Research Article

Photovoltaic Performance of ZnO Nanorod and ZnO : CdO Nanocomposite Layers in Dye-Sensitized Solar Cells (DSSCs)

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Triphenylene diamine sensitizer comprising donor, electron conducting, and anchoring group is synthesized for a potential application in dye-sensitized solar cells. Absorption spectrum, electrochemical and photovoltaic properties of triphenylene diamine have been investigated. Two different electrodes are used for dye-sensitized solar cells. The performances of ZnO nanorod electrodes are compared to ZnO : CdO nanocomposite electrode. Also, the theoretical calculations for HOMO and LUMO orbitals are used to estimate the photovoltaic properties of organic sensitizer in the design stage. ZnO : CdO nanocomposite electrode-based dye-sensitized solar cell sensitized with organic sensitizer exhibits higher efficiencies than ZnO nanorod electrode. For a typical device, a solar energy conversion efficiency (η) of 0.80 based on ZnO : CdO nanocomposite is achieved under simulated AM 1.5 solar irradiation (100 mW cm^{-2}) with a short circuit photocurrent density (J_{sc}) of 3.10 mA/cm^2 , an open-circuit voltage (V_{oc}) of 480 mV, and a fill factor (FF) of 0.57. These results suggest that the ZnO : CdO nanocomposite system is a good selection and a promising candidate for electrode system in dye-sensitized solar cells.

1. Introduction

The modern society has intensively consumed energy resources, a large portion of which is accounted for by fossil fuel, such as petroleum, coal and natural gas. Development of alternative, renewable sources of energy is essential to reduce emission of carbon dioxide and other harmful substances when fossil fuel is burnt, as well as attain stable energy provision. Solar energy is one of several promising clean energy sources that could contribute to a stable energy supply and mitigate global environmental issues. In particular, the direct creation of electric energy is made possible through a solar cell. Much attention is now being focused on solar cells as potential energy-conversion systems. Dye sensitized nanocrystalline solar cells (DSSC) are of great interest as a cost-effective alternative to conventional silicon photovoltaics. The photoanode in DSSC is a mesoporous metal oxide film, sensitized by a monolayer of dye molecules. Upon visible light absorption, excited sensitizer molecules inject an electron into the conduction band of metal oxide. These carriers are transported and collected by a contact electrode [1, 2]. Among the other metal oxides such as SnO_2 , In_2O_3 ,

and WO_3 , ZnO nanostructures are promising materials for photovoltaic materials in solar cell. ZnO has large exciton binding energy (60 MeV) with the 3.4 eV energy band gap. Physical properties are similar to TiO_2 but its electron mobility is higher by 2-3 orders of magnitude [3–5].

A sensitizer, as the light-harvesting component in a dye-sensitized solar cell (DSSC), is of paramount importance to photovoltaic performance. The sensitizer is attached to the surface of a mesoporous wide band-gap semiconductor serving as electron transporter [6–8]. The interest in metal-free, organic dyes with high extinction coefficients has grown in recent years for organic solar cell research. In order to investigate organic dyes and, in the longer run, prepare an efficient solar cell dye, a number of different organic dyes are designed and synthesized [9–13]. Dye-sensitized solar cells (DSSCs) appear to be highly promising alternatives to more expensive solar cell technologies. Considering the current maximal level of overall conversion efficiency (η) under simulated sunlight for DSSCs (12%), improvements in efficiency and durability would certainly facilitate widespread utilization of this technology. It is clear that there are a number of factors determining the efficiency of solar cells,

but the structural and physical properties of the sensitizer are clearly important ones [14, 15].

In this study, triphenylene diamine-based organic sensitizer is synthesized for dye sensitized solar cell application. Theoretical calculations for HOMO and LUMO orbitals of triphenyl diamine sensitizer are used to estimate the photovoltaic properties of organic sensitizer. Electrochemical properties are also investigated. Dye sensitized solar cell is operated with 4 μm thicknesses of ZnO nanorod electrode. To obtain the better efficiency in dye sensitized solar cell, ZnO : CdO nanocomposite structure is prepared. Efficiencies of ZnO : CdO nanocomposite-based dye sensitized solar cell are compared to ZnO nanorod-based dye sensitized solar cell. Results show that ZnO : CdO nanocomposite electrodes have higher efficiencies than ZnO nanorods. And ZnO : CdO nanocomposite electrodes are promising materials for dye sensitized solar cells.

