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Pyrocatechol violet sensitized Ho-TiO$_2$/ZnO nanostructured material: as photoanode for dye sensitized solar cells

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Abstract

In this work TiO$_2$, Holmium doped (Ho–TiO$_2$) Titanium oxide nanoparticles (NPs) and the corresponding nanostructured combinations (Ho–TiO$_2$/ZnO NC) were successfully synthesized through sol gel method and reflux techniques respectively. The prepared nano materials were characterized with the help of x-ray diffraction Analysis (XRD), UV–visible spectroscopy, Scanning Electron Microscopy (SEM), Energy dispersive x-ray Analysis (EDX) and Fourier Transform infrared spectroscopy (FT–IR). The absorption spectra of nano materials were used for band gaps calculation. The band gap of pure TiO$_2$ NPs was found to be 3.10 eV which was effectively tuned to 2.65 eV by the doping of Holmium at different concentrations. XRD patterns confirmed the crystalline nature and purity of the synthesized nano materials. Morphology and elemental composition of the material were investigated using SEM and EDX respectively. FTIR helped in detecting the functional groups and grafting of the dye on the surface of nanoparticles. The nano materials were used as Photo-anodes in dye sensitized solar cells (DSSC). Pyrocatechol Violet dye was used as a photo-sensitizer. P3HT (polymer), a hole conducting polymer, was employed as a solid state electrolyte. I–V measurements were used for characterization of fabricated solar cells. Ho–TiO$_2$/ZnO nanomaterial photosensitized with Pyrocatechol violet dye gave the highest percentage efficiency of 1.51. Other characteristic parameters of the fabricated devices such as short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), maximum power point (MPP) and fill factor were found to be 11.2 mA cm$^{-2}$, 0.41 V, 1.55(mW cm$^{-2}$) and 0.33 respectively.

1. Introduction

The alarming increase in energy consumption is the most basic and prominent challenge that we face today. As the human population increases the demand for energy intensifies. World is going through a critical situation i.e. the extensive utilization of energy is 14 terawatts (TW) for 7 billion people. It is expected that this energy demand will increase more than 24 terawatts (TW) in upcoming 40 years [1]. The consumption of petroleum products with the constantly expanding requirements is immensely problematic. Natural energy from sunlight being freely accessible to everyone, clean and environmental friendly is considered to be the greatest blessing for mankind in the 21st century [2]. The energy generated from sunlight is easily convertible to electricity with the help of solar light harvesting devices. Such devices have already been applied in solar light lamps, calculators and satellites. Currently, innovative technological concepts are being focused on the dye sensitized solar cells (DSSCs). DSSCs are reliable devices in comparison to other PV devices of third generation solar cells in terms of economic and fabrication aspects [3]. In contrary to other solar cells, DSSCs use semiconductor material and photosensitizer. A sensitizer is usually a dye which is adsorbed on the surface of wide band gap semiconductor. The sensitizer absorbs the solar radiations efficiently per unit area and generates electron. The photoengraved electrons are then injected to the conduction band of semiconductor. The charge separation at interface helps to reduce the electron hole recombination hence maximize the soar to electrical energy conversion. Recently Zn-Porphyrin-Sensitized Nanocrystalline TiO$_2$ Films power conversion efficiency for DSSC is reached to 10.4% [4].
For DSSC record power conversion efficiency is 12% for small cells and for minimodules is about 9% [5]. The aim of all the generations of PV devices is to reduce the cost and yielding a more durable and stable device with a better efficiency [6–8]. There are four basic components of DSSC, photo anode, dye, electrolyte and counter electrode. Photo anode consists of conducting glass with screen printed nano materials (semiconductor). The electron is injected into conduction band of nanomaterials from the dye. These electrons go through the external circuit to counter electrode where reduction occurs and the dye is regenerated by the redox couple of the electrolyte [5, 9]. P3HT (poly 3-hexylthiophene is a p-type organic semiconductor polymer. It plays the same role in DSSC as the liquid electrolyte does. Its LUMO level is higher than the LUMO of dyes hence acting as a good hole conductor in solid state heterojunction solar cells [10, 11]. This advantage makes them durable and stable in comparison to earlier cell designs [12]. Different semiconductor metal oxides (TiO₂), ZnO, ZnS, Cu₂O, Al₂O₃, MgO, SnO₂, and SrTiO₃, their composites and core shells nanomaterials have been used as photo anode with a layer of dye (photo sensitizer) coated on their surfaces [13–18].

