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Low temperature fabrication of high performance p-n junction on the Ti foil for use in large-area flexible dye-sensitized solar cells☆

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ABSTRACT

A p-n junction of poly (3,4-ethylenedioxythiophene) (PEDOT) - dye-sensitized TiO_2 is introduced into the large-area flexible dye-sensitized solar cell (DSSC) as an anode. This p-n junction is fabricated using a cyclic voltammetry electropolymerization of PEDOT onto a Ti foil substrate, and then treated in the aqueous ammonia, finally subjected to coating TiO_2 by a doctor-scraping technique, all of preparations and treatments are carried out under low temperature. The obtained p-n junction forms a single directional pathway for electron transport which benefites the charge separation. The large-area (10 cm^2) flexible DSSC with the p-n junction demonstrates an enhanced photovoltaic conversion efficiency of up to 6.51% compared to 4.89% for the DSSC without the p-n junction due to its low series resistance and charge-transfer resistance, high effective electron lifetime for recombination. As a result, the DSSC fabricated using the p-n junction can be suitable for high powered DSSC applications.

1. Introduction

Dye-sensitized solar cells (DSSCs) represent a low-cost alternative to conventional photovoltaic devices and have recently attracted much research interest [1], attributable to their easy fabrication, good stability, and high conversion efficiency [2–5]. In order to overcome some problems in general DSSCs in which TiO_2 porous films are solidified on a conductive glass substrate, flexible DSSCs based on metal foils or polymer substrates have attracted wide researches, due to their light weight, good flexibility, impact-proof, and low cost [6–8]. Besides, the flexible DSSC has been seen as the 3rd generation photovoltaic cell as well as the organic photovoltaic (OPV) device [9], owing to its shape or surface can be devised and constructed, and the technique of large-scale roll-to-roll (R2R) processing and rapid coating can be used in the flexible DSSC, which further decreases the cost and broadens the application for the flexible DSSC. Where the R2R process has been utilized for the industrial production of the OPV materials [10–12], and the OPV cell shows good operational stability under the consensus stability testing protocols (ISOS standards) [13] and reaches one-day energy pay-back for the factories [14]. Ti foils and Ti meshes have been utilized to manufacture large-area flexible DSSCs as anode and counter electrode materials, due to theirs flexibility and relatively low sheet resistance compared to those of the conducting glass substrate [15–17]. Ti-based materials have superior corrosion resistances in the contacting I_3^-/I^- electrolyte because of the passive oxide film of TiO_2 on these substrates.

As we have seen, the research of novel architectures and high performance flexible electrodes, such as that with a p-n junction structure, good electroconductivity, and excellent flexibility is still a challenge for the science development [18]. Looking for a suitable p-type hole transporting material which can match with the n-type semiconducting material of TiO_2 is a key issue to form a p-n junction in the flexible DSSC. Recently, Heng et al. reported a p-n junction of CuI-TiO_2 which was introduced to the flexible DSSC and showed an enhanced efficiency of 4.73% [19]. As extensively used p-type conducting polymers, e.g., polypyrrole [20,21], polyaniline [22,23], and poly (3,4-ethylenedioxythiophene) (PEDOT) [24–30], have received considerable attention in DSSCs. These p-type conducting polymers are advantageous over other small molecules owing to their low cost, good stability, and simple easy preparation of designable structures. Among them, PEDOT has already been reported as a cost-effective and stable counter electrode for catalyzing the reaction of I_3^-/I^- redox couple in DSSCs [24–26]. In addition,

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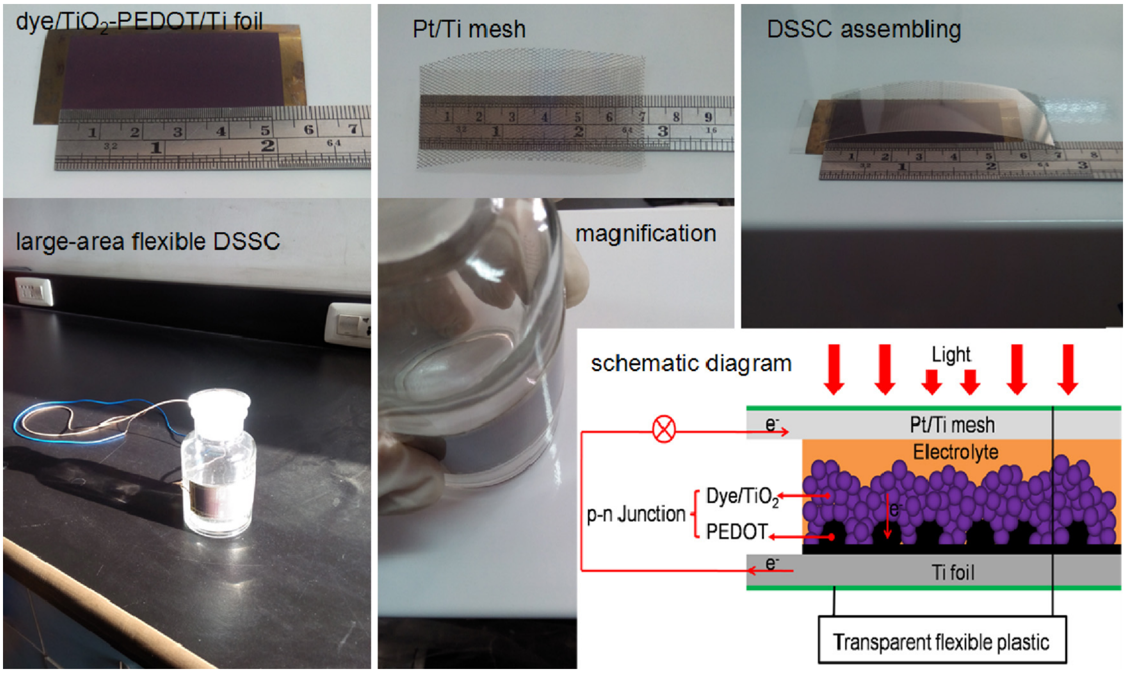


Fig. 1. Photographs and schematic diagram of the p-n junction based flexible dye-sensitized solar cell.

