

In Situ Prepared Transparent Polyaniline Electrode and Its Application in Bifacial Dye-Sensitized Solar Cells

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Dye-sensitized solar cell (DSSC) has been widely recognized as a potential alternative to the conventional silicon solar cell for its low-cost and high conversion efficiency.^{1,2} A standard DSSC consists of a dye-sensitized TiO₂ photoanode, a iodide/triiodide redox electrolyte, and a counter electrode. The counter electrode, which serves to reduce I₃⁻ to I⁻ to complete the cycle of electron transfer, plays an important role in DSSC.^{3,4} It is typically made of platinized F-doped SnO₂ (FTO), due to the high catalytic activity and conductivity of platinum. However, since Pt is a noble metal and the two current methods^{5,6} (sputtering and thermal decomposition) used for preparing Pt counter electrodes are both high energy-consuming, consequently the cost and the energy payback time of DSSCs will be increased, which could be the limiting factors for the large-scale commercial application of them. Therefore, many functional materials have been studied to replace Pt as counter electrodes for more cost-effective DSSCs, such as various carbon-based materials including carbon black,⁷ activated carbon,^{8,9} graphite,⁹ carbon nanotubes,^{10,11} and graphene.¹² Recently, conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT)^{13,14} and polyaniline (PANI)^{15–17} attract more and more research interest as promising candidates for a Pt counter electrode due to their excellent catalytic activities and extremely low cost, especially for PANI, a “classic” conducting polymer that can be easily obtained and has good conductivity and environmental stability.¹⁸

Consider that the conventional DSSCs can only be operated by introducing light from the side of FTO glass (front illumination), for the counter electrodes are typically opaque. Another solution to the reduction of cost could be the design of bifacial DSSCs, which have the advantage of higher light-harvesting efficiency, for their capabilities of utilizing the incident light from both sides,

ABSTRACT Highly uniform and transparent polyaniline (PANI) electrodes that can be used as counter electrodes in dye-sensitized solar cells (DSSCs) were prepared by a facile *in situ* polymerization method. They were used to fabricate a novel bifacially active transparent DSSC, which showed conversion efficiencies of 6.54 and 4.26% corresponding to front- and rear-side illumination, respectively. Meanwhile, the efficiency of the same photoanode employing a Pt counter electrode was 6.69%. Compared to conventional Pt-based DSSCs, the design of the bifacial DSSC fabricated in this work would help to bring down the cost of energy production due to the lower cost of the materials and the higher power-generating efficiency of such devices for their capabilities of utilizing the light from both sides. These promising results highlight the potential application of PANI in cost-effective, transparent DSSCs.

KEYWORDS: polyaniline · transparent · counter electrode · cost-effective · bifacial dye-sensitized solar cell

which could help to further bring down the cost of energy production.^{19,20} The bifacial DSSCs require transparency of the counter electrodes. Despite the fact that the semitransparent Pt electrode could be prepared by depositing a thin layer of Pt on a transparent substrate, a main problem that could always be encountered is its high reflectance,²¹ let alone its high cost mentioned before. On the other hand, for carbon-material-based counter electrodes, the thickness is required to be up to several micrometers to get the desired conductivity and catalytic activity,^{7–12} which makes it difficult for them to be transparent. Several methods have been proposed to prepare high-quality transparent PANI films,^{22–24} but none has been applied in DSSC yet. Interestingly, the emeraldine PANI and N3 or N719 dye possess complementary absorption properties in the visible range, which means when the light passes through a thin PANI film, the loss of energy that can be utilized by N3 or N719 dye could be minimized. Thus, it is possible to fabricate efficient bifacial DSSCs with transparent PANI counter electrodes. Particularly, when the photoanodes are also prepared to be transparent or semitransparent, bifacially

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active transparent DSSCs could be obtained. In practice, transparent DSSCs would be more preferable for their versatile applications as power-generating windows, especially in the area of building integrated photovoltaics (BIPV).

In this paper, we report a novel transparent PANI counter electrode which was prepared by *in situ* polymerization of aniline monomers on FTO glass. The microstructure and the optoelectrochemical properties of the PANI film were well studied. A bifacially active transparent DSSC, as shown in Figure 1, was also successfully fabricated and characterized.

