Chemical Physics Letters 483 (2009) 124–127

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

UV-reduction of graphene oxide and its application as an interfacial layer to reduce the back-transport reactions in dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 15 September 2009
In final form 22 October 2009
Available online 24 October 2009

ABSTRACT

A mixture of graphene oxide (GO) and TiO_2 nanocomposites was reduced photocatalytically by UV-irradiation and applied as interfacial layer between a fluorine doped tin oxide (FTO) layer and a nanocrystalline TiO_2 film. Impedance spectra implied a decreased back-transport reaction of electrons. The graphene–TiO_2 interfacial layer effectively reduced the contact between I_3^- ions in the electrolyte and FTO layer, which inhibited back-transport reaction. The introduction of graphene–TiO_2 increased V_{oc} by 54 mV and the photoconversion efficiency was improved from 4.89% to 5.26%.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their low production cost and relatively high energy conversion efficiency [1,2]. Highest photovoltaic conversion efficiencies so far reported for DSSCs is about 11% [3]. TiO_2 nanoparticles with average particle size 15–20 nm are typically deposited as a porous layer with a thickness of 10–12 µm on a transparent conductive oxide (TCO) [4,5]. Electrons generated by the dye molecules have to pass through numerous grain boundaries in order to reach TCO through the conduction band of TiO_2. It was suggested that the rough surface of fluorine doped tin oxide (FTO) glass might short circuit the cells [6]. When the thick TiO_2 layer is formed by doctor blade method, the rough FTO surface may not be covered uniformly by the TiO_2 particles (for example Degussa P25 has particle size 25 nm). This can lead to the formation of some voids between the TiO_2 nanoparticles and FTO glass interface [7]. In addition, TiO_2 nanoparticles have a tendency to form large colloids in suspension or paste. Some parts of the FTO surface are not covered by TiO_2 and can directly contact with electrolytes, thereby decreasing V_{oc} by the electron back-transport reaction $[\mathrm{FTO}(2e^-) + I_3^- \rightarrow \mathrm{FTO} + 3I^-]$. Therefore, controlling the interface between FTO and TiO_2 layer is essential for the formation of efficient DSSCs.

Two-dimensional graphene has attracted much attention on account of their remarkable electronic properties with 0 eV band gap in which the filled valence band touches the conduction band [8], highlighting its application in future optoelectronic devices [9,10]. However, the electrical resistance of graphene oxide is quite high. Many studies have been reported the reduction of graphene oxides, such as, chemical reduction using reducing agents [11], high temperature annealing [12] and UV-assisted photocatalytic reduction [13]. However, hazardous chemicals (hydrazine or $NaBH_4$) are used for chemical reduction, and temperatures ∼1100 °C are required for thermal reduction.

This Letter reports the UV-assisted photocatalytic reduction of graphene oxide mixed with TiO_2 nanoparticles without the need for hazardous chemicals and high temperature annealing. This graphene–TiO_2 was applied as an interfacial layer between FTO layer and nanocrystalline TiO_2 (NC-TiO_2) film. Although many researchers reported the use of carbon based materials in DSSCs but most of them are carbon based counter electrodes [14,15] or carbon nanotube (CNT)-TiO_2 hybrid based working electrodes [16]. Two-dimensional flat graphene sheets incorporated with small TiO_2 nanoparticles (<10 nm) applied as an interfacial layer makes it unique compared to other carbon based materials such as CNT and carbon black to decrease the contact between FTO surface and electrolyte, thereby reducing the back-transport reaction of electrons in the FTO and NC-TiO_2 film interface.

2. Experimental

Graphene oxide (GO) was prepared through Hummer's method [17]. All chemicals and materials were used without any further purification. Graphene oxide was reduced by following procedure reported elsewhere [13]. Firstly, TiO_2 colloidal suspension (0.05 M) was prepared by drop wise addition of titanium (IV) isopropoxide (Fluka) to a vigorously stirred solution of ethanol. The colloidal suspension was continuously stirred prior to its use to prevent agglomeration of the particles. Graphene oxide (1.5 mg/ml) was added to the TiO_2 colloidal suspension and sonicated for

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0009-2614/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cplett.2009.10.066

30 min to disperse of GO sheets with TiO_2 particles. UV-assisted reduction of graphene oxide was performed by 450 W xenon arc lamp for about 2 h.

