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GRAPHENE EFFECT ON EFFICIENCY OF TiO_2-BASED DYE SENSITIZED SOLAR CELLS (DSSC)

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Abstract. *Graphene embedded TiO_2 films as photo-electrodes for dye sensitized solar cells (DSSC) was fabricated. Firstly, colloidal paste of TiO_2/Graphene was prepared by carefully mixing of a certain amount of graphene with TiO_2 commercial paste, then it was used to spread TiO_2 films and finely annealed at 450°C to form nanocomposite TiO_2/graphene electrodes. The SEM images and Raman scattering were used to examine the morphology and microstructure as well as the existence of graphene in TiO_2 electrode films. The electrodes after being sensitized with dye "N179" were combined with Pt counter electrodes and iodine-based electrolyte to make DSSC cells. I-V characteristics of the DSSC cells were recorded at room temperature. The open-circuit voltage (V_{oc}), the short-current density (J_{sc}) and the photoelectric conversion efficiency η) of the DSSC cells were estimated. The results show that the graphene content added into TiO_2 electrode films has affected on V_{oc}, J_{sc} and η of cells in the nonlinear form. The efficiency reached a maximal value with a graphene concentration of 0.005 wt %. It is supposed to be related with an improving the charge transfer in the working photo-electrode of DSSC.*

Keywords: graphene sheets (GS), dye sensitized solar cells (DSSC).

Classification numbers: 88.40.fh, 88.40.H-.

I. INTRODUCTION

Recently, improving the open-circuit voltage, the short-circuit current and consequently the efficiency of dye-sensitized solar cells (DSSC) have been receiving much attention. As we known that in DSSC devices the charges (electron-hole pairs) are normally generated from the dyes impregnated in mesoporous TiO_2 layer due to absorb the incident light, then these charges were separated and transferred into electrodes in both sides to give electrical energy. In order to improve energy transfer efficiency of DSSC devices it should be improved: i) the charges generation process of dye materials; ii) the electron-hole pairs separated process. In the DSSC solar cells the optically generated electrons and holes are separated due to the HOMO energy level of the dye has laid higher than the valence band of TiO_2; iii) the charges transfer process from dye materials to the electrodes through mesoporous TiO_2 layer and electrolyte. By these ways many researches have been paid to find out new giving high optical absorption with high quantum efficiency. Using semiconductor quantum dots as dye materials in quantum dot-sensitized solar cells (QDSSC) have improved the optical absorption, then it plays a role of an additional charge generation. In other case the metallic nanoparticles added mesoporous TiO_2 layer have improved in charge transfer process due to plasmonic resonance absorption [1]. In addition, many investigations show that to enhance efficiency of TiO_2-based DSSCs, electrons from dye should be easily transferred from dye to the surface of TiO_2 nanoparticles and then to the FTO electrode [2–5] and it can be done by improving the electronic conductivity of TiO_2 layer. Graphene has gained lots of attention due to its great transparency and high conductivity. At room temperature, the electron mobility in graphene is larger than 15000 cm^2/Vs. Therefore one can hope that graphene embedded at the surface of TiO_2 nanoparticles may improve the charge transfer process in DSSC devices. Recently, graphene was used for a photocatalysis [6–8]. Zhang *et al.* [6] reported the enhancement of the hydrogen evolution on TiO_2/graphene-nanocomposites. They recorded an increase of hydrogen evolution of 1.6 times larger for TiO_2/2.0 wt% graphene in comparison to Degussa P25. However, application of graphene for the DSSC so far is rarely reported until now, so a more detailed study in this object is thus required. Graphene is a great candidate due to its interesting characteristics, especially in the electrochemistry field. In this paper we present results on the research of TiO_2-based DSSC embedded with graphene.

II. EXPERIMENT

Graphene sheets were prepared by a plasma-assisted electrochemical exfoliation process [9]. First, 10 mg of graphene was dispersed into 6 ml of terpineol to get a solution, then the solution was ultrasonically stirred for 30 minutes. The solution obtained after stirring was added to TiO_2 paste in ratios of 0.005, 0.01, 0.05 and 0.10 wt%. The mixture was carefully mixed to get a homogeneous paste for spreading film working electrode (see Fig. 1). The TiO_2-based working electrodes were fs fabricated by following steps: First the FTO substrates were cleaned by ultrasonic stirring in decon solution for 45 minutes, and ultrasonically stirred again in deionized water. After that the FTO substrates step by step were ultrasonically stirred in ethanol, acetone and deionized water for 15 minutes at a temperature of 50°C. Finally, the substrates were dried

