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Effect of photo-doping on performance for solid-state dye-sensitized solar cell based on 2,2′7,7′-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene and carbon counter electrode

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ABSTRACT

Photo-doping is a process to optimize solid-state dye-sensitized solar cells based on 2,2′7,7′-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene (spiro-OMeTAD). We investigate the effect of photo-doping on performance for solid-state DSSC based on spiro-OMeTAD and carbon counter electrode. The efficiency is improved to 4.09% by optimizing doping level under standard solar conditions (AM1.5G 100 mW cm^{-2}). Results indicate that photo-doping has significant influence on charge transferring properties at TiO_2/spiro-OMeTAD and spiro-OMeTAD/carbon interface, which is consistent with the change of photovoltaic performance.

1. Introduction

Dye-sensitized solar cell (DSSC) has been regarded as one of the most promising alternatives to the conventional silicon-based photovoltaic device due to its easy fabrication and abundance of materials [1,2]. Though a high conversion efficiency up to 12.3% could be achieved for solar energy, the conventional DSSC meet with drawbacks for its practical application due to the use of liquid electrolyte, which always relates to the complex encapsulation and the solvent leakage. Replacements for the liquid electrolyte with a solid hole-transporting material (HTM) seem to be more viable for its practical application. One of the most efficient HTMs for solid-state DSSC is 2,2′,7,7′-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD) [3]. Over the past decade, great attention has been devoted to spiro-OMeTAD and significant improvements have been achieved for solid state DSSC based on spiro-OMeTAD [4–13]. Recently, the effect of oxygen on the performance for devices based on spiro-OMeTAD was investigated [14]. Moreover, the oxygen-induced doping level in spiro-OMeTAD increase from 3.5% to 10.5% after illuminating [14]. This means photo could accelerate the oxidation of spiro-OMeTAD by oxygen, which is the so-called photo-doping [11]. In most publications on spiro-OMeTAD based solid-state DSSC, the opitmized efficiency could be obtained after photo-doping. However, few paper report the detailed effect of photo-doping on the performance for spiro-OMeTAD based solid-state DSSC.

In this work, we investigate the effect of photo-doping on the performance for solid state DSSC based on spiro-OMeTAD and carbon counter electrode. Carbon counter electrode by screen printing avoid the sophisticated facility for Au or Ag electrodes [15]. A metal free indoline dye (D102) with a strong absorption coefficient was used as the sensitizer. Solution containing spiro-OMeTAD was drop casted onto the porous carbon counter electrode. The devices were fabricated under ambient atmosphere, which is benefit for spiro-OMeTAD based DSSCs [14]. The performance measured immediately after drying of spiro-OMeTAD was quite poor. However, the performance was increased gradually as the light soaking time increased. The energy conversion efficiency without photo-doping was only 0.82%, by introducing photo-doping the efficiency was improved to 3.6% at 0.86 sunlight intensity. For an optimized device with 12 min doping, we achieved an efficiency of 4.09% under simulated AM1.5 solar illumination of 100 mW cm^{-2}. This efficiency is comparable to that for Au counter electrode with spiro-OMeTAD and the D102 dye [4]. To the best of our knowledge, this

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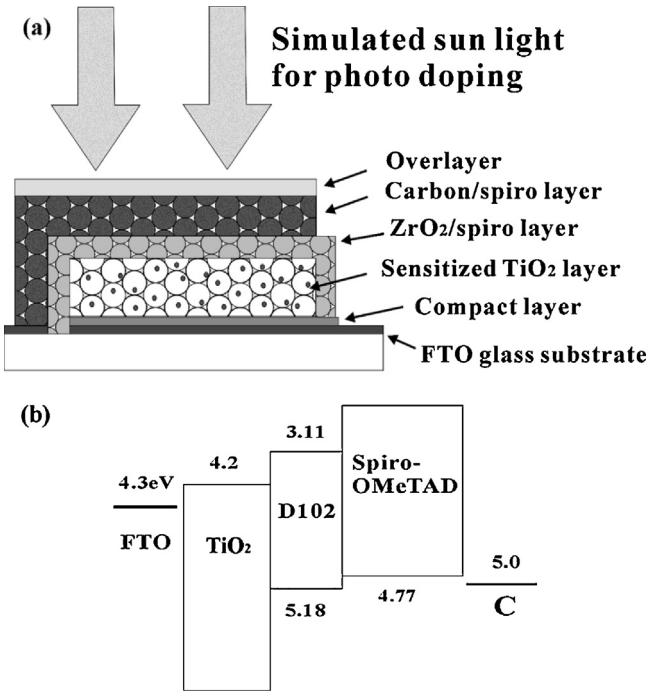

Fig. 1. (a) A schemed structure of device based on spiro-OMeTAD and carbon counter electrode and (b) the energy levels of materials.

is the first time that the influence of photo-doping on interface properties and performance for solid-state DSSC based on spiro-OMeTAD and carbon counter electrode is reported.

