Influence of CdS Morphology on the Efficiency of Dye-Sensitized Solar Cells

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ABSTRACT: Cadmium sulfide (CdS) used in dye-sensitized solar cells (DSSCs) is currently mainly synthesized by chemical bath deposition, vacuum vaporization, spray deposition, chemical vapor deposition, electrochemical deposition, sol−gel, solvothermal, radio frequency sputtering, and hydrothermal process. In this paper, CdS was synthesized by hydrothermal process and used with a mixture of titanium dioxide anatase and rutile (TiO\(_2\) (A+R)) to build the photo-anode, whereas the counter electrode was made of nanocomposites of conductive polymer polyaniline (PANI) and multiwalled carbon nanotubes (MWCNTs) deposited on a fluorine-doped tin oxide substrate. Two morphologies of CdS have been obtained by using hydrothermal process: branched nanorods (CdSBR) and straight nanorods (CdSNR). The present work indicates that controlling the morphology of CdS is crucial to enhance the efficiency of DSSCs device. Indeed, the higher power conversion energy of 1.71% was achieved for a cell CdSBR−TiO\(_2\) (A+R)/PANI−MWCNTs under 100 mW/cm\(^2\), whereas the power conversion energy of 0.97 and 0.83% for CdSNR−TiO\(_2\) (A+R)/PANI−MWCNTs and TiO\(_2\) (A+R)/PANI−MWCNTs, respectively. Therefore, by increasing the surface to volume ratio of CdS nanostructures and the crystallite size into those structures opens the way to low-cost chemical production of solar cells.

1. INTRODUCTION

The dye-sensitized solar cell (DSSC) has been extensively studied and appears as a powerful substitute to other thin-film solar cells, like silicon solar cells, largely because of the low cost of the materials used and its relatively simple fabrication process. In DSSCs, light absorption and charge-carrier transport occur in different steps (dissimilar to what happen in solar cells using inorganic p−n junctions).\(^3\)−\(^9\) DSSCs comprise three key parts: a transparent conducting oxide dispersed on glass, a layer of mesoporous metal oxide semiconductor that is photosensitized by a monolayer of dye molecules fixed onto the oxide surface, and a counter electrode, which is most frequently a platinum-coated fluorine-doped tin oxide (FTO) substrate. The cell is filled by an electrolyte to ensure hole transport and close the circuit.\(^1\)\(^0\)\(^1\)\(^1\)

By incorporating a photoanode made of titanium dioxide (TiO\(_2\)) nanostructures using ruthenium-dye sensitizers, certain DSSCs demonstrated a power conversion efficiency greater than 12.5%.\(^1\)\(^2\) Currently, DSSCs based on zinc oxide (ZnO) continue to show low efficiency numbers, compared to TiO\(_2\)-based DSSCs. The photocatalytic features of TiO\(_2\) are dependent on its crystalline phase, its pore structure, its specific surface area, and its crystallite size. TiO\(_2\) occurs in three crystalline phases: rutile (the thermodynamic stable phase), anatase and brookite (the two metastable phases). Numerous studies have established the anatase phase of TiO\(_2\) as a highly effective photocatalytic material for multiple uses.\(^1\)\(^3\)

It is still poorly understood why the anatase phase exhibits higher photocatalytic activity than rutile phase. TiO\(_2\) acts as a catalyst in the ultraviolet region because of its wide band gap (~3.2 eV) and this restricts its ability to harvest light. To overcome this drawback, sensitized composites of two or more semiconducting materials with offset band gaps and positions are used (Bi\(_2\)S\(_3\), CuInS\(_2\), CdTe, CdS, CdSe, PbS are examples). These semiconductors capture light in the visible region and function as useful sensitizers due to their capacity to transfer electrons to larger band gap semiconductors, including TiO\(_2\).\(^1\)\(^4\)

Cadmium sulfide (CdS) recently became a promising alternative material because of its 2.3 eV direct band gap (\(\sim 3.2\) eV) and this restricts its ability to harvest light. To overcome this drawback, sensitized composites of two or more semiconducting materials with offset band gaps and positions are used (Bi\(_2\)S\(_3\), CuInS\(_2\), CdTe, CdS, CdSe, PbS are examples). These semiconductors capture light in the visible region and function as useful sensitizers due to their capacity to transfer electrons to larger band gap semiconductors, including TiO\(_2\).\(^1\)\(^4\)

