Effect of annealing temperature on optical properties and dye absorbance capacity of ZnO-CdS nanocomposite

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Abstract

ZnO-CdS nanocomposite material has been synthesized by Chemical Co-precipitation method. The prepared nanocomposite material has been characterized by UV-visible (UV-vis) spectrophotometer and X-ray diffractometer (XRD). The optical band gap of prepared material lies between 3.6 eV to 4.0 eV. The synthesized nanocomposite material has been annealed at two different temperatures 160^o C and 200^o C. The results of UV-visible characteristic and XRD analysis show that the optical and structural property of the material depends on the temperature at which it has been annealed. A natural dye from beet root extract has been synthesized and has absorbance in visible region. The synthesized nanocomposite material is deposited over the glass plate using spin coater. The thin film of synthesized ZnO-CdS nanocomposite when annealed at higher temperature absorbs more dye than the film annealed at lower temperature. Copyright © 2017 VBRI Press.

Keywords: ZnO-CdS nanocomposite, photovoltaic devices, dye-sensitized solar cells (DSSCs), natural dyes, annealing temperature.

Introduction

The increasing world energy demand, depletion of fossil fuels and increasing pollution level have forced human to seek clean and renewable energy technologies. Photovoltaic technology which is based on solar energy is of great interest in the area of clean and sustainable energy technologies. Dye-sensitized solar cell (DSSC) is considered one of the low cost photovoltaic technologies **[1]**. The efficiency of DSSC has been achieved up to 13% **[2]**. The structure of DSSCs comprises of transparent conducting oxide (TCO) over which a wide band gap semiconducting nanomaterial is deposited, then photosensitizer (dye) is absorbed over it and electrolyte is filled between the counter electrode and photoelectrode **[1]**. The semiconducting material deposited TCO is called photoelectrode. Metal oxides like Titanium dioxide (TiO_2) **[3-5]**, Zinc oxide (ZnO) **[6, 7]**, Stannic oxide (SnO_2) **[8]** etc and their composites have been used as semiconducting material in the DSSCs. The metal complex based dyes like N719, N3 and ruthenium polypyridyl complexes etc are mostly used in DSSC applications **[9]**. The efficiency of DSSCs highly depends upon the used photosensitizer, photoelectrode material and electrolyte.

The metal oxide nanomaterials are easy to synthesize in different morphologies like spherical structure, one dimensional structure (nanowires and nanotubes) and core-shell structure. The factors related to photoelectrode which affect the performance of DSSCs are the size, morphology and thickness of thin film of semiconducting material **[7, 10]** and the annealing temperature of photoelectrode **[11]**. Besides other factors, annealing temperature of photoelectrode is one of the important factors which may affect the performance of the DSSC. For ZnO nanoparticles, it has been reported that the amount of dye absorbed by the ZnO film firstly increases with increase in annealing temperature of the film and after a particular temperature it starts decreasing **[11]**.

Metal complex based photosensitizers contain some heavy metals which are inexpensive and have bad impact on the environment **[9]**. For overcoming the problem, many natural dyes are being synthesized and studied as they are low cost and environment friendly. Natural dyes prepared from beet root extract **[12]**, spinach extract **[13]**, ipomoea extract **[13]** etc. has been used in DSSCs.

In the present work, we have synthesized ZnO-CdS nanocomposite and natural dye from beet root extract. We have shown the effect of annealing temperature on the optical properties of the synthesized nanomaterial and its dye absorbance capacity. The efficiency of DSSCs depends mainly on the amount of dye absorbed by the photoelectrode material; hence, the present work is fruitful in the improvement of performance of DSSCs.

Experimental

Materials/ chemicals details

Zinc acetate dihydrate (Rankem), sodium hydroxide pallets (Merck), cadmium acetate dehydrated (SDFCL), sodium sulfide fused flakes (Fisher Scientific), ethylene glycol monoethyl ether (Merck) and ethyl alcohol were used with no further purification.

ZnO-CdS nanocomposite synthesis

The nanostructured ZnO-CdS nanomaterial was synthesized by Chemical Co-precipitation method. Four 100 mL aqueous solutions of cadmium acetate, sodium sulfide, zinc acetate and sodium hydroxide solutions were prepared separately at constant stirring (0.02 mole of each). Firstly, the sodium sulfide solution was mixed with cadmium acetate solution drop wise with constant stirring. The color of the solution was changed from transparent solution to greenish-yellow. After constant stirring for 90 minutes, the zinc acetate solution was mixed in it drop-wise. After constant stirring of 15 minutes, the sodium hydroxide solution was mixed in it. The solution was stirred constantly for 60 minutes. Then the obtained precipitate was washed several times with distilled water and dried at room temperature (say sample S_1). The sample was annealed at two different temperatures 160^{o}C (say sample S_2) and 200^{o}C (say sample S_3) for the same time interval of one hour.

