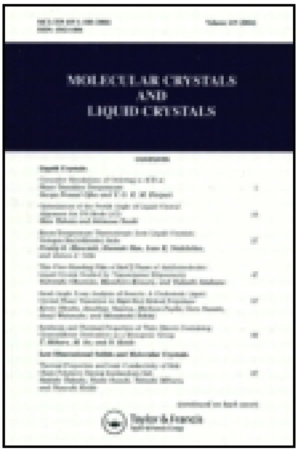

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Improved Efficiency of Dye-Sensitized Solar Cell Using Graphene-Coated Al_2O_3-TiO_2 Nanocomposite Photoanode

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Improved Efficiency of Dye-Sensitized Solar Cell Using Graphene-Coated Al_2O_3-TiO_2 Nanocomposite Photoanode

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Dye-sensitized solar cells (DSSCs) were fabricated using graphene-coated Al_2O_3 (GCA)-TiO_2 nanocomposite electrodes. The GCA-TiO_2 pastes were prepared by simply blending the GCA particles with TiO_2 particles without any complex treatments. The DSSC with 1 wt.% GCA-TiO_2 exhibited much better overall energy conversion efficiency, when compared to the DSSCs with TiO_2 alone and with carbon nanotube-TiO_2. It can be attributed to efficient electron transport through the GCA-TiO_2 to the transparent conducting oxide, resulting in significantly enhanced electron lifetime.

Keywords Dye-sensitized solar cell; electron lifetime; electron transport; graphene-coated Al_2O_3; nanocomposite; TiO_2

Introduction

Dye-sensitized solar cells (DSSCs) based on mesoporous TiO_2 have been extensively studied as low-cost alternative to commercial Si-based solar cells [1–4]. The TiO_2 films composed of nanoparticles smaller than 30 nm don't develop the depletion layer at an interface between the TiO_2 and electrolyte, leading to large back electron

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transfer from the conduction band of the TiO_2 to the electrolyte [3,5]. To suppress the back electron transfer, efforts [6] have been carried out; (1) composite electrodes using metal oxides with different band gaps, (2) nanostructures whose direction is perpendicular to the transparent conducting oxide (TCO), and (3) incorporating the conductive materials in the TiO_2 mesoporous films.

Carbon-based materials (e.g., carbon nanotube, graphene, etc.) incorporated into the TiO_2 matrix have been studied for the DSSCs [6–8] pertaining to the (3) above. It has recently been reported that incorporating the graphene in the mesoporous TiO_2 is a promising method to benefit the charge separation, because the graphene is a zero band gap material and provides excellent electron mobility [6–8]. However, it requires additional, lengthy pre-treatment processes such as electrostatic stabilization and chemical functionalization methods, leading to long process time [7,9,10], because the strong van der Waals π-π interaction and/or folding and wrinkling of the graphene sheets lead to their tendency to aggregate, resulting in inferior cell performance.

This paper reports the TiO_2 films incorporated by the graphenes without any complex, additional pre-treatment. The graphene-coated Al_2O_3 (GCA) nanoparticles were prepared and mixed with the TiO_2 nanoparticles, because, if the graphene is coated on the nanoparticle, it should hinder the interaction and aggregation between the graphene sheets, improving the cell performance with the reduced process time. The GCA-TiO_2 composite pastes for the DSSCs were prepared by simply dispersing the GCA particles with the TiO_2 nanoparticles without any complex pre-treatments. For comparison, the TiO_2 electrodes without the GCA and with the carbon nanotube (CNT) were fabricated using the similar preparation process. The DSSC with the 1 wt.% GCA-TiO_2 exhibited much higher cell efficiency than the others, due to the significantly enhanced electron lifetime.

Experimental

For the synthesis of the GCA nanoparticles, AlN powders were heated for 20 h at 1400°C in a gas mixture of argon and 10 vol.% CO at 200 ml/min. The GCA nanoparticles could be synthesized by the reverse reaction of Eq. (1) below.

$$Al_2O_3(s) + 3C(s) + N_2(g) \rightarrow 2\ AlN(s) + 3\ CO(g) \tag{1}$$

AlN powders were first prepared by calcining a (hydroxo)(succinato)Al(III) complex at 1300°C for 5 h under a flow of nitrogen. The powders in an alumina crucible were set in an alumina tube and heated at a rate of 5°C/min to 1400°C in a gas mixture of argon and 10 vol % CO at a flow rate of 200 ml/min. The reverse reaction of Eq. (1) occurred at 1400°C so that the graphene-coated Al_2O_3 particles could be synthesized by calcining the AlN powders at 1400°C for 20 h under a flow of 10 vol % CO/Ar [11].

