Optical and electrical properties of organic dye sensitized Cr–ZnO and Ni–CdO nanoparticles

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Abstract

In this work presents an approach for the selection of dye sensitized Cr–ZnO and Ni–CdO nanoparticles as a photo anode material for the applications of DSSCs. The 4 wt% Cr–ZnO and Ni–CdO nanoparticles were synthesized through simple and fast microwave combustion method. X-ray diffraction (XRD) was used for the detection of crystalline phases and size of the synthesized nanomaterials. It confirms the existence of hexagonal wurtzite phase of Cr–ZnO (30–35 nm) and cubic phase of Ni–CdO (43–45 nm) nanoparticles. SEM and TEM micrographs of Cr–ZnO and Ni–CdO reveal that the synthesized samples are prismatic and spherical shaped, respectively. Optical absorption of Cr–ZnO and Ni–CdO nanoparticles before and after sensitization with Trypan Blue (TB), SPADNS (SPD) and Evans Blue (EB) dyes were examined through UV–Visible spectroscopy. The results show that the selected dyes improve the absorption edge of Cr–ZnO and Ni–CdO nanoparticles to longer wavelength side. HOMO and LUMO energy levels of the dyes were calculated by cyclic voltammetry. I–V characteristics of Cr–ZnO and Ni–CdO films before and after sensitization with dyes revealed the influence of dye sensitization on photo conductivity of Cr–ZnO and Ni–CdO nanoparticles.

Keywords Bandgap · Cr–ZnO · Dyes · Evans blue · Photoconductivity · Ni–CdO

1 Introduction

In an efficient dye sensitized solar cell (DSSC), a sensitizer (dye) is one of the important key components which improve the efficiency of solar energy conversion. Over the past decades, the ruthenium (Ru) complex based DSSCs were developed by researchers, which have shown high light to energy conversion efficiencies of over 11% [1]. However, high cost of synthesis, problematical steps of compound purification, very less yield of product and environmental concern have limited the potential applications of Ru complexes. These disadvantages of Ru based complexes have given an insight for the development of metal free organic sensitizers. These dyes are used in the DSSCs due to their various significant advantages

such as high absorption co-efficient, easy for synthesis and purification, less toxic, affordable cost and eco-friendliness [2]. The recent reports highlighted the highest photo conversion efficiency of DSSCs from organic sensitizers is greater than 13.5% indicates that the organic dye sensitizers are also proves to be the significant materials for DSSCs compared to Ru, Ce and Zn transition metal sensitizers. The anchoring modes of the dye molecules to the crystalline semiconductor surface are of essential significance, the interaction and the extent of electronic coupling between the lower unoccupied state (LUMO) of dye and the conduction band of semiconductor influencing directly the overall cell performance [3]. Anchoring with wide band gap semiconductor surface (ZnO, TiO₂, SnO₂) has been achieved by using a number of essential

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functional groups present in the dye molecules, such as carboxylic acid ($-\text{COOH}$), sulfonic acid ($-\text{SO}_3\text{H}$), Nitro ($-\text{NO}_2$), acetylacetone derivatives ($-\text{CH}_3\text{COCHCOCH}_3^-$) and salicylate ($-\text{C}_7\text{H}_5\text{O}_3^-$). Among these, the sensitizers with functional group $-\text{SO}_3\text{H}$ gained more prominence due to the different possibilities of binding modes (mono-dentate or bi-dentate) on the surface of semiconductors [4–6]. Generally, the electronic and optical properties of dye molecules have contributed to understanding the type of dye-semiconductor interaction. It was observed that dyes having a sulphonic acid group as an anchoring group, the absorption of dye molecule was preferred by bi-dentate bridging with transfer of proton to nearby oxygen. The dye anchoring on surface of semiconductor by monodentate was found less stable compared to other forms of binding.[7]. But several researchers were used $-\text{SO}_3\text{H}$ contained dyes and achieved better efficiency of Gratzel cell. R. Parthiban et al. were revealed that the Evans blue sensitized ZnO device has shown the efficiency of 0.1% and it depends on the electronic structure of dye and semiconductor used

[8]. S.A. Kazmi et al. reported that the 2.5% of efficiency was achieved by methyl orange anchor- TiO_2 Ag DSSCs [9].

