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Optical, spectral and photovoltaic characterization of natural dyes extracted from leaves of *Peltophorum pterocarpum* and *Acalypha amentacea* used as sensitizers for ZnO based dye sensitized solar cells

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ABSTRACT

The ZnO nanorods were synthesized using hydrothermal method. The morphologies, crystalline nature and optical properties of the synthesized ZnO nanorods were characterized by X-ray diffractometer, High-resolution scanning electron microscopy [HRSEM], and UV–Vis absorption spectroscopic studies. A thin layer of ZnO nanorods were spread on transparent conducting FTO coated glass plate using Doctor Blade method. Natural dyes extracted from *Peltophorum pterocarpum* and *Acalypha amentacea* leaves with solvents such as water and ethanol were used as sensitizers to fabricate dye sensitized solar cells (DSSCs). The extracted dyes were characterized by Fourier transform infrared (FTIR) and UV–Visible absorption spectroscopy. The FTIR confirms the presence of anthocyanin, carotene and chlorophyll molecules in the dye extracts. The influence on the different parameters such as open circuit voltage (V_{OC}) short circuit current (J_{SC}), fill factor (FF), and power conversion efficiency (η) of the dye sensitized solar cells (DSSCs) were analyzed. The ZnO nanorods provide high specific surface area for dye adsorption and the pathway is efficient for electron transportation.

1. Introduction

The growing demand for renewable energy sources, dye sensitized solar cells (DSSCs) have been intensively investigated as alternative candidate for the next generation solar cells due to their relatively high conversion efficiency and low production cost when compared with silicon solar cells [1,2]. A dye-sensitized solar cell (DSSC) is a device that converts light into electrical energy using dye molecules based on the sensitization of the semiconductor electrode material. TiO_2 and ZnO semiconductors have limited absorption capacity in the visible light region, dye sensitizers have been employed to improve the amount of excited electrons generated upon light absorption. Synthetic ruthenium based complex dyes, such as N719 and N3, are the most common dyes used in DSSCs. Although both dyes have a good photoelectric conversion efficiency, their long term use in DSSCs is not sustainable because of the limited sources of ruthenium, and high cost associated with the production of ruthenium complex dyes [3–6]. Thereby, directing research to naturally occurring and abundant dyes is a potential substitute.

DSSCs consists of two conducting glass electrode coated with porous nanocrystalline wide band gap semiconductor oxide film, such as ZnO nanoparticles which have the dye adsorbed onto their surface, whereas the counter electrode, is coated with platinum or graphite, there is an electrolyte solution that contains the redox couple that regenerates the dye [7–9]. ZnO nanostructures have attracted much attention due to their potential application as dye sensitized solar cells (DSSCs) for over ten years [10–11]. As a typical *n*-type semiconductor, various ZnO nanostructures were prepared by various methods including electrochemical deposition, chemical vapor deposition, pulsed laser deposition, and hydrothermal processes [12–14]. Among these structures, ZnO nanorods or nanowires synthesized by hydrothermal method were widely used as photoanodes in DSSCs [15]. ZnO nanoparticle DSSCs have shown the second highest efficiency after TiO_2. Additionally, there is a wealth of information regarding the processing and properties of ZnO nanowires or nanorods and a large variety of morphologies that are accessible by either vapor deposition, hydrothermal or solution growth methods [16,17]. ZnO shows higher electronic mobility, making it more desirable as a promising photoanode material for DSSC. In principle, to improve the power conversion efficiency of DSSC, it is very important to obtain the photoanode with high surface area and with low electron recombination rate [18,19]. To date, the investigation of natural dyes has been mainly limited to TiO_2 based DSSCs

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[20,21]. However, examining their performance in ZnO based DSSCs are important towards achieving highly efficient DSSCs.

In this work, we have reported our efforts in the synthesis of ZnO nanorods by hydrothermal method which was employed as photoanode for DSSCs. The morphology, crystalline structure and optical properties of the synthesized ZnO nanorods were characterized. A large specific surface area of ZnO helps in improving the anchorage of dye molecules. The application of natural dyes in ZnO based DSSCs was attempted to improve the device performance. The dyes were extracted from *Peltophorum pterocarpum* and *Acalypha amentacea* leaves with two different solvents such as water and ethanol. The spectral and optical absorption of dye extracts were studied by FTIR and UV–Visible absorption spectroscopy respectively. The J-V characterization was carried out to analyze the power conversion efficiency of the fabricated dye sensitized solar cells.

