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A novel hierarchical Pt- and FTO-free counter electrode for dye-sensitized solar cell

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Abstract

A novel hierarchical Pt- and FTO-free counter electrode (CE) for the dye-sensitized solar cell (DSSC) was prepared by spin coating the mixture of TiO₂ nanoparticles and poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) solution onto the glass substrate. Compared with traditional Pt/FTO CE, the cost of the new CE is dramatically reduced by the application of bilayer TiO₂-PEDOT:PSS/PEDOT:PSS film and the glass substrate. The sheet resistance of this composite film is 35 Ω sq⁻¹ and is low enough to be used as an electrode. The surface morphologies of TiO₂-PEDOT:PSS layer and modified PEDOT:PSS layer were characterized by scanning electron microscope, which shows that the former had larger surface areas than the latter. Electrochemical impedance spectra and Tafel polarization curves prove that the catalytic activity of TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE is higher than that of PEDOT:PSS/FTO CE and is similar to Pt/FTO CE's. This new fabricated device with TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE achieves a high power conversion efficiency (PCE) of 4.67%, reaching 91.39% of DSSC with Pt/FTO CE (5.11%).

Keywords: TiO₂ nanoparticles; PEDOT; PSS; Dye-sensitized solar cells; Counter electrode; Composite film

Background

Dye-sensitized solar cells (DSSCs) have attracted considerable interests due to their simpler fabrication and low production costs compared with conventional silicon-based solar cells [1,2]. A traditional DSSC consists of a transparent photoanode with dye-sensitized mesoporous thin-film-like TiO₂ or ZnO, I⁻/I₃⁻ redox electrolyte, and a counter electrode (CE) with a catalytic layer deposited on FTO substrate. As one of the most crucial components of DSSC, the CE works as a catalyst for the reduction of I₃⁻ to I⁻, and the materials used in catalytic layer and conductive substrates significantly affect the performance and costs of the DSSCs. Platinized FTO is the most common material for CE as it has good conductivity and high catalytic activity. However, noble metal platinum is expensive, scarce, and easy to be eroded by the I⁻/I₃⁻ electrolyte [3,4]. Moreover, the Pt catalytic layer is usually prepared by thermal annealing or electrodeposition method, and

both methods require high temperature (450°C), which is beyond the sustaining ability of plastic substrates to realize the flexible DSSCs. The common FTO substrates are very expensive and hard, also preventing the production of flexible DSSCs. Therefore, it is imperative to develop Pt- and FTO-free CEs with low cost and good catalytic activity for DSSCs.

Many reported materials have been used as the substitute for Pt-based CEs like conductive polymers (polyaniline [5], polypyrrole [6], poly(3,4-ethylenedioxy-thiophene) (PEDOT) [7], carbon materials (graphene [8], carbon black [9], carbon nanotube [10], etc.), and most of them have lower catalytic activity than Pt [11]. In order to achieve a cost-effective Pt-free CE, PEDOT:PSS has attracted much attention because of good catalytic activity, better film-forming property, low cost, and easy coating [12-14]. Modified PEDOT:PSS has potential to replace TCO in organic electronics for its high conductivity [15]. Though with many of strengths, the catalytic ability of DSSC with PEDOT:PSS/FTO CE still exists a distance from Pt/FTO CE and needs to be further improved.

Consequently, in this work, a hierarchical TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE was used in the fabrication of DSSC. The TiO₂-PEDOT:PSS layer was fabricated utilizing

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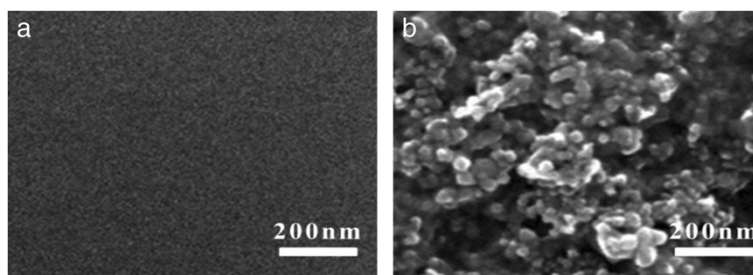


Figure 1 SEM images of PEDOT:PSS film (a) and TiO₂-PEDOT:PSS composite film (b).

the mixture of PEDOT:PSS and TiO₂ nanoparticles. The neat PEDOT:PSS layer acts as a high conductive electrode in order to develop charge passageway. This hierarchical TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE performed better catalytic activity than the PEDOT:PSS/FTO CE, and as a result, the DSSC using TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE also performs good photovoltaic properties.