Till now, several authors reports the numerous were metal free organic dyes with $-\text{SO}_3\text{H}$ group sensitized nano-structured solar cells. Out of all these dyes we select the Trypan blue, SPADNS and Evans blue for our work. Because, Trypan blue and Evans blue dyes are the azo dyes, which have strong absorption coefficient in the visible and near IR region, relatively long time excited-state life time and easily soluble in organic solvents. Over the past few years, these dyes were much attention in variety of potential applications in the textile industry and biomedicine. Very little interest of these dyes on DSSCs was observed recently [10]. Similarly, SPADNS dye is made from spadns inorganic reagent which is low-cost, easily available, gives a good yield of product and not degrades at low intensity [11]. The optical and electrical performance of several organic dyes with TiO_2 and ZnO nanoparticles were studied and reported, but the trypan blue, evans blue and SPADNS are used first time in Cr-ZnO and Ni-CdO nanomaterials.

Trypan blue

SPADNS

Evans blue

In this study, azo chromophore ($-N=N-$) based organic dyes (Trypan blue, SPDANS and Evans blue) as photosensitizers have been applied to adsorption of 4 wt% Cr–ZnO and Ni–CdO nanoparticles. The synthesized Cr–ZnO and Ni–CdO nanoparticles were characterized through XRD and SEM. The redox potential of all the dyes was determined by cyclic voltammetry (CV). The effect of dyes on the absorption and photo conductivity properties of synthesized Cr–ZnO and Ni–CdO nanoparticles has been examined through UV–Vis and I–V characteristic studies.

2 Materials and characterizations

All the chemicals were of analytical grade and were used as received without further purification. Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 98%], cadmium nitrate hexahydrate [$Cd(NO_3)_2 \cdot 6H_2O$, $\geq 99\%$], ethylene glycol, nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$, $\geq 97\%$], chromium (III) sulphate basic [$Cr_2(SO_4)_3 \cdot 6H_2O$, 98%], trypan blue ($C_{34}H_{24}N_6Na_{24}O_{14}S_4$, 75%) and evans blue ($C_{34}H_{24}N_6Na_{24}O_{14}S_4$, 85%) were procured from Himedia chemicals. SPADNS ($C_{16}H_9N_2Na_3O_{11}S_3$, 80%) dye was procured from Merck Chemicals. Double distilled water (H_2O), ethyl alcohol (C_2H_5OH) and acetone (CH_3COCH_3) were used for washing of nanomaterials and preparation of dye solutions.

The crystal structure and crystallite size of synthesized Cr–ZnO and Ni–CdO nanoparticles were determined by using high resolution X-ray diffractometer provided with Cu-K α radiation at $\lambda = 0.154060$ nm from an angle $2\theta = 30^\circ$ to 80° . The size distribution and morphology of the samples were analyzed by field emission scanning electron microscope (FESEM) [Model: FE-SEM Carl Zeiss AG-ULTRA 55]. The cyclic voltammetric studies of dyes were performed on an electrochemical work station (Model: CH Instruments 660D). The Optical absorption properties of Cr–ZnO and Ni–CdO nanoparticles with and without dye sensitization was characterized through UV–Vis–NIR spectrophotometer (Model: USB 4000, Ocean Optics), the current–voltage characteristics of pure and dye sensitized Cr–ZnO and Ni–CdO samples were performed on a Kiethley source meter (Model: Kiethley Instruments Inc.2401) controlled by the Kick start software.

