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Citation	電気材料技術雑誌. 2001, 10(2), p. 53-56
Version Type	VoR
URL	https://hdl.handle.net/11094/81657
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Improvement of photovoltaic properties in composite films of conducting polymer-C₆₀-carbon nanotube

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Conducting polymers with the extended π -conjugation in their main chains have attracted much attention not only from a fundamental viewpoint but also from the viewpoint of their practical application¹⁾ as materials suitable for electronic and optoelectronic devices such as light-emitting diodes and photovoltaic devices.²⁻⁴⁾ Among various conducting polymers, poly(3-alkylthiophene) (PAT) has attracted much attention as a soluble and even fusible polymer, because of their unique optical and electrical properties.¹⁾

Previously, the fabrication of conducting polymer/fullerene composite devices based on the effective photoinduced charge transfer between conducting polymers and C₆₀ has been demonstrated. C₆₀ was found experimentally to be an optically active acceptor for conducting polymers, causing quenching of the photoluminescence (PL)²⁻⁴⁾ and enhancement of photoconductivity.³⁻⁵⁾ That is, composites films consisting of a polymer and C₆₀ exhibited a strong donor-acceptor (D-A) type photovoltaic effect.²⁻⁵⁾

Carbon nanotube also attracts much attention as a new material, which is studied in various application field using the geometric and physical chemistry feature. Since it is possible to store a lot of gas per unit mass, it has a possibility for the application as gas storage. Besides, it is promising for the application as a field emission electron source, since the tip of a nanotube are acute and an aspect ratio is very large and chemically stable.

In this study, the preparation of multiwall carbon nanotube (MWNT) grown by organic vacuum chemical vapor deposition (CVD) and the electrical and photovoltaic properties of composite films of conducting polymer - C₆₀ - MWNT are reported.

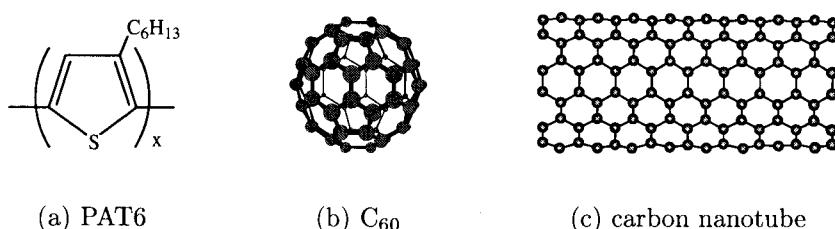


Fig. 1: Molecular structures of PAT6(a), C₆₀(b) and carbon nanotube(c) used in this study.

The molecular structures of PAT, C_{60} and carbon nanotube used in this study are shown in Fig. 1. PAT was obtained by the polymerization from the corresponding monomer utilizing $FeCl_3$ as a catalyst. Details of the preparation and purification method were already reported in previous paper.⁶⁾ Among various forms of poly(3-alkylthiophene), poly(3-hexylthiophene) (PAT6) with alkyl chain length $n=6$ was used in this experiment. C_{60} purchased from Bucky USA Co. was used.

MWNT were prepared by the method of vacuum CVD at 850 °C, using Fe - phthalocyanine (Fe-Pc) as a starting material. The SEM micrographs are shown in Fig. 2. MWNTs made from Fe-Pc have mainly the form of straight bundles of MWNTs of almost equal length of about 5-10 μm as compared with those made of Ni - phthalocyanine.