A huge effort has been focused on controlling the shape and size of CdS nanocrystals. As a result, several new methods have been published for synthesizing CdS nanostructures, especially CdS nanowires.\(^1\)\(^9\) Inducing the formation of branches on existing nanowires or nanorods results in enlarged surface areas that can boost charge-transportation channels and increase light absorption. These techniques may have significant industrial applications in optoelectronics.\(^2\)\(^0\)
Numerous chemical and physical techniques have been employed, such as colloidal, solvothermal, vapor deposition, template, and laser ablation methods, to synthesize CdS micro/nanostructures.21 Yao et al. and Peng et al. synthesized CdS nanowires by using laser ablation of a metal catalyst mixed target and CdS.22,23 Solution deposition protocols, with or without organic surfactants, chemical vapor deposition, and high-temperature thermal decomposition methods, were used to synthesize one-dimensional CdS nanostructures. These structures include nanobelts,22,24 nanowires,22,25 nanorods,22,26 and nanotubes.20,23,27 Chen et al. have developed a simple one-step, no template hydrothermal technique for fabricating CdS nanorod arrays on an indium tin oxide substrate.20,28 Hydrothermal process was defined by Byrappa and Yoshimura (2008) as any homogeneous (nanoparticles) or heterogeneous (bulk materials) reaction occurring at high temperature and pressure larger than 1 atm.29 Hydrothermal fabrication has numerous benefits compared to other conventional processes. The technique can produce homogeneous and pure-phase materials, as well as speeding up reaction rates by improving solid and fluid species interactions. Indeed, hydrothermal fluids have lower viscosity, higher diffusion rates, which consequently enable efficient mass transport. These are a number of practical and environmental benefits to this process: pollution free (reactions are completed within a closed system), low energy consumption, better dispersion, better shape regulation, improved control of nucleation, simplicity of the technique, and cost effectiveness.29 Hossain et al. presented CdS deposited by chemical bath deposition (CBD) on TiO2 to fabricate DSSCs, and the conversion efficiency was 1.13%.30 Abdelah et al. reported an improvement in the conversion efficiency of DSSCs (~1.25%) by producing porous CdS via CBD.31 The incorporation of carbon nanotubes (CNTs) and polyaniline (PANI) enhances the DSSC performance. Benetti et al. were the first to fabricate CNTs–polymer composites by mixing epoxy resin with multiwalled carbon nanotubes (MWCNTs).32 Conductive PANI-packed nanotubes might produce innovative materials with very useful optical, electronic, or thermal characteristics.

In this study, TiO2(A+R) were deposited by spray-coating onto CdS nanorods, which were prepared by hydrothermal deposition technique on top of a commercial FTO transparent glass. Branched cadmium sulfide (CdSBR) or straight cadmium sulfide nanorods (CdSNR) with TiO2(A+R) were used as a photoelectrode in DSSCs, whereas PANI–MWCNTs nanocomposites were used as a counter electrode. The DSSC fabrication and characterization are described in Sections 2 and 3, respectively.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Ethylene glycol (CH2OH)2, ditetrabutylammonium cis-bis(isothiocyanato)bis-(2,2-bipyridyl-4,4-dicarboxylato) ruthenium(II) (N719 dye) C58H86N8O8RuS2 95%, thiourea ≥99.0%, multiwalled carbon nanotubes >99%, titanium(IV) oxide rutile TiO2 99.99%, L-glutathione reduced ≥98.0%, and titanium(IV) oxide anatase TiO2 99.7% were all purchased from Sigma-Aldrich. Iodine I2 was purchased from Mallinckrodt chemical work. Fluorine-doped tin oxide (FTO) glass substrate, with a resistivity of 12–17 Ω cm, was purchased from Nanocs. N,N-Dimethylformamide (DMF), acetone (C3H6O), cadmium nitrate Cd(NO3)2·4H2O, hydrochloric acid (HCl), potassium iodide (KI), and ethanol (C2H5OH) were purchased from Fisher Scientific. Aniline C6H5N ≥99% and sulfuric acid H2SO4 were purchased...
from Alfa Aesar. All of the chemicals were used without any further purification.

2.2. Fabrication of the Photoanode. FTO-coated glass with dimensions of 2.5 x 2.5 cm² was used as substrate. Prior to the deposition, the substrate was cleaned ultrasonically within acetone, methanol, and deionized water (DI water, 18.20 MΩ cm) for 5 min each. CdSNR and CdSBR were synthesized to fabricate the photoanode of the DSSC. Initially, CdSNR was synthesized by an hydrothermal approach, specifically an aqueous solution with thiourea, cadmium nitrate, and glutathione was prepared according to the following molar ratio (1:1:0.6) and stirred for a few minutes. Then, the solution was transferred into a Teflon-lined stainless steel autoclave (20 cm³ capacity). Finally, the FTO substrate was placed into the autoclave and then loaded into the oven at 200 °C for 3.5 h. The sample was rinsed with DI water after being cooled down naturally to room temperature. Then, the sample was naturally dried in air at room temperature.