RESULTS AND DISCUSSION

A highly uniform and transparent PANI electrode has been prepared (Figure S1 in Supporting Information), and the molecular and the crystal structures of the PANI were investigated by ATR-FTIR (Figure S2) and

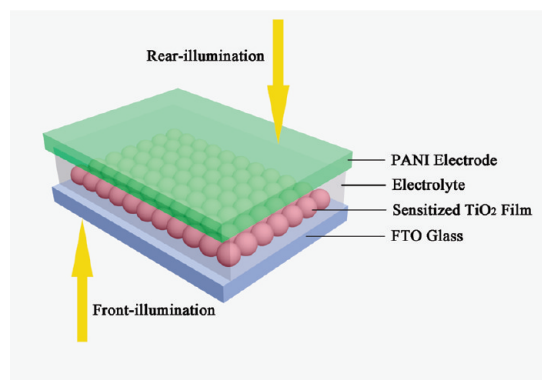


Figure 1. Schematic illustration of the bifacial DSSC based on transparent PANI counter electrode.

XRD (Figure S3), respectively. The microstructure of the PANI electrode was observed by SEM. As shown in Figure 2a, the PANI film is homogeneous and smooth with uniform grain size around 200 nm. A more detailed image presented in Figure 2b further reveals that the grains are all composed of small granules with diameters about 20 nm and exhibit similar cauliflower-like shapes. Consequently, this type of morphology will render PANI film with high surface area, which is favorable for good catalytic activity.¹⁷ The tilted views shown in Figure 2c,d also confirm the homogeneity of the PANI film, and the average film thickness is determined to be *ca.* 250 nm, as well.

Cyclic voltammetry was used to investigate the catalytic activity of PANI electrode toward the I^-/I_3^- redox couple. In comparison, the Pt electrode was also studied under the same condition. Two pairs of redox waves were observed on both electrodes; the left and the right pairs are explained to be the oxidation and reduction of I^-/I_3^- and I_2/I_3^- , respectively (see Figure 3).⁸ As mentioned before, the counter electrode in a DSSC serves to catalyze the reduction of I_3^- to I^- , thus the characteristics of the left pair of peaks were of research interest. The peak current density could be used to evaluate the catalytic activity of the counter electrodes.^{8,12,17} The apparent catalytic activity of PANI was found to be better than that of Pt for its higher peak current density. This result suggests that the PANI could be used as an efficient counter electrode in DSSCs.

Figure 4a shows the representative $J-V$ characteristics of the DSSCs with PANI and Pt counter electrodes under 1 sun illumination (AM 1.5, 100 mW/cm²). The device employing PANI counter electrode gave a short

