



# Complexation of polyaniline and graphene for efficient counter electrodes in dye-sensitized solar cells: Enhanced charge transfer ability



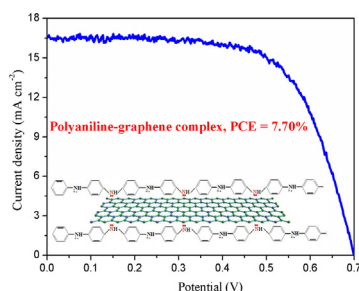
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## HIGHLIGHTS

- Aniline–graphene complexes were synthesized by a reflux technique.
- PANi–graphene complex CEs were electro-polymerized by a CV approach.
- Covalent bond between PANi and graphene can accelerate the charge transfer between them.
- A conversion efficiency of 7.70% was obtained from PANi–8 wt% graphene complex CE-based DSSC.

## GRAPHICAL ABSTRACT



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## ABSTRACT

With an aim of significantly enhancing charge-transfer ability of counter electrodes and therefore photovoltaic performances of dye-sensitized solar cells (DSSCs), here we pioneerly report the complexation of polyaniline (PANi) and graphene as well as their employment as counter electrodes (CEs) in efficient DSSCs. Owing to the covalent bond between PANi (N atoms) and graphene (C atoms), charge transfer kinetics is dramatically elevated, which can be confirmed by the enhancement on electrocatalytic activity toward triiodides and a decrease in charge-transfer resistance. A power conversion efficiency of 7.70% is determined from DSSC using PANi–8 wt% graphene complex CE in comparison with 6.40% from pure PANi CE-based DSSC. The high conversion efficiency, facile charge-transfer in combination with simple preparation, relatively low cost, and scalability demonstrates the potential use of PANi–graphene complexes in robust DSSCs.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs), electrochemical devices converting solar energy into electricity, are potential solutions to energy depletion, environmental pollution, and ecological destruction [1–4]. To date, an impressive light-to-electric power conversion efficiency of 12.3% has been recorded from liquid electrolyte-based DSSC [5]. However, the commercialization of

DSSCs is always obstructed by high-cost of Pt counter electrode [6]. By addressing this issue, it is a prerequisite to develop cheap CEs with honors of good electrocatalytic activity toward triiodides and rapid charge transfer ability. Conducting polymers such as polyaniline (PANi) and carbon materials such as graphene are preferred alternative CE materials [7,8]. The single use of PANi or graphene in CE always generates associated problems. For example, PANi has excellent redox behaviors but the charge-transfer ability is relatively low because of its organic semiconductor nature, whereas graphene, a single-layer material of sp<sup>2</sup>-bond-carbon atoms in a hexagonal lattice, has an excellent electrical conduction in two dimensions, but the redox performances are unsatisfactory.

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Previous researches are focusing on chemical, physical or electrochemical combination of PANi and graphene [9–11]. The disadvantage of the proposed approaches is relatively high interfacial resistance between PANi and graphene, which gives a low charge-transfer kinetics. The power conversion efficiencies of the DSSCs fabricated using traditional PANi–graphene CEs are in the level of ~7% [12–14].

To integrate the redox behavior of PANi and electron-conduction of graphene well, we report here the reflux synthesis of aniline–graphene complexes, in which aniline monomers are bonded onto graphene via covalent bonding between N atoms (electron donor) and C atoms (electron acceptor). The PANi–graphene complex CE electrochemically deposited on FTO conductive glass generate a promising power conversion efficiency of 7.70%, which is much higher than 6.40% from pure PANi CE-based DSSC.

## 2. Experimental

### 2.1. Reflux synthesis of aniline–graphene complexes

The aniline–graphene complexes were synthesis by a reflux process. In details, five aniline–graphene mixtures with graphene (the average diameter was around 500 nm) dosages of 1, 4, and 8 wt% were sealed in a three-neck flask filled with high-purity N<sub>2</sub> gas. In dark, the mixtures were refluxed for 6 h at 184 °C to obtain the target aniline–graphene complexes.

### 2.2. Deposition of PANi–graphene complex CEs

The fabrication of PANi–graphene complex CEs was on an electrochemical workstation (CHI660E): In details, a cleaned fluorine doped tin oxide (FTO, 12 Ω sq<sup>-1</sup>) glass was used a working electrode, a Pt plate was a CE, and an Ag/AgCl was a reference electrode. The supporting electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution dissolved aniline–graphene complex. A cyclic voltammetric method was employed at a sweep rate of 200 mV s<sup>-1</sup> for 50 repeating cycles. After deposition, the electrodes were washed several times in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution and deionized water, dried in vacuum at 60 °C for 24 h. As a comparison, PANi-only CE was also prepared under the same synthesis conditions.