To functionalize CdSBR, the resultant CdSNR was rinsed in dilute HCl with a ratio (1:9) for 30 s and then cleaned with DI water. The product was then placed into a fresh solution, and the hydrothermal approach was repeated for 3.45 h at 200 °C to get the branched CdS structure (CdSBR). A mass of 3 g from each titanium dioxide phase (anatase and rutile, TiO2(A+R)) was mixed with acetic acid and DI water (10:90%) to create a suspension. After stirring it for nearly 35 min, the suspension was sonicated for 3 h. The resultant suspension is then oxidized to I3⁻/I⁻, and reduced state of the redox couple (RE), which consequently transfers to the conduction band (CB) of TiO2(A+R) results by the oxidation of the dye molecules, which consequently transfers the electron into the CB of CdS. The oxidized dye molecules were regenerated by electrons coming from the reduced state of the redox couple (RE), which consequently oxidized to I3⁻ (OX). Finally, the I3⁻ was regenerated by accepting electron from the counter electrode.

3. CHARACTERIZATION

The morphology and the structure of the CdS nanorods were observed within a scanning electron microscope JEOJSM7000F with energy dispersive X-ray analysis (EDS). The crystallinity of the products was studied by X-ray diffraction (XRD) and carried out on a Rigaku Miniflex 600 X-ray diffractometer using Cu Kα radiation with a 1.54056 Å wavelength. Raman spectroscopy was also used to characterize the CdSBR and CdSNR. Optical absorption of the samples and substrate were recorded by acquiring the spectra with a UV-vis spectrometer from 300 to 900 nm. Current–voltage (I–V) characteristics were evaluated and measured using a Keithley 2400 source meter in the dark and under illumination at AM 1.5. The solar light simulator had an intensity of 100 mW/cm².
4. RESULTS AND DISCUSSION

The CdS nanorods (CdSNR) and branched nanorods (CdSBR) have been characterized by scanning electron microscopy (SEM, Figure 4). CdSNR and CdSBR were grown by using a hydrothermal process to cover uniformly the FTO substrate. As shown in Figure 4a,b, the dimensions of the vertically ordered CdSNR are $\sim 100$ nm in diameter, $\sim 230$ nm in length, which are consistent with the dimensions reported by Chen et al.\textsuperscript{37} The hexagonal cross-section of the CdSNR was clearly observed in Figure 4a. Furthermore, the EDS analysis exhibited the presence of Cd and S elements with a ratio $\sim$1:1, whereas the compositions for Cd and S in the compound are 48.55 and 51.45\%, respectively, as shown in Figure 4e,f. EDS analysis of the CdSBR revealed that the composition of Cd = 51.09\% and S = 48.91\%. Figure 4c,d shows the CdSBR morphology at low and high magnifications, which indicate a uniform coverage of CdSBR onto the surface of the FTO substrate. CdSBR consists of straight CdSNR backbones with length of $\sim 250$ nm and hexagonal branches dimensions of $\sim 200$ nm length and $\sim 100$ nm diameter. As expected, the reaction time for hydrothermal process has an effect on the dimensions of CdSNR and CdSBR. The presence of thin branches along the CdSNR backbones, which form the CdSBR structure, improves the performance of DSSCs due to a decrease in recombination.

The fractal geometry characterizes the scaling structure of a surface by a number $D_{\text{fractal}}$ called the fractal dimension that varies between 2 (when the surface is flat) and 3. Considering the growth of thin films, the surface contains lakes within islands and islands within lakes, which we will refer to simply as islands. When the islands are characterized by a surface with a fractal dimension $D_{\text{fractal}}$ the coastlines formed by the islands sectioning by a plane are with a dimension $D_{\text{coast}} = D_{\text{fractal}} - 1$. The surface of the island $A$ is linked to its radius $R$ by the relationship $A \propto R^D$. And the perimeter of the island $P$ is linked to the fractal dimension of the thin-film $D_{\text{fractal}}$ with the

![Figure 4](image4.png)

**Figure 4.** Top-view and cross-sectional SEM images of as-prepared CdSNR at different magnifications (a, b), top view and cross-section of CdSBR grown by two steps hydrothermal process on FTO (c, d), EDS spectra for CdSNR and CdSBR (e, f).