2. Experimental methods

2.1. Synthesis of ZnO nanoparticles

ZnO nanorods were prepared by hydrothermal method [22]. Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was used as a zinc source. In a typical reaction 3.357 g of $Zn(Ac)_2.2H_2O$ (5.08×10^{-7} mol L^{-1}) was dissolved into 30 ml of distilled deionized water (DDW). 4.0 g NaOH (3.33×10^{-6} mol L^{-1}) was dissolved in 30 ml of distilled deionized water (DDW). The NaOH solution was added drop wise to $Zn(Ac)_2.2H_2O$ solution and the stirring was continued for 30 min and $Zn(OH)_2$ was formed. The mixture was transferred into a Teflon lined autoclave and was heated in an oven at 200 °C for 7 h. Then cooled up to room temperature, the obtained solid product was centrifuged, washed three times with distilled deionized water (DDW) and once with ethanol in order to remove the residues, and dried at 400 °C for 4 h to obtain ZnO nanoparticles.

2.2. Preparation of natural dye

Peltophoroum pterocarpum and *Acalypha amentacea* leaves were collected and the samples were washed with running tap water to get rid of the dust particles. After washing, the samples were shade dried for four weeks at room temperature. The samples were then crushed with mortar and pestle to coarse powder. Maceration is a technique used in extracting dye from plant that involves leaving the pulverized plant to soak in a suitable solvent in a closed container. Here we used distilled water and ethanol as solvents. About 25 g of coarse powdered leaves of *P. pterocarpum* were dissolved in 100 ml of solvents such as water and ethanol separately and kept for 48 h with occasional stirring. After 48 h the extracts were filtered by decantation followed by filtration using whatman filter paper to obtain clear solutions. The same procedure was repeated to extract dye from *A. amentacea* leaves (Fig. 1). To prevent the dye from light exposure, the extracted dyes were covered with aluminum foil.

2.3. Preparation of electrolyte

The I^-/I_3^- is a common electrolyte in organic solvents, such as acetonitrile, which was used in this study. Lithium ion was added to facilitate electron transport. This electrolyte is suitable for ion diffusion and infiltrates well into the ZnO film, exhibiting the highest efficiency among all DSSCs. The electrolyte solution was prepared by dissolving 0.3 M of Lithium Iodide (LiI) and 0.03 M of Iodine (I_2) in *tert*-butyl alcohol and acetonitrile in 1:1 vol ratio, which can be used as charge transport mediator between photoanode and counter electrode in DSSC.

2.4. Fabrication of DSSC

The FTO glass (Fluorine doped tin oxide) (sheet resistance 7.5 kΩ/cm^2) was used as the current collector. The FTO plate was first cleaned using an ultrasonic bath with acetone, ethanol, and water for about 15 min respectively. FTO glasses were rinsed well with distilled water and air dried which are used as anode and cathode in DSSC. Scotch tape was used as a spacer to control the film thickness and to provide non-coated areas for electrical contact. The prepared ZnO nanorods were made as paste by mixing with polyethylene glycol binder and coated on FTO by doctor blade technique to prepare DSSC photoanode. The prepared ZnO film was air dried at 70 °C for 30 min and the films were annealed at 450 °C for 1 h to eliminate the polymer binder. The coated glasses were soaked in *Peltophorum pterocarpum* and *Acalypha amentacea* dye extracted with water and ethanol for 12 h. After the dye-sensitization process, the photoanode was washed with ethanol to remove the unanchored dye molecules and air dried. A platinum coated FTO glass plate was used as the counter electrode. The dye-covered ZnO electrode and Pt counter electrode were assembled as a sandwich-type cell. The electrolyte solution was injected in between the cells which act as charge transport mediator between photoanode and counter electrode in DSSC.

2.5. DSSC assembly

The ZnO nanoparticles coated on FTO glass was placed facing upward, and the conductive side of the platinum coated counter electrode faced the ZnO film. A DSSC was assembled by introducing liquid electrolyte (0.3 M of Lithium Iodide (LiI) and 0.03 M of Iodine (I_2) in *tert*-butyl alcohol and acetonitrile in 1:1 vol ratio) into the space between the ZnO electrode (photo anode) and the counter electrode (cathode) by capillary action (Fig. 3). The two electrodes were clipped together using two binder clips to prevent the electrolyte from leaking.

2.6. Characterization and measurements

The absorption spectrum of *Peltophorum pterocarpum* and *Acalypha*

Fig. 1. *Peltophorum pterocarpum* tree with leaves and dyes.