J. Mater. Environ. Sci. 7 (5) (2016) 1589-1596
ISSN: 2028-2508
CODEN: JMESC

Effect of Reaction Time on the Synthesis of Cadmium Selenide Nanoparticles and the Efficiency of Solar Cell

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Received 13 Sep 2015, Revised 22 Feb 2016, Accepted 05 Mar 2016
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Abstract

Cadmium selenide nanoparticles were synthesized by solvothermal method using cadmium acetate, $Cd(CH_3COO)_2$ and selenous acid (H_2SeO_3) at 60 °C, and at different reaction times of 4, 8,12 and 16 hours. The synthesized nanoparticles were characterized by XRD, UV, PL, Raman, SEM and EDX spectral analysis. X-ray diffraction analysis confirmed a hexagonal, wurtzite structure and grain sizes were found to be of 15.8, 10.5, 6.7 and 111.7nm at 4, 8, 12 and 16 hours respectively. The absorption and photoluminescence spectra of the CdSe nanoparticle showed a red shift as the particle size was reduced. The band gap energy was computed from the absorption data and was found to be 1.62, 1.76, and 1.8 eV for 4, 8 and 12 hours reaction time respectively. The dielectric constant, dielectric loss, and conductivity of CdSe nanoparticles were studied over a range of frequency (50 Hz – 5 MHz) and temperature (40 °C-140 °C). Both dielectric constant and dielectric loss decreased with the increase in frequency and temperature. A solar cell was fabricated using TiO_2 as a photo anode, CdSe as a counter electrode, alizarine dye as sensitizer and I^-/I^{3-}as electrolyte, and the maximum conversion efficiency of the solar cell was found to be 3.28 %.

Keywords: *chalcogenide, Solvothermal, dielectric constant, solar cell, I-V characteristics.*

1. Introduction

Energy crisis and environment degradation have stimulated a great deal of interest in exploring renewable and environment friendly energy sources. At present, technologies to utilize solar energy have attracted world-wide attention. Although the thin film solar cells based on crystalline Si could provide high quantum conversion efficiency, the high cost of semiconductor grade silicon wafers has turned the attention of researchers towards developing cheaper materials which may be purely inorganic or may contain organic material as an essential part of the device. As a promising alternative to silicon-based solar cell, new photovoltaic systems like dye-sensitized solar cell [1-3], organic solar cell [4] and multifunctional solar cell [5] play a vital role in the development of renewable energy. Dye–sensitized solar cell (DSSCs), based on nanocrystalline TiO_2 is a low cost, environment friendly, and large photovoltaic effect alternative to other solar cell materials. These cells are composed of a wide band gap semiconductor (like TiO_2, ZnO) deposited on a transparent conducting substrate (FTO), a redox electrolyte I^-/I^{3-} couple and a counter electrode of CdSe, which acts as the cosensitizer of DSSC.

Inorganic semiconductors have several advantages as the band gap of semiconductor quantum dots (QD) can be tuned by size to match the solar spectrum. The large intrinsic dipole moments can lead to rapid charge separation and a large extinction coefficient which is known to reduce the dark current and increase the overall efficiency which can generate multiple charge carriers with a single photon. Recently, various nano-sized semiconductors such as CdS [6], CdSe [7], CdTe [8] Sb_2S_3 [9-10], Bi_2S_3 [11] have been studied for photocatalyst and solar cell applications. Among these sensitizers, CdSe has shown much promising application as an impressive senstizer which has strong absorption capability of the solar spectrum. Quasi solid-state dye sensitized solar cell (DSSCs), based on $TiCl_4$ treated and untreated nanoporous TiO_2 electrodes using alizarin dye, (CAS no-72-48-0) (oxidised) as photosensitizer were fabricated to improve the photo conversion efficiency (PCE) from 3.57 % to 5.12 % [12], yet there is a need to optimize their chemical and physical properties for improving device performance. DSSC based on Ru-complex photo sensitizers, such as N_3, N_{719} and black dyes has shown high photo conversion efficiency (PCE) [13]. In the recent years, metal free organic dyes have been explored as an alternative to Ru-complexes because of the low material costs, easy to synthesize and show high molar extinction coefficients [14]. The extent of diffusion of dye into nano crystalline TiO_2 matrix significantly affects the efficiency and photo current in DSSCs. The electron transport between the dye and nanocrystalline semiconductor interface is a key step in the energy conversion process as photoexcited electrons in dye molecules are transferred to an external circuit through these semiconductor films.

