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Fe–tannic acid complex dye as photo sensitizer for different morphological ZnO based DSSCs

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ABSTRACT

In this paper we have synthesized different morphological ZnO nanostructures via microwave hydrothermal methods at low temperature within a short time. We described different morphologies of ZnO at different $Zn(NO_3)_2$/KOH mole ratio. The ZnO nanostructures were characterized via X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and UV–vis spectrophotometry. All ZnO structures have hexagonal wurtzite type structures. The FESEM images showed various morphologies of ZnO such as plate, rod and nanoparticles. Dye sensitized solar cells have been assembled by these different morphological structures photo electrode and tannic acid or Fe–tannic acid complex dye as sensitizer. We have achieved at maximum efficiencies of photovoltaic cells prepared with ZnO plate in all dye systems. The conversion efficiencies of dye sensitized solar cells are 0.37% and 1.00% with tannic acid and Fe–tannic acid complex dye, respectively.

1. Introduction

Solar energy is the clean, green and plentiful renewable energy sources [1]. In 1991, O'Reagen and Gratzel developed dye sensitized solar cells (DSSCs) which were interested in many researcher's due to their low cost and environmental friendly applications [2–4]. The DSSCs comprise of a photo anode (metal oxide semiconductor), a dye sensitizer (organometallic or organic dye), an electrolyte (redox couple) and a counter electrode (catalyst) [5]. In DSSC, a photon excitation of the dye sensitized and dye molecule injected an excited electron into conductivity band of photo anode [5,6]. Dye molecules which lost electrons are then oxidized. The injected electron travels through the counter electrode and concurrently extracted to load electrical energy. The injected electron transferred to electrolyte and electron bereft dye to replace the electron [6].

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor having a variety of application in sensors, photodetectors, and DSSCs [7,8]. Depending on the preparation methods for ZnO, different morphological properties can be obtained. Various morphologies of ZnO nanostructures have been used in DSSC, such as nanoparticles, nanoporous films, nanowires, nanosheets, tetrapods, nanorods, and nanospheres [7–13]. The power conversion efficiency of ZnO-based DSSCs are lower than that of TiO_2-based DSSCs. The conversion efficiency of ZnO-based DSSCs was explained by dissolution of ZnO, dye-Zn^{2+} aggregates formation and lower injection efficiency, etc. However, ZnO has higher electron mobility than TiO_2. Consequently, there is a significant enhancement in the electron transport in DSSCs using ZnO with different morphologies in photo anodes [7].

In DSSCs, the dyes play a key role in sunlight absorption and conversion of sunlight to electric energy. The highest efficiency of DSSCs formed by Ru-complex dyes and TiO_2 reached 11–12%. However, Ru based dyes have several disadvantages such as costly produced noble metal contains in their structures including toxic materials and difficulty in synthesis [2]. Thousands of dyes have been synthesized and used in DSSCs until nowadays, and they can be divided into four categories. The first type sensitizers are the metal complexes dyes. The second type sensitizers are porphyrin and phthalocyanine. These dyes have some disadvantages such as poor solubility and difficulty in attachment on semiconductor's surface. The third type sensitizers are organic dyes. They are included in coumarin, indoline, carbazole, tetrahydroquinoline, triarylamine, triphenylamine, and perylene dyes. These dyes have some advantages such as low cost, easy synthesis and less environmental pollution problems due to presence of non-toxic metals in their structures, although they are poor chemical and light stability [14]. The fourth type sensitizers are natural dyes. The natural dyes are promising alternative to organic dyes for DSSC application [15]. Natural dyes include several pigments such as cyanin, carotenoids, tannins, chlophyll, anthocyanins, and betanins [2,5,14]. They are environmental friendly, cheap and have easy preparation methods. However, they have several disadvantages such as lower conversion efficiency and chemical stability.

