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Composite films of carbon black nanoparticles and sulfonated-polythiophene as flexible counter electrodes for dye-sensitized solar cells

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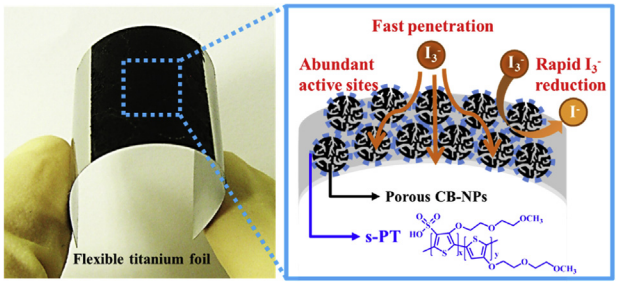
HIGHLIGHTS

- Carbon black/sulfonated-polythiophene (CB-NPs/s-PT) worked as counter electrodes.
- Water-soluble s-PT conductive binder was first used in dye-sensitized solar cells.
- Flexible CB-NPs/s-PT film gave a good cell efficiency (η) of 9.02% at 100 mW cm^{-2}.
- At weak light illuminations, a cell with CB-NPs/s-PT still exhibited good η's.
- Low-cost CB-NPs/s-PT gave great potential to replace Pt and for indoor devices.

GRAPHICAL ABSTRACT



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ABSTRACT

A composite film based on carbon black nanoparticles and sulfonated-poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) (CB-NPs/s-PT) is formed on a flexible titanium foil for the use as the electro-catalytic counter electrode (CE) of dye-sensitized solar cells (DSSCs). The CB-NPs provide the large amount of electro-catalytic active sites for the composite film, and the s-PT polymer serves as a conductive binder to enhance the inter-particle linkage among CB-NPs and to improve the adhesion between the composite film and the flexible substrate. The flexible CB-NPs/s-PT composite film is designed to possess good electro-catalytic ability for I^-/I_3^- redox couple by providing large active sites and rapid reduction kinetic rate constant of I_3^-. The cell with a CB-NPs/s-PT CE exhibits a good cell efficiency (η) of 9.02 ± 0.01% at 100 mW cm^{-2}, while the cell with a platinum CE shows an η of only 8.36 ± 0.02% under the same conditions. At weak light illuminations (20–80 mW cm^{-2}), a DSSC with CB-NPs/s-PT CE still exhibits η's of 7.20 ± 0.04–9.08 ± 0.02%. The low-cost CB-NPs/s-PT CE not only renders

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high cell efficiency to its DSSC but also shows a great potential to replace the expensive platinum; moreover it is suitable for large-scale production or for indoor applications.

1. Introduction

Recently, electro-catalytic reduction of triiodide ions (I_3^-) at the counter electrode (CE) of a dye-sensitized solar cell (DSSC) becomes a very important issue, not only from the point of view of power conversion efficiency (η) of the DSSC, but also from the viewpoint of cost of fabrication of the cell. Triiodide ions (I_3^-) are strongly electron-deficient; thereby a slow electro-catalytic reduction of I_3^- ions can lead to severe energy loss in a DSSC owing to their susceptibility for recombination reactions with the photo-induced electrons. Generally, a Pt film provides a great electro-catalytic ability to the CE of a DSSC, and thereby renders for the DSSC a high power conversion efficiency. However, Pt is very expensive and often reacts with the iodide electrolyte [1]. To replace platinum, several types of materials have been investigated, *e.g.*, alloys [2–4], conducting polymers [5–7], carbon-based materials [5,6,8–12], transition metal compounds [5,13], and the pertinent composite materials [5,14–17]. Among all these materials, composite materials often exhibit a better electro-catalytic ability, because one component of a composite material can nullify the defects of others [18,19]. Composite materials can be easily designed in such a way to exhibit various properties, *e.g.*, oriented electron transfer pathways, fast charge transfer electro-catalytic ability, porous morphology, and high conductivity. For achieving low-cost and high performance, plenty of combinations of conducting polymers and carbon-based materials were widely studied; these composites were intended for obtaining good electro-catalytic ability for I_3^- reduction and good η for the pertinent DSSCs.

