Copper doped ZnS quantum dot as sensitizer in solar cell

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Copper ion doped ZnS quantum dots have been synthesized and introduced as sensitizer in solar cells. The quantum dots, synthesized using simple chemical method, has been characterized by using UV-Visible absorption spectroscopy, X-Rray Diffraction spectroscopy, and Trans-Electron Microscopy to study the influence of different concentrations of Copper ion doping on quantum dots. The successful doping is confirmed using Energy Dispersive X-Ray spectroscopic study. The Current density – voltage characteristics of the fabricated solar cells are studied and the photovoltaic parameters are compared for each cell. Better performance in terms of photo-conversion efficiency has been obtained for Cu ion doped ZnS quantum dot sensitized solar cells.

1. Introduction

Nanotechnology finds its widespread use in various fields of electronics in recent times. Nanoparticles such as Quantum Dots have an impressive ability to harvest a wide range of wavelengths of sunlight and as a result they are of recent interest among researchers and scientists for their application as sensitizers in solar cells. Also, they have the property of multiple exciton generation from single incident photon absorption. Additionally, simple and low cost fabrication methods and size dependent tunable band gap in quantum dots add to its merits [1]. While quantum dot sensitized solar cells (QDSSCs) are derivatives of dye sensitized solar cells [2-4], but they are advantageous than dyes as, quantum dots are cheaper than organic dyes and more stable towards water and oxygen [5]. Commonly used organic dyes have strong absorbance at around 350–700 nm and only weak absorption in the infrared (IR) [6-9], whereas QDs have size-dependent band gap that can absorb sunlight in both the IR and visible regions [10]. Semiconductor quantum dots are hence considered a more practical alternative to organic dyes as sensitizers in solar cell structures. Fig. 1 shows the basic structure and working of a typical QDSSC.
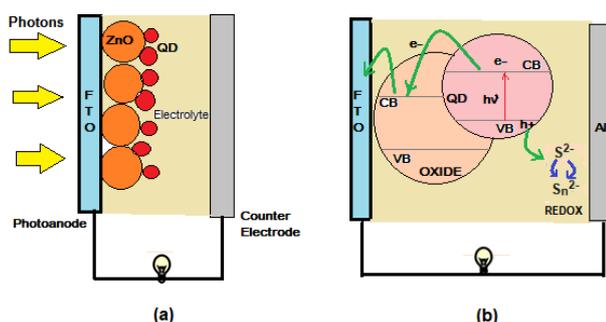

Fig. 1. (a) General structure of a QDSSC, (b) Operation of a typical QDSSC (color online)

An additional advantage of quantum dots (QDs) is that by altering the physical properties of QDs, one can alter the opto-electronic properties. With reducing the size of quantum dots, the electronic band gap increases [11]. Doping of quantum dots with transition metal ions is considered as one of the simplest and most effective method for increasing the efficiency of sensitized solar cells [12]. The dopant ions alters the charge separation and recombination dynamics in QDSSCs by creating extra intermediate electronic states in the bandgap region of QDs [13]. Also, by adding the dopant ions, the quantum dot crystal needs to re-adjust their structure in order to accommodate the dopant ions. This is known as nucleation effect in quantum dots, which in turn alters the opto-electronic properties of quantum dots [14,15].

In the present article the effect of Cu ion doping on ZnS quantum dots is investigated as sensitizer in ZnO oxide based QDSSC. ZnS thin film acts as n-type semiconductor having a wide direct band gap energy of $E_g = 3.65$ eV (bulk). This is the largest band gap value among all of the semiconductors made from II-IV compound. The sp electron-hole pair in the ZnS QD interacts with the 3d electron of the dopant Cu ions and because of the of the quantum confinement effect for the sp-state the opto-electronic properties in Cu doped ZnS QDs gets highly enhanced [14, 16]. A simple chemical one pot synthesis is adopted for preparation of ZnS quantum dots on polyvinyl alcohol (PVA) matrix. The main function of PVA capping matrix is only to control the growth of QDs during synthesis while itself not taking part in the chemical reaction [15]. Undoped and three different concentrations (2%, 4% and 6%) of Cu-ion doped ZnS quantum dots are synthesized and then applied over the ZnO layer as sensitizing layer in solar cells. A simple dip coating technique is utilized for deposition of quantum dot sensitizing layer on the photoelectrode surface. Current density- voltage characteristic is obtained for the solar cells and in enhanced efficiency is reported for Cu ion

doped QDSSCs, compared to that of undoped ones. In this paper, the syntheses of ZnS quantum dots as well as the fabrication steps of solar cells have been described in details in the 'Experimental' section. Characterization of the synthesized samples and the photovoltaic characteristics are provided in details in the 'Results and Analysis' section. The whole work is summarized and concluded in the end.