TiO₂ having wide band gap (3.2 eV) has been employed as a feasible electron acceptor for dye sensitized solar cells [15, 19]. In the beginning it gave low efficiency (1%) which was tremendously enhanced when Gratzel used porous TiO₂ as anode material [20, 21]. Low cost, high structure stability and photosensitivity of TiO₂ attracted the attention of researchers to develop new products [22, 23]. In the struggle for enhanced efficiency TiO₂ has been subjected to cationic doping, anionic doping, and multi-element doping [24]. Charge recombination at the interface of the semiconductor/dye/electrolyte due to diverse trapping sites and the high grain boundaries among the TiO₂ NPs inhibit the overall conversion efficiency and performances of DSSC. To minimize issue, TiO₂ is combined with nanostructured metal oxide materials of wide band such as ZnO [14], Cu₂O, SnO₂, SrTiO₃ [16], Al₂O₃, and MgO to develop heterojunction system. These developments have significantly reduced electron-hole pair recombination [25–27].

Many researchers have already revealed the beneficial effects of ZnO/TiO₂ composites as photoanodes for DSSC. However, they got low photovoltaic efficiency. In the present work ZnO and Ho-doped TiO₂ nanoparticles synthesized by reflux technique were used to generate TiO₂/ZnO and Ho-doped TiO₂/ZnO heterojunction combinations with various concentrations of Holmium. This was done with the aim to compare the efficiencies of these two heterojunction systems under the same experimental conditions and to investigate the impact of holmium doping on TiO₂ with a particular reference to its role in the Ho-TiO₂/ZnO heterojunction system. These heterojunctions (TiO₂/ZnO, Ho-TiO₂/ZnO) displayed better photovoltaic response in DSSC than bare TiO₂ due to linkage of Zn–O–Ti. The enhanced response could also be attributed to the formation of a passivation layer of ZnO loaded on TiO₂ surface. This layer reduces charge carrier’s recombination and improves the fast transport of free electrons. Pyrocatechol violet dye was used as a photosensitizer in this work which further boosted the efficiency.

2. Materials and methods

All the reagents and chemicals were analytical grade. Titanium tetraisoproxide (C₁₂H₂₈O₄Ti), holmium (III) nitrate pentahydrate (Ho(NO₃)₃·5H₂O), zinc acetate dihydrate (ZnC₄H₆O₄·2H₂O), sodium hydroxide and 2-propanol were purchased from Sigma Aldrich and used without further purification.

2.1. Synthesis of TiO₂ NPs.

Sol-gel technique was used for synthesis of the TiO₂ nanoparticles. First of all 100 g Titanium (IV) isopropoxide was added to (200 g) of iso-propanol. The mixture was stirred for 5 min utilizing a magnetic stirrer. This gave us an alkoxide solution. Now a mixture of 25.33 g water and 127 g iso-propanol was prepared and then added drop wise to the alkoxide solution. The mixture was stirred for 24 h at ambient temperature. The precipitate was dried at 100 °C in oven and then calcined at 500 °C and 1000 °C in a furnace. The same Sol-gel technique was employed for the synthesis of Ho-TiO₂ NPs except the addition of weighed amount of Holmium salt (Holmium (III) nitrate pentahydrate) (1%–3%) to TTIP solution before the hydrolysis step.

