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RESEARCH ARTICLE

Studies of high-efficient and low-cost dye-sensitized solar cells

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Abstract Dye-sensitized solar cell (DSSC) is a new type of photoelectric device. To commercialize DSSC successfully, it is necessary to further improve the efficiency of energy conversion and reduce its cost. Nitrogen-doped (N-doped) TiO_2 photoanode, the carbon counter electrode (CE), and a new type of hybrid photoanode were investigated in this study. The conversion efficiency of the DSSC reached by 10.10% as the DSSC was fabricated with the N-doped photoanode, and this efficiency is much higher than that of the undoped-DSSC with 8.90%; as the low-cost carbon was used as CE, the efficiency of the DSSC was 7.50%, it was as samilar as that of Pt CE (7.47%); the hybrid DSSC with multilayer photoanode by the film-transfer technique achieved a panchromatic response and a superposed short circuit current density (J_{SC}) by using two complementary dyes.

Keywords high-efficiency, dye-sensitized solar cell (DSSC), hybrid, nitrogen-doped (N-doped) TiO_2, carbon counter electrode (CE)

1 Introduction

Dye-sensitized solar cells (DSSCs) developed by Grätzel have attracted considerable interest as a low-cost alternative to silicon solar cells [1]. However, it is necessary to further improve the energy conversion efficiency and reduce the cost of DSSCs for successful commercialization.

One important way to improve the efficiency of DSSC is broadening the absorption spectra of dyes. Many attempts have been carried out, including tandem DSSCs, hybrid DSSCs, and co-sensitized DSSCs [2–14]. The tandem and co-sensitized methods improved the efficiencies of DSSCs to a certain extent. However, the problem is that tandem DSSCs require a strict adjustment of the transmittance of the top cells and restrictions on the short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) of the two cells [2]. Although co-sensitized DSSCs avoid the disadvantages of tandem DSSCs, undesirable competitive adsorption and interactions between dyes can easily cause a decrease in the conversion efficiency of DSSCs [3]. To solve these problems, a new type of hybrid DSSC with a multilayer photoanode prepared by a simple and low-cost film-transfer technique has been developed. The results showed that the hybrid structure achieved a panchromatic response and a superposed J_{SC} by using two complementary dyes AP and ZnPc without the significant decrease in V_{OC}.

Semiconductor oxide photoelectrode is known to be one of the key components that affect the energy conversion efficiency of DSSCs. TiO_2 is a typical semiconductor oxide material for photoelectrodes. However, oxygen deficiencies found in the pure TiO_2 crystal structure may cause the shortened lifetime of DSSCs [15–18]. To solve this problem, we have developed a DSSC system based on N-doped TiO_2, which successfully achieved high energy conversion efficiency [19]. In this paper, a simple method was used to prepare the needle-like N-doped TiO_2 nanocrystals from commercial TiO_2 powders. The DSSC fabricated by the N-doped photoanode prepared by our approach achieved a high conversion efficiency of 10.10%, which is much higher than the value of 8.90% for the undoped-DSSC. Furthermore, the electron injection, electron transport time and electron lifetime were studied and the details will be available in a future paper.

To reduce the cost of DSSCs, it is important to explore substitutes for Pt to make DSSCs more competitive among various photovoltaic devices. One approach is to replace Pt with abundant, non-precious materials not susceptible to price inflation during high demand. Carbon materials attract the most attention due to their high catalytic activity, low cost, and excellent corrosion resistance against the redox couple among non-Pt catalytic materials. We

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synthesized a well-ordered mesoporous carbon (Com) with a modified one-pot chemical method. The DSSC using Com counter electrode (CE) yielded an efficiency of 7.50%, which is similar to the value of DSSCs using Pt CE (7.47%). We also compared the performance of several kinds of carbon materials used as CE catalytic materials with the traditional Pt CE in the DSSC system. They were activated carbon (Ca), carbon black (Cb), and multi-wall carbon nanotube (MWCNT, Cn).

