

Effect of TiO₂–graphene nanocomposite photoanode on dye-sensitized solar cell performance

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Abstract. In this research work, graphene–TiO₂ photoanodes with various graphene concentrations (0, 0.5, 1, 1.5 and 2 wt%) were deposited on fluorine tin oxide glass substrates as working electrodes for dye-sensitized solar cells. The structure, morphology, surface composition and dye adsorption of the photoanodes were investigated by X-ray diffraction, field emission scanning electron microscopy, X-ray photoelectron spectroscopy and UV–VIS–NIR spectroscopy, respectively. The photocurrent–voltage characteristics of the dye-sensitized solar cells were examined using a solar simulator. The results indicated that the dye adsorption on photoanode surfaces increases with the increase in the graphene content. In addition, dye-sensitized solar cells efficiency increases with the increase in the graphene content to 1.5 wt% and then decreased. The efficiency of the dye-sensitized solar cell, based on the TiO₂–1.5 wt% graphene nanocomposite, increased by 42% with respect to the pristine sample.

Keywords. Photoanode; graphene; nanocomposite; dye-sensitized solar cell; efficiency.

1. Introduction

Growing concerns about environmental pollution, such as global warming, carbon dioxide emission from vast uses of fossil fuels and the increasing demand for energy sources, are the driving force for the use of clean and renewable energy sources.^{1–3}

Among renewable energy sources, semiconductor-based solar cells such as silicon-based p–n junction solar cells have attracted a great deal of attention as a clean renewable energy source.⁴ However, semiconductor-based solar cells have limitations, such as high cost and environmentally hazardous waste produced in the fabrication process. Photoelectrochemical dye-sensitized solar cells (DSSCs) have been considered as a substitute for semiconductor solar cells because of their low cost, relatively high conversion efficiency and nontoxicity.^{4,5}

A DSSC contains a semiconductor photoanode, a layer of dye attached to the photoanode, a counter electrode and an electrolyte. Titanium dioxide (TiO₂) is one of the most promising nanocrystalline semiconductor materials used as a photoanode in the DSSCs due to its low cost, chemical stability and optical properties.^{6,7} The TiO₂ photoanode has a key role throughout the light-to-electricity conversion in the DSSCs. It contains electron movement from the dye molecules to the TiO₂ conduction band and electron transfer to the external circuit.⁸

However, charge recombination is a main negative factor that limits DSSC performance. In other words, the back-electron transfer in the TiO₂ photoanode–electrolyte interface before reaching the collecting electrode, such as fluorine-doped tin oxide (FTO), is assumed to be the major recombination pathway, which reduces the DSSC efficiency.² It is predicted that improving the conduction pathways from the location of the photo-generated carriers to the collecting electrode would considerably enhance the DSSC efficiency.

To prevent recombination and improve transport, there are several approaches used, including (1) the use of composite semiconductor photoanode with different bandgaps, (2) insertion of some doping elements in the TiO₂ photoanode and (3) incorporating charge carriers to direct the photogenerated electron.

Some researchers indicate that a composite photoanode, such as TiO₂/SnO₂ improved DSSC efficiency.^{9,10} In addition, the insertion of doping elements such as zirconium, aluminium, ruthenium and niobium promoted charge transfer and increased DSSC efficiency.⁹ In recent years, one-dimensional (1D) and two-dimensional (2D) nanomaterials such as carbon nanotubes (CNTs) and graphene sheets have been incorporated into TiO₂ photoanodes to enhance DSSC performance. However, DSSC efficiency was improved limitedly by the addition of CNTs in the TiO₂ photoanode. The graphene may be more favourable than CNTs for charge separation due to its excellent conductivity and good contact with TiO₂.¹¹

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TiO₂ can attach to the graphene to form graphene bridges. These graphene bridges reduce the TiO₂–TiO₂ connections and act as an electron transfer from the TiO₂ conduction band to the collective electrode.

In this way, charge recombination could be suppressed and DSSC efficiency is enhanced.^{4,10,12} In this research, TiO₂–graphene nanocomposite photoanodes were deposited on conductive glass substrates. Then, DSSC performance, based on the various TiO₂–graphene photoanodes, was investigated.

