Application of Carbon Nanotubes to Counter Electrodes of Dye-sensitized Solar Cells

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In order to search for an efficient counter electrode in a dye-sensitized solar cells, three kinds of nano-carbon materials were examined. When single wall carbon nanotubes (SWCNTs) were used as a carbon electrode, the conversion efficiency of the cells is 4.5%. This value is comparable to Grätzel-type dye-sensitized solar cell (counter electrode: platiun-suputtered fluorine-doped tin oxide) under the same experimental condition.

Recently, dye-sensitized solar cells (DSC) has attracted much attention because of low cost of raw materials and relatively high photon to current conversion efficiency for simple and low energy consuming fabrication process.[1] Dye-sensitized solar cells are expected as inexpensive-widespread model of solar cells, and wide investigation has been undertaken.

A fluorine-doped tin oxide (FTO) substrate coated with a catalytic amount of platinum is used as counter electrode in dye-sensitized solar cell. Although this electrode is expensive, yet it has been used because of its high electrochemical activity. A low cost electrode with high electrochemical activity is an important requirement to enhance the practical utility of the dye sensitized solar cells.

Sometimes carbon is also used as a catalyst of counter electrode in dye sensitized solar cell, because the overvoltage of iodide/triiodide reduction at carbon catalyst is kept low. Kay et al. have applied carbon film to counter electrode of DSC and good conversion efficiency is obtained.[2] Recently, new carbon materials, e.g. nanotubes having nanometer-sized molecular structure, are examined from a point of view of applicability to electrode of various devices because it has high conductivity and large surface area. Several attempts to apply carbon nanotubes to counter electrode of solid-state solar cells have already been reported.[3–5] But these devices are not practical because of their low efficiency.

In this letter, we report the experimental results on the nano-carbon materials such as single wall carbon nanotubes (SWCNTs), carbon filaments[6] (multi-walled carbon tubes with 1 µm diameter and 10–40 µm length) and nanohorns[7] (corn-shaped carbon cages with 5 nm diameter and 20 nm length) to examine their applicability to the counter electrode of the dye-sensitized solar cells. In dye-sensitized solar cells with liquid electrolyte, conversion efficiency should become higher by use of nano-carbon electrode, because contact between the electrode and electrolyte is good even in nano fibrous materials and this is expected to enhance the electrochemical activity of electrode.

SWCNT (purified sample) was purchased from Carbon Nanotechnologies Inc. Carbon filament and nanohorn were prepared by reported procedures.[6,7] Using these materials, two kinds of carbon films were prepared by the following methods. Method (a): Carbon materials (20 mg) were ultrasonically suspended in water (50 ml). About five drops of the suspension were spread on an FTO substrate (substrate area: 1 cm^2, sheet resistance: 13.5 Ω $square^{-1}$, purchased from Nippon Sheet Glass) at 60 °C. After the suspension was dried, the spreading and drying procedures were repeated five times. Method (b): The carbon suspension prepared by the method (a), was filtered by the Teflon membrane filter[8] (pore size 100 nm, diameter 35 mm) and dried at 60 °C.

Nanocrystalline TiO_2 film was prepared by the previously described method.[9] TiO_2 colloidal paste (particle size: 13 nm, purchased form Solaronix) was spread on FTO substrate. A mixed suspension of ZrO_2 (JRC-ZEO-1: particle size 36 nm, reference catalyst obtained from the Catalysis Society of Japan) and TiO_2 (JRC-TIO-5: particle size 0.5–1 µm) was applied to the TiO_2 layer as a light reflecting layer,[2] subsequently fired at 500 °C. A ruthenium dye, *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4-carboxilic acid-4′-tetrabutylammonium carboxilate)ruthenium(II) (N719 dye: purchased from Solaronix) was used as a sensitizer for the TiO_2 particles. The electrolyte consisted of 0.05 M (1 M = 1 mol dm^{-3}) iodine, 0.10 M lithium iodide, 0.30 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.50 M 4-*tert*-butylpyridine in 3-methoxyacetonitrile. A conversion efficiency was measured under simulated sun light (AM 1.5, 100 mW cm^{-2}). The area of the TiO_2 photoelectrode was 0.25 cm^2.

The efficiencies of solar cells using carbon film deposited on FTO electrode (prepared by method (a)) were measured in order to examine catalytic activity of the carbon material. The schematic structure of the cell is shown in Figure 1(a). current density-voltage curves of the cell are shown in Figure 1(b) and the conversion efficiencies (η) are summarized in Table 1. Platinum coated FTO (Pt/FTO) electrode which is usually used in dye-sensitized solar cell, shows the highest conversion efficiency (5.4%). Among the carbon coated FTO electrodes, the most efficient electrode is SWCNT/FTO (3.5%), followed by the carbon filament/FTO (2.5%) and the nanohorn/FTO (2.4%). When the counter electrode is only FTO, conversion efficiency is very low (0.1%). This result clearly shows that the carbon film works as electrochemical catalyst. The electrochemical activity of carbon film may be explained in terms of the size of surface area in carbon materials. Specific surface areas (S) of the carbon materials are measured and the results were summarized in Table 1. SWCNT has the highest specific surface area (764 m^2 g^{-1}). The carbon filament (300 m^2 g^{-1}) and nanohorn (350 m^2 g^{-1}) also have relatively large specific surface area, but these values are smaller than that of SWCNT. This indicates that electrochemical activity is enhanced by the large surface area of the carbon materials.

