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DIELECTRIC AND CONDUCTIVITY STUDIES OF CADMIUM SELENIDE NANOROD AND THE EFFICIENCY OF SOLAR CELL

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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 80 ^{o}C. The synthesized nanoparticles were characterized by XRD, UV, PL, SEM, and EDX spectral analysis. X-ray diffraction analysis confirmed a hexagonal; wurtzite structure and the crystallite size was found to be 6.7 nm. Red shift of emission spectrum was observed as the particle size reduced in the photoluminescence spectra of the CdSe nanoparticles. The band gap energy was determined from the absorption spectra as 1.81 eV. The dielectric constant, dielectric loss, and conductivity of CdSe nanoparticles were studied over a range of frequency (50 Hz – 5 MHz) and temperature (40 ^{o}C-140 ^{o}C). Both dielectric constant and dielectric loss were decreased on raising the frequency and temperature. The solar cell was fabricated using CdSe as a counter electrode, TiO_2 as a photo anode, ruthenium dye as sensitizer and I^-/I_3^-as an electrolyte, and the maximum power conversion efficiency of solar cell was found to be 3.08%.

Key Words: Solvothermal, Dielectric Constant, Solar Cell, J-V Characteristics & Chalcogenide

Introduction

The dielectric constant is one of the important properties which determine the capability of storing electric charges by the material and the capability of transferring the electric charge. The dielectric constant is different from material to material. Most of the bulk electronic properties as well as the surface properties of a material like the coulombic interaction between excitons, reflection coefficient, and refractive index etc., depend on the dielectric constant of the medium. CdSe with low dielectric constant, low dielectric loss in the high frequency regions [1], and enhanced optical quality with lesser defects are of vital importance for the fabrication of materials for ferroelectric, photonic and electro-optic devices. The dielectric constant arises due to the existence of various types of polarization mechanisms like electronic, ionic, orientation and space-charge polarization [2]. The space charge polarization depends on the purity and perfection of the sample, which influence at high temperature and is not observed in the low frequency region. The materials with high dielectric constant led to power dissipation factor and with low dielectric constant due to less number of dipoles per unit volume lead to minimum losses [3]. High dielectric constant at low frequency materials is very important for their potential capacitors, memory devices, sensors and solar cells [4].

Cadmium selenide (CdSe), an II–VI semiconductors exists in a crystalline forms viz. wurtzite (hexagonal), Zinc blende (cubic) and sphalerite (cubic) [5], have been the subject of investigations in recent years [6], which provide excellent and unique properties based upon shape and size of nanostructures [7]. In the NPs, the confinement of arriers perturbs the semiconductor band structure resulting in the series of discrete energy states in the conduction and valence bands. The strength of the quantum confinement in the materials depends upon the relative size of the NPs and the band gap, depends on the effective mass and dielectric constant of the materials, $\varepsilon=4\pi^2 \mu e^2$, where μ is the effective mass of the electron and hole, ε is dielectric constant at high frequency, and e is the electronic charge.

The nanocrystalline semiconductor is interesting due to their electrical and optical properties related to the quantum confinement of electrons [8]. The dielectric behavior of CdSe depends on chemical composition and on the surface morphology which is controlled by different factors like pH, reaction time, temperature, rate of addition of reactants etc., In the present work, CdSe nanoparticles was synthesized by solvothermal method at 80°C, and structural, optical, morphological, elemental analysis were investigated. Solar cell was fabricated using TiO_2 as photo anode, CdSe as photo cathode, I^-/I_3^- as an electrolyte and ruthenium dye as sensitizers for measuring efficiency. The frequency and temperature dependence dielectric constant, dielectric loss, ac conductivity and energy of activation were also investigated.

Experimental:

All the reactants were of analytical grade and were used without further purification. Cadmium acetate and selenous acid were taken as 1:1 ratio and dissolved in water by continuous stirring and capping agent, ethylene glycol was added with stirring for an hour. The reducing agent, hydrazine hydrate was added with stirring and refluxed at 80°C for 12 hours. The red coloured, colloidal solution was centrifuged at 3000 rpm for complete separation of solid precipitate.

