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ORIGINAL PAPER: SOL-GEL AND HYBRID MATERIALS FOR ENERGY, ENVIRONMENT AND BUILDING APPLICATIONS

The performance of CdS quantum dot sensitized ZnO nanorod-based solar cell

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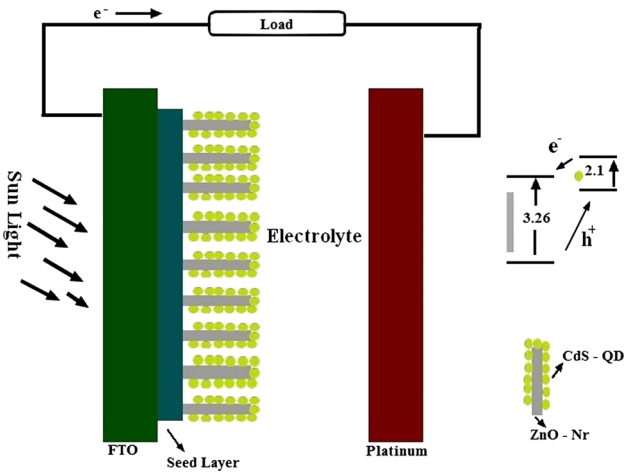
Abstract ZnO nanorods (NRs) have been grown by sol–gel dip-coating method on FTO glass plates. The CdS quantum dots (QDs) were deposited on the as-prepared ZnO NRs by successive ionic layer adsorption and reaction method. The structural characteristics of the ZnO NRs, CdS QD and CdS QD-sensitized ZnO NRs films have been studied using X-ray diffraction method. ZnO NRs exhibit hexagonal structure. CdS QD had a size of 2 nm. The FESEM image showed the presence of CdS quantum dots on the ZnO NRs. From the optical studies, the optical band gap energy of ZnO thin film was found to be 3.26 eV and the band gap energy of CdS quantum dot was observed to be 2.1 eV. The optical absorption edge was found at 370 nm for ZnO NRs and at 460 nm for the CdS QD. The PL spectra of the prepared ZnO NRs and CdS QDs sample exhibit a strong emission peak at 395 and 688 nm. Solar cells have been fabricated using the CdS quantum dot sensitized ZnO nanorods, and the efficiency of the cell was 1.3 %.

Graphical Abstract



Keywords Sol–gel method · ZnO nanorods · CdS quantum dot · Solar cell · J–V characteristics

1 Introduction

ZnO is a promising material with unique properties of UV emission, optical transparency, electric conductivity, piezoelectricity, and has a wide band gap (3.37 eV), large exciton binding energy (60 meV) at room temperature, high mechanical, thermal stabilities and radiation hardness. ZnO is widely used in piezoelectric transducers, gas sensors, optical wave guide, transparent conductive films, varistors, solar cell window layer and bulk acoustic wave devices [1–6]. ZnO semiconductor thin films have attracted many researchers because of their good optical and electrical properties which make them suitable to be used in solar cell applications. ZnO

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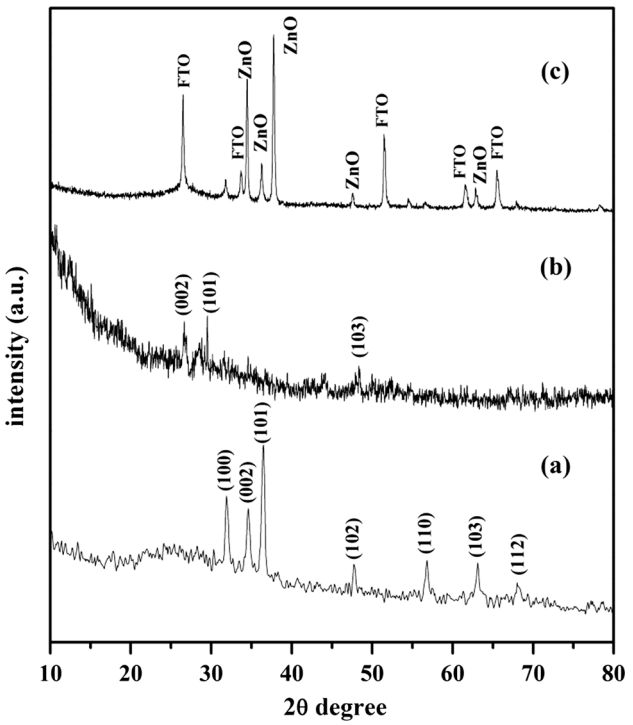