Methods

Preparation of TiO₂ photoanodes

TiO₂ paste was blade-coated on FTO substrates and subsequently sintered at 450°C for 30 min. After cooling down to room temperature, the samples were put into 40 mmol/L TiCl₄ solution at 70°C for 30 min and then sintered at 450°C for 30 min. Finally, after cooling down to 80°C, the as-prepared TiO₂ photoanodes were soaked in the ethanol solution of N719 dye for 24 h.

Preparation of the counter electrodes

In total, we have prepared four kinds of CEs, including Pt/FTO, PEDOT:PSS/FTO, TiO₂-PEDOT:PSS/FTO, and TiO₂-PEDOT:PSS/PEDOT:PSS/glass. The Pt/FTO CE was prepared by spraying H₂PtCl₆ solution on the pre-cleaned FTO substrate and subsequently sintered at 450°C for 15 min. The PEDOT:PSS/FTO and TiO₂-PEDOT:PSS/FTO CEs were fabricated by spin coating PEDOT:PSS

(Clevis PH 1000, purchased from Heraeus, Hanau, Germany) solution and TiO₂-PEDOT:PSS solution onto FTO substrates, respectively. The TiO₂-PEDOT:PSS/PEDOT:PSS/glass was obtained by spin coating PEDOT:PSS mixed with 6% volume of ethylene glycol (EG) on glass substrate (5,000 rpm/s for 30 s) and sintered at 120 °C for 15 min. This process was repeated four times. Then, the TiO₂-PEDOT:PSS (40 mg P25 powder added in 1 ml PEDOT:PSS solution) solution was spin-coated on top of the PEDOT:PSS layer at 1,000 rpm/s for 40 s and sintered at 120°C for 15 min. Finally, the resultant substrates were immediately put into EG for 30 min and then dried in the oven at 120°C for 15 min.

Fabrication and characterization of DSSCs

The processed TiO₂ photoanodes have an active area of 0.16 cm², and these prepared CEs were assembled together with 60-μm surlyn film, respectively. The I⁻/I₃⁻ electrolyte was injected through the interspace and sealed with paraffin.

The sheet resistance of the catalytic layers was measured using a four-probe tester (model RTS-8, Four Probe TECH, Guangzhou, China). The surface morphologies of CEs were scanned by field emission scanning electron microscope (quanta 200 F, FEI, OR, USA). Electrochemical impedance spectroscopy (EIS) and Tafel polarization

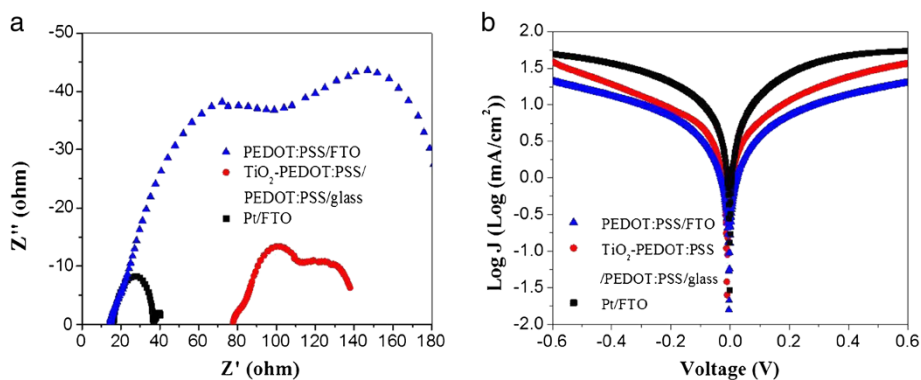


Figure 2 Electrochemical characters. Nyquist plots (a) and Tafel polarization curves (b) of DSSCs based on PEDOT/FTO CE, TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE, and Pt/FTO CE.

curves were measured using an electrochemical workstation (model CHI600, CH Instruments, Inc., Austin, TX, USA) at room temperature. The current density-voltage characteristics of photocurrent density-photovoltage were simulated at AM 1.5G illumination (100 mV cm^{-2} , XES-301S, SAN EL, Osaka, Japan) and recorded by a Keithley source meter (Keithley, Cleveland, OH, USA).

Results and discussion

The sheet resistance of different CEs, PEDOT:PSS/FTO CE, TiO_2 -PEDOT:PSS/FTO CE, TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE, and Pt/FTO CE, is 6.3, 7.5, 35, and $7.2 \Omega \text{ sq}^{-1}$, respectively. Though the sheet resistance of TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE is larger than that of TiO_2 -PEDOT:PSS/FTO CE and Pt/FTO CE, it is still qualified, i.e., the sheet resistance below $100 \Omega \text{ sq}^{-1}$ can be used as electrode [16,17].