2.1 Synthesis of 4 wt% Cr–ZnO and Ni–CdO nanoparticles

In the present work, the 4 wt% Cr–ZnO nanoparticles were prepared by microwave combustion method in the water medium. The stoichiometric ratio of zinc (II) nitrate and chromium (III) sulphate basic were dissolved in 100 ml of doubly distilled water. The 1:1 molar ratio of urea to metal

nitrate was added, which acts as a fuel. The obtained solution was kept for stirring for 30–40 min. The resultant homogeneous mixture was kept in a microwave oven and exposed to 60% power of microwave radiation for 20 min. A pale yellow paste like precipitate was settled at bottom of the beaker. The resultant product was washed 3–4 times with double distilled water and ethanol, and dried at 333 K for 6 h. Finally resulting powder was calcinated at 500 °C for 2 h in a muffle furnace and finally a fine crystalline powder of Cr–ZnO was obtained. The similar procedure has been followed for the synthesis of Ni–CdO nanoparticles and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) used as the source of dopant.

3 Results and discussions

3.1 XRD analysis

Figure 1a shows the powder XRD (X-ray diffraction) patterns of pyramid shaped Cr–ZnO nanoparticles. The five strong diffraction peaks are noticed at 31.53° , 34.26° , 36.03° , 47.41° and 56.40° which can be assigned to diffraction from (100), (002), (101), (102) and (110) planes respectively, according to JCPDS card No. 36–1451. This reveals that the prepared nanoparticles were Cr–ZnO with a hexagonal wurtzite structure [10]. Similarly, Fig. 1b shows the powder XRD pattern of prepared Ni–CdO nanoparticles. The Figure specifies phase purity and morphological parameters of synthesized Ni–CdO nanoparticles. The six major diffraction peaks were observed in the XRD pattern of Ni–CdO nanoparticles at various diffraction angles, corresponding to (111), (200), (220), (311), (222) and (400) directions. All the peaks of XRD graph indexed the face centred cubic structure of Ni–CdO nanoparticles, which is in good agreement with the JCPDS card no. 78–0653 with lattice constants; $a = b = c = 4.7063$ Å [12]. The peaks appearing in X-ray diffraction pattern of Cr–ZnO and Ni–CdO are well matched with X-ray diffraction pattern of undoped ZnO and CdO nanoparticles (supplementary data Fig. 1S) and no additional peaks corresponding to secondary phases were emerged in the 4 wt% of Zn^{2+} and Ni^{2+} doping. The result shows that the obtained Cr–ZnO and Ni–CdO nanomaterials have good crystalline phase and high purity. The crystallite size of synthesized nanoparticles has been calculated from Debye–Scherrer equation:

$$\text{Crystallite size } (D) = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ is the wavelength of X-ray used (0.154 nm), β is the full width at half maxima in radians and θ is the Bragg's

Fig. 1 XRD pattern of 4 wt% Cr-ZnO (a) and Ni-CdO (b) nanoparticles

Table 1 Crystallite size of the synthesized Cr-ZnO and Ni-CdO nanoparticles

Samples	Crystallite size
4 wt% Cr-ZnO	40.30 nm
4 wt% Ni-CdO	48.43 nm

diffraction angle. The calculated crystallite size was tabulated in the Table 1 [13, 14].

3.2 FE-SEM and EDAX analysis

The FE-SEM is one of the most frequently used analytical methods, used for the identification of surface morphology of the synthesized nanomaterials. Figure 2a–b represents the scanning electron micrograph of 4 wt% Cr-ZnO and Ni-CdO nanoparticles. The images illustrate that the synthesized Cr-ZnO and Ni-CdO nanoparticles have got hexagonal prism and spherical-like structures, respectively [15]. Figure 2c–d are illustrates the EDAX micrograph of Cr-ZnO and Ni-CdO nanoparticles. The EDAX spectrum of 4 wt% of Cr-ZnO and Ni-CdO show an evidence for the presence of Cr, Zn, Ni, Cd and O, respectively [16].

3.3 TEM analysis

Figure 3a–b shows the TEM images of 4 wt% Cr-ZnO and Ni-CdO nanoparticles prepared by the microwave heating method. The photomicrograph shows the well crystallite

nature and reveals grain size ranges from 38 to 63 nm for Cr-ZnO and 50–80 nm for Ni-CdO nanoparticles. This is well matched with the crystallite size calculated from XRD using Scherrer's formula [17].