Fabrication of Solar Cell Using TiO_2/ CdSe Film:

Photoanode, TiO_2 paste was prepared by dissolving 0.5 g of TiO_2 in 1 mL of water and 1 mL of acetone. TiO_2 paste was then coated on fluorine doped tin oxide (FTO) glass (3.5 cm x 2 cm) by doctor blading technique [9], and sintered at 300 °C for 3 hours The solar cell was fabricated using CdSe as the counter electrode coated on FTO glass films, TiO_2 as photoanode using ruthenium dye as the sensitizer and iodide solution as an electrolyte.

Instrumentation:

The synthesized CdSe sample was characterized by using X-ray diffractometer (MAC Science MO3XHF22) with Cu(k_α) radiation (λ=1.5405Å) in the 2θ range of 20-80°. Optical UV-vis absorption spectra of CdSe were 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 HIOKI 3532-50 LCR HI TESTER. The current-voltage measurement of solar cell was characterized by GS610 YOGOKAWA source measure unit.

Results and Discussion:

X-Ray Diffraction Analysis:

The XRD pattern of CdSe nanoparticles (Fig.1) reveals hexagonal wurtzite structure due to the existence of the peaks (101), (102), (103), (110), (112), and (200) (JCPDS-ICDD No-19-0191). The peaks are sharp and narrow, confirming the good crystallinity and fine crystallite size. The crystalline size of nanoparticles was determined [10] by using Scherer formula

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

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 crystallite size of the cadmium selenide nanoparticles was found to be 6.7nm .

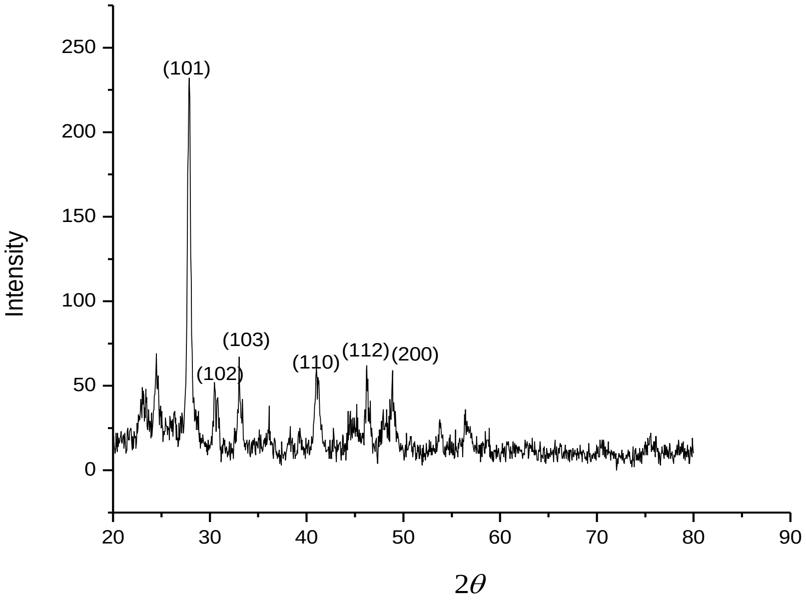


Figure 1: XRD spectrum of CdSe at various reaction time

UV-Visible Spectral Analysis:

Solid state UV-vis absorption spectra were recorded in the region of 200-800 nm (Fig 2). The optical band gap (E_g) of CdSe nanoparticles was calculated from the absorption peak using the formula

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

Where h is the planck's constant, c is the velocity of light and λ is the wavelength at which absorption peaks were obtained.

Band gap was calculated by plotting $(\alpha h\nu)^2$ versus hν (Tauc's plot) of the CdSe nanoparticles (Fig 3). The band energy of bulk CdSe material is 1.7 ev [10] and the increase in band gap value 1.81 eV could be attributed to the decrease in the crystallite size of CdSe nanoparticles.