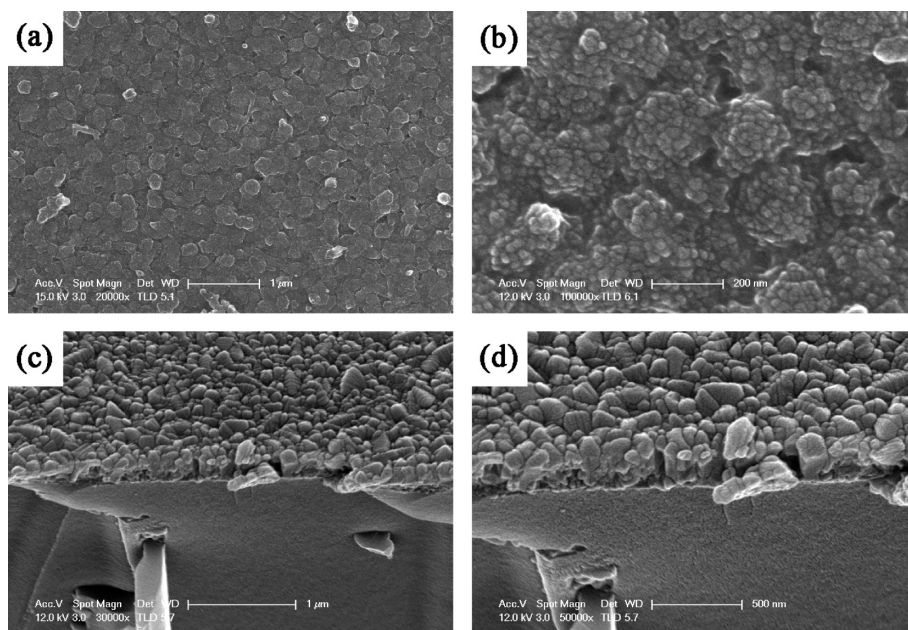


Figure 2. SEM images of the PANI film grown on FTO glass, (a) top view, low magnification; (b) top view, high magnification; (c) tilted view, low magnification; (d) tilted view, high magnification.

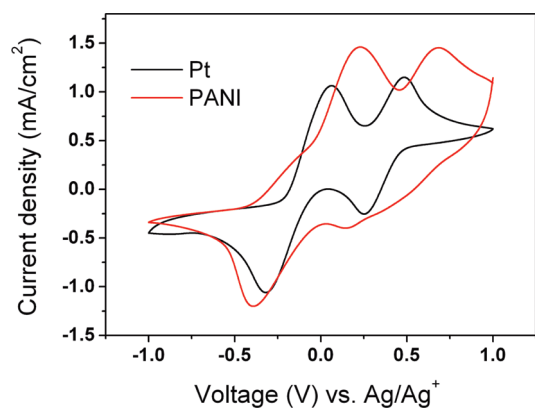


Figure 3. Cyclic voltammograms for Pt and PANI electrodes obtained at a scan rate of 50 mV/s in 10 mM LiI , 1 mM I_2 acetonitrile solution containing 0.1 M LiClO_4 as supporting electrolyte.

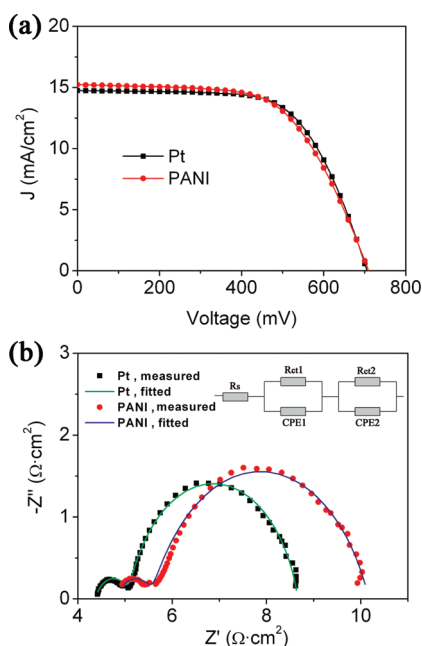


Figure 4. (a) J - V characteristics of DSSCs employing Pt and PANI counter electrodes measured under 100 mW/cm^2 , AM 1.5 simulated irradiation. The active area is 0.25 cm^2 . (b) Nyquist plots of Pt- and PANI-based DSSCs obtained at open circuit conditions under 100 mW/cm^2 , AM 1.5 simulated irradiation with active area of 0.25 cm^2 . The symbols are experimental data, and the solid lines are fitted results according to the inset equivalent circuit.

circuit current density (J_{sc}) of $15.24 \text{ mA}/\text{cm}^2$, an open circuit voltage (V_{oc}) of 710 mV, and a fill factor (FF) of 0.60, resulting in a power conversion efficiency (PCE) of 6.54%, which was comparable to that of 6.7% when the counter electrode was switched to Pt (see Table 1). The same devices were then subjected to electrochemical impedance spectroscopy (EIS) analysis to further investigate the correlations between the properties of the counter electrodes and the J - V performances of the devices. Figure 4b shows the EIS spectra measured under 1 sun illumination at open circuit conditions.

