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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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\textsubscript{2} nanoparticles with average particle size 15–20 nm are typically deposited as a porous layer with a thickness of 10–12 \(\mu\)m 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\textsubscript{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\textsubscript{2} layer is formed by doctor blade method, the rough FTO surface may not be covered uniformly by the TiO\textsubscript{2} particles (for example Degussa P25 has particle size 25 nm). This can lead to the formation of some voids between the TiO\textsubscript{2} nanoparticles and FTO glass interface [7]. In addition, TiO\textsubscript{2} nanoparticles have a tendency to form large colloids in suspension or paste. Some parts of the FTO surface are not covered by TiO\textsubscript{2} and can directly contact with electrolytes, thereby decreasing \(V\text{oc}\) by the electron back-transport reaction [\(\text{FTO}(2e^-) + I_3^- \rightarrow \text{FTO} + 3I^-\)]. Therefore, controlling the interface between FTO and TiO\textsubscript{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.

A mixture of graphene oxide (GO) and TiO\textsubscript{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\textsubscript{2} film. Impedance spectra implied a decreased back-transport reaction of electrons. The graphene–TiO\textsubscript{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\textsubscript{2} increased \(V\text{oc}\) by 54 mV and the photoconversion efficiency was improved from 4.89\% to 5.26\%.

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\textsubscript{4}) are used for chemical reduction, and temperatures \(-1100\) \(^\circ\)C are required for thermal reduction.

This Letter reports the UV-assisted photocatalytic reduction of graphene oxide mixed with TiO\textsubscript{2} nanoparticles without the need for hazardous chemicals and high temperature annealing. This graphene–TiO\textsubscript{2} was applied as an interfacial layer between FTO layer and nanocrystalline TiO\textsubscript{2} (NC-TiO\textsubscript{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\textsubscript{2} hybrid based working electrodes [16]. Two-dimensional flat graphene sheets incorporated with small TiO\textsubscript{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\textsubscript{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\textsubscript{2} colloidal suspension \((0.05 \text{ M})\) 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 \((1.5 \text{ mg/ml})\) was added to the TiO\textsubscript{2} colloidal suspension and sonicated for...
30 min to disperse of GO sheets with TiO2 particles. UV-assisted reduction of graphene oxide was performed by 450 W xenon arc lamp for about 2 h.

Reduced graphene–TiO2 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 TiO2 paste (Degussa P25) was cast over graphene–TiO2 interfacial layer by doctor blade technique and successive sintering at 500 °C for 30 min. The nanocrystalline TiO2 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 I2, 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/cm². AM 1.5 simulated sunlight by using 450 W xenon arc lamp (HL 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–TiO2 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 10⁻¹–10⁹ Hz at room temperature.

3. Results and discussion

Fig. 1a shows the change in color from light brown¹ 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 TiO2 particles as witnessed by the chemical reduction of GO sheets [18,19]. Charge separation occurs upon UV-irradiation of the TiO2 particles as witnessed by the chemical reduction of GO sheets [18,19]. charge separation occurs upon UV-irradiation of the TiO2 particles as witnessed by the chemical reduction of GO sheets [18,19].

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.
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–TiO₂ nanocomposites were applied as interfacial layer between FTO and nanocrystalline TiO₂ layer in DSSCs. The low roughness of graphene–TiO₂ interfacial layer provided better adhesion between the FTO substrate and NC-TiO₂ layer than without any interfacial layer. The introduction of 500 nm thick graphene–TiO₂ 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/TiO₂ 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–TiO₂ interfacial layer.

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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.

References