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Photoelectrical Properties of Composites from Organic Vacuum CVD - grown Multiwall Carbon Nanotubes and Conjugated Polymer

S. Lee[+,++], T. Sonoda[+], H. Kajii[+], H. Araki[+] and K. Yoshino[+]

[+] *Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, 565-0871, Japan*
[++] *Heat Physics Department, Uzbek Academy of Sciences, Tashkent, Uzbekistan*

Composite of multiwall carbon nanotubes (MWNT) and conjugated polymers (CP) have been studied. MWNTs were prepared by the method of chemical vapor deposition (CVD) using metal phthalocyanine as starting material.

We have examined the transport and photophysical properties of the composite film of poly(3-hexylthiophene) - MWNTs with different volume fractions of MWNTs. Temperature dependence of the dark conductivity and the magnetoresistance of the porous MWNT mat and the nano-composite film have shown that the transport in MWNT/polymer composite is determined by two mechanisms: tunneling between tubes and bundles and semi-metallic conduction along the tubes.

The enhancement of photoconductivity of composite films has been found near percolation threshold with maximum at ca. 3 vol.%. The enhanced photoresponse was observed due to the efficient charge separation and collection of photogenerated charge carriers in C_{60}-doped P3HT + MWNT composite film.

Introduction

Semiconducting conjugated polymers with an extended π-conjugation in their main chains have attracted much attention not only from fundamental view points but also from practical interest as materials for electrical and optoelectronic devices such as electroluminescence devices and photocells. They exhibit numerous unique phenomena such as a drastic change in electrical, optical and magnetic properties upon doping. Especially, when a molecular dopant can interact with a host matrix due to its specific electronic energy scheme new functionalities are expected to appear.

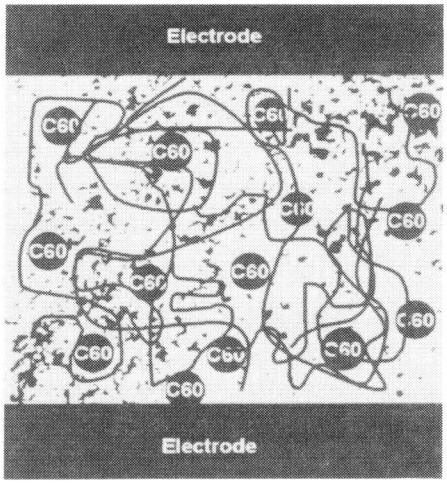

Fig.1 Distributed network of conducting MWNT in polymer matrix which can sufficiently improve the collection efficiency of polymer photocell.

However, the commercial application of conducting polymers is hindered by the low mobility of charge carriers. Discoveries of spheroidal fullerene C_{60} and higher fullerenes and tubular fullerenes[1] have opened new fascinating opportunities for polymer researchers.

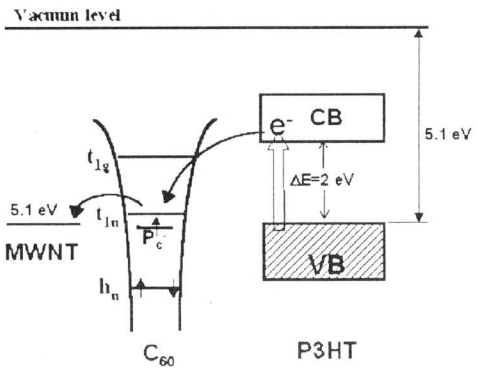

Fig. 2 The scheme of electronic transfer processes in C_{60}-doped P3HT/MWNT composite film.

The purpose of this paper is to show that a composite from MWNT and conjugated polymer can solve the problem by formation of distributed network of conducting MWNT in polymer matrix (see Fig. 1) which can sufficiently improve the collection of photogenerated charge carriers. The energy scheme of electron transfer processes in MWNT-C_{60}-doped P3HT composite is shown in Fig. 2. MWNTs can efficiently collect the photogenerated electrons because of high work function (~5.1 eV) of graphite-like MWNT. The preparation of composite from MWNT

grown by vacuum CVD and conjugated polymer and its transport and photophysical properties are reported. The unique properties of carbon nanotubes as dopants for conjugated polymers are emphasized.

Preparation and experimental methods

MWNTs were prepared by the method of vacuum chemical vapor deposition at 700 °C, using metal phthalocyanine such as Ni- or Fe – phthalocyanine (Ni-Pc or Fe-Pc) as starting material.[2] MWNTs grow from Ni-Pc at higher rate than from Fe-Pc and are typically 40~200 nm in diameter and 20~40 μm in length (Fig.3).

