



Modified conducting polymer films having high catalytic activity for use as counter electrodes in rigid and flexible dye-sensitized solar cells



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HIGHLIGHTS

- Triton makes PEDOT chain transforms from coiled benzoid to linear quinoid structure.
- Triton modified PEDOT:PSS is conductive and exhibits optical transmittance of 93%.
- The catalytic activity the Triton modified PEDOT:PSS is better than that of Pt.
- PEDOT:PSS/Triton-based DSSC shows a higher efficiency than that of Pt-based DSSC.

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ABSTRACT

We report replacing platinum based counter electrode (CE) in dye-sensitized solar cell (DSSC) with conducting polymer based CE. Conducting polymers are prepared through mixing poly-(3,4-ethylene-dioxythio phene):poly-(styrene sulfonic acid) (PEDOT:PSS) with Triton. The polymer mixture is spin-coated on indium tin oxide (ITO)-coated glass substrate and ITO-coated polyethylene naphthalate plastic substrate to form a CE for use in both rigid and flexible DSSCs, respectively. The PEDOT:PSS-Triton polymer not only is transparent (up to 93%) and highly conductive but also exhibits better catalytic activity than the expensive platinum. The DSSC fabricated using the PEDOT:PSS-Triton conducting polymer CE shows better performance or higher power conversion efficiency than that using Pt-based CE, either rigid or flexible.

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1. Introduction

Nowadays, dye-sensitized solar cell (DSSC) remains as one promising renewable energy capturing particular attention among researchers owing to its low cost, facile fabrication, and better efficiency under dim light as compared with other types of photovoltaics [1–3]. Studied issues cover, but are not limited to, all the components of DSSCs, namely the dye [4], the hole transport material [5], the photoanode [6], and the counter electrode (CE) [7]. It appears that many of the efforts have been made for the study of photoanode and CE. With regard to the photoanode, some of the recent interests include the development of novel TiO₂ beads [8–11] and low-temperature synthesis of the photoanode for flexible DSSCs (FDSSCs) [9–12]. In terms of the CE, most of the

attentions have been paid to the development of the catalytic layer as follows.

Pt is a stable material having excellent electrical conductivity and high catalytic activity, suitable for use as a CE. However, the cost of Pt is an unequivocal drawback and as a result there is a need to replace the Pt with a low cost material. Carbon based materials and conducting polymers appear to be the mostly investigated. Carbon black, activated carbon, carbon nanotube, graphite, and graphene have been studied for this purpose. Murakami et al. used carbon black coated FTO-glass as a CE to achieve an excellent conversion efficiency (9.1%) and a high fill factor (~72%) [13]. However, a very thick layer of carbon black (at least 14.47 μm) is required to exhibit catalytic activity comparable to that of Pt and to reduce the charge transfer resistance (R_{ct}), leading to an obvious drawback that the CE becomes opaque and therefore bi-facial illumination is less possible. Imoto et al. utilized a variety of activated carbon powder coated on FTO-glass as the CE of DSSCs [14].

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Similarly, the activated carbon layer has to be as thick as 30 μm to obtain only a slightly better conversion efficiency (3.89%) than that of the one having a sputtered Pt CE (3.61%), only around 100 nm thick. Nam et al., have reported significantly high conversion efficiency (~10%) by using multi-walled carbon nanotubes (MWCNTs) on FTO-glass as the CE [15]. The preparation of the 5 μm MWCNTs requires a quite complex process and a high temperature of 550 °C. Also, no catalytic activity information was given. Veerappan et al. employed sub-micrometer-sized colloidal graphite as the CE without the use of a transparent conducting oxide (TCO) [16]. Similar with other carbon-based CEs, a thick graphite electrode (9 μm) was used to achieve an efficiency only 85% of that of the one using Pt as the CE. Through utilizing functionalized graphene coated FTO-glass as the CE, Roy-Mayhew et al. conducted a very comprehensive study on the electrochemical performance; however, the resulting efficiency (4.99%) is lower than that (5.54%) of the cell with a Pt CE [7].

