Improving the performance of dye-sensitized solar cells with TiO$_2$/graphene/TiO$_2$ sandwich structure

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Abstract
This study investigates the extent to which the TiO$_2$/graphene/TiO$_2$ sandwich structure improves the performance of dye-sensitized solar cells (DSSCs) over that of DSSCs with the traditional structure. Studies have demonstrated that the TiO$_2$/graphene/TiO$_2$ sandwich structure effectively enhances the open circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), and photoelectrical conversion efficiency ($\eta$) of DSSCs. The enhanced performance of DSSCs with the sandwich structure can be attributed to an increase in electron transport efficiency and in the absorption of light in the visible range. The DSSC with the sandwich structure in this study exhibited a $V_{oc}$ of 0.6 V, a high $J_{sc}$ of 11.22 mA cm$^{-2}$, a fill factor (FF) of 0.58, and a calculated $\eta$ of 3.93%, which is 60% higher than that of a DSSC with the traditional structure.

Keywords: Graphene; Solar cells; Sandwich structure; TiO$_2$

Background
Dye-sensitized solar cells (DSSCs) are attracting attention globally because of their low cost, high energy conversion efficiency and potential applications [1-4]. Graphene has been extensively utilized in organic photovoltaic (PV) cells owing to its excellent optical and electrical characteristics, which are exploited in transparent conductive films or electrodes [5-8]. Some researchers have reported on composite graphene-TiO$_2$ photoelectrodes in DSSCs [9-12]. Fang et al. [9,10] discussed the effect of the amount of graphene on the structures and properties of DSSCs. DSSCs with the optimal composite TiO$_2$ film can achieve a photoelectrical conversion efficiency of 7.02%. Graphene is also commonly used in graphene-based counter electrodes in DSSCs [13-15]. The conventional counter electrode is platinum (Pt) because of its outstanding conductivity, catalytic activity, and stability when in contact with an iodine-based electrolyte. The expensive Pt can be replaced with graphene films in DSSCs without significantly sacrificing photoelectrical efficiency. This replacement can simply reduce the cost of the fabrication process [13]. Zhang et al. [14] grew DSSCs with graphene-based counter electrodes, which exhibited a photoelectrical conversion efficiency of as high as 6.81%. Double-layer photoelectrodes have been used to increase the photoelectrical conversion efficiency of DSSCs. Many investigations have focused on modifying the nanostructures of TiO$_2$ photoelectrodes to nanospheres, nanospindles, nanorods, nanowires, and others [16-20]. Many special nanostructures of photoelectrodes can increase the scattering of light and improve the performance of DSSCs [16,17].

This work develops a new TiO$_2$/graphene/TiO$_2$ sandwich structure for photoelectrodes. A thin layer of graphene was inserted into the traditional TiO$_2$ photoelectrode layer, making it a double layer. DSSCs with the traditional structure were also fabricated and the characteristics of the prepared DSSCs were compared. The DSSC with the TiO$_2$/graphene/TiO$_2$ sandwich structure exhibited excellent performance and higher photoelectrical conversion efficiency. This improvement is associated with the increase in electron transport efficiency and the absorption of light in the visible range.

Methods
Preparation of TiO$_2$ photoelectrodes
The TiO$_2$ slurry was prepared by mixing 6 g of nanocrystalline powder (P25 titanium oxide; Evonik Degussa Japan

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Preparation of graphene
The graphene film was prepared using a radio-frequency magnetron sputtering system with a carbon target (99.99%, Optotech Materials Co., Ltd, Taichung, Taiwan). The photoelectrodes were dried and annealed at 450°C for 30 min.
graphene film was deposited on the surface of the first photoelectrode layer. The working pressure of the chamber was maintained at 3 mTorr. The constant RF power was 90 W; the flow rate of argon was 90 sccm, and the deposition time was 2 min.

