Fabrication of TiO2/CdS heterostructure photoanodes and optimization of light scattering to improve the photovoltaic performance of dye sensitized solar cells (DSSCs)

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Research Article

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Abstract

Currently, the TiO2/CdS photoanodes based dye sensitized solar cells (DSSCs) have shown extraordinary developments in the photo conversion efficiency. In this report, pristine TiO2, CdS and various molar ratios of TiO2/CdS photoanodes were prepared by one step microwave irradiation route and followed by doctor blade method. The sheet like morphology of the TiO2 and CdS nanoparticles were clearly evident from the SEM and TEM images. A significant reduction band gap with enhanced light absorption and rapid prevention of electron hole pair was explored by UV-DRS and PL studies. The photocurrent density-voltage (J-V) and electrochemical impedance (EIS) characteristics were analyzed for assembled solar cell. The photo-conversion efficiency of 12.8% was obtained with the configuration TiO2/CdS (200 mg) that represent a 2.5 fold increment compared to bare TiO2 (5.33%) as well as commercial Pt (6.11%). The experimental results are discussed.

1. Introduction

Recently, Photovoltaic cell (PV) has poor conversion power efficiency from light to electricity. Behind the overlay of many PV device that produce over than 41% of the incident light output electricity and semiconductor materials have a performance was lower than 20% as a results of the greatest usage of enterprise. Because, these PVs can translate only the quarter part of the light output obtained. This performance can restrict by certain chemical composition of the component [1-3]. Solar energy is also one of the greatest significant power renewable resources due to its continuous supply and economic compatibility [4-7]. Solar cells, which transfer solar energy directly into electrical energy and heat, can decrease energy costs incurred by alternate energy generation. It is well known that titanium oxide (TiO2) is one of the important photoanodes in the DSSCs due to its outstanding physico-chemical properties, suitable electronic structure and band-gap energy [8-10]. In pristine TiO2, electron mobility is also too limited and thus lower solar cell transfer efficiency [11, 12]. A large number of works has been done to increase light quality in a visible light area by concentrating on the development of high-performance sensitizers [13–16]. A substrate to absorb photographs in the full sunlight spectrum remains a task. Semiconductor materials like CdSe, CdS, Bi2S3, PbS, CdTe2 and CuInS4, and so on that adsorb visible light may act as sensitizers even though they are capable of transmitting electricity to wide semiconductors such as pristine ZnO and TiO2 [17]. Variety of methods have been used to fabricate the TiO2/CdS heterostructure such as Hydrothermal. Solvothermal, microwave dielectric, chemical bath deposition, sol gel and chemical co-precipitation methods and so on.

Among these, Microwave irradiation has an absorption function that makes it easy to heat up the solution uniformly. The effect is uniform ionization and rapid crystal growth, leading to the development of limited distribution crystallites [18]. Compared to other traditional approaches, microwave irradiation synthesis has the benefit of a fast response time, which is due to the occupying power produced by microwave electrical or magnetic factors that produce friction and molecular interactions. In the present investigation, the novel TiO2/CdS binary photoanodes was synthesized by facile microwave irradiation
method for the first time without employing the hydrothermal process. The constructed TiO$_2$/CdS binary photoanodes exhibits high photo-conversion efficiency and good electro catalytic activity with long term stability performance than bare TiO$_2$ and CdS. The origin of this high photovoltaic property was investigated through various experimental studies such as powder X-ray diffraction (XRD), TEM, UV-Vis DRS, SEM, XPS and Photovoltaic were studies. The improved photovoltaic mechanism of the proposed DSSC was also discussed in detail.

2. Experimental

2.1 Materials

All the chemicals used were analytical grade used without any further purification. They are Titanium isopropoxide (TTIP, 99% Sigma–Aldrich), cadmium nitrate [Cd(NO$_3$)$_2$.4H$_2$O] (98% Fisher Scientific) and sodium thiosulfate [Na$_2$S$_2$O$_3$.5H$_2$O] (98% Sigma–Aldrich).