Poly(3-alkylthiophene) was prepared by the method already reported.[3] We have chosen the poly(3-alkylthiophene) because this polymer is stable and soluble in common solvents such as toluene, benzene or chloroform. What is more important is that MWNTs form a stable dispersion in polymer solution because highly soluble long side-chain polymer completely wraps the nanotubes and suppresses the flocculation of bundles into large aggregates. The fast flocculation of carbon nanotubes usually occurs in colloidal solution. It was proposed that the strongly curved nanotube surface is more reactive than the flat graphite sheet and causes the strong polymer/nanotube interface strength.[4]

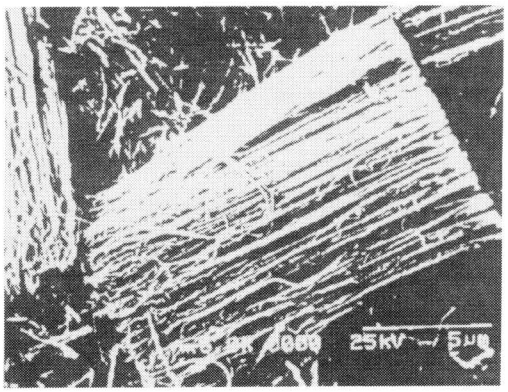

Fig. 3 SEM micrographs of MWNT prepared by the vacuum CVD using Fe – phthalocyanine as starting material.

The solution of MWNTs and CP were prepared by sonication of the purified MWNTs in toluene and mixed with the solution of poly(3-hexylthiophene) (P3HT). The nano-composite films with thickness of 1~12 μm were formed by casting on a glass plate with thermally evaporated gold electrodes.

The temperature dependence of conductivity was measured with a standard two-probe and four-probe technique using the physical property measurement system (Quantum Design). Magnetotransport measurements were performed with a magnetic field applied perpendicular to the sample.

The absorption spectra were measured using a Hewlett-Packard 8452 diode array spectrophotometer. A high intensity Xenon lamp (500W) was used as UV-Visible light source for measurement in broad UV-visible-near IR spectral range in combination with the excitation monochromator with order sorting filters and a 1200 g/mm grating blased at 300 nm. The spectral response of the device was corrected for the response of the lamp-monochromator system by measuring the calibration spectrum with a UV-enhanced Si photodiode (Hamamatsu Photonics, S1337-1010BQ) placed in the sample position. Photosensitivity and current-voltage characteristics were measured by a Keithley 617 picoammeter with a built-in voltage source. All photoconductivity measurements were carried out in a vacuum optical cryostat in vacuum of about 10^{-5} torr at room temperature.

RESULTS AND DISCUSSION

We have examined the transport and photophysical properties of the nano-composite film of P3HT - MWNTs with different volume fractions of MWNTs. With increasing volume fraction of MWNTs in CP the conductivity of composite increases drastically undergoing insulator-to-conductor transition at relatively low concentration of MWNTs.

For the case of composites with low percolation threshold, the Fermi-Dirac type expression was proposed which is valid at all volume concentration:[5]

$$\log(\rho) = \log(\rho_f) + \frac{\log(\rho_m) - \log(\rho_f)}{1 + \exp[b(p - p_c)]}$$

where ρ_m is the matrix resistivity, ρ_f – the final composite resistivity, b - an empirical parameter. We obtained the value of percolation threshold p_c= 5.7 vol.% by fitting the data with this formula (solid line in Fig.4). Many parameters may influence the percolation threshold such as dopant/matrix interactions, dopant shape and distribution. The further more elaborate study is needed.

Thermal fluctuation induced tunneling model usually quite well describes the conductivity of composites of conducting particles in dielectric matrix:[6]

$$\sigma = \sigma_0 \exp[-T_1/(T+T_0)],$$

where σ_0 is a constant, $T_1 = wA\varepsilon_0^2/8\pi k$, $T_0 = 2T_1/\pi\chi w$, $\chi = \sqrt{2mV_0}/h^2$ and $\varepsilon_0 = 4V_0/ew$, e and m the electron charge and mass, V_0 – the potential barrier height, w – the interparticle distance, A – the area of the capacitance formed by the junction.

