Carbon/F-doped SnO$_2$ nanowires array counter electrode for dye sensitized solar cell

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F-doped SnO$_2$ nanowires array coated with carbon on stainless steel substrate was investigated as counter electrode (CE) for dye-sensitized solar cell (DSSC). With increasing the carbon coating time, the conductivities of F-doped SnO$_2$ nanowires increased and the charge transfer resistances of the CEs decreased. The overall energy conversion efficiencies of DSSCs with an active area of 0.25 cm^2 sensitized by a N719 dye reached up to 9.28% (AM1.5, 100 mW cm^{-2}) by using the electrodes. It is found that the photovoltaic performance was deeply affected by the carbon coating time.

1. Introduction

Dye-sensitized solar cell (DSSC) is an attractive and promising device as a clean energy source because of its potential for high efficiency and low-cost production [1, 2]. In general, a typical DSSC consists of a nanocrystalline titanium dioxide (TiO$_2$) electrode sensitized with a dye fabricated on a transparent conducting oxide-coated (TCO) glass substrate, a counter electrode coated with a layer of catalyst, and an electrolyte solution containing I^-/I_3^- redox ions between the two electrodes. The overall redox reaction in DSSC can be summarized as $I_3^- + 2e^- \leftrightarrow 3I^-$. Tri-iodides produced near the dye-sensitized TiO$_2$ reduce at the counter electrode (CE). The tri-iodides reducing process, equal to the producing, is one of the most important factors to the photovoltaic performance of DSSC [3].

Traditionally, a thin layer of Pt [4-6] or graphite [7, 8] solid films are deposited onto electrical conductive substrates such as transparent conductive oxide coated glass or stainless steel foil to catalyze the tri-iodides reduction process [9]. However, the catalytic performances are not satisfied to meet the practical demand [10]. Recently many fruitful works have been reported that using one dimensional (1D) nanomaterials as catalysts benefits the efficiencies greatly [11-14]. These works obtained favorable results through increasing the internal surface area of catalysts.

To further improve the performance, imparting porosity to the current collector becomes urgent and necessary [15]. In this work, we propose a nanostructured CE consisting of a layer of carbon/F-doped SnO$_2$ nanowires array (CFTO). The carbon in the electrode serve as the catalysts for reducing tri-iodides, meanwhile the F-doped SnO$_2$ nanowires array serves as the electrical conductive pathways to collect current. Both of the surface area of catalyst and current collector are increased by employing this electrode.

2. Experimental details

To prepare the CFTO CE, a layer of F-doped SnO$_2$ nanowires array was firstly deposited on several stainless steel foils (304, 2.5 mm in thickness, Zhejiang Hemudu Co. Ltd) via a vapor-liquid-solid (VLS) mechanism referring to a previous report [16] except that the mixed powders of Sn and SnF$_2$ in a weight ratio of 95:5 were used as the source materials and a 5-nm-thick sputtered Pt was used as the catalyst. Second, the prepared substrates were immersed into a sucrose solution (30 g sucrose, 100 ml deionized water) with different time of 0, 15, 30 and 45 min respectively. Lastly all the prepared substrates were dried in a quartz resistance tube furnace at 500 ^{o}C for 3 h [17].

The morphology and crystal structure of a typical CFTO CE were characterized by scanning electron microscopy (SEM, JEOL JEM-6320F) and X-ray diffraction (XRD, Bruker-AXS D8) using the CuKα line at 1.54 Å. The *I-V* measurements of individual F-doped SnO$_2$ nanowires with different carbon coating time were performed using an HP4140B semiconductor test system.

3. Results and discussion

Fig. 1(a) shows the top view SEM image of a typical prepared CFTO CE. The electrode looked like a lawn and consisted of nanowires 50-60 nm in diameter. Pt nanoparticles could be clearly seen in the top of each nanowire. The nanowire density of the CFTO determined by counting nanowires in a representative area of a SEM image was estimated to be 3×10^7 /mm^2. Fig. 1(b) presents the XRD pattern. The diffraction peaks can be well indexed to the tetragonal cassiterite structure of SnO$_2$ (JCPDS card: 41–1445) and hextragonal graphite structure of carbon (JCPDS card: 75-1621).
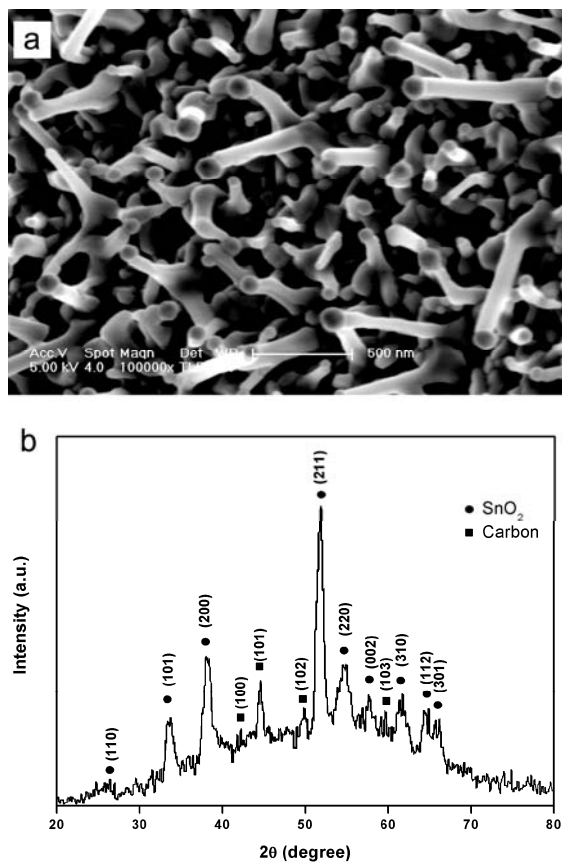
Fig. 1. The top view scanning electron microscopy (SEM) image (a) and x-ray diffraction (XRD) pattern (b) of a typical prepared CFTO CE.

