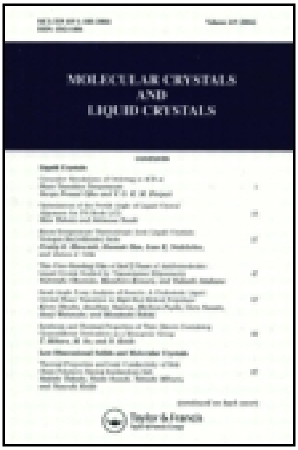

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Photovoltaic Device Using Composite Films of Polymer and Carbon Nanotube Cut by Acid Treatment

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PHOTOVOLTAIC DEVICE USING COMPOSITE FILMS OF POLYMER AND CARBON NANOTUBE CUT BY ACID TREATMENT

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Single-wall carbon nanotube-polymer composite having high electric conductivity was employed for organic photovoltaic cells. Acid treatment by a mixture of H_2SO_4/HNO_3 cut the long entangled carbon nanotubes and improved dispersion into polymers. The composite films showed high electric conductivity depending on the concentration of CNTs. The photovoltaic cell, which has a layered structure composed of a spin-coated nanotube-polymer composite film and a deposited pigment film, showed about three times higher value of short-circuit photocurrent than that not including nanotubes. This result was attributed to the improvement of carrier transport in the polymer film.

Keywords: acid treatment; carbon nanotube; conducting polymer; photovoltaic cell

INTRODUCTION

Carbon nanotubes (CNTs) are promising materials having excellent chemical and physical stability and distinctive structure with high aspect ratio, which are expected to be applied for field emission cathodes. From the viewpoint of organic electronics, CNTs are also promising materials having long and pure π-electron systems leading to high carrier mobility. If one can apply CNTs for organic electronics, the most critical weak point of organics, low mobility or high resistivity, can be overcome and the performance of organic electronic devices can be improved.

However, CNTs cannot form a uniform film by themselves. As a way for adapting for organic electronics, carbon nanotube-polymer composites have been studied [1,2]. They have been applied for a hole blocking layer in organic light emitting diodes [3] or a charge injection layer [4]. Another

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important application of the composite film is an organic photovoltaic cell. In polymer photovoltaic cells, the performance is mainly limited by the efficiency of collecting the photogenerated carriers through the polymer to the electrodes, because of high resistivity of polymer. Therefore, high electric conductivity of CNTs are expected to improve the carrier transport in the polymer and enhance the collection efficiency of photogenerated carriers. So far, some attempts have been reported using multi-wall nanotubes (MWNTs) and poly (*p*-phenylene vinylene) [5], and single-wall nanotubes (SWNTs) and poly thiophene [6]. However, remarkable improvement has not been achieved.

One of problems on the CNT-polymer composite films is that uniform dispersion of CNTs is not easy because long nanotubes tend to aggregate and entangle themselves. In this study, we employed an acid treatment method reported on single-wall nanotubes (SWNTs) [7]. Acid treatment by a mixture of H_2SO_4/HNO_3 is expected to cut the long entangled nanotubes and improve dispersibility into polymers. In addition, we evaluated the photovoltaic property of a layered structure device, composed of a spin-coated composite film and a deposited organic pigment film to prevent a short-circuit due to the film ununiformity.

EXPERIMENTAL

SWNTs made by the HIPCO process were supplied from Carbon Nanotechnologies Inc. Cutting CNTs were performed following the reported method [7], but the purification process was omitted because the supplied samples were enough pure. The CNTs of 10 mg were dispersed into a 3:1 mixture of H_2SO_4/HNO_3 of 40 ml, and sonicated for 10 hours. Then, the dispersions were neutralized by KOH and filtered by a micropore filter having a diameter of 0.1 μm. A surface active reagent of Triton X-100 (*t*-Octylphenoxypolyethoxyethanol, SIGMA Aldrich) was added before filtration with a concentration of less than 0.1%. The filtrate was centrifuged and evaporated.

The cut CNTs in THF solvent were mixed with poly(2-methoxy,5-(2′-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) solution with various concentration. The dispersions were spin-coated on a glass substrate after sonication for 3 h. The structure of CNTs and the composite films were observed by scanning electron microscope (SEM, Hitachi S-4700). The local electric property of the composite film was evaluated by current mode of atomic force microscope (current mode AFM, Seiko Instruments SPI-3800).