**DSSC assembly**

The electrolyte was composed of 0.05 M iodide, 0.5 M lithium iodide, and 0.5 M 4-tert-butylpyridine (TBP) in propylene carbonate. A 100-nm-thick layer of platinum was sputtered onto the ITO substrate as an electrochemical catalyst to form the counter electrode. Cells were fabricated by placing sealing films between the two electrodes, leaving two via holes through which the electrolyte could be injected. The sealing process was performed on a hot plate at 100°C for 3 min. Then, the electrolyte was injected into the space between the two electrodes through via holes. Finally, the via holes were sealed using epoxy with a low-vapor transmission rate. DSSCs with different structures were prepared to examine the effect of structure on the properties of the DSSC. Sample 1 was fabricated with a traditional structure and a single TiO$_2$ photoelectrode layer, which was spin-coated at a rotation
rate of 4,000 rpm. Sample 2 also had the traditional structure with a single TiO₂ photoelectrode layer, which was spin-coated at a rotation rate of 2,000 rpm. Sample 3 had the sandwich structure of TiO₂/graphene/TiO₂ on ITO glass, and the deposition of the TiO₂ photoelectrodes was performed at rotation rate of 4,000 rpm.

**Characterization**

The crystalline microstructure of the products was elucidated using a PANalytical X’Pert Pro DY2840 X-ray diffractometer (PANalytical B.V., Almelo, The Netherlands) with Cu-Kα radiation (λ = 0.1541 nm) in the scanning range 2θ = 30° and 70°. The surface morphology and vertical structure were analyzed using a LEO 1530 field-emission scanning electron microscope (One Zeiss Drive Thornwood, New York, USA). The optical absorption properties were measured in the range of 300 to 900 nm using a Hitachi U-2001 ultraviolet-visible spectrophotometer (Chiyoda, Tokyo, Japan). The photocurrent voltage (I-V) characteristics were measured using a Keithley 2420 programmable source meter under 100 mW cm⁻² irradiation (Keithley Instruments Inc., Cleveland, OH, USA). Simulated sunlight was

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**Figure 4** UV-vis absorption spectra of DSSCs with different structure (a) before and (b) after dye loading.
provided by a 500-W xenon lamp (Hong Ming Technology Co, Ltd, Taiwan) that had been fitted with an AM-1.5 filter. The active area of each DSSC, which was exposed to the light, was 0.3 × 0.3 cm².

Results and discussion

Figure 1 presents the phase structure of the TiO₂ photoelectrodes in the samples. Clearly, most peaks were indexed to anatase TiO₂ (JCPDS No. 21-1271). Only one peak, at θ = 27.41°, corresponded to rutile TiO₂ (JCPDS No. 76-0317). The strong similarity of the patterns of that were obtained from the samples indicates that the phase structures of the samples were all the same although the structures of the DSSCs differed.

Figure 2a shows the surface morphology of the TiO₂ photoelectrode. The TiO₂ nanoparticles have a mean diameter of 50 nm. Sufficient interspaces in the photoelectrode layer facilitated the loading of dye into the film. Figure 2b,c,d shows the cross-sectional scanning electron microscopy (SEM) images of the three prepared DSSCs - samples 1, 2, and 3, respectively. The thicknesses of the photoelectrodes in samples 1 and 2 were 4 and 9.5 μm, respectively, as presented in Figure 2b,c. However, the thickness of the first TiO₂ layer in sample 3 was 4 μm and that of the second layer was 6.5 μm. The thickness of the two photoelectrode layers differed although the spin-coating parameters were the same because different substrates were used during spin-coating. The graphene layer served as the substrate when the second photoelectrode layer had been deposited. The thickness of the photoelectrode of sample 3 is almost the same as the one of sample 2.

Figure 3a,b presents the Raman scattering spectra of the graphene film that was deposited on the glass substrate using the process that was described in the ‘Preparation of graphene’ section. The spectra include important peaks that correspond to the D band (approximately 1,350 cm⁻¹), the G band (approximately 1,580 cm⁻¹), and the 2D band (approximately 2,700 cm⁻¹) [21]. The D band originates from defects owing
to the disorder of the sp²-hybridized carbon atoms. The G band is associated with the doubly degenerate E₂g mode. The 2D peak is associated with the second-order modes of the D band. The Raman spectra indicate that the prepared graphene layer exhibits two-dimensional properties.