The GCA-TiO_2 composite films were prepared by simply dispersing the GCA (1, 3, and 5 wt.% over TiO_2) and commercial TiO_2 (P25) nanoparticles in ethanol without any additional pre-treatment on the graphene. The GCA-TiO_2 films were fabricated by doctor-blading the GCA-TiO_2 pastes on the FTO (F-doped SnO_2) transparent conducting oxide (TCO) followed by calcination at 450°C for 30 min. For comparison, the mesoporous TiO_2 films without the GCA and with the 1 wt.% carbon nanotube (CNT) were prepared. The scattering layer consisting of the rutile TiO_2 particles (250 nm) was deposited on the films. The photoanodes were immersed in N719 dye solution overnight. The N719 dye is $RuL_2(NCS)_2{:}(TBA)_2$, where the L and TBA are 2,2′-bipyridine-4,4′-dicarboxylic acid and tetrabutylammonium, respectively. The dye-adsorbed photoanodes and Pt counter electrodes were sandwiched and a liquid electrolyte containing the redox couple (I^-/I_3^-) was then introduced in between. All of the samples have similar film thickness (about 10 μm) and an active area of the dye-adsorbed photoanodes was about 0.24 cm^2.

Photovoltaic current-voltage characteristics of the DSSCs were measured under 1 Sun illumination (100 $mWcm^{-2}$, AM1.5) verified by an AIST-calibrated Si-solar cell. The Bode diagrams were measured using the electrochemical impedance analyzer in the frequency range of 1 Hz to 100 kHz under the 1 Sun at open-circuit potential.

Results and Discussion

Figure 1 shows the high resolution-transmission electron microscopy (HR-TEM) image of the graphene sheets in the graphene-coated Al_2O_3 (GCA). The GCA particles were in a range of 20 to 40 nm in a size. Two or three parallel dark fringes were observed at the edge of GCA and the spacing between fringes is 0.34 nm. It is corresponding to the spacing between the (002) planes of graphite, indicating the two or three graphene sheets coated on the alumina particles.

Figure 2 shows the absorbance spectra of the N719 dyes detached using 0.1 M NaOH aqueous solution from the TiO_2 (sample 1) and the GCA-TiO_2 nanocomposite electrodes, where the 1, 3, and 5 wt.%-GCA-TiO_2 films are referred to as the samples 2, 3, and 4, respectively. The amount of the adsorbed dyes decreased with the increase of the GCA content in the mesoporous TiO_2 films, indicating that the

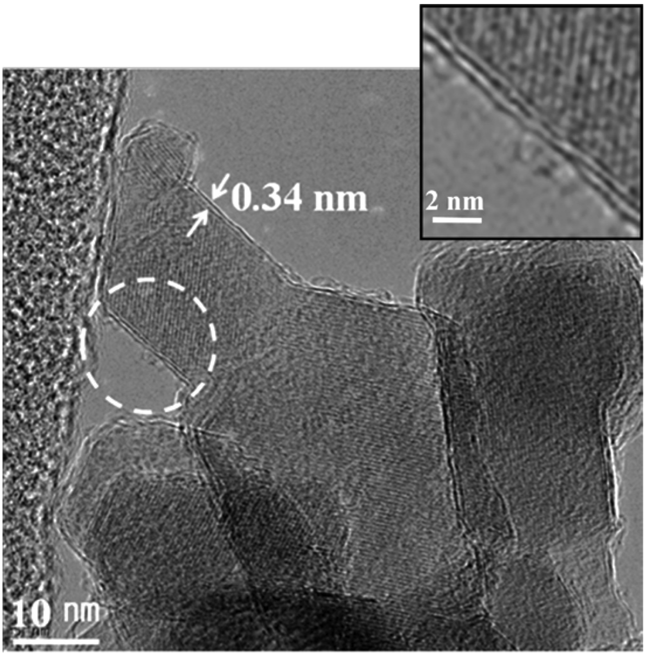

Figure 1. HR-TEM image of the synthesized graphene-coated Al_2O_3 particles.

