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# Titanium dioxide/graphene anode for enhanced charge-transfer in dye-sensitized solar cell

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ABSTRACT

Enhancement of power conversion efficiency has been a persistent objective for dye-sensitized solar cell (DSSC). We represent here the feasibility of incorporating graphene into mesoscopic $TiO_2$ with an aim of reducing electron loss within an anode. Results indicate that the short-circuit current density has been markedly enhanced due to the facile transfer of photogenerated electrons along graphene network from conduction band of $TiO_2$ nanocrystallites. An optimal power conversion efficiency of 7.56% is recorded from the DSSC employing 0.03 wt% graphene integrated $TiO_2$ in comparison with 5.21% for pristine $TiO_2$ based solar cell.



## 1. Introduction

Dye-sensitized solar cell (DSSC) [1–3], a photoelectrochemical device directly converting solar energy into electricity with no emissions, has attracted growing interests because of its superiorities in easy fabrication, relative high efficiency, environmental-friendliness, and scalable materials. A typical DSSC comprises of an inorganic semiconductor anode generally having $TiO_2$, liquid electrolyte containing $I^-/I_3^-$ redox couples, and a Pt counter electrode. With an aim of enhancing power conversion efficiency, reducing fabrication expense, and elevating long-term stability, many efforts have been made such as design of extraordinary $TiO_2$ structures [4,5], synthesis of cost-effective counter electrodes [6–8], and fabrication of quasi-solid or full-solid electrolytes [9,10]. The researchers have focused on creating the anodes with light enhancement effects [11–13], the interference effect of incident light reflected from $TiO_2/CaF_2$ ($SiO_2$, $GeO_2$) and $CaF_2$ ($SiO_2$, $GeO_2$)/electrolyte interfaces can markedly elevating the light intensity for dye irradiation and excitation. More recently, a class of transparent metal selenide alloy counter electrodes have been successfully fabricated by a mild solution method for bifacial DSSCs [14,15], which have superiority of generating electricity on both sides and help bring down the cost of solar-to-electric conversion [16].

We report here an avenue of enhancing solar cell efficiency by integrating graphene with $TiO_2$ nanocrystallites. The original intention of this design is to conducting electrons from conduction band of $TiO_2$ nanocrystallite to graphene, therefore shortening electron migration length. Moreover, the large interfacial resistance between adjacent $TiO_2$ nanoparticles increases the probability of trapping electrons. The direct transfer of photogenerated electrons FTO layer along graphene can significantly elevate electron density for electricity generation. The anodes and photovoltaic performances of their solar cells are optimized by controlling graphene dosage. This concept of reducing electron loss and shortening electron migration length is also of significance for other solar cells, such as quantum dot-sensitized solar cells, perovskite solar cells, and organic–inorganic hybrid solar cells.

## 2. Experimental

### 2.1. Preparation of graphene integrated $TiO_2$ colloids

The graphene integrated $TiO_2$ colloids were prepared as follows. Under vigorous agitation at room temperature, 100 mL of

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deionized water was mixed with 10 mL of titanium tetrabutanolate. After 30 min the mixture was pump-filtrated to obtain dehydrated filter powders. Subsequently, 10 mL of acetic acid and 0.8 mL of nitric acid were added dropwise to these filter powers in a flask. After agitating for 15 min at 80 °C, the volume of the mixture was adjusted to 170 mL by adding deionized water. The reactant was further agitated at 80 °C for 15 min in a sealed atmosphere and then transferred into a Teflon−lined autoclave for heating at 200 °C for 12 h. A homogeneous mixture consisting of 70 mL of the white colloid and 0.4 g of commercial P25 was formed under ultrasonic irradiation for 30 min and then transferred to another Teflon-lined autoclave, which was subsequently heated at 200 °C for 12 h. After removing the supernatant liquid, the colloid was mixed with 0.8 g of poly(ethylene glycol) ($M_w$ = 20,000), 1 mL of OP emulsifier, and stoichiometric graphene (The dosages of the graphene were controlled at 0.02, 0.03, 0.04, and 0.07 wt%) were concentrated at 80 °C to obtain graphene integrated $TiO_2$ colloids.

### 2.2. DSSC assembly

FTO glass substrates (12 Ω square$^{-1}$) with a size of 2 × 2 cm$^2$ were thoroughly rinsed with deionized water and anhydrous ethanol and then dried by an $N_2$ gas stream. Graphene integrated $TiO_2$ photoanodes were fabricated by coating graphene integrated $TiO_2$ colloid onto cleaned FTO substrates using a doctor-blade method. The size of the resultant graphene integrated $TiO_2$ film was controlled at 0.5 × 0.5 cm$^2$ with an average thickness of 10 μm. The air-dried colloids were calcined in a muffle furnace at 450 °C for 30 min. The heating temperature was controlled at a speed of 2 °C min$^{-1}$ from 25 to 130 °C and then at 6 °C min$^{-1}$ to 450 °C. The FTO glass supported graphene integrated $TiO_2$ were immersed in a 0.50 mM N719 ethanol solution for 24 h to obtain the dye-sensitized $TiO_2$/$CaF_2$ anodes. A DSSC device was assembled by sandwiching liquid electrolyte between a dye-sensitized graphene integrated $TiO_2$ anode and a Pt counter electrode (purchased from Dalian HepatChroma SolarTech Co., Ltd).