2 Experiment

2.1 Fabrication of DSSCs

Dye-sensitized hybrid electrodes (area: 0.16 cm^2), N-doped and undoped TiO_2 electrodes (area: 0.16 cm^2) were assembled with platinized counter electrodes.

Photoanodes for the carbon CEs were prepared from the TiO_2 films (8 μm, area: 0.2 cm^2) of 20 nm-sized particles (Degussa, Germany) followed by a sintering process at 500°C and then cooling to 80°C. The TiO_2 films were immersed in a 5×10^{-4} M solution of N719 dye (Solaronix SA, Switzerland) in acetonitrile/*tert*-butanol ($v : v = 1 : 1$) for 16 h.

The photoanodes and corresponding CEs were assembled to form a solar cell by sandwiching a redox (I^-/I_3^-) electrolyte solution. The electrolyte was composed of 0.03 M I_2, 0.06 M LiI, 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile.

2.2 Characterization

The UV-Vis-NIR absorption spectra were recorded using UV–550 (Japan) UV–Vis spectrophotometers. The current-voltage curves were conducted by a Keithley digital source meter (Keithley 2601, USA). The intensity of the incident light was 100 $mW \cdot cm^{-2}$. The instrument was equipped with a 300 W solar simulator (Solar Light Co., INC., USA) that served as the light source. The photon flux was determined by a power meter (TES–1333R, Taiwan) and a calibration cell (BS–520, s/n 019, Bunkoh-Keiki Co., Ltd., Japan).

3 Results and discussion

3.1 Hybrid DSSC

The new type of hybrid DSSC with a multilayer photoanode developed by our group was prepared by a simple and low-cost film-transfer technique. The structure of the multilayer photoanode consists of an adhesive TiO_2 bottom layer/Dye 1/, a transferred porous P25 layer/Dye 2/, and a scattering layer (ST41). The sintered adhesive bottom layers that lie on the F-doped SnO_2 glass (prepared by the doctor-blade technique) were first sensitized with Dye 1 (AP) [20]. The hybrid photoanode was fabricated using the bottom layer sensitized with Dye 1 (AP) to transfer the porous P25/ST41 scattering layer under friction [21,22]. After compression, the obtained anode was then dipped into the solution of Dye 2 (ZnPc).

AP and ZnPc are two model dyes with independent spectral absorption in the visible and near-IR (NIR) region. Figure 1 shows the absorption spectra of AP, ZnPc, and hybrid of AP/ZnPc absorbed onto the TiO_2 films. The absorption band in the range of 300–580 nm is assigned to AP. On the other hand, the absorption band of ZnPc is observed to be between 500 and 800 nm. The absorption spectra of the hybrid photoanode showed the sum adsorption of the AP and ZnPc as comparable to a panchromatic response in the range of 300–800 nm. Through an investigation of photoelectrical performances, the J_{SC} of the hybrid cell was found to be 10.73 $mA \cdot cm^{-2}$, almost equivalent to the sum value of 10.74 $mA \cdot cm^{-2}$ for the AP cell (8.65 $mA \cdot cm^{-2}$) and ZnPc cell (2.09 $mA \cdot cm^{-2}$). The V_{OC} of the hybrid cell was between the values of two single devices, but closer to the larger one. The photoelectric characteristics can be interpreted in Eqs. (1) and (2):

$$J_{SC\ hybrid} = J_{SC1} + J_{SC2}, \tag{1}$$

$$V_{OC2} << V_{OC\ hybrid} < V_{OC1}. \tag{2}$$

The developed film-transfer technique is also simple, convenient, low-cost and highly efficient. It is very easy to fabricate the multilayer-structured hybrid photoanode by using three or more dyes to further broaden the absorption