Fig. 1 X-ray diffraction pattern of (*a*) ZnO NRs, (*b*) CdS QD and (*c*) CdS QD-sensitized ZnO NRs-based thin film

with different structures like vertically aligned nanorods, bundle-like nanorods and flower-like structures have been synthesized by several methods [7, 8]. There are many methods available for the growth of ZnO NR-based thin films like hydrothermal synthesis [9], electrochemical deposition [10], sputtering [11] and sol–gel dip-coating method [12]. Among these several methods, sol–gel dip-coating method is a low-cost method, which does not use high vacuum process and high-temperature conditions.

Semiconductor quantum dots are used in solar cell application because of the tunable optical band gap which can be easily achieved through quantum confinement effect by varying their size [13]. There are several types of semiconductor quantum dots such as CdS, CdSe and CdTe which are capable of absorbing light in visible region, and serve as sensitizer as they can transfer electrons to large band gap semiconductors such as ZnO. Among these semiconductor quantum dots, CdS has been paid great attention in quantum dot sensitized solar cell application due to its high potential in light harvesting in the visible region [14]. In addition, it is also possible to use hot electron to generate multiple electron–hole pairs (exciton) per photon through the impact ionization effect. CdS quantum dot with the tunable band gap of 2.4–4.0 eV can provide new opportunities to harvest light from the visible spectrum of solar light [15].

Compared to conventional dye-sensitized solar cell, the semiconductor QD has high extinction coefficients, which

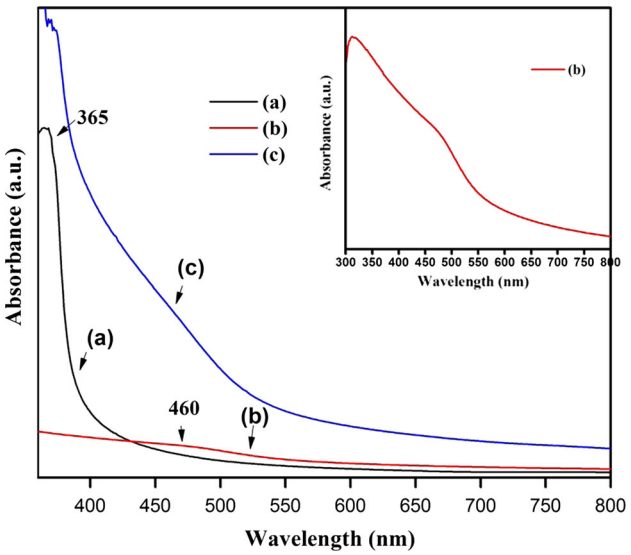

Fig. 2 Absorption spectra of (*a*) ZnO nanorods, (*b*) CdS quantum dot and (*c*) CdS QD-sensitized ZnO nanorods thin film

reduce the dark current and increase the overall performance of the solar cell efficiency [16].

In the present work, CdS QDs-sensitized ZnO NR-based thin films have been synthesized by sol–gel dip-coating method. The performance of CdS quantum dot sensitized ZnO NRs-based solar cells has been investigated.