The device structure of a photovoltaic device is shown in Figure 1. After spin-coating of the composite film on an ITO glass substrate, a perylene pigment (Me-PTC, 3,4,9,10-perylenetetracarboxylic 3,4:9,10-bis-methyl-

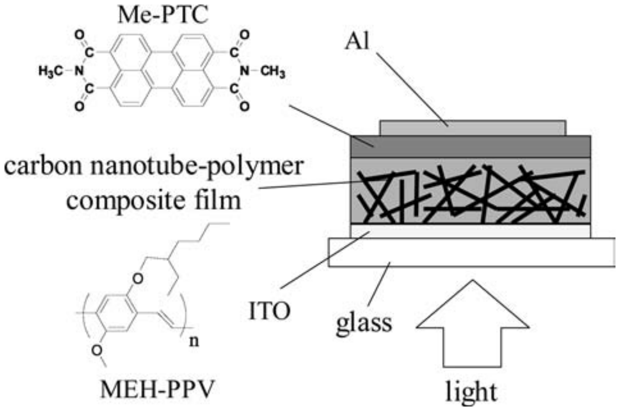

FIGURE 1 The device structure of the photovoltaic cell. The carbon nanotube-polymer composite film was spin-coated on an ITO glass substrate. The organic pigment layer was deposited on it.

imide) was deposited with a thickness of 100 nm. The top Al electrode was deposited with a thickness of 20 nm. The photovoltaic performance was evaluated under illumination of solar simulator (AM1.5) from ITO side, using source-measure unit (Keithley, model 236). The action spectrum for monochromatic light was also measured. All the measurements were performed at room temperature and under atmospheric conditions.

RESULTS AND DISCUSSION

The structural properties of the CNTs and the CNT-polymer composite film were evaluated by SEM. Figures 2(a) and 2(b) shows the CNTs before the acid treatment and after, respectively. Long and mesh structures of the pristine CNTs, whose length reache several microns, were not observed in the treated CNTs. This can be attributed to a result of the acid treatment cutting the long structure of nanotubes. Figure 2(c) showed the CNT-polymer composite films with a CNT concentration of 10 wt%. The CNTs dispersed in the MEH-PPV had some cluster structures, but fibril structures based on nanotubes were observed when the cluster was magnified (Fig. 2(d)).

The electric properties of the composite films were evaluated using a single-layer sandwiched cell (ITO/composite film/Al). Figure 3 shows the current-voltage characteristics for CNT concentrations of 0, 5, 20wt%. The conductivity estimated from the current at 1 V increased from 8.4×10^{-12} for 0, to 4.9×10^{-9} for 5, and 1.1×10^{-6} S/cm for 20wt%,

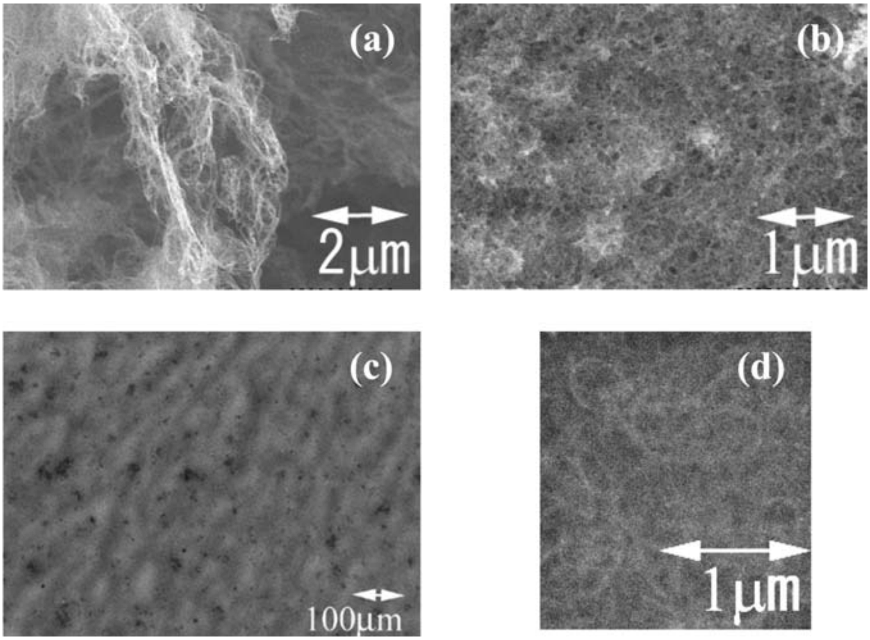

FIGURE 2 Scanning electron microscope images of (a) pristine single-wall nanotubes, (b) after acid treatment, (c) dispersed in MEH-PPV, (d) magnified image of (c).