2. Experimental

2.1 Fabrication of DSSCs

For the fabrication of the photoanodes, FTO-coated glass substrates, 25 × 25 mm² (FTO, Solaronix, Switzerland, 15 Ω sq⁻¹), were first ultrasonically cleaned in ethanol, acetone and water for 30 min, respectively. Graphene–TiO₂ nanocomposite photoanode was deposited on the FTO substrates as follows:

Seven grams of TiO₂ powder (TECNAN, 25 nm particle size), graphene sheets (0, 0.5, 1, 1.5 and 2 wt%) and 30 ml ethanol (Sigma Aldrich, 99.5%) were mixed in a dried agate mortar for 40 min. Then, 1 ml tetrabutyl orthotitanate (Sigma Aldrich, 97%) was added to the above paste, and the final mixture was stirred for 1 day to obtain the desired paste. The obtained pastes were deposited on the FTO substrates by the doctor blade method. The films were dried at 100°C for 1 h. Finally, the film was annealed at 450°C for 1 h. For sensitization, a dye solution is obtained by mixing of 20 mg of N719 dye (Solaronix, Switzerland) in 100 ml ethanol. Then, the photoanodes were immersed in a dye solution for 24 h. Pt counter electrodes were prepared by depositing a Plastisol solution (Solaronix) on the FTO substrates with doctor blade method, and then heated at 400°C for 30 min in air. The Pt/FTO prepared electrodes were coupled with photoanodes. The electrodes were separated by a Surlyn film (Solaronix) and sealed together by heating. A thin layer of electrolyte was introduced into the inter electrode space. The electrolyte used was 0.5 M LiI, 0.05 M I₂, 0.5 M 4-tert-butylpyridine in acetonitrile.

2.2 Characterization

The structure and morphology of the photoanodes were determined using a Bruker X-ray diffractometer (XRD, D8ADVANCE, Germany, Ni-filter, CuKα radiation λ = 1.5406 Å) and field emission scanning electron microscopy (FE-SEM, Hitachi S4160, Cold Field Emission, voltage 20 kV). The surface chemical composition of the photoanode was analysed by X-ray photoelectron spectroscopy (XPS) using an AlKα source (1486.6 eV). The X-ray source was operated at 15 kV with a current of

10 mA. The adsorption of the dye on the photoanodes was measured by a UV–VIS–NIR spectroscopy (JASCO, V 670).

Photocurrent–voltage characteristics of the DSSCs under AM 1.5 G illumination (100 mW cm⁻²) were investigated using a solar simulator (Palm Sense MODEL). DSSC efficiency was evaluated from¹³

$$\eta = \frac{FF \cdot J_{SC} \cdot V_{OC}}{P_{in}}, \quad (1)$$

where V_{OC} is the open-circuit voltage, J_{SC} the short-circuit current, P_{in} the input power density and FF the fill factor, respectively.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of TiO₂ and graphene–TiO₂ photoanodes. As can be seen, all samples contain both anatase and rutile phases and the graphene did not affect the crystalline phases. In this research work, we used TiO₂ with both anatase and rutile phases. It is believed that a combination of anatase and rutile phases has higher photo-reactivity than either anatase or rutile alone.¹⁴ The effect of TiO₂ photoanode mixing on the anatase and rutile phases in the DSSC performance can be related to two factors, including (1) electrons migrating from the rutile conduction band (CB) to the anatase CB and (2) possible electron transfer between anatase–rutile grain boundaries. During illumination, electrons were inserted from the dye molecules to the rutile CB, and then moved to the anatase CB, as the anatase CB is located below the rutile CB. Electron transfer from the rutile CB to the anatase CB enhances the possibility of electron injection. Then, the charge recombination rate at the photoanode–electrolyte interface is reduced and DSSC performance increases.²

Figure 2 shows the FE-SEM images of the TiO₂ nanoparticles and graphene sheet. The average particle size of