Figure 4 displays the UV-vis spectra of photoelectrodes with different structures before and after they were loaded with dye. Clearly, the photoelectrode with the TiO₂/graphene/TiO₂ sandwich structure has a higher absorption than those with the traditional structure both before and after loading with dye. Dye loading substantially increases the absorption in the short wavelength region (400 to 600 nm) perhaps because of the absorption of light by the N719 dye. The DSSC with the TiO₂/graphene/TiO₂ sandwich structure exhibited the greatest increase in absorption after dye loading perhaps because of the interface between the graphene and the TiO₂ film and the upper photoelectrode with more porous structure, which retained more dye.

Figure 5 presents the energy level diagram of the DSSC with the TiO₂/graphene/TiO₂ sandwich structure. Under illumination, electrons from the photoexcited dye are transported to the conduction band (CB) of TiO₂ via the CB of the graphene and TiO₂. The transportation path via the CB of graphene is in addition to the traditional path. Owing to the excellent electrical conduction of the graphene, the graphene layer bridges behave as a channel for transferring electrons and rapidly transport the photoexcited electrons [22]. The graphene is homogeneous throughout the system, and the excited electrons are captured by the graphene without any obstruction. The collected electrons can be rapidly and effectively transported to the CB of TiO₂ through graphene bridges. In the interface of graphene and TiO₂, the resistance through which charges are transported is reduced relative to the DSSC without graphene bridge and the recombination and back-reaction processes are suppressed.

Figure 6 plots the photovoltaic performance of the DSSCs that were fabricated with the traditional structure and the sandwich structure on ITO substrate. Table 1 summarizes the photovoltaic parameters of these fabricated DSSCs. The model used to calculate shunt resistance (Rsh) and series resistance (Rs) is taken from [23]. Clearly, the DSSCs with the sandwich structure have higher photoelectrical conversion efficiency (3.93%) than those with the traditional structure (2.46%). This improvement in photoelectrical conversion efficiency in the DSSCs arises mainly from increases in Jsc and Voc. The sandwich structure also slightly increases FF. The recombination of the electrons is suppressed and an additional path for the transportation of photogenerated electrons is available, increasing Jsc. Moreover, the photoelectrodes with the TiO₂/graphene/TiO₂ sandwich structure have a smaller absorption edge, as presented in Figure 3, so the DSSC with the TiO₂/graphene/TiO₂ sandwich structure can absorb light over a wide range of wavelengths and, therefore, has a higher Voc.

Conclusions
This work proposed a simple and convenient method to enhance the performance of DSSCs by using a low-cost and easy fabrication process. DSSCs with three structures were fabricated, and the characteristics of these DSSCs, including the Jsc, Voc, and photoelectrical conversion η of these DSSCs, were investigated. Clearly, the induced graphene film and sandwich structure markedly improve the performance of the DSSCs. This improvement in performance is associated with an increase in the absorption of light, a wide range of absorption wavelengths, shorter charge transportation distances, and the suppression of charge recombination when the graphene is applied.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
LCC wrote the paper and designed the experiments. CHH prepared the samples. PSC, XYZ, and CJH did all the measurements and analyzed the data. All authors read and approved the final manuscript.

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References
1. Grätzel M: Perspectives for dye-sensitized nanocrystalline solar cells. Prog Photovolt Res Appl 2003, 11:171–185.
2. O’Regan B, Grätzel M: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. Nature 1991, 353:737.
3. Grätzel M: Solar energy conversion by dye-sensitized photovoltaic cells. Inorg Chem 2005, 44:6841.
4. Grätzel M: Photoelectrochemical cells. Nature 2001, 414:338–344.
5. Du X, Slachta I, Barker A, Andrei FY: Approaching ballistic transport in suspended graphene. Nat Nanotechnol 2008, 3:491.
6. Nar RR Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, Peres NM, Geim AK: Fine structure constant defines visual transparency of graphene. Science 2008, 320:1308.
7. Bae S, Kim H, Lee Y, Xu XF, Park JS, Zheng Y, Balakrishnan J, Lei T, Kim HR, Song Yi, Kim YJ, Kim KS, Ozyilmaz B, Ahn JH, Hong BH, Iijima S: Roll-to-roll production of 30-inch graphene films for transparent electrodes. Nat Nanotechnol 2010, 5:574–578.