TABLE 1. EIS and J - V Parameters of DSSCs with Pt and PANI Counter Electrodes^a

| electrodes | R_s ($\Omega \cdot \text{cm}^2$) | R_{ct} ($\Omega \cdot \text{cm}^2$) | V_{oc} (mV) | J_{sc} (mA/cm^2) | FF | PCE (%) |
|------------|--------------------------------------|--|----------------------|---|-------|---------|
| FTO/Pt | 4.37 | 0.72 | 706 | 14.75 | 0.643 | 6.69 |
| FTO/PANI | 4.83 | 0.75 | 710 | 15.24 | 0.604 | 6.54 |

^a Note: The sheet resistances of bare FTO, Pt/FTO, and PANI/FTO were measured to be $13(\pm 1)$, $10(\pm 0.5)$, and $12(\pm 0.5) \Omega/\text{sq}$, respectively.

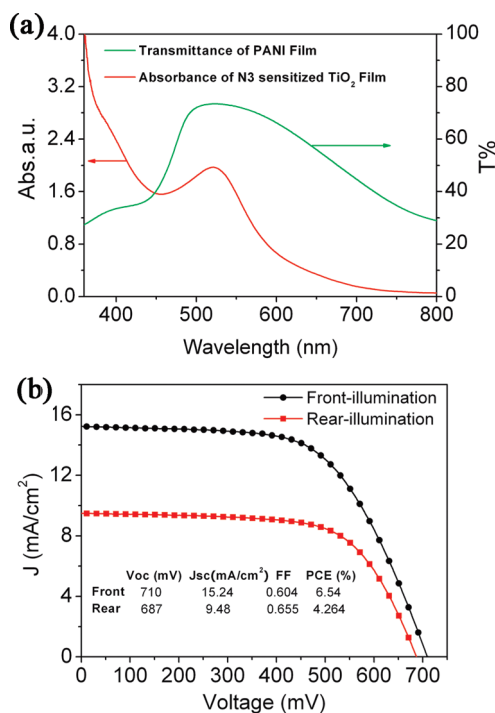


Figure 5. (a) UV-vis spectra of transparent PANI electrode and N3 sensitized TiO_2 film. (b) J - V characteristics of PANI-based bifacial DSSCs under front (solid circle) and rear illumination (solid square) measured at AM 1.5 simulated irradiation ($100 \text{ mW}/\text{cm}^2$).

Similar EIS spectra were observed for PANI- and Pt-based devices, and the interpretation of such EIS spectrum has been well-established.^{25,26} The semicircle at the highest frequency region describing the electron transport at the counter electrode/electrolyte interface was at the focus of this work. By fitting the experimental data with the inset equivalent circuit, charge transfer resistance (R_{ct}) at the counter electrode/electrolyte interface could be derived (see Table 1). The R_s in the equivalent circuit means ohmic series resistance of the device which could be read directly from the onset of the first semicircle. It could affect the fill factor of the device. Since R_{ct} of the PANI electrode was slightly higher than that of Pt, the improvement of J_{sc} was attributed to the high surface area of the PANI electrode due to its porous nature according to the results of SEM and CV and confirmed by AFM with a rms roughness of about 40 nm. The decrease of FF resulted from the increase of R_s for the higher sheet resistance of the PANI electrode.



Figure 6. Digital photograph of a large-area bifacially active transparent DSSC fabricated in this work. The cell was sealed with Surlyn, and the electrolyte was introduced through a drilled hole on the counter electrode.

The thin PANI film showed excellent transparency range from 450 to 750 nm with its maximum transmittance of 74% at 510 nm; meanwhile, the absorption of N3 dye was mainly in the range of 450 to 650 nm (see Figure 5a). It should be noted that the complementary absorption properties of PANI film and N3 dye are crucial for high performance of the bifacial DSSC mentioned in this work when the light was cast from the rear side. Figure 5b shows the J - V characteristics of the bifacial DSSC corresponding to front and rear illumination. When irradiated from the rear side, the device exhibited an efficiency of 4.26%, which approaches 65% that of front illumination. The reduced J_{sc} was the main reason for the efficiency loss. We attribute the reduction of J_{sc} to the lower light intensity cast on the dye-sensitized TiO_2 film for the lower transmittance of PANI film than that of FTO glass. The decrease of V_{oc} and the improvement of FF are also caused by the same reason. The detailed relationships between the light intensity and the characteristics of DSSCs have been well formulated elsewhere.^{27,28} Figure 6 gives a demonstration of a completed bifacial DSSC fabricated in this work.