Conducting polymers have also been used as CE materials. Saito et al. applied chemically polymerized p-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-TsO) to the CE [17]. The resulting efficiency (~3.6%) was comparable with the one having a Pt CE because of the comparable electrical resistance as well as catalytic activity. In addition, it is worth noting that the PEDOT-TsO was deposited on FTO-glass and the optimized thickness was around 2 μm . High surface area polyaniline (PANI) was deposited on FTO-glass and used as a substitute of Pt [18]. The PANI electrode improves the catalytic activity owing to the high surface area. The conversion efficiency reaches 7.15%, which is slightly higher than that of the one with a Pt CE (6.9%). DSSC having a polypyrrole (PPy) nanoparticle based CE (deposited on FTO-glass) shows an improved conversion efficiency, as compared to the one having a Pt CE [19]. The cell performance was improved due to reduced R_{ct} and higher electro-catalytic activity provided by the PPy. However, the preparation of PPy is very complicated too. Lee et al. have obtained a higher conversion efficiency (7.88%) using PProDOT-Et₂ [poly(3,3-diethyl-3,4 dihydro-2H-thieno-[3,4-b] [1,4]doxepin)] as the CE (on FTO-glass) [20]. The resulting cell efficiency is slightly higher than the one with a sputtered-Pt (7.77%) CE. The improved performance is attributed to the wire-like structure that increases the effective surface area, but the thickness of the CE is unknown. Chen et al. utilized Poly-(3,4-ethylenedioxythio phene):poly-(styrene sulfonic acid) (PEDOT:PSS) modified with either dimethyl sulfoxide (DMSO) or DMSO and carbon black (CB) as the CE on FTO-glass [21]. The cell having the DMSO/CB CE exhibited a conversion efficiency of 5.81% under 100 mW cm^{-2} , which is marginally higher than that (5.66%) of the one consisting of a Pt CE. The DMSO and CB improve the conductivity (low R_{ct}) and catalytic activity (low Nernst diffusion resistance) of the PEDOT:PSS. Hong et al. added 1 wt% graphene into PEDOT:PSS and obtained a cell efficiency of 4.5%, which is lower than that (6.3%) of the one having a Pt CE [22]. They also showed the optical transmittance of the 60 nm thick CE reached a peak of nearly 88% in the wavelength range of 390–780 nm, which is helpful for bi-facial illumination. Yeh et al. deposited a 7.2 μm thick TiN nanoparticles/PEDOT:PSS composite layer on Ti foil as a CE [23]. The electro-catalytic activity of the CE was attributed to not only the inherent superior electrical conductivity of TiN but also the surface roughness as well as porous morphology of the composite CE, and the resulting cell efficiency was 6.67%. It is also worth noting that the resulting cells are not flexible type as the photoanodes were deposited on FTO-glass. Xu et al. have also used TiN-PEDOT:PSS on FTO-glass and obtained a relatively high conversion efficiency (7.06%), as compared to 6.57% for Pt CE [24]. This CE was considered to provide a combined network that endows more favorable and efficient interfacial active sites.

Although the above Pt-free CEs show somewhat improved cell

performance, there are a few issues that have not been addressed. Almost all the CEs have a thickness in the micron range, indicating poor light transmittance and therefore preventing bi-facial illumination that would increase the utilization of the sun light. Also, it is only recently that highly conductive, post-treated PEDOT:PSS was employed to replace ITO for preparing ITO-free photoanode for use in organic solar cells [25]. Furthermore, all the Pt-free CEs were deposited on TCO-glass or Ti foil, indicating that these CE materials cannot function to replace TCO. Moreover, all the cells demonstrated are rigid type; however, with the growing flexible electronics, the development of a flexible version of DSSCs is inevitable.

In this research, we have used PEDOT:PSS as the CE in FDSSCs. It has been reported that the conductivity of PEDOT:PSS can be increased by the addition of various additives, including ethylene glycol (EG) and DMSO, which transform the PEDOT:PSS from benzoid-dominated to quinoid-dominated structure [25,26]. In addition, surfactant Zonyl FS-300 was shown to enhance the conductivity of PEDOT:PSS in ITO-free electrode in rigid cells [27]. Here, we demonstrate that through the use of a common additive, Triton-X, not only the electrical conductivity but also the electro-catalytic activity of PEDOT:PSS are enhanced. The catalytic and conductive properties were characterized by both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The resulting flexible cell efficiency is very similar to that of one with a Pt CE. Furthermore, the intensity-modulated photocurrent spectroscopy (IMPS) analysis is reported. Finally, we also show that our PEDOT:PSS CE exhibits higher optical transmittance than Pt CE through back-side illumination.

2. Experimental

PEDOT:PSS was mixed with Triton X-100 at various weight percentages via ultrasonic agitation. The mixture was then spin-coated on glass, ITO-glass, and ITO-coated polyethylene naphthalate (PEN) substrates at predetermined spin rates of 500 rpm for 20 s, followed by 800 rpm for 120 s. The spin-coated films were annealed at 120 °C for 5 min in ambient. The resulting CEs are designated as PPTw, where w represents the weight percentage of Triton X-100 in the PEDOT:PSS mixture. Photoanodes were fabricated on ITO-glass and ITO-PEN by employing screen printing and electrophoresis method, respectively. To fabricate rigid photoanodes, paste consisting of TiO₂ powders (P25 from Degussa, Germany), ethyl cellulose, terpineol, and ethanol was first prepared. The obtained TiO₂ paste was then screen-printed on ITO-glass to create a coating. Subsequently, the coating was annealed at 450 °C to form photoanode having a thickness of 13.5 μm . Apart from the rigid one, in order to make flexible photoanodes, electrophoresis method was utilized to fabricate the photoanode [12]. The resulting TiO₂ photoanodes were then immersed in commercial N719 dye (5×10^{-4} M) for 18 h.

Three types of testing cells were then fabricated: three-electrode cells, symmetric cells, and complete DSSCs or FDSSCs. The three-electrode cell consists of a PPTw-ITO-glass working electrode, a Pt CE, and a Pt reference electrode. The electrolyte was an acetonitrile solution containing 10 mM I₂, 50 mM LiI, and 500 mM LiClO₄. The symmetric cell was made out of two identical PPTw-ITO-glass electrodes and an electrolyte composed of 0.1 M LiI, 0.05 M I₂, 0.5 M 4-tert-Butylpyridine, and 0.6 M 1-Propyl-2,3-dimethylimidazolium iodide in 3-Methoxypropionitrile (MPN) solvent. Combining these, the DSSCs consist of dye-loaded TiO₂ photoanode, the aforementioned MPN-based electrolyte, and PPTw CE. The resulting DSSCs are either rigid or truly flexible one, depending on the type of the substrate used.

Microstructures of PEDOT:PSS and PPTw were examined via Raman microscopy (RENISHAW), equipped with a 632.8 nm He-Ne

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