Table 1 Photovoltaic parameters of DSSCs fabricated with different structures

| Sample label | Jsc (mA cm⁻²) | Voc (V) | FF | η (%) | Rsh (Ω) | Rs (Ω) |
|--------------|---------------|--------|----|-------|--------|-------|
| 1            | 4.46          | 0.56   | 0.55| 1.38  | 9,888  | 1     |
| 2            | 8.044         | 0.55   | 0.56| 2.46  | 7,785  | 1     |
| 3            | 11.22         | 0.6    | 0.58| 3.93  | 7,558  | 3     |
8. Wang X, Zhi L, Tao N, Tomovic Z, Li J, Muller K: Transparent carbon films as electrodes in organic solar cells. Angew Chem Int Ed 2008, 47:2990–2992.
9. Fang X, Li M, Guo K, Zhu Y, Zhangqiang H, Liu X, Chen B, Zhao X: Improved properties of dye-sensitized solar cells by incorporation of graphene into the photoelectrodes. Electrochim Acta 2012, 65:174–178.
10. Fang X, Li M, Guo K, Liu X, Zhu Y, Sebo B, Zhao X: Graphene-compositing optimization of the properties of dye-sensitized solar cells. Sol Energy 2014, 101:176–181.
11. Sun S, Gao L, Liu Y: Enhanced dye-sensitized solar cell using graphene-TiO2 photoanode prepared by heterogeneous coagulation. Appl Phys Lett 2010, 96:033113.
12. Tsai T-H, Chiou S-C, Chen S-M: Enhancement of dye-sensitized solar cells by using graphene-TiO2 composites as photoelectrochemical working electrode. Int J Electrochem Sci 2011, 6:3333–3343.
13. Gong F, Wang H, Wang Z-S: Self-assembled monolayer of graphene/Pt as counter electrode for efficient dye-sensitized solar cell. Phys Chem Chem Phys 2011, 13:17676–17682.
14. Zhang DW, Li XD, Li HB, Chen S, Sun Z, Yin XJ, Huang SM: Graphene-based counter electrode for dye-sensitized solar cells. Carbon 2011, 49:5382–5388.
15. Choi H, Kim H, Hwang S, Han Y, Jeon M: Graphene counter electrodes for dye-sensitized solar cells prepared by electrophoretic deposition. J Mater Chem 2011, 21:7548.
16. Park JT, Roh DK, Chi WS, Patel R, Kim JH: Fabrication of double layer photoelectrodes using hierarchical TiO2 nanospheres for dye-sensitized solar cells. J Mater Chem 2012, 18:4440–455.
17. Qiu Y, Chen W, Yang S: Double-layered photoanodes from variable-size anatase TiO2 nanospindles: a candidate for high-efficiency dye-sensitized solar cells. Angew Chem 2010, 122:3757–3761.
18. Lin XF, Song DM, Gu XQ, Zhao YL, Qiang YH: Synthesis of hollow spherical TiO2 for dye-sensitized solar cells with enhanced performance. Appl Surf Sci 2012, 263:816–820.
19. Kim A-Y, Kang M: High efficiency dye-sensitized solar cells based on multilayer stacked TiO2 nanoparticle/nanotube photoelectrodes. J Photochem Photobiol A Chem 2012, 233:20–23.
20. Bakhtiyar A, Mohammadi MR, Dadar H, Fray DJ: Improved efficiency of dye-sensitized solar cells aided by corn-like TiO2 nanowires as the light scattering layer. Electrochim Acta 2013, 90:302–308.
21. Ferrari AC, Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov KS, Roth S, Geim AK: Raman spectrum of graphene and graphene layers. Phys Rev Lett 2006, 97:247401.
22. Yang N, Zhai J, Wang D, Chen Y, Jiang L: Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells. ACS Nano 2010, 4:887–894.
23. Murayama M, Mori T: Evaluation of treatment effects for high-performance dye-sensitized solar cells using equivalent circuit analysis. Thin Solid Films 2006, 509:123–126.

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