In this paper, CdSe nanoparticles, as cosensitizer, were prepared at various reaction times of 4, 8, 12 and 16 hours, to understand the effect of reaction time on the morphology and size of the synthesized CdSe nanoparticles. The quantum conversion efficiency was measured by fabricating the solar cell using the synthesized CdSe as photo cathode which could act as co sensitizer, nanoporous TiO_2 as anode, alizarine dye (CAS no-72-48-0) as sensitizers and I^-/I^{3-}as electrolyte.

2. Materials and Methods

2.1 Experimental

All the reactants used were of analytical grade and were used without further purification. Cadmium acetate and selenous acid were taken as 1:1 ratio and were dissolved in water by continuous stirring, and capping agent, ethylene glycol was added and the stirring was continued for an hour. The reducing agent, hydrazine hydrate was added while stirring and it was refluxed at 60 ^oC for 4, 8 and 12 hours. The resultant red coloured, colloidal solution was centrifuged at 3000 rpm for complete separation of solid.

2.2 Fabrication of solar cell using TiO_2/ CdSe film

Photoanode, TiO_2 paste was prepared by 0.5 g of TiO_2 in 1 mL of water and 1 mL of acetone. The homogeneous, monolayer of TiO_2 paste was then coated on fluorine doped tin oxide (FTO) glass (3.5 cm x 2 cm) by doctor bladding technique [15], and sintered at 300 ^oC for 3 hours. The solar cell was fabricated using CdSe as the counter electrode coated on FTO glass films, TiO_2 as photoanode using alizarin dye as the sensitizer (CAS no-72-48-0) and iodide solution as an electrolyte.

2.3 Instrumentation

The synthesized CdSe was characterized by using X-ray diffractometer (MAC Science MO3XHF22) with Cu(k_α) radiation (λ=1.5405 Å) in the 2θ range of 10-80^o. Optical Uv-Vis absorption spectra of CdSe was recorded using (Shimadzu Uv-Vis 2700 Spectrometer). Photoluminescence (PL) spectrum was recorded at room temperature using a Cary-Eclipse-(EL08083851) spectrometer. Morphology was characterized by a scanning electron microscope SEM, JSM-7000. Dielectric measurements were recorded by using H10KI 3532-50 LCR HI TESTER. The current-voltage measurement of solar cell was characterized by GS610 YOGOKAWA source measure unit.

3. Results and Discussion

3.1 X-ray diffraction analysis:

The XRD pattern of CdSe nanoparticles (Fig.1) reveals hexagonal wurtzite structure due to the existence of the peaks (100, 102, 103, 110, 200). The peaks are sharp and narrow, confirming the good crystallinity and fine grain size. The crystalline size of nanoparticles was determined [16] by using Scherer formula :

$$D = K\lambda/\beta \text{ Cos } \theta \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where λ is the wavelength of X-ray radiation (1.54 Å), β is the angular line width at half of the maximum intensity, θ is Bragg diffraction angle and K is a constant (0.9). The calculated crystallite size of the cadmium selenide nanoparticles at different reaction time (Table-1) clearly shows that the size of nanoparticle decreased as the reaction time increases from 4 to 12 hours and further increase of reaction time to 16 hours converts the nanoparticles into macro crystallite size aggregate particles (111.7 nm) with the change in the colour of particle from red to black. The size of particles obtained with the reaction time of the 16 hours is not in the nano range, it is not considered for the fabrication solar cell.

