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A freeze-dried graphene counter electrode enhances the performance of dye-sensitized solar cells

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ABSTRACT

A flexible graphene/polyimide (PI) counter electrode without a fluorine-doped tin oxide (FTO) layer has been fabricated for dye-sensitized solar cell (DSSCs) applications. The flexible counter electrode consists of polyimide double-sided tape as a substrate beneath a graphene film acting as the conductive and catalytic layer. Chemically reduced graphene oxide (rGO) on the PI electrode (rGO-PI) shows comparable catalytic activity to that of the reference sputtered platinum/FTO counter electrodes (Sputter-Pt/FTO). A DSSC with a freeze-dried rGO-PI (FD-rGO-PI) counter electrode shows an overall conversion efficiency (η) of 5.45%, while that of the conventional Sputter-Pt/FTO electrode is 5.52%. The DSSC with a thermally dried rGO-PI (Gel-rGO-PI) counter electrode (not freeze-dried) exhibits a smooth morphology and much poorer performance ($\eta = 1.61\%$). Field emission scanning electron microscopy, electrochemical impedance spectroscopy, and cyclic voltammetry measurements demonstrate that the FD-rGO-PI electrode possesses a porous structure, numerous edges, minimum charge-transfer resistance and a higher electrocatalytic activity toward the I_3^-/I^- redox couple than that of the Gel-rGO-PI electrode. The high electrocatalytic activity, facile preparation procedure, absence of FTO, and material flexibility render the FD-rGO-PI electrode an ideal alternative to conventional DSSC counter electrodes.

1. Introduction

Dye-sensitized solar cells (DSSCs) are conventionally composed of a mesoporous nanocrystalline TiO_2 film, a light sensitive dye, an electrolyte containing the I^-/I_3^- redox couple, and a counter electrode [1]. The counter electrode (CE) is typically prepared by depositing platinum (Pt) onto a fluorine-doped tin oxide (FTO) glass substrate. The Pt counter electrode in a DSSC collects electrons from the external circuit and catalyzes the reduction process within the iodide liquid electrolyte, thereby ensuring the continuity of electron transfer [2]. The Pt metal not only provides high catalytic activity but also is highly resistant to the corrosive liquid electrolyte [3,4]. However, to fabricate a highly catalytic Pt CE, heat treatment at temperatures greater than 380 °C is often required. These temperatures are incompatible with plastic substrates. In addition, Pt and FTO substrates are substantial contributors to the cost of DSSCs. To reduce material costs and achieve desired flexibility in DSSCs, carbon material is often considered as an alternative [5–11]. Graphite, amorphous carbon (carbon black) [5,6], nano- or micro-carbon [6–8], and carbon nanotubes (single layer, double layers and multilayers) [9–11] have all been utilized for this purpose. Graphene has been identified as an ideal CE candidate due to its high charge carrier mobility [12], good catalytic activity [13], and desirable chemical stability [14]. Many reports have demonstrated that graphene CEs perform comparably to Pt CEs [15–19]. However, in these materials, graphene is coated or sprayed onto transparent conducting oxide films (TCO glass), which require subsequent heat treatment. This heat treatment is incompatible with flexible polymer-containing CEs. Recently, Aotila et al. has fabricated a carbon-based CE for DSSCs based on an electropolymerized poly(3,4-ethylenedioxythiophene) (PEDOT) material and a single-walled carbon nanotube film, achieving an efficiency of 4.0%, approximately 93% of Pt-based solar cells (4.3%) [20]. Hou et al. also used PEDOT-polystyrene sulfonate as a catalytic layer and achieved an efficiency of 5.34%. However, no traditional Pt CE data were reported for comparison [21]. Sun et al. employed a polyaniline/carbon composite as a catalytic layer and flexible graphite as the conducting substrate, achieving an efficiency of 7.36%, approximately 93% of the efficiency of Pt-based solar cells (7.87%) [22]. Conducting polymer/graphene composite has been also applied to DSSC counter electrode by many research groups [23–25]. Hong et al. reported an efficiency of 4.5% using a counter electrode made by a graphene/PEDOT-poly(styrenesulfonate) (PEDOT-PSS) composite [23]. Wang et al. achieved an efficiency of 6.09% using a polyaniline/graphene counter electrode [24], which was close to its Pt CE counterpart 6.88%. Park et al. prepared a graphene/PEDOT without TCO and reached a comparable efficiency 6.26% to that of Pt/TCO counter electrode (6.68%)[25]. A printable graphene enhanced composite counter electrode for flexible dye-sensitized solar cells was also reported, i.e. the efficiency of flexible DSSCs using TiC/graphene/PEDOT counter electrode (4.5%) can be slightly higher than that of Pt CE (4.3%) [26]. The use of graphene materials and its composites or derivatives for flexible energy devices has become increasingly important [27].

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In this study, graphene materials were synthesized using a modified Hummers' chemical oxidation [28] and a modified Ti^{+3} ion reduction process [29], where flexible graphene materials were coated onto polyimide double-sided tape. By using this flexible graphene/PI film, a cost effective, FTO-free, high performance DSSC was fabricated.

