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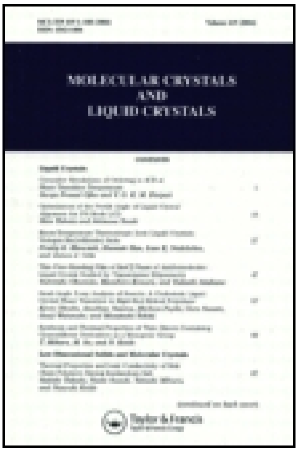

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# Efficiency Characteristics of Dye-Sensitized Solar Cells (DSSCs) by Incorporation of $TiO_2$-Reduced Graphene Oxide Composite Electrodes

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*We successfully fabricated the $TiO_2$-based photoelectrode doped with reduced graphene oxide (rGO) to improve the power conversion efficiency of dye-sensitized solar cells (DSSCs). The ratio of rGO was 0.3∼1.5 wt%. The DSSCs with the $TiO_2$ photoanode incorporated 0.3 wt% rGO showed a maximum power conversion efficiency of 6.26% which is 44% higher than the pristine $TiO_2$ photoelectrode. We concluded the introduction of rGO doped at 0.3 wt% ratio contributed to reducing the resistance of the surface and the interface of the photoelectrode from the observation of electrochemical impedance spectroscopy(EIS).*

**Keywords** Dye-sensitized solar cells; graphene; $HNO_3$-treatment; photoelectrode

## Introduction

Dye-sensitized solar cells (DSSCs) have received great attention due to easy fabrication and low production cost compared with conventional silicon–based solar cells. The highest power conversion efficiencies in recent report is about 13%. The theoretical value of the energy conversion efficiency on DSSCs is about 33%, so many efforts have been made to achieve improved efficiency [1]. The photoelectrode of DSSCs is generally made of $TiO_2$ paste. The $TiO_2$ based photoelectrode is chemically adsorbed to the dye molecules, which provides the surface area to fix dye molecules. Because of electron transport by photogeneration that occurs in random transit path between $TiO_2$ nanoparticles, however, there is a possibility of the recombination of electron. To reduce the electron recombination and improve the electron mobility, many studies have been reported; porous structure formation [2], induction of the charge carriers by direct photogeneration [3], etc. In this study, the photoelectrodes of $TiO_2$-reduced graphene oxide (rGO) were manufactured by a $HNO_3$-treatment method and the influence of different amounts of the graphene on the properties of DSSCs were studied.

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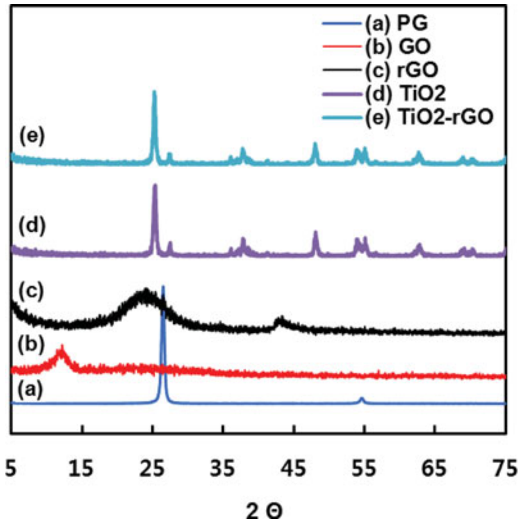

**Figure 1.** XRD Patterns of (a) pristine graphite, (b) graphene oxide, (c) reduced graphene oxide, (d) $TiO_2$ without rGO, (e) $TiO_2$ with rGO.

## Experiments

Graphene oxide(GO) was prepared using a Hummer's method [4]. $TiO_2$/GO powder was prepared with the different GO ratio of 0.3∼1.5 wt%. The solution mixture of $TiO_2$-rGO composite electrodes were made as follows. After the $TiO_2$/GO powder was added in DI water:$HNO_3$ solution (120:1 ratio), the solution mixture was sonicated for the redispersion of GO for 1h and then stirred at 80°C for 8 h. $N_2H_4$ was added in the mixture and then it was stirred at 90°C for 2 h. After that, the $TiO_2$/rGO reactant was dried under vacuum at 100°C for 12 h. The mixture of $TiO_2$/rGO powder, DI water, ethanol, and PEG (polyethylene glycol) was mixed well in a paste mixer. The $TiO_2$/rGO photoelectrodes were sensitized by dipping them in N719 dye solution for 24 h. The DSSCs were assembled by sandwiching a HPE (Dyesol co.) electrolyte layer between the $TiO_2$/rGO electrodes and Pt-coated electrodes. The morphology of the electrode composites was measured using XRD, FE-SEM. The electrochemical properties were measured by electrochemical impedance spectroscopy(EIS) for 0.3, 0.6, 0.9, 1.2 and 1.5 wt % of the rGO-doped photoelectrode.