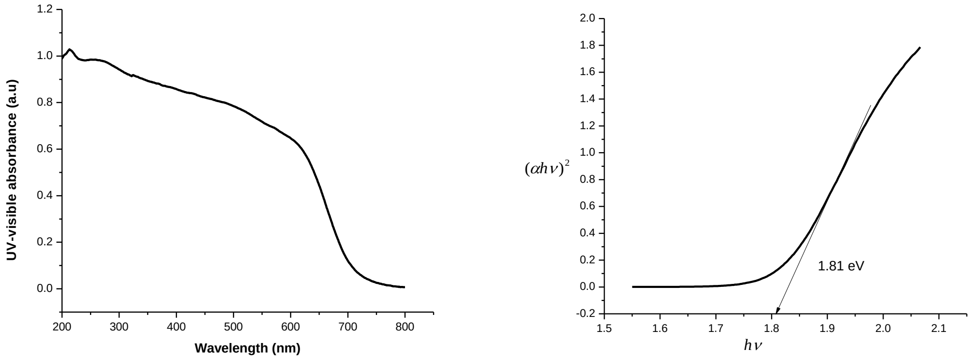


Figure 2: UV-visible absorption spectra of CdSe nanoparticles & Figure 3: Tauc plot for CdSe nanoparticles

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 [11]. The particle size of cadmium selenide nanoparticles was found to be 15.74 nm.

Photoluminescence (PL) Spectral Analysis:

Photoluminescence spectrum of the CdSe nanoparticles (fig 4), showed the broad emission band at wavelength (420 nm) 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 is observed in nanomaterials and confirm the nanocrystalline nature of CdSe nanoparticles [11]. The PL emitted as light by the photocathode layer (CdSe) would reach the active region of the PN junction, thus increasing the solar cell photocurrent.

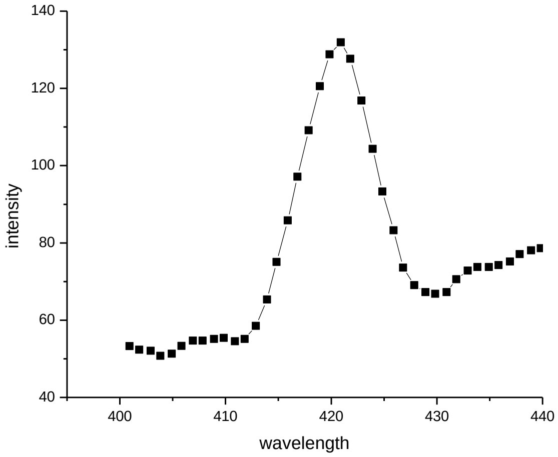


Figure 4: Photoluminescence emission spectra of CdSe nanoparticle.

Scanning Electron Microscope:

The FESEM analysis was used and the morphology of the synthesized CdSe nanoparticles, revealed a nanorod morphology (Fig-5) .

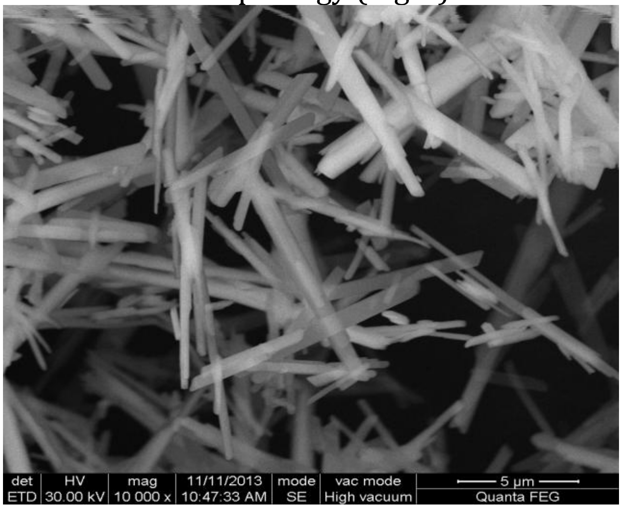


Figure 5: FESEM image of CdSe nanoparticle at 80^{o}C

Energy- Dispersive X-Ray Spectral Analysis:

Fig-6 shows EDX spectra of CdSe nanoparticles. The peaks of Cadmium (Cd), selenium (Se) have been observed, which confirm the presence of CdSe nanoparticles and no other prominent peaks for other element were observed showing the purity of CdSe.