2. Experimental details

2.1. Synthesis of GO

A modified Hummers' method was employed to synthesize the graphene oxide (GO). In a flask, 1 g of graphite (Alfa, 7 ~ 10 μm, purity ≥ 99%), 0.75 g of Na_2SO_4 (MERCK) and 30 mL of concentrated H_2SO_4 (95–97%) were mixed and ice cooled for 30 min. Gradually, 2.25 g of $KMnO_4$ (99%) was added into the ice cold solution and stirred for 2 h. After stirring at room temperature for 48 h, 300 mL of de-ionized water was added and the mixture was stirred for an additional 30 min. Then, 30 mL of H_2O_2 (35%) was added and stirred for another 1 h. The residuals were collected using centrifugation and re-washed with de-ionized water twice and ethanol once. Two GO pastes were made. One GO was freeze-dried under vacuum and the other was not. The freeze-drying of GO residuals occurred in a freeze-dryer (FD-5030, PanChum Sci. Corp. Taiwan) at −47.7 °C and 69.3 Pa for 2 days. The freeze-dried materials were then dispersed and stirred in ethanol for one day with a GO to ethanol ratio of 0.1 g GO to 1 mL ethanol. The other GO paste was obtained by heating the GO residuals at 60 °C in an oven for 4 h. Both GO residuals were then re-dispersed in ethanol (2:1) and stirred into pastes. The GO pastes were then coated onto polyimide (PI) double-sided tape with a doctor-blade, as described in the following section.

2.2. Preparation of counter electrodes

Three different counter electrodes were prepared: Gel-rGO-PI, FD-rGO-PI, and Sputter-Pt/FTO. "rGO" represents a reduced GO. The Gel-rGO-PI counter electrode was prepared using non-freeze-dried GO paste on polyimide tape, following a drying process at 80 °C. The resultant film/PI was immersed in a $Ti–Ti^{3+}$ metal-ion solution at 120 °C for 30 min. This method is a modified version of previous work [29] where Ti metal particles were not employed. In this solution, the GO film was reduced to a graphene film. The reduced GO film/PI was washed with water three times. The FD-rGO-PI counter electrode was obtained using the freeze-dried GO paste and the same processing as described for Gel-rGO-PI. The resultant rGO film on the PI polymer substrate was estimated by FESEM at approximately 20 μm in thickness. The Sputter-Pt/FTO counter electrode is a traditional Pt counter electrode, synthesized by sputtering Pt on an FTO glass substrate and annealing at 380 °C. Sputtering was performed with a Cressington 108 auto-sputter system at 20 mA for 150 s.

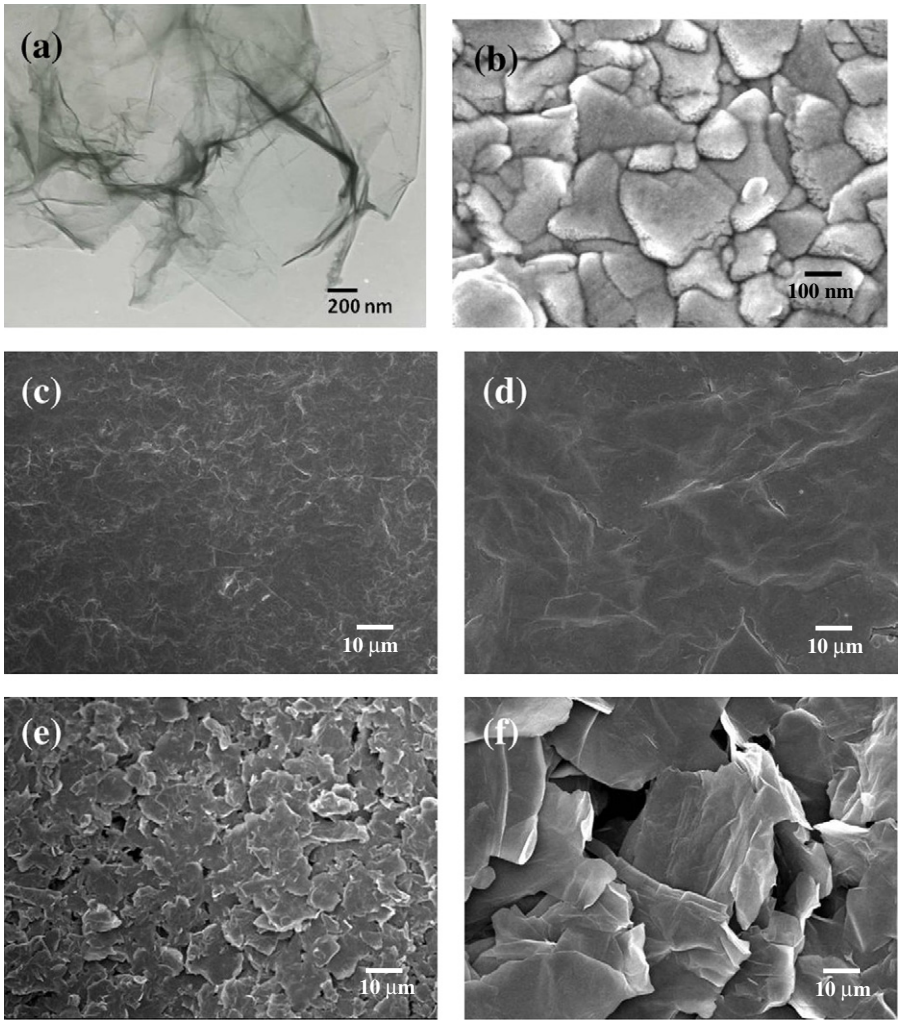

Fig. 1. (a) TEM image of an rGO sheet not yet coated on PI substrate, (b) FESEM image of Sputter-Pt/FTO, (c) (d) FESEM image of Gel-rGO-PI, ×1000 and ×10,000 magnification, respectively. (e) (f) FD-rGO-PI, ×1000 and ×10,000 magnification, respectively.