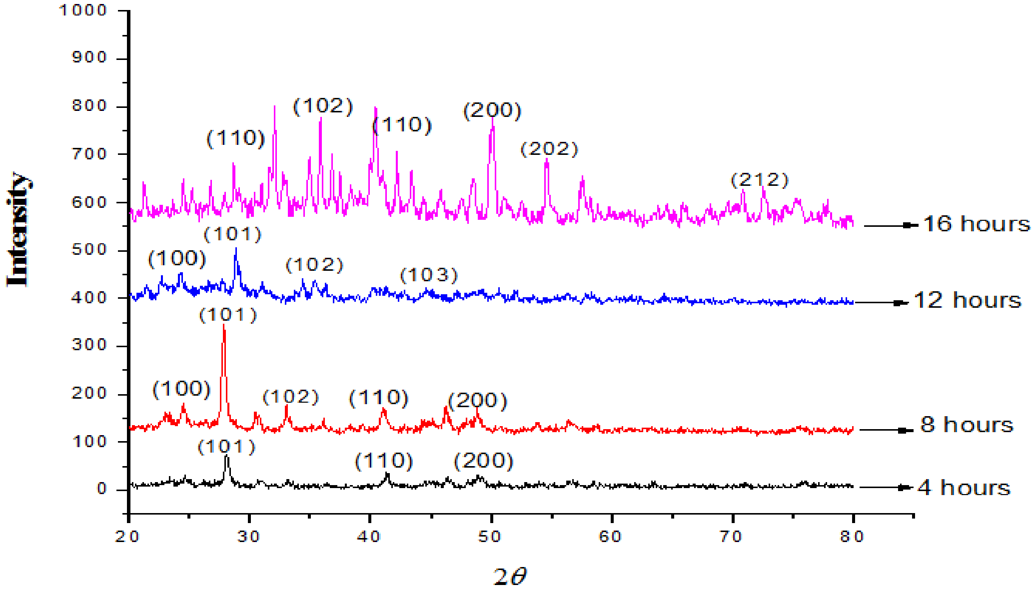


Figure 1 : XRD spectrum of CdSe at various reaction time.

Table 1 : Crystallite size of the CdSe at different reaction time

Sample	2θ	β	Cos θ	D nm
CdSe (4 hrs)	27.89	0.0090	0.9702	15.8
CdSe (8 hrs)	28.27	0.01360	0.9697	10.5
CdSe (12 hrs)	28.59	0.02110	0.9690	6.7
CdSe (16 hrs)	31.99	0.0013	0.9612	115.5

3.2 Uv-Visible spectral analysis

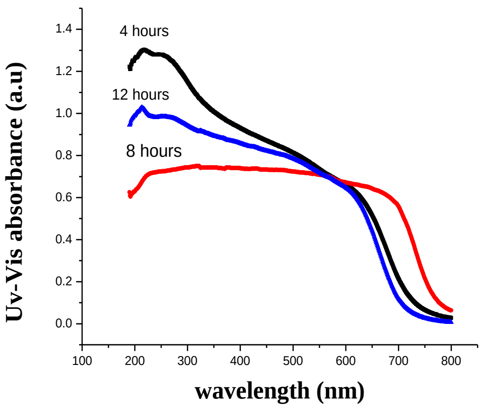
Solid state Uv-Vis absorption spectra was recorded in the region of 100-800 nm (Fig.2) which shows excitonic peaks at 490, 454, and 409 nm at different reaction times of 4, 8 and 12 hours respectively. The optical band gap (E_g) of CdSe nanoparticles was calculated from the absorption peak using the formula

$$Eg = hc/\lambda \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

where h is the planck's constant, c is the velocity of light and λ is the wavelength at which absorption peaks were obtained. The band gap value was found to be 1.62 eV, 1.76 eV, and 1.8 eV at 4, 8 and 12 hours of reaction time respectively. The band gap value was also calculated using Tauc's plot using the relationship of the absorption coefficient and the incident photon energy of semiconductor [17],

$$\alpha(h\vartheta)\ \alpha\ (h\vartheta - Eg)^{n} \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

where α is absorption coefficient, hν is the energy of the incident photon respectively. By plotting $(\alpha h\nu)^2$ versus hν (Tauc's plot) of the CdSe nanoparticles (Fig 3). The band gap energy of bulk CdSe material is 1.74 ev [17] and the increase in band gap value from 1.6 eV to 1.8 eV could be attributed to the decrease in the crystallite size as the reaction time of CdSe was increased from 4 to 12 hours.