The electron transport measurements on individual CFTO nanowires were carried out at room temperature, as exemplified in Fig. 2. The conductivity of the pure F-doped SnO_2 nanowire was found to be 123.5 S/cm. By coated with a layer of carbon, the conductivity was increased to a certain extent. With different deposition time of 15, 30 and 45 min, the conductivities of CFTO nanowires were 263.8 S/cm, 312.5 S/cm and 328.3 S/cm respectively.
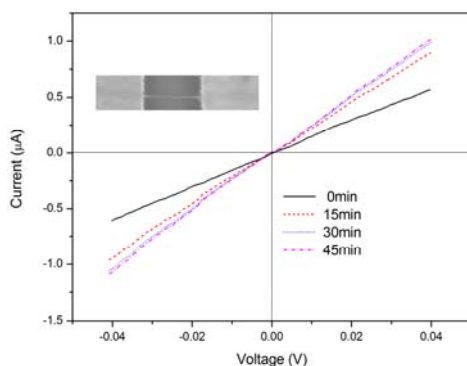

Fig. 2. Room temperature I-V characteristics of CFTO nanowires with different carbon coating time.

Charge transfer resistance (R_{ct}) is an index to the catalytic performance of CE [18]. Therefore in this work the catalytic performance of the prepared CFTO CEs were evaluated through measuring R_{ct} in symmetric thin layer cells consisting of two identical electrodes stacking with a hot-melt film (Surlyn) in between by electrochemical impedance spectroscopy (EIS) [19]. The liquid electrolyte injected into the interelectrode consisted of 0.5 M 4-tert-butylpyridine (TBP), 0.1 M LiI, 0.05 M I_2 and 0.6 M 1-propy-2, 3-dimethylimidazolium iodide in metho-xypropionitrile (MPN). The EIS measurements were performed using a sinusoidal perturbation of 10 mV at zero bias potential over the frequency range of 0.01-10⁵ Hz with an IM6/IM6e (Zahner, Germany) electrochemical analyzer.

The EIS results and the equivalent circuit [20-22] for the electrochemical symmetric cells are shown in Fig. 3. By using the circuit and fitting plots with the Thales software, R_{ct} of the CFTO CEs with different carbon coating time of 0, 15, 30 and 45 min were taken as 1.9, 1.2, 1.0 and 0.75 Ω cm², respectively. Compared with R_{ct} values reported previously [6], the R_{ct} values obtained here are far below, which indicates that the catalytic performance of the prepared CFTO are superior. There are several reasons which may contribution to the high performance. On one hand, it may be attributed to the positive synergistic catalysis of the capped Pt on the top of each nanowire and the coated carbon; On the other hand, the increased surface area of carbon layer is supposed to make it excellent in catalyzing [23]. Furthermore, it is believed that the electrical conductive F-doped SnO_2 nanowires make great contribution as they have direct 1D electronic pathways allowing for efficient electron transport [15, 24].
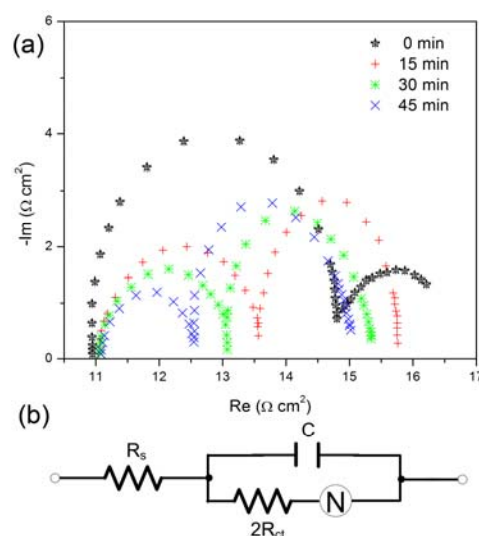

Fig. 3. Nyquist plots (a) and the corresponding equivalent circuit (b) for the symmetric cells based on CFTO CEs with different carbon coating time. The electrode area was 0.36 cm² and the interelectrode distance was set to 100 μm. R_s: serial resistance; $2R_{ct}$: charge transfer resistance of the two electrodes; R_n: Nernst impedance.

