-VI group of semiconductor in the design and performance of hybrid solar cell structure.

References

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