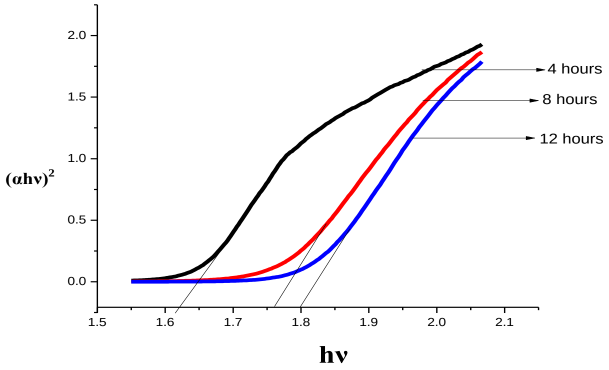


Figure 2 : UV-Visible absorption spectra of CdSe nanoparticles **Figure 3 :** Tauc plot for CdSe nanoparticles

The particle size of CdSe nanoparticles was computed from the absorption of the wavelength of Uv-Vis spectra (Table 2) by using Hyperbolic band model [18]:

$$R = \sqrt{2\pi^2}\, h^2 E_g b/m^*(Egn^2 - Egb^2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where R is a quantum dot radius (2R is the diameter representing particle size), E_{gb} – Bulk band gap (1.7 ev for CdSe), E_{gn} – band gap of nanoparticles (calculated from absorption peak), h – Planck's Constant, M* - effective mass (1.18 x 10^{-3} Kg for CdSe).

Table 2 : The particle size and band gap energy at different reaction time

Sample	Band gap energy (eV)	Particle size (nm)
CdSe (4 hrs)	1.62	18.29
CdSe (8 hrs)	1.76	15.74
CdSe (12 hrs)	1.8	6.1

When the reaction time was raised from 4 to 12 hours, the particle size was decreased from 19 nm to 14.2 nm (Table 2) and correspondingly the effective band gab value increases (Fig 4).

3.3 Photoluminescence (PL) spectral analysis

Photoluminescence spectra (Fig.5) of the CdSe nanoparticles at different reaction time shows only a single peak at 419, 420, and 421 nm at 4, 8, and 12 hours respectively and the intensity of the PL for the CdSe nanoparticles increases with an increase in the reaction time from 4 to 12 hours. The PL peak was broad and asymmetric at 8 hours of reaction time and became narrower and symmetric as the reaction time was increased from 8 to 12 hours (fig.5). The broad emission band at lower wavelength (420nm) may be attributed due to the presence of deep level trapping site and electron hole recombination trap state or imperfection site. Such a lattice phenomena are observed in nanomaterials and these results confirm the nanocrystalline nature of CdSe nanoparticles [18].

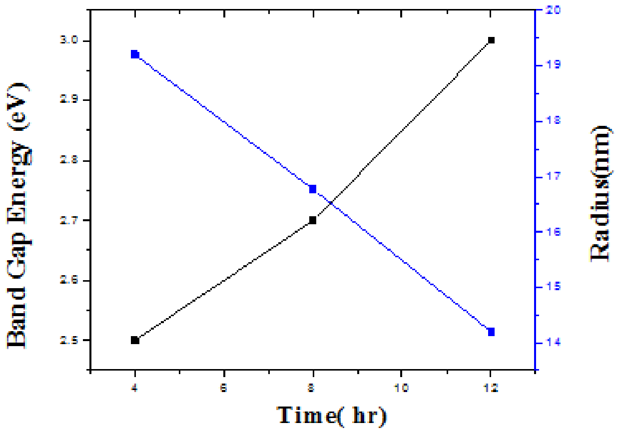


Figure 4 : Variation of effective band gap and crystalline size at different reaction time