respectively. On the other hand, in the case of non-treated CNTs dispersed into the polymer, the conductivity cannot be evaluated due to a short-circuit. Thus, the acid-treatment was revealed to be effective for improvement of dispersibility, as a result, high electric conductivity depending on the CNT concentration was obtained.

Figure 4 shows a current mode AFM image of the composite films on an ITO substrate. The bright area corresponds to high conductivity area. On the whole, this distribution of bright areas agreed with the distribution of CNT clusters observed by SEM, and covered the area to a certain extent. Therefore, the obtained high conductivity is not due to a pinhole shortcircuit between two electrodes, but due to dispersion of highly conductive CNTs.

Next, we applied this composite film for a photovoltaic device. Unfortunately, a single layer device of the composite did not show a photovoltaic effect owing to large dark current. Therefore, we fabricated a layered device of a spin-coated composite film and a deposited Me-PTC film (Fig. 1), and compared the photovoltaic effect with a MEH-PPV/Me-PTC device including no CNT. The I-V characteristics under illumination are shown in Figure 5. The positive voltage corresponds to positively bias of

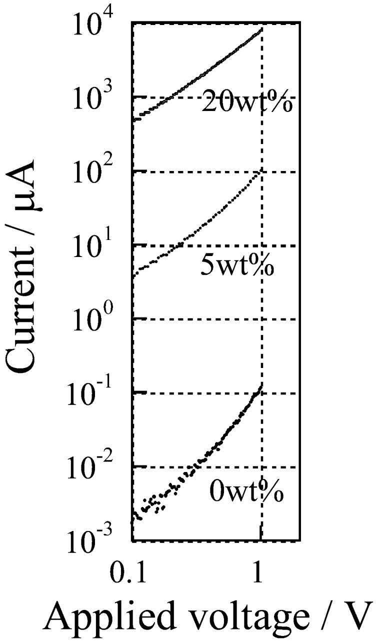

FIGURE 3 Current-voltage characteristics of the carbon nanotube-polymer composite film sandwiched by ITO and aluminum electrode. The concentration of nanotubes are shown in the figure.

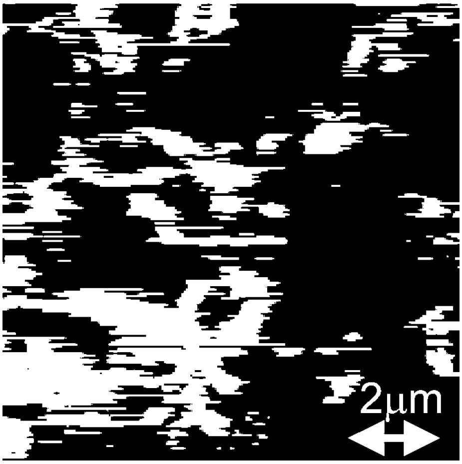

FIGURE 4 Current AFM image of the composite film on an ITO glass substrate. The contrast of image corresponds to the local current under applied voltage of 10 V.

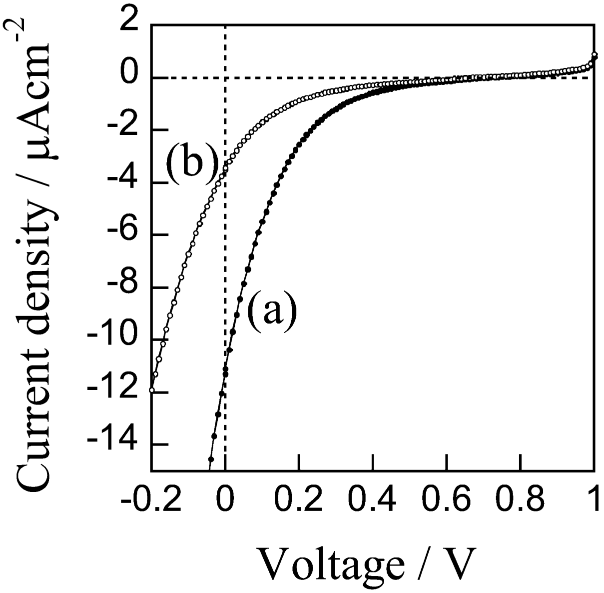

FIGURE 5 Current-voltage characteristics of the photovoltaic cell under illumination of a solar simulator (AM1.5) from the ITO side. (a) ITO/composite film/Me-PTC/Al, (b) ITO/MEH-PPV/Me-PTC/Al. The positive voltage corresponds to positive bias of the ITO electrode.

