Thin Solid Films 573 (2014) 112–116

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Dye-sensitized solar cells based on porous conjugated polymer counter electrodes

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ARTICLE INFO

Article history:
Received 23 March 2014
Received in revised form 7 November 2014
Accepted 10 November 2014
Available online 15 November 2014

Keywords:
Dye-sensitized solar cells
Electrochemical deposition
Poly-3-methyl-thiophene
Counter electrode
Porous structure
Nanostructure

ABSTRACT

In this paper, we report platinum-free dye-sensitized solar cells that were fabricated using a grown porous poly-3-methyl-thiophene (P3MT) counter electrode. The growing of the porous P3MT was performed by an electrochemical deposition method. This method is easy and affordable unlike the common expensive deposition methods. The morphology of P3MT films was studied by scanning electron microscopy images. It was observed that polymer layers grown with a current density of 2 mA/cm^2 have a clear porous and rough structure as compared to layers grown with a lower current density. To understand the reaction kinetics and the catalytic activities of the counter electrodes with P3MT for $3I^-/I_3^-$ redox reaction, cyclic voltammetry (CV) was performed. Based on the analysis of CV, it was shown that this layer can be used as a counter electrode for dye-sensitized solar cells. The electro deposition conditions during the growth of polymer layers such as current density, the morphology of polymer films and the duration of polymerization have a significant role in the current–voltage characterization of the fabricated solar cells. The performance of the fabricated solar cells was improved by optimization of these parameters. The highest efficiency of 2.76% was obtained by using porous P3MT in the counter electrode.

1. Introduction

Since dye-sensitized solar cells (DSSCs) were introduced by Grätzel [1], they have attracted much attention as cheap and next-generation solar cells. Their maximum conversion efficiency of over 10% [2] suggests that they are a promising type of solar cells. For commercial usages, it is important to develop low-cost materials and to achieve maximum efficiency for the cells. A typical DSSC consists of a transparent conductive substrate, a porous thin-film photoelectrode composed of titanium dioxide (TiO_2) nanoparticles, dyes, an electrolyte, and a counter electrode [3]. The requirements for the counter electrode in a DSSC are effective reduction of oxidized species and good chemical stability in the electrolyte systems used in DSSCs [4]. So far, various materials have been used as counter electrodes of DSSCs [5–7]. Platinum (Pt) is a cathode most commonly used in DSSCs. Recently, several attempts have been made to replace high-cost Pt counter electrodes with conjugated polymers because of their high electrochemical activity. Poly(3,4-ethylenedioxythiophene) (PEDOT) is the most preferred conducting polymer which is considered for use as a counter electrode in DSSCs [8–16]. In many studies, researchers have observed that pure polymer counter electrodes have a lower efficiency than Pt-based DSSCs [8,10,11,16]. In order to enhance the performance of polymer-based DSSCs, other materials such as graphene or nanoparticles are incorporated with polymer to increase the film surface area, conductivity and catalytic activity. For example, Hong et al. [11] incorporated graphene with PEDOT. They obtained an increased efficiency of ~4.5% compared to ~2.3% for pure PEDOT-based cells. Saito et al. [8] used polymerized p-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-TsO) as counter electrodes and obtained a conversion efficiency of ~3.6% under 100 mW/cm^2. Electrochemical polymerization of PEDOT has been carried out in the presence of different anions and polymerization potentials with the reported efficiency of 4.2% [14]. Improving the performance of dye-sensitized solar cells has also been reported. According to Nazeeruddin et al. [15], the improvement was done based on a PEDOT counter electrode and using synthesized highly porous PEDOT films. Other polymers such as polypyrrole (PPy) and polyaniline (PANI) can be used as a counter electrode in dye-sensitized solar cells [17–21]. Recently, Tang et al. [22] synthesized PPy and PANI nanostructures by chemical and electrodeposition techniques. They used double-layered PANI consisting of a nanoparticle and a nanofiber layer as a counter electrode and reported an efficiency of 6.58%. In this study, we use poly-3-methyl-thiophene (P3MT) as a counter electrode. The advantages of P3MT, compared with those of other polymers in the polythiophene derivations, include less susceptibility to oxidation during electrochemical processes [23] and possession of the highest electric conductivity within the polythiophene family [24]. In addition,

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http://dx.doi.org/10.1016/j.tsf.2014.11.034
0040-6090/

P3MT is not soluble in most solvents, which can result in better chemical stability and is compatible with liquid electrolytes in dye-sensitized solar cells [25]. Researchers have investigated the photovoltaic properties and application of P3MT in various structures [26–30]. In this paper, we report an effective way of producing porous P3MT layers that can be used as counter electrodes in DSSCs due to their relatively high catalytic properties. P3MT films can be deposited on conductive substrates using inexpensive low-temperature deposition techniques [31,32], which is one of the advantages of polymer-based counter electrodes. In this study, we demonstrate that, by controlling the growth conditions, porous P3MT structures can be obtained, and that they are potentially appropriate for the construction of dye-sensitized solar cells.

2. Experimental procedure

2.1. TiO_2 paste

TiO_2 nanoparticles with diameters of 20 nm and 400 nm were synthesized by acetic acid-catalyzed hydrolysis of titanium isopropoxide (97%, Aldrich), followed by autoclaving at 220 °C for 12 h. To prepare a screen-printable paste, the water in the autoclaved TiO_2 colloid solution was replaced by ethanol. Ethyl cellulose (Aldrich), lauric acid (98%, Fluka) and terpineol (97%, Fluka) were added to the ethanol solution of the TiO_2 particles, and then ethanol was removed from the solution using a rotary evaporator to obtain viscous pastes.