Reduced graphene–TiO_2 solution was spin coated over FTO glass (15 Ω/□, Solaronix SA) substrate at 1500 rpm for 30 s and the resulting film was annealed at 500 °C for about 30 min in argon atmosphere. Then TiO_2 paste (Degussa P25) was cast over graphene–TiO_2 interfacial layer by doctor blade technique and successive sintering at 500 °C for 30 min. The nanocrystalline TiO_2 film was sensitized with N719 solution (535-tris TBA, Solaronix, 13 mg dissolved in 50 ml ethanol) for 24 h. Pt coated FTO glass was used as counter electrode. The electrolyte used in DSSCs consists of 0.5 M LiI, 0.05 M I_2, 0.5 M 4-tert-butylpyridine in mixed solvent of acetonitrile and propylene carbonate (1:1). DSSCs without any interfacial layer were also prepared for comparison.

The transmittance of the interfacial films on FTO was measured by UV–Vis spectrophotometer (Hewlett Packard 8453). The DSSCs were illuminated under 100 mW/cm^2, AM 1.5 simulated sunlight by using 450 W xenon arc lamp (LH 151, Spectral Energy Co.). The incident light intensity was calibrated with a radiometer photometer (ILT 1400-A). Four samples for each with and without interfacial layer were made for *J*–*V* measurement, and the reproducibility of the effect of interfacial layer was quite good. The morphology of the graphene–TiO_2 interfacial layer was examined by an AFM (Xe-100, Park Systems) and a field emission scanning electron microscope (FE-SEM, JSM-6700, JEOL). Impedance spectra were measured by an impedance analyzer (IM6 ex, Zahner Elektrik). The spectra were scanned in a frequency range of 10^{-1}–10^6 Hz at room temperature.

3. Results and discussion

Fig. 1a shows the change in color from light brown[1] to dark brown to black as the GO is reduced. The color change was caused by partial restoration of the π network within the carbon structure, as witnessed by the chemical reduction of GO sheets [18,19]. Charge separation occurs upon UV-irradiation of the TiO_2 particles [20]. In the presence of ethanol, the holes are scavenged to produce ethoxy radicals and electrons accumulate within TiO_2 particles. These accumulated electrons interact with GO sheets in order to reduce certain function groups [13]. The sheet resistance (R_s) of GO–TiO_2 layer on glass prior to UV-irradiation was 782.30 kΩ/□ using a four-point probe method. After 2 h of UV-irradiation, the sheet resistance became 17.30 kΩ/□. Since both samples (before and after UV-reduction) contained same concentration of TiO_2, the contribution of TiO_2 to the decrease of sheet resistance is expected to be constant.

The spin coated graphene–TiO_2 over the FTO glass substrate was analyzed by AFM. Fig. 1b shows the AFM image of a single graphene sheet of the graphene–TiO_2 composite. The graphene sheet is coupled with TiO_2 nanoparticles. The interaction of TiO_2 nanoparticles with graphene oxide sheets can be through physisorption, electrostatic binding or through charge transfer [21]. The line profile (Fig. 1c) of AFM image showed that the average height of TiO_2 particles on graphene sheet was <10 nm. However, some large particles ~20 nm in diameter were also observed. These large TiO_2 particles are attributed to agglomeration of TiO_2 colloids in the solution. The average rms surface roughness (R_a) of the commercial FTO (Fig. 2a) and graphene–TiO_2 interfacial layers were 15 and 6.26 nm, respectively. Graphene–TiO_2 interfacial layer coated the rough FTO layer, which led to more uniform surface, as shown in Fig. 2b. The cross-sectional SEM image in Fig. 2c showed that a graphene–TiO_2 interfacial layer with a thickness of 500 nm was adhered tightly to the FTO layer. In comparison, significant amount of voids were observed between the FTO surface and NC-TiO_2 film for the DSSCs without any interfacial layer (not shown here).

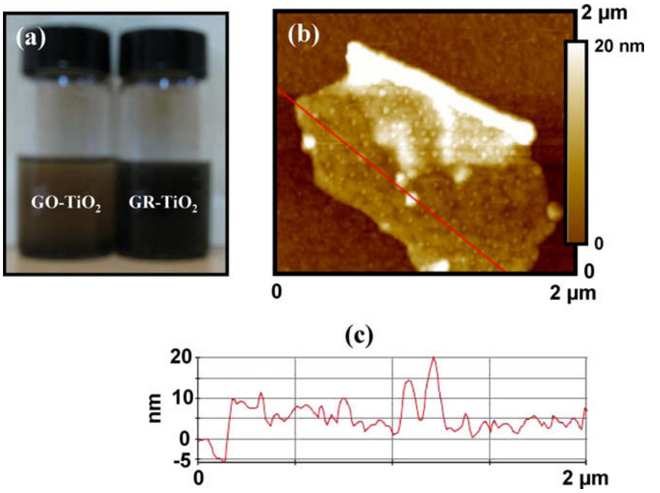

Fig. 1. (a) The changes of color of 0.05 M TiO_2 solution with 1.5 mg/ml GO before and after UV-irradiation for 2 h, (b) AFM images of GO–TiO_2 nanocomposites films (size of 2 µm × 2 µm) over FTO substrate and (c) line profile of the AFM image of GO–TiO_2 composite.