3.4 FT-IR analysis of with and without dye-sensitized 4 wt% Cr-ZnO and Ni-CdO nanoparticles

Figure 4a represents the FT-IR spectra of 4 wt% Cr-ZnO nanoparticles. The broad band in the range of $430\text{--}498\text{ cm}^{-1}$ represents the stretching vibration of Zn–O. The broad absorption peaks at $3417\text{--}3508\text{ cm}^{-1}$ assigned the stretching vibration of –O–H group present in the physical adsorption on the sample, whereas absorption characteristic peaks at 1628 cm^{-1} represents the bending vibration of –O–H group. In Cr-ZnO, the band frequency of 1113 cm^{-1} represent the asymmetric stretching vibration of C–O and the poor band at 613 cm^{-1} represents the stretching frequency of Cr–O bond [18]. Similarly, Fig. 4b displays the FT-IR spectra of synthesized 4 wt% Ni-CdO nanoparticles. The broad peak at $3290\text{--}3550\text{ cm}^{-1}$ represents the formation of hydroxyl (–O–H) group in the adsorbed water molecule, while the peak at 1636 cm^{-1} is assigned their bending mode of vibration. The bands in the range of $400\text{--}700\text{ cm}^{-1}$ are corresponding to stretching vibrations of Cd–O bond. A peak observed at 1451 cm^{-1} is due to presence residual carbonate ions [19]. Figure 4c and d represent the FT-IR of TB, SPD and

Fig. 2 FE-SEM and EDAX images of 4 wt% Cr-ZnO (**a, c**) and 4 wt% Ni-CdO (**b, d**) nanoparticles

Fig. 3 TEM images of 4 wt% Cr-ZnO (**a**) and 4 wt% Ni-CdO (**b**) nanoparticles

EB dyes sensitized 4 wt% Cr-ZnO and Ni-CdO nanoparticles. From these figures, the peaks at $1230\text{--}1268\text{ cm}^{-1}$, $2917\text{--}2935\text{ cm}^{-1}$ are assigned to aromatic C-N and alkyl

C-H groups respectively. Broad peak at 3442 cm^{-1} represents the both O-H and N-H groups are present in the surface of prepared dye sensitized nanoparticles films [20].

Fig. 4 IR spectra of **(a)** 4 wt% Cr-ZnO, **(b)** 4 wt% Ni-CdO, **(c)** TB, SPD, EB dyes sensitized 4 wt% Cr-ZnO, **(d)** TB, SPD, EB dyes sensitized 4 wt% Ni-CdO

3.5 UV-visible analysis of Cr-ZnO and Ni-CdO nanoparticles.

Figure 5a illustrates the optical reflectance spectrum of 4 wt% Cr-ZnO and Ni-CdO nanoparticles. The reflectance spectra have been recorded in the wavelength range 200–800 nm at room temperature. The reflectance spectrum has been used to derive the optical bandgaps of 4 wt% Cr-ZnO and Ni-CdO nanoparticles. The diffused reflectance of Cr-ZnO and Ni-CdO nanocrystals are analyzed by Kubelka–Munk relation:

$$[F(R)] = (1 - R)^2 / 2R \quad (2)$$

where R is the diffused reflectance of the sample and F[R] is the Kubelka–Munk function [21]. The optical band gap of Cr-ZnO and Ni-CdO nanoparticles was calculated by

plotting the graph of $[F(R)h\nu]^2$ against photon energy in eV. The linear part of the curve was extrapolated to $(h\nu)^2 = 0$ (X-axis). Figure 5b and c shows the plot of photon energy in eV versus $[F(R)h\nu]^2$ for synthesized nanoparticles. It shows the energy gap for all the synthesized samples as a function of Cr and Ni doping concentration [22]. The optical band gap was found to be 3.07 eV for Cr-ZnO and 1.94 eV for Ni-CdO nanoparticles [23].