2.2. Synthesis of undoped TiO₂/ZnO and Ho-TiO₂/ZnO nanostructured material

Reflux technique was applied to incorporate ZnO with undoped TiO₂ and Ho-TiO₂ NPs to generate TiO₂/ZnO and Ho-doped TiO₂/ZnO nanostructured materials respectively. 0.548 g of zinc nitrate dihydrate (ZnC₄H₆O₄·2H₂O) was used in this reaction as a Zinc precursor salt. The salt was dissolved in deionized water (250 ml) by stirring for 15 min. The pre-synthesized undoped and Ho-doped TiO₂ NPs (0.1997 g) were added to the above reaction mixture followed by drop wise addition of 0.1 M NaOH aqueous solution. The solution was further stirred for 5 h to ensure proper dispersal. The resulting product was refluxed for 3 h at 120 °C. In the subsequent step the solution was cooled down at ambient temperature, which was followed by centrifugation at 2000 rpm. The solution was washed with ethanol and deionized water several times during centrifugation to
eradicate un-reacted $O_2^-$ ions from the solution. After 6 h the dried sample was annealed in furnace for 2 h at 450 °C to get undoped TiO$_2$/ZnO and Ho-TiO$_2$/ZnO.

2.3. Sensitization of synthesized nanomaterials with pyrocatechol violet dye
In order to sensitize the nanostructured material with Pyrocatechol violet dye, solutions of different concentrations of dye ranging from $1.5 \times 10^{-7}$ to $4 \times 10^{-7}$ M were prepared from the stock solution (1 mM) by dilution. Each of these solutions was mixed with 3 ml of ($1 \text{ mg ml}^{-1}$) solution of the synthesized nonmaterial. These solutions were kept magnetically stirring for 18 h at room temperature. The samples were centrifuged and washed to remove the un-grafted dye molecules and then optically analyzed through UV-visible spectroscopy. A schematic of working of DSSCs is shown in figure 1.

2.4. Device fabrication for DSSC
2.4.1. Preparation of P3HT solution and active layer of synthesized nanomaterials
20 mg of Poly-3-hexylethiophene (P3HT) was dissolved in 1 ml of chloroform at 60 °C for 15 min in the presence of Argon atmosphere. The nanohybrid material (grafted material) 46 mg ml$^{-1}$ was transferred to chloroform. Photoactive active blend is a combination of dye grafted nanostructured materials blended with P3HT. P3HT is a conducting polymer. It plays a dual role i.e. as an electrolyte and as a photosensitizer, because it absorbs in UV-visible region [10, 11, 28]. The same procedure was followed for the preparation of photoactive blend of hybrid nanomaterials of Ho-TiO$_2$ and their respective nanostructured materials (TiO$_2$/ZnO, Ho-TiO$_2$/ZnO).

2.4.2. Substrate treatment
ITO coated glass slabs having dimensions of 3 × 2 cm$^2$ and thickness of about 80 nm were employed as a substrate for device fabrication. About 1/3 (small portion) of the glass sheet was etched for one hour with the help of hydrochloric acid. The remaining portion was covered with scotch tape. Finally these slabs were rinsed with acetone and deionized water and were dried overnight.

2.4.3. PEDOT: PSS spin coating
Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is used to improve the surface morphology and smoothness of ITO. It hinders the diffusion of oxygen through the anode [29, 30]. The device in present research work is a solid state heterojunction solar cell. It is a sub type of DSSC. It was spin coated on the surface of ITO at 4000 rpm for 45 s and an acceleration of 6500 rpm. After spin coating 0.3 cm portion of PEDOT: PSS was removed with the help of water. And then the substrate was annealed for 15 min at 50 °C to get a uniform morphology of polymer and make it ready for the deposition of photoactive layer.
2.4.4. Deposition of the active layer
The active blend which consists of dye sensitized nanomaterials as photoanode and P3HT as a hole conducting layer in the ratio of 70:30 was used as a photoactive layer. Its deposition was achieved at 1800 rpm with an acceleration of 1600 rpm for 20 s. It was followed by another spin at 600 rpm in order to remove any traces of solvent [31].

2.4.5. Cathode deposition
The cathode is made up of Al metal and deposited on the top of active layer by thermal evaporation under high vacuum conditions. Consequently 80 nm thick strips of aluminum were made to extract and guide electrons to the external circuit. After cathode deposition the fabricated devices were annealed at 85 °C for 15 min for achieving of uniform surface of the photoactive materials.

