



Fabrication of CdS nanorods and nanoparticles with PANI for (DSSCs) dye-sensitized solar cells



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ABSTRACT

A thin film and core-shell dye-sensitized solar cell containing cadmium sulfide (CdS) are fabricated by using low cost solution processes. Cd nanoparticles (NPs) and nanorods (NRs) are embedded within the dye-sensitized solar cells structures and investigated. The morphology of CdS_{NPs} and CdS_{NRS} were controlled and characterized with multiple techniques including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Raman scattering, and optical absorption. The inclusion of CdS thin film in zinc oxide/polyaniline (ZnO/PANI) hybrid solar cells increases the energy conversion efficiency from 0.125% to 1.35%. The energy conversion efficiency of the core-shell devices was found higher than that of the corresponding planar structures fabricated under similar conditions. By increasing the crystallinity and absorption, the energy conversion efficiency of the CdS_{NRS} device was increased to 2.44%.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are promising for several applications in building integrated photovoltaics (BIPV), such as power-generating windows, and shingles (Jasim, 2011). Graetzel et al. have produced low cost DSSCs with a solar conversion efficiency better than 10% (Bin Ahmad and Murakami, 2011; O'Regan and Gratzel, 1991; Gratzel, 2001; Grätzel, 2004). These DSSCs not only are environmentally responsible, but they are also low-cost and can be tuned to various colors (depending on the sensitizing dye used).

The performance of the DSSCs is largely governed by the properties of its photoanode. The photoanode of the DSSC includes a mesoporous film of a metal oxide that lies on a transparent conductive glass substrate. Metal oxides including titanium dioxide (TiO₂), zinc oxide (ZnO), tin dioxide, niobium pentoxide and indium (III) oxide have been employed as photoanode materials for the DSSCs. Dye molecules, which are attached to the surface of the oxide film, capture incident light. Excitation of these molecules by incoming photons stimulates the injection of electrons into the oxide layer. Two properties of the oxide film that are imperative to the robust harvesting of light and the efficient pro-

duction of energy would be: superior electron transport characteristics, and a surface area at the interface that can be as large as possible (Chang et al., 2012).

N-type CdS semiconductor with band gap equal to 2.42 eV has a large number of possible uses in light-emitting diodes, lasers, solar cells, nonlinear integrated optical, optical waveguides, and electronic devices (Yoon and Suh, 2002; Mohammed et al., 2016). CdS has also been studied for using as a buffer layer in Copper-Indium-Gallium-Selenide (CIGS) solar cells. Because of its possibility for widely use in commercial applications (Yoon and Suh, 2002; Chen et al., 2011), the n-type CdS semiconductors have been methodically investigated, especially in its nanocrystalline form. Nano size CdS are particular interested for researchers who would like to know the shape and size of crystals affect the solar cell efficiency (Ramprasad et al., 2012).

A number of techniques have been used to produce CdS nanocrystalline thin films. Some of them use chemical methods and the others use physical methods. Among these are RF sputtering (Choi et al., 1998; Tomita et al., 1994), sol-gel, solvothermal, and hydrothermal processes (Abdulelah et al., 2016; Qingqing et al., 2006; Li et al., 2009), successive ionic layer adsorption and reaction (SILAR) (Pathan and Lokhande, 2004), spray deposition, pulsed-laser deposition, electrodeposition (Choi et al., 1998), vacuum evaporation (Kim et al., 1994), chemical vapor deposition (CVD) (Choi et al., 1998; Berry et al., 1992), chemical bath deposition (CBD) (Rieke and Bentjen, 1993; Lanning and Armstrong,

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1992), and even screen printing (Park et al., 1992). Among these, the hydrothermal methods represent significant technologies for fabricating nanocrystalline thin film structures at low temperature (Li et al., 2009). This technique produces high purity and homogeneity, narrow particle size distributions, crystal symmetry and many other unique properties (Phuruangrat et al., 2009; Yoshimura and Byrappa, 2008).

Despite its broad applicability, the chemical bath deposition (CBD) method has some known limitations: the yield is low in this technique, the reactants often do not mix completely, and there is little control during the processing. The limitations often produce ineffective homogeneous colloidal layers of CdS (Choi et al., 1998). Thus, CBD although ideally suited for thin-film applications, is not suitable for applications requiring thicker films. The thickness of cadmium sulfide films, if made by using CBD method, reaches the saturation point when the thickness ranges from (0.05–0.2) μm . For depositions requiring longer reaction times, the thicker films tend to form dual layers. The inner layer is quite adherent, but the outer layer is less adhesive, even though there is no visible difference (Hossain and Takahashi, 2012; Oladeji and Chow, 1997). However, working within these known limitations can yield very successful results.

In this paper, we report the results of CdS_{NRS} prepared by hydrothermal technique and the results of CdS_{NPs} prepared by a chemical bath deposition method. The properties of these CdS thin films were studied and presented. The CdS_{NRS} and CdS_{NPs} thin films were then fabricated into DSSCs. The properties of these two types of DSSCs were studied and compared. The results are presented, and conclusion based on our findings is given at the end. By using similar conditions, the data found that the energy conversion efficiency of the devices is higher than reported in reference (Abdulah et al., 2016) that prepared CdS_{NPs} by chemical bath deposition.