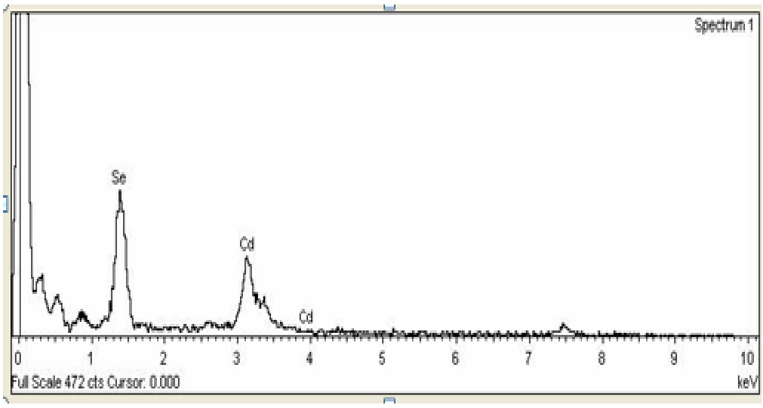


Figure 6: EDX spectral analysis of CdSe nanoparticles

Dielectric Studies

The capacitances, dielectric constant, dielectric loss of the material are important parameters in selecting the material for the device fabrication.

Dielectric Constant:

The dielectric constant was measured in the frequency range 50 Hz to 5 MHz and the temperature range of 40 °C - 140 °C. The dielectric constant was evaluated using the relation

$$\varepsilon_r = cd/A\varepsilon_0 \qquad \text{..........................(4)}$$

Where d is the thickness, and A is the area of the sample, ε_0 is the permittivity of free space ($8.85\text{x}10^{-12}C^2N^{-1}M^{-2}$), ε_r is the dielectric constant and c is the capacitance. The frequency dependence of dielectric constant of CdSe nanoparticles with temperature are given in fig-7, which reveals that the dielectric constant decreases with increase in frequency and then reaches almost a constant value in the higher frequency region. The high value of dielectric constant at low frequencies can be attributed to lower electrostatic binding strength, arising due to the space charge polarization, which depends on the purity and perfection of the sample. The very low value of dielectric constant at higher frequencies is important for the fabrication of materials towards photonic and electro-optic devices [12]. CdSe with high dielectric constant at low frequency and low dielectric constant at high frequency could be considered as a potential material for fabricating photonic devices and solar cell.

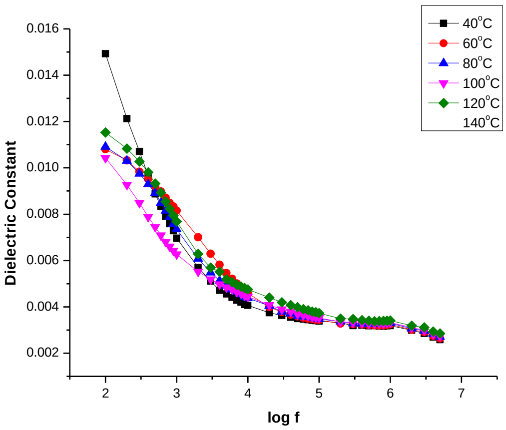


Figure 7: Dielectric constant (ε_r) Vs log frequency at different temperature

Temperature and Frequency Dependence of Dielectric Loss:

Dielectric loss represents loss of energy on heating a dielectric material in a varying electric field. The variation of dielectric loss of CdSe nanoparticles are given in fig 8. As the frequency increases, the dielectric loss is found to decrease exponentially and attains constant values similar to dielectric constant. At high frequencies as the polarization decreases the dielectric loss also decreases, as the particles are not getting sufficient time to generate phase angle. Thus at high frequencies the contribution of orientational or dipole polarization vanishes and the effect is only for electronic polarization which is instantaneous. At high frequencies the very low dielectric loss related with the purity of nanomaterials having negligible defects with good optical quality which could be useful in the design of optical devices [13].