PEDOT is also potentially applicable as a hole transporting material in a solid-state DSSCs [27–30]. For instance, Koh et al. were successful at improving the power conversion efficiency significantly up to 6.80% by using PEDOT, and the active area of the DSSC was 0.16 cm^2 [30].

In this paper, integrating the merits of the Ti-based substrates and PEDOT, we report on low temperature fabrication a new p-n junction of dye-sensitized TiO_2-PEDOT/Ti and using in a large-area flexible DSSC with an active area of 10 cm^2 (shown in Fig. 1).

2. Experimental

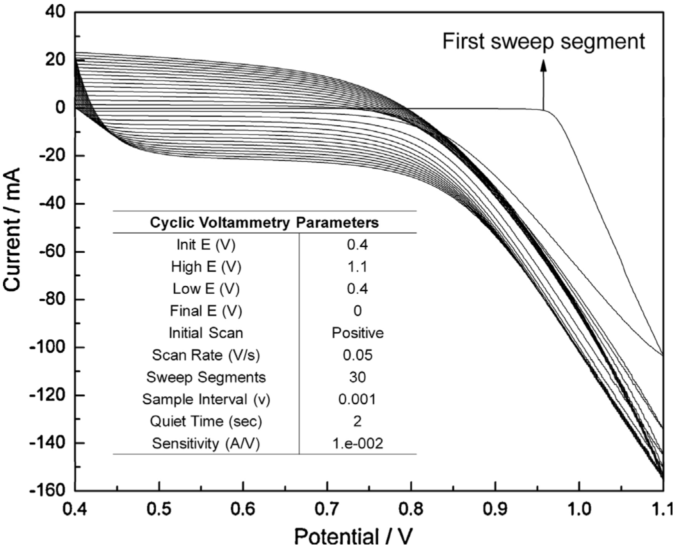
2.1. Materials

3, 4-ethylenedioxythiophene monomer (EDOT) was purchased from Aldrich, USA. Sodium dodecyl sulfate (SDS), lithium pechlorate ($LiClO_4$), aqueous ammonia, hydrofluoric acid, ethanol, iodine, lithium iodide, tetrabutyl ammonium iodide, 4-tert-butyl-pyridine, and acetonitrile were purchased from Shanghai Chemical Agent Ltd., China (Analysis purity grade). Titania nanopowder (P25) was purchased from Degussa, Germany. Sensitized-dye N719 [cis-di(thiocyanato)-N,N′-bis (2,2′-bipyridyl-4-carboxylic acid-4-tetrabutylammonium carboxylate) ruthenium (II)] was purchased from Dyesol, Australia. The above agents were used without further purification.

2.2. Fabrication of the flexible p-n junction

PEDOT was electrodeposited on the Ti foil by the cyclic voltammetry (CV) measurement from an aqueous solution containing 2.0 mM EDOT, 10 mM SDS, and 10 mM $LiClO_4$. A three-electrode cell with an Electrochemical Workstation (CHI660D, Shanghai Chenhua Device Company, China), comprised of the Ti foil (0.03 mm thickness, purchased from Baoji Yunjie Metal Production Co., Ltd., China) working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode was used. Before the plating, Ti foil samples with rectangular dimension of 2.5 cm × 5.5 cm were cleaned with mild detergent and rinsed in distilled water. The Ti foil samples then immersed in hydrofluoric acid solution with suitable concentration for 2 min and rinsed in distilled water again. The cleaned Ti foil was designated as sample A. The CV plating PEDOT on the cleaned Ti foil was carried out at a “High E” of 1.1 V. The value of “Init E” was same as the “Low E”, the CV parameters were shown in Fig. 2 in detail. For comparison, the value of “Sweep Segments” was changed, and the samples plated under “Sweep Segments” = 15, 30, and 45 were designated as sample B, C, and D, respectively. The obtained PEDOT/Ti samples were rinsed in distilled water and then immersed in an aqueous ammonia for 12 h to change their conductive state to semiconductor state. Finally, the samples were drying at 80 °C in a vacuum drying oven (Suzhou Jiangdong Precision Instrument Co., Ltd., China).

The TiO_2 colloid (prepared according to our previous report [31]) was coated on the cleaned Ti foil and different PEDOT/Ti samples using a doctor-scraping technique, respectively. The thickness of



Cyclic Voltammetry Parameters	
Init E (V)	0.4
High E (V)	1.1
Low E (V)	0.4
Final E (V)	0
Initial Scan	Positive
Scan Rate (V/s)	0.05
Sweep Segments	30
Sample Interval (v)	0.001
Quiet Time (sec)	2
Sensitivity (A/V)	1.e-002

Fig. 2. Cyclic voltammetry for the electrodeposition of PEDOT on the Ti foil.