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Three-dimensional Conducting Polymer Films for Pt-free Counter Electrodes in Quasi-solid-state Dye-sensitized Solar Cells

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ABSTRACT

Three-dimensional (3D) poly(3,4-ethylenedioxythiophene) (PEDOT) films were demonstrated as an efficient Pt-free catalyst in dye-sensitized solar cells (DSSCs). The 3D PEDOT films were fabricated by the deposition of a polystyrene (PS) bead (diameter = 1 μm) monolayer on fluorine-doped tin oxide (FTO) glass, followed by electrochemical polymerization (EP) of ethylenedioxythiophene (EDOT) monomer. For comparison, a flat PEDOT film and Pt counter electrodes were additionally prepared by solution casting polymerization (SCP) and the thermal reduction of a spin-coated H_2PtCl_6 solution, respectively. When these films were implemented as counter electrodes in quasi-solid-state DSSCs with a nanogel electrolyte, the cell efficiency of the 3D PEDOT film prepared by EP for 30 sec reached 5.05%, which is higher than those of the flat PEDOT (4.11%) and Pt counter electrode (4.59%). The improved efficiency of the 3D PEDOT-based cell is attributed to its higher electrocatalytic performance and improved light reflectance, as determined by cyclic voltammogram (CV), incident photon-to-current efficiency (IPCE), and electrochemical impedance spectroscopy (EIS) analyses.

1. Introduction

A tremendous amount of research has been focused on dye-sensitized solar cells (DSSCs) since their introduction in the 1990s by the Gratzel group [1]. DSSCs have been nominated as an attractive next generation photovoltaic device because the costs of the components and fabrication process are much lower than those of conventional silicone photovoltaics. In addition, they demonstrated a high energy conversion efficiency. Yella *et al.* [2] reported the highest efficiency of 12.3% using Co(II/III)tris(bipyridyl)–based redox couples while Chung *et al.* [3] fabricated an all solid-state DSSC with an increased efficiency of 10.2% and an enhanced stability. Basically, a photoanode [4,5], electrolyte [6,7], sensitizing dye [8,9], and counter electrode [10,11] are essential components of a DSSC, all of which play a pivotal role in improving the efficiency and stability.

Among the components, the counter electrode must have a superior catalytic activity considering that the reduction reaction of I_3^- to I^- takes place, which thereby affects the regeneration of the oxidized dye at the photoanode. Typically, the counter electrode is made of platinum (Pt) due to its superior electrocatalytic properties and high electrical conductivity. However, given the fact that Pt is extremely expensive, is in limited supply, and even unstable in corrosive electrolytes, it is imperative to develop a Pt-free counter electrode for practical applications. Therefore, towards this goal, recent research has been focused on the development of a Pt-free counter electrode using carbon [12,13], metal sulfides [14,15], conducting polymers [16,17], transition metal nitrides [18,19], and graphene [20]. In recent years, a number of groups have investigated poly(3,4-ethylenedioxythiophene) (PEDOT) to take advantage of its high conductivity, catalytic activity, transparency, and low cost [21–27]. Due to its fascinating properties, many trials have been conducted to implement PEDOT as a counter electrode of DSSCs.

Three methods are generally used for the synthesis of PEDOT: 1) electrochemical polymerization (EP), 2) solution casting polymerization (SCP), and 3) vapor phase polymerization. Several groups have used the EP method for the fabrication of PEDOT films implemented as a counter electrode for DSSCs. For example, Ahmad *et al.* fabricated a DSSC employing porous PEDOT films derived from an ionic liquid with an efficiency of 7.93%, which is lower than that using a Pt counter electrode [22]. Xiao *et al.* reported a high efficiency DSSC using a PEDOT/multi-wall carbon nanotube (MWCNT) composite counter electrode due to the high electrical conductivity of MWCNTs [23]. The Bisquert group fabricated one-dimensional PEDOT nanotube arrays using ZnO wires as templates, demonstrating a much improved efficiency utilizing its higher effective area than that of a flat PEDOT counter electrode [24]. Various

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PEDOT films have also been fabricated by the SCP method. For example, Lee *et al.* prepared PEDOT nanofibers with diameters of 10-50 nm using sodium dodecyl sulfate as nanoreactors [25]. This highly porous structure showed an enhanced conversion efficiency (9.2%) compared to the cell with bulk PEDOT films (6.8%). Recently, the Park group prepared a nanopatterned PEDOT counter electrode using the spin-coating of PEDOT on pre-patterned substrates, which could increase both the catalytic surface area and light reflection [26]. However, with the spin-coating of the PEDOT solution, it is hard to control the thickness, which inherently limits the increase of the film thickness, thereby requiring an additional process such as layer-by-layer deposition [27].

In this paper, we first report the preparation of three-dimensional (3D) PEDOT films and their use as a counter electrode in DSSCs. The preparation procedure involves deposition of a polystyrene (PS) bead (diameter = 1 μm) monolayer on fluorine-doped tin oxide (FTO) glass, followed by the EP of ethylenedioxythiophene monomer. A flat PEDOT film was also prepared by the SCP method for comparison with the 3D PEDOT films. A conventional Pt counter electrode was prepared by spin-coating of a 7 mM H_2PtCl_6 solution and a subsequent thermal reduction process. Quasi-solid-state DSSCs employing a nanogel electrolyte were fabricated with various counter electrodes. Current density-voltage (J-V) curves, cyclic voltammogram (CV), incident photon-to-current efficiency (IPCE), and electrochemical impedance spectroscopy (EIS) measurements were used to characterize the device performance, catalytic activity, and light reflectance properties.