3.6 Electrochemical properties of dyes

The electrochemical properties measured from cyclic voltammetry is used identify the molecular orbital energy levels dye molecules. The molecular orbital levels of organic dye molecules have two energy levels i.e., HOMO and LUMO. The highest occupied molecular orbital (HOMO) is

Fig. 5 Optical reflectance of synthesized nanoparticles (a), Kubelka–Munk plot of Cr–ZnO (b) and Ni–CdO (c) nanoparticles

an outer energy level that acts as electron donor and lowest unoccupied molecular orbital (LUMO) is the deepest energy level that acts as electron acceptor (from HOMO level). When selecting the organic dyes used for DSSCs, this is very important to know the band gap, HOMO and LUMO values of dyes [24]. Figure 6 shows the cyclic voltammograms of 0.1 mM solutions of commercial Trypan Blue (TB), SPADNS (SPD) and Evans blue (EB) dyes in 0.1 M of KCl solution in the potential range from 0.2 to -1.6 eV versus SCE (standard calomel electrode). The electrochemical glass cell consists of standard calomel electrode as a reference electrode, platinum wire as an auxiliary electrode

and pencil graphite electrode as a working electrode. The potential were reference to ferrocene/ferrocenium (Fc/Fc^+) as internal reference [25]. A 100 mV/s scan rate was employed for the present cyclic voltammetric studies. The cyclic voltammograms of dyes exhibit a single well shaped reduction peak in the negative potential region and no oxidation peak was seen in the reverse scan. This clearly indicates that the dyes show the irreversible redox process. Moreover, the reduction peaks obtained from the cyclic voltammetry are helps to calculating the LUMO energy levels of selected metal free organic dye molecules (TB,

Fig. 6 Cyclic voltammograms of (a) solvent, (b) Trypan blue, (c) SPADNS and (d) Evans blue dyes

SPD and EB). The LUMO and HOMO levels of dyes have been calculated using the following equations (Table 2):

$$E_{\text{LUMO}}/E_{\text{HOMO}} = -(4.8 + E_{\text{onset}}^{\text{red}}/E_{\text{onset}}^{\text{oxd}}) \quad (3)$$

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (4)$$

$$E_{\text{HOMO}} = E_{\text{LUMO}} - E_g \quad (5)$$

$$E_g = \frac{1240}{\lambda_{\text{onset}}} \text{eV}$$

where, $E_{\text{onset}}^{\text{oxd}}$ is the onset oxidation potential and $E_{\text{onset}}^{\text{red}}$ is the onset reduction potential of the dyes and 4.8 eV is the energy level of ferrocene below the vacuum level. The $E_{\text{LUMO}}/E_{\text{HOMO}}$ of the TB, SPD and EB dyes are $-4.05 \text{ eV}/-6.12 \text{ eV}$, $-4.16 \text{ eV}/-6.21 \text{ eV}$ and $-4.12 \text{ eV}/-6.18 \text{ eV}$, respectively [26].

Table 2 Absorption maxima, HOMO and LUMO values of TB, SPD and EB dyes

Dye	λ_{max} (in abs.)	$E_{\text{onset}}^{\text{red}}$ (V)	E_{LUMO} (eV)	E_{HOMO} (eV)
Trypan blue	597 nm	-0.75	-4.05	-6.12
SPADNS	603 nm	-0.63	-4.16	-6.21
Evans blue	607 nm	-0.68	-4.12	-6.18

Fig. 7 Optical absorption spectrum of (A) Trypan blue (B) SPADNS (C) Evans blue dyes sensitized Cr–ZnO nanoparticles

3.7 UV–visible absorption analysis of dye-sensitized Cr–ZnO and Ni–CdO nanoparticles

Figure 7(A–C) shows the optical absorption spectra of dyes (TB, SPD and EB) in solution, pure Cr–ZnO nanoparticles and dyes sensitized on the Cr–ZnO nanoparticles. The figures show the significance difference between the absorption spectra of dyes loaded Cr–ZnO nanoparticles and TB, SPD and EB dyes in the visible region. Figure 7A(e)–C(e)

represents the absorption spectra of dyes in solution, which show the stronger absorption peaks at 597 nm, 603 nm and 607 nm, respectively [27]. It reveals that the absorption maxima for all the dyes are in the visible range. On the other hand, absorption spectra of individual dyes in solution show the different bands at lower wavelength (UV-region). The band at lower wavelengths are assigned to the π – π^* transition of the aromatic ring. The band at visible region assigned to the n – π^* transition of lone pair present in the azo chromophore ($-N=N-$) of

