

DYE-SENSITIZED SOLAR CELLS BASED ON TiO₂-GRAPHENE COMPOSITE ELECTRODE

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable interests because of their relatively low cost and high efficiency for the photoelectrical conversion of solar cells since Gratzel's group introduced nanostructured TiO₂ film into anode electrodes [1]. Although 11% conversion efficiency was obtained [2, 3] further improvements are still necessary. The major bottleneck is the transport of photogenerated electrons across the TiO₂ nanoparticle network, which competes with the charge recombination. To suppress the recombination and improve the transport, there are several strategies including (1) using composite metal oxides as the semiconductor with different band gaps [4], (2) preparing the porous structure whose direction is perpendicular to the conducting substrate [5-10] and (3) introducing charge carriers (1D nanomaterials) to direct photogenerated electron [11-13]. Graphene, consisting of a single atomic layer of graphite, has generated increasing interest because of its unique properties and potential applications [14]. To date, various synthetic methods, such as mechanical exfoliation, epitaxial growth, chemical and electrochemical reductions of graphite oxide and bottom-up organic synthesis, have been developed for producing graphene [15]. Among them, the reduction of exfoliated graphene oxide (GO) was proven to be an effective and reliable method to produce graphene nanosheets (GNS) owing to its low cost and massive scalability. Recently, graphene-based composite materials have triggered more attention due to the synergistic contribution of two or more functional components and many potential applications. Remarkable, the requirement to obtain graphene as individual sheets and to maintain it in the reduced form still remains a great challenge in designing composite systems. Great efforts have been made to uniformly incorporate

GNS into composite materials and explore their applications in various fields, which include quantum dots [16], metal nanoparticles [17], metal oxides [18], and conducting polymers [19] and so on. Therefore, new strategies to synthesize graphene-based composite nanosheets are indispensable. Particularly, the utilization of various carbonaceous materials, such as mesoporous carbon [20] and carbon nanotubes [21], as the building block for the TiO₂-based composites for potential photocatalysts has been investigated extensively. Based on the unique properties of the graphene, considerable efforts have been made to incorporate GNS into TiO₂ based composite materials [22]. For example, Li's group prepared a chemically bonded TiO₂-graphene nanocomposite photocatalyst with graphene oxide and P25 using a facile one-step hydrothermal method, which showed high photodegradation performance for methylene blue [10]. Yangqiao et al. reported a Enhanced dye-sensitized solar cell using graphene-TiO₂ photoanode prepared by heterogeneous coagulation method [23]. Furthermore, a strong tendency for aggregation makes graphene intrinsically graphite, which not only alters the electro-optical properties of the graphenes, but also prevents their interfacing with other materials. Therefore, novel and facile approaches to preparation of homogenous colloidal suspensions of high-quality TiO₂-GNS remain a great challenge.

In this report, using a simple direct mixing method, we describe preparation and characterization of a TiO₂-GNS composite used as the materials for the DSSC working electrode. The energy conversion efficiency and the electrochemical impedance of the fabricated cells have been determined. With this method, no orderly arrangements of GNS have been observed on the conductive substrate; however, a comparable improvement in the energy conversion

efficiency of our DSSCs to those with well aligned GNS electrode has been achieved. Importantly, our technique could be compatible to a large scale production using existing DSSC fabrication technology.

2. Experimental details

2.1 Synthesis of graphene nanosheets (GNS)

Graphene oxide was prepared via a modified Hummer's method [24, 25] starting from natural graphite flakes (98%, 50 mesh, Hyundai Coma Ind. Co., Korea). The graphite flakes (3g; 2-5 mm in lateral size) were first incubated in H₂SO₄ (98%, 12ml) without stirring and kept at 80°C for 4.5h. The solution was then cooled down to room temperature and sonicated in water bath for 2h to obtain tens of micron-sized graphite flakes. It is noted that the sonication time is crucial for the size of the resulting graphene oxide sheets; the shorter the sonication time, the larger the GO sheets. Subsequently, the solution was diluted with 0.5L de-ionized (DI) water and left overnight. The pre-oxidized graphite powder was obtained after filtering the solution using 200nm Nylon Millipore filters, followed by washing with DI water. To exfoliate the pre-oxidized graphite powders into single-layer GO sheets, the powder (2 g) and 10.0-15.0 g KMnO₄ was added into H₂SO₄ not exceeding 125ml under ice-bath cooling and stirred for 2h. The solution was diluted in DI water (250ml), then 20ml H₂O₂ (30%) added to it at room temperature. After precipitation for 12h, the upper supernatant was collected and centrifuged, where the GO powders were obtained as precipitates. To remove the metal ions existing in the GO powders, they were dissolved in HCl solution (HCl:H₂O =1:10 (volume ratio)) and recovered from centrifugation. The GO powders were further dissolved in DI water and recovered after centrifugation to remove the unwanted HCl [26].