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Tannins are water-soluble polyphenolic compounds which are important classes of secondary metabolites and have molecular weight ranged to 500–20,000 Da [16]. Since ancient time tannins are able to tan animal skins from leather. Tannins are a type of polyphenols extracted from different parts of trees such as in barks, fruits, leaves and woods [16,17]. Tannins are water-soluble compounds and their modified forms are used as adsorbent for metals from wastewater [16–18]. Tannins are divided in four major groups: gallotannins, ellagitannins, complex, and condensed tannins [16]. Tannic acid is a specific commercial form of gallotannin which are esters of glucose and gallic acid.

Tannic acid has a unique form of polyphenol and used in different subjected area. We have used tannic acid and Fe–tannic acid for DSSCs application because there is not any application of tannic acid as a dye for solar cell in the literature. The Fe tannic acid complex is a stable dye and it can conform to dye sensitized solar cell application. Ever since, O'Reagen and Gratzel [3] invented the first dye sensitized solar cell in 1991 numerous research effort have focused on DSSCs based different natural dye, organic dye etc. due to the environmental friendliness and low cost product. The researchers have effort for improvement the cell efficiency. Many researchers have improved separately different type of dyes, but these dyes are insufficient in providing the expected efficiencies and hence researchers have been looking for a new type dyes and/or alternatives. We thought that the tannic acid and especially Fe–tannic acid complex which has higher efficiencies can become potential alternative natural dye for DSSCs.

In the present work, the photo-sensitizing properties of tannic acid and Fe–tannic acid complex dyes on different morphological ZnO nanostructure based photoanodes have been studied for DSSC application. Fe–tannic acid complex dye was synthesized in using tannic acid and $FeCl_3$. The light absorption characteristics of the dyes were investigated using UV–Vis spectrophotometer. To the best of our knowledge, the tannic acid and Fe–tannic acid complex dyes have never been used as sensitizer in DSSC and the present work provides a comprehensive view on the use of these dyes in the DSSC. The ZnO nanostructures were synthesized by microwave assisted hydrothermal method, and the crystalline structure and morphologies of the prepared ZnO nanostructures were investigated by XRD and SEM, respectively. The photoanode was prepared by coating various ZnO nanostructures layer on FTO coated glass substrate. The photovoltaic parameters of DSSCs fabricated of these natural dyes were measured under simulated solar light and the results were discussed and compared.

2. Experimental section

2.1. Materials

In the current study, the used materials are mentioned as follows: Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich), potassium hydroxide (KOH, Merck), tannic acid (Merck), iron (III) chloride-hexahydrate($FeCl_3 \cdot 6H_2O$, Sigma Aldrich), di-tetrabutylammonium *cis*-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (N719 dye, Sigma Aldrich), fluorinated tin oxide glass (FTO glass, Sigma Aldrich 7 Ω/sq.), ethyl cellulose (Sigma Aldrich), ethanol (Merck), dihydrogen hexachloroplatinate (IV) hexa hydrate ($H_2PtCl_6 \cdot 6H_2O$, Alfa Aesar), 2-propanol (Sigma Aldrich), Lithium iodide (LiI, Merck), Iodine (I_2, Riedel de Haen), 4-*tert* butyl pyridine (Sigma Aldrich).