2. Experimental

The structure of the monolithic solid-state DSSC is schematically presented in Fig. 1, where from bottom to top is the FTO glass substrate, TiO_2 compact layer, dye sensitized TiO_2 nanocrystalline layer, ZrO_2 spacer layer, mesoscopic carbon layer and spiro-OMeTAD overlayer. The fluorine-doped SnO_2 substrates were etched with zinc power and HCl (1 M) to form two detached electrode pattern before being ultrasonically cleaned with detergent, deionized water and ethanol successively. After that, the patterned substrates were coated with a 100–200 nm compact TiO_2 layer by aerosol spray pyrolysis at 450 °C. After cooling down to room temperature naturally, a nanoporous TiO_2 layer was deposited on top of the compact layer by screen printing and then sintered at 500 °C for 30 min. Followed, a 4 μm ZrO_2 spacer layer and a 6 μm mesoscopic carbon layer was printed on the top of the mesoporous TiO_2 layer successively, and then the films were sintered at 400 °C for 30 min. After cooling down to 70 °C the samples were soaked in D102 solution (0.5 mM in CH_3CN:t-BuOH (1:1)) overnight in the dark. After sensitization, the films were rinsed in dry ethanol for 3 times (10 min every time) and dried in air flow. Then, a chlorobenzene solution containing 0.17 M Spiro-OMeTAD (Merk), 0.2 mM $Li(CF_3SO_2)_2N$ (Aldrich) and 0.1 mM *tert*-buytlpyridine (Aldrich) was drop-casted onto the carbon layer. The devices were subsequently dried at 60 °C in dark. Finally the cells were illuminated from the back side at open circuit under simulated sunlight for photo-doping. Similar photovoltaic properties can be obtained when the cells are illuminated from the front side. It is noticeable that all devices were not sealed since air is necessary for the oxidation of spiro-OMeTAD under illumination [14].

Table 1
The photovoltaic performance of devices with different time of photo-doping at 0.86 sunlight intensity. The film thickness of nanoporous TiO_2 layer is 0.9 μm. The cell active area (with a mask) is 0.13 cm^2.

Illuminating time (min)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	*FF*	η (%)
0	2.19	766	0.42	0.82
2	4.09	784	0.47	1.75
5	5.89	803	0.47	2.58
10	5.94	818	0.60	3.39
15	5.56	831	0.67	3.6

3. Results and discussion

Fig. 2a shows the SEM cross section of the solid state DSSC based on carbon counter electrode and spiro-OMeTAD. It is clear that mesoscopic TiO_2 layer, ZrO_2 layer, carbon counter electrode and spiro-OMeTAD overlayer are ordinally deposited on FTO glass. The inset in Fig. 2a is the SEM of a carbon counter electrode film in which graphite and carbon black particles could be seen clearly. Fig. 2b displays that spiro-OMeTAD is distributed uniformly in the pores of the mesoscopic TiO_2 and ZrO_2 layer. This indicates a good pore filling of spiro-OMeTAD for this monolithic structure.

Fig. 3 shows the photocurrent–photovoltage curves of devices with different illuminating time under 0.86 sunlight intensity and the corresponding photovoltaic performance is displayed in Table 1. For the undoped device we get a short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*FF*) of 2.19 mA cm^{-2}, 766 mV, and 0.42, respectively, yielding an overall conversion efficiency (η) of 0.82%. This device suffers from a low J_{sc} and FF. When increase the illuminating time to 2 min, 5 min, and

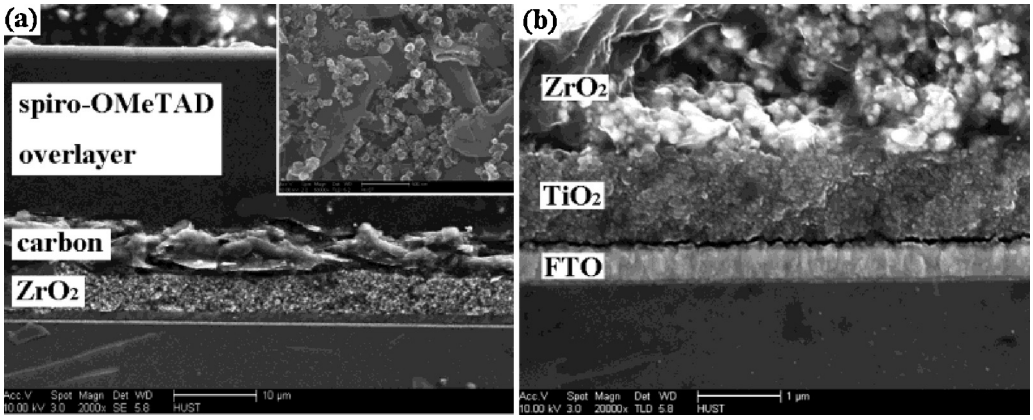

Fig. 2. The SEM images of the cross section of the solid state DSSC based on carbon counter electrode and spiro-OMeTAD under (a) low and (b) high magnification. Insert picture: the surface feature of carbon counter electrode.