Next, we measured the efficiency of the solar cells using carbon film (prepared by method (b)) as a counter electrode substrate. The schematic structure of the cell and their current density-voltage curves are shown in Figure 2(a) and 2(b), respectively. The conversion efficiencies (η) are summarized in Table 2. It is obvious that only SWCNT electrode shows high

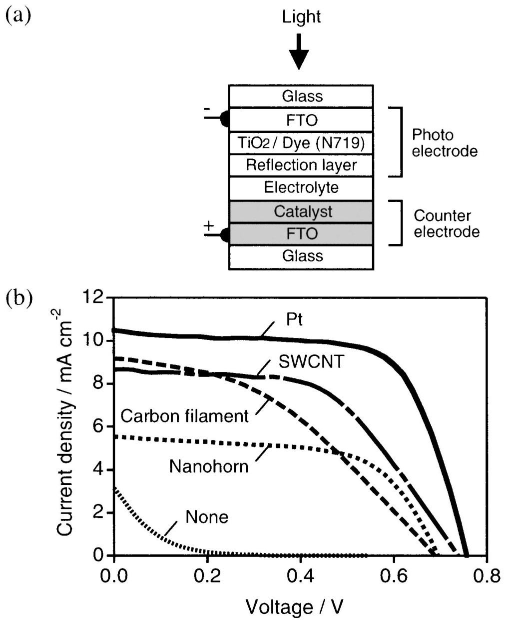

Figure 1. (a) Schematic diagram of dye-sensitized solar cell with carbon catalyst spread on FTO substrate. (b) Photocurrent density-voltage characteristics of the cells under 1.5 AM, 100 mW cm^{-2} illumination.

Table 1. Conversion efficiency (η) of the cells and specific surface area (S) of carbon materials

Catalyst	η/%	S/m^2 g^{-1}
SWCNT	3.5	764
Carbon filament	2.5	350
Nanohorn	2.4	300
Pt	5.4	—
None	0.1	—

conversion efficiency. The SWCNT electrode (4.5%) shows 85% efficiency of that in Pt/FTO electrode. Carbon filament (0.2%) and nanohorn (0.04%) show low efficiency. The difference in the efficiency of each carbon electrode results from resistance of carbon electrode together with the catalytic activity of carbon materials. Sheet resistance (R) was measured by four point method and the results are summarized in Table 2. SWCNT electrode shows very small resistance (1.8 Ω square^{-1}) but that of carbon filament (990 Ω square^{-1}) and nanohorn (>1000 Ω square^{-1}) are high. Low resistance of SWCNT is attributed to a metallic or semiconducting property of individual SWCNT and good contact among them arising from the tangle of the fibrous structure of SWCNTs. The SWCNT film prepared by method (b) shows durability to scratches because mechanical strength of the film is also increased by tangle of the molecules. This feature enhances practical utility of the SWCNT film for electrical devices. The resistance of the carbon filament is relatively high because contact between thick fibers is not good. In the case of nanohorns, the contact among their short fibers is also weak and this causes a high resistance and fragileness of the nanohorn film.

In conclusion, among carbon materials, SWCNT shows high electrochemical activity in iodide/triiodide redox reaction because of its high surface area. Moreover, SWCNT fibers can easily take the form of highly conductive films by the filtration of water suspension. According to those two advantageous characteristics, SWCNT electrode is suitable for counter electrode for dye-sensitized solar cells.

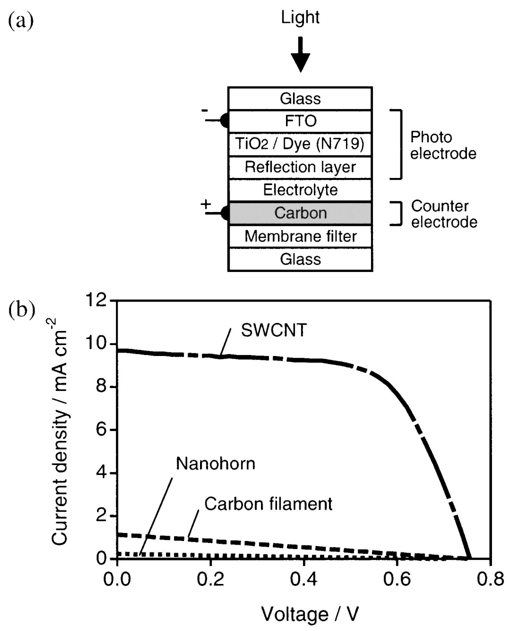

Figure 2. (a) Schematic diagram of dye-sensitized solar cell with carbon film as a counter electrode. (b) Photocurrent density-voltage characteristics of the cells under 1.5 AM, 100 mW cm^{-2} illumination.

Table 2. Conversion efficiency (η) of the cells and sheet resistance (R) of carbon electrodes

Electrode	η/%	R/Ω square^{-1}
SWCNT	4.5	1.8
Carbon filament	0.2	990
Nanohorn	0.04	>1000

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