## Results and Discussion

We prepared and characterized the DSSCs with $TiO_2$-rGO composite electrodes treated with different GO ratio of 0.3∼1.5 wt% using a $HNO_3$-treatment method. Figure 1 shows the XRD patterns of the Pristine graphite (PG), graphene oxide (GO), rGO, $HNO_3$-treated $TiO_2$ powder and $HNO_3$-treated $TiO_2$-rGO composite powder. The pattern of graphite has a peak centered at $2\theta = 26.6^\circ$, corresponding to a d-spacing of 3.34Å as shown in Fig. 1(a), which is absent in the GO sample in Fig. 1(b). While a new peak at $2\theta = 12.1^\circ$ is arisen, corresponding to the (002) inter-planar spacing of 7Å. After reducing GO in hydrazine hydrate after $HNO_3$-treatment, the basal spacing decreases from 7Å of the pristine GO to 3.56Å in the reduced sample (Fig. 1(c)), indicating that the graphene has been successfully obtained. Figure 1(d) and 1(e) show the XRD patterns of $TiO_2$ and $TiO_2$-rGO powder treated with $HNO_3$, respectively, showing different rutile contents. The $TiO_2$ powder without rGO

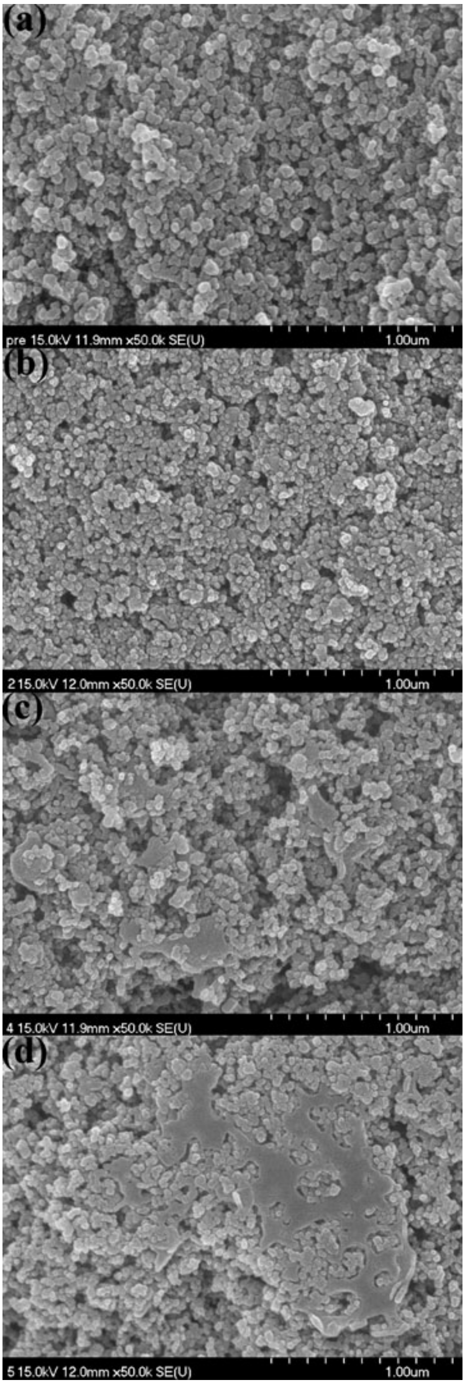

**Figure 2.** SEM images of (a) $TiO_2$ electrode, (b) $TiO_2$-rGO composite electrode (0.3 wt%), (c) $TiO_2$-rGO composite electrode (0.9 wt%), (d) $TiO_2$-rGO composite electrode (1.2 wt%).

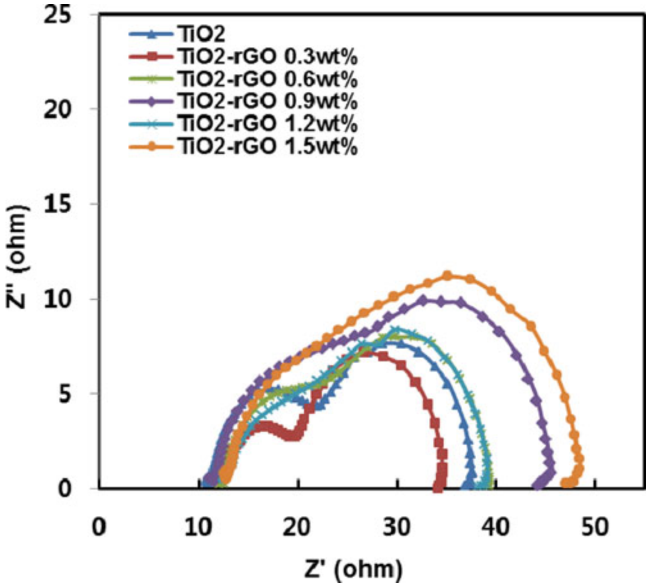

**Figure 3.** Nyquist plots of DSSCs with different $TiO_2$-rGO photoelectrodes under 100 mW/cm$^2$, AM 1.5 simulated illumination at active area of 0.25 cm$^2$.

shows rutile content of 17.8%, while the $TiO_2$ the powder with 0.3 wt% rGO shows rutile content of 12.2%. It can be seen the decreased rutile content about 5% by addition of 0.3 wt% rGO. With increase of the rGO content in the range of 0.3∼1.2 wt%, the rutile contents were changed from 12 to 15%. These results indicated that when GO turned into rGO during reduction process by $HNO_3$-treatment, it facilitated rutile turn into anatase for a certain GO addition ratio, and thus the rutile content was reduced.