The surface morphologies of pristine PEDOT:PSS film and TiO_2 -PEDOT:PSS composite film are depicted in Figure 1a,b, respectively. As is shown in the two images, the surface of modified PEDOT:PSS film is almost smooth, while the TiO_2 -PEDOT:PSS composite film is rough and has a large surface area which is good for catalytic reduction of I_3^- . In TiO_2 -PEDOT:PSS composite film, as shown in Figure 1b, the thin catalytic layer is composed of TiO_2 nanoparticles, and their diameter ranges from 20 to 50 nm. These nanoparticles are uniformly dispersed in PEDOT:PSS, forming a network structure, beneficial for electron conduction. Therefore, the performance of DSSCs with TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CEs could be greatly improved by the addition of TiO_2 nanoparticles.

A typical EIS spectrum for a DSSC exhibits three semicircles in the Nyquist plot, as is shown in Figure 2a. Traditionally, the first semicircle in high-frequency region corresponds to charge transfer resistance (R_{ct}) of the CE/electrolyte interface, while the second semicircle in the middle-frequency region represents charge transfer and recombination resistance in the TiO_2 /dye network [18,19]. The low-frequency semicircle is attributed to the Nernst diffusion impedance of the I^-/I_3^- redox couple. From Figure 2a, we can obviously see that the spectra of TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE has a smaller semicircle than that of the PEDOT:PSS/FTO CE, which indicates that TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE has a better catalytic activity than PEDOT:PSS/FTO CE. The simulated values of series resistance (R_s), charge transfer resistance (R_{ct}), and diffusion element (Z_{w1}) of corresponding cells calculated by Zview software are shown in Table 1. The simulated R_{ct} and Z_{w1} of TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE (1.51 and $4.02 \Omega \text{ cm}^2$, respectively) are lower than those of PEDOT:PSS/FTO CE (4.47 and $11.28 \Omega \text{ cm}^2$, respectively), indicating that the addition of TiO_2 nanoparticles greatly improves the catalytic activity for the redox reaction. The R_s value of TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE is higher than that of PEDOT:PSS/FTO CE due to a lower

Table 1 Electrochemical impedance spectra (EIS) parameters of PEDOT/FTO CE, TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE, and Pt/FTO CE

Counter electrode	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	Z_{w1} ($\Omega \text{ cm}^2$)
PEDOT:PSS/FTO	4.22	4.47	11.28
TiO_2 -PEDOT:PSS/ PEDOT:PSS/glass	23.26	1.51	4.02
Pt/FTO	4.91	5.73	-

conductivity of PEDOT:PSS layer than that of FTO substrate, and the result is in accordance with the conclusion from the sheet resistance. However, the R_{ct} of TiO_2 -PEDOT:PSS/PEDOT:PSS/glass composite CE is lower than that of Pt/FTO CE ($5.73 \Omega \text{ cm}^2$) which is opposite to the traditional standpoint that a smaller R_{ct} may lead to a higher fill factor (FF) and η in photovoltaic performance. However, for TiO_2 -PEDOT:PSS/PEDOT:PSS/glass CE, the charge transfer of the CE/electrolyte interface is mainly illustrated by the second semicircle of the spectra. Similar findings have been reported by He et al. [20] and Roy-Mayhew et al. [8], and they contend that the second semicircle is due to the electrolyte/CE interface.

Furthermore, Tafel polarization curves were carried out on the same dummy cells used in EIS measurement to investigate the interfacial charge transfer properties of CE/electrolyte, and the corresponding results are shown in Figure 2b. The exchange current (J_0) = 0.58 mA, calculated from the intersection of the linear cathodic and anodic Tafel polarization curves [16,21], was derived from the TiO_2 -PEDOT:PSS/PEDOT:PSS/glass composite film and higher than that of PEDOT:PSS/FTO film (0.14 mA). Correspondingly, the catalytic activity of TiO_2 -PEDOT:PSS/PEDOT:PSS/glass composite CE is much higher than that of PEDOT:PSS/glass CE, which demonstrates that the big