2 Experimental technique

ZnO nanorods have been prepared by a two-step simple chemical method. In the first step, ZnO seed layer has been prepared using sol–gel dip-coating method. 0.3 mol of

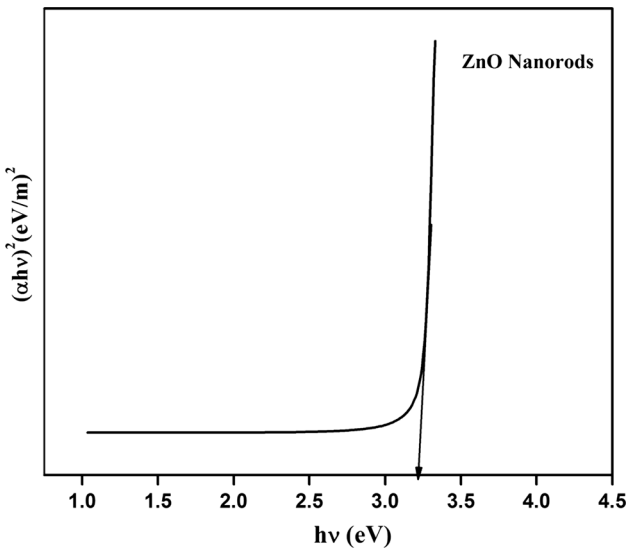

Fig. 3 Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of ZnO nanorods-based thin film

Zinc acetate dihydrate ($(CH_3COO)_2$ $Zn{\cdot}2H_2O$) was dissolved in a mixture of ethanol and ethanolamine (1:0.025) at room temperature. The resultant solution was stirred for 1 h to yield a homogeneous, clear and transparent solution using magnetic stirrer. The dip-coating method has been used to prepare thin films of ZnO using the prepared solution onto FTO glass substrates. After deposition, annealing of the samples was carried out for the removal of solvent and residual organics and film densification. The films were annealed at 300° C for 1 h, and these films form the ZnO seed layer. In the second step, an aqueous solution was prepared by dissolving zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and hexamine ($(CH_2)_6N_4$) in deionized water. The concentration of zinc nitrate and hexamine was kept at 0.2 and 1 mol/L, respectively. The ZnO seed layer-coated substrates were vertically dipped in the (zinc nitrate + hexamine) solution, and the solution was heated in a laboratory oven and maintained at 90 °C for 4 h. At the end of the growth period, the substrates were removed from the solution and were thoroughly washed with deionized water to remove the residual salt from the surface and annealed at 450 °C for 1 h.

CdS quantum dots have been deposited onto ZnO nanorods thin film by successive ionic layer adsorption and reaction method. 0.1 M of cadmium nitrate in ethanol was taken as cationic pre-cursor solution, and 0.1 M of sodium sulfide in ethanol was taken as anionic precursor. The ZnO nanorods thin film was dipped in cationic solution for 15 s for adsorption of cadmium ions and rinsed in deionised water to remove loosely bounded Cd-species. Then, it was dipped in anionic solution for 15 s and rinsed in deionised water. The sulfide ions react with adsorbed cadmium ions forming CdS on ZnO nanorods thin film. The chemical process was repeated to get a uniform coating. The obtained film was then dried at 100 °C for 1 h, and the prepared CdS quantum dot was annealed at 300 °C for 1 h because annealing is widely used to enhance the performance of the solar cell [17].

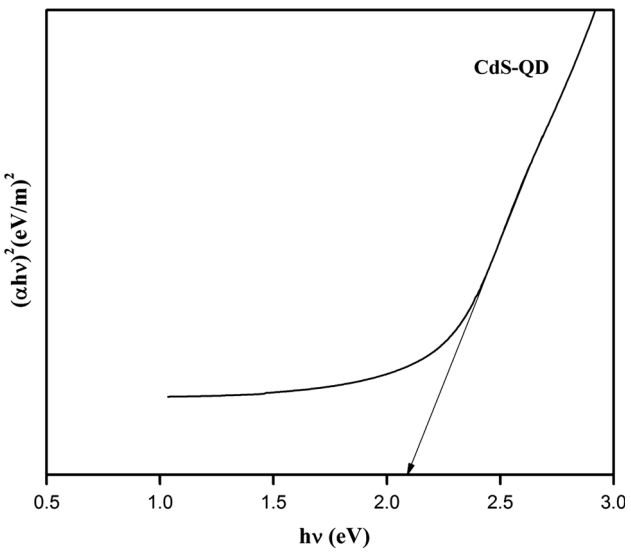

Fig. 4 Plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of CdS quantum dots-based thin film