2. Experimental

To prepare the capping matrix, 5 gm of PVA powder is added in 100 ml of double distilled water and stirred with the help of magnetic stirrer for 2 hrs at around 90^0C until the solution turns transparent and viscous. The solution is given one day time for stabilization in dark chamber. In order to prepare the ZnS solution, at first 4 gm of $ZnCl_2$ is dissolved in double distilled water of 100 ml with a constant heating at an temperature 90 °C and stirring for 3 hrs. A few drop of HNO_3 is added to maintain the pH value of the solution. The prepared solution of $ZnCl_2$ is air cooled then added to the previously prepared PVA solution with mild heating and stirring using a magnetic stirrer. Simultaneously, to obtain the sulphide ions, 3 gms of Na_2S pallet is added to 100 ml of double distilled water with constant stirring and mild heating to obtain an aqueous solution. This aqueous solution of Na_2S is then added dropwise to the to ZnS solution, with stirring and hating at 90 °C until milky white precipitate is obtained. The milky white precipitate is the indication of ZnS formation.

The prepared ZnS solution is separated into four separate flasks to carry out the doping. In three of the flasks 2%, 4% and 6% $CuCl_2$ (by weight) is added respectively [16]. After moderate heating and stirring, the prepared samples are kept undisturbed for a whole day. Next day, the samples are washed thrice using double distilled water so that any unwanted byproduct of the reaction gets dissolved, leaving behind only the quantum dot samples.

The next part of the experiment is to prepare QDSSCs using the prepared quantum dots as sensitizer. To prepare the oxide layer for the photoelectrode, Znic Accetate ($ZnC_2H_3O_2$) and Sodium Hydroxide (NaOH) is mixed using ethanol as solvent to obtain ZnO. Four separate FTO coated glass (resistivity <10 ohm/sq.) plates are taken and ZnO film is deposited on the conducting surface by simple tape template and doctors blade technique. The ZnO coated FTO glass plates are then heated at 90^0C and air annealed at 500 °C so that the ZnO layer becomes hard on the FTO plates. This ZnO coated glass plate are immersed in the previously prepared Cu doped (0%, 2%, 4% and 6%) ZnS quantum dot solutions. Each plate is dipped for about 60 seconds each which results in formation of ZnS QD layer on the oxide [17]. In a separate beaker, a polysulphide electrolyte is prepared by mixing 2M of Soduim Sulphide (Na_2S) and 3M of Sulphur (S) [18]. Few drops of the electrolyte solution is added to the ZnO-ZnS deposited FTO glass photoelectrode plate before

sandwiching it with a thin aluminum plate (counter electrode). Thin glass cover slip are used as spacers in between the photoanode and Aluminum cathode to avoid any kind of short between the two electrodes. Scotch tapes and clips are used to hold the two electrodes together and metal crocodile probes are connected to each plate to act as electrode points.

The synthesized samples are tested by UV/VIS spectrophotometer to study their optical properties and X-Ray diffraction spectrometer is used to study their crystal structure. High resolution transmission microscope (HRTEM) images of the samples are taken to confirm the formation of quantum. Energy disruptive X-ray (EDX) spectroscopy is carried out to confirm the successful doping and also to obtain the exact percentage of elements present in each samples. To measure the photo current in the devices, the transparent photoelectrode side of each cell are illuminated by artificial white light using a 500 W Xenon Lamp (100 mW cm^{-2}) with an area of illumination of 0.3 cm^{-2}. The photocurrent is measured using a Keithley multimeter. The analysis and extraction of parameters from the current density – voltage (JV) curves is done using Open Photovoltaic Analysis Platform (OPVAP).