2.2 Fabrication of DSSCs

In the preparation of working electrode (WE) for DSSC, FTO glass substrates purchased from Pilkington (~10 ohm/cm²) were used. Prior to use the FTO substrates were cleaned by ultrasonication in de-ionized water, acetone and isopropyl alcohol for 15 min each and then dried before O₂ plasma

cleaning. The composition of TiO₂-GNS composite electrodes are shown in Table 1. 0.2g of poly ethylene glycol (PEG MW 10000) was dissolved with the mixed solvent containing 2 ml of D.I. water and 2.5 ml of ethanol. Then 1.0 g of TiO₂ was added to make the suspension of TiO₂. After the suspension was dispersed TiO₂ electrodes were prepared by doctor-blade technique on fluorine-doped tin oxide (FTO) glass for comparison. For the preparation of graphene composite electrodes, 0.1mg of GNS was added into the suspension (0.01%). After that, it was stirred for about 30 min to let GNS dispersed in the suspension well, until it can anchor TiO₂ perfectly: then TiO₂-0.01% electrode was prepared. Also, the electrodes with 0.02, 0.025, 0.03, 0.06, 0.2wt% content of GNS were prepared (TiO₂-GNS0.02%, TiO₂-GNS0.025%, TiO₂-GNS0.03%, TiO₂-GNS 0.06% and TiO₂-GNS0.2%) in the same way. Then they were annealed at 450°C for 1h, then cooled to 80°C and immersed in to the N3 dye solution with a concentration of 3x10⁻⁴ M in ethanol for 24 hr. The organic solvent-based liquid electrolyte was prepared from the solution of 0.6 M dimethylpropylimidazolium iodide, 0.1 M of iodine, 0.5 M tert-butylpyridine, and 0.1 M of lithium iodide in 3-methoxyacetonitrile. Pt sputtered on FTO was used here as the counter electrode. Sandwich type cell assembly was made by clamping the N3 Dye sensitized TiO₂-GNS composite working electrode, a drop of electrolyte and Pt counter electrode with two clips.

Table.1. Composition of TiO₂-GNS composite working electrodes.

| Samples | TiO ₂ (g) | GNS (mg) | PEG (g) |
|----------------------------|----------------------|----------|---------|
| TiO ₂ | 1.0 | 0.0 | 0.2 |
| TiO ₂ -GNS0.01% | 1.0 | 0.1 | 0.2 |
| TiO ₂ -GNS0.02% | 1.0 | 0.2 | 0.2 |
| TiO ₂ -GNS0.03% | 1.0 | 0.3 | 0.2 |
| TiO ₂ -GNS0.06% | 1.0 | 0.6 | 0.2 |
| TiO ₂ -GNS0.2% | 1.0 | 2.0 | 0.2 |

2.3 Characterization and Measurements

The morphology of the films was investigated by field emission scanning electron microscope (FESEM) (Hitachi S-4500 model). Fourier transform-Infrared (FT-IR) spectra were recorded on a FT/IR-4100 spectrometer with KBr pellets in the 4000-400cm⁻¹ region. Ultraviolet-Visible (UV-vis)

