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A New Front Contact Counter Electrode with Multiwall Carbon Nanotube Array for Dye-sensitized Solar Cells

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A new kind of front contact counter electrode with multiwall carbon nanotube array on a nonconductive substrate and a thin metal layer was designed for dye-sensitized solar cells. Under standard AM 1.5 irradiation (100 mW cm^{-2}), a device with such counter electrode yielded an overall conversion efficiency of 2.53%.

Dye-sensitized solar cells (DSCs) have been widely studied for its low cost and high efficiency during the past two decades.[1] A typical DSC is composed of a thin TiO_2 nanocrystal film adsorbed with dyes on a conductive glass, electrolyte, and a counter electrode.[2] In such a structure, a counter electrode which is normally composed of a catalytic layer on a fluorine-doped tin oxide (FTO) substrate plays a key role. It serves to transfer electrons coming from the external circuit back to the redox electrolyte. Hence, good conductance and catalytic activity are necessary for the counter electrode. So far, platinum is mostly used as catalyst in DSCs for its excellent catalytic activity and is favorable for high efficiency DSCs.

Nevertheless, platinum is quite expensive as it is well known. What is more, it has been found that the catalytic activity of platinum can diminish[3] and that the metal can even dissolve[4] when in contact with electrolyte. To reduce the cost of DSC, cheaper carbon materials were applied as counter electrodes as alternatives.[5–7] Of those carbon materials, carbon nanotubes showed the best performance. To further decrease the cost, FTO substrate, which accounts for a large portion of the cost, was replaced by some other substrates such as membrane filters on glass.[7] Up to now, the search for new kinds of counter electrode is still an active field of research.

In this letter, a new counter electrode was introduced to DSCs. Multiwall carbon nanotube array (MWCA) as catalyst was prepared on a nonconductive silicon substrate instead of FTO glass. A thin metal layer was deposited on top of the nanotube array and connected with the external circuit, which faced electrolyte in front of the array. The new counter electrode is referred to here as front contact counter electrode (FCCE) (Figure 1a).

All chemicals and solvents used in the present work were purchased from Fluka of puriss quality. Transparent films (10 μm thick layer) of 20 nm TiO_2 particles were used as photoanodes (photoanode fabrication details are given in the Supporting Information[12]). The ruthenium dye (2,2′-bipyridyl-4,4′-dicarboxilate)$_2$(NCS)$_2$, N719) was used as the sensitizer. The electrolyte solution was composed of 50 mM iodine (I_2), 500 mM lithium iodide (LiI), and 500 mM *tert*-butylpyridine dissolved in 3-methoxypropionitrile.

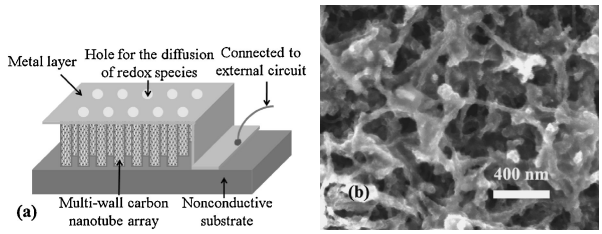

Figure 1. (a) Schematic illustration of the FCCE counter electrode, which is composed of a nonconductive substrate, MWCA, and a Z-like thin Ti layer and (b) scanning electron micrograph (SEM, LEO 1530, German) of surface of MWCA.

MWCA with a thickness of ca. 35 μm on silicon substrate was used as electrode and prepared as described earlier.[8] XRD results confirmed the well-prepared MWCA by this method (given in the Supporting Information[12]). Due to the nonconductivity of silicon substrate a thin Ti layer with a thickness of ca. 5 nm was sputtered on the top of MWCA to connect the nanotubes and conduct the electrons from the external circuit to the nanotubes, as shown in Figure 1b. The thickness of Ti layer was determined by the sputtering time and the degree of vacuum. The thin Ti layer could not cover the rough surface of MWCA completely due to the length difference of carbon nanotubes, and thus there are lots of pores on the surface. The pores range from tens of nanometers to several micrometers, which favors the diffusion of redox species.

The TiO_2 electrodes and the new FCCEs were assembled into devices followed by an injection of the electrolyte (See the Supporting Information[12]). Surlyn was used as sealing material and the thickness was 60 μm. Figure 1 shows the overall structure of a DSC with FCCE electrode. In this structure, MWCA orients to the TiO_2 film which will reduce the diffusion length of I_3^- ions from TiO_2 surface to counter electrode. MWCA with large surface area will be good enough for the reduction of I_3^-. The absence of FTO layer is well compensated by a porous metal layer on top of MWCA to complete the circuit. The photovoltaic performance of this kind of DSC was studied below.

Photocurrent–voltage curves were plotted with a 450 W xenon lamp (Oriel, USA) calibrated with a standard Si solar cell (Peccell, Japan), simulating AM 1.5 solar light (1Sun). Impedance measurements were performed with a computer-controlled electrochemical work station with an impedance analyzer (CHI 604a, Shanghai, China) in a two-electrode configuration.