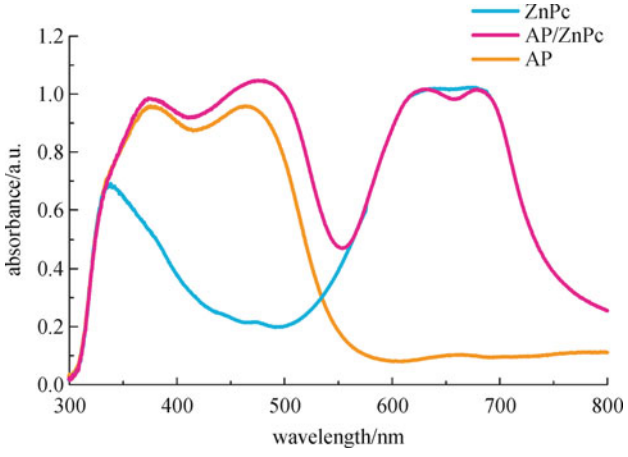

Fig. 1 UV-Vis absorption spectra of AP, ZnPc, hybrid of AP/ZnPc absorbed onto the TiO_2 films

spectrum of DSSC, thus breaking restrictions on the semiconductors and dyes in conventional DSSCs.

3.2 N-doped photoanode

N-doped and undoped photoanodes were prepared by a simple method from commercial TiO_2 powders. Commercially-available ST-01 (Ishihara Sangyo Kaisha, Ltd.) was used to prepare N-doped TiO_2 through a simple dry method. In brief, nanocrystalline N-doped ST-01 was prepared by sintering pure TiO_2 powders at 500°C for 3 h under dry N_2 and NH_3 gas flow. For comparison, pure ST-01 was also treated under the same conditions without nitrogen source and the obtained sample was denoted as undoped ST-01. The screen-printable N-doped and undoped TiO_2 colloidal pastes were prepared according to the procedure developed by our group [23]. A screen-printing technique was used to fabricate the films. Then, the obtained films were sensitized with N719.

The photoelectrical performances of DSSCs based on the N-doped and undoped TiO_2 electrodes are shown in Table 1. The DSSC fabricated by the N-doped photoanode prepared by our approach achieved a high conversion efficiency of 10.10%, which is much higher than the value of 8.90% for the undoped DSSC. Our results show that the N-doped DSSCs possess higher photocurrent and enhanced open circuit photovoltage. Finally, the synergetic effect of higher dye uptake, faster electron transport and higher photovoltage contributes to a higher conversion efficiency of N-doped DSSCs. The details will be shown in a future paper.

3.3 Carbon CE

Among the four kinds of carbon materials, Ca, Cb, and Cn were purchased. The Com was synthesized with a modified one-pot chemical method [24,25]. The experimental details will be shown in another paper. The transmission electron microscopy (TEM) images in Fig. 2 showed that the Com powder was well-ordered and built by rows of carbon walls with accumulated small-sized carbon particles. Figure 2(b) showed the cross-section of the ordered carbon walls presenting a mesoporous structure. The well-ordered mesoporous structure provided the Com a large surface area. Such a configuration was beneficial to diffuse the redox couple in the electrolyte.

We investigated the impact of the sprayed carbon paste onto the performance of carbon CEs and determined the proper spray time duration. Under optimal conditions, the energy efficiencies of the DSSCs using the four carbon CEs and traditional Pt CE are 6.57% (Ca), 6.25% (Cb), 7.02% (Cn), 7.50% (Com) and 7.47% (Pt). The *I-V* curves are shown in Fig. 3. We conclude that the Com CEs show excellent catalytic activity for triiodide reduction among the four carbon materials, which can match the performance of Pt CE.

Table 1 Performance of the DSSCs based on N-doped and undoped TiO_2 electrodes

titania electrode	V_{OC}/mV	J_{SC}/(mA·cm^{-2})	*FF*/%	η/%
N-doped ST-01	778±10	19.05±0.07	0.68±0.01	10.1±0.2
undoped ST-01	756±13	17.40±0.10	0.68±0.01	8.9±0.3