![Figure 5](image5.png)

**Figure 5.** AFM image of straight CdS nanorods onto the FTO substrate (a), AFM of branched CdS nanorods onto the FTO substrate (b).
relation \( P \propto R^{D_{\text{fractal}}} \). So, the relationship linking the perimeter with the surface is a power law given by \( P = \mu A^{\alpha_{\text{fractal}}} \), where \( \mu \) is the proportionality factor between the perimeter and the surface, \( \alpha_{\text{fractal}} = D_{\text{fractal}}/2 \). The atomic force microscopy

Figure 6. UV–vis absorption spectra of CdS\(_{\text{NR}}\), CdS\(_{\text{BR}}\), and FTO (a), band gaps of CdS\(_{\text{NR}}\) and CdS\(_{\text{BR}}\) (b), XRD patterns of CdS\(_{\text{NR}}\), CdS\(_{\text{BR}}\), and FTO (c), Raman spectra of CdS\(_{\text{NR}}\) and CdS\(_{\text{BR}}\) (d).

Figure 7. Tilted-view SEM images of as-prepared CdS\(_{\text{BR}}\)–TiO\(_{2}\)(A+R) at high magnification (a), tilted-view of MWCNTs (b), top-view of PANI (c), top-view of PANI–MWCNTs nanocomposite (d).
(AFM) measurements are carried out with a Bruker Dimension-Icon AFM (peak force) in tapping mode ($f = 300 \text{ kHz}$). The tip was a silicon AFM probe Tap300 Al-G with a constant force of 40 N/m. AFM images are shown in Figure 5. The fractal dimension was extracted with the WSxM software.\(^4\) The measured fractal dimensions of straight and branched CdS nanorods are $1.670 \pm 0.049$ and $1.705 \pm 0.045$, respectively. Further analysis showed that the typical densities of CdSBR and CdSNR are $\sim 57$ and $\sim 46$ nanorods/\(\mu\)m\(^2\), respectively. Figure 6a illustrates the absorbance spectra from (300–900) nm of CdSNR, CdSBR, and FTO substrate. The CdSBR structure absorbs mainly in the visible region ranging from 326 to 573 nm, whereas the CdSNR structure absorbs in the region ranging from 320 to 520 nm. Since, both structures absorb mainly the violet and blue wavelengths, the remaining transmitted light will exhibit the complementary color to the wavelengths absorbed, i.e., yellow–orange. Apparently, the absorbance peak for the CdSBR structure is higher than that of CdSNR, which is attributed to the high surface area covered by CdSBR compared to CdSNR and thus absorbing and harvesting more photons. The band gaps of CdS\(_{\text{NR}}\) and CdS\(_{\text{BR}}\) were established to be 2.37 and 2.28 eV, respectively, as shown in Figure 6b, which indicates that the absorption edge of CdS\(_{\text{NR}}\) is identified to be at lower wavelength than that of the CdS\(_{\text{BR}}\). On Figure 6c, the XRD patterns of as-prepared CdS\(_{\text{NR}}\), CdS\(_{\text{BR}}\), and FTO are presented. The hexagonal wurtzite phase of CdS is confirmed and the intensity peak (002) at $2\theta = 24.6^\circ$ referring the formation of the CdS\(_{\text{BR}}\) grown on FTO with better crystallization than CdS\(_{\text{NR}}\). The mean crystallite sizes of CdS\(_{\text{NR}}\) and CdS\(_{\text{BR}}\) have been determined by using the Debye–Scherrer’s equation, $D = \frac{K\lambda}{\beta \cos \theta}$, where $\lambda$ is the wavelength of the X-ray radiation in nanometer (nm), $D$ is the crystallite size, $\beta$ is the full width at the half-maximum of the peak, $\theta$ the diffraction angle, and $K$ is a constant, usually taken as 0.94.\(^{34,41−43}\) The measurements indicate that the mean crystallite sizes were 42.97 ± 4.2 and 49.37 ± 1.5 nm for CdS\(_{\text{BR}}\), CdS\(_{\text{RR}}\), respectively. On Figure 6d, the Raman spectra of the as-prepared CdS\(_{\text{NR}}\) and CdS\(_{\text{BR}}\) are shown at room temperature. The longitudinal optical phonon modes 1LO and 2LO of CdS were measured at 297 cm\(^{-1}\) and at 600 cm\(^{-1}\) for both structures. These values are in agreement with the literature.\(^{44−46}\) It can be clearly seen that there is no difference in the peak position between the Raman spectra of CdS\(_{\text{NR}}\) and CdS\(_{\text{BR}}\) because the same growth technique was used. However, there is a difference in the shape of the peak, which indicates a better crystalline structure for CdS\(_{\text{BR}}\) compared to CdS\(_{\text{NR}}\).\(^{34}\) This enhanced crystalline structure is confirmed by XRD in Figure 6c.
The morphology of the CdSBR/TiO2(A+R) is presented in Figure 7a, it is seen obviously that the surface of CdSBR was perfectly attached to the TiO2(A+R) nanoparticles. Figure 7b displays the typical SEM image tilted view at low and high magnifications of MWCNTs deposited on FTO. The good coverage of nanotube network onto the FTO substrate is visible in the Figure 7b, due to the dissolution of the MWCNTs in the DMF. Figure 7c shows the SEM image of PANI network after polymerization onto the FTO substrate. Figure 7d demonstrates a good interface between PANI−MWCNTs due to the diffusion of MWCNTs between the porous PANI film.

