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A flexible polypyrrole-coated fabric counter electrode for dye-sensitized solar cells

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HIGHLIGHTS

- Conductive fabric with resistance of 1.5 Ω sq^{-1} is achieved by Ni coating.
- Polypyrrole with sufficient electrocatalytic activity is synthesized on Ni-coated fabric.
- DSSCs fabricated using PPy/Ni-coated fabric counter electrode exhibit an efficiency of 3.30%.

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ABSTRACT

The current dye-sensitized solar cell (DSSC) technology is mostly based on fluorine doped tin oxide (FTO) coated glass substrate. The main problem with the FTO glass substrate is its rigidity, heavyweight and high cost. DSSCs with a fabric as substrate not only offer the advantages of flexibility, stretchability and light mass, but also provide the opportunities for easy implantation to wearable electronics. Herein, a novel fabric counter electrode (CE) for DSSCs has been reported employing a daily-used cotton fabric as substrate and polypyrrole (PPy) as catalytic material. Nickel (Ni) is deposited on the cotton fabric as metal contact by a simple electroless plating method to replace the expensive FTO. PPy is synthesized by *in situ* polymerization of pyrrole monomer on the Ni-coated fabric. The fabric CE shows sufficient catalytic activity towards the reduction of I_3^-. The DSSC fabricated using the fabric CE exhibits power conversion efficiency of ~3.30% under AM 1.5.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant interests as promising alternatives for the photovoltaic conversion of solar energy due to their potentially low production costs and relatively high solar-to-electric conversion efficiencies [1–7]. Typically, DSSCs consist of a mesoporous dye-sensitized TiO_2 photoanode, an iodide/triiodide (I^-/I_3^-) redox electrolyte, and a counter electrode (CE). The CE plays an important role in DSSCs, which serves to collect electrons from external circuit and to catalyze I^-/I_3^- redox-coupled regeneration reaction in electrolyte.

Platinized fluorine-doped tin oxide (FTO) glass CE has been widely used in DSSCs due to its good electric conductivity and excellent catalytic activity for I_3^- reduction of platinum (Pt). However, large-scale commercial application of platinized CE is restricted by its high cost and high energy-consuming preparation (sputtering and thermal decomposition). Therefore, extensive studies have been carried out for the development of Pt-free CE in DSSCs. So far, many functional materials have been employed in Pt-free CE, such as carbon-based materials [8–11] and conducting polymers [12–18]. As a well-known conducting polymer, polypyrrole (PPy) has received more and more attention as a potential candidate for platinized CE because of its low cost, facile synthesis, high catalytic activity and remarkable environmental stability [14–18].

FTO glass is also one of the expensive components in DSSCs. The cost of conductive glass is estimated to account for about 30% of the total material cost of DSSCs [19]. Moreover, the rigid, fragile and

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heavy-weight feature will bring transport problem for the FTO glass based DSSCs. Novel substrates such as metal foils or plastic foils coated with indium-doped tin oxide [20–22] have been used to fabricate flexible CEs to achieve the requirements for portable electricity and high-throughput industrial roll-to-roll production. However, the cost of these flexible substrates is even much higher than that of FTO glass.

Fabrics are flexible and porous materials made by weaving or pressing fibers, which gives them important properties, such as flexibility, stretchability, and light mass. Among the fabrics, cotton (natural cellulose) is indeed the most commonly used material, because of its process easiness, relative cheapness and good mechanical properties. In this paper, we report a novel flexible CE employing a daily-used cotton fabric as substrate. Nickel (Ni) is coated on the cotton fabric as metal contact by a simple low temperature electroless plating method to replace the expensive FTO. The CE is prepared with PPy as catalytic material, which is synthesized by *in situ* polymerization of pyrrole monomer on the Ni-coated fabric. Fabric-based DSSCs are expected to meet the various requirements of electronic textiles and wearable electronics. In addition, the technologies for fabric coating are very mature in textile industries, which can benefit the roll-to-roll production of DSSCs on fabrics.

