Spray-coated Carbon Nanotube Counter Electrodes for Dye-sensitized Solar Cells

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(Received March 28 2005, Accepted July 22 2005)

Carbon Nanotube(CNTs) counter electrode is a promising alternative to Platinum counter electrode for dye sensitized solar cells (DSSCs). In this study, CNT counter electrodes having different visible light transmittance were prepared on fluorine-doped tin oxide (FTO) glass surface by spray coating method. Microstructural images show that there are CNT-tangled region coated on FTO glass counter electrodes. Using such CNT counter electrodes and screen printed TiO_2 electrodes, DSSCs were assembled and its I-V characteristics have been studied and compared. Light energy conversion efficiency of DSSCs increased with decreasing in light transmittance of CNT counter electrode. Efficiency of DSSCs having CNT counter electrode is compatible to that of Pt counter electrode.

Keywords : Spray coating, CNT, Counter electrode, Dye-sensitized solar cell, Nano, TiO_2

1. INTRODUCTION

There is great interest in Dye Sensitized Solar Cells (DSSCs) due to high conversion efficiency and simple production methods. Since Gratzel published his breakthrough report in nature[1], many studies have been carried out on DSSCs consisting of mesoporous TiO_2 electrode, sensitizer and electrolyte. Here, counter electrodes have not much studied because of excellent catalytic properties of Platinum[2].

TCO itself has extremely poor catalytic property for iodine reduction[3,4]. In this reason, it is required to modify TCO with good catalytic materials such as Platinum[5], Carbon[6,7]. Pt has been widely used as a catalyst[2]. High efficiency of DSSC (~11 %) was obtained by using Pt coated FTO glass counter electrode [8]. However, Pt is not suitable for large size DSSCs because of its cost and difficulties in large area coating. In order to overcome such limits, we investigated CNTs. Until now, few groups used activated carbon layer or CNT for DSSCs and obtained low efficiency[9]. In this case, it is essential for electrodes to promote electron-transfer reaction, not to degrade its electro-chemical property and to retain low voltage during redox coupling, and to have high electrical conductivity. Also, it requires large effective area for catalytic reaction. Especially, 3D structure is expected to enhance electron-transfer reaction within electrolyte by enlarging effective reaction area. However, it is difficult to fabricate Pt in 3-dimensional (3D) configuration.

Carbon nanotubes (CNTs) are promising alternative to Pt as a catalysis, due to their novel physical and electrochemical properties which have caused considerable excitement. This material system can be easily fabricated in the form of 3D electrode. In this respect, we report novel method for fabricating 3D CNT electrodes in conjunction with TCO glass, especially to fabricate transparent CNT-contained counter electrodes.

2. EXPERIMENTAL PROCEDURE

2.1 CNT counter electrode preparation

CNT slurry was prepared by adding commercially available, finely dispersed multi wall CNTs (diameter ~ 20 nm, length ~5 um) with 3 % CMC added-water-alcohol followed by 10 hours stirring. This slurry is sprayed on FTO glass substrate (Ashai FTO, 8 Ω/□, 80 % transmittance in visible region), using spray gun (Nozzle dia ~0.3 mm). Distance between the substrate and spray gun was around 200 mm. Transmittance of the counter electrode has controlled by number of sweeps and spraying time of CNT slurry on FTO surface. CNT-coated FTO glasses were annealed at 100 °C for 1 hr in ambient atmosphere. To compare the performance of the spray-coated CNT counter electrode, Pt-counter electrodes also prepared on similar FTO substrate by DC magnetron sputtering.

2.2 TiO_2 electrode preparation

TiO_2 paste was prepared by mixing TiO_2 powder (Degussa, P25) with 2.5 pH deionized water, followed by magnetic stirring. This paste kept in ball milling for one hour. Using this paste, approximately 10 μm thick layer was screen-printed on transparent F-doped SnO_2/glass substrate (Ashai FTO, Sheet resistance 8 Ω/□ and 80 % transmittance in the visible region). After drying in room temperature for 30 minutes, TiO_2 films were sintered at 500 °C for 30 minutes. In order to sensitize TiO_2 films, sintered TiO_2 electrodes were immersed in a solution of 0.02 mg/cc red dye $(RuL_2(NCS)_2$ [L=2,2'-bipyridine-4,4'-dicarboxylic acid] in ethanol for 24 hours at room temperature. Excess dyes are removed by rinsing the electrode in absolute ethanol.

2.3 Cell construction

Dye-sensitized TiO_2 electrode was directly staked on CNT counter electrode. Surlyn sheet (thickness, 50 μm) was kept between two electrodes to avoid the direct contact. Uniform TiO_2 electrodes were used to construct DSSCs with different transmittance of CNT counter electrodes. So we can compare the performance of the counter electrode as a function of its transmittance and also with Pt counter electrode. The electrolyte containing I^-/I_3^- redox couple was introduced into the gap by capillary effect. The spacer was sealed with heat press. Single side Cu tape and Ag paste were used to make an electrical contact. Here the effective area of the DSSCs was 0.25 cm^2. Cross section view of the DSSC is shown in Fig.1.