3. Characterization techniques used
The crystalline structure and phase composition of the synthesized nanomaterials was determined with the help of x-rays diffractometer (PANalytical XPERT high score’s Diffractometer). FTIR (BRUKER Platinum ATR) spectroscopy was used for identification of different functional groups present in a compound. The optical studies were carried out with the help of UV-visible (Shimadzu-1700) double beam spectro-photometer. In order to record absorption spectrum, the sample solution was prepared and with the help of absorption spectrum, optical energy gap (band gap) was calculated. Scanning electron microscopic images were obtained by JEOL JAD-2300 and this technique was used to study the morphology and size of the nanoparticles. Energy dispersive x-ray analysis (EDX) coupled with scanning electron microscopy was used for the identification of elemental composition of materials.

4. Results and discussion

4.1. UV-visible spectroscopic studies
Figure 2(a) shows the UV-visible spectra of undoped TiO2 NPs and Ho-TiO2 NPs. The spectrum of undoped TiO2 nanoparticles dispersed in deionized water shows a broad absorption centered at 300 nm. Maximum absorption peaks for 1%, 2%, 3% Holmium doped TiO2 NPs were observed at 305 nm, 310 nm and 315 nm respectively. From the spectra it is noticed that the maximum absorption of Holmium doped TiO2 nanoparticles is shifted towards the longer wavelength i.e. demonstrated bathochromic shift as compared to the Pure TiO2 NPs [32]. The UV-visible spectra of TiO2/ZnO and Holmium doped TiO2/ZnO nanostructured materials are shown in figure 3(a). The absorption peak of TiO2/ZnO NPs occur at 371 nm. The corresponding spectra of different doping percentages of Holmium (1%, 2% and 3%) (Ho doped TiO2/ZnO) reveal a pronounced red shift to 378 nm, 379 nm and 381 nm respectively the red-shift of Ho doped TiO2/ZnO NPs compared to that of the pure TiO2 NPs is probably due to strong electronic coupling between the TiO2 and ZnO [33]. The band gaps of synthesized nanomaterials were calculated from UV-visible spectra using the following equation.

\[
\alpha h\nu = A (h\nu - E_g)^n
\]

Where \( \alpha \) represent the absorption coefficient, \( h\nu \) is the energy of photon, ‘A’ represents the proportionality constant and it is different for different materials while \( n \) is the fitting parameter that depend on electronic transitions [34]. The optical band gap of Pure TiO2 was calculated, which came out to be 3.06 eV and the band gaps of 1%, 2% and 3% Holmium doped TiO2 NPs are shown in figure 2(b). The energy gap (figure 3(b)) value for TiO2/ZnO heterojunction was calculating to be 2.98. With increasing percentage of Holmium, TiO2/ZnO heterojunctions showed significant reduction in band gaps (table 1) [35].

4.1.1. UV-visible spectroscopy of pyrocatechol violet dye grafted nanomaterials
Pyrocatechol violet dye, contains two different types of anchoring groups which are sulfonate (SO3−) and catechol. It was used as a photo-sensitizer. The UV-vis study of Pyrocatechol violet dye reveals that the dye shows three peaks of absorption. The first peak is observed at 278 nm and the second at 325 nm. These two peaks occur in UV region due to n–π∗ transition and the third broad absorption appears at 428 nm and occur in visible range of electromagnetic radiation due to the aggregated dye molecule at low energy as shown in figure 4 (plot a). The UV-visible spectrum of PV dye grafted on the surface of the TiO2 NPs is shown in figure 4 (plot b). A dramatic change in optical behavior of the nanohybrid materials was observed. The interaction between dye and nanoparticles can be explained by comparing the absorption spectra of pure dye and the nanomaterials grafted with dye. The spectrum of pure dye shows three broad absorptions centered at 278 nm, 325 nm and 428 nm, whereas the nanostructured material grafted with different concentrations of dye ranging from 10 μM to 30 μM.
show two absorption peaks. The first broad peak appears at 300 nm wavelength which confirms the presence of TiO$_2$ NPs in the nanohybrid materials. More interestingly the broad peaks of dye were disappeared (at 278 nm and 325 nm) and a new band at the region of 600–700 nm was appeared. In case of pure dye and nanoparticles it was not present which confirms that there is some type of interaction between the dye and NPs [31, 36]. The change in absorption spectra of dye and dye grafted NPs highlights that the dye is successfully chemisorbed on the surface of NPs. The spectra of grafting of PV dye on Ho doped TiO$_2$, TiO$_2$/ZnO, and Ho-TiO$_2$/ZnO, materials grafted with different concentrations of dye ($10$–$30$ $\mu$M) are shown in figure 4. A red shift was observed in the first peak as compared to pure TiO$_2$ NPs. Disappearance of the two first peaks of dye and the appearance of a new peak at 665 nm in grafted sample confirm that there is some sort of interaction between the dye and Ho-TiO$_2$. The same trend was followed by TiO$_2$, Ho-TiO$_2$, and respective nanocomposites when grafted with dye. Changes in the electronic spectra of the grafted material are almost the same as explained earlier for the grafted TiO$_2$ NPs. These changes in the spectra of grafted dye confirm the successful chemisorption of dye on NPs. The absorption of the NPs in the visible region can enhance efficiency of the device.

