Plastic and Solid-state Dye-sensitized Solar Cells Incorporating Single-wall Carbon Nanotubes

Nobuyuki Ikeda and Tsutomu Miyasaka*
Graduate School of Engineering, Toin University of Yokohama, 1614 Kurogane-cho, Aoba, Yokohama 225-8502

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A clay-like conductive material comprising single-wall carbon nanotube and imidazorium iodide derivative was combined with dye-sensitized mesoporous TiO_2 layer formed on a plastic substrate. A thin, plastic, solid-state photocell was devised, which works with a highest conversion efficiency of 2.3% under simulated sunlight intensity of 23 mW cm^{-2}.

Recent advancements in plastic electronics and printable electronics[1] are stimulating manufacture of solid-state organic electronic devices by simple coating and printing processes. Dye-sensitized solar cells (DSCs), which are generally manufactured by enclosing iodine-based liquid electrolytes, also requires liquid to solid conversion to prevent the leakage of liquid components. Glass to plastic conversion of DSCs is also sought after to meet high-speed roll-to-roll continuous manufacture processes, which lead to a dramatic cost reduction by applying screen printers to the entire process. To this end, development of solid-state or quasi-solid-state DSCs has been the subject of recent intense studies.[2–4] We have previously reported a solid-state DSC using a conductive composite of polymer-loaded carbon black and ionic liquid; the cell attained a power conversion efficiency of 4.07% on a glass substrate.[5] This practice demonstrated that a soft conductive material of current rectifying ability is capable of eliciting high-density photocurrent by making good electric junction with the porous TiO_2 surface. In this report, we show preparation of full-plastic DSC with a solid-state structure that incorporates a clay-like layer comprising single-wall carbon nanotube (SWCNT) and ionic liquid. This is the first trial in the solidification of full-plastic DSC, which was realized by iodine-free assembling method and achieved high conversion efficiency up to 2.3%.

Indium-tin-oxide (ITO)-coated polyethylene naphthalate (PEN) (thickness, 200 μm; sheet resistance, 13 Ω sq.$^{-1}$; transmittance, 80%, Peccell Technologies) was coated with a 7 μm-thick mesoporous TiO_2 layer by doctor-blading of a binder-free nanocrystalline TiO_2 paste, which has been prepared as reported previously.[6] The TiO_2 layer was sensitized by monolayer adsorption of ruthenium complex dye (N719), *cis*-bis(thiocyanato-*N*)bis(4,4′-tetrabutylammonium hydrogen dicarboxylato-2,2′-bipyridine-κ^2N)ruthenium(II) (Peccell Technologies, Inc). The SWCNT-based conductive composite was prepared by triturating 30 mg of a solid powder of SWCNT (Carbon Nanotechnologies, Inc.) in the presence of 400 mg of an ionic liquid, 1,3-diethyleneoxide derivative of imidazolium iodide (1,3-di(2-(2-(2-(2-methoxy)ethoxy)ethoxy)ethoxy)ethylimidazolium iodide, abbriviated as EOImI (See Supporting Information[15]), on an agate mortar. This mixing yielded SWCNT–EOImI composite in the form of a highly viscous black paste which is clay-like solid state and is free of volatile components. A 90-μm thick layer of this hard paste was sandwiched by the dye-sensitized TiO_2 layer and an ITO–PEN counter-electrode (cathode). The surface of the counter ITO–PEN cathode underwent no treatment for loading of catalyst, such as Pt. All processes were conducted in aerated conditions. The SWCNT–EOI composite layer tightly contacts the mesoporous dye/TiO_2 layer and ITO–PEN cathode to form a thin solid-state full-plastic photocell with an effective irradiation area of 0.24 cm^2. Photocurrent density–voltage (*I*–*V*) characteristics were measured on a Keithley 2400 source meter combined with a solar simulator for AM1.5 light irradiation (Peccell Technologies, PEC-L10).

Figure 1 shows *I*–*V* characteristics of the SWCNT-based plastic photocell. On irradiation at 1 sun intensity (100 mW cm^{-2}), the photocell gave a short-circuit photocurrent density (J_{sc}) of 6.81 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 0.66 V. Overall power conversion efficiency was 1.63%. The efficiency increased to 2.33% with low current density at 1/4 sun intensity (23 mW cm^{-2}). This reflects a relatively high internal electric resistance due to the composite layer as shown by a low fill factor (*FF*), 0.36, that controls the efficiency. However, it is worthy of attention that a full-plastic cell with the iodine-free solidified structure achieves fairly high performance. Improvement of *FF* up to 0.65, by optimizing the composite material and the current-collection structure, can reach 3% efficiency, which approaches the level of our glass-type solidified DSCs.[5,7] In Figure 1 and in Table 1, other full-plastic cells are compared as references which were assembled using multi-wall carbon nanotube (MWCNT, Showa Denko Co.) and a carbon black (CB, commercially available as acetylene black) in the EOI-mixed composite. It was found that SWCNT works best over other kinds of carbon.

SWCNT, consisting of rolled-up graphene sheet, is known to exhibit metallic or semiconducting property depending on the chiral vector (chiral angle and diameter) of nanotube that determines the band structure.[8–10] This is, however, not the case for MWCNT, which is a crude mixture of various types of tubes.