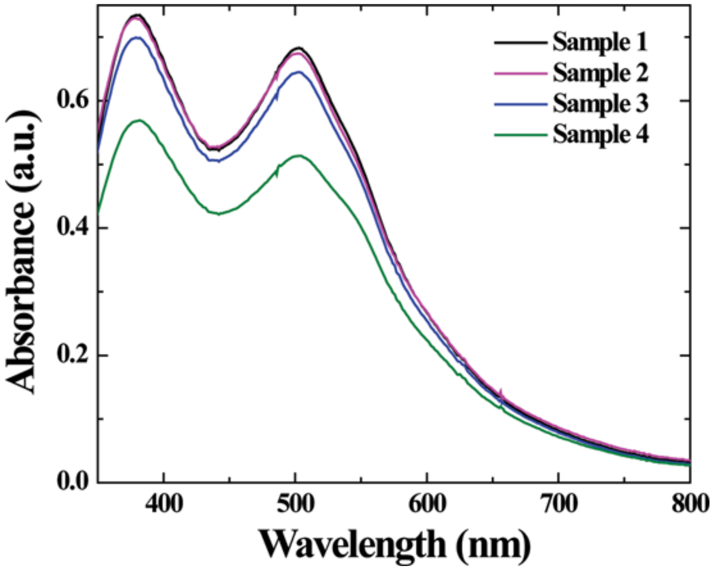

Figure 2. Absorbance spectra of the N719 dyes detached from the TiO_2 (sample 1) and the 1, 3, and 5 wt.% GCA-TiO_2 films (denoted as the samples 2, 3, and 4, respectively).

TiO_2 surface area for the dye adsorption was reduced by the incorporation of the GCA. However, it should be noted that the amount of the dye adsorbed in the 1 wt.% GCA-TiO_2 film was slightly lower without apparent difference than that of the TiO_2 film.

Figure 3 shows the Bode plots of the samples 1, 2, and 4, respectively, measured at open circuit potential under the 1 Sun illumination. It is known that the

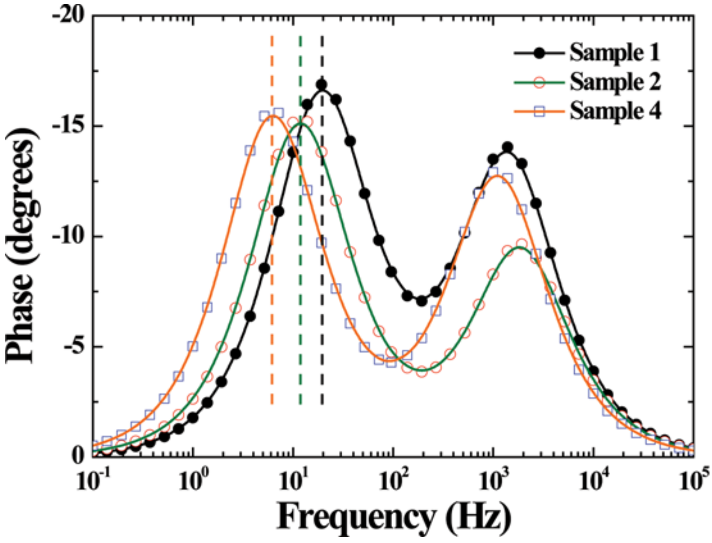

Figure 3. Bode plots of the samples 1, 2, and 4, respectively, measured at V_{oc} under the 1 Sun illumination.