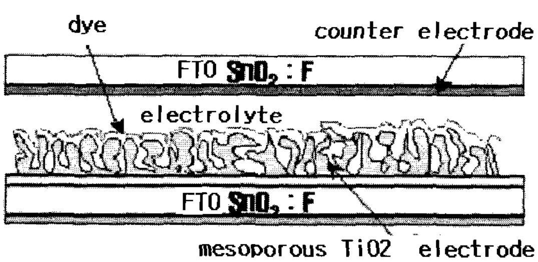


Fig. 1. Schematic diagram of dye sensitized solar cell.

2.4 Characterization

Light transmittance and absorption of CNT and Pt counter electrodes were measured by fluorescent spectrophotometer. Field emission scanning electron microscope (FE-SEM) was used to study the micro-structure of electrodes. Sheet resistance of the electrode was measured with four-point probe. Alpha-step (Tencor Alpha-step 200) profile meter) was employed to measure thickness of TiO_2 electrode. Photocurrent–Voltage characteristics of DSSCs having TiO_2 electrode and different counter electrode were measured using solar simulator attached with Keithley 2400 source meter.

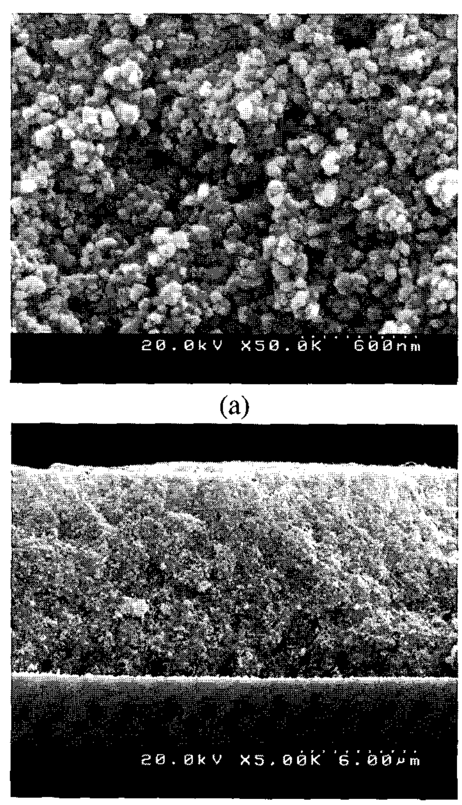
3. RESULTS AND DISCUSSION

3.1 Microstructure of electrodes

Figure 2 shows plan-view and cross section view micrographs of spray-coated TiO_2 electrodes. There are many open pores around TiO_2 particles observed on the plan-view. This TiO_2 electrode was used for assembling dye-sensitized solar cell.

Photographs of spray-coated CNT counter electrodes with different transmittance are shown in Fig. 3. Such counter electrode with high transmittance may have few coverage of CNT on FTO glass. In this case, measurement of light transmittance also confirms that surface area of CNT counter electrode on FTO glass increases with increasing spraying time in the range of 10 sec to 1 min.

FE-SEM micrographs of FTO glass surface and CNT-counter electrodes were showed in Fig. 4. One can see



(b)

Fig. 2. FE-SEM micrographs of nanocrystalline TiO_2 electrodes prepared by screen-printing.
(a) plan-view and (b) cross section-view.

many triangular facets from FE-SEM micrograph (see Fig. 4(a)) of the surface of F-doped SnO_2 (FTO). High resolution FE-SEM micrograph (Fig. 4(b)) shows that tangled-CNT tubes provides open pores on surface of FTO glass. We expect that these tangled CNTs may be in 3-dimensional configuration. This means that spray-coated CNT counter electrodes may have larger surface area than those in the cases of normal carbon and Pt counter electrodes. Counter electrodes with different transmittance have prepared by adjusting the spraying time in the range of 10 sec to 1 min. Fig. 4(c), (d), and (e) show FE-SEM micrographs of CNT counter electrodes for 60 %, 30 %, and 0 % transmittance respectively.

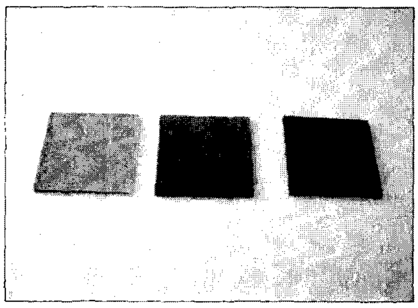


Fig. 3. Photographs of spray coated CNT counter electrodes (From left: 60 %, 30 %, and 0 % transmittance).