In conclusion, a novel transparent PANI electrode has been prepared on FTO with a thickness of about 250 nm by *in situ* polymerization. The PANI film was found to be quite porous on the nanoscale and exhibited higher apparent catalytic activity toward the reduction of I_3^- than that of Pt. Furthermore, the thin film showed excellent transparency in the visible region, which allowed us to fabricate transparent bifacial DSSCs. In our preliminary results, the device employing PANI counter electrode yielded a promising front-illuminated power conversion efficiency of 6.54%, which was comparable to 6.69% of Pt-based device, while the rear-illuminated efficiency was 4.26%. This type of transparent DSSC has an advantage of higher power-to-weight ratio, for it can utilize the light from both sides. Especially, when applied with a reflecting background such as with a static concentrator, the energy output efficiency could be much enhanced.^{29,30} Consequently, the cost for energy production could be reduced, and it could have a wide range of application areas as electricity-generating windows.

EXPERIMENTAL SECTION

Preparation of PANI and Pt Electrodes. In a typical procedure, 25 mmol aniline was first dissolved in 50 mL of 0.4 M HCl solution, then another 50 mL of 0.4 M HCl containing 8.3 mmol ammonium persulfate (APS) was added under vigorous stirring, followed by immersing a piece of well-cleaned FTO glass in the solution. After being kept at 4 °C for 30 min, the FTO glass was taken out and rinsed with DI water; then the PANI on the nonconductive side was removed. Finally, the PANI/FTO was redoped in 1 M HCl for 4 h, then rinsed and dried at 80 °C in vacuum for 30 min. The precipitates in the solution were also collected and treated the same way for XRD characterization. Then, the Pt electrode was prepared by depositing a thin layer of Pt on FTO using magnetron sputtering.

Fabrication of DSSCs. TiO_2 paste was first synthesized by hydrothermal method, then it was doctor-bladed on FTO glass and sintered at 500 °C for 30 min; this procedure was repeated twice. The TiO_2 photoanode was then immersed in a 0.5 mM N3

ethanol solution and kept at 60 °C for 12 h, then rinsed with ethanol and dried. The DSSCs were assembled by sandwiching the sensitized TiO_2 photoanode with Pt or PANI counter electrode by introducing an electrolyte containing 1 M PMII (1-methyl-3-propyl imidazolium iodide), 0.04 M LiI, 0.03 M I_2 , 0.1 M GuSCN (guanidinium thiocyanate), 0.5 M TBP (4-*tert*-butylpyridine) in acetonitrile, and propylene carbonate ($v/v = 1:1$) between them.

Characterization. The molecular structures of PANI were investigated by ATR-FTIR (Nicolet 6700, USA) and XRD (D8 Advance, Bruker, Germany). Scanning electron microscopy, SEM (JEOL, 6700F, Japan), and atomic force microscopy, AFM (SPM 9500J3, Shimadzu, Japan), were used to study the microstructures of the PANI electrode. UV-vis spectra were recorded on UV-2550 spectrometer (Shimadzu, Japan). Cyclic voltammetry was performed on CHI 660C (Shang Hai, China) electrochemical station with a Pt wire as auxiliary electrode, a Ag/Ag^+ electrode as reference electrode, and PANI/FTO or Pt/FTO as working electrode in an acetonitrile solution containing 10 mM LiI, 1 mM

I_2 , and 0.1 M LiClO₄ as supporting electrolyte at a scan rate of 50 mV/s. The $J-V$ characteristics were measured under AM 1.5 simulated illumination (Newport, 91192) with a power density of 100 mW/cm², and the active area was controlled by a 0.25 cm² mask. For comparison, the same piece of photoanode was used for both PANI and Pt counter electrodes. Electrochemical impedance spectroscopy (EIS) measurements were also performed on CHI 660C with the frequency ranging from 100 kHz to 0.1 Hz at open circuit conditions under 100 mW/cm² irradiation.

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Supporting Information Available: Digital photograph and AFM image of the PANI electrode are presented, the FTIR and XRD spectra are also provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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