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Thickness-self-controlled synthesis of porous transparent polyaniline-reduced graphene oxide composites towards advanced bifacial dye-sensitized solar cells

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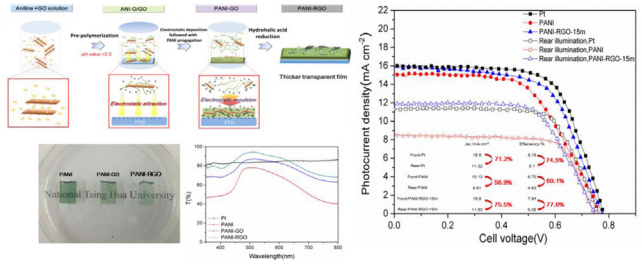
HIGHLIGHTS

- A two-step approach is demonstrated to fabricate a porous, ultrathin PANI-RGO electrode.
- The thickness can be self-controlled by pH adjustment.
- The well-designed PANI-RGO electrodes exhibit excellent photovoltaic performances.
- The incorporation of RGO raises the transparency of PANI and photo harvest.
- A universal approach is well-designed to fabricate PANI-RGO-based conductive thin films.

GRAPHICAL ABSTRACT



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ABSTRACT

A powerful synthesis strategy is proposed for fabricating porous polyaniline-reduced graphene oxide (PANI-RGO) composites with transparency up to 80% and thickness from 300 to 1000 nm for the counter electrode (CE) of bifacial dye-sensitizing solar cells (DSSCs). The first step is to combine the *in-situ* positive charge transformation of graphene oxide (GO) through aniline (ANI) prepolymerization and the electrostatic adsorption of ANI oligomer-GO to effectively control the thickness of ultrathin PANI-GO films by adjusting pH of the polymerization media. In the second step, PANI-GO films are reduced with hydroiodic acid to simultaneously enhance the apparent redox activity for the I_3^-/I^- couple and their electronic conductivity. Incorporating the RGO increases the transparency of PANI and facilitates the light-harvesting from the rear side. A DSSC assembled with such a transparent PANI-RGO CE exhibits an excellent efficiency of 7.84%, comparable to 8.19% for a semi-transparent Pt-based DSSC. The high light-harvesting ability of PANI-RGO enhances the efficiency retention between rear- and front-illumination modes to 76.7%, compared with 69.1% for a PANI-based DSSC. The higher retention reduces the power-to-weight ratio and the total cost of bifacial DSSCs, which is also promising in other applications, such as windows, power generators, and panel screens.

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1. Introduction

Bifacial dye-sensitising solar cells (DSSCs) have recently attracted the attention of several research groups [1–5] because of a higher light-harvesting efficiency regarding the ability of both-side incident illumination absorption. This property substantially reduces the cost of energy generation and the limitation of the incident angle and direction of DSSCs. Moreover, the transparent property renders the bifacial DSSCs a highly promising device for building-integrated photovoltaic systems and portable power generators in which the bifacial DSSCs must combine with transparent substrates, such as building windows, lampshades, portable device displays, and panel screens [1–5]. Accordingly, the design and fabrication of a transparent counter electrode (CE) with a high ability for reducing I_3^- to I^- to complete the cycle of electron transport is highly demanded.

Platinum is a common active component of the CE in DSSCs because of its excellent redox activity for the I_3^-/I^- couple. Thus, transparent thin-layer Pt CEs have been fabricated through sputtering or thermal deposition [3,6]. However, the high cost, the high energy-consuming process, and the high reflectance of thin Pt films restrict the realisation of a bifacial DSSC module [7]. Accordingly, numerous functional materials, including carbon-based nanomaterials and conducting polymers, have been proposed to replace Pt as alternative materials of CEs in DSSCs. Carbon-based nanomaterials, such as carbon black [8], activated carbon [9,10], graphite [10–12], carbon nanotubes [13,14], graphene [15–17], and carbon nanotube-graphene composites [18,19], have been well studied. However, the catalytic activity of carbons for reducing I_3^- to I^- primarily derives from defects and oxygen-containing functional groups that block the electron transport on the graphene plane. Consequently, a certain thickness is required to achieve favourable electronic conductivity and acceptable catalytic activity. In other words, the photovoltaic performance of bifacial DSSCs with a carbon-based CE is generally lower than that of a device with a Pt CE [16,17]. However, conductive polymers such as poly(3,4-ethylene-dioxythiophene) [20], polyaniline (PANI) [3,21–25], polypyrrole (PPy) [26], and poly(3,3-diethyl-3,4-dihydro-2*H*thieno-[3,4-*b*] [1,4] dioxepine) (PProDOT-ET2) [27], have also been employed as CEs in DSSCs. Amongst these conducting polymers, PANI is particularly suitable for the CE of bifacial DSSCs because of its environmental stability, simple and environmentally friendly processing [28], and complementary light absorption to N719 and N3 dyes, which maximise the use of rear illumination for DSSCs [3].