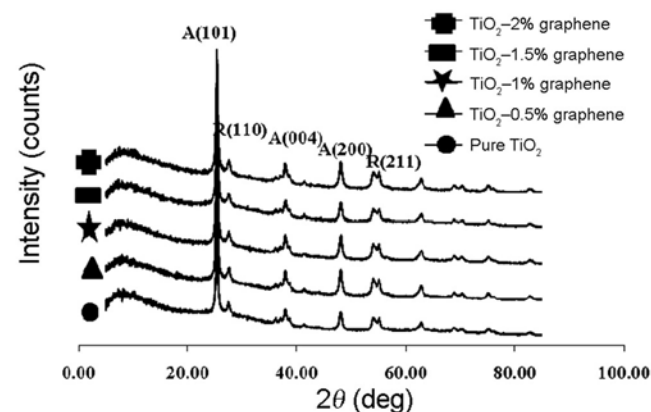


Figure 1. XRD pattern of photoanodes based on the different graphene concentrations.

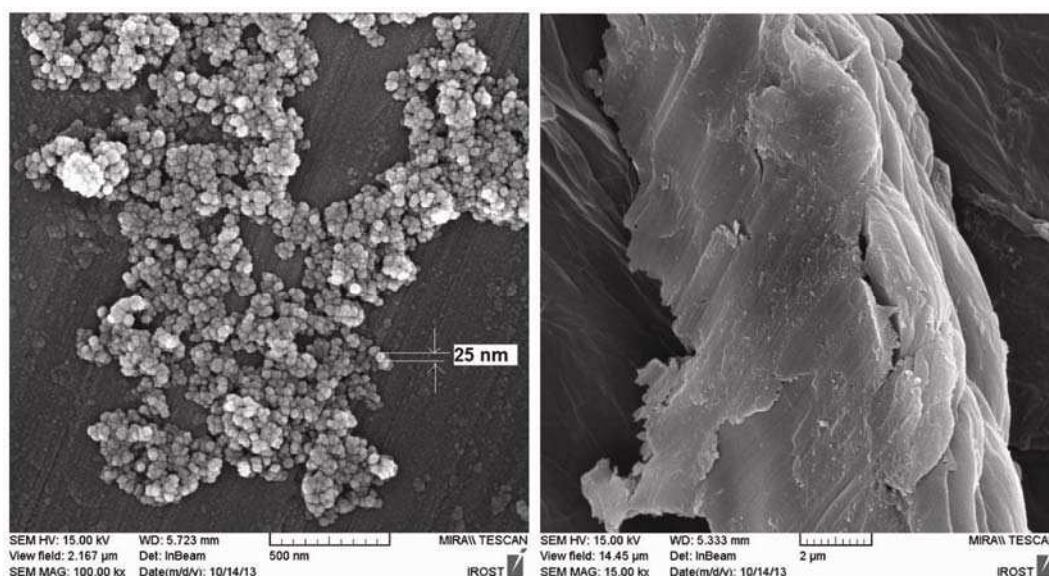


Figure 2. FE-SEM TiO₂ nanoparticles (left) and graphene sheet (right).

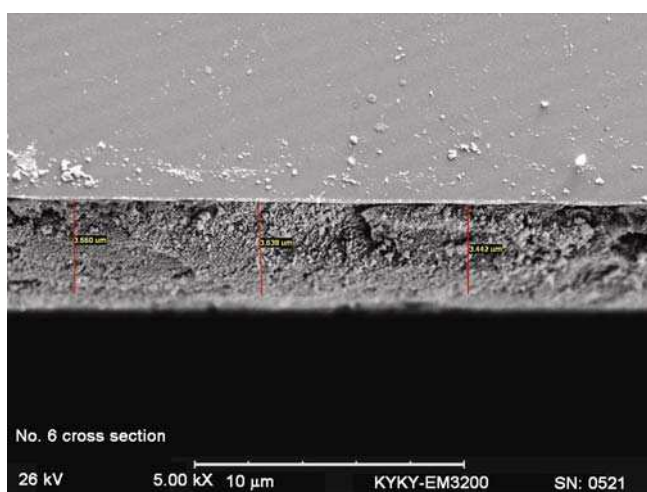


Figure 3. FE-SEM cross-section image of the TiO₂-1.5 wt% graphene photoanode.

the TiO₂ is 25 nm. In addition, figure 3 shows a cross-section of the TiO₂-1.5 wt% graphene photoanode. The thickness of the photoanode is 3 μm.