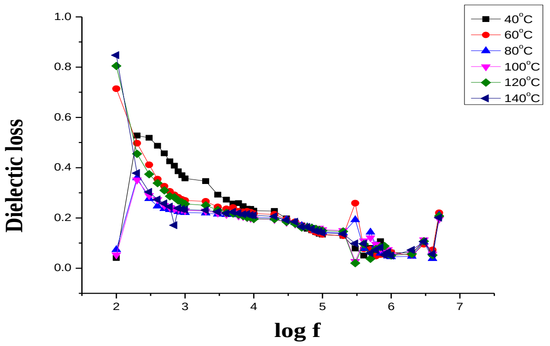


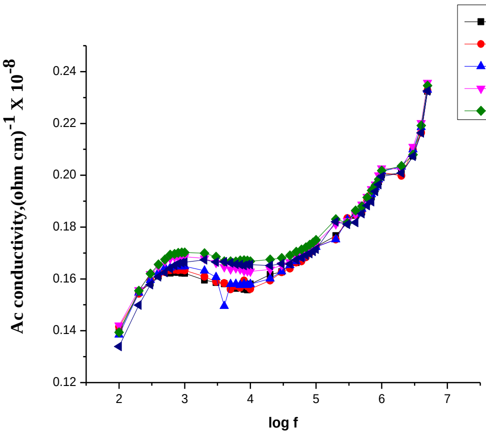
Figure 8: Dielectric loss Vs log frequency at different temperature

Temperature and Frequency Dependence of AC Conductivity:

The Ac conductivity was calculated by using the equation

$$\sigma_{Ac} = \varepsilon_r \, \varepsilon_o \, \omega \tan \delta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Where ε_o is the permittivity of free space (8.85×10^{-12} C^2 N^{-1} M^{-2}) , ε_r is the dielectric constant, ω is the angular frequency ($\omega = 2\pi f$, f= frequency of applied field) and $\tan\delta$ is the dielectric loss. The Ac conductivity of CdSe nanoparticles as a function of log f at different temperature is shown in Fig 9. The increase in Ac conductivity with the increase in temperature is the characteristics of the semiconducting nature of the sample [14]. Due to the thermionic emission and tunnelling of charge carriers across the barrier, the conductivity increases with the temperature, because of small size of the particles, the charge carriers reach the surface of the particles more and easily enable the electron transfer by thermionic emission or tunneling to enhance the conductivity [15].



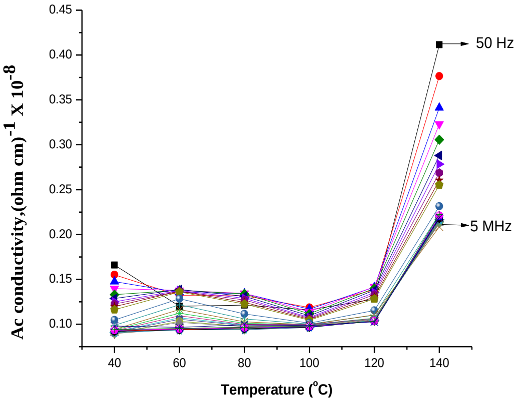


Figure 9: AC conductivity Vs frequency at different temperature Fig 10 Ac conductivity Vs temperature at different frequency

DC Conductivity:

Temperature and frequency dependence of DC electrical conductivity of sample was given in (Fig 11), in which conductivity increases with temperature which is attributed to improvement of charge density. Due to temperature effect, the inter-grain boundary area decreases i.e. there is a decrease in the scattering of the electron. Consequently, the carrier concentration and mobility in the inter-grain domains also increase which increases the conductivity.