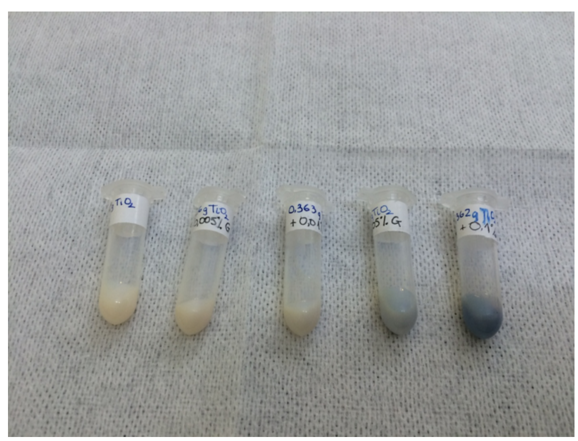

Fig. 1. Graphene/TiO_2 paste with different weight concentration of graphene.

at 120˚C for 10 minutes. Three TiO_2 layers step by step were spread onto the FTO substrates. The first layer served as the blocking layer was prepared with a thickness of 50 nm. It contains fine TiO_2 nanoparticles of 5 nm in size. The second layer with a thickness of about 12 μm was made by spreading the TiO_2/graphene paste. The last layer with a thickness of 3 μm served as the reflective layer was spread by the paste of TiO_2 nanoparticles of about 80-100 nm in size. The multilayer working electrode was thermally annealed at 470˚C for 30 minutes to remove the remaining solvents. Next step the electrode was soaked in TiCl4 50 mM solution for 30 minutes, cleaned in deionized water, dried and annealed at 470˚C for 30 minutes. Finally, the electrode was sensitized by the "N179" dye sensitizer to get a ready working electrode of the DSSC solar cells.

The morphology and material compound of the synthesized samples were identified by SEM and Raman scattering, respectively. UV-VIS absorption spectra of the films were recorded by using a Shimadzu UV-1800 spectrometer. Solar cell devices in configuration of FTO/blocking layer/Graphene-TiO_2+ N179/reflex-layer/(I^-/I^{2-}) electrolyte/Pt were manufactured and their photocurrent-voltage (I/V) characteristics were recorded under irradiation of a 150 W xenon lamp equipped with an AM 1.5G filter (Newport) that its light intensity was adjusted to 1-sun conditions (100 mW/cm^2) by using a Keithley 2400 source meter.

III. RESULTS AND DISCUSSION

Figure 2(a) presents a cross-section image of the TiO_2 film deposited onto a glass substrate. It shows that the TiO_2 film has a thickness of about 12.3 μm. Figures 2b and 2c present SEM images of the films of TiO_2 and TiO_2 embedded with 0.01 wt% of graphene. The surface morphology of the graphene-embedded film looks very similar to the original TiO_2 film. It means the embedding of graphene did not change morphology of the TiO_2 film.

In the aim to check the existence of graphene and phase structure of TiO_2 materials in the film Raman scattering at room temperature of the films was carried out. Figure 3 presents the Raman spectra of the TiO_2 films. The Raman lines were observed at energies of 147, 398, 516 and 640 cm^{-1} which correspond to the vibration modes of TiO_2 anatase. There are two Raman lines at 1333 cm^{-1} and 1577 cm^{-1} belong to the D and G modes of graphene, respectively. These D and G modes are better observed in the inset. This confirms the presence of graphene that was embedded into the TiO_2 film.

The embedding of graphene has affected on the UV-Vis absorption of TiO_2 films. The absorption spectra of TiO_2 films embedded with graphene of various different contents (namely 0.005, 0.01, and 0.1 wt %) are presented in Fig. 4.

The absorption of the TiO_2 films vs. graphene content slightly increases in a wavelength range from 350 to 800 nm. Such a small increase in absorption may have a weak contribution in the improvement of the characteristic parameters of the DSSC devices. The efficiency of one solar cell could be improved as the charge generation, charge separation and charge transfer processes should be simultaneously enhanced. Graphene is an excellent conductor. Therefore the embedding graphene into TiO_2-based working electrode could have to improve the charge transfer in TiO_2 working electrode and then enhances efficiency of the DSSC solar cells. In the aim to look for influences of graphene on the open-circuit (V_{oc}), the short-circuit current (J_{sc}) and the photoelectric conversion efficiency (η) of the solar cell, the I/V characteristics of the DSSC solar cells at room temperature were measured. The measured characteristics are presented in Fig. 5.