Figure 4 shows the FE-SEM images of the TiO₂ and TiO₂-graphene photoanodes. Figure 4 shows that the TiO₂ photoanode film is porous. The pore size in the TiO₂ photoanode was increased by the insertion of graphene. It means that the addition of graphene made a larger pored photoanode. Some researchers investigated and reported the reason for this phenomenon in the TiO₂ containing CNTs. They ascribed it to the good separation ability of the CNTs among the TiO₂ photoanode nanoparticles.

Therefore, graphene, due to its specific 2D structures, could lead to more effective separation than CNTs. Thus, the high porosity of the TiO₂-graphene films was

obtained.⁵ In addition, the fabrication of the porous photoanode has a positive effect on DSSC efficiency. The porous structure is expected to approach a higher surface area. There are more sites for dye adsorption in the TiO₂-graphene photoanode in comparison to the conventional TiO₂ photoanode. So, a higher amount of dye adsorption induced by incorporating graphene, as illustrated in figure 5, is expected to lead to enhancement in the DSSCs performance.

Figure 6 shows the XPS spectra of the photoanodes with and without graphene. The C 1s peak of the photoanode with graphene is stronger than that without it, proving that graphene was inserted into the TiO₂ photoanode.¹¹

The current density-voltage (J - V) characteristics and DSSCs efficiencies based on the different photoanodes are reported in table 1 and figure 7.

The results indicated that the J_{SC} first increased with the increased graphene concentration, reaching a peak value of 8.835 mA cm⁻² at a graphene concentration of 1.5 wt%, and then decreased to 3.615 mA cm⁻² at 2 wt%. However, the V_{OC} remained almost unchanged (0.61–0.68 V). The initial increase and subsequent decrease of J_{SC} can be explained by the formation of more conductive sites by graphene, which considerably decreases the transport resistance for photogenerated electrons. The J_{SC} corresponds to the ejected electron numbers throughout the external circuit, while V_{OC} is associated with the difference between the Fermi level of TiO₂ under illumination and the Nernst potential of the I^-/I_3^- redox couple in the electrolyte.³ The almost unchanged V_{OC} of the DSSC, based on TiO₂ and TiO₂-graphene photoanodes, shows that the Fermi level of the TiO₂-graphene photoanode is not affected by the graphene incorporation. Like the J_{SC} , the overall efficiency increases first, and then decreases