As references, Pt (purchased from Dalian HeptaChroma Solar-Tech, Co., Ltd, China), pure PANi, pure graphene, and PANi–8 wt% graphene mixture CEs were also performed under the same conditions. The synthesis of PANi CE was similar to that of PANi–graphene complex CEs. The supporting electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution dissolved 0.1 mol of aniline. Graphene CE was prepared by dissolving graphene in 12.5 g L<sup>-1</sup> of polyvinylidene difluoride in N-methyl-2-pyrrolidone (mass ratio of graphene to polyvinylidene difluoride was 95:5) and casting onto a cleaned FTO glass substrate. The film thickness was controlled at around 3 μm, then the coated FTO substrate was vacuumly dried at 60 °C for 24 h. Similarly, the PANi–8 wt% graphene mixture CE was also prepared according to the above procedures.

### 2.3. Assembly of DSSCs

A layer of TiO<sub>2</sub> nanocrystal anode film with a thickness of 10 μm was prepared by a sol-hydrothermal method and casted onto a cleaned FTO glass substrate. After being calcined at 450 °C for 30 min, the resultant TiO<sub>2</sub> films were further sensitized by immersing into a 0.5 mM ethanol solution of N719 dye (purchased from DYESOL LTD). The DSSC was fabricated by combining the dye-sensitized TiO<sub>2</sub> anode and FTO supported PANi–graphene complex CEs. A redox electrolyte consisted of 100 mM of tetraethylammonium iodide, 100 mM of tetramethylammonium iodide, 100 mM of

tetrabutylammonium iodide, 100 mM of NaI, 100 mM of KI, 100 mM of LiI, 50 mM of I<sub>2</sub>, and 500 mM of 4-tert-butyl-pyridine in 50 ml acetonitrile.

### 2.4. Electrochemical characterizations

The cyclic voltammetry (CV) curves were recorded in a supporting electrolyte consisting of 50 mM LiI, 10 mM I<sub>2</sub>, and 500 mM LiClO<sub>4</sub> in acetonitrile. Electrochemical impedance spectroscopy (EIS) measurements were also carried out in a frequency range of 0.01 Hz ~ 10<sup>5</sup> kHz and an ac amplitude of 10 mV at room temperature. Tafel polarization curves were recorded by assembling symmetric cell consisting of FTO–PANi–graphene complex|liquid electrolyte|FTO–PANi–graphene complex.

### 2.5. Photovoltaic test

The photovoltaic test of the DSSC was carried out by measuring the current–voltage (*J–V*) characteristic curves using an Electrochemical Workstation (CHI660E, Shanghai Chenhua Device Company, China) under irradiation of a simulated solar light from a xenon-mercury arc lamp (CHF-XM-500W, Beijing Trusttech Co., Ltd) in ambient atmosphere. The incident light intensity was calibrated using an FZ-A type radiometer from Beijing Normal University Photoelectric Instrument Factory to control it at 100 mW cm<sup>-2</sup> (AM 1.5). Each DSSC device was measured five times to eliminate experimental error and a compromise *J–V* curve was employed. The fill factor (*FF*) and light-to-electric energy conversion efficiency (*η*) was calculated according to the equations:

$$FF = \frac{P_{\max}}{J_{SC} \times V_{OC}} = \frac{J_{\max} \times V_{\max}}{J_{SC} \times V_{OC}} \quad (1)$$

$$\eta(\%) = \frac{P_{\max}}{P_{in}} \times 100\% = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \times 100\% \quad (2)$$

where *J*<sub>SC</sub> is the short-circuit current density (mA cm<sup>-2</sup>), *V*<sub>OC</sub> is the open-circuit voltage (V), *P*<sub>in</sub> is the incident light power, *P*<sub>max</sub> is the maximum power output, *J*<sub>max</sub> (mA cm<sup>-2</sup>) and *V*<sub>max</sub> (V) are the current density and voltage at the point of maximum power output in the *J–V* curves, respectively. The relative humidity is around 25%.

### 2.6. Other characterizations

The morphologies of the resultant PANi or PANi–graphene complex CEs were observed with a scanning electron microscope (SEM, S4800). Fourier transform infrared spectrometry (FTIR) spectra were recorded on a PerkinElmer spectrum 1760 FTIR spectrometer by an ATR model. The UV–vis spectra were measured on a UV-3200 spectrophotometer by dissolving the samples in acetone. The fluorescence emission spectra were recorded at room temperature using a Fluorolog3-P spectrophotometer. The emission spectrum was collected using a conventional setup at excitation wavelengths of 500 nm.

## 3. Results and discussion

UV–vis adsorption spectra of graphene, aniline, aniline–8wt% graphene mixture, and aniline–graphene complexes with various graphene dosages were diluted in acetone to reveal the complexing mechanism of aniline molecules onto graphene. As is shown in Fig. 1a, no peak is observed in the UV–vis spectrum ranging from 350 to 700 nm. In comparison with the UV–vis spectrum of aniline–graphene mixture, new absorption peaks at 366, 452, 513, and 554 nm are observed, suggesting the successful complexation of

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