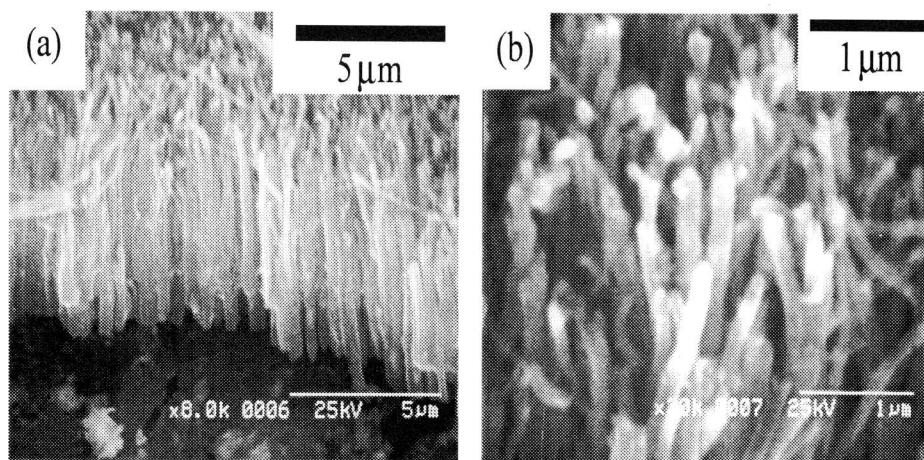


Fig. 2: SEM micrographs of MWNT prepared by the vacuum CVD using Fe-phthalocyanine as a starting material.

PAT6 was dissolved in toluene, which is convenient for spin coating or casting. C_{60} were doped with PAT6 at an appropriate ratio. The solution of composites were prepared by sonication of the purified MWNTs in toluene and mixing with the C_{60} doped solution of PAT6. The thin films was fabricated from the composite solution by spin coating or casting onto cleaned indium-tin-oxide (ITO)-coated quartz substrates with a sheet resistance of 10 Ω/\square . An aluminum (Al) layer was deposited by thermal evaporation through a shadow mask under a pressure of 10^{-4} Pa onto the composite films as a counterelectrode to the ITO. The electrode area of the photocell was 2×2 mm^2 .

A high intensity Xenon lamp (350 W) was used as UV-Visible light source for measurement in broad UV-visible-near IR spectral range in combination with the monochromator with order sorting filters and a 1200 g/mm grating blased at 300nm. The spectral response of the device was corrected for the response of the lamp-monochromator system by measuring the calibration spectrum with UV-enhanced Si photodiode placed in the sample position. All measurements were carried out in a vacuum optical cryostat at room temperature.

We investigated the transport and photophysical properties of MWNTs in PAT6 films. With increasing the volume fraction of MWNT in PAT6, the conductivity of the composite increases drastically at relatively low concentration of MWNT, as shown in Fig. 3, which can be explained in terms of percolation process of conduction.

Figure 4 shows the spectral dependence of photosensitivity of composite films of PAT6 - C₆₀ - MWNT. We suppose that the enhancement of photocurrent is mainly caused by the improved collection of charge carriers. The effect of exciton dissociation at polymer/MWNT interface should be also taken into account.

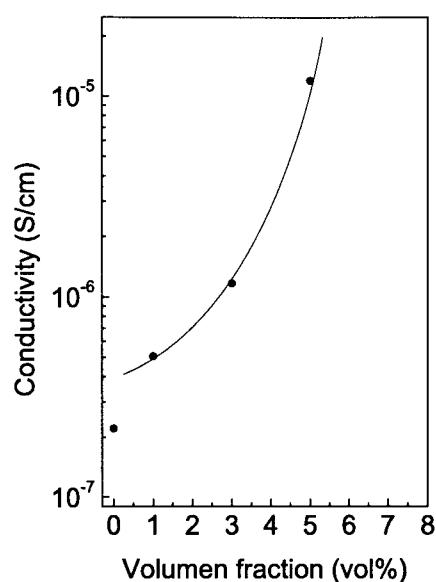


Fig. 3: Dependence of electrical conductivity on volume fraction of MWNT in PAT6.