The UV−vis light absorption of rutile is more efficient compared to anatase, however, the reflectivity of anatase is higher than rutile in the UV−vis region.47 Therefore, a mixture of anatase and rutile provides better optical properties for the photoanode. On Figure 8a, the UV−vis absorption spectra of dye-sensitized CdSBR + TiO2(A+R) dye-sensitized CdSNR + TiO2(A+R) + TiO2(A+R) and dye were recorded. It is noticed, as expected, that the absorbance of sensitized CdSBR + TiO2(A+R) is higher than CdSNR + TiO2(A+R) in the 450−500 and 575−675 nm regions due to increasing the surface area of CdSBR + TiO2(A+R) in comparison to CdSNR + TiO2(A+R). Although the absorption peak of TiO2(A+R) Shows up near 540 and 700 nm, it shows that the presence of CdS enhances light absorption edge in the visible light regions at around 400−540 and 550−700 nm by harvesting more photons.48 Figure 8a shows a typical XRD patterns of TiO2(A+R) before and after annealing. The largest intensity of XRD peaks of TiO2(A+R) after annealing as compared to product before annealing indicates a better crystallization due to the removal of DI water from the nanoparticles.

The current density versus voltage (J−V curves) of the DSSCs are shown at room temperature under illumination and dark conditions in Figure 9a,b respectively. The device parameters for each DSSC, i.e., the photoelectric conversion efficiency (PCE), short circuit current (Jsc), open-circuit voltage (Voc), fill factor (FF), shunt resistance (Rsh), and series resistance (Rs) are enlisted in Table 1.

Among all of the DSSCs devices, CdSnR−TiO2(A+R)/PANI−MWCNT shows a significantly higher PCE (1.71%) than CdSBR−TiO2(A+R)/PANI−MWCNT (0.98%) and TiO2(A+R)/PANI−MWCNT (0.83%). The incorporation of CdSnR into TiO2(A+R) as photoanode improves the charge transport and reduces the recombination of charges due to the larger surface area, which results in a continuous path for electrons and more dye-binding sites. Moreover, the branched structure of CdS (CdSBR) absorbs more light than the straight structure of CdS (CdSNR), which consequently exhibits strong higher power conversion efficiency.49 Thus, it is reasonable to say that the PCE is enhanced by the morphology of CdSBR due to larger crystallite size for CdSBR 37 ± 1.5 nm in comparison to CdSNR 42.97 ± 4.2 nm, meaning less grain boundaries, which consequently increase the electrical conductivity, and therefore the efficiency of solar cell is improved.

The performance of the displayed CdSBR in DSSCs could be compared with previous studies based on CdS prepared by CBD. Table 2 shows highest power conversion efficiency for the presented work, which in terms refers that the current design of CdS synthesized via hydrothermal process is very effective for enhancing the performance of DSSCs.

| technique to prepare CdS | PCE (%) | refs |
|-------------------------|---------|-----|
| CBD                     | 1.13    | 30  |
| CBD                     | 1.04    | 50  |
| CBD                     | 1.25    | 31  |
| hydrothermal process    | 0.90    | 9   |
| hydrothermal process    | 2.44    | previous work 34 |
| hydrothermal process    | 1.71    | this work |

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crystallite size, better junctions, and uniform morphology. To design DSSCs devices, three cells were fabricated with one hybrid counter electrode PANI–MWCNTs, and the most efficient device was CdS$_{BR}$–TiO$_2$(A+R)/PANI–MWCNTs due to the high surface area of the hybrid working electrode compared to CdS$_{NR}$–TiO$_2$(A+R) and TiO$_2$(A+R) devices. Therefore, CdS$_{BR}$ morphology is an interesting nanostructure to improve the efficiency of DSSCs.

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