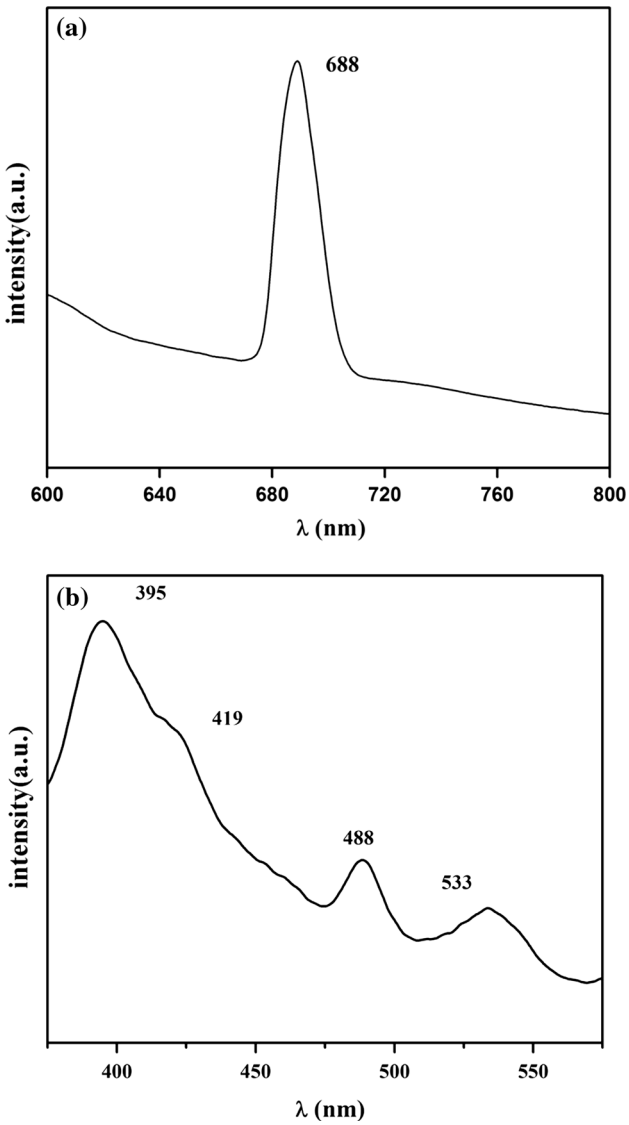

Fig. 5 Room temperature photoluminescence emission spectra of **a** CdS quantum dot, **b** ZnO nanorods

3 Results and discussion

3.1 X-ray diffraction studies

Figure 1 shows the X-ray diffraction pattern of (a) ZnO nanorods (b) CdS quantum dots (c) CdS QD-sensitized ZnO NRs. The diffraction peaks of the ZnO nanorod-based