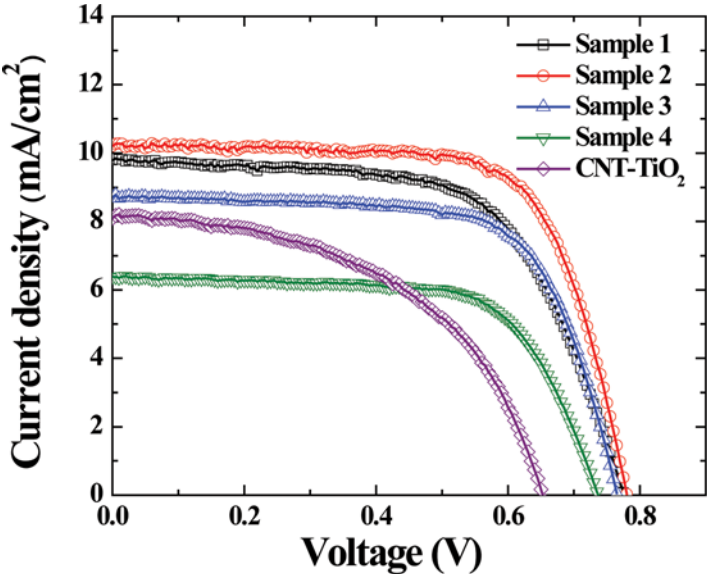

Figure 4. Photocurrent-voltage characteristics of the samples 1 to 4 and the DSSC with the 1 wt.% CNT-TiO_2 film.

meddle-frequency region (1 – 100 Hz) relates directly to the electron transfer process in the film photoanode [6,7]. The electron lifetime (τ_e) in the mesoporous films can be estimated using the equation $\tau_e = 1/(2\pi\ f_{mid})$, where the f_{mid} is a frequency peak in the middle-frequency region. The shift of the f_{mid} peak from high frequency to low frequency reveals a more rapid electron transport process. The estimated electron lifetime was 4.3, 11.5, and 22.1 ms for the samples 1, 2, and 4, respectively. Therefore, the GCA incorporated in the mesoporous TiO_2 film significantly increased the electron lifetime, indicating the enhanced charge separation or suppressed recombination rate.

Figure 4 shows the photocurrent-voltage characteristics of the samples 1 to 4 and the DSSC with the 1 wt.% CNT-TiO_2, which are summarized in Table 1. All of the DSSCs with the GCA-TiO_2 films exhibited higher fill factors (FFs) than the DSSC with the TiO_2 alone, due to better electron transport through the GCA-TiO_2 to the TCO. Furthermore, the DSSC with the 1 wt.% GCA-TiO_2 exhibited higher short-circuit current (J_{sc}), open-circuit potential (V_{oc}), and fill factor than the DSSC with the TiO_2 alone, resulting in significantly improved overall energy-conversion efficiency (η). It can be attributed to the reduced recombination rate caused by the

Table 1. Photovoltaic properties of DSSCs composed of different electrodes

Samples	GCA loading (wt.%)	J_{sc} /mAcm^{-2}	V_{oc} /mV	FF /%	η /%
Sample 1	0	9.75	771	61.48	4.6
Sample 2	1	10.23	778	68.10	5.4
Sample 3	3	8.66	764	67.56	4.5
Sample 4	5	6.33	734	65.78	3.1
1 wt.% CNT-TiO_2	0	8.11	657	50.62	2.7

longer electron lifetime. Although the sample 4 exhibited longer electron lifetime than the sample 2, the cell efficiency of the DSSCs (samples 3 and 4) was abruptly decreased. The absorbance data of the Figure 2 showed that the amount of the adsorbed dye was significantly decreased as the GCA content increased over 3 wt.%. The lower cell efficiencies of the samples 3 and 4 can be attributed to the significantly decreased amount of the adsorbed dye, because it reduces the concentration of the electrons photoexcited from the dye molecules. The DSSC with the CNT-TiO_2 was also compared, as shown in Table 1. The DSSC with the CNT-TiO_2 exhibited much lower cell efficiency than the other DSSCs. It may be due to the aggregation of the CNTs, because the CNT-TiO_2 film was prepared by the simple blending procedure without any acid treatment [6,7]. The comparative performance tests have been repeated many runs, and the results are reproducible.

Conclusions

The GCA-TiO_2 nanocomposite electrodes were prepared by simply dispersing the GCA (1, 3, and 5 wt.% over TiO_2) with the TiO_2 particles without any additional, complex pre-treatment on the graphenes. The DSSCs with the 1 wt.% GCA-TiO_2 exhibited significantly improved cell efficiency, compared to the DSSCs with the TiO_2 alone and with the CNT-TiO_2, due to the enhanced electron lifetime that leads to the efficient charge separation or reduced charge recombination. It suggests that the graphene-incorporated TiO_2 films could be fabricated by mixing the GCA particles with the TiO_2 particles without any pre-treatment of the graphene, resulting in the significantly improved cell performance with the reduced process time. We expect that the GCA-TiO_2 films should provide good insight on the nanocomposite electrodes for the DSSCs.

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