2.2. Polymerization of 3-methylthiophene

The P3MT electro deposition was carried out in an acetonitrile solution containing 0.1 M 3-methylthiophene (3MT) (98%, Aldrich) and 0.1 M tetrabutylammonium tetrafluoroborate (Merck) at room temperature. Polymerization was carried out by applying different constant current densities (Galvanostatic method). The applied current densities varied between 1.0 and 2.5 mA/cm^2. Fluorine-doped tin oxide glass (FTO) substrates were used as the anode in the electrochemical polymerization process, and a platinum plate of a similar surface area was used as the cathode. The separation between the electrodes was kept around 2 cm. The electrochemically deposited P3MT layer was subsequently reduced in 1 M hydrazine (NH2-NH2) in a tetrahydrofuran solution for 1 min.

2.3. Solar cell fabrication

To prepare the devices, the fluorine-doped tin oxide glass (FTO) substrates were used with a sheet resistance of 8 Ω/cm^2. These substrates were washed with deionized water, acetone, ethanol, and 2-propanol, and finally rinsed with water. A layer of TiO_2 (20 nm, anatase) paste was deposited by a doctor-blading method on the top of the FTO layers. After the film was dried at 120 °C, another layer of TiO_2 (400 nm, anatase) paste was coated as a light-scattering layer, and the deposited film was annealed at 550 °C for 1 h to produce a mesoporous TiO_2 film. When the temperature decreased to 80 °C, the prepared samples were soaked in a 0.3 mM dye solution (a solvent mixture of acetonitrile and tert-butyl alcohol in the volume ratio of 1:1) for 24 h at room temperature. Di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II)(N719) was used as a sensitizer. Various P3MT counter electrodes were prepared for the DSSCs as described in Section 2.2. The DSSC samples were assembled using a dye-adsorbed TiO_2 working electrode and P3MT films as a counter electrode. Then, a liquid electrolyte (0.5 M lithium iodide and 0.05 M iodine in acetonitrile) was injected into the midst of the sandwiched electrodes.

2.4. Solar cell characterization

The current–voltage (J–V) characteristics of DSSCs were measured using a Keithley 2400 digital source meter under AM1.5G (100 mW/cm^2) illumination with a solar light simulator (300 W, Xenon lamp) calibrated by a reference Si solar cell. The current–voltage characteristics of the DSSCs were used to determine the short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (Eff.) of those solar cells. The active area of the DSS cells was 0.25 cm^2.

The catalytic activity of the counter electrode was measured by cyclic voltammetry (CV) in a three-compartment cell using an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, Netherlands). While the prepared polymeric counter electrodes were used as the working electrode, Platinum (Pt) foil and Ag/Ag+ served as the counter electrode and the reference electrode respectively. The scan rate used was 100 mV/s, while the electrolyte was an acetonitrile solution containing 10 mM LiI, 1 mM I_2, and 100 mM tetrabutylammonium tetrafluoroborate. The morphology of the polymer films was also monitored using scanning electron microscope (SEM) images. The images were recorded using the TESCAN SEM system. The operating voltage of the system was 15 kV. The thickness of the polymer films was determined by cross-sectional SEM images. An Ocean Optics spectrometer, model HR 4000, was used for absorption measurements.

3. Results and discussion

3.1. Properties of polymer counter electrodes

The as-grown polymer layers were incorporated with electrolyte ions through an electrochemical approach. By reducing the polymers, the ions could be removed from the surface [25]. The photovoltaic study reported here is based on P3MT reduced chemically with hydrazine. The as-grown P3MT films appeared in a deep blue color, but the reduced P3MT films displayed a purplish red color. The absorption spectrum of the P3MT layer is shown in Fig. 1. In this spectrum, two local maxima are observed; one in the region near 1.5 eV and the other, which is more intense, in the region close to 2.4 eV. According to Sun and Frank [33] and Nicho et al. [34], these peaks correspond to a bipolaron band and the π–π* transition respectively. Using the method described by dos Reis et al. [32], the energy gap was calculated around 2.14 eV. The absorption spectrum and the energy gap were found consistent with the reports of P3MT synthesis by the electrochemical deposition method [32,35–37].

Since the morphology of electrochemically grown P3MT is critical to the final solar cell structure, different growth conditions were applied in order to obtain more favorable porous polymer layers. It was found that,

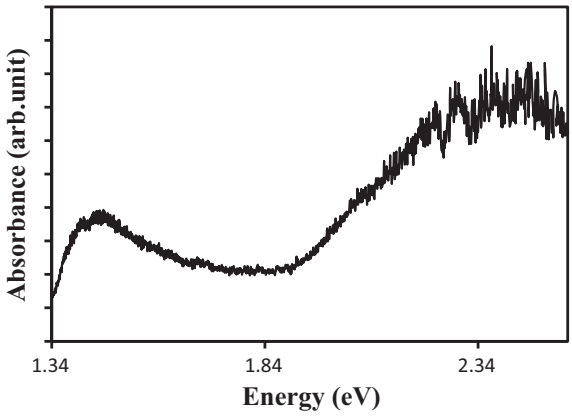

Fig. 1. The absorption spectrum of electrochemically deposited layer of P3MT (chemically reduced by hydrazine).