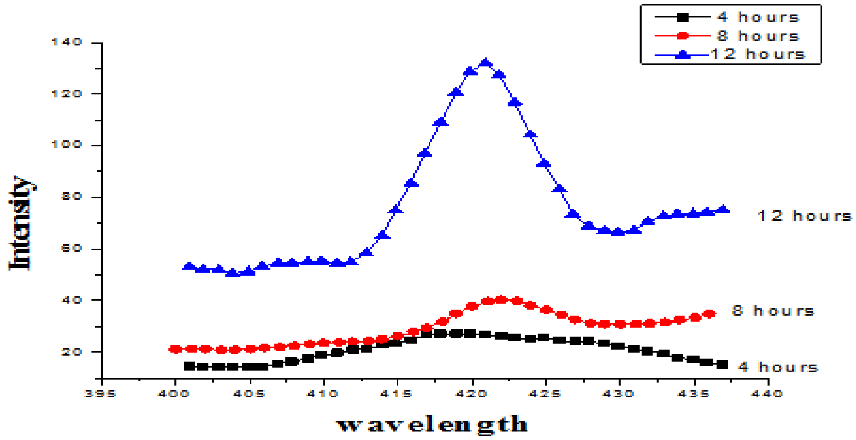


Figure 5 : Photoluminescence emission spectra of CdSe nanoparticles at various reaction time.

3.4 Raman spectral analysis:

Raman spectrum of CdSe nanoparticles was recorded in the range of wave number 100 to 4000 cm^{-1} (Fig. 6). The presence of strong fundamental and weak overtones modes at 235.31 and 457.42 cm^{-1} correspond to the 1 LO (Longitudinal optical) and 2 LO peaks of phonon vibrations. These vibrations match well with vibration of hexagonal, wurtzite structure of CdSe nanoparticles [19]. The absence of further peaks in the Raman spectrum supports the purity of synthesized CdSe nanoparticles.

3.5 Scanning Electron microscopic analysis:

Fig. 7 shows the scanning electron micrographs of CdSe nanoparticles at various reaction times 4, 8 and 12 hours respectively which clearly reveals a large variation in the morphology of CdSe nanoparticles: a large agglomeration of undistinguishable morphology at 4 hours, formation of needle type morphology at 8 hours, and a well defined rod formation at 12 hours. The enhancement of well defined morphological crystallites was observed as the heating time was increased from 8 to 12 hours.

3.6 Energy- Dispersive X-ray spectral analysis

The EDX spectrum of CdSe (Fig.8) showed prominent peaks only for cadmium and selenium ions with an error of 1.09 % and 1.72 % respectively (Table-3) and the purity of the synthesized CdSe was confirmed due to the presence of peaks only for Cd and Se ions.

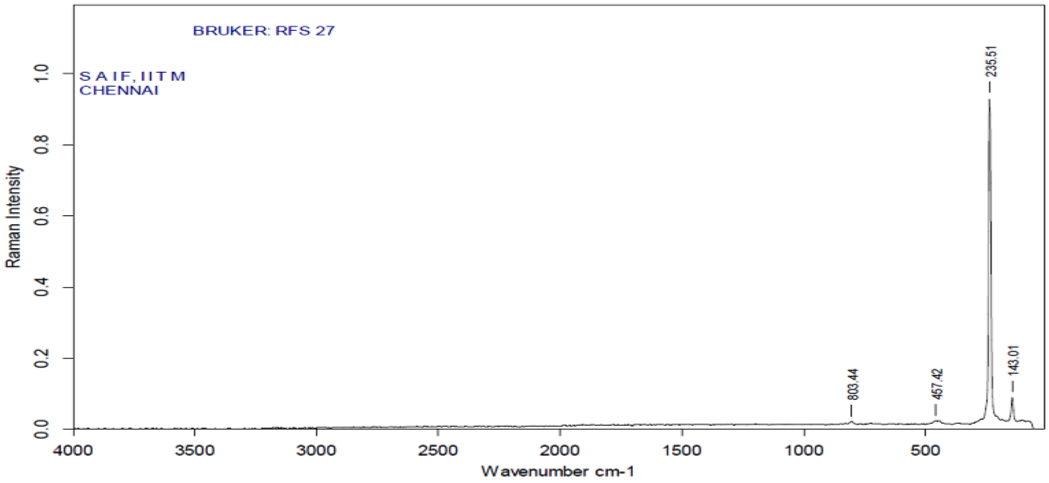
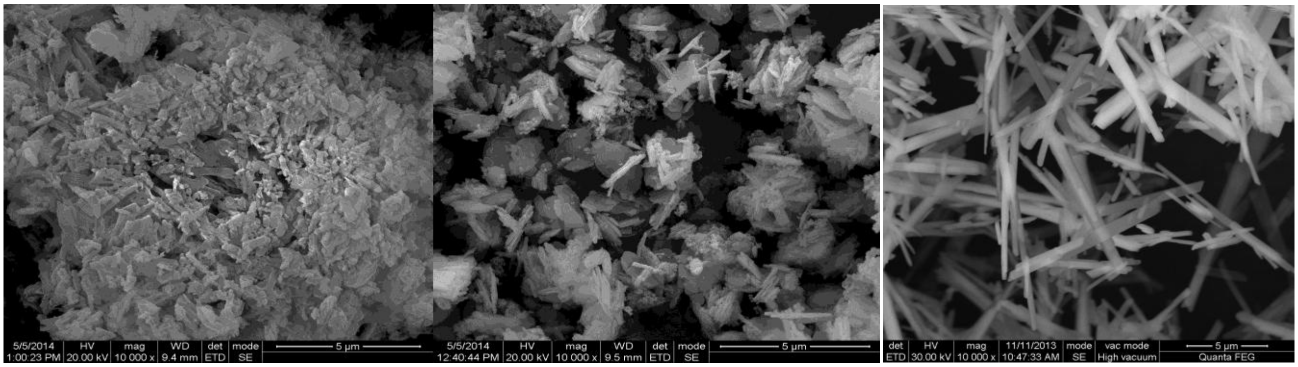


