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A composite catalytic film of Ni-NPs/PEDOT: PSS for the counter electrodes in dye–sensitized solar cells

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ABSTRACT

As the catalytic material for the counter electrode (CE) of a dye-sensitized solar cell (DSSC), a composite film of nickel nanoparticles (Ni-NPs) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was deposited on an FTO glass substrate, by using a home-made polymeric dispersant, poly(oxyethylene)-segmented imide (POEM). Scanning electron microscopy (SEM), atomic force microscopy (AFM), and energy dispersive X-ray spectroscopy (EDX) were used to characterize the films. A solar-to-electricity conversion efficiency (η) of 7.81% was achieved for the DSSC using Ni-NPs/PEDOT: PSS, while the DSSC with the Pt CE showed a $\eta$of 7.63%. The best composite film showed a high stability, when it was subjected to potential cycling for 100 cycles in an electrolyte containing the redox couple, iodide/triiodide (I^-/I_3^-), while the Pt film showed a considerable decrease in its stability. In replacing the conventional sputtered Pt film as the CE in a DSSC, the Ni-NPs/PEDOT: PSS film exhibited multiple advantages of higher power conversion efficiency, higher stability of the catalytic film, and less expensive material cost. The photovoltaic parameters of the cells were substantiated by incident photon-to-current conversion efficiency (IPCE) spectra, electrochemical impedance spectroscopy (EIS), Tafel polarization plots, and cyclic voltammetry (CV).

1. Introduction

The structure of a dye-sensitized solar cell (DSSC) consists of a dye-adsorbed nanocrystalline TiO_2 photoanode, an electrolyte, and a counter electrode (CE) [1]. A thin film composed of platinum (Pt) has been widely used as the catalytic material for the CE of a DSSCs, owing to its high conductivity and excellent electro-catalytic ability for the reduction of triiodide (I_3^-) to iodide (I^-) at the CE [2]. However, platinum is one of the rare noble metals and considered to be expensive in cost [3]. Fabrication of CEs with other cheaper metals is expected to bring down the production cost of the cells, especially when it is a matter of large-scale production.

In order to replace Pt for CEs, several transition metal compounds, such as TiN [4], Mo_2N [5], W_2N [5], MoC [6], WC [6], MoS_2 [7], WS_2 [7], CoS [8], NiS [9], NbO_2 [10], WO_2 [11] have been investigated. Their electro-catalytic ability is comparable to that of Pt [12–14]. Some of these transition metal compounds show not only a remarkable electro-catalytic ability, but also a good conductivity [15,16]. These transition metal compounds also find other applications, *e.g.*, super capacitors [17], fuel cells [18], and sensors [19]. Among these transition metal compounds, nickel based compounds, such as NiS, Ni_3S_2 [9,20], $Ni_{12}P_5$ [21], and sulfur-doped NiO [22], were proved to show superior electro-catalytic ability, when they were used as counter electrode materials in DSSCs. A nickel incorporated carbon nanotube/nanofiber composite CE rendered for its DSSC a solar-to-electricity conversion efficiency (η) of 8.32%, which was much better than that of the DSSC (7.96%) with a platinum counter electrode (Pt-CE) [23]. Graphene supported nickel nanoparticles (GP-Ni) was used as the catalytic film for the CE of a DSSC; the cell showed a higher η (2.19%) compared to that of the cell with Pt (2.00%), and this was attributed to a better electro-catalytic ability of the film with GP-Ni [24]. Nickel nanoparticles (Ni-NPs) enhance the performance of a CE in a DSSC, owing to their excellent electro-catalytic ability, superior conductivity [25] and long-term stability [26,27]. Nickel nanoparticles were reported to have been used as the conducting material on a paper substrate for a DSSC, in the place of transparent conducting oxide (TCO) [28]; however nickel nanoparticles cannot be attached easily to a substrate because of their high density.

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Conducting polymers, such as polyaniline (PANI) [29,30], polypyrrole (PPy) [31,32], PEDOT [33], PEDOT:PSS [34], and PProDOT–Et_2 [35], have also been widely investigated as CE materials for DSSCs, because of their unique properties, such as low-cost, good stability, tunable conductivity, good electro-catalytic ability, changeable structure, and environmental compatibility. Among these conducting polymers, PEDOT:PSS has attracted much attention for about a decade now [36]. It has several advantages, *e.g.*, easy synthesis, able to exist and be dispersed in an aqueous phase, easy fabrication, good adhesion to a substrate, good stability, and ability to fix other materials into its structure. Due to these reasons, PEDOT:PSS has been used to fix some materials in it, *e.g.*, graphene [37], PPy [38], and TiN [39], which otherwise are associated with the problems of poor adhesion to the substrate. However, the flat structure of PEDOT:PSS and its organic group of PSS limit its electro-catalytic ability and conductivity, respectively. In order to solve the problem of its poor conductivity, some researchers used graphite, which has good conductivity attributable to its abundance in sp^2 orbits [40]. To solve the problem of flat structure of PEDOT:PSS, which limits its electro-catalytic ability, carbon black is often incorporated in it to increase its surface area and thereby its electro-catalytic ability [40].