2.2 Synthesis of TiO$_2$, CdS and TiO$_2$/CdS nanocomposite samples

The synthesis process of photoanodes was convoluted in numerous steps. In order to prepare TiO$_2$ sample, 10 ml of TTIP was hydrolyzed with mixed solution of water and ethanol (1:1). After that NaOH was added to the TiO$_2$ in order to increase the PH value of the solution as 9. The resultant product was placed to microwave oven and irradiated at 140 °C for 10 min. Finally, the product was dried at conventional mode (100 °C for few hours). In the preparation of CdS nanoparticles, 0.5 g of Cd(NO$_3$)$_2$.4H$_2$O and 2 g of Na$_2$S$_2$O$_3$.5H$_2$O was separately diluted with 50 ml of deionized water (DI). The mixture was placed to microwave oven and irradiated at 140 °C for 10 min. Finally, the product was dried at conventional mode (100 °C for few hours). In TiO$_2$/CdS nanocomposite preparation, the various amounts of CdS (25, 50 and 100 mg) were mixed with TiO$_2$ with mechanical grinding method. The different ratio of CdS (25, 50 and 100 mg) with TiO$_2$ was marked as TiO$_2$/CdS25, TiO$_2$/CdS50 and TiO$_2$/CdS100, respectively.

2.3 DSSC fabrication setup

The present solar cell device is sandwich type, which is consists of photoanode, cathode and electrolyte solution, respectively. The photoanode and cathode of DSSC is fabricated using TiO$_2$/CdS and commercial platinum (Pt) paste deposition on FTO substrate using doctor blade method [19]. Then the photoanode was immersed in N719 dye solution. 0.6 M iodide/triiodide liquid electrolyte was injected between photoanode and cathode, respectively. AM1.5, 100 mWcm$^{-2}$ solar stimulator was used to monitor the photocurrent vs. voltage characteristics. The active surface area of the DSSC was 0.16 cm$^2$ (0.4 x 0.4 cm$^2$).

2.4 Characterization techniques
X-ray diffraction (XRD) (Japan, XD-3A) using CuKα radiation and a scintillation counter detector were used to identify the crystalline structure of the samples. The morphological and optical properties of the samples were analyzed by Hitachi SU8010 type SEM instrument, H-600-II, Hitachi type TEM analytical instrument, UV–Vis spectrophotometer (UV-2550, Shimadzu, Japan). The electronic structure and chemical composition of the sample were determined by XPS (AXIS-165 Shimadzu, Japan). Autolab Potentiostate ECO CHEMIE was used to monitor the electrochemical performance.

3. Results And Discussion

3.1 Structural characteristics

The crystallinity structure is investigated using the Powder XRD pattern and the pertinent pattern is seen in the Figure 1. The sharp peaks in X-ray diffraction of pristine TiO$_2$ assay suits well with the TiO$_2$ anatase phase with tetragonal crystalline structure (JCPDS N. 89-4921) with the following matched miller orientation planes of (101), (004), (200) (015), (211) and (204) respectively. While the wurtzite structure of CdS was confirmed with relative diffraction planes of (002), (110), (103), and (112), consequently. The results matched perfectly with the standard data (JCPDS No.65–3414). The mixture orientation plane of TiO$_2$ ((101), (200), (211), (204)) and CdS ((002), (110), (103), and (112)) in the composite samples reveal the formation of heterostructure between them. It was renowned that no other additional or impurity phases were found in the pattern, which resembles the high product purity. The anatase and wurtzite structure of TiO$_2$ and CdS was further confirmed by Raman spectroscopy, which is shown in Figure 2. The Raman modes of 517 cm$^{-1}$ ($A_{1g}$ antisymmetric bending quivering of O-Ti-O), and 638 cm$^{-1}$ ($E_g$) [20], confirmed the anatase phase of TiO$_2$. The high intensity bands assigned to CdS at 300 cm$^{-1}$ and 604 cm$^{-1}$ [21]. The increase of cds content in the TiO$_2$ were significantly enhanced the property, which was identified by the Raman intensity modes. This attributed to the structural distortion between heterostructure crystal matrices.

3.2 Morphological analysis

Figure 3 (a-c) shows the SEM images of pure TiO$_2$, CdS and TiO$_2$/CdS100, samples respectively. The sheet like and spherical nanoparticles were identified in the pristine TiO$_2$ and CdS nanoparticles. In the TiO$_2$/CdS100 composite, the CdS nanoparticles are anchored on the surface of TiO$_2$ nanosheets. Further the TEM image of pristine TiO$_2$ sample clearly expose the wrinkle type ultrathin nanosheets (diameter in several micrometers) were identified (Fig. 3d). The clear individual spherical nanoparticles (30-40 nm) of CdS were also noticed in the corresponding TEM picture (Fig. 3e). The CdS nanoparticles were clearly decorated on the TiO$_2$ nanosheets surface in the TiO$_2$/CdS100 composite (Fig. 3f). The elemental mapping of TiO$_2$/CdS100 composite clearly exhibits the presence of the key elements of Ti, O, Cd and S (Fig. 3 g-j). The results yet again substantiate the formation of heterostructure between TiO$_2$ and CdS.