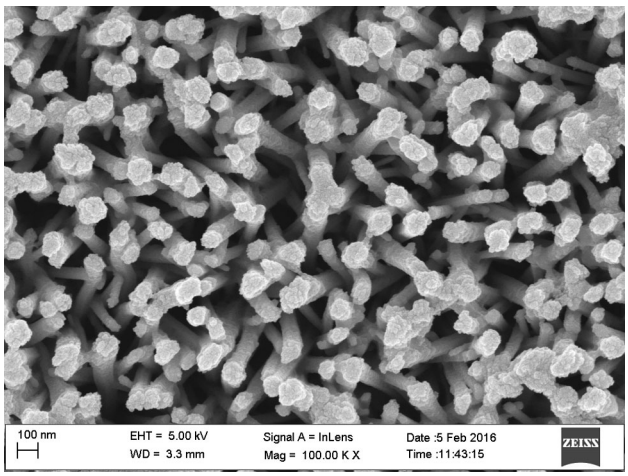

Fig. 6 FESEM image of prepared CdS QD-sensitized ZnO nanorods

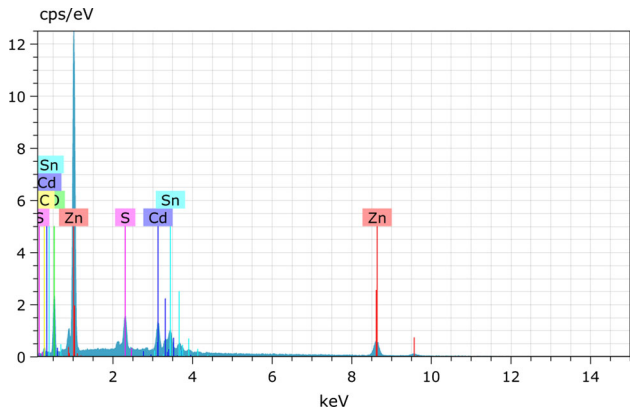

Fig. 7 EDAX spectra of CdS QD-sensitized ZnO nanorods

films have been indexed as (100), (002), (101), (102), (110), (103) and (112) planes of ZnO. All the diffraction peaks in the pattern correspond to the hexagonal phase of ZnO. The lattice parameters have been calculated using the formula

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \quad (1)$$

From the above equation, the lattice parameters a and c are found and they are 3.2 and 5.2 Å, respectively, which are in good agreement with the reported standard values (JCPDS No. 36-1451). Figure 1b is the diffraction pattern of CdS QD, and the diffraction peaks at 2θ (degree) of 29.5°, 26.7° and 48.1° are indexed as (002), (101) and (103) of CdS (JCPDS No. 41-1049). The grain size of ZnO NRs and CdS QD films has been calculated using Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