We measured the surface areas, the pore volume and the pore size distribution of $TiO_2$ particles with and without rGO by a Brunaver-Emmett-Teller(BET) and a Barret-Joyner-Halenda (BJH) plot. The surface areas of $TiO_2$ and $TiO_2$-rGO were about 54.3 and 56.5 ± 0.2 m$^2$/g, respectively. We found that the increment of surface area of $TiO_2$-rGO composite compared to $TiO_2$ was attributed to the development of mesopores. We also measured the pore size distributions of the nanoporous $TiO_2$-rGO particles. However, the pore size distributions showed to be same, the pore volume of $TiO_2$-rGO was increased, as determined by BJH plot. These results indicated the increase of the surface areas and pore volume was caused by the addition of rGO, which can be induced the increase of the dye absorptions.

The morphology of the $TiO_2$ and the $TiO_2$-rGO composite electrodes with different content of rGO was observed using FE-SEM, as can be seen in Fig. 2. The $TiO_2$-rGO(0.3 wt.%) photoelectrode film exhibits the most compact morphology and its particles size was decreased as shown in Fig. 2(b). The porosities of $TiO_2$-rGO (0.3 wt%) films comparing with the $TiO_2$ film were more uniform. The decrease of agglomeration between the particles in $TiO_2$-rGO (0.3 wt%) film was observed due to the improvement of dispersibility of the rGO. The increased porosities would result in the increase of the surface areas which in turn induced the increase of the dye absorptions and the enhancement of the photoelectric properties. As can be seen in Fig. 2(c) and (d), however, it can be seen the agglomeration morphology with increasing GO content, which would result in the decrease of the surface

**Table 1.** Solar cell performance of the DSSCs with different $TiO_2$-rGO composite electrodes

| Samples | $V_{oc}$ (V) | $J_{sc}$ ($mA/cm^2$) | FF (%) | $\eta$ (%) |
|---|---|---|---|---|
| Pristine $TiO_2$ | 0.63 | 11.86 | 58.09 | 4.33 |
| 0.3 wt% rGO | 0.67 | 15.72 | 59.68 | 6.26 |
| 0.6 wt% rGO | 0.6 | 11.62 | 57.8 | 4.05 |
| 0.9 wt% rGO | 0.6 | 8.79 | 59.41 | 3.16 |
| 1.2 wt% rGO | 0.59 | 9.91 | 60.45 | 3.55 |
| 1.5 wt% rGO | 0.59 | 7.38 | 55.93 | 2.42 |

areas and in turn induced the decrease of the dye absorptions and the inhibition of the electron transfer.

Figure 3 shows electrochemical impedance spectroscopy (EIS) for 0.3, 0.6, 0.9, 1.2 and 1.5 wt % of the rGO-doped photoelectrodes. In EIS observations, the Nyquist plots of the impedance characteristics were obtained from the dependence of the real axis resistance Z or $Z_{re}$ and imaginary axis resistance Z or $Z_{im}$ along with the angular frequency. The radius of the middle semicircle of $TiO_2$ photoelectrode doped with 0.3 wt% rGO shorted than that of rGO. These results were inferred by providing the electron pass way and reducing the surface resistance. The decreased resistance came from the reduced chances of the electron recombination. When rGO was added more than 0.3 wt%, then, the radius of the middle semicircle was increased. It might seem to increase charge recombination due to inhibition of the electron transfer dependent on the agglomeration of the rGO.

Table 1 shows open circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF), and power conversion efficiency ($\eta$) of each samples. The doping ratio of 0.3 wt% rGO shows the maximum efficiency of 6.26%, while that of pristine $TiO_2$ sample shows 4.33%. The increase of $J_{sc}$ in the DSSC means the increase of current velocity and dye adsorption. It might be explained that reduction of contact resistance between $TiO_2$ and rGO, electron trapping phenomena, and increase the dye adsorption.

## Conclusions

We successfully fabricated the $TiO_2$ based photoelectrode doping with reduced graphene oxide(rGO) to improve the power conversion efficiency of dye-sensitized solar cells(DSSCs). The ratio of rGO was 0.3∼1.5 wt%. The DSSCs with the rGO doped at 0.3 wt% ratio showed a maximum power conversion efficiency of 6.26%. The conversion efficiency of the rGO doped device was enhanced up to 44% compared with the pristine $TiO_2$ photoelectrode. We concluded the introduction of rGO doped at 0.3 wt% ratio contributed to reducing the resistances of the surface and the interface of the photoelectrode from the EIS analysis. The internal resistance of the photoelectrode directly affects the power conversion efficiency.

## Acknowledgment

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