4.2. XRD studies
In figure 5(i) (a) diffraction peaks in the XRD pattern of TiO$_2$ are positioned at angles of 25.05$^\circ$, 37.83$^\circ$, 48.02$^\circ$, 54.87$^\circ$ and 62.60$^\circ$ corresponding to crystal planes (101), (004), (200), (211) and (200) of TiO$_2$ NPs respectively [33]. It was found that the rare earth metals inhibit the transition between anatase to rutile phase during the heat treatment. This inhibition in transformation stabilizes the anatase phase by the bonding of (holmium) to TiO$_2$ NPs [37]. So It was found that both undoped and Holmium doped samples exist in anatase phase and have
tetragonal structure according to JCPSD card number 00-001-0562. Additionally, with increasing concentration of holmium, the broadening in width and weakness in intensity of diffraction peaks of anatase phase occurred. So, it is interpreted that holmium doping retards the growth of nano crystallites because bonds of Ti–O–Ho formed during the calcinations inhibit the transfer and rearrangement of Ti and O in particles [38]. Figures 5i (b)–(d) specifies XRD patterns of 1%, 2% and 3% Ho doped TiO₂. No characteristic peak of the holmium oxide is observed in XRD pattern of doped samples. It indicates that either the Ho ions are highly

![Graph](image-url)

**Figure 3.** (a) UV-visible Spectra of undoped TiO₂/ZnO (solid line), 1% Ho-TiO₂/No (dash), 2% Ho-TiO₂/No (dot), 3%Ho-TiO₂ (dash dot) (b) Band gap of undoped TiO₂/ZnO (solid line), 1% Ho-TiO₂/ZnO (dash), 2% Ho-TiO₂/ZnO (dot) and 3% Ho-TiO₂/ZnO (dash dot).

| S. NO | Compounds names          | Band gaps values (eV) |
|-------|--------------------------|-----------------------|
| 1     | TiO₂ NPs                 | 3.10                  |
| 2     | 1% Ho-TiO₂ NPs          | 3.01                  |
| 3     | 2% Ho-TiO₂ NPs          | 2.99                  |
| 4     | 3% Ho-TiO₂ NPs          | 2.96                  |
| 5     | TiO₂/ZnO heterojunction | 2.98                  |
| 6     | 1%Ho-TiO₂/ZnO heterojunction | 2.67            |
| 7     | 2%Ho-TiO₂/ZnO heterojunction | 2.66          |
| 8     | 3%Ho-TiO₂/ZnO heterojunction | 2.65          |
dispersed or Ho ions are incorporated in crystalloid of the TiO$_2$ NPs \cite{39}. The diffraction peaks of TiO$_2$/ZnO and Ho doped (1\%, 2\% and 3\%) TiO$_2$/ZnO nanostructured materials correspond to (100), (002), (101), (110), (103), (201) crystal planes indicating wurtzite structure for ZnO in accordance with JCPDS card number (79–0208) as shown in figures 5ii(a)–5ii(d). Due to strain and stress effect, the TiO$_2$ (101) peak intensifies. This reveals that the ZnO is covered by TiO$_2$ NPs \cite{33}. More ever the peak at 34.37° (002 crystal plane) correspond to the hexagonal ZnO wurtzite structure \cite{40}. The average crystallite size of the nanomaterials were calculated from the XRD data by using the Debye–Scherrer formula shown in equation 1 and summarized in table 2.
4.3. SEM studies