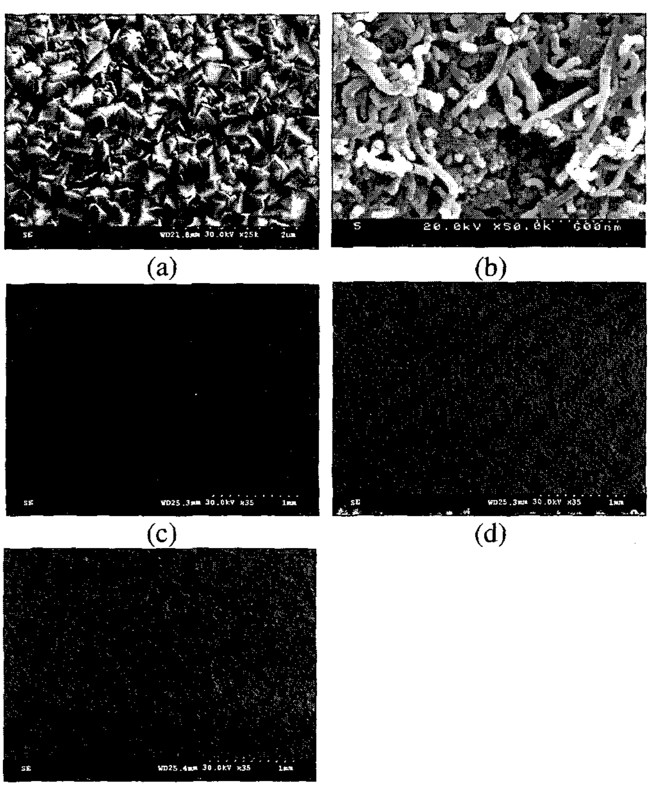


Fig. 4. FE-SEM micrographs of CNT-counter electrodes as a function of transparency. (a) FTO glass, (b) CNT (high resolution), (c) 60 %, (d) 30 %, and (e) 0 %.

3.2 Photocurrent-voltage curves of DSSCS

Figure 5 shows photocurrent-voltage curve of DSSCs for different CNT counter electrodes, measured under simulated solar light (AM 1.5, 100 mW/cm^2). For comparison, obvious mirror-like sputtered-Pt was also used for counter electrode. As a result, photocurrent density gradually increased with inversely increasing in transmittance of CNT counter electrode. In the case of DSSCs having fully covered CNT counter electrode, maximum current density of 11.5 mA/cm^2 was observed. This result is comparable with that of Pt counter electrode.

Here, in the case of CNT counter electrode, enhanced efficiency of DSSCs may due to high surface area. This means that catalytic behaviors of CNT-electrode increased with increasing surface area of CNT on FTO glass. In order to increase such efficiency, we need to do full coverage of CNT on glass as counter electrode. However, to use DSSCs in transparent window applications, we need mutual compromise between the efficiency and transparency of DSSCs. Summery of the I-V measurements of DSSC with different counter electrodes are showed in Table 1.

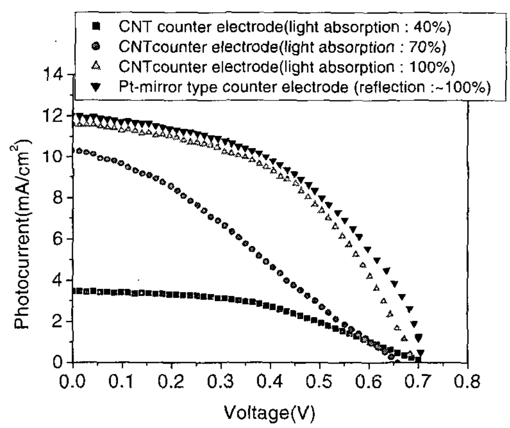


Fig. 5. Photocurrent-voltage curve of DSSCs for different counter electrodes.

Table 1. Summery of photocurrent-voltage characteristics of DSSC for different counter electrodes.

Transmittance of CNT counter electrode %	Open-circuit voltage V_{oc} (Volt)	Short-circuit current density J_{sc} (mA/cm^2)	Fill factor	Efficiency %
60	0.706	3.4	50	1.20
30	0.658	10.2	33	2.21
0	0.690	11.5	49	3.88
0 (Platinum)	0.710	12.0	48	4.08

4. CONCLUSION

Dye-sensitized solar cells (DSSC) were prepared, using spray coated, different light transmittance CNT counter electrodes and screen printed TiO_2 electrode. Microstructural images show that irregularly CNT-tangled region coated on FTO glass counter electrodes. I-V characteristics of DSSCs consists of different transmittance CNT counter electrode have been studied in simulated solar light and compared with conventional DSSCs which consists of sputtered Pt counter electrode. DSSCs light energy conversion efficiency increase with decrease in CNT counter electrode's light transmittance. CNT counter electrode is at least compatible to that of Pt counter electrode. This study shows spray coating is one of suitable fabrication method for preparing highly effective CNT counter electrodes for semi transparent DSSCs in order to use window applications.

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