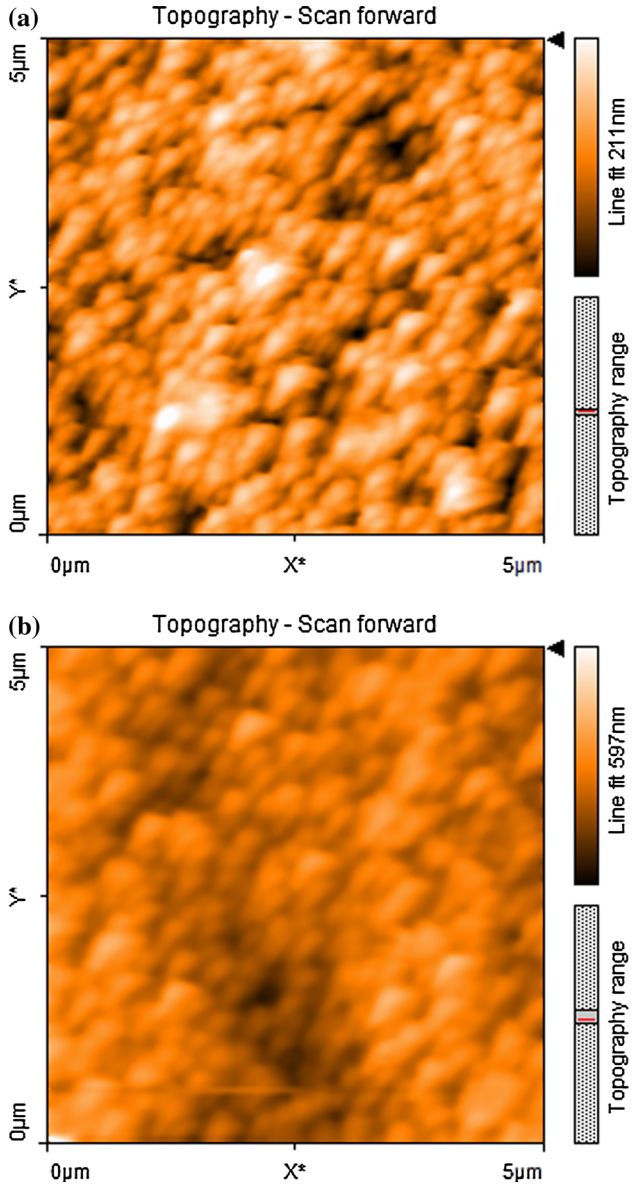

Fig. 8 AFM image of **a** ZnO NRs-based thin film and **b** CdS QD-sensitized ZnO NRs

where, D is the grain size, K is a constant taken to be 0.94, λ is the wavelength of the X-ray radiation, β is the full width at half maximum and θ is the angle of diffraction. The grain size has been calculated and was found to be 23 and 2 nm for ZnO nanorods and CdS quantum dots, respectively. The diffraction peaks of CdS quantum dot sensitized ZnO nanorods-based film are shown in the Fig. 1c. The peaks were found to be slightly shifted. The shift in the peak of ZnO nanorods may be due to the presence of CdS quantum dot.

3.2 UV analysis

Optical absorption spectra of ZnO nanorods, CdS quantum dots and CdS-sensitized ZnO nanorods-based thin film are shown in Fig. 2. The absorption edge of the ZnO nanorod is observed to be present at 365 nm, and absorption edge of the CdS quantum dots is present at 460 nm. The absorption edge of CdS quantum dot sensitized ZnO nanorods has been shifted toward longer wavelength 470 nm (Red Shift). The absorption of light by ZnO nanorods sensitized by CdS was found to be more, and this increase in light absorption is due to the presence of CdS in ZnO nanorods.

The optical band gap energy has been calculated using the equation

$$\alpha h\upsilon = A\left(E_g - h\upsilon\right)^n \tag{3}$$

$$\alpha = \left(\frac{2.303\log\left(\frac{1}{T}\right)}{t}\right) \tag{4}$$

where, α is the absorption co-efficient [18], t is the thickness of the thin film, v is the frequency of the incident radiation, A is the constant, E_g is the band gap of the material, h is the Planck's constant and n is equal to 1/2 for direct transition. Figures 3 and 4 show the plot of $(\alpha h\upsilon)^2$ versus photon energy of $h\upsilon$ for ZnO NRs and CdS QD. The optical energy gap values for the prepared samples were calculated from this plot. The optical band gap of the prepared ZnO nanorods has been found to be 3.26 eV, and optical band gap of the prepared CdS quantum dot has been found to be 2.1 eV.

3.3 PL analysis

Figure 5a shows the emission spectra of CdS QD excited at 460 nm. A strong red emission peak at 688 nm is observed in the visible region. The FWHM of the quantum dot emission peak is 16.59 nm. Figure 5b shows the ZnO NRs PL spectra excited at 325 nm. There are four peaks 395, 419, 488 and 533 nm present in the spectrum. 395-nm peak is attributed to UV near band edge emission, and the peak at 533 is attributed to green emission which is due to antisite defect of oxygen [19]. The peaks at 419 and 488 nm are attributed to band energy free exciton and bound exciton, respectively [20].

3.4 FESEM analysis

Figure 6 shows the FESEM image of CdS quantum dot sensitized ZnO nanorods. The FESEM image shows the morphology of vertically aligned ZnO nanorods of hexagonal shape which have grown uniformly with average diameter of 100 nm.

3.5 EDAX analysis

Energy-dispersive X-ray analysis (EDX) pattern of CdS-sensitized ZnO nanorods is shown in Fig. 7. The compositional analysis shows that the prepared film has Zn, O, Cd and S. Sn present in the spectra is due to the FTO glass plate.

3.6 AFM analysis

Figure 8a shows the atomic force microscopic image of ZnO NRs. The image shows well-defined particle like structure with granular topography and indicates the presence of small crystalline grains. It can be seen that the structure appears to be homogeneous with porosity consistent with a high surface area structure.