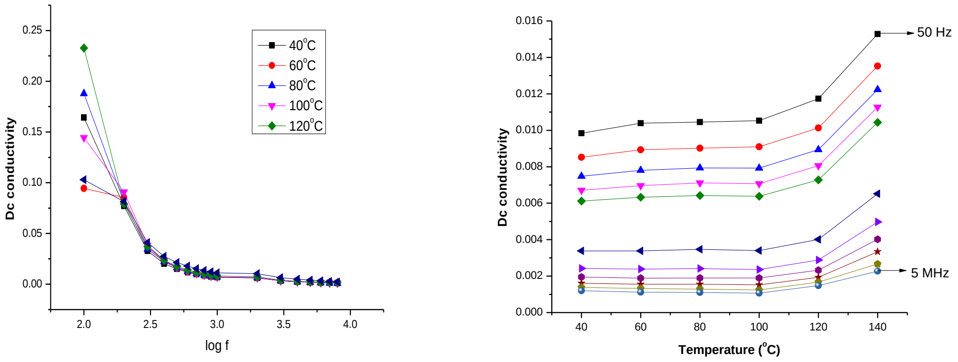


Figure 11: Dc conductivity Vs frequency at different temperature & Figure 12: Dc conductivity Vs temperature at different frequency

Activation Energy:

The temperature dependence of electrical conductivity (σ_{ac}) of CdSe nanoparticles follows the Arrhenius equation [24].

$$\sigma_{Ac} = \sigma_o \exp^{(-Eact/KBT)} \qquad \text{…………………..(6)}$$

where, K_B is Boltzmann constant, σ_o is the ideal conductivity of mono crystalline structure, σ_{ac} is the electrical conductivity and E_{act} represents the activation energy, that will raise the free energy of an atom or a molecule to cross over the energy barrier [16]. It is clear from the figure that there are two transport mechanisms, giving rise to two activation energies Ea_1 and Ea_2. At higher temperature range (354 – 393 K) the value of Ea_1 is 0.34eV, the conduction mechanism is due to carrier excited into the extended states beyond the mobility edge and at lower temperature range (313 – 353 K); the value of Ea_2 is 0.12eV, the conduction mechanism is due to carrier excited into localized states at the edge of the band.

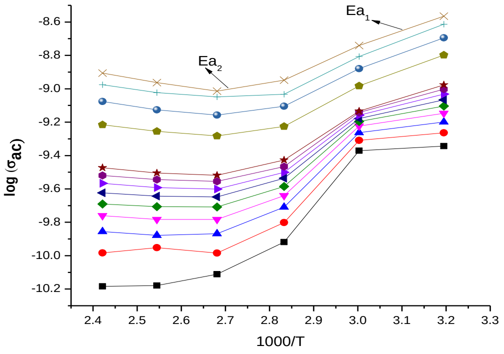


Figure 12: Variation of ln(σ) vs 1000/T of CdSe nanoparticles.

Energy Gap:

The energy gap (Eg) is the difference in energy between the highest point in the valence band and the lowest point in the conduction band (Ec) and it is considered as the lowest energy to transform charge carrier from the top of valence band to the bottom of conduction band which represents one of the important optical properties of semiconductors [17].

$$\sigma_{ac}(\omega) = A\omega^{s} \qquad \text{......................(10)}$$

Where A is a constant, ω is a angular frequency, and s represents the exponential factor, where s is given as

$$s = d(\ln\sigma_{ac}(\omega))/d\ln(\omega) \qquad \text{......................(11)}$$

The value s can be calculated from the slope of $\ln\sigma_{ac}$ against $\ln(\omega)$.

Solid materials have energy band, with so many adjacent energy levels. The number of these levels is equal to the number of atoms in the crystal. The band, therefore, seems to be continuous but it is actually discrete with forbidden region which are called energy gaps. The energy gap value was found to be 1.808 ev for cadmium selenide nanoparticles, which is comparable with the value of band gap calculated using Tauc's plot method.