2. Experimental

2.1. Materials

Fluorine-doped tin oxide (FTO) glasses (TEC8, 8 ohms sq^{-1}) were provided by Pilkington. Monodisperse polystyrene (PS) beads with a diameter of 1 μm dispersed in deionized water (9.7 wt%) were purchased from Bangs Lab. Fumed silica (SiO_2, 7 nm), titanium(IV) chloride ($TiCl_4$, 99%), poly(ethylene glycol dimethyl ether) (PEGDME, M_n = 500 $gmol^{-1}$), iodine (I_2), 1-methyl-3-propyl imidazolium iodide (MPII), chloroplatinic acid hexahydrate (H_2PtCl_6, $6H_2O$), $LiClO_4$ (99.99%), 3,4-ethylenedioxythiophene (EDOT), poly(vinyl pyrrolidone) (PVP, M_n = 10,000 $gmol^{-1}$), iron(III) p-toluenesulfonate hexahydrate (Fe(III) tosylate), sodium dodecyl sulfate, and pyridine were purchased from Sigma-Aldrich and were used as received.

2.2. Preparation of the PEDOT counter electrode via a SCP method

First, 0.252 g of pyridine and 0.02 g of PVP, which is a retardant of the highly active oxidant (Fe(III) tosylate) and a surfactant polymer, respectively, were dissolved in 4 g of butanol [28]. After complete mixing, an EDOT monomer (0.262 g) was added to the above solution. The homogeneous EDOT oligomer solution was spin-coated on FTO glass at 1,500 rpm for 20 sec and kept in an oven at 70°C for 20 min to undergo polymerization. Then, it was washed with methanol to remove the residuals.

2.3. Deposition of a PS monolayer on FTO glass

A PS monolayer was deposited on FTO glass according to a previously reported procedure [29]. First, the PS solution (9.7 wt%) was diluted with an equal volume of absolute ethanol and then, 100 μl of the diluted PS solution was spin-coated on a 2cm × 2 cm of silicon wafer which was cleaned with absolute ethanol. The wafer was then slowly immersed into a glass vessel containing deionized water, where the PS spheres on the silicon wafer were simultaneously transferred to the water surface with an unordered array. A 2% sodium dodecyl sulfate solution was one-dropped onto the water surface, where the surface tension leads to a closed packed array. Then, a monolayer of PS on the water surface was lifted off using FTO glass. To enhance the necking of the PS beads, the PS layer on the FTO glass was kept in an oven at 110 °C for 5 min.

2.4. Preparation of the PEDOT counter electrode via the EP method

The electrochemical system consisted of three electrodes including the PS/FTO glass, Pt wire, and Ag/AgCl as a working electrode, counter electrode, and reference electrode, respectively. 3D PEDOT films with different morphologies were synthesized on a FTO substrate using 0.1 M $LiClO_4$ as the supporting electrolyte, 0.015 M EDOT monomer, and acetonitrile as a solvent at a constant potential of 1.2 V while varying the polymerization time.

2.5. Fabrication of DSSCs

DSSCs with an area of 0.20 cm^2 were fabricated according to previously reported procedures [30–32]. The viscous TiO_2 paste was cast onto the FTO substrate using a doctor blade method and calcined at 450 °C for 30 min. The TiO_2 films were sensitized with a 0.1 mM N719 dye (Solaronix SA) solution in absolute ethanol at room temperature for 24 hours and then rinsed with absolute ethanol and dried with nitrogen gas. A nanogel electrolyte consisting of PEGDME, SiO_2, MPII, and I_2 was prepared as a quasi-solid-state electrolyte and drop-casted onto the photoanode [30]. The thermally reduced Pt counter electrode was fabricated by the spin-coating of a 7 mM H_2PtCl_6 solution in isopropyl alcohol, followed by calcination at 450 °C for 30 min. Finally, the cells were placed in a vacuum oven for a day to ensure complete evaporation of the solvent and then sealed with epoxy resin.

2.6. Characterization

A field emission scanning electron microscope (FE-SEM, SUPRA 55VP, Germany, Carl Zeiss) at an accelerating voltage of 2 kV was used to characterize the morphology of the PEDOT films. The solar cell performance was measured using a solar simulator under a one sun illumination condition (100 $mWcm^{-2}$) (1,000 W xenon lamp, Oriel, 91193) where a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si + KG filter, Certificate No. C-ISE269) was used for calibration. The EIS measurements were carried out at frequencies ranging from 50000 Hz to 0.01 Hz using a CompactStat electrochemistry analyzer (IVIUM Technologies) under AM 1.5 (at 100 $mWcm^{-2}$) light conditions and the data was analyzed using Z-view software (v 2.8, Scribner Associates, Inc). The IPCE measurements were performed using a 150 W Arc Xe lamp source and a specially designed IPCE system (HS-Technologies, PE-IPCE). The CV curves were obtained using a three electrode system composed of a PEDOT/FTO working electrode, Pt wire counter electrode, and an Ag/AgCl reference electrode dipped in an acetonitrile solution containing 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$ in the range of -0.6 to 1 V at a scan rate of 50 mV/s.

3. Results and Discussion

3.1. Morphology and catalytic properties of the 3D PEDOT films

The fabrication procedure of the 3D PEDOT films is shown in Fig. 1. In the first process (P1), a monolayer of PS beads with a diameter of 1 μm was deposited on FTO glass using a previously reported procedure [29]. As shown in Fig. 2**a**, the closely packed PS