Fig. 3a shows the transmittance spectra of the bare FTO and graphene–TiO_2 interfacial layers coated on the FTO substrate. The transmittance of the bare FTO substrate was ~82%, which decreased to 75% by the introduction of graphene–TiO_2 interfacial layer over FTO. However, the transmittance of the graphene–TiO_2/FTO substrate was high enough to use in DSSC.

The influence of the graphene–TiO_2 interfacial layer on the performance of the DSSCs was investigated. Fig. 3b shows the *J*–*V* characteristic curves. The cells with graphene–TiO_2 interfacial layer showed a considerably improved open-circuit voltage (V_{oc}), compared to that of the cell without interfacial layer. With the use of graphene interfacial layer, the open-circuit voltage increased from 0.687 (±0.003) V to 0.741 (±0.005) V but the fill factor remained almost same. A small decrease in the short-circuit current density (J_{sc}) was observed and this may be due to the decrease in visible light transmittance of the electrode from 82% to 75% (Fig. 3a) with the introduction of graphene–TiO_2 interfacial layer. The photoconversion efficiency increased from 4.89% to 5.26% with graphene–TiO_2 interfacial layer. Also, the DSSC with graphene–TiO_2 interfacial layer showed a substantial reduction of dark (back-transport reaction) current in *J*–*V* curves under dark conditions (not shown here). The Nyquist plots (Fig. 3c) measured in the dark under a forward bias of −0.7 V, showed the radius of the middle semicircle increased with the introduction of graphene–TiO_2 interfacial layer, indicating that the electron recombination resistance augments with the interfacial layer.

As mentioned earlier, a thick TiO_2 layer formed by the doctor blade method cannot cover the rough FTO surface uniformly without void formation because of the rough surface of FTO layer. Iodide (I^-) ions in the electrolyte migrate from the counter electrode to the nanopores of TiO_2 transfer the electrons to the highest occupied molecular orbital level of the dye adsorbed on TiO_2 and then converted to I_3^- ions. Some of the I_3^- ions in the electrolyte penetrate the porous TiO_2 and can directly contact with FTO surface, thereby collecting the electrons from the FTO surface through back-transport reaction [22]. As shown in Fig. 4, the presence of the graphene–TiO_2 interfacial layer between FTO and NC-TiO_2 in the DSSC may inhibit the direct contact between I_3^- ions and FTO electrode, thereby effectively preventing the back-trans-

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[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

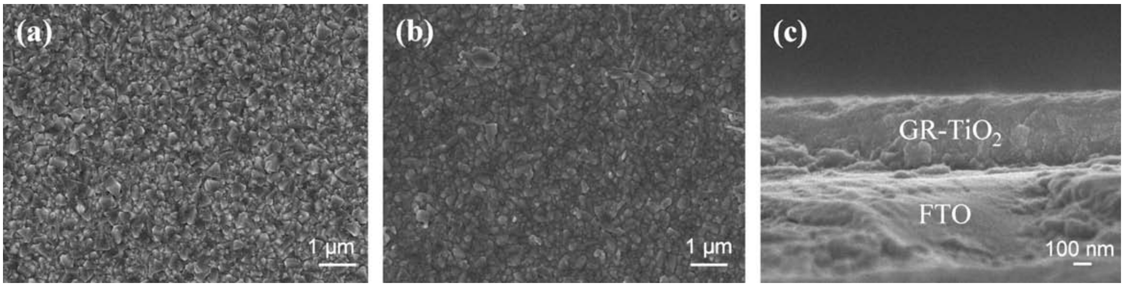

Fig. 2. FE-SEM surface images of (a) bare FTO surface and (b) TiO_2–GO interfacial layer over FTO. (c) Cross-sectional images of the TiO_2–GO interfacial layer.