2. Experiments

2.1. Reagents and materials

Cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, thioacetamide CH_3CSNH_2 $\geq 99.4\%$, potassium iodide KI, acetone $\text{C}_3\text{H}_6\text{O}$ and ethanol $\text{C}_2\text{H}_6\text{O}$ were purchased from Fisher Scientific; thiourea $\geq 99.0\%$, L-Glutathione reduced $\geq 98.0\%$, Di-tetrabutylammonium cis-bis (isothiocyanato)bis (2,2-bipyridyl-4,4-dicarboxylato)ruthenium(II) (N-719 dye) $\text{C}_{58}\text{H}_{86}\text{N}_8\text{O}_8\text{RuS}_2$ 95%, and ethylene glycol (CH_2OH)₂ were purchased from Sigma Aldrich; cadmium acetate $\text{Cd}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ $\geq 98.0\%$, zinc oxide ZnO $\geq 99.9\%$, aniline $\text{C}_6\text{H}_7\text{N}$ $\geq 99\%$, and sulfuric acid H_2SO_4 were purchased from Alfa Easar; iodine I_2 was from mallinckodi chemical work. All the chemicals were used as received without further purification. Trimethylaluminum (TMA) $\text{Al}(\text{CH}_3)_3$, diethylzinc (DEZ), $\text{Zn}(\text{C}_2\text{H}_5)_2$, and water (H_2O) were employed as the basic precursors to grow aluminum doped zinc oxide AZO, they were from Stream chemicals. Teflon-lined stainless steel autoclave (acid digestion vessels) from Parr instruments company. Fluorine doped tin oxide (FTO) coated glass substrate, with a resistivity of 12–17 Ωcm was used as an electrode, and was purchased from Nanocs.

2.2. Preparation of (AZO)

FTO glass slides were ultrasonically cleaned by acetone, ethanol and deionized water for 5 min each, and finally dried by nitrogen gas. AZO was deposited by utilizing atomic layer deposition (ALD) technique using DEZ, TMA and distilled water vapor as precursors on FTO glass as an electrode. The selected substrates were placed in a Cambridge Nanotech Fiji F200 ALD reactor. AZO was

deposited at 200 °C process temperature. High purity argon was used as the process gas and the background pressure in the chamber during deposition was 750 mTorr. A DEZ and H_2O pulses briefly increased the pressure by 30–40 mTorr. Note that this particular ALD reactor is designed for traditional thermal as well as plasma-enhanced processes. The process was repeated for 18 cycles leading to a highest conducting AZO film of thickness 80 nm.

2.3. Preparation of CdS precursors

Two precursors of CdS were prepared by chemical bath deposition and hydrothermal techniques. The process is an ammonia free solution with pH (6–7), which refers to slightly acidic or neutral, this procedure was used here to prevent etching of AZO (Armstrong, 2014). A precursor solution of CdS was prepared by chemical bath ammonia free deposition through dissolving the appropriate amounts of cadmium acetate and thioacetamide in deionized water which produces CdS_{NPs} through reactions between Cd^{2+} and S^{2-} ions in a solution, the concentration of cadmium acetate and thioacetamide was $\sim 0.0001\text{ M}$ and 0.0002 M respectively (Choi et al., 1998). The precursor deposited by ammonia free chemical bath on an AZO/FTO glass, the CdS_{NPs} were deposited at 80 °C for 1.5 h and the solution was stirred by using a magnetic stirrer at 100 rpm to get the desire thickness.

The straight CdS_{NRS} were synthesized on an AZO/FTO glass by hydrothermal approach (Chen et al., 2011), AZO/FTO placed in 20 ml Teflon lined stainless steel autoclave, which had been filled with an aqueous solution from cadmium nitrate, thiourea and glutathione with a molar ratio of 1:1:0.6, the autoclave was placed in the oven at 200 °C for 3.5 h. Then the autoclave was cooled to room temperature. The CdS_{NRS}-AZO/FTO glass was taken out and rinsed with DI water and dried by argon gas (Li et al., 2009). It should be mentioned that CdS is toxic, and must be follow the laboratory safety instructions when handle it (Abdulah et al., 2016).

2.4. Preparation of ZnO, PANI and dye N719

Different nanomaterials like ZnO and TiO_2 are employed as n-type with CdS to fabricate DSSCs, ZnO has an energy band like that of TiO_2 . The flexibility in thin film synthesis and morphology of ZnO increased with increasing its electron mobility than the TiO_2 (Chang et al., 2012; Quintana et al., 2007; Gao et al., 2007). 6 g of ZnO nanopowders and 10 ml of DI water were mixed and ultrasonically dispersed for 10 min to get a needed solution, then the mixture was deposited by using airbrush technique onto the FTO/AZO/CdS_{NPs} and FTO/AZO/CdS_{NRS} devices to produce a dense ZnO layer which was subsequently annealed in an oven at 450 °C for 30 min. The resultant ZnO layer was then immersed in a dye bath prepared by dissolving 0.01 g of the dye (N719) in 10 ml ethanol. The samples were left in a dye bath for about 18 h to get an FTO/AZO/CdS_{NRS}-ZnO/N719 electrode. PANI were prepared by electrochemical method the electrochemical oxidative polymerization (Gašparac and Martin, 2001). The solution was prepared by dissolving 2 M aniline monomer in a 1 M of sulfuric acid, at 2 V constant voltage, the deposition occurred at room temperature on another FTO to form a surface area of 1.5 cm^2 PANI/FTO and using platinum as a counter electrode for the solar cell device.

2.5. Solar cell fabrication

Few drops of the electrolyte were adding on top of the FTO/AZO/CdS_{NRS}-ZnO/N719 and PANI/FTO device, the solvent was prepared by using 0.127 g from I_2 , and 0.83 g of KI. The electrodes were dissolved in 10 ml glycol. After 5 s the electrolyte will dry out and electrodes will be sandwiched together to form a photovoltaic (DSSCs) device by using binder clips. The schematic diagram of

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