The photovoltaic performance (I–V) parameters (short circuit current density (J_{sc}), open circuit voltage (V_{oc}), filling factor (FF), and photon-to-electron conversion efficiency (η)) of the DSC employing FCCE (device **a**) are listed in Table 1. For

Table 1. Photovoltaic characteristics of the DSCs made with different counter electrodes under illumination of AM 1.5 full sunlight[a]

Device	Counter electrode	J_{sc} /mA cm^{-2}	V_{oc} /mV	*FF*	η /%
a	FCCE	7.3	679	0.51	2.53
b	Pt layer on FTO glass	11.9	700	0.58	4.90
c (**d**)	Pt (Ti) layer on silicon substrate	— (—)	— (—)	— (—)	— (—)

[a]The cell active area was 0.28 cm^2.

comparing the catalytic activity of FCCE, several kinds of counter electrodes were also used in DSC. Counter electrode with a thermally deposited Pt layer on FTO glass was applied to device **b**. Counter electrodes with a sputtered Pt layer and a Ti layer, both of which are ca. 5 nm thick, on silicon substrates were applied to device **c** and **d**, respectively. *I–V* parameters of device **b**, **c**, and **d** are also listed in Table 1. *I–V* curves of devices **a**, **b**, and **c** are plotted in the Supporting Information.[12]

As shown in Table 1, device **c** or **d** shows no photovoltaic behavior while device **a** does, which proves that MWCA and FCCE function effectively. The photovoltaic performance parameters obtained with device **a** are 7.3 mA cm^{-2}, 679 mV, 0.51 and 2.53%. The overall efficiency of device **a** is half of that of device **b**, which is attributed to the lower current density. Normally, MWCA is a crude mixture of different carbon tubes and particles caused by the preparation process,[9] which lead to a metallic MWCA. Such metallic nature will result in a decrease of catalytic activity and then reduction of the redox couple. Hence, J_{sc} is partly impaired.

Electrochemical impedance spectra (EIS) were used to scrutinize the catalytic activity of FCCE. At high bias voltage, a transport resistance of the substrates and external contacts (R_s), the charge-transfer resistance at counter electrode (R_{ce}) and the recombination resistance between the film and I_3^- in electrolyte (R_{ct}) could be easily obtained from Nyquist plots, as well as the resistance of diffusion of redox species in the electrolyte (R_{sol}).

Figure 2 shows Nyquist plots of device **a** and device **b** at a bias of −0.7 V. Take device **a** as an example, R_s is determined by the real part of the start point of the curve as shown in Figure 2. The real parts of the semicircles from left to right in the curve are assigned to R_{ce}, R_{ct}, and R_{sol}, respectively.[10] All those parameters can be extracted by Z-View software (v2.1b,

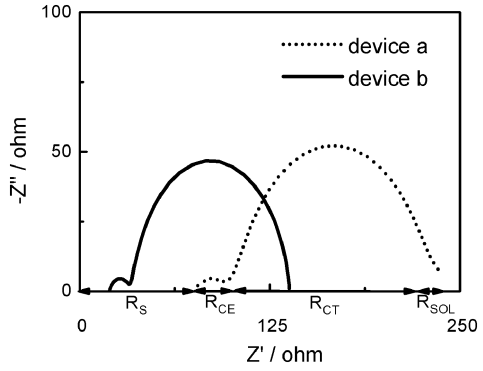

Figure 2. Nyquist plots of device **a** with FCCE and device **b** with normal Pt-loaded counter electrode at $-V_{oc}$.

Table 2. Impedance elements inside the DSCs made with different counter electrodes at a bias of −0.7 V[a]

Device	R_s	R_{ce}	R_{ct}	R_{sol}
a	74	22	138	14
b	18	10	102	16

[a]All the units are ohm. The cell active area was 0.28 cm^2.

Scribner Associate, Inc., USA) fitting and based on the EIS model described elsewhere[11] and listed in Table 2.

It can be seen that device **a** has a larger R_s than that of device **b**. It means that the series resistance of FCCE is larger than that of a normal count electrode. In our FCCE the Ti layer will account for such R_s due to its nanoscale thickness on a non-conductive substrate. The larger R_s reduces V_{oc} and *FF* of device **a** in Table 1. On the other hand, R_{ce} of device **a** is larger than that of device **b**, which means that thermally prepared Pt electrode has better catalytic activity. This result is consistent with above discussion. Higher purity of MWCA may be helpful to improve catalytic performance of FCCE. R_{sol} of device **a** is equal to device **b**, which implies that the design of FCCE will not obstruct the diffusion of ions between two electrodes of DSC.

In summary, a new FCCE with MWCA was developed for DSCs. The use of MWCA and nonconductive substrate is promising to reduce the cost of DSC and improve the long-term stability. Further work is in progress, such as reducing the series resistance, purifying MWCA, and developing new and cheaper nonconductive substrates, to optimize the FCCE used in DSCs for better photovoltaic performance.

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12 Supporting Information is available electronically on the CSJ-Journal Website, http://www.csj.jp/journals/chem-lett/index.html.