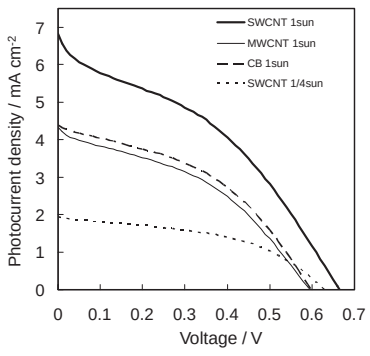

Figure 1. Photocurrent density–voltage characteristics for the SWCNT-based solid-state plastic dye-sensitized solar cell under incident intensities of 1 sun (100 W cm^{-2}, solid line) and 1/4 sun (23 mW cm^{-2}, dotted line). Data obtained with MWCNT and CB are compared as references.

Table 1. Photovoltaic performances of ITO–PEN/dye-TiO_2/CNT-EOI/ITO–PEN solid-state plastic dye-sensitized photocells measured under simulated solar irradiation (AM1.5)

Carbons	Light intensity	J_{sc}/mA cm^{-2}	V_{oc}/V	*FF*	η/%
SWCNT	1 sun	6.81	0.66	0.36	1.63
MWCNT	1 sun	4.33	0.60	0.39	1.01
CB	1 sun	4.39	0.60	0.42	1.10
SWCNT	1/4 sun	1.94	0.63	0.46	2.33

MWCNTs have more metallic nature. By adsorption of oxygen in air, semiconducting SWCNT tends to exhibit p-type nature in conduction and current rectification.[11] This would indicate that the SWCNT can function like a hole conductor in junction with the surface of dye-coated n-type TiO_2. It has been found that SWCNT also works as an efficient cathode catalyst (hole acceptor from iodine) in DSC as.[12] Use of MWCNT resulted in lower photovoltaic performance, yielding a similar efficiency to CB (Table 1). For MWCNT and CB that lack current rectification ability, back electron transfer (short-circuiting) matters at the surface of carbon in contact with dye-coated TiO_2, which must significantly reduce the photocurrent density. This is assumed to be a main reason why SWCNT achieves relatively high performance in J_{sc} and V_{oc}.

The presence of redox-active ionic liquid (EOImI) is prerequisite for driving the photovoltaic mechanism. Its role is to fill the mesoscopic interior of dye-adsorbed TiO_2 where no space is available for SWCNT to occupy. Quasi-solidification of liquid electrolytes by mixtures of ionic liquids and carbon nanotubes has been studied for DSC fabrication (glass type) by using iodine as electron acceptor.[13] In our method, iodine is omitted. Addition of iodine to the composite paste simply reduced the performance, as shown in Table 2. Highest efficiency was realized with the iodine-free system. A similar phenomenon was found for our polymer/carbon-based DSCs using glass substrates.[5] As for the effect of SWCNT content in the composite, best *I–V* performance was obtained by maximizing the SWCNT content, which gives a clay-like feature. Action spectrum of external photon-to-current conversion quantum efficiency (EQE) shows a maximum EQE exceeding 30% at around 530 nm where optical absorption peak of the dye occurs (See Supporting Information[15]).

EOImI functions as a redox shuttle in the mesopore interior by electronically bridging the photoactive dye monolayer and SWCNT. Electron transport from SWCNT to the photo-oxidized dye may proceed by electron-exchange mechanism at the EOImI molecules adsorbed on the TiO_2 surface.[13,14] Figure 2 illustrates the electron/hole transport scheme in the mesoscopic structure.

Table 2. Influence of the content of I_2 (wt %) added in the SWCNT–EOI layer on the photovoltaic performance of ITO–PEN/dye-TiO_2/SWCNT–EOI/ITO–PEN solid-state dye-sensitized photocells measured under simulated solar irradiation of 1 sun (AM1.5)

Iodine content	J_{sc}/mA cm^{-2}	V_{oc}/V	*FF*	η/%
0%	6.81	0.66	0.36	1.63
2.4%	2.36	0.63	0.42	0.63
4.8%	1.99	0.63	0.43	0.54
8.3%	1.04	0.53	0.43	0.24
12.0%	0.67	0.48	0.37	0.12

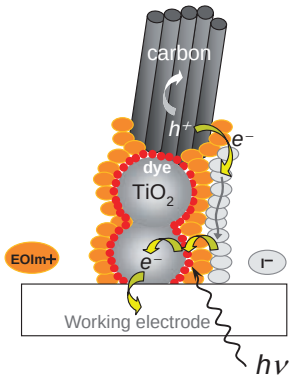

Figure 2. Schematic illustration for the charge-transport processes at the interfaces of dye-sensitized TiO_2 and SWCNT-based composite following the photoexcitation of the dye.

This mechanism can be driven by the presence of a trace amount of iodine, which is not necessarily added as an initial component but photoelectrochemically produced inside the mesopore by the reaction of dye with EOImI.

A thin, flexible solar cell (thickness, 500 μm) easily assembled by the present method is fairly stable under air and works without sealing the electrodes (See Supporting Information[15]).

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