Recently, composites of PANI and carbon nanomaterials have attracted considerable attention because the introduction of nanocarbons effectively enhances the catalytic activity of PANI, resulting in the superior performance of DSSCs [29-32]. Drop-casting and Spin-coating is an easy way to fabricate transparent PANI/nanocarbon CE but this method only can be conducted in fabricating small devices, lacking practicability. To prevent the catalytic film from peeling off the substrate, several investigations involving electro- polymerisation to simultaneously deposit PANI and nanocarbons onto the substrate have been conducted [30-32]. However, no literature proposes an effective approach to fabricating a transparent PANI/nanocarbon CE, possibly due to that electropolymerisation generally produces a compact layer that depresses the penetration of electrolytes. As a result, the optimal performance was obtained at several micrometres of composites [22]. Chemical deposition using electrostatic adsorption to combine PANI and RGO or carbon nanotubes with a layer-by-layer structure has also been proposed while the low transparency, caused by the high content of nanocarbons, restricts the use of this method with bifacial DSSCs [33,34]. An interfacial polymerization has been proposed and successfully fabricated a transparent PANI/nanocarbon film [35]. However, this method requires the use of organic solvent and rigorous parameter control for modulating thickness of films. Moreover, the thin film easily peels off from the substrate because of weak interaction between film and substrate. These reasons restrict the practicability of this method to prepare a transparent PANI/nanocarbon CE. Accordingly, preparing a transparent PANI/nanocarbon CE for bifacial DSSCs with excellent performances is a big challenge.

This study presents a simple, two-step approach to fabricating transparent thin films consisting of PANI and RGO using 1) an *in-situ* positive charge transformation of GO through aniline pre-polymerisation onto GO (denoted as ANI-O/GO) and electrostatic adsorption of positively charged ANI-O/GO onto fluorine-doped tin oxide (FTO), and 2) chemical reduction of PANI/GO films with hydroiodic acid (Scheme 1). In this approach, PANI not only acts as a spacer to prevent the restacking of RGO during the reduction process but also reverses the net negative charge to a positive charge around the surface of the GO during the pre-polymerisation (i.e., the ANI-O/GO formation step). The latter effect supplies an electrostatic driving force for ANI-O/GO particles to adsorb onto the negatively charged FTO surface (similar to self-assembly). Moreover, the thickness of the PANI-GO films can be self-controlled by adjusting the pH value of the precursor solution from this unique deposition mechanism. Here, the extensive oxygen groups on the well-dispersed GO in the aniline precursor solution to work as nucleation sites of the PANI propagation, leading to clear enhancement in the electrolyte-accessible area and larger short-circuit current density (J_{SC}). Furthermore, hydroiodic acid was used to prevent possible exfoliation of films caused by gas evolution when other strong reducing agents, such as sodium borohydride or hydrazine, were adopted. The RGO constructs great conductive paths within PANI, leading to faster electron transfer and larger fill factor (FF). Thus, the well-designed polyaniline-reduced graphene oxide (PANI-RGO) electrodes retained a fairly high transparency (despite contain RGO) and exhibited an excellent photovoltaic performance. Such an outstanding performance has not been achieved before because of the lack of effective transparency retention of the PANI/nanocarbon electrodes [30-32,36].

In this study, the microstructure and electrocatalytic activity of PANI-RGO and polyaniline-graphene oxide (PANI-GO) with various deposition times are examined systematically to propose the unique deposition mechanism of this novel synthesis approach. In addition, transparent bifacial DSSCs were successfully fabricated and characterised. The incorporation of RGO raised the transparency of CEs and enhanced the rear-illumination performance of DSSCs. Moreover, this transparent PANI-RGO electrode with excellent electrochemical activities is promising for other electrochemical systems, such as photo-electro-chromic devices [37], supercapacitors [38], and sensors [39], responding to the gradually increasing demand for transparent devices.

2. Experiment

2.1. Preparation of graphene oxide (GO)

Graphene oxide was prepared from raw graphite powders by a modified Hummers' method according to our previous study [40]. In a typical process, 0.25 g graphite, 0.125 g $NaNO_3$, 12 ml H_2SO_4 (98%), and 0.75 g $KMnO_4$ were added into a flask with continuous stirring for about 15 min in an ice bath. Then, this solution was ultrasonically aged in an ice bath for 3 h (Delta, 40 kHz and 200 W). Subsequently, 12 ml deionized (DI) water was added slowly into the above solution which was continuously stirred for 12 h. Finally, hydrogen peroxide was added to react with the residual permanganate and manganese dioxide. Rinsing with DI water,