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An investigation of the dye-sensitized solar cell performance using graphene-titania (TrGO) photoanode with conventional dye and natural green chlorophyll dye

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ABSTRACT

Development of innovative low-cost and efficient DSSCs (dye-sensitized solar cell) device for solar energy conversion is essential. In this present study, the performance of DSSCs based on graphene-titania (TrGO) photoanode using conventional N719 (synthetic dye) and natural green chlorophyll dye (organic dye) were extensively studied, analysed and discussed. TrGO was successfully synthesized via one step sol precipitation peptization technique using titanium (IV) isopropoxide (TTIP) and reduced graphene oxide (rGO) as starting materials. It was found that TrGO-2 exhibited the highest photocurrent generation among samples regardless of dye type. DSSCs device fabricated using N719 dye showed 9.15 mA cm^{-2} of photocurrent with 3.95% efficiency whereas DSSCs device using natural chlorophyll green dye exhibited photocurrent density of 3.43 mA cm^{-2} with 0.67% efficiency. From the Tauc plot, band gap was narrowed from 3.17 eV of TiO_2 to 2.78 eV of TrGO considering the graphene extended the absorption range of the film to the visible light region. The main reason was associated with the better surface contact of the TiO_2 dopants with the rGO film resulting in a lower charge transfer resistance.

1. Introduction

Historically, M. Gratzel and O'Regan successfully demonstrated the first 3rd-generation solar cells known as DSSCs which converted the light energy into electricity via the electron-transfer event between the dye (sensitizer) and the metal oxide in 1991 [1–6]. In 2005, Nazeeruddin et al. [4] reported that the champion DSSCs sensitized with N719 dye (ruthenium complexes) illustrated approximately 10% of power conversion efficiency under AM 1.5. However, DSSCs using ruthenium complexes suffered from shortcomings in terms of their high cost (due to the limited production of ruthenium) and hazardous nature of ruthenium (non-environmental friendliness of the heavy metal) [7].

In recent years, dyes derived from natural sources as the photosensitizer for DSSCs have been extensively studied as the possible inexpensive and eco-friendly alternatives to the conventional material with high light-harvesting efficiency, [5,8,9]. In order to bring the renewable solar energy to the point of commercial readiness, substantial research efforts towards the development of hybrid semiconductor/photoelectrode for high-efficient DSSCs have been developed.

Accordingly, natural dyes especially cyanine, chlorophyll, anthocyanin, carotene and flavonoid have been extensively studied as sensitizers in DSSCs. This is attributed to the fact that the electronic structures of the plant pigments have the ability to interact with sunlight and turn it into an electric current by altering the wavelength [10]. In the present study, green chlorophyll extracted from the pandan leaves (*Pandanus amarylliforus*) was extracted as the natural green chlorophyll dye pigment. Specifically, chlorophyll could be classified as a unique pigment ascribed to its ability to conduct photosynthesis converting the light energy to transduction energy in plant. Additionally, chlorophyll (a mixture of 2 pigment complexes, namely chlorophyll a and b) is an attractive candidate as the sensitizer in DSSCs attributed to its tendency to absorb blue and red lights. Also, many research works have been focussed on the preparation of porphyrin-type organic dye from chlorophyll due to its low lost, ease of preparation and eco-friendly. Although the commercialized N719 (ruthenium transition metal polypyridyl complexes) is the most widely used synthetic dye with photoelectric conversion efficiency (PCE) of > 10% [11], DSSCs equipped with natural dyes as the sensitizers have several advantages over the synthetic N719 dye considering the latter contains heavy metal and is not cost effective.

In other respect, it has been reported that DSSCs photoanode composed by the thick mesoporous TiO_2 nanoparticles (~ 10 to 15 μm)

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network would serve as a large-specific-surface-area anchoring site for the dye molecules to absorb in the photoanode. In an open literature, titanium dioxide (TiO_2) itself has recorded a remarkable high photo-conversion efficiency (PCE) in DSSCs. However, TiO_2 tends to suffer from shortcomings in terms of its relatively large band gap, which results in the fast recombination rate. One possible explanation is that the injected electron tends to travel in the random colloidal particle matrix and grain boundaries of TiO_2, creating a random transfer route followed by the trap-limited diffusion process [12]. In other words, the charge carrier recombination rate increases tremendously, which leads to the reduction of the PCE in DSSCs. Taking these facts into serious consideration, it is of great important to introduce a highly conductive material in metal oxide semiconductor to enhance the PCE.

Correspondingly, reduced graphene oxide (rGO) which is inexpensive and abundance has been attracted tremendous research interest in the field of photovoltaic DSSCs [13–18]. Due to its remarkable properties such as good flexibility, zero bandgap, high mobility carrier coupled with large surface area, graphene appeared as one of the promising carbonaceous materials that has been widely used as photoanodes in DSSCs device [19–23]. It is noteworthy to mention that the rGO has a matching conduction band with TiO_2 and thereby, a rapid charge transfer could be triggered between the rGO and TiO_2 surface. Also, the photo-induced electrons can move through rGO bridge rather than TiO_2 – TiO_2 grain boundary as a result of the diminished charge recombination [24]. In view of these facts, the combination of TiO_2 and rGO to produce the TiO_2/rGO composites is an alternative route to further improve the conduction pathways and PCE of DSSCs from the point of photo-induced electrons at photoanode to the charge collector electrode.