diffuse reflectance spectra of the TiO_2 and TiO_2/GNS were obtained using an UV-vis spectrophotometer (UV-670). The current density versus voltage (J - V) characteristics of the solar cell devices in the dark and under white light illumination were measured with an AM 1.5G solar simulator (300 W, Newport, USA) in $100 \text{ mW}/\text{cm}^2$ conditions, adjusted with a standard PV reference cell (2 x 2 cm, a monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) with a Keithley 2400 source-measure unit. The all photovoltaic properties such as open circuit voltage (V_{oc}), Short circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (EFF) were calculated from J - V curves. The electrochemical impedance spectroscopy (EIS) measurements were performed with a computer controlled Autolab, Versastat-3. The magnitude of alternative signal was set to 10 mV. A conventional cell with three electrode system was used for EIS measurements with 2.5mM $\text{Fe}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) solution as supporting electrolyte, composite with varying percentage of GNS in TiO_2 were used as WE and Pt as a counter electrode and Ag^+/Ag as a reference electrode.

3. Results and discussion

From the SEM images (Figure 1), we found that the GNS were well-dispersed among the TiO_2 nanoparticles, and there was good contact between the Graphene and TiO_2 nanoparticles. When the content of GNS exceeded from 0.06 to 0.2wt%, the surface area of the TiO_2 with adsorbent dyes significantly decreased and the number of cracks on the surface of the porous TiO_2 electrode increased, resulting in a lower current density. If the TiO_2 film containing too many GNS, the bare surface of the GNS, which are not covered dyes would increase the electron recombination process on the working electrode surface, resulting in a lower V_{oc} . With the higher GNS loading, there will be light harvesting competition between N3 dye and GNS, and the dye adsorption was reduced because the TiO_2 is surrounded by GNS. At the same time, the excessive GNS can act as a kind of recombination center instead of providing an electron pathway, and the short circuit will happen easily. All of these lead to the decrease of the total efficiencies [27]. UV-vis spectroscopy was used to measure the dye-

absorption ability of TiO_2 -GNS film which would be related to the film surface and porous morphology. Figure 2 shows the UV-vis absorption spectra of dye which is obtained by immersing the dye-coated electrode in N3 dye for 24 hours. As the result, TiO_2 containing 0.01wt% GNS shows the greatest absorption ability as shown by the highest absorption intensity of N3 dye at the wavelength of both 535nm. The increase of GNS content resulted in the decrease of dye-desorption corresponded to the agglomeration and dense packing of TiO_2 particles as observed from SEM.

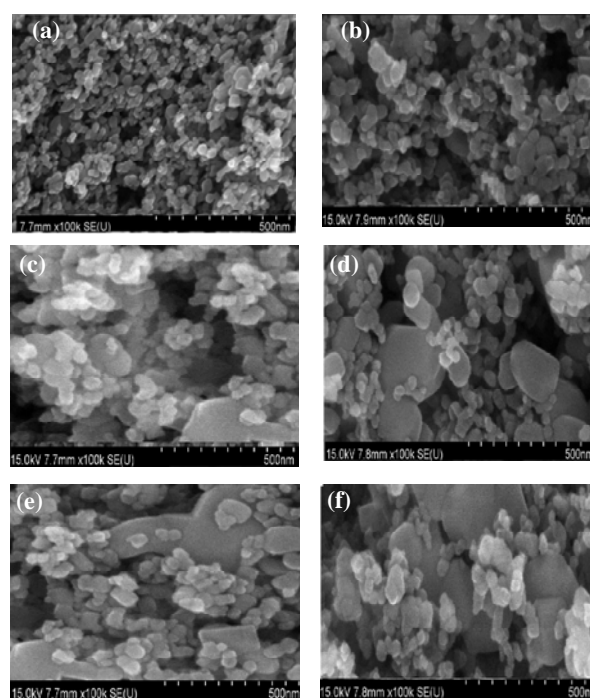


Fig.1. SEM images of (a) 0 (b) 0.01 (c) 0.02 (d) 0.03 (e) 0.06 and (f) 0.2wt% GNS incorporated TiO_2 film.