The morphologies of the synthesized undoped TiO\textsubscript{2} NPs, Ho-TiO\textsubscript{2} NPs, and their corresponding nanostructured heterojunctions were analyzed through SEM images. Figures 6(a) and 6(b) represent the SEM images of undoped TiO\textsubscript{2} NPs, Ho-TiO\textsubscript{2} NPs respectively. These clearly show the approximate spherical morphologies with little agglomeration of the particles. It is revealing that agglomeration and irregular structure is noticed in undoped TiO\textsubscript{2} NPs. In Ho-TiO\textsubscript{2} NPs the particles are slightly homogenously dispersed. This means that holmium incorporation improves deagglomeration [15]. The SEM images of TiO\textsubscript{2}/ZnO and Ho-TiO\textsubscript{2}/ZnO nanostructures are depicted in figures 6(c) and 6(d) respectively. In both images the ZnO nanostructure was observed to be well dispersed over the TiO\textsubscript{2} NPs.
rods are uniformly dispersed throughout TiO2 NPs and Ho-TiO2 NPs. All the nano rods seem to be mutually separated without agglomeration [41].

4.4. EDX studies

Energy dispersive x-ray spectroscopy has been used to identify the presence of elements in the synthesized materials. The weight % of different elements present in the materials is given in the table 3. The stoichiometric ratio of Zn and Ti was found to be almost 1:1 (figure 7(a)). In case of Ho-TiO2 (figure 7(b)). The ratio of holmium was also found to be in accordance with the theoretical value. For Ho doped TiO2/ZnO (figure 7(c)). An equamlar ratio of Zn and Ti with a minute ratio of dopant was observed.

Table 3. EDX data of TiO2/ZnO, Ho-TiO2 and Ho-TiO2/ZnO.

| Sr.no | Samples       | wt% O | wt% Zn | wt% Ti | wt% dopant |
|-------|---------------|-------|--------|--------|------------|
| 1     | TiO2/ZnO      | 30.37 | 33.47  | 36.16  | —          |
| 2     | Ho-TiO2       | 61.81 | —      | 37.10  | 1.09       |
| 3     | Ho-TiO2/ZnO   | 31.67 | 31.96  | 35.92  | 0.45       |

Figure 7. EDX patterns of (a) TiO2/ZnO, (b) Ho-TiO2 and (c) Ho-TiO2/ZnO.
4.5. FTIR studies

Fourier Transforms Infrared spectra of undoped TiO$_2$ NPs Ho-doped TiO$_2$ NPs and their respective nanostructured heterojunctions were recorded in the wave number range of 400–4000 cm$^{-1}$ for the identification of chemical bonds and functional groups in the compound. Bonding of Ti–O–Ti reveals the formation of TiO$_2$ NPs (figure 8(a)). Calcination at 500 °C leads to considerable sharpening of transmission or absorption bands in 400–900 cm$^{-1}$. It indicates the formation of anatase phase of TiO$_2$ NPs. The peak at 3458 cm$^{-1}$ corresponds to the O–H stretching of the alcohol [42]. At 1216 cm$^{-1}$ band is due to the bending mode of Ti–O–Ti. Transmission band at 1435 cm$^{-1}$ signifies symmetric stretching vibration of carboxalate group. The bands at 2970 cm$^{-1}$ and 2946 cm$^{-1}$ correspond to symmetric and asymmetric vibration of alkyl chain respectively. The band at 1738 cm$^{-1}$ confirms the reaction between the acetic acid and TTIP [43, 44].