Observing the obtained I-V curves one can find that the V_{oc} and J_{sc} are dependent on graphene concentration in a nonlinear form. With a low graphene concentration (about 0.005 wt %) both the V_{oc} and J_{sc} increase. This increase is probably due to the increase of the charge transfer from the dye to TiO_2 resulting in the increase of the charge density in the conduction band of TiO_2. With a higher graphene concentration (above 0.01 wt %) first the V_{oc}, then both the V_{oc} and J_{sc} significantly decrease. This may be related to the increase of the recombination processes in TiO_2 nanoparticles as well as a short current caused by direct contacts of graphene with FTO electrode. The estimated V_{oc}, J_{sc} and the efficiency η of DSSC solar cells embedded with graphene are presented in Table 1. It can be seen from the obtained results that the efficiency of the DSSC solar cell embedded with 0.005 wt% of graphene reached a largest value, namely 4.03% that increased about 15% in comparison to that of the devices without graphene.

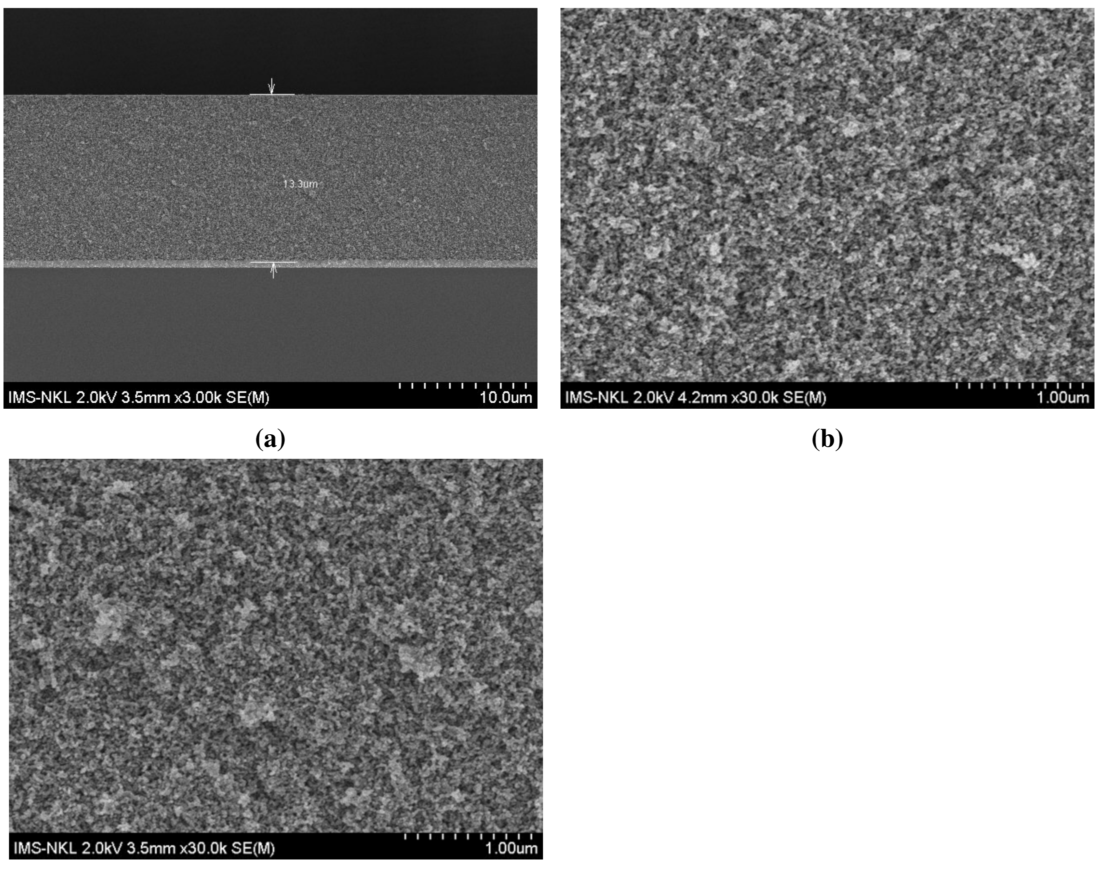

Fig. 2. FESEM images of the TiO_2 and TiO_2 embedded with graphene films, (a) – the cross-section of the TiO_2 film, (b) – SEM image of the TiO_2 film, (c) – SEM image of the TiO2 film embedded with 0.01 wt% of graphene.