3. Results and analysis

Fig. 2 shows the obtained absorption spectra of the synthesized undoped as well as Cu doped ZnS quantum dots. It can be observed from the figure that strong absorbance edge occurs at 230 nm for undoped ZnS and for Cu doped ZnS the corresponding absorption edges are at 227 nm, 216 nm, and 196 nm for 2%, 4%, and 6% doping concentrations respectively. Absorption edge is the wavelength at which there is a sudden increase in absorption in samples which in turn corresponds to the respective bandgap of the quantum dots. The absorption edge is determined by drawing a tangent on the point of sudden increase of absorption, to meet the the x- axis. It can be noted that absorption edge shows slight blue shifts towards lower wavelength in case of doped QDs. This slight shifting in absorption edge in doped samples is the effect of the quantum confinement produced because of the increased nucleation [19]. This slight blue shift in spectra is also considered as an indication for successful doping of quantum dots. From the absorbance edge, particle size has been estimated by hyperbolic band model [20, 21].

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^*(E_{gn}^2 - E_{gb}^2)}} \qquad (1)$$

Here, R is the quantum dot radius to be calculated, whereas, m* (effective mass of the specimen), h (Planck's constant). E_{gb} (bulk band gap) are constant for each material. Thus the size of quantum dots is varying with the increase in E_{gn} (the quantum dot band gap), which is determined from the absorption edge in the Uv-Vis spectrum. The other values used in the present estimation are as follows, bulk band gap (E_{gb}) for ZnS: 3.65eV,

electron effective mass of ZnS at room temperature: 3.64×10^{-31} Kg [14] and the planks constant: 6.626×10^{-34} Js. The data from absorption spectra is presented in Table 1.
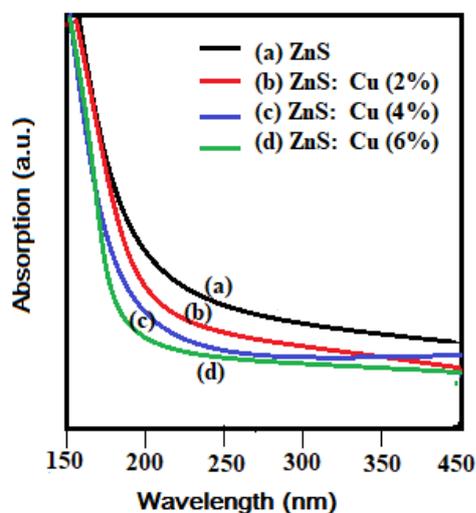

Fig. 2. UV-Visible absorption spectroscopy of a) ZnS, (b) 2% Cu-doped ZnS, (c) 4% Cu-doped ZnS and (d) 6% Cu-doped ZnS quantum dots (color online)

Table 1. Data from absorption spectra

QD sample	Absorption edge (nm)	Bandgap (eV)	Estimated Size (nm)
ZnS	230	5.63	10.86
ZnS:Cu (2%)	227	5.46	11.47
ZnS:Cu (4%)	216	5.74	10.52
ZnS:Cu (6%)	196	6.32	9.02

Fig. 3 shows the obtained XRD characteristics of each of the ZnS samples. The average particle size (crystallite size) is estimated by using Debye-Scherrer formula [22,23]:
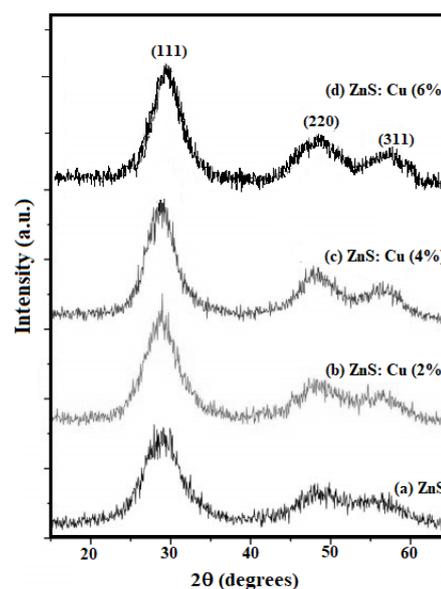
$$D = \frac{0.9\lambda}{WCos\,\theta} \qquad (2)$$