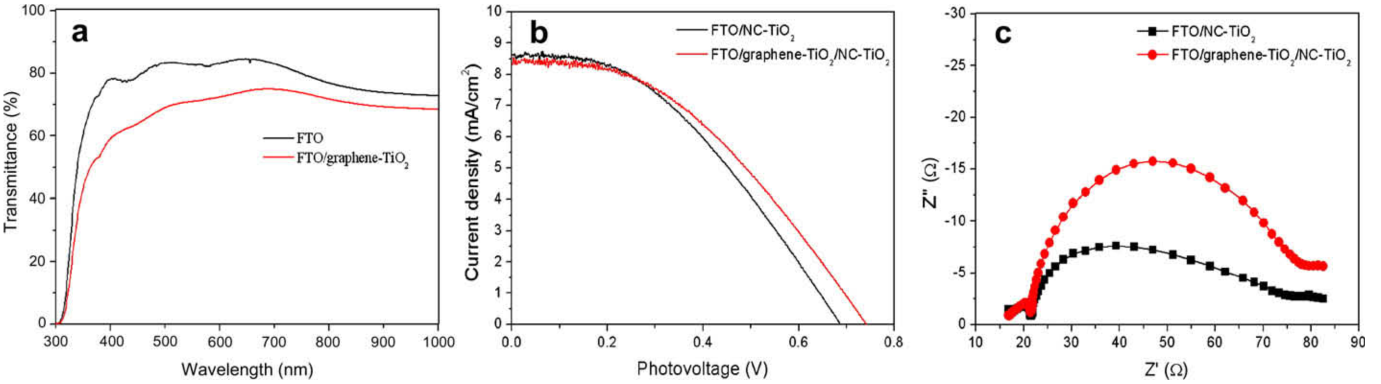

Fig. 3. (a) UV–Vis transmission spectrum of bare FTO and graphene–TiO_2 coated FTO substrate, (b) *J–V* characteristics curves and (c) impedance spectra (Nyquist plots) of the DSSCs with and without graphene–TiO_2 interfacial layer.

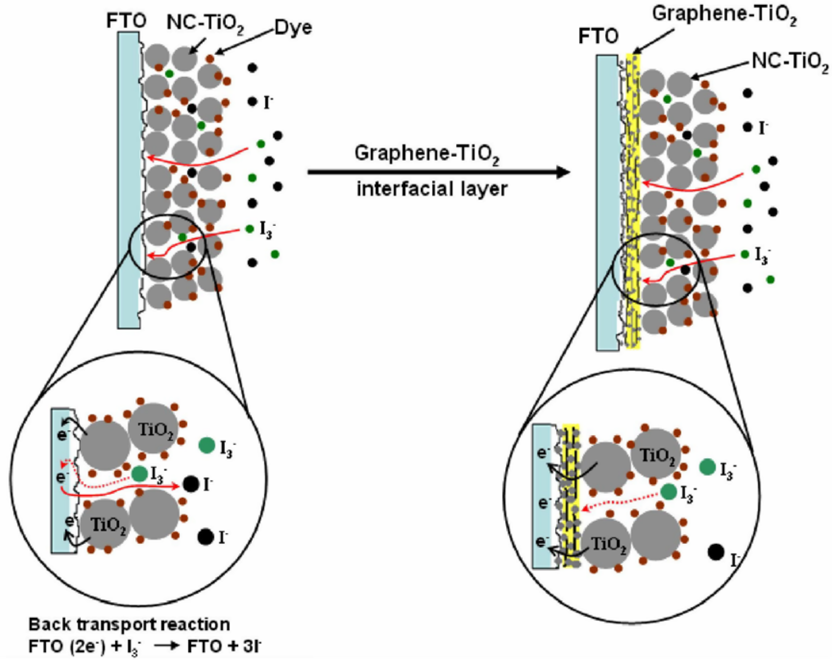

Fig. 4. Schematic representation and mechanism of applied graphene–TiO_2 interfacial layer to prevent back-transport reaction of electrons.

port of electrons from the FTO electrode to the I_3^- ions and thus increasing V_{oc}.

By introducing graphene–TiO_2 interfacial layer in the DSSCs, the open-circuit voltage (V_{oc}) increased. Therefore it can be stated that, the back-transport of electrons from the FTO electrode to the I_3^- ions was suppressed by the introduction of graphene–TiO_2 interfacial layer. Two-dimensional graphene sheet acts a barrier between FTO layer and electrolyte and thus increasing the open-circuit photovoltage (V_{oc}).

4. Conclusion

Graphene oxide in the GO–TiO_2 nanocomposites was successfully reduced by UV-assisted photocatalytic reduction. The reduced graphene–TiO_2 nanocomposites were applied as interfacial layer between FTO and nanocrystalline TiO_2 layer in DSSCs. The low roughness of graphene–TiO_2 interfacial layer provided better adhesion between the FTO substrate and NC-TiO_2 layer than without any interfacial layer. The introduction of 500 nm thick graphene–TiO_2 interfacial layer resulted in a 54 mV increase in the open-circuit voltage (V_{oc}) due to retardation of the back-transport reaction in the FTO/TiO_2 interface. It is believed that the two-dimensional graphene sheets significantly decrease the direct contact of the electrolyte with the FTO substrate. The photoconversion efficiency increased from 4.89% to 5.26% after introducing the graphene–TiO_2 interfacial layer.

Acknowledgements

This research was supported by a grant from the University Restructuring Program (funded by the Ministry of Education and Human Resources Development) of Chungju National University. Also, this work was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.10.066.

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