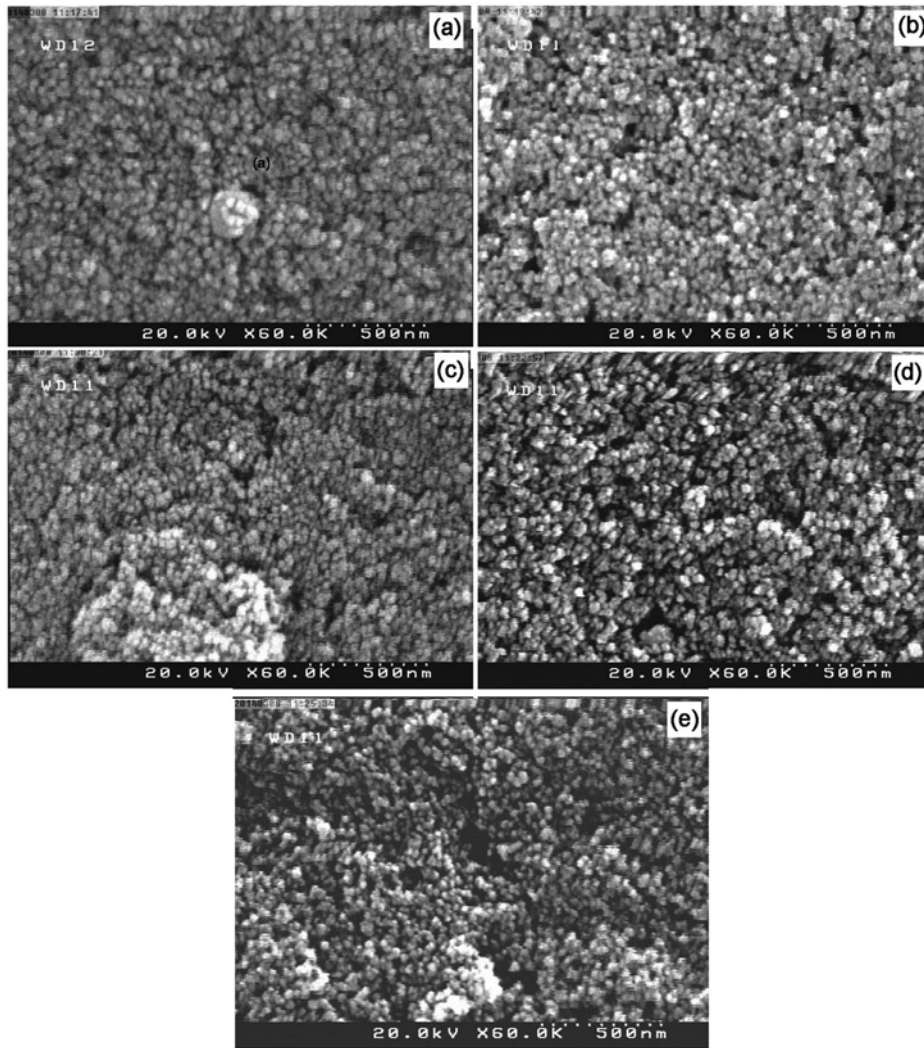


Figure 4. FE-SEM images of the photoanodes based on the different graphene concentrations: (a) 0, (b) 0.5, (c) 1, (d) 1.5 and (e) 2 wt%.

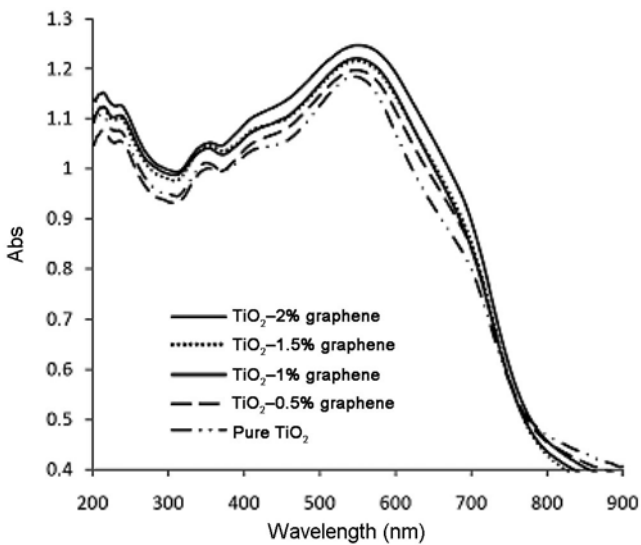


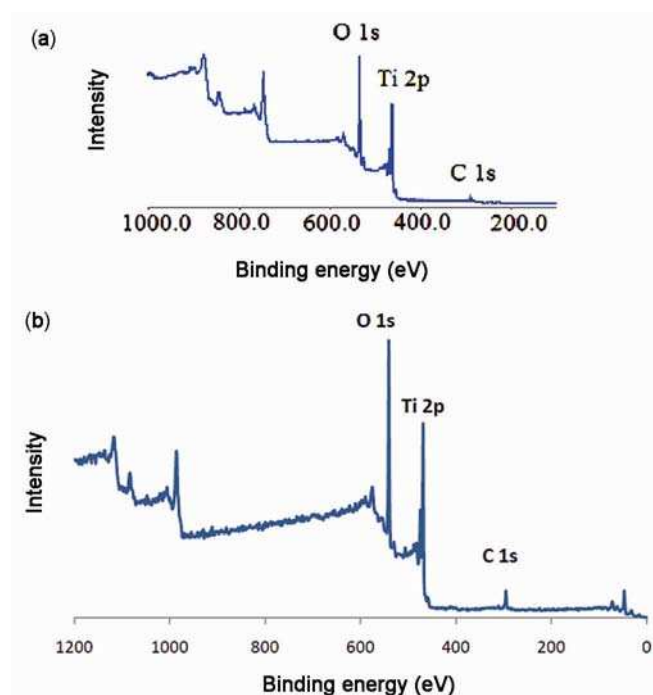
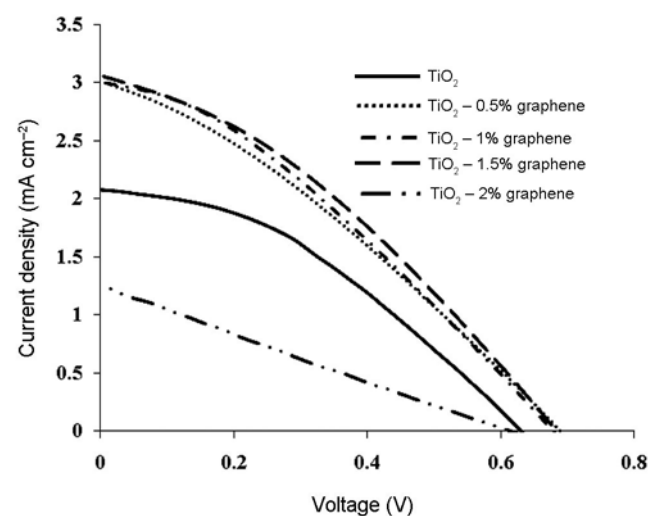
Figure 5. Dye adsorption on the photoanodes based on the different graphene amounts.