2. Experimental

2.1. Materials. Tetraphenylbenzidine, triphenyl phosphine, POCl_3 , cyanoacetic acid, and piperidine are purchased from Aldrich. Solvents are of spectroscopic grade and are used without any further purification.

2.2. Synthesis and Characterization of Triphenylene Diamines. The synthesis of TPD dye is conducted in two steps with moderate yields. Tetraphenylbenzidine is supplied from Aldrich company. First reaction is the Vilsmeier reaction, to form aldehyde product.

In the second reaction, the aldehyde is condensed with cyanoacetic acid by means of the Knoevenagel reaction in the presence of piperidine to form the target compound of TPD.

2.3. Synthesis and Characterization of TPD Dye

2.3.1. Synthesis Method of TPD. Aldehyde product and acrylic acid product are synthesized in the following procedure.

(1) *Step (synthesis of 4-[[4'-(diphenylamino)biphenyl-4-yl](phenyl)amino]benzaldehyde).* POCl_3 (1.36 mmol, 0.2 g) is stirred in a two-necked flask at 0°C for 1 hour in dried DMF under argon atmosphere. After additional stirring for 1 h at room temperature, this solution is added to a stirred solution of 5 g (0.0097 mol) of N,N'-Bis(diphenyl)benzidine in 20 mL of 1,2-dichloroethane. This reaction mixture is stirred for another hour at 60°C and allowed to cool to room temperature. Hereafter, the mixture is poured into a solution of 10 g sodium acetate in 100 mL water, and this mixture is extracted three times with dichloromethane. The combined organic layers are washed twice with water and dried over magnesium sulfate. After filtration and evaporation of the solvent, a yellow solid is obtained. The desired monoformylated product is isolated from this crude product by column chromatography using silica gel and solvent as the eluent, 4-[[4'-(diphenylamino)biphenyl-4-yl](phenyl)amino]benzaldehyde, yellow crystals; molecular structure is analysed with ^1H NMR spectrum. ^1H NMR

(CDCl_3): (ppm), 9.83 (1H, s, -CHO), 7.71 (2H, d, Ar-H), 7.55 (2H, t, Ar-H), 7.48 (2H, t, Ar-H), 7.21 (21H, m, Ar-H).

(2) *Step (Synthesis of (2Z)-2-(cyanomethyl)-3-{4-[[4'-(diphenylamino)biphenyl-4-yl](phenyl)amino]phenyl}acrylic acid, TPD).* To a solution of 4-[[4'-(diphenylamino)biphenyl-4-yl](phenyl)amino]benzaldehyde (0.16 mmol, 72.3 mg) and cyanoacetic acid (0.32 mmol, 27.95 mg) in a mixture of tetrahydrofuran : methanol (1 : 1) is added catalytic amount of piperidine, after which the solution is stirred for 2 h at 40°C . The solvent mixture is evaporated under reduced pressure and the resulting material is extracted with chloroform and 0.1 M HCl solution, washed with water, and dried over magnesium sulfate. The product is purified by column chromatography using silicagel and chloroform:methanol as the eluent. Molecular structure is characterized with IR and ^1H NMR spectrum, mass and elemental analysis. IR (KBr): cm^{-1} , 3551, 3412, 3031, 2214, 1583, 1487, 1392, 1323, 1270, 1178, 1074, 1028, 1003, 959, 818, 788, 749, 723, 693, 667. ^1H NMR ($\text{DMSO}-d_6$): (ppm), 7.88 (1H, s, -CH=), 7.79 (2H, d, Ar-H), 7.60 (4H, q, Ar-H), 7.36 (6H, m, Ar-H), 7.15 (5H, m, Ar-H), 7.10 (10H, m, Ar-H). MS/(ESI/100 eV): m/z : 583. $\text{C}_{40}\text{H}_{29}\text{N}_3\text{O}_2$ (583): Calcd: C 82.31%, H 5.01%, N 7.20%, O 5.48%; found: C 82.33%, H 5.00%, N 7.23%, O 5.48%.