In general, conducting polymers/carbon-based composites can be simply classified into three types: (1) pyrrole type [20–22], (2) aniline type [23–28], and (3) thiophene type [29–35]. As regards to type (1), many polypyrrole (PPy)-based composite films were investigated, *e.g.*, graphene oxide/PPy (GO/PPy, η = 8.14%) [36,37], graphene quantum dot/PPy (GQD/PPy, η = 5.27%) [38], nanographite/PPy (NG/PPy, η = 7.40%) [39], carbon black nanoparticle/PPy (CB/PPy, η = 7.20%) [40,41], single-walled carbon nanotubes/PPy (SWCNT/PPy, η = 8.30%) [42], and multi-walled carbon nanotubes/PPy (MWCNT/PPy, η = 7.42%) [43–45]. In regard to type (2), lots of polyaniline (PANI)-based composites were studied, *e.g.*, graphene/PANI (GN/PANI, η = 7.78%) [46–49], GO/PANI (η = 7.41%) [50–52], nanographite/PANI (NG/PANI, η = 7.36%) [53,54], CB/PANI (η = 6.77%) [41], MWCNT/PANI (η = 7.21%) [55,56], and SWCNT/GO/PANI (η = 6.88%) [57]. In regard to type (3), among the thiophene-based conducting polymers, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is a well known water soluble conducting polymer, and is often used for preparing composite electro-catalytic materials with carbon-based materials for DSSCs, *e.g.*, GN/PEDOT:PSS (η = 4.50%) [58,59], CB/PEDOT:PSS (η = 7.01%) [60,61], MWCNT/PEDOT:PSS (η = 8.30%) [62,63], and carbon fiber/PEDOT:PSS (η = 5.61%) [64]. These carbon/PEDOT:PSS composites show good electro-catalytic ability for I_3^- reduction, and can be prepared via a simple, large-scale, and cheap process. However, the efficiencies of DSSCs with carbon/PEDOT:PSS are limited, due to the inclusion of the non-conducting PSS component within the PEDOT:PSS. Therefore, another water-soluble conducting polymer with high conductivity is required.

In this work, we introduced a novel thiophene-based water-soluble conducting polymer, sulfonated-poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) (s-PT), for the first-time application in the DSSCs. By adding the nano-porous carbon black nanoparticles (CB-NPs) into the s-PT polymer matrix, the composite film can provide a nano-porous morphology and a good adhesion to the flexible titanium foil. Therefore, the nano-porous CB-NPs/s-PT composite film can provide large surface area, fast electrolyte penetration, and rapid reaction rate for I_3^- reduction. The good cell efficiencies of a DSSC with CB-NPs/s-PT composite CE reveal its compatibility at indoor, especially for weak to medium sunlight applications (20–60 mW cm^{-2}). In brief, the composite CB-NPs/s-PT film is a promising substitution for Pt due to its outstanding properties, *i.e.*, good electro-catalytic ability for I_3^- reduction, low-cost, simple preparation process, and easy for large-scale production.

2. Experimental

2.1. Materials

Titanium (IV) tetraisopropoxide (TTIP, >98%), methanol (MeOH, >99.5%), ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.5%), lithium perchlorate ($LiClO_4$, ≥98.0%), 2-methoxyethanol (≥99.5%), tetrabutylammonium triiodide ($TBAI_3$, >97%), and sulfonated-poly(thiophene-3-[2-(2-methoxyethoxy)-ethoxy]-2,5-diyl) aqueous solution (2% s-PT dispersed in 1,2-propanediol/isopropanol/water at the ratio of 3/2/1) were all obtained from Sigma Aldrich. Acetonitrile (ACN, 99.99%), nitric acid (HNO_3, *ca.* 65% solution in water), and dichloromethane (DCM, 99.99%) were received from J. T. Baker. Lithium iodide (LiI, analytical grade), iodine (I_2, analytical grade), and poly(ethylene glycol) (PEG, MW ~20,000) were purchased from Merck. Acetone (99%), 4-tert-butylpyridine (tBP, 96%), and tert-butyl alcohol (tBA, 96%) were bought from Acros. 3-Methoxypropionitrile (MPN, 99%) was procured from Alfa Aesar. Transparent TiO_2 paste (TL paste, Ti–nanoxide HT/SP, with an average particle size of 13 nm) and Surlyn® (SX1170–25, 25 μm) were supplied by Solaronix (S.A., Aubonne, Switzerland). The commercial light scattering TiO_2 particle, ST-41, with an average particle size of 200 nm, was obtained from Ishihara Sangyo, Ltd. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was acquired from Tokyo Chemical Industry Co., Ltd. Titanium foil (Ti foil) was obtained from Nilaco Corporation, Tokyo, Japan. Fluorine-doped tin oxide (FTO, TEC-7, 7 Ω $sq.^{-1}$) conducting glass was obtained from NSG America, Inc., New Jersey, USA. Carbon black nanoparticle (black pearl® 2000) was supplied by Cabot Corporation.

2.2. Preparation and characterization of various electro-catalytic films

Titanium foils (Ti foils) and FTO glasses were first cleaned with a neutral cleaner and then washed with de-ionized water, acetone, and isopropanol sequentially. To obtain a highly efficient standard Pt film, we preliminary prepared two kinds of Pt films onto the cleaned Ti foils via two different routes: (i) direct-current (DC) sputtering and (ii) hydrothermal reduction methods; the fabrication details were given in the Supplementary information. In Fig. S1