In Ho-doped TiO$_2$ NPs the vibration band at 445 cm$^{-1}$ corresponds to the metal oxide single bond in bending mode, in case of Ho–O. The band at 1631 cm$^{-1}$ is attributed to the presence of water of hydration within Ho$_2$O$_3$ shown in figure 8(b) [45]. In case of TiO$_2$/ZnO heterojunction (figure 8(c)) the aromatic rings C–H stretching occur at 3011 cm$^{-1}$. The absorption frequency band in region from 400–1000 cm$^{-1}$ corresponds to the bonding of Ti–O–Ti and shows the successful formation of TiO$_2$. The peak at 1211 cm$^{-1}$ indicates Ti–O–Ti vibrations. The peak at 1726 cm$^{-1}$ corresponds to the carbonyl bond clearly indicating the non-hydrolytic sol-gel reaction of TTIP and acetic acid to form ester [42, 44]. Sharp band at 509 cm$^{-1}$ indicates the Zn–O stretching mode [46]. In Holmium doped TiO$_2$/ZnO nanostructured heterojunction (figure 8(d)) peak at 445 cm$^{-1}$ signifies the bending mode of the Ho–O.

4.5.1. FTIR Studies of PV dye grafted nanomaterials

FTIR spectrum of Pyrocatechol Violet dye (PV) is shown in figure 9(a). Broad band at 3262 cm$^{-1}$ corresponds to the stretching mode of hydroxyl group (O–H) of water which was used as a solvent. The carbonyl bond (C=O) stretching mode appeared at 1737 cm$^{-1}$. Vibrations of C–O occur at 1365 cm$^{-1}$. The sulfonic acid group (SO$_3^-$) vibration contributes to the absorption at 1216 cm$^{-1}$ [44, 47, 48]. Pyrocatechol Violet grafted undoped TiO$_2$, Ho-doped TiO$_2$ NPs and their respective nanostructured heterojunctions were investigated through FTIR.
spectroscopy and their spectra are shown in figures 9(b)–9(e). The spectra of dye grafted nano materials were compared with the pure dye spectrum in order to confirm and investigate the successful grafting of the dye on the surface of the nano materials. From the spectra of the grafted nano materials it was observed that all the peaks are slightly shifted from their original positions as compared to the pure dye. The disappearance of solfonic acid group (SO$_3^-$) vibrations contributing to absorption at 1216 cm$^{-1}$ and the appearance of new peaks confirm the successful grafting of dye molecules on the surface of nanoparticles. It means that dye is successfully chemisorbed.

4.6. Photovoltaic characteristic of DSSC

The I–V curves of DSSCs assembled with synthesized nanomaterials (Ho-doped samples and dye grafted samples) are shown in figures 10 and 11 respectively. Their corresponding performance parameters are summarized in tables 4 and 5 respectively. Two types of solar cells were fabricated, the one having no