Notes: *FF*: fill factor; η: conversion efficiency

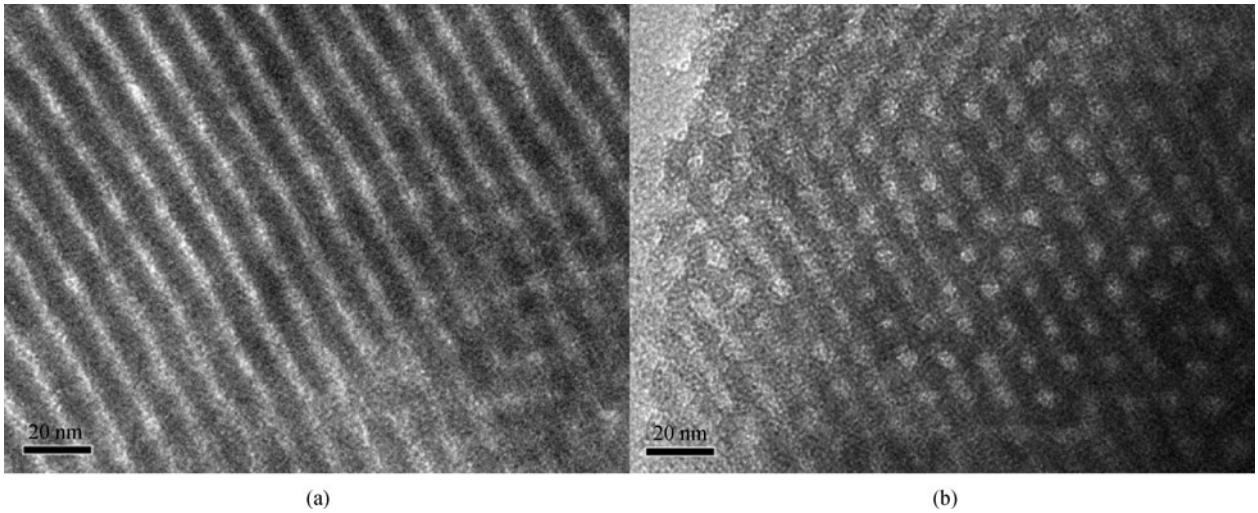

Fig. 2 TEM images of the well-ordered Com. (a) Top view; (b) cross-section

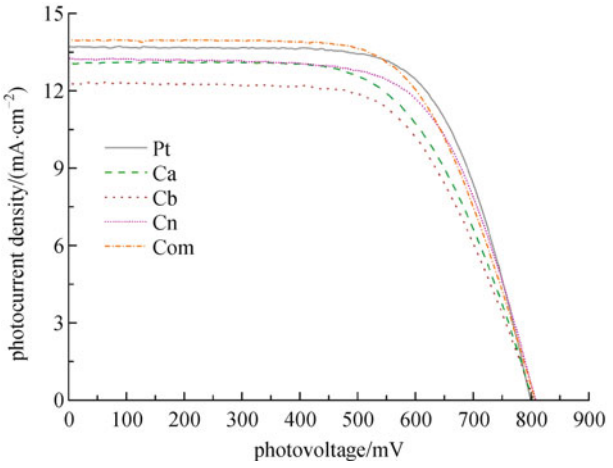

Fig. 3 *I-V* curves for DSSCs using the four kinds of CEs and the Pt electrode

4 Conclusions

In conclusion, we successfully developed a new type of hybrid photoanode and the N-doped photoanode for high-efficient DSSCs as well as the carbon CEs for low-cost DSSCs. The hybrid DSSCs with multilayer photoanodes by the film-transfer technique achieved a panchromatic response and a superposed J_{SC} by using two complementary dyes without the significant decrease in V_{OC}.

The DSSC fabricated by the N-doped photoanode of our simple approach achieved a high conversion efficiency of 10.10%, which was much higher than the value of 8.90% for the undoped-DSSC. Moreover, N-doped DSSCs possess higher photocurrent due to a higher dye uptake. Furthermore, an enhanced open circuit photovoltage was obtained in N-doped DSSCs. Therefore, N-doped TiO_2 nanocrystals prepared by our approach are ideal semiconductor materials for DSSCs.

We synthesized a well-ordered Com with a modified one-pot chemical method. Com CE was used in the DSSC system, as well as other three kinds of carbon CEs. The high performance of DSSC using Com CE yields an efficiency of 7.50%, comparable to that of Pt CE (7.47%). This demonstrates its promising potential for replacing Pt.

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