Here, 'λ' and 'θ' (theta) are wave length of X-ray (0.1541 nm) and the glancing angle respectively. While, 'W' and 'D' are FWHM (full width at half maxima) and particle diameter (crystallite size) respectively. The crystalline planes corresponding to the first, second and third XRD peaks are (111), (220), and (311) respectively [18]. From the X-ray diffraction peaks, the average crystallite size of quantum dots has been estimated using (2) and found to be in the range of 9.61-11.2 nm. Further, by comparing the X-ray diffraction with the help of ICDD (International Center Diffraction Data) JCPDS - 00.001.0792, it has been revealed that ZnS quantum dots are "wurtzite" in structure [22]. The data and estimated sizes from the XRD analysis is shown in Table 2.

Fig. 3. XRD spectroscopy of a) ZnS, (b) 2% Cu-doped ZnS, (c) 4% Cu-doped ZnS and (d) 6% Cu-doped ZnS quantum dots

Table 2. Data from X-ray diffraction spectra

QD sample	Diffraction angle 2θ (degrees)	W (radian)	Crystalline Plane	Size $D = 0.9\lambda\,/W\cos\theta$ (nm)	Avg. Size (nm)
ZnS	30	0.0263	111	11.56	11.22
	48	0.0210	220	11.13	
	56	0.0178	311	10.97	
Zn:Cu (2%)	29	0.0265	111	11.48	10.64
	48	0.0208	220	10.39	
	56	0.0177	311	10.05	
ZnS:Cu (4%)	29	0.0265	111	10.39	10.08
	47	0.0208	220	10.22	
	55	0.0178	311	9.64	
ZnS:Cu (6%)	28	0.0266	111	10.12	9.61
	48	0.0210	220	9.42	
	56	0.0181	311	9.31	

The High Resolution Transmission Electron Microscope (HRTEM) images (Fig. 4) confirms that the size of QDs is in the range 9-11 nm, which is in close agreement to the sizes estimated from XRD pattern and absorption spectroscopy. Fig. 5 shows the Selected Area Electron Diffraction (SAED) pattern of the prepared ZnS QDs. Each concentric circle corresponds to a unique crystalline plane in the crystal of ZnS. Thus the SAED pattern shows that the ZnS QDs are polycrystalline in nature [22].

Energy dispersive X-ray (EDX) spectra of the synthesized doped and undoped ZnS samples are provided in Fig. 6. The presence of strong peaks can be observed in all four spectra that corresponds to Zn and S. One can also observe the extra peaks of Cu present in Fig. 6 (b), (c) and (d) which confirm the presence of Cu ions in the doped samples. Each spectrum also shows the percentage of each element present in each sample. Thus from EDX study we can confirm the successful doping of ZnS specimen quantum dots with desired percentage of Cu ions has been achieved.
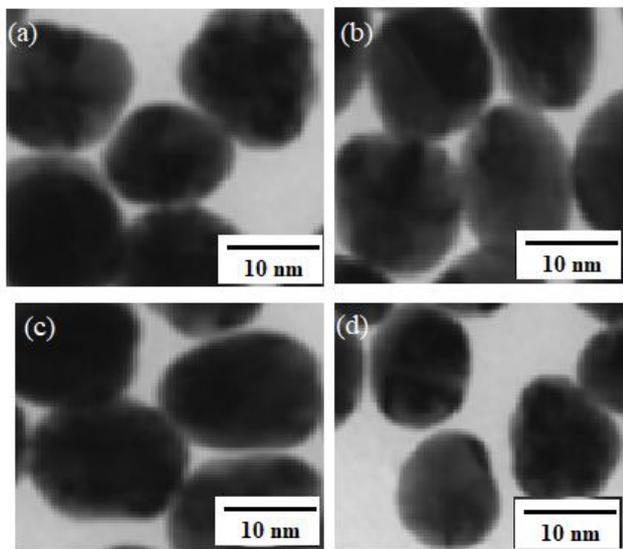