Figure 1 shows the molecular structure of organic sensitizer. Absorption spectrum of TPD is taken in chlorobenzene solvent (Figure 2). It shows that organic sensitizer absorbs in the visible region between 380–550 nm.

2.4. Synthesis of ZnO Nanorods and CdO Nanostructures. ZnO nanorods and CdO nanostructures are synthesized from zinc salt and Cadmium salt in water solution using hydrothermal reaction. Microwave method is used for the synthesis of ZnO and CdO nanostructures. In a typical experiment, zinc acetate is dissolved in 25 mL deionized water in a beaker. The concentration of zinc acetate dehydrate is 0.55 M. The solution is stirred with magnetic bar at 100°C for 1 hour until a transparent mixture is obtained. Subsequently, solution is loaded into a 100 mL Teflon-lined container. Then solution is irradiated by microwave energy in the microwave oven at 200°C for 60 minutes (CEM MARS-5, frequency 2.45 GHz, maximum power 700 W, multimode oven). Then the solution is poured into a beaker and heated at 200°C until water is evaporated. After wet precipitate is dried in an oven at 90°C for 12 h. Finally, white powder is calcined in a furnace at 200°C for 36 hours. For CdO synthesis, we followed the same experimental method using cadmium acetate dehydrate. White powder is calcined at 450°C for 36 hours. Brown CdO nanoparticles are obtained. To obtain ZnO : CdO nanocomposite, ZnO is mixed with 5% CdO nanostructures.

3. Results and Discussion

3.1. AFM Image of Thin Film of Organic Sensitizer. Morphology of organic material is another important factor for DSSCs. The surface morphology of thin film of triphenylene diamine is prepared in chlorobenzene solvent on FTO glass by using spin coater in 1500 rpm. Atomic force microscopy (AFM)

(Z)-2-Cyano-3-4-[4-(4-diphenylaminophenyl)(phenyl)anilino]phenyl-2-propenoic Acid, TPD

FIGURE 1: Molecular Structure of TPD Dye.

FIGURE 2: Absorption Spectrum of Organic Sensitizer in Chlorobenzene Solvent.

FIGURE 3: Atomic Force Microscopy of Organic Sensitizer on FTO Glass.

image is taken in noncontact mode (Figure 3). These measurements are performed under ambient conditions using a commercial scanning probe microscope. The AFM topographic image obtained is processed using the XEI program. Atomic force microscopy image of TPD which has 16.84 nm rms value is shown in Figure 3 on FTO glass.

FIGURE 4: Ground State Optimization of Dye.

3.2. Theoretical Calculations of HOMO and LUMO Frontier Orbital of Organic Sensitizer. All ground-state geometry optimization and HOMO-LUMO orbital calculations are performed with the Gaussian 03 program package. Figure 4 shows the ground state optimization of organic dye. The HOMO is primarily comprised of π framework of the triphenylene diamine, with significant contributions from π electrons of the diphenylamino substituents (Figure 5(a)) whereas LUMO is very clearly confined to the π system of anchoring group (Figure 5(b)).

3.3. SEM and XRD Analysis of ZnO and ZnO: CdO Nanoelectrodes. The crystal structures of the ZnO nanorods are investigated using XRD. The XRD pattern reveals that with the use of calcination method, ZnO nanorods are formed. The diffraction peaks positioned at 2θ values of 31.8, 34.5, 36.3, 47.6, 56.6, 62.9, 66.3, 68.0, 69.2, 72.5, and 76.9° can be indexed to the hexagonal wurtzite phase of zinc oxide. The Nano-CdO materials are characterized using X-ray diffraction analysis (XRD). The XRD pattern shows the formation of nano-CdO materials. The diffraction peaks positioned at 2θ values of 32.9, 38.2, 55.2, 65.8, 69.2, 81.9° can be indexed to the phase of Cadmium oxide. Figure 6 shows the SEM images of ZnO nanorod (a) and ZnO: CdO nanocomposite (b).