(figure 7). The improvement in DSSC performance, which is mainly due to the increase in J_{SC} for the graphene-TiO₂ photoanode, will be discussed in the following. Generally, there are several steps during the light-to-electricity conversion in DSSCs. The presumed light-to-electricity conversion in the DSSCs follows these steps^{8,15}



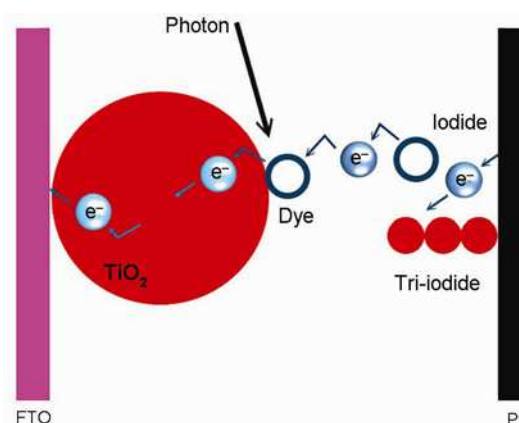
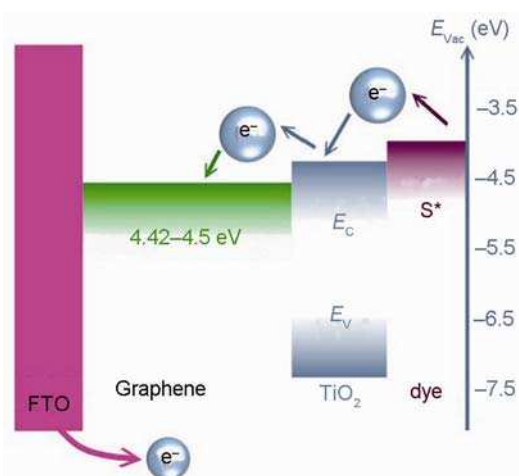
Table 1. Photovoltaic parameters of DSSCs assembled with photoanodes containing various amounts of graphene.

Graphene content, wt%	J_{SC}	V_{OC}	FF	$\eta\%$
0	6.01	0.63	0.13	0.49
0.5	8.71	0.69	0.11	0.65
1	8.77	0.68	0.11	0.67
1.5	8.84	0.68	0.12	0.7
2	3.62	0.61	0.08	0.19

**Figure 6.** XPS spectra of (a) TiO₂ and (b) TiO₂-1.5 wt% graphene photoanode.**Figure 7.** J - V curves of the DSSCs based on the different TiO₂-graphene photoanodes.