Fig. 6. EDX spectra of (a) ZnS , (b) 2% Cu-doped ZnS, (c) 4% Cu-doped ZnS and (d) 6% Cu-doped ZnS quantum dots
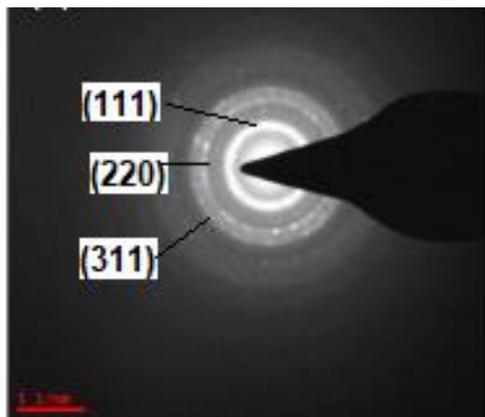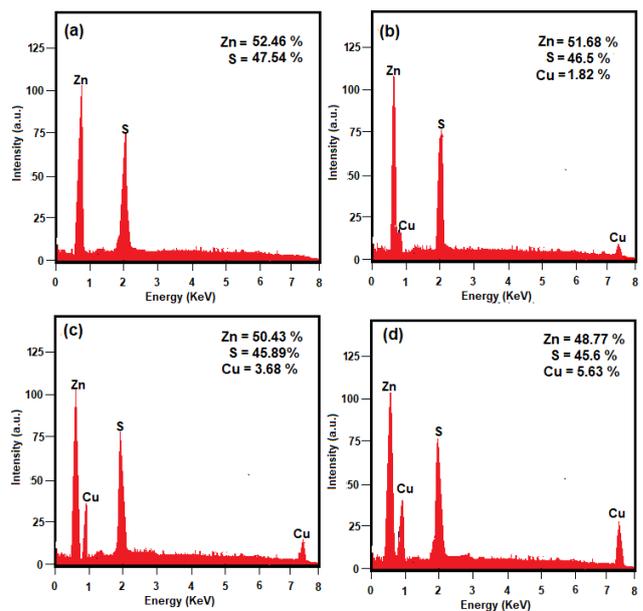

Fig. 4. HRTEM image of (a) ZnS, (b) 2% Cu-doped ZnS, (c) 4% Cu-doped ZnS and (d) 6% Cu-doped ZnS quantum dots
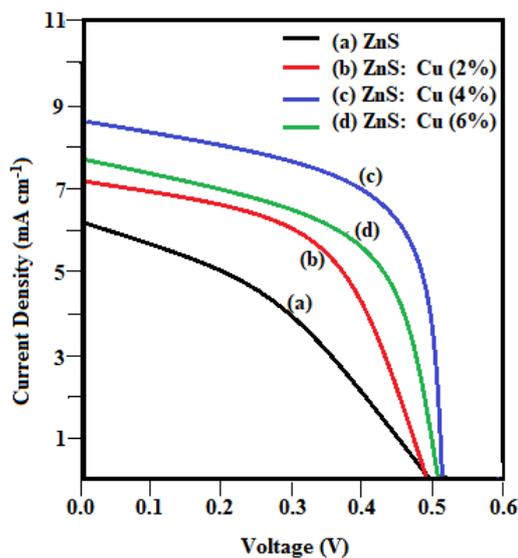

Fig. 7. Current density- voltage characteristics of ZnO based QDSSC with (a) ZnS, (b) 2% Cu-doped ZnS, (c) 4% Cu-doped ZnS and (d) 6% Cu-doped ZnS quantum dots (color online)

Fig. 5. SAED patterns of synthesized ZnS quantum dots

The current density–voltage (J–V) characteristics for each of the fabricated solar cells are shown in Fig. 7. The transparent side of each cell is illuminated by artificial white light using a 500 W Xenon Lamp (100 mW cm^{-2}) with an area of illumination of 0.3 cm^{-2} and the current density (J) v/s voltage (V) values are measure. The short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) is obtained from each of the J–V curves. Fill factor (FF) and power conversion efficiency (η) is calculated by using the equations (3) and (4), respectively [16]. The solar cell parameters for each devices are presented in Table 3.

$$FF = \frac{J \max . V \max}{Jsc.Voc} \qquad (3)$$

$$\eta = \frac{Voc \times Jsc \times FF}{Pin} \qquad (4)$$

Table 3. Photovoltaic parameters of pure ZnS and Cu^{+2} doped ZnS sensitized ZnO solar cell at different doping concentrations