To confirm the electrode performance, DSSCs with an active area of 0.25 cm^2 were fabricated using the prepared CFTO CEs. The cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) is(tetrabutylammonium) (N719 dye, Solaronix SA) was used without purification and was dissolved in an absolute ethanol solution with a concentration of 0.3 mM. The TiO$_2$ photo electrode was prepared using a previously published procedure [25] and sensitized by staining it with the prepared dye for 24 h. Then the CFTO CE and prepared TiO$_2$ photo electrode was sandwiched together using a hot-melt film (Surlyn) as a spacer. Finally an electrolyte same with that injected in the symmetric cells mentioned above was introduced into the space between the sandwiched cell. Fig. 4 shows a schematic diagram of the prepared DSSC with a load.
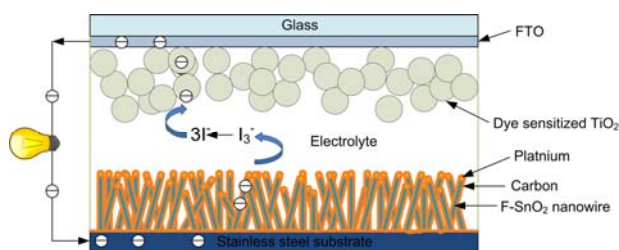

Fig. 4. Schematic diagram of the fabricated DSSC with a CFTO CE. The electrons generated near the dye sensitized TiO$_2$ flow through the electrical conductive F-doped SnO$_2$ (FTO) nanowires array and return back to the electrolyte under the combination catalytic effect of Pt nanoparticles and carbon.

The current-voltage characteristics of the fabricated cells were measured under standard air mass (AM1.5, 100 mW cm^{-2}) provided by a solar simulator using a digital source meter (Keithley 2400). Fig. 5 shows the J-V characteristics of DSSCs with different CFTO CEs. It can be seen that the open circuit voltage (V_{oc}) current density (J_{sc}), fill factor (FF) and conversion efficiency (η) of DSSC with the CFTO CE increased gradually with the increase of carbon coating time, as listed in Table 1. The regularly increased J_{sc} revealed that the conductivity of the direct 1D electronic pathway in the CFTO CEs has great influence to the charge transport time (τ_d). The gradually increased FF and η confirmed that the coated carbon layer has strong effect to the photovoltaic performance.
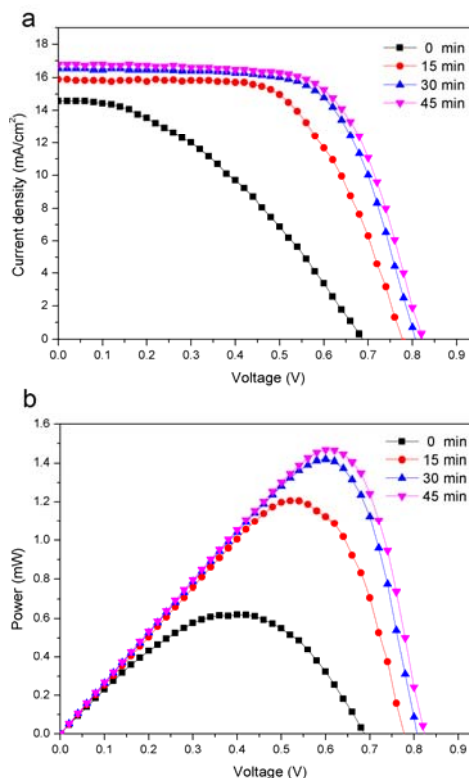

Fig. 5. J-V characteristics of DSSCs using CFTO CEs with different carbon coating time. All cells were measured at 100 mW cm^{-2} (AM1.5).

Table 1. Summary of DSSCs performances using CFTO CEs with different carbon coating time (Short-Circuit Current Density, J_{sc}; Open - Circuit Voltage, V_{oc}; Fill factor, FF; and Overall Conversion Efficiency, η).

Time of carbon coating [min]	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	$\eta(\%)$
0	14.8	686	0.47	3.96
15	16.3	783	0.60	7.64
30	16.5	816	0.66	8.92
45	16.7	827	0.67	9.28

4. Conclusions

In conclusion, we have shown that the CFTO CE is highly effective at catalyzing the tri-iodides reducing process. The charge transfer resistance of the electrode gradually decreased by increasing the carbon coating time, which leads to a gradual enhancement in V_{oc}, J_{sc}, FF and significant improvement of conversion efficiency. DSSC sensitized with a N719 dye with an active area of 0.25 cm^2 showed conversion efficiency as high as 9.28% by using the CFTO CE. The results presented here are of particular significance because they offer us a practical way to improve the CE catalytic performance greatly.

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