### 2.3. Photovoltaic tests

Photovoltaic tests were carried out on the DSSC by measuring the characteristic photocurrent-voltage (*J-V*) curves using an electrochemical workstation (CHI660E, Shanghai Chenhua Device Company, China) under irradiation from a simulated solar light (a 100 W xenon arc lamp, XQ–500 W) in an ambient atmosphere. The incident light intensity was controlled at 100 mW cm$^{-2}$ (AM1.5). Each *J-V* curve was repeatedly measured for at least five times and a modest *J-V* curve was used.

### 2.4. Characterizations

The morphologies of the resultant $TiO_2$/$CaF_2$ were observed with a scanning electron microscope (S-3500N, Hitachi, Japan). The optical absorption spectra were recorded on a UV–vis spectrophotometer (Agilent 8453) at room temperature. X-ray diffraction (XRD) profiles of the resultant nanocrystallites were recorded on an X-ray powder diffractometer (X'pert MPD Pro, Philips, Netherlands) with Cu Kα radiation (λ = 1.5418 Å) in the 2θ = 20–70°, operating at a 40 kV accelerating voltage and a 40 mA current. For the electrochemical impedance spectroscopy (EIS) measurements, the DSSCs were scanned from 0.1 Hz to 2 MHz at an ac amplitude of 10 mV.

## 3. Results and discussion

Fig. 1a displays the top-view SEM photograph of pristine $TiO_2$ anode. At the first glance, the electrode surface is homogeneous and no aggregation is observed. The mesoporous structure provides channels for dye diffusion and adsorption [17]. Moreover, the loose structure is also beneficial for the diffusion of liquid electrolyte containing $I^-/I_3^-$ redox couples for dye recovery. The undetection of graphene in the SEM image of 0.03 wt% graphene integrated $TiO_2$ anode (Fig. 1b) may be attributed to a low dosage of graphene. It is noteworthy to mention that the average $TiO_2$ particle size is 15–20 nm in graphene integrated $TiO_2$ anode, whereas it is approximately 25 nm for pristine $TiO_2$ anode. The adding of graphene to $TiO_2$ colloid may inhibit the aggregation of positively charged $TiO_2$ colloidal particles. The lamellar graphene is expected to block aggregation effect of $TiO_2$ colloidal particles during calcination process. A superiority of forming ultrafine $TiO_2$ nanoparticles is to elevate dye adsorption due to increases specific surface area.

Fig. 2a shows the XRD patterns of pristine $TiO_2$ and graphene integrated $TiO_2$ anodes, demonstrating diffraction peaks centered at 2θ = 25.3, 37.8, 48.1, 53.9, 55.1, 62.8, and 68.9° in the pristine $TiO_2$ pattern due to attribution of (101), (004), (200), (105), (211), (204), and (116) planes [12,13], respectively. All the diffraction peaks corresponding to anatase $TiO_2$ can be identified in XRD patterns of graphene integrated $TiO_2$. Similarly to SEM result, no diffraction peaks corresponding to graphene is detected because the graphene dosage is lower than the limit for XRD identification or the peak overlap of graphene for (002) at ~25° [18]. To demonstrate the dependence of crystalline $TiO_2$ structure on graphene dosage, the crystallite size is determined by Scherrer equation and the structural parameters are summarized in Table 1.

$$L = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

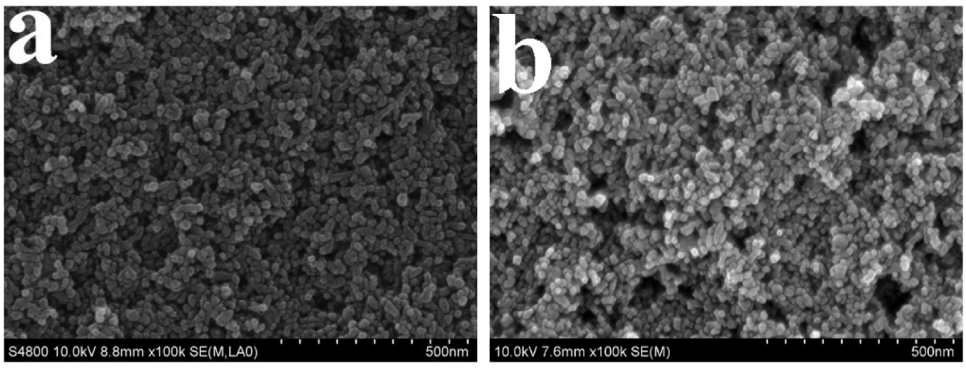


**Fig. 1.** Top−view SEM photographs of (a) pristine $TiO_2$ and (b) 0.03 wt% graphene integrated $TiO_2$ anodes.