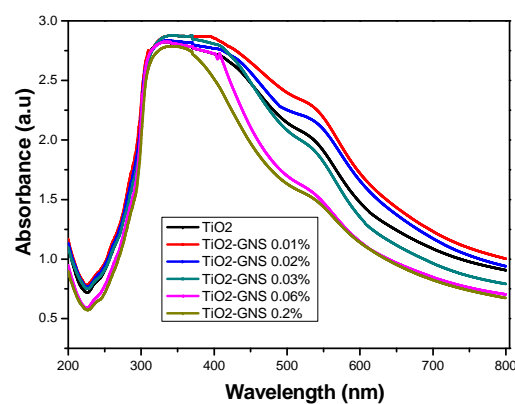


Fig.2. Optical absorption spectra of N3 dye from TiO_2 films containing 0~0.2wt% GNS.

Figure 3 shows the FTIR spectra of GNS (curve 1), TiO₂ (curve 2), and as prepared TiO₂-GNS (curve 3). Pure TiO₂ showed a low wavelength band around 690 cm⁻¹, which corresponds to the vibration of Ti-O-Ti bonds (curve 2). For TiO₂-GNS (curve 2), the broad absorption at this low wavelength (below 1000cm⁻¹) was attributed to the vibration of Ti-O-Ti bonds in TiO₂, similar to that in the spectrum of TiO₂. The absorption band appearing at ca. 1600cm⁻¹ clearly showed the skeletal vibration of the graphene, attributed to C=O stretching. This skeletal vibration peak was also observed in the FTIR spectrum of graphene prepared by reduction of GO (curve 1). However, in the as-prepared TiO₂-GNS, the broad absorption below 1000 cm⁻¹ was much plumper than the corresponding peak in pure TiO₂. In fact, this peak can be looked at as a combination of Ti-O-Ti vibration and Ti-O-C vibration (798 cm⁻¹) [28]. The presence of Ti-O-C bonds indicated that, during the reduction, graphene oxide, with the residual carboxylic acid functional groups, firmly interacted with the surface hydroxyl groups of TiO₂ nanoparticles and finally formed the chemically bonded TiO₂-GR composites [29].

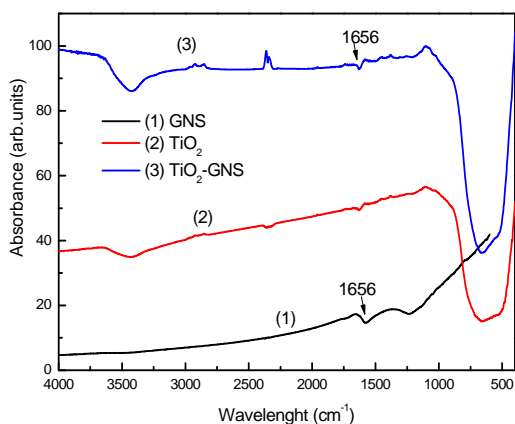


Fig.3. FTIR spectra of GNS, TiO₂ and TiO₂-GNS composites.

The comparative photovoltaic performance of the DSSCs based on working electrode and composite working electrodes prepared by varying composition of GNS is shown in Figure 4. Voc, JSC, FF and EFF values obtained for each DSSC are summarized in Table 2. DSSC with TiO₂ working electrode has shown EFF of 5.0%. For the composite, it is observed that both Jsc and EFF increase initially with increase in GNS content. Amongst the different composite working electrodes, the DSSC with a

TiO₂-GNS0.01% working electrode had the highest Jsc of 11.28 mA cm⁻², resulted in a good EFF of 5.73% which is comparable to the one using the TiO₂ electrode (4.53%). At the best conditions, the incorporation of GNS at 0.01wt% in the TiO₂ films increases the conversion efficiency by approximately ~27%, compared to the conversion DSSCs. Furthermore, for 0.01 wt % TiO₂-GNS, value of short circuit photocurrent density (Jsc) is found to be increased by ~30% from 8.67 to 11.28mA cm⁻², when compared to as prepared TiO₂ electrode. The strong enhancement of Jsc of the DSSCs with 0.01wt% GNS suggests that GNS should play an important role in enhancing the conductivity of the TiO₂ films. However, at higher GNS contents, the solar conversion efficiency decrease, which should be explained by the solar energy loss from the optical absorption of the carbon materials.