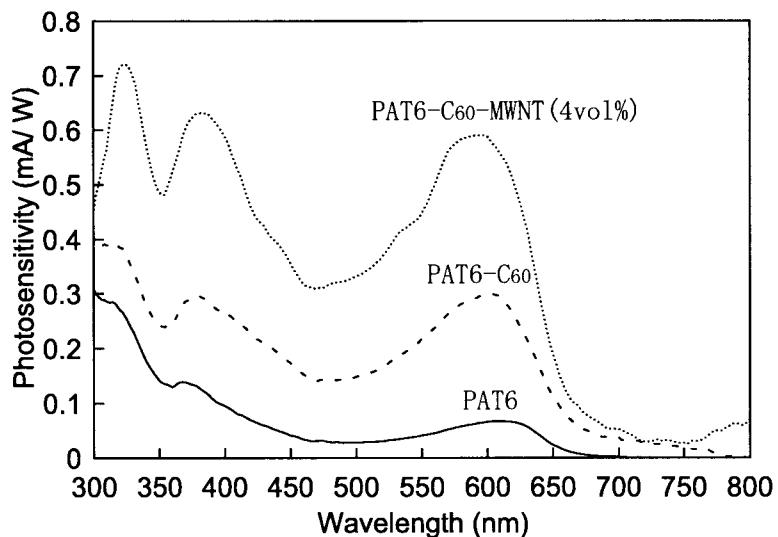


Fig. 4: Spectral dependence of photosensitivity of composite films of PAT6 - C₆₀ - MWNT.

Furthermore, we studied photovoltaic properties of devices with poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS) as hole transport layer. The molecular structures of PEDOT and PSS are shown in Figs. 5(a) and 5(b), respectively. The film of PEDOT;PSS was fabricated from their solution by spin coating onto cleaned ITO-coated quartz substrates, followed by drying at 90 °C for 20 minutes in vacuum, as shown in Fig. 5(c).

In current-voltage measurements under irradiation, the photocurrent is enhanced at short circuit condition, it is explained by the higher built-in field. The work function of PEDOT;PSS

is 0.5 eV higher in comparison with that of ITO. The open circuit voltage, however, remains unchanged. The thin film heterostructure photovoltaic cells of PEDOT;PSS and composite of PAT6 - C₆₀ - MWNT are now in progress.

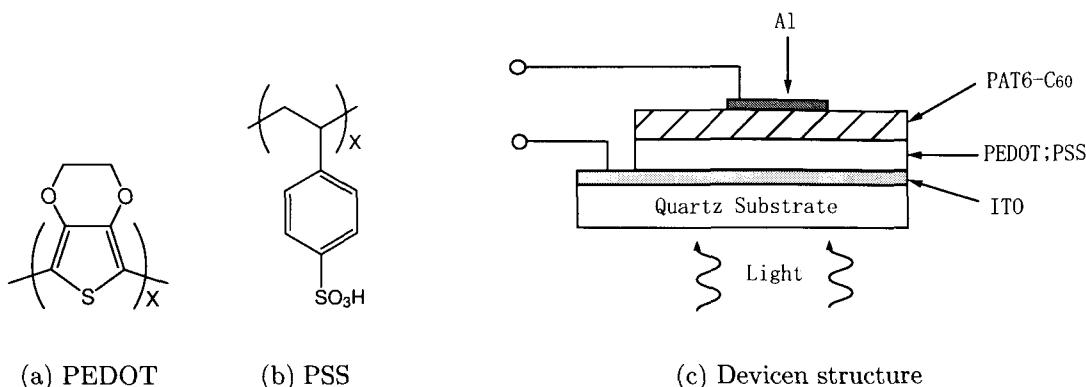


Fig. 5: Molecular structures of PEDOT(a) and PSS(b), and device structure of photovoltaic device(c)

In conclusion, electrical and photovoltaic properties in composite films of PAT6 - C₆₀ - MWNT were studied. In composite films of PAT6 - MWNT, the increase of conductivity at relatively low concentration of MWNTs was obtained. It can be explained in terms of conduction by percolation threshold. In composite films of PAT6 - C₆₀ - MWNT, the enhancement of the photocurrent was realized.

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