In this work, we used PEDOT: PSS for incorporating the poly(oxyethylene)-segmented imide (POEM)-dispersed Ni-NPs in its structure, and used this composite material as the electro-catalytic film for the CE of a DSSC. The polymer PEDOT: PSS acts as a kind of linker for Ni-NP to improve the electron-transfer among them. Moreover, the PEDOT:PSS was also intended to enable a good contact between the Ni-NPs and the substrate. On the other hand, Ni-NPs could improve the conductivity of PEDOT:PSS film. In addition, the composite film showed higher roughness compared to that of PEDOT:PSS film; this higher roughness means a higher surface area for the film and thereby a higher electro-catalytic ability for it. The DSSC using Ni-NPs/PEDOT:PSS showed an η of 7.81%, while the DSSCs with bare PEDOT:PSS and bare Ni-NPs showed η's of 4.36% and 0.24%, respectively. The η of the DSSC using Ni-NPs/PEDOT:PSS (7.81%) is better than that of the cell with a Pt-CE (7.63%).

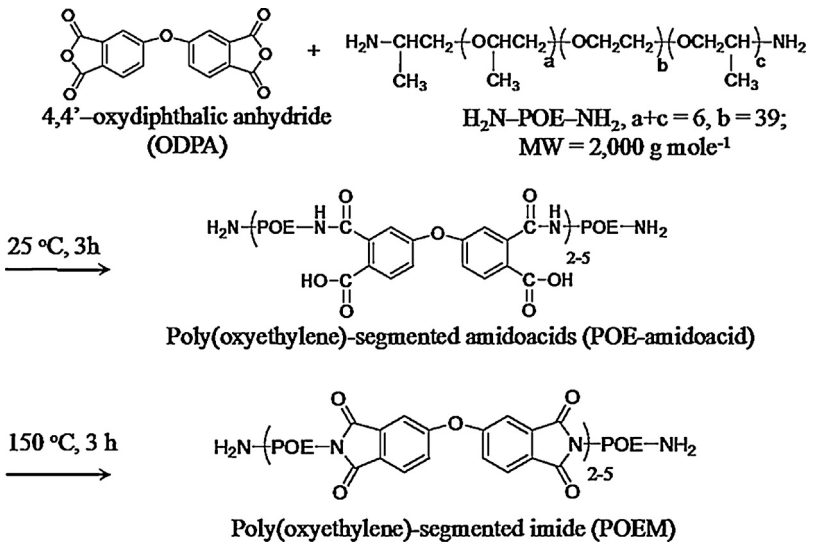
2. Experimental Section

2.1. Materials

Nickel nanoparticles (Ni-NPs, diameter≈35 nm, 95+%) were obtained from Echo Chemical Company (Miaoli, Taiwan). PEDOT:PSS aqueous solution (PH 500, 1.0∼1.4 wt% dispersion in water) was received from Heraeus. Lithium iodide (LiI, synthetic grade) and iodine (I_2, synthetic grade) were acquired from Merck. Acetone (99+%), 4–*tert*–butylpyridine (*t*BP, 96%), and *tert*–butyl alcohol (*t*BA, 96%) were procured from Acros. Titanium (IV) tetraisoproproxide (TTIP, > 98%), acetylacetone (AA, > 99.5%), dimethyl sulfoxide (DMSO, ≥ 99.5%), ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.5%), lithium perchlorate ($LiClO_4$, ≥ 98.0%), and 2–methoxyethanol (≥ 99.5%) were bought from Aldrich. Acetonitrile (ACN, 99.99%) and Nitric acid (HNO_3, ca. 65% solution in water) were supplied by J. T. Baker. 3–methoxypropionitrile (MPN, 99%) was delivered by Fluka. 1,2–dimethyl–3–propylimidazolium iodide (DMPII), transparent TiO_2 paste (TL paste, Ti–nanoxide HT/SP, 13 nm), and cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(*tetra*- butylammonium) (N719 dye) were provided by Solaronix (S.A., Aubonne, Switzerland). Commercial light scattering TiO_2 particles (ST–41, 200 nm) were obtained from Ishihara Sangyo, Ltd.

2.2. Preparation of the photoanode and counter electrode

A TiO_2 colloid was synthesized by adding 72 ml of TTIP to 430 ml of 0.1 M nitric acid, with constant stirring and heating at 88°C for 8 h. The colloid was cooled down to room temperature, transferred to an autoclave (PARR 4540, U.S.A.), and heated at 240 °C for 12 h; this rendered uniform TiO_2 nanoparticles of *ca.* 20 nm in size. Then the colloid was concentrated to 13 wt%. After that, a scattering layer paste (SL paste) was prepared by adding to the concentrated-TiO_2 colloid, 100 wt% of ST–41 particles and 25 wt% of the home-made polymeric dispersant, POEM with respect to the weight of TiO_2 nanopaticles. The POEM dispersant was prepared according to our previous reports [41,42] by the procedure shown in Scheme 1, and was used to prevent the aggregation of TiO_2 nanoparticles in the films and to prevent the films from being cracked during drying. In the next stage, the TiO_2 photoanode was prepared by the TL paste and SL paste mentioned above. Fluorine–doped SnO_2 (FTO, TEC–7, 7 Ω $sq.^{-1}$, NSG America, Inc., New Jersey, USA) conducting glass was first cleaned with a neutral cleaner and then washed with deionized water, acetone, and isopropanol, in sequence. The conducting surface of the FTO was treated with a solution of TTIP and 2–methoxyethanol (weight ratio of 1:3) for obtaining a good contact layer between the conducting glass and the TiO_2 film. A 15 μm porous TiO_2 film was coated on the treated FTO by a doctor blade technique. This porous TiO_2 film consisted of two TiO_2 layers, one



Scheme 1. Synthetic procedure for poly (oxyethylene)-segmented imide (POEM).