The root-mean-square surface roughness of the ZnO NRs film was found to be 33 nm. The higher surface roughness is due to the crystalline nature of the film. Figure 8b shows the CdS QD-sensitized ZnO NRs atomic force microscope image, and the root-mean-square surface roughness of the film was found to be 59 nm.

3.7 J–V characteristics

Solar cell with structure FTO/ZnO–CdS/electrolyte/Pt has been fabricated. The iodine redox electrolyte was used in the fabricated solar cell. The current density–voltage (J–V) characteristics of CdS quantum dot sensitized ZnO nanorod-based solar cell are shown in Fig. 9.

The solar cell conversion efficiency (η) is given by

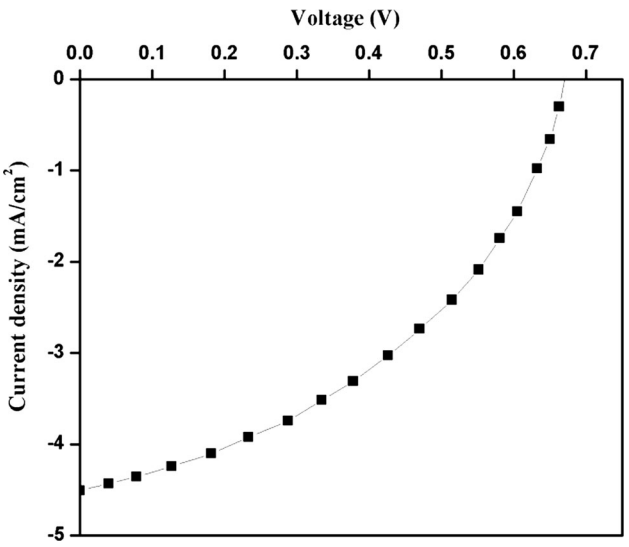

Fig. 9 J–V characteristics of CdS quantum dot sensitized ZnO nanorods-based solar cell

Table 1 Solar cell energy conversion from literature

S. no	Authors	Material	Efficiency (%)	References
1	Thambidurai et al.	CdS quantum dot sensitized ZnO nanorods	0.69	[21]
2	Raja et al.	CdS quantum dots sensitized ZnO nanostructured Al doped ZnO solar cells	1.37	[22]
3	Patil and Singh	CdS quantum dots sensitized ZnO nanorods-based solar cells coated over steel substrate	0.76	[23]
4	Qi et al.	CdS quantum dot sensitized solar cells with ZnO nanowire arrays	0.72	[24]

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \quad (5)$$

where J_{sc} is the short-current density, V_{oc} is the open-circuit voltage, FF is the fill factor and P_{in} is the incident light power. The CdS quantum dot sensitized ZnO nanorods solar cell exhibited an efficiency of 1.3 % with short-circuit current density (J_{sc}) of 4.5 mA cm^{-2}, open-circuit voltage (V_{oc}) of 0.67 V and fill factor (FF) of 0.43. Table 1 shows the solar cell energy conversion efficiency of CdS quantum dot sensitized ZnO nanorod-based solar cells reported by different authors [21–24].

4 Conclusion

CdS quantum dot sensitized ZnO NRs has been synthesized by simple chemical method. The X-ray diffraction pattern revealed the formation of ZnO thin film with hexagonal phase, and CdS quantum dot had a size of 2 nm. The absorption edge of the ZnO nanorod was observed at 365 nm, and absorption edge of the CdS quantum dots was found at 460 nm. Emission spectra of the prepared ZnO nanorods and CdS quantum dots have been studied by photoluminescence spectrum. The surface roughness value was calculated using AFM analysis, and the root-mean-square surface roughness of the CdS quantum dot sensitized ZnO nanorods film was found to be 59 nm. CdS quantum dots sensitized ZnO nanorod-based solar cell has been fabricated, and its efficiency was 1.3 %.

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