Synthesis of natural dye from beet root extract

The natural dye from beet root extract was synthesized. The beet root was washed and peeled off properly. Then the small chopped pieces of beet root (50 g) was crushed and dipped in 100 mL ethanol for about one hour and then heated in boiling water indirectly. For removing solid drags, the extract was centrifuged and filtered off.

Preparation of nanomaterial thin film and dye loading

The synthesized nanocomposite material (S_1) was dispersed in Ethylene glycol monoethyl ether with the help of ultrasonicator and deposited over three glass plates of equal area using spin coater. The films were annealed at three different temperatures 200^{o}C (T_1), 240^{o}C (T_2) and 280^{o}C (T_3) for one hour. For dye loading over the deposited films, the three films were dipped in the synthesized dye for about 90 minutes.

Characterizations

For optical properties of the synthesized nanomaterial, UV-visible characteristics of the samples were taken using Unicam-5267. XRD characterization of the samples S_1, S_2 and S_3 were taken using AXRD Bench top for structural analysis of as synthesized ZnO-CdS nanocomposite. For observing the effect of annealing temperature over dye loading capacity of synthesized nanomaterials, UV-visible characterization of the three dye loaded films (T_1, T_2 and T_3) were taken.

Results and discussion

UV-visible characteristic of as synthesized nanocomposite material

For investigating the effect of annealing temperature on optical properties of synthesized nanomaterials, UV-visible characteristic of the three samples S_1, S_2 and S_3 were taken. **Fig. 1** shows the Tauc plot of the three samples. The band gap of as synthesized material is between 3.6 nm-4.0 nm. The band gap of as synthesized material is determined by the equation:

$$\alpha = A\,(h\nu - E_g)^n / h\nu$$

where, α is the absorption coefficient, E_g is the absorption band gap, A is constant and n depends on type of transition, n may have values 1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and indirect transitions. As CdS and ZnO have direct allowed transitions **[14]**, we have chosen n = 1/2. The band gap of the material is calculated from the $(\alpha h\nu)^2$ vs hν plot (Tauc plot). The plot shows that the band gap of the synthesized nanomaterial decreases with increase in annealing temperature. This is due to increase in crystallite size of the nanomaterial with increase in annealing temperature, and as the surface area decreases with increase in crystallite size, the band gap is found to decrease with increase in annealing temperature. Increment in crystallite size of the synthesized nanomaterial with annealing temperature is verified by the XRD analysis also.

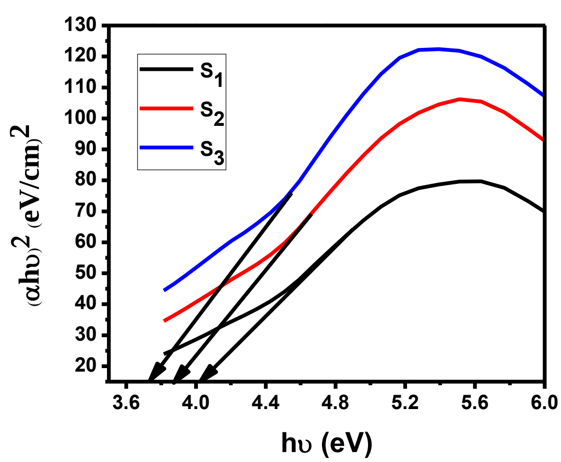

Fig. 1. Plot of $(\alpha h\nu)^2$ versus hν.

Structural analysis of as synthesized nanocomposite

The XRD pattern of as synthesized nanocomposite samples S_1, S_2 and S_3 is shown in **Fig. 2**. The peaks at 31.85^o, 34.40^o, 36.25^o, 56.60^o and 62.75^o are due to ZnO in hexagonal phase and 26.20^o, 43.30^o and 52.30^o are due to CdS in hexagonal phase. The crystallite size of nanomaterial is calculated using Debye Scherrer formula d = 0.9λ / βcosθ, where λ is wavelength of X-ray used, β is full width at half maxima and θ is the angle at which intensity of peak is highest. Here, λ of X-ray used is 0.154

nm. The crystallite size of the CdS nanoparticles in the synthesized nanocomposite is found to be 3.07 nm for S_1, 3.60 nm for S_2 and 3.82 nm for S_3. The crystallite size of ZnO nanoparticles in the synthesized nanocomposite is found to be 14.13 nm for S_1, 14.90 nm for S_2 and 16.76 nm for S_3. The crystallite size of both ZnO and CdS increases with increase in annealing temperature.