dyes [28]. Figure 7A(a)–C(a) show the optical absorption spectra of Cr–ZnO. It reveals that the highest absorption maxima occur at 390 nm which indicates that Cr–ZnO nanoparticles absorption of light in the range of ultra violet region. Figure 7A(b–d) show the different concentration of dyes loaded Cr–ZnO nanoparticles, which revealed the interaction of the dyes with Cr–ZnO and combines effect obtained from the UV–Visible spectra. The slightly broadened absorption spectra (compared to dyes in solution) obtained from dye sensitized Cr–ZnO clearly confirmed that anchoring of dyes with Cr–ZnO surface [29].

In addition, among the concentration of dye, the Cr–ZnO films sensitized with 3 mM TB, 3 mM SPD and 1 mM EB dyes have got much strong optical absorption compared to the other concentration of dyes. At higher concentrations of no further increase in the optical absorption was observed. This revealed that the adsorption saturation limit of TB, SPD and TB dyes on Cr–ZnO is 3 mM, 3 mM and 1 mM, respectively [30].

In the similar way, the absorption spectra of dyes in solution and adsorbed on the Ni–CdO surface is displayed in the Fig. 8(A–C). The spectra of 3 mM, 3 mM and 1 mM

Fig. 8 UV–Visible absorbance spectrum of (A) Trypan blue (B) SPADNS and (C) Evans blue dyes sensitized 4 wt% Ni–CdO nanoparticles

of dye loaded shows the broadened spectra in the range between 478 and 750 nm and slightly shifted absorption peak confirms the good interaction of dyes on the surface of Ni–CdO nanoparticles [20]. The careful observation of all the dye loaded spectra of Cr–ZnO and Ni–CdO nanoparticles, the spectra of dyes loaded Cr–ZnO (upto 430–815 nm) nanoparticles shows excellent broadness compared to dyes sensitized Ni–CdO (478–750 nm). Hara et al. [31] were reported the reason for red shift of the absorption peak by organic dyes coated on the undoped metal oxide surface. They revealed the red shift may be attributed to a strong binding interaction (J-type of aggregate) between the anchoring group of the dyes and the metal oxide surface [32]. Although J-aggregate of organic dyes is very high significance for the solar energy harvesting, it is also important to notice that only the dye which strongly attached to the oxide surface by the anchoring group will contribute to the change in the conductivity of the device. The optical absorption spectra of all the dyes coated semiconducting materials illustrates that the TB, SPD and EB dyes are completely chemisorbed with Cr–ZnO and Ni–CdO surfaces and that these dyes absorb light of suitable wavelengths. This indicates that the selected commercial TB, SPD and EB dye molecules can be used as photo-sensitizers for wide band gap semiconductors [33].

3.8 I–V characteristics of dye sensitized Cr–ZnO and Ni–CdO nanoparticles

Figure 9a, b illustrates the current–voltage (I–V) characteristics of TB, SPD and EB dyes sensitized 4 wt% Cr–ZnO

nanoparticles under dark and UV-light illumination conditions. Figure 9a shows the current intensity of dyes sensitized 4 wt% Cr–ZnO samples under dark condition. From these curves, it can be carefully seen that the dyes sensitized Cr–ZnO samples shows low current intensity compared bare Cr–ZnO sample. This decrease of current intensity after dye sensitization is due to the blocking effect of the dye and as well as surface relaxation effect [32]. Subsequently, UV–Vis light is illuminated on the surface of dyes sensitized Cr–ZnO, the excited electrons present in the LUMO levels of dyes are easily jumped into the conduction band (CB) of Cr–ZnO ($E_{CB} = -4.204$ eV) nanoparticles. This leads to improve the charge carriers on the surface of Cr–ZnO and slightly improves the current intensity of Cr–ZnO samples. The similar result was reported by R. Parthiban et al., in case of Evans blue sensitized ZnO solar cells. They explain the reason for slightly increase of current in the dyes loaded ZnO under light condition. Based on the DFT of Evans blue dye, the electronic density in the ground state of dye molecules is actually distributed mainly in the aromatic (C–N), amine (N–H) and alkyl (C–H) groups, excluded in the SO_3^- anchoring group. Furthermore, the electrons are excited due to light illumination on the surface of dye–ZnO film. It illustrated that on illumination of photon energy, the electron density is shifted towards the SO_3^- anchoring group (electron acceptor), that favours the electron impinges on to the surface of semiconducting materials. It is also informed that the electrons in the excited state are not distributed much in the anchoring group, which indicates that the injection of electrons on the semiconductors surface is