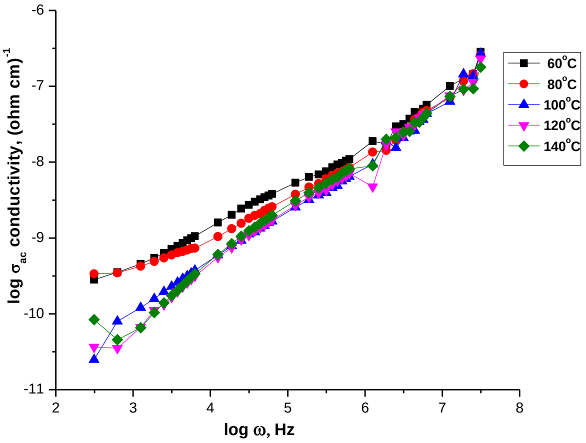


Figure 12: Temperature dependence of AC conductivity of CdSe as a function of log ω (frequency)

Current Density With Potential:

Solar cell was fabricated using TiO_2 as a photo anode, ruthenium dye as sensitizer and I^-/I_3^-as electrolyte, and CdSe as a counter electrode and the photovoltaic performance of the solar cell was performed by measuring photocurrent Vs Voltage (fig 13).

The efficiency of a solar cell is defined as the output power density divided by the input power density. If the incoming light has a power density P_{in}, the efficiency will be

$$\eta = P_m/P_{in} = Jsc.Voc.FF/P_{in}$$

The fill factor, FF is defined as the ratio of the maximum power output product (P_m) to the product of short circuit photo current and open circuit voltage.

$$FF = \frac{Pm}{Jsc \; x \; Voc} = \frac{Jmp \; x \; Vmp}{Jsc \; x \; Voc} \qquad \text{...................... (7)}$$

Where J_{mp} and V_{mp} represent the photocurrent density and photovoltage corresponding to the maximal power point respectively. The four quantities Jsc, Voc, FF, and η are used to characterize the performance of a solar cell. The photovoltaic parameters are given in table -4.

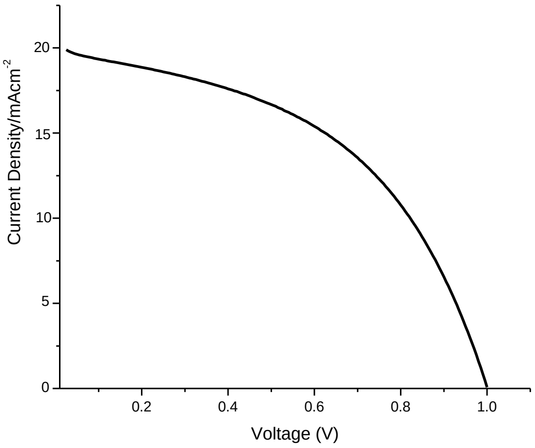


Figure 13: Photocurrent density –voltage (I-V) curve of CdSe nanoparticles.

Table 2 Photovoltaic parameters of the CdSe based DSSCs.

Parameters	CdSe
Voc [V]	1.0
Jsc [mA]	20
FF [%]	0.54
η [%]	3.08

The solar cell was fabricated, and the maximum quantum conversion efficiency was found to be 3.08% for synthesized cadmium selenide nanoparticles.

Conclusion:

Cadmium selenide nanoparticles were prepared by solvothermal method and characterized by XRD, UV-visible, PL, EDX and SEM spectral analysis. The powder X-ray diffraction analysis revealed that the synthesized CdSe nanoparticles are in hexagonal wurtzite structure with average crystallite size of 6.34 nm. The EDX spectral analysis confirmed the purity of CdSe nanoparticles. The band gap of CdSe nanoparticles were calculated using UV- spectral analysis as 1.81 eV. The well defined rod like morphological SEM image was observed. The dielectric constant and dielectric loss were found to decrease and attain constant value on raising the frequency. The variation of Ac conductivity with temperature proved the CdSe nanomaterials as semiconducting materials. The hybrid DSSC using quantum dot CdSe as photocathode, nanocrystalline TiO_2 as photoanode, ruthenium dye as sensitizer and I^-/I_3^- as electrolyte were fabricated and the quantum conversion efficiency was found to be 3.08%.

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