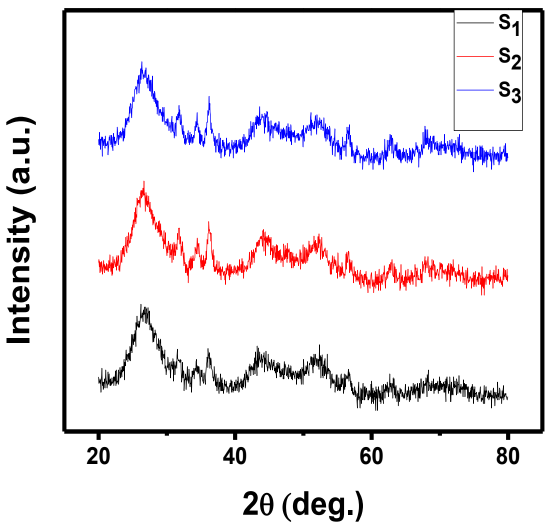

Fig. 2. XRD characteristic of ZnO-CdS nanocomposite material.

UV-visible characteristic of as synthesized natural dye

Fig. 3 show the UV-visible characteristic of as synthesized dye from beet root extract. The plot shows that the dye has good absorbance in visible region, highest at 415 nm.

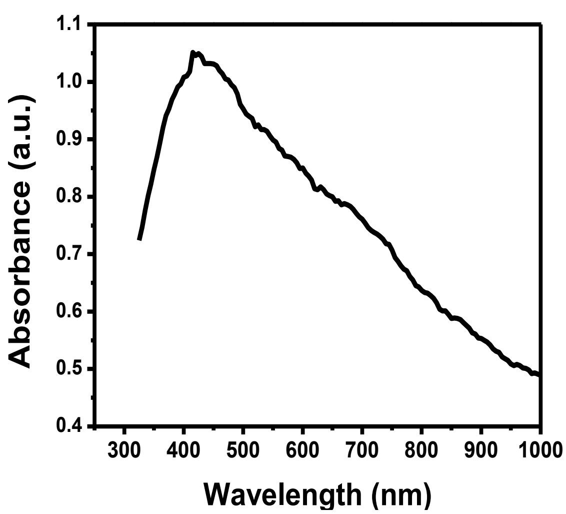

Fig. 3. UV-visible characteristic of synthesized natural dye.

Dye loading capacity of synthesized nanomaterial

UV-visible characteristic of dye loaded thin film of synthesized nanomaterial annealed at three different temperatures 200^o C (T_1), 240^o C (T_2) and 280^o C (T_3) was taken and shown in **Fig. 4**. The synthesized dye has absorbance in visible region, highest at 415 nm (**Fig. 3**). Since all the three films were annealed for same time interval (one hour) and dipped in the dye for same time duration (90 minutes), we can say that the film which shows higher absorbance in visible region has absorbed more dye. The graph (**Fig. 4**) shows that the thin film annealed at higher temperature shows higher absorbance, hence we can conclude that the amount of dye absorbed by the thin film of synthesized ZnO-CdS nanomaterial has increased with increase in annealing temperature. With increase of annealing temperature, there may occur following changes which increase the dye absorbance: a) there may occur some morphological modifications in the film and particles become more porous to absorb more amount of dye, b) the organic material used in the deposition process of nanomaterial film or synthesis process of nanomaterial which may prevent the dye loading over the nanomaterial film are vaporized at higher temperature, so the thin film annealed at higher temperature contain less organic material content and the surface of nanoparticles become more free for dye absorbance **[11]**.

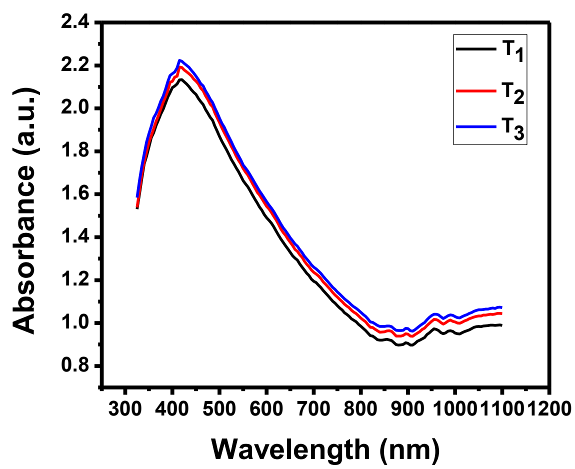

Fig. 4. UV-visible characteristic of dye loaded nanomaterial film.

Conclusion

The band gap of synthesized ZnO-CdS nanocomposite material has been found to decrease with increase of annealing temperature. The crystallite size of the synthesized nanocomposite material increased with increase in annealing temperature. Hence the optical and structural property of the synthesized ZnO-CdS nanocomposite depends on the temperature at which it has been annealed. The dye absorbance capacity of synthesized nanomaterial film increased with increase in annealing temperature of the film. So the selection of annealing temperature of the photoelectrode film of particular nanomaterial in DSSCs is important for its performance.

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Author's contributions

Conceived the plan: Monika Tandon and Pratima Chauhan; Performed the expeirments: Monika Tandon; Data analysis: Monika Tandon; Wrote the paper: Monika Tandon and Pratima Chauhan. Authors have no competing financial interests.

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