3.4. Electrochemistry of Triphenylene Diamine Consisting of Anchoring Groups. E_{HOMO} and E_{LUMO} values of triphenylenediamine comprising anchoring groups are calculated by

FIGURE 5: HOMO and LUMO Frontier Orbitals of Organic Sensitizer, HOMO Level (a), LUMO Level (b).

FIGURE 6: SEM image of ZnO nanorod (a) and ZnO : CdO nanocomposite (b).

using cyclic voltammograms. Solutions of TPD dye are prepared in dichloromethane (10^{-3} M). A three electrode cell set-up employed for the measurements consisted of glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl reference electrode, all placed in a glass vessel. Tetrabutylammonium hexafluorophosphate (TBAPF₆), 0.1 M, is used as supporting electrolyte. Ferrocene is used as internal reference electrode. Table 1 summarizes the voltammetric behavior of 10^{-3} M solution of TPD. E_{HOMO} and E_{LUMO} levels are calculated from the onset potentials of oxidation and reduction and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc⁺) to be 4.8 eV below the vacuum level. Results shows that TPD sensitizer can inject electrons to conduction band of metaloxide semiconductor.

3.5. Photovoltaic Device Fabrication and Characterization of DSSCs. The construction of the dye sensitized solar cell device requires first cleaning of the fluorine doped tin oxide (FTO) coated glass substrates in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol. TPD has been used to manufacture solar cell devices to explore current-voltage characteristics using 4 μm thickness of ZnO nanorod electrode and 4 μm ZnO : CdO nanocomposite electrode (ZnO: 5% CdO) for comparison to electrode efficiencies. Electrodes are immersed into the TPD solution (0.5 mM in a mixture of acetonitrile: tert-butanol; chlorobenzene (volume ratio: 1:1:3) containing and kept

TABLE 1: Redox potentials of TPD derivatives.

	$E_{\text{oxidation}}^a$ (Volt)	$E_{\text{reduction}}^b$ (Volt)	$E_{\text{ferrocene}}^c$	E_{HOMO}^d	E_{LUMO}^e	$E_{\text{Band Gap}}^f$
[TPD]	0.85	-1.08	0.39	5.26	3.33	1.93

^aFirst oxidation potentials of TPD.

^bReduction potentials of TPD.

^cPotentials of ferrocene, internal reference electrode.

^dHOMO energy level of TPD.

^eLUMO energy level of TPD.

^fEnergy Band Gap of TPD.

at room temperature overnight. TPD adsorbed ZnO and ZnO : CdO coated glasses are washed with pure chlorobenzene. The stained electrode and Pt-counter electrode are assembled into a sealed sandwich-type cell by heating with a hot-melt ionomer film (Surlyn 1702, Du-Pont) as a spacer between the electrodes. Platinized FTO glasses are used as counter electrode. Platinization of counter electrodes is done by coating of FTO glasses with 1% solution of hydrogen hexachloroplatinate (Aldrich) in 2-propanol and annealing at 400°C for 30 min. Cells are prepared in sandwich geometry. Surlyn 1702 (DuPont) frame is used as a spacer and a thermoplastic sealant between the two electrodes. Cells prepared in this way are then sealed by heating at 100°C. A drop of electrolyte solution (electrolyte of 0.6 M N-methyl-N-butyl-imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I₂ + 0.5 M

FIGURE 7: Schematic drawing of dye sensitized solar cells.

4-*tert*-butylpyridine (TBP) in acetonitrile) is placed on the drilled hole in the counter electrode of the assembled cell and is driven into the cell via vacuum backfilling. Finally, the hole is sealed using additional Bynel and a cover glass (0.1 mm thickness). Active areas of the cells are adjusted to 1 cm². *I*-*V* data collection is made by using Keithley 2400 Sourcemeter and LabView data acquisition software. *I*-*V* characteristics of dye sensitized solar cell in dark and under illumination are shown in Figure 6.

The entire energy conversion efficiency, η , is calculated by means of the following equations:

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{light}}, \quad (1)$$

here, V_{oc} is open circuit voltage (V), I_{sc} is short circuit current (mA/cm²), and FF is fill factor:

$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}, \quad (2)$$

where, V_{max} and I_{max} are voltage and current at the point of maximum power output of cell.