The working principle of the DSSCs is illustrated in figure 8. It is well known that the back-electron transfer at the TiO₂ photoanode-electrolyte interface is assumed to be the main reason for the decline in DSSC efficiency.²

According to the above results, it is noted that graphene causes remarkable enhancement in DSSC performance. DSSC performance was improved by the incorporation of graphene, due to two major factors: the first is the increased electron lifespan. In the TiO₂ photoanode, the photogenerated electrons must move through the thick TiO₂ film before arriving at the FTO substrate, and have a great chance of being recombined by the photo-generated hole. In the TiO₂-graphene nanocomposite photoanode, the TiO₂ conduction band is approximately -4.21 eV, whereas graphene has a work function (-4.42 eV) close to that of the FTO (-4.4 eV), as indicated in figure 9. In other words, the energy level of graphene is between the TiO₂CB and FTO. Under illumination, the CB of the TiO₂ captures the photogenerated electrons from the dye molecules. As the TiO₂ is supported by graphene, the excited electrons are received by the

**Figure 8.** Working principle of the DSSCs.¹⁶**Figure 9.** Schematic energy level diagram.¹²

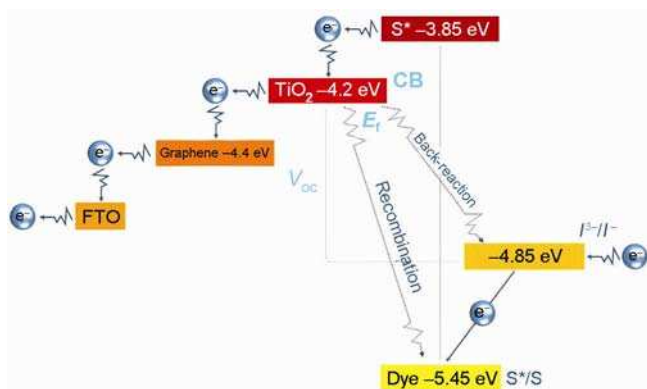


Figure 10. Schematic of the graphene effect on the charge recombination prevention in the TiO_2 -electrolyte interface.

graphene. Graphene, due to its excellent electrical conduction, acts as an electron transfer path, and then collected electrons can transfer rapidly to the FTO.^{11,12}

Hence, the graphene incorporated into the TiO_2 photoanode behaves as the electron acceptor and transferor for efficient charge separation and fast photogenerated electron transport to prevent charge recombination.¹⁶ The second is the increased dye adsorption: graphene improved the adsorptivity of the dye molecules on the TiO_2 -graphene photoanode as indicated in figure 5. As indicated above, the incorporation of graphene affected the surface morphology of the photoanodes and created more sites for dye molecule adsorption. It caused more light to be gathered and caused more electrons to be injected from the excited state of the dye into the TiO_2 CB, which improved the DSSC efficiency.^{2,3} However, when the graphene content was increased above its optimum value (1.5 wt%), DSSC efficiency decreased (table 1). This can be ascribed to two factors: the first graphene may absorb some light and thus, there is a light yielding rivalry between the dye and graphene, with the increase in the graphene content. In addition, it has been shown that graphene can absorb light in a wide wavelength range of 200–800 nm. Therefore, light absorption by the dye was reduced because the TiO_2 was surrounded by graphene. It means that the heavy incorporation of graphene into the DSSC has a negative result on the J_{SC} and conversion efficiency. The second graphene can behave as a recombination centre rather than producing an electron pathway. Excessive graphene increases the recombination of electron-hole pairs in the DSSC and then decreases DSSC efficiency.^{11,16}

In summary, it is concluded that graphene has both positive and negative effects on DSSC efficiency. As a positive effect, graphene accelerates electron transfer, reduces electron-hole recombination (figure 10), and then increases DSSC efficiency. Negatively, the graphene can act as a recombination centre for electron-hole pairs and thus decrease DSSC efficiency.

4. Conclusions

DSSCs based on TiO_2 -graphene photoanodes with various graphene concentrations were fabricated. The graphene concentration's effects on the DSSCs efficiency were investigated. The results are as follows:

- (1) Graphene incorporation increased dye adsorption on the TiO_2 -graphene photoanode.
- (2) Graphene incorporation in the TiO_2 photoanode first increased DSSC efficiency and then decreased it as the graphene amount was increased.
- (3) The maximum DSSC efficiency was obtained with the TiO_2 -1.5 wt% graphene photoanode.
- (4) The minimum DSSC efficiency was obtained with the TiO_2 -2 wt% graphene photoanode.

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