2.2. Synthesis of ZnO structures

$Zn(NO_3)_2 \cdot 6H_2O$ (4.425 g, 0.015 mol) was dissolved in 60 mL of distilled water, and KOH(0.4 g, 0.007 mol) was added under stirring and then the stirring was continued for 30 min, firstly all reactants were dissolved and then $Zn(OH)_2$ formed. The pH value of the system was fixed at 6–7 of neutral state and the present sample was coded to ZnO-1. $Zn(NO_3)_2 \cdot 6H_2O$ (4.425 g, 0.015 mol) was dissolved in 60 mL of distilled water and KOH (1.3 g, 0.023 mol) was added under stirring and then the stirring was continued for 30 min, firstly all reactants dissolved and then $Zn(OH)_2$ formed. The pH value of the system was fixed at 7–8 of soft alkaline state and the current sample was coded to ZnO-2. $Zn(NO_3)_2 \cdot 6H_2O$ (4.425 g, 0.015 mol) was dissolved in 60 mL of distilled water and KOH (1.85 g, 0.033 mol) was added under stirring and then the stirring was continued for 30 min, firstly all reactants dissolved and then $Zn(OH)_2$ formed. The pH value of the system was fixed at 9–10 of alkaline state and this sample was coded to ZnO-3. Finally mixtures were added to double walled Teflon digestion vessels. All the synthesis were performed in using MARS5 (CEM Corp.) microwave hydrothermal system. The operation temperatures, power and times of the reactions vessels were set at 100 °C, 380 W and 30 min, respectively. After the microwave hydrothermal treatment, the resultant slurry was washed in three times with distilled water, two times ethanol and finally dried overnight in an oven kept at 70 °C.

2.3. Complexation of Fe–tannic acid dye

0.01 M tannic acid of 10 mL and 0.01 M $FeCl_3 \cdot 9H_2O$ 4 mL were added in sample caps and mixed for vortex. The Fe^{3+} solution was added dropwise into tannic acid solution to avoid the formation of Fe–tannic acid precipitate. The complexation occurs rapidly, but if it is added over 4 mL Fe solution, the complex falls down. The 5 mM N719 dye solution was prepared in acetonitrile and chosen as reference dye.

2.4. Solar cell fabrication

The ZnO paste was prepared by the addition of 0.05 g of aqueous ethyl cellulose onto 0.5 g of ZnO materials in a mortar under vigorous grinding with pestle and mixed with 5 mL ethanol. Thus prepared uniform ZnO paste was coated on FTO/glass by a doctor blade technique. The thin films were dried at room temperatures and calcined in air at 450 °C for 1 h. The thin film of photoanode was separately immersed into tannic acid, the Fe–tannic acid complex and N719 dye solutions which were kept in dark for 24 h. Subsequently, the samples were rinsed with ultrapure water and dried at room temperatures. Counter electrode was prepared by spreading a droplet of 5 mM $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol on a FTO substrate and heated at 400 °C for 20 min in air. The used electrolyte was 0.1 M LiI, 0.05 M I_2, 0.5 M 4-*tert* butyl pyridine in acetonitrile.

2.5. Characterization of ZnO structures and solar cell

The powder X-ray diffraction patterns were recorded as PANalytical Empyrean with Cu Kα ($\lambda = 1.54$ Å) at 45 kV voltage and 40 mA current. A scan rate, step size and 2θ range of the samples was 0.1°/s, 0.013° and 10–90°, respectively. Scanning electron micrographs were obtained in FEI Quanta FEG 450 (FE-SEM) and Energy dispersive X-ray spectroscopy (EDS) analysis APOLLO X SSD (EDAX) detector was used as an elemental composition of the studied samples. The UV–vis absorption spectra of tannic acid dyes and UV–vis diffuse reflectance spectra (DRS) of the ZnO samples were recorded on Shimadzu UV-2401PC spectrophotometer. Fourier Transform Infrared spectra (FTIR) of the samples were recorded in the range of 500–4000 cm^{-1} using Attenuated Total Reflectance (ATR) technique. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) on electrochemical workstation (CHI 660C) with a traditional three electrode system. The working, counter and reference electrodes were a glassy carbon, Pt-wire and Ag/AgCl electrodes, respectively. The performances of devices were recorded thought the measurement of (J–V) curves on a CHI 660C electrochemical workstation with a 100 mW/cm^2 light illumination of Oriel LCS-100 AM 1.5 solar simulator. Electrochemical impedance spectroscopy (EIS) measurement was carried out under 100 mW/cm^2 light illumination in the frequency range of 0.1 Hz to 100 kHz at their open circuit potential.