3.3 Optical characteristics
UV-Vis DRS was implemented to discern the skill of light absorption and optical band gap energy of the samples. Figure 4a) shows the UV absorption spectra of all the samples. The absorption values of pristine TiO$_2$ and CdS were located at 410 and 480 nm, respectively. The K-M model [22, 23] has been utilized to extrapolate the band gap energy and the relevant band gap plot is shown in Figure 4b). The calculated band gap energy of TiO$_2$ and CdS was 3.02 eV and 2.58 eV. The light absorption ability is significantly improved in the visible light region when the loading amount of CdS is increased into TiO$_2$. After combination of CdS with TiO$_2$, the band gap energy was gradually decreased from 3.02 eV to 2.25 eV. This could be due to the heterostructure combination adequate to extended light absorbance ability, which is favorable to enhancing the DSSC power conversion efficiency in the photovoltaic field. The luminescence and charge transfer process of the samples were further analyzed by room temperature photoluminescence spectra with excitation wavelength of 350 nm and the emission spectrum is shown in Figure 5. The abroad emission intensity in the visible light (440 nm) and green light (545 nm) region is perceived in TiO$_2$ and CdS samples, respectively. The composite sample cover the emission nature in the visible to green emission region. This may be due to the high luminescence properties of heterostructure combination, which is suitable for optoelectronic device applications. Remarkably, the emission intensity peak was decreased gradually while increasing the CdS content. It was noted that TiO$_2$/CdS100 sample shows highly reduced emission intensity than compared to other samples. This could be due to the suppress recombination process of electron-hole pair.

### 3.4. Surface area and chemical composition analysis

Figure 6 (a) & (b) shows the N$_2$ adsorption-desorption with pore size distribution curves of pure TiO$_2$, CdS and TiO$_2$/CdS100, samples respectively. The clear H3 hysteresis loop with type IV isotherm could be noticed in all the samples. Hence, all the samples belong to the mesoporous nature [24-27]. The type IV isotherm is due to the highly porous nature of nanosheets with uniform size of the nanoparticles. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size of TiO$_2$/CdS100 composite sample is found to be 103.5 m$^2$/g and 23.5 nm. The pore size and surface area is higher than pristine TiO$_2$ (66.8 m$^2$/g and 37.8 nm) and CdS (45.7 m$^2$/g and 43.5 nm). The high porous nature of the TiO$_2$/CdS100 composite sample is due to the uniform size nanoparticles of CdS were successfully decorated on the ultrathin TiO$_2$ nanosheets surface. Chemical environment and surface element analysis was explored through XPS and the TiO$_2$/CdS100 composite sample XPS spectra is shown in Figure 7. Figure 7 a) shows the survey spectra with wide range analysis, which is mainly exhibits the major elements of Ti, Cd, O and S. The high magnification spectra of Ti 2p exhibits the binding energies of ∼465.1 eV and 458.1 eV are ascribed to the Ti2p$_{1/2}$ and Ti2p$_{3/2}$, respectively (Fig. 7b). The Cd 3d core level XPS spectrum (Fig. 7c) has two peaks at 404.1 eV (Cd 3d$_{5/2}$) and 410.1 eV (Cd 3d$_{3/2}$). The high resolution S 2p spectra (Fig. 7d) shows two peaks at 161.4 eV and 164.1 eV, which are related to the S2p$_{1/2}$ and S 2p$_{3/2}$. The deconvolution of the XPS spectrum for the O 1s peak is presented in Fig. 7e which is composed of three peaks at 529.1, 531.51 and 533.5 eV. These peaks can be consigned to the incident of the Ti-O, C-O, bonds and even S-O/S=O bonds (in sulfate sort) present in the composite.
3.5. Photovoltaic studies