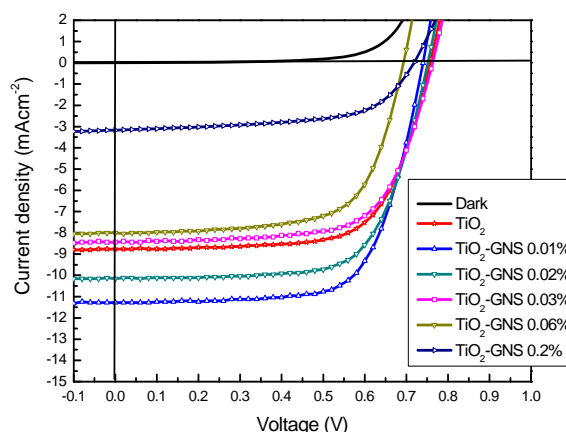


Fig.4. Photocurrent density-voltage characteristics of different working electrodes.

Figure 5 shows Nyquist plots recorded for TiO₂, and TiO₂-GNS electrode in the frequency range of 1 Hz to 100 KHz. It is observed that, with the introduction of GNS, through in small amount, the semicircle in the plot became shorter, which indicated a decrease in the solid state interface layer resistance and the charge transfer resistance on the surface [30]. Overall, both the electron accepting and transporting properties of GNS in the composite could contribute to the suppression of charge recombination.

In summary, TiO₂ nanoparticles and GNS were directly mixed at different concentrations and then Doctor blade method on the FTO conductive glass substrate. The small amount of the GNS resulted in

the greater active film surface; whereas, the large amount of the conductive carbon material resulted in the agglomeration of TiO₂ particles. UV-Vis measurement showed that the addition of GNS at the concentration of 0.01wt% increased the dye absorbance ability on the TiO₂ films. Further increase of the amount of GNS in the working electrode resulted into the reduced dye-adsorption ability on the film surface. The degradation of the DSSCs performance at the GNS content of 0.02% or higher are preliminarily discussed in terms of the TiO₂ surface structure. Comparison of J-V characteristics measurement with the conventional TiO₂ electrode, the presence of GNS at the concentration of 0.01wt% revealed an increase in a short-circuit photocurrent of 30% and an overall energy conversion efficiency of 27%. The electrical conductivity and effective surface area play a major role in determining the energy conversion efficiency of the GNS-incorporated DSSCs.

Table.2. Photovoltaic properties of the DSSCs with TiO₂-GNS composite working electrodes.

| Samples | J _{sc} (mA/cm ²) | V _{oc} (V) | FF | EFF (%) |
|----------------------------|---------------------------------------|---------------------|------|---------|
| TiO ₂ | 8.67 | 0.76 | 0.68 | 4.53 |
| TiO ₂ -GNS0.01% | 11.28 | 0.74 | 0.69 | 5.73 |
| TiO ₂ -GNS0.02% | 10.1 | 0.75 | 0.68 | 5.21 |
| TiO ₂ -GNS0.03% | 8.4 | 0.76 | 0.70 | 4.31 |
| TiO ₂ -GNS0.06 | 8.0 | 0.69 | 0.67 | 3.72 |
| TiO ₂ -GNS0.2 | 3.17 | 0.72 | 0.60 | 1.37 |

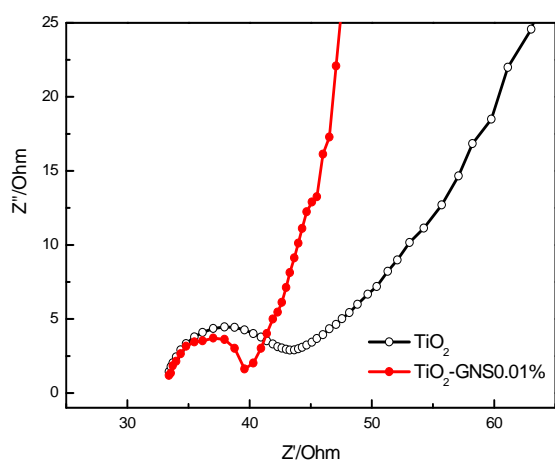


Fig.5. Nyquist plots measured for TiO₂, and TiO₂-GNS0.01% working electrodes.

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