Figure 9. FTIR spectra of (a) Pyrocatechol Violet dye, (b) PV–TiO$_2$, (c) PV–Ho–TiO$_2$, (d) PV–TiO$_2$/ZnO, (e) PV–Ho–TiO$_2$/ZnO.
photosensitizer (Pyrocatechol violet dye), and the active layer is made up of the undoped TiO2 NPs, Holmium doped TiO2 NPs and their respective nanostructured combinations simply blended with P3HT polymer. The other type of cells contained the photosensitizer grafted nanomaterials and the active layer is made up of the grafted undoped TiO2 NPs, Holmium doped TiO2 NPs and their respective nanostructured combinations which are blended with P3HT polymer. Different parameters were measured from I–V curves such as Short
A successful synthesis of pure and Holmium doped (Ho-TiO2 NPs) TiO2 was carried out by using sol gel method. Reflux technique was adopted to synthesize the corresponding nanostructured heterojunctions (Ho-TiO2/ZnO/Dye). It was found that the synthesized nanoparticles exhibited anatase phase and tetragonal structure. From UV-visible spectra band gaps were calculated for pure TiO2 NPs as well as for Holmium doped Titania. The band gap of undoped TiO2 NPs was found to be 3.10 eV which was effectively tuned to 2.96 eV by the doping of Holmium at different concentrations. For corresponding nanostructured combination (Ho-TiO2/ZnO), the band gap was further narrowed down to 2.65 eV. XRD pattern revealed the crystallinity and average crystallite size. The average crystallite size of pure and 1%, 2%, 3% Holmium doped NPs were found to be 9.67, 6.54, 7.9 and 6.06 nm respectively. The corresponding undoped and Holmium doped nanostructured materials were found to have average crystallite sizes of 23.84, 12.9, 19.34 and 25.0 nm respectively. SEM revealed that TiO2 NPs had spherical shape whereas ZnO was found in the form of nanorods. Elemental analysis confirmed the exact elemental compositions of the materials in the same ratios in which they were mixed. Successful grafting of the dye on the surface of nano materials was confirmed by the significant shifting of the peaks in FT-IR and UV-visible spectroscopies. The I–V measurements showed that the Holmium doped TiO2/ZnO and Ho-TiO2/ZnO/dye nanostructured heterojunctions serve as effective junctions for the generation of photocurrent which is comparable to the updated devices but the overall efficiency is reduced due to the leakage of current or transport of electrons and holes toward the respective electrode. This is a big challenge and under investigation in our group.

Table 5. The calculated parameters form the I–V measurements curves of PV sensitized undoped, Ho-TiO2 NPs and their respective nanocomposites based solar cell.

| Device Composition | Jsc (mA/cm²) | Voc (V) | MPP (mW/cm²) | Fill factor | Efficiency (η%) |
|--------------------|--------------|---------|--------------|-------------|-----------------|
| P3HT-TiO2 Light    | 2.4          | 0.43    | 0.50         | 0.48        | 0.5             |
| P3HT-TiO2-PV dye   | 5.61         | 0.43    | 1.13         | 0.46        | 1.11            |
| P3HT-Ho-TiO2-PV dye| 6.56         | 0.41    | 0.91         | 0.33        | 0.9             |
| P3HT-TiO2/ZnO-PV dye nanocomposite | 8.3 | 0.41 | 1.16 | 0.34 | 1.16 |
| P3HT-Ho-TiO2/ZnO-PV nanocomposite | 11.2 | 0.41 | 1.55 | 0.33 | 1.51 |

5. Conclusion

A successful synthesis of pure and Holmium doped (Ho-TiO2 NPs) TiO2 was carried out by using sol gel method. Reflux technique was adopted to synthesize the corresponding nanostructured heterojunctions (Ho-TiO2/ZnO/Dye). It was found that the synthesized nanoparticles exhibited anatase phase and tetragonal structure. From UV-visible spectra band gaps were calculated for pure TiO2 NPs as well as for Holmium doped Titania. The band gap of undoped TiO2 NPs was found to be 3.10 eV which was effectively tuned to 2.96 eV by the doping of Holmium at different concentrations. For corresponding nanostructured combination (Ho-TiO2/ZnO), the band gap was further narrowed down to 2.65 eV. XRD pattern revealed the crystallinity and average crystallite size. The average crystallite size of pure and 1%, 2%, 3% Holmium doped NPs were found to be 9.67, 6.54, 7.9 and 6.06 nm respectively. The corresponding undoped and Holmium doped nanostructured materials were found to have average crystallite sizes of 23.84, 12.9, 19.34 and 25.0 nm respectively. SEM revealed that TiO2 NPs had spherical shape whereas ZnO was found in the form of nanorods. Elemental analysis confirmed the exact elemental compositions of the materials in the same ratios in which they were mixed. Successful grafting of the dye on the surface of nano materials was confirmed by the significant shifting of the peaks in FT-IR and UV-visible spectroscopies. The I–V measurements showed that the Holmium doped TiO2/ZnO and Ho-TiO2/ZnO/dye nanostructured heterojunctions serve as effective junctions for the generation of photocurrent which is comparable to the updated devices but the overall efficiency is reduced due to the leakage of current or transport of electrons and holes toward the respective electrode. This is a big challenge and under investigation in our group.
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