In the present research study, a novel method (one step sol precipitation peptization technique) to encapsulate TiO_2 into the rGO photo-anode film was developed with the aim to enhance the photocurrent of DSSCs by minimizing the electron transfer resistance in the device and intensifying the electron transport rate. Innovative approaches by using one step sol precipitation peptization technique to synthesis hybrid of TiO_2/rGO composites as photoanode are crucial for developing efficient DSSCs system. Notably, one-step one step sol precipitation peptization technique contributed well TiO_2 particles in well crystalline formed without agglomeration on rGO sheets. Furthermore, the performance of the photoanode sensitized with natural dye has also been studied to evaluate the photocurrent performances and absorption compatibility between the natural dye and TiO_2/rGO photoanode. It is also of great important to tailor the morphology of the photoanodes by optimizing the ratio of TiO_2 and rGO in the composites to provide more conductive pathways for photo-induced electron transfer. To the best of our knowledge, there have been very limited reports of one-step synthesis of TrGO composite through sol precipitation peptization technique that resulted in high PCE in DSSCs. Therefore, this study aims to optimize the TiO_2/rGO ratio for improving the PCE in the natural green chlorophyll- and N719-sensitized DSSCs.

2. Materials and methods

2.1. Material

Natural graphite powder (< 20 μm), analytical grade sulphuric acid (H_2SO_4, 95.0–98.0%), phosphoric acid (H_3PO,85.0%), potassium permanganate ($KMnO_4$,99.9%), hydrogen peroxide (H_2O_2, 30 wt%), hydrochloric acid (HCl, 37.0%), hydrazine solution 37%, titanium (IV) isopropoxide (TTIP, 97.0%), ethanol (EtOH, 99.0%), nitric acid (HNO_3, 68.0%), fluorine tin oxide (FTO) conducting glass slides (7 Ω/sq) and triton X-100 laboratory scale were purchased from Sigma Aldrich. N719 (ruthenizer 535-bis TBA) and electrolyte EL-HPE were supplied by Dyesol.

2.2. Preparation of graphene oxide (GO) and reduced graphene oxide

Huang's method for the preparation of graphene oxide (GO) [21] was adopted in the present study [18]. Accordingly, the one-pot chemical oxidation of graphite was carried out at room temperature for 3 days to allow the oxidation of graphite for the preparation of GO. The solution was then subjected to centrifugation at 10,000 rpm to form the GO gel. The dried GO powder was then subjected to reduction process to prepare the reduced graphene oxide. Specifically, GO solution was prepared by adding the GO powder to a flask containing 3 mg/ml of purified water. The hydrazine solution was immediately added to the GO solution, followed by refluxing in an oil bath at 80 °C overnight. The black precipitate was then filtered and dried to obtain the rGO powders.

2.3. Synthesis of TrGO (graphene-titania) nanocomposite

In the present work, the precursor solution [solution A] was prepared by dissolving 11 ml TTIP in 50 ml propanol. In the meanwhile, 0.01 g rGO powders were dispersed in 50 ml DI water, followed by sonication for 2 h. 1.5 ml nitric acid serving as an oxidizing agent was then added to the as-prepared rGO solution to prepare solution B. Solution A was added dropwise into the solution B with a constant stirring and then allowed to stand for aging for 6 h at 80 °C. Next, the collected sol was dried at 60 °C to obtain the TrGO nanocomposite powder. Finally, the nano-powder was annealed at 450 °C for 6 h, and then allowed to cool until it has reached room temperature. The same procedures were repeated to prepare TrGO nano-composites containing different weight percentages of rGO; TrGO-1 0.01 g, TrGO-2 0.03 g and TrGO-3 0.05 g, respectively.

2.4. Preparation of TiO_2 paste and TrGO paste

Fluorine-doped tin oxide covered glass (FTO) was used as the substrate in the present work to fabricate the photoanode. Accordingly, the FTO glass was first soaked in acetone and then subsequently cleaned in an ultrasonic bath for about 15 min to remove all contaminants present on the surface of the substrate, followed by rinsing with DI water and isopropanol. To prepare TrGO paste, 2.0 g TrGO powder was initially dispersed into 10 ml absolute ethanol and left to stir at room temperature for 2 h, followed by sonication for approximately 30 min until a homogeneous suspension was formed. Finally, a drop of trixton-100 was added to the solution. Adopting the doctor blade technique, the TrGO paste was spread on the FTO substrate, followed by drying at room temperature for about 30 min and heating at 100 °C for 10 min to prepare the photoanode electrode. The semiconductors were then subjected to a final thermal sintering process at 450 °C for 30 min. For the sake of comparison, a pure TiO_2 paste and photoanode were fabricated using the same procedure as of those TrGO.

2.5. Dye preparation

Two different types of dyes (i.e., conventional N719 dye and natural extracted green chlorophyll dye) were prepared in the present study. Correspondingly, N719 (ruthenizer 535-bis TBA) was diluted with ethanol to prepare the 0.5 mM N-719 dye ethanol solution. In the meanwhile, Soxhlet extraction method was adopted to extract the natural green chlorophyll dye from pandan leaves. Specifically, 10 g of pandan leaves (source of chlorophyll) was initially cut into smaller pieces and filled in the net cloth. 250 ml ethanol was used as the solvent for the extraction process. Following this, extraction of dye pigment was carried out in a Soxhlet extractor overnight. Next, the chlorophyll pigment solution was placed in rotary evaporator to prepare the chlorophyll pigment in gel form.(Fig. 1)