Fig. 9 I–V characteristics of Trypan blue, SPADNS and Evans blue dyes sensitized 4 wt% Cr–ZnO in dark condition and UV-light condition

very less effective. The lower electron density distribution in the acceptor group is attributed to the very slight increment of light current (compared to dark current) was observed in the I–V characteristics [34]. Moreover, in the case of SPADNS and Trypan blue dyes sensitized Cr–ZnO nanoparticles were show the less shift of photo voltage towards lower side under light condition. This is due to these dyes also contains sulphonic acid group as an acceptor part similar to Evans blue dye. This sulphonic acid group is more acidic compare to other anchoring groups ($-\text{COOH}$, $-\text{OH}$ etc.) and which affect the electron injection process over on the semiconductor surface [35]. Figure 10a, b show the I–V characteristics of Trypan blue, SPADNS and Evans blue dyes sensitized 4 wt% Ni–CdO nanoparticles. The results of current intensity values reveal similar trend of I–V characteristics of Cr–ZnO samples. The carefully compare the current intensity of dyes sensitized 4 wt% Cr–ZnO and 4 wt% Ni–CdO nanoparticles, which show the well current intensity was observed in dye sensitized 4 wt% of Cr–ZnO ($E_{\text{CB}} = -4.204$ eV) compared dyes loaded Ni–CdO ($E_{\text{CB}} = -4.315$ eV) nanoparticles. This is due to good interaction between dye molecules and Cr–ZnO nanoparticles. The measured current intensity of before and after dyes sensitization of samples were noticed in the Table 3. The remarkable increase in the current intensity of dyes coated Cr–ZnO and Ni–CdO samples may result in higher efficiency in the dye sensitized solar cells [36].

Table 3 Current intensity of dyes sensitized Cr–ZnO and Ni–CdO nanoparticles

Dyes sensitized samples	Dark condition Current intensity (A)	Light condition Current intensity (A)
2 wt% Cr–ZnO	0.2298	0.2814
TB sensitized Cr–ZnO	0.1753	0.4347
SPD sensitized Cr–ZnO	0.1592	0.3421
EB sensitized Cr–ZnO	0.1972	0.4642
4 wt% Ni–CdO	0.3411	0.4004
TB sensitized Ni–CdO	0.3224	0.4420
SPD sensitized Ni–CdO	0.3002	0.4048
EB sensitized Ni–CdO	0.2880	0.4529

4 Conclusions

The effect of dyes on the optical and electrical properties of Cr–ZnO and Ni–CdO nanoparticles were studied. The absorption spectrum of TB, SPD and EB dyes sensitized 4 wt% Cr–ZnO and 4 wt% Ni–CdO nanoparticles show the broader peaks compared to bare 4 wt% Cr–ZnO and 4 wt% Ni–CdO nanoparticles. The current–voltage (I–V) measurement under dark as well as UV–Vis. light illumination conditions showed the photosensitive behaviour of dye sensitized Cr–ZnO and Ni–CdO nanoparticles. The increased current intensity of dye sensitized Cr–ZnO and Ni–CdO nanoparticles was clearly indicated the possibility of using these nanoparticles in the fabrication of dye sensitized solar cells (DSSCs).

Fig. 10 I–V characteristics of Trypan blue, SPADNS and Evans blue dyes sensitized 4 wt% Ni–CdO nanoparticles in dark and light condition

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Human and animal rights Humans/animals are not involved in this work.

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