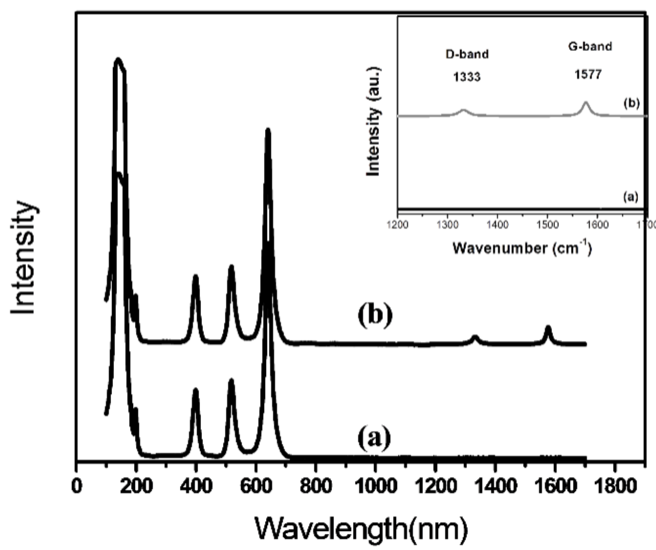

Fig. 3. Raman spectra of TiO_2 film (a) and TiO_2 graphene-embedded film (b). Inset exhibits Raman lines of the D and G band of graphene.

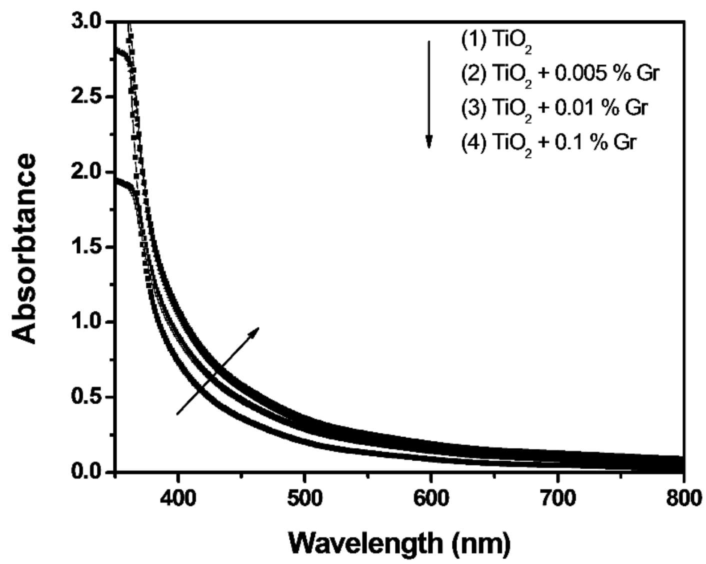

Fig. 4. UV-vis absorption of the TiO_2 films.

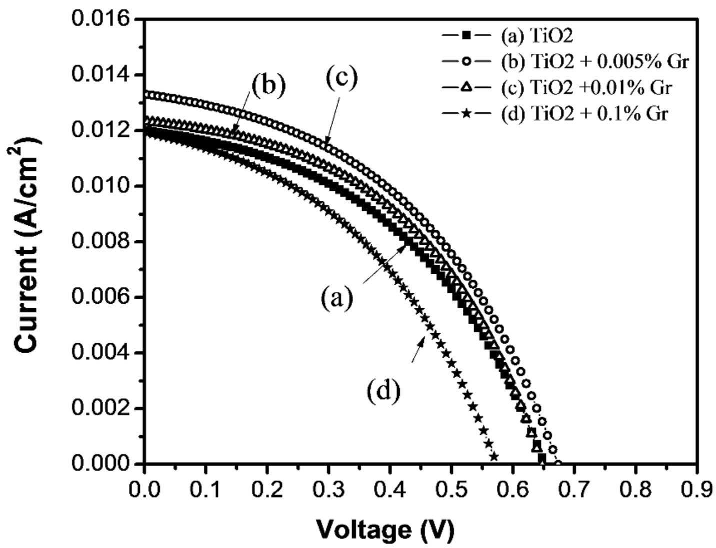

Fig. 5. I/V curves of the TiO2-based DSSC solar cells embedded with graphene of various different concentrations.

Table 1. Characteristic parameters of the TiO_2-based DSSC solar cells embedded with different concentrations of graphene.

Graphene (%)	Short-cut current J_{sc}(mA)	Open-circuit Voltage V_{oc}(V)	Efficiency η (%)
0.00 (TiO_2)	12.22	0.647	3.5
0.005	13.55	0.68	4.03
0.01	12.46	0.64	3.83
0.10	12.22	0.615	3.1

IV. CONCLUSION

DSSC solar cells with a structure of FTO/TiO_2+graphene/Dye/Electrolyte/Pt were successfully manufactured. The graphene concentration has clearly affected to V_{oc}, J_{sc}, and η of the DSSC solar cells. The DSSC cell embedded with 0.005 wt% graphene has a maximal efficiency of about 4.03 % which is 15% larger than that of the DSSC solar cell without graphene. The enhancement in the photoelectric conversion efficiency of the DSSC solar cells has been supposed to be related with the increase of the charge transfer in TiO_2 working electrode.

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