Figure 7 shows the schematic illustration of dye sensitized solar cell.

3.6. Performance of Dye Sensitized Solar Cells. The TPD sensitizer has been used to manufacture solar cell devices to explore current-voltage characteristics by using 4 μ m ZnO electrode and 4 μ m ZnO : CdO layers. Under standard global AM 1.5 solar conditions, the organic sensitizer is tested for other electrode using 4 μ m ZnO nanorod and 4 μ m ZnO : CdO nanocomposite electrode for better comparison to electrode efficiency. Dye sensitized solar cell using 4 μ m ZnO nanorod electrode exhibits a short-circuit photocurrent

TABLE 2: Photovoltaic performance of ZnO and ZnO : CdO-based dye sensitized solar cells.

	J_{sc} (mAcm ⁻²)	V_{oc} (mV)	FF	η (%)
ZnO	1.61	600	0.60	0.58
ZnO : CdO	3.10	480	0.57	0.80
Z907	11.54	772	0.66	5.72

FIGURE 8: *J*-*V* curve of ZnO and ZnO : CdO-based DSSCs.

density (J_{sc}) of 1.61 mA/cm², an open-circuit voltage (V_{oc}) of 600 mV, and a fill factor (FF) of 0.60, corresponding to an overall conversion efficiency, η of 0.58%. Normally, ZnO has lower efficiency than TiO₂ electrode because of ZnO crystal defects. Ruthenium Z907 gives higher efficiency in TiO₂ with overall conversion efficiency of 5.72 and short circuit photocurrent density of 11.54 mA/cm² in our laboratory condition. For this reason, *n*-type ZnO is doped with *n*-type CdO nanomaterial to improve the crystal quality of ZnO nanorods. 5% CdO nanostructures are mixed with ZnO nanorods to improve the crystal quality of ZnO nanorods. 4 μ m ZnO : CdO nanocomposite electrode is used for improving the dye sensitized solar cell efficiency. We have tested several ratios of ZnO : CdO composite, %5 CdO ratio is the optimum ratio for our experiments. ZnO : CdO-based dye sensitized solar cell using TPD sensitizer gives a short-circuit photocurrent density (J_{sc}) of 3.10 mA/cm², an open-circuit voltage (V_{oc}) of 480 mV, and a fill factor (FF) of 0.57, corresponding to an overall conversion efficiency η of 0.80%. ZnO nanorod electrode shows lower efficiency than ZnO : CdO electrode. Figure 8 shows the *J*-*V* curve of all dye sensitized solar cells. And all photovoltaic characterization results are shown in Table 2. Results show that ZnO : CdO nanocomposite is a good selection and improves the solar cell efficiency. According to SEM images in Figure 6, ZnO morphology is completely changed after doping with 5% CdO. Crystal morphology effects the dye sensitized solar cell efficiency.

In line with these statements, the higher efficiency is reported under standard conditions obtained for TPD sensitizer using $4\ \mu\text{m}$ ZnO: CdO layers. ZnO: CdO nanocomposite-based solar cells shows remarkably good efficiencies according to ZnO nanorod for the application of DSSCs.

4. Conclusion

In this paper, we have successfully fabricated dye sensitized solar cells using ZnO nanorod electrode and ZnO: CdO nanocomposite electrode. We report the good efficiency obtained with $4\ \mu\text{m}$ ZnO: CdO layers under standard conditions for TPD dye that performs a short-circuit photocurrent density (J_{sc}) of $3.10\ \text{mA}/\text{cm}^2$, an open-circuit voltage (V_{oc}) of 480 mV, and a fill factor (FF) of 0.57, corresponding to an overall conversion efficiency η of 0.80%. ZnO nanorod-based DSSC gives a short-circuit photocurrent density (J_{sc}) of $1.61\ \text{mA}/\text{cm}^2$, an open-circuit voltage (V_{oc}) of 600, and a fill factor (FF) of 0.60, corresponding to an overall conversion efficiency η of 0.58%. As a conclusion, ZnO: CdO electrode exhibits higher efficiencies than ZnO nanorod electrode.

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