Figure 6 : Raman spectra of cadmium selenide nanoparticles.



(a) (b) (C)

Figure 7 : SEM image of CdSe nanoparticles at 60 ^{o}C at different reaction times, (a) 4 hours, (b) 8 hours, (C) 12 hours.

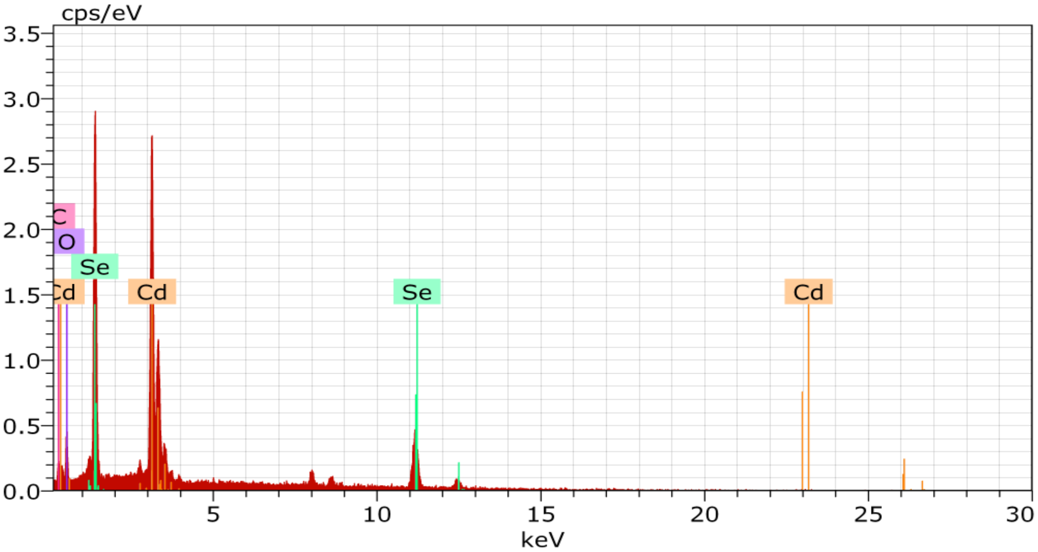


Figure 8 : EDX spectral analysis of CdSe nanoparticles.

3.10 Current density with potential:

Solar cell was fabricated using TiO_2 as a photo anode, alizarine dye as sensitizer and I^-/I^{3-}as electrolyte, and the synthesised CdSe at three different reaction time as counter electrode and the photo current was measured (Fig. 10) by varying the applied potential. The photovoltaic parameters and the efficiency of η was calculated (Table-4) using the equation 8 and 9 given below [17]:

$$\eta = \frac{\mathrm{Voc\ Isc\ FF}}{Pin} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$FF = \frac{Imp\ x\ Vmp}{Isc\ \ x\ Voc} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (9)$$

where, Voc - open circuit potential, Isc - short circuit current, FF - fill factor, η - power conversion efficiency.