The present DSSC device was sandwich type, which is schematically expressed in Figure 8a). The fabricated DSSC was tested for photo current density – voltage (J-V) characteristics under AM 1.5 solar condition with intensity of 100 mwcm\(^{-2}\). Figure 8b) shows the J-V curves, which shows the photovoltaic parameters of photoelectric conversion efficiency (\(\eta\)), open current voltage (\(V_{oc}\)), fill factor (FF) and current density (\(J_{sc}\)). The results are précised in Table 1. The optimized TiO\(_2\)/CdS100 photoanode show high current density (22.45%) and photo-voltage (932 mV), which results in high PCE of 12.8%. the PCE of TiO\(_2\) and CdS was found to be 5.33 and 3.21%, respectively. The fabricated DSSC was also examined to incident photon to electron conversion efficiency (IPCE) and the plot is display in Figure 8c). The highest IPCE values reaches to 93.5% for optimized TiO\(_2\)/CdS100 photoanode than compared with other photoanode samples (at wavelength of 480 nm). The improved IPCE of the composite electrode is attributed to the recombination of lower charge, this leads to greater efficiency gathering of charges and cost effective charging at the interface of the TiO\(_2\)/CdS/FTO. In the examination of long term stability test (Fig. 8d), the experiment was carried out with various time solar light illuminations (0-600 h). The results reveal that no major changes in PCE arise throughout the period of testing (approximately 600 h). This could be due to the long term cyclibility of the DSSC. Charge transport and recombination resistance behavior was further analyzed by electrochemical impedance spectra (EIS) analysis. Figure 9 a) shows the Nyquist plot with equivalent circuit (inset) of the all the photoanodes with corresponding circuit. There are two semicircles smaller (lower frequency region) and higher (higher frequency region) was found in the Nyquist plot. The second semicircle was taken to find out the recombination resistance and charge transport properties. The EIS results establish that the optimized TiO\(_2\)/CdS100 photoanode show lower RCT (24.5 \(\Omega\)) and Rs (5.8 \(\Omega\)) than compared with other photoanode samples. Moreover, the photoanode show longer electron life time (12.5 ms). The EIS parameters values are also summarized in Table 2. The improved mechanism of the DSSC is shown schematically in Figure 9c). The integration of CdS as a photoanode into TiO\(_2\) increases the transport of charges and decreases the recombination of charges because of the greater surface area, resulting in a consistent electron pathway and more dye-binding domains. In addition, the heterostructure consumes more light than the straight bare TiO\(_2\) and CdS. Hence it has higher power conversion efficiency. Moreover, the heterostructure could provide more active site, which means less grain borders, which consequently enhances electrical conductivity and furthermore boosts solar cell performance [28].

4. Conclusions

In the present investigation, the incorporated CdS can fascinate the structural, optical and photovoltaic properties of TiO\(_2\) photoanodes. The sheet like morphology of the TiO\(_2\) and CdS nanoparticles were clearly evident from the SEM and TEM images. The photocurrent density-voltage (J-V) and electrochemical impedance (EIS) characteristics were analyzed for assembled solar cell. The photoconversion efficiency of 12.8% was obtained with the configuration TiO\(_2\)/CdS (200 mg) that represent a 2.5 fold increment compared to bare TiO\(_2\) (5.33%) as well as commercial Pt (6.11%). The enhanced PCE
of the TiO\textsubscript{2}/CdS composite is due to the photogenerated electrons can move from CdS to TiO\textsubscript{2} more quickly, ensuring that two dimensional constructs, and their near interfacial touch. Moreover, CdS behaves as an supply of electrons for TiO\textsubscript{2}. This special arrangement for electron-hole transition allows for photogenic electrons-holes with a certain electrical potential energy in CB and VB, thereby improving photo-conversion efficiency of DSSC.

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Tables

| Parameters        | TiO₂ | Cds | Pt  | TiO₂/CdS25 | TiO₂/CdS50 | TiO₂/CdS100 |
|-------------------|------|-----|-----|------------|------------|-------------|
| Jsc (mA/cm²)      | 12.8 | 6.45| 15.23| 16.81      | 18.51      | 22.45       |
| Voc (mV)          | 670  | 601 | 721 | 742        | 878        | 932         |
| Fill Factor       | 65.1 | 63.4| 68.4| 74.1       | 83.1       | 88.5        |
| Efficiency η (%)  | 5.33 | 3.21| 6.11| 8.22       | 9.71       | 12.8        |
| Samples       | $R_s/\Omega cm^2$ | $R_{ct}/\Omega cm^2$ | $r/\text{ns}$ |
|--------------|----------------|----------------------|-------------|
| CdS          | 9.4            | 79.4                 | 4.2         |
| TiO$_2$      | 8.2            | 64.2                 | 6.5         |
| TiO$_2$/CdS25| 7.2            | 48.9                 | 7.8         |
| TiO$_2$/CdS50| 6.4            | 38.7                 | 9.2         |
| TiO$_2$/CdS100| 5.8           | 24.5                 | 12.5        |