Samples	Voc (V)	Jsc (mA cm^{-2})	FF	η %
ZnS	0.48	6.2	0.51	1.52
ZnS:Cu 2% doped	0.48	7.3	0.58	2.03
ZnS:Cu 4% doped	0.52	8.6	0.59	2.64
ZnS:Cu 6% doped	0.51	7.8	0.56	2.22

For the undoped QDSSC 1.52% efficiency was obtained, whereas, for the Cu doped ZnS QDSSCs the efficiency value obtained are 2.03%, 2.64%, and 2.22% for 2%, 4%, and 6% doping concentrations respectively. It can be observed that there is a significant increase in current density and efficiency for the Cu doped QDSSCs. The reason for this can be traced to the transition metal ion property of Copper ions. Copper has electronic configuration of $[Ar]4s^2 3d^{10}$ [24]. Being transition metal copper loses the s electrons before the d electron by nature [15, 17]. In case of neutral atoms, although ns orbitals has slightly lower in energy but the they can be considered having a very small difference in the energy of ns and (n -1)d orbitals. However, in ionic state, energy of the (n -1)d orbitals is considerably less than that of that ns electrons, as a result of which the ns electron is the the highest-energy electrons and is removed before the (n -1)d electron [17, 19]. This result in d-d transition in Copper ions when used as dopant in QDSSCs, which in turn results in an enhancement in electron conduction and improved current density (J_{sc}) in Cu ion doped ZnS quantum dot sensitized solar cell [19]. But it can also be observed that the solar cell performance degrades for higher values of Cu doping. The reason being, excess of Cu ions creates unwanted mid-gap states in the band gap region of quantum dots, that causes electrons to get trapped in them. This decreases the amount of charge recombination with holes and with the polysulfide electrolyte [24]. It also adversely effects the redox operation in the solar cell and hence the overall efficiency and performance deteriorates.

There is a significant increase in open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}), compared to that of undoped samples. The enhancement in current density can be attributed to the photo assisted d-d electronic transition in Cu doped quantum dot sensitizing layer. As a result of which, there is also a notable improvement in fill factor (FF), which in turn leads to enhancement of overall photo conversion efficiency (η) in doped quantum dot sensitized solar cell. Efficiency as high

as 2.64% is obtained at 4% Ni-doping concentration of ZnS quantum dots which is significantly higher than that of the pure ZnS QDSSCs and those of the previously reported ZnS-QD/ZnO based QDSSCs [25].

4. Conclusions

ZnS quantum dots are prepared by chemical method and different concentrations of Cu ion doping is done on synthesized quantum dots. The UV-Visible Absorption Spectroscopy shows slight blue shift in the absorption edge of Cu doped ZnS quantum dots due to increase in nucleation rate. The X-ray diffraction pattern shows that there is almost no visible change in the patterns, which indicates damage done to the ZnS structure due to doping, as they have similar XRD patterns. The average size of synthesized quantum dots is found to be within the range of 9-11 nm from the high resolution transmission electron microscope images which matches that of the estimated size from absorption and XRD analysis. The different crystalline planes of ZnS quantum dots can be easily identified from the SAED pattern which confirms that the ZnS quantum dots are polycrystalline in nature. The EDX study of each of the prepared samples confirms that the Cu ions have been successfully doped into the ZnS quantum dot crystal in desired weight percentages (0%, 2%. 4% and 6%).

The synthesized quantum dots are introduced on a ZnO photoelectrode solar cell as sensitizer and the solar cell parameters are obtained for white light illuminated condition. Significant improvement in solar cell parameters as well as in efficiency is obtained for doped quantum dot sensitized solar cells. A 4% Cu doped ZnS quantum dots on ZnO thin films exhibits a highest short-circuit current density (J_{SC}) of about 8.6 mA/cm^2, open circuit voltage (V_{OC}) of 0.52 V, fill factor (FF) of 0.59. Power conversion efficiency (η) of around 2.64% is obtained for the 4% Cu doped ZnS quantum dot sensitized device, which can be considered as a significant improvement compared to undoped solar cell performance.

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