2. Experimental

2.1. Ni deposition on cotton fabrics

Plain weave 100% cotton fabrics (182 g m^{-2}) in white color were used as the substrates. Electroless nickel (Ni) plating was carried out by multi-step processes including pre-cleaning, activation, electroless Ni plating and post-treatment followed by rinsing and drying. In the pre-treatment stage, the fabric samples were precleaned with a 5% non-ionic detergent at pH 7.0 and 40 °C for 20 min. The samples were then rinsed with deionized water. Surface sensitization was conducted by immersing of the samples into an aqueous solution containing 50 g L^{-1} nickel sulfate ($NiSO_4 \cdot 6H_2O$) and 40 mL L^{-1} 38% hydrochloric acid (HCl) at 25 °C for 10 min. The specimens were subsequently rinsed with deionized water and activated through immersion into a solution containing 10 g L^{-1} sodium borohydride ($NaBH_4$) and 10 g L^{-1} sodium hydroxide (NaOH) at 25 °C for 10 min. Then, the specimens were rinsed with a large volume of deionized water for more than 5 min to prevent contamination of the plating bath. After that, the activated specimens were coated via an autocatalytic reaction in the Ni-plating solution at 70 °C for 2 h. The composition of the plating bath was as follows: 25 g L^{-1} $NiSO_4$, 28 g L^{-1} succinic acid ($C_4H_6O_4$), 20 g L^{-1} DL-malic acid ($C_4H_6O_5$) and 25 g L^{-1} sodium hypophosphite ($Na_2H_2PO_2$). The pH of the plating bath was adjusted to 8.0 using NaOH aqueous solution. In the post-treatment stage, the Ni-coated fabrics were rinsed with deionized water at 40 °C for 20 min immediately after the electroless nickel plating and then dried at 60 °C.

2.2. Preparation of PPy/Ni-coated fabrics

The Ni-coated fabrics were immersed in an aqueous solution of pyrrole (1.0 M), cetyltrimethylammonium bromide (CTAB, 0.01 M) and sodium dodecyl benzene sulfonate (SDBS, 0.01 M) for 30 min under magnetic stirring. The polymerization was carried out at 5 °C for 2 h by gently adding an aqueous solution of 0.5 M iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as oxidant agent to the stirred bath. The PPy/Ni-coated fabrics were then washed with deionized water and ethanol to extract the byproducts and remaining reagents, and vacuum-dried at 60 °C to constant weight.

2.3. DSSC fabrication

The TiO_2 (P25, Degussa) paste was coated on FTO glass using the doctor-blade method with Scotch tape as the spacer. The TiO_2 film was dried in air and sintered at 450 °C for 1 h. The obtained TiO_2 film had a thickness of ~10 μm and an area of ~0.36 cm^2. The electrode was then immersed in a solution of 0.3 mM N719 (bis(-tetrabutylammonium)-cis-(dithiocyanato)-*N*,*N*′-bis(4-carboxylato-4′-carboxylic acid-2,2′-bipyridine) ruthenium, Solarnix) in ethanol for 24 h at room temperature. After that, the TiO_2 electrode was rinsed thoroughly with ethanol and dried under a dry air stream. The DSSC was fabricated by sandwiching the sensitized TiO_2 electrode and fabric CE using a sheet of stretched parafilm as the spacer. The backside of the cell was sealed by polymer film [23]. The electrolyte was injected between the photoanode and CE using a syringe. The electrolyte containing 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.025 M LiI, 0.04 M I_2, 0.05 M guanidium thiocyanate (GuSCN), and 0.28 M 4-tertbutylpyridine (TBP) in dry acetonitrile was used. The Pt CE was prepared by depositing a drop of 50 mM solution of H_2PtCl_6 in isopropanol onto FTO substrates followed by annealing at 450 °C in air for 15 min.

2.4. Characterization and measurement

The electrical conductivity of the samples was measured at room temperature by a four-point probe resistivity system (RTS-9, Probes Tech., China) with copper electrodes and a 5 N pressure at room temperature and relative humidity of 65%. The morphologies of the samples were examined by scanning electron microscopy (SEM, JSM-6510LV, JEOL, Japan). Double-sided conductive carbon tape was used to attach the samples to the microscope stage. The samples were sputtered with gold to get good electrical contact and avoid charging. The composition of the Ni-coated sample was examined using an energy dispersive spectrometer (EDS, EDAX, USA). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded using a TGA-FTIR spectrometer (Tensor 27, Bruker, Germany) in the range from 4000 to 600 cm^{-1} with 8 scans and a resolution of 2 cm^{-1}. The Scotch tape test was performed; in this test a piece of Scotch tape is placed on the fabric and removed. The sample fails the test if any of it remains on the Scotch tape [24]. In order to test the corrosion resistance of Ni and PPy to electrolytes, the samples were immersed in electrolyte solution for 2 h and the transmittance of electrolytes was recorded by UV-2550 spectrometer (Shimadzu, Japan) before and after immersion. Less transmittance change of electrolytes is an indication of better corrosion resistance. The *J*–*V* characteristics were measured under AM 1.5 simulated illumination (Sciencetech, SS150) with a power density of 100 mW cm^{-2}. Electrochemical impedance spectroscopy (EIS) measurements were carried out on Autolab PGSTAT302N (Metrohm AG, Switzerland) with the frequency ranging from 0.01 Hz to 100 kHz. For the EIS measurements, the symmetric cell configuration with two identical fabric or FTO CEs was used. The symmetric cell was constructed by sandwiching two identical CEs separated with a sheet of stretched parafilm. Two pieces of microscope glass were utilized to stabilize the fabric cell. The cell was sealed in polymer pouches. The same electrolyte for the DSSC fabrication was injected.