Table 3 : Elemental analysis of cadmium selenide nanoparticles

EI AN Series	Unn. C [wt.%]	Norm C [wt.%]	Atom C [at.%]	Error [wt.%]
Cd 48 L-series	36.04	44.10	14.36	1.19
Se 34 K-series	21.95	26.86	12.45	0.71
O 8 K-series	16.47	20.16	46.12	3.75
C 6 K-series	7.26	8.88	27.06	2.16
Total	81.71	100.00	100.00	

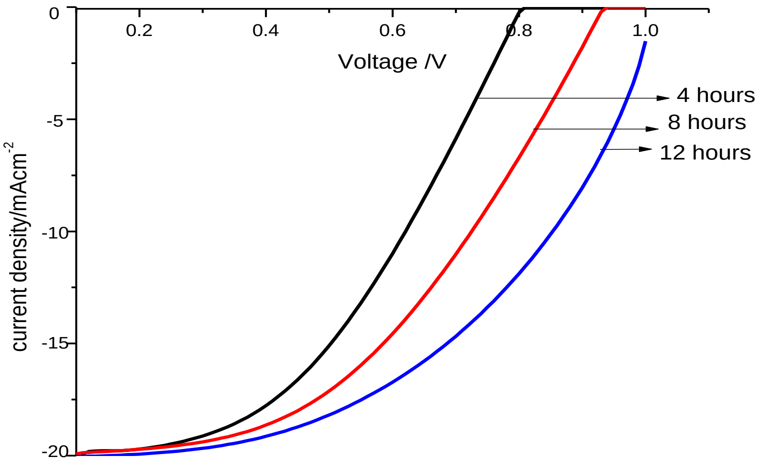


Figure 10 : Photocurrent density –voltage (I-V) curve of CdSe nanoparticles.

Table 4: Photovoltaic parameters of the CdSe based DSSCs.

Parameters	4 hour	8 hour	12 hour
Voc [mV]	0.8	0.94	1.0
Isc [µA]	19.8	19.9	20
FF [%]	0.4554	0.4586	0.54
Ƞ [%]	2.0714	2.451	3.28

The efficiency of fabricated DSSC depends on the reaction time which is clearly shown by the EIS parameters of the CdSe-based DSSC, i.e., the efficiency of the solar cell was improved from 2 to 3.28 % as the reaction time of CdSe was raised from 4 to 12 hours.

Conclusion

Cadmium selenide nanoparticles were prepared by solvothermal method at different duration of reaction time 4, 8, 12 and 16 hours and characterized by XRD, UV-Visible, PL, Raman, EDX and SEM spectral analysis. The powder X-ray diffraction analysis revealed that the synthesized CdSe nanoparticles are in wurtzite structure with average crystallite size of 15, 10, 6.34, and 111.7 nm at the reaction time of 4, 8, 12 and 16 hours respectively. The particle size was found to be macrosize on increasing the reaction to 16 hours. The EDX spectral analysis and Raman spectral analysis confirmed the purity of CdSe nanoparticles. The band gap of CdSe nanoparticles were calculated from UV- spectral data as 1.62, 1.76 and 1.8 eV for 4, 8 and 12 hours respectively. A well defined morphological SEM image was observed at 12 hours duration of reaction time. The dielectric constant and dielectric loss were found to decrease and attain constant value on raising the frequency. The increase in ac conductivity with temperature proved the CdSe nanomaterials as semiconducting materials. The hybrid DSSC using nano CdSe as photocathode, nanocrystalline TiO_2 as photoanode, alizarine dye as sensitizer I^-/I^{3-} as electrolyte was fabricated and the maximums quantum conversion efficiency was found to be 3.28%.

Acknowledgement-The authors are greatful for UGC (UGC reference no: F.No.41-1005/2012 (SR) for its generous funding.

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