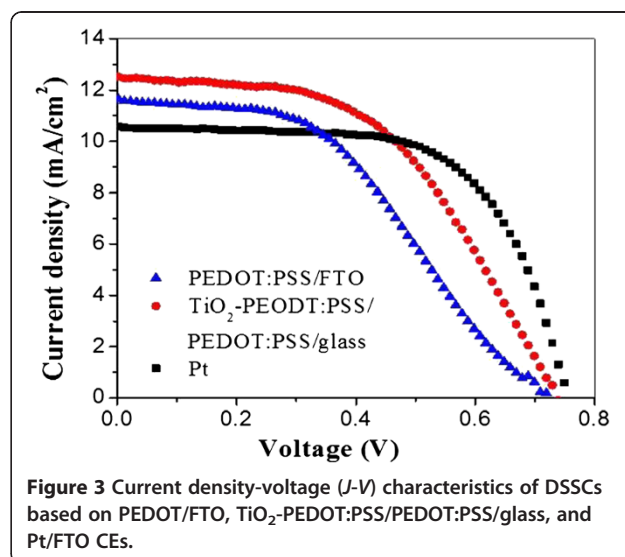


Figure 3 Current density-voltage (J - V) characteristics of DSSCs based on PEDOT/FTO, TiO_2 -PEDOT:PSS/PEDOT:PSS/glass, and Pt/FTO CEs.

Table 2 The performances of dye-sensitized solar cells with different CEs measured under an AM 1.5G illumination

Counter electrode	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	η (%)
PEDOT:PSS/FTO	0.72	11.63	0.43	3.64
TiO ₂ -PEDOT:PSS/PEDOT:PSS/glass	0.73	12.45	0.51	4.67
Pt/FTO	0.75	10.54	0.63	5.11

surface area of TiO₂ nanoparticles enhances the reduction of I₃⁻ to I⁻ remarkably. Though the J_0 of TiO₂-PEDOT:PSS/PEDOT:PSS/glass composite CE is smaller than that of Pt/FTO CE (1.2 mA), the former still exhibits superior catalytic activity and has great potential to act as CE for DSSC.

Figure 3 presents the photocurrent density-voltage (J - V) curves of DSSCs using PEDOT:PSS/FTO CE, TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE, and Pt/FTO CE, respectively, and the related photovoltaic parameters are shown in Table 2. There is little difference in V_{oc} values of these three cells. The FF of the DSSC with PEDOT:PSS/FTO CE is just 0.43 because of the poor catalytic activity of PEDOT:PSS solution. After modified by the TiO₂ nanoparticles, the DSSC with TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE has obtained higher FF of 0.51 and thus higher $\eta = 4.67\%$ (increasing 22% compared with 3.64% for the DSSC with PEDOT:PSS/FTO CE). This is mainly due to the reduced charge transfer resistance and porous diffusion impedance because of the large electrochemical surface area in the porous TiO₂-PEDOT:PSS layer. Compared with DSSC based on Pt/FTO CE, the one with TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE has lower FF, but its overall efficiency has already reached 91.39% of the one with Pt/FTO CE. It is noticeable that the performance of TiO₂-PEDOT:PSS/PEDOT:PSS layers can be further enhanced by optimization of their weight ratio and the film thicknesses, referring to the previous studies using TiO₂-PEDOT:PSS/FTO CE [22]. With such an excellent performance, the TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE has great potential to be a substitute for Pt- and FTO-based CEs which are very expensive and account for a large part of the cost. At the same time, due to the low preparation temperature, the TiO₂-PEDOT:PSS/PEDOT:PSS composite film can be applied in flexible cells and make them more functional and lightweight.

Conclusions

In summary, we utilize a facile wet method to fabricate a novel hierarchical Pt- and FTO-free CE for the dye-sensitized solar cell. It is found that the TiO₂ doped PEDOT:PSS catalytic activity layer will dramatically affect the electrochemical properties of the final device. By adjusting the composition of TiO₂, the properties of CE have been optimized preliminarily. Because of the large active area of TiO₂ nanoparticles, the proposed composite

CE shows excellent enhancement in the conductivity and the superior catalytic activity for the reduction of I₃⁻ to I⁻. The conversion efficiency is increased by 22% than that of the DSSC with PEDOT:PSS/FTO CE and is comparable to that of the DSSC with traditional Pt/FTO CE. After further optimization, the TiO₂-PEDOT:PSS/PEDOT:PSS/glass CE can be more cost-effective, high efficient, and flexible to replace Pt and FTO CEs and more broadly used for future commercial applications.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

XZ did most of the experiments and drafted the manuscript. ML designed and figured out the research idea and rewrote the paper. DS did part of the research experiments. PC participated in the design of the study. ZrZ, YZ, CS, and ZhZ took part in the discussion of the research. All authors read and approved the final manuscript.

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