the ITO electrode. As a result, the device using the CNT-polymer composite showed about three times higher value of short-circuit photocurrent (curve (a), 11.1 μA/cm^2) than that not including CNT (curve (b), 3.4 μA/cm^2). Both devices showed the almost same open circuit voltage around 0.7 V. Thus, dispersion of CNTs into the polymer layer was revealed to enhance the short-circuit current.

There are two aspects in the effect of dispersing CNTs into polymers. One is a transporting effect, which utilize the high conductivity and high mobility of CNTs and improves the collection efficiency of photogenerated carriers to the electrodes. The other is a charge transfer effect, which assist the photogeneration of electrons and holes based on some electronic interactions between nanotubes and polymers. To investigate this point, an action spectrum of this device was measured under illumination from the ITO side (Fig. 6). The action spectrum showed a valley around a wavelength of 500 nm, corresponding to the absorption peak of MEH-PPV. On the other hand, photocurrent peak at 580 nm corresponds to the absorption peak of Me-PTC. These results clearly show that the photogeneration occurs at the MEH-PPV/Me-PTC interface. In other

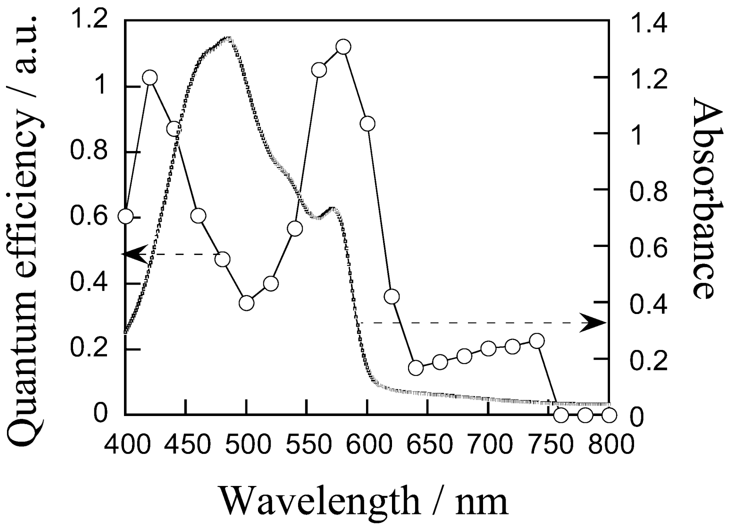

FIGURE 6 Action spectrum of the photovoltaic cell using the composite film under monochromatic light illumination from the ITO side. Absorption spectrum of the film is also shown.

words, photogeneration does not occur at the bulk of the composite film. This result leads us to a conclusion that dispersion of CNTs into the polymer improved carrier transportation and collection efficiency of the photogenerated carriers.

There are some difficulties to use the composite films for photogeneration leading to a single-layered photovoltaic cell. For that purpose, it is important to enhance semiconducting characteristics of the composite films. As well known, carbon nanotubes can be both metallic and semiconducting, depending on the periodic unit of carbon bonding. In addition, CNTs usually contain considerable amount of metal particles as a catalyst. Therefore, the composite films show metallic properties rather than semiconducting, which results in deterioration of photovoltaic effect. For practical application of CNTs for organic electronics, one has to remove metallic nanotubes and metal particles, and enhance semiconducting characteristics of the CNT-polymer composite.

CONCLUSION

In conclusion, single-wall carbon nanotube-polymer composite films were prepared by using acid cutting method to improve the dispersion. The composite films showed high electric conductivity depending on the concentration of nanotubes. The photovoltaic cell composed of the composite film and deposited pigment film showed higher short-circuit photocurrent three times larger than that not including nanotubes. This improvement was attributed to enhancement of carrier transport in the polymer film.

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