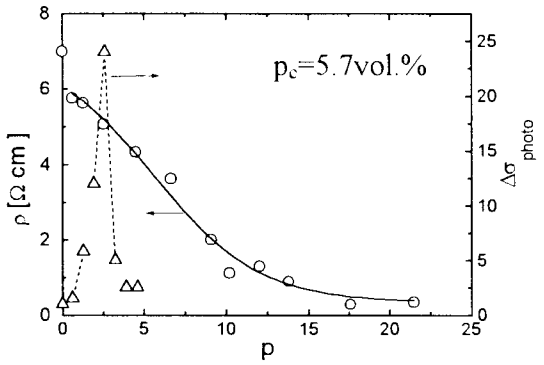

Fig. 4 Dependence of electrical resistivity (open circles) on the volume fraction of MWNT (The solid line is a best fit) and PC enhancement of MWNT-doped P3HT film (open triangles) upon excitation with Ar laser (488 nm, 20mW/cm^2). MWNTs were made from Ni-Pc.

However, the fitting of temperature dependence of conductivity over broad temperature range has shown that the thermal fluctuation induced tunneling model strongly deviates from experimental curve at low temperature (Fig.5a). The experimental data is almost temperature independent at low temperatures and saturate at relatively high temperature than predicted by the model. The possible explanation is that the thermal fluctuations of barrier height becomes too small at low temperatures. The highly anisotropic geometry of dopant with large aspect ratio have to be taken into account. Similar deviations were observed for highly structured carbon black-polymer composites. The very weak temperature dependence of conductivity of heavily doped sample (18 vol.%) and pure MWNT mat supports such explanation (Fig.5b).

The quite strong coupling between MWNTs can be deduced from the weak temperature dependence of both samples and hopping between the nanotubes is not a dominating process in conductivity. However, the relatively low value of conductivity of porous MWNT's mat indicates the small number of contacts with not strong enough intertube/interbundle coupling and the high degree of disorder. The heavily MWNT-doped (far above percolation threshold) polymer films show one order less conductivity but similar temperature dependence.

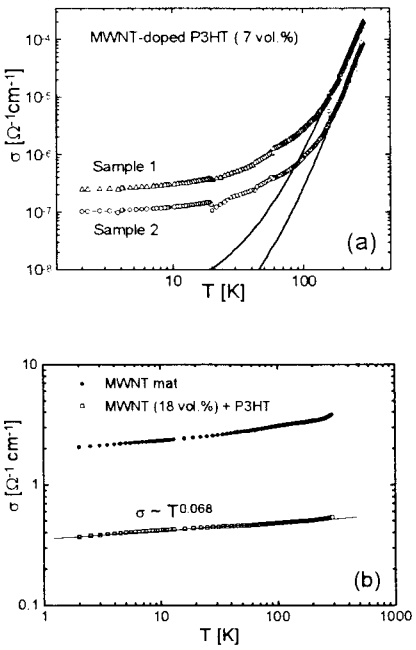

FIG. 5 Temperature dependence of electrical conductivity of nano-composite film of semiconducting polymer with 18 vol.% of MWNTs.

We have observed the clear positive transverse magnetoresistance in composite and MWNT mat. The magnetoresistance of pure crystalline graphite usually obey a relation:[7]

$$\Delta\rho/\rho = BH^2$$

where B is proportional to $\mu_e\mu_h$. Magnetoresistance of our samples obeys this relation for $\Delta\rho/\rho < 1\%$ and H<3 Tesla and starts to deviate and saturate at higher value. The average mobility was estimated about 330 cm^2/Vs which is much lower than the hole mobility $\mu_h \approx 10^4$ cm^2/Vs in graphite but close to the value of $\mu_h \approx 220$ cm^2/Vs obtained for MWNTs.[8] Our results, very surprisingly, is similar to the ones of study of a single

multiwalled carbon nanotube[9] which has also shown the semi-metallic behavior of a single MWNT with the clear positive magnetoresistance. This fact confirms the quite high quality of our vacuum CVD-grown MWNTs with relatively low concentration of defects.

We can conclude from our experimental data that the transport in MWNT/polymer composite is determined by two mechanisms: tunneling between tubes and bundles and semi-metallic conduction along the tubes.

The enhancement of photoconductivity of composite films has been found at near percolation threshold with maximum at ca. 3 vol.%. Figure 4 (open triangles, dashed line for eye guide) shows the photoconductivity enhancement of MWNT-doped P3HT film upon excitation with Ar laser (488 nm, 20mW/cm^2).

The spectral dependence of photoconductivity of C_{60}-sensibilized P3HT + MWNT composite film was carried out in surface geometry with in-plane electrodes at low electric field of $5x10^3$ V/cm to avoid the effects of photoinjection from electrodes, electric filed induced exciton dissociation and electric field dependent mobility which complicate the interpretation of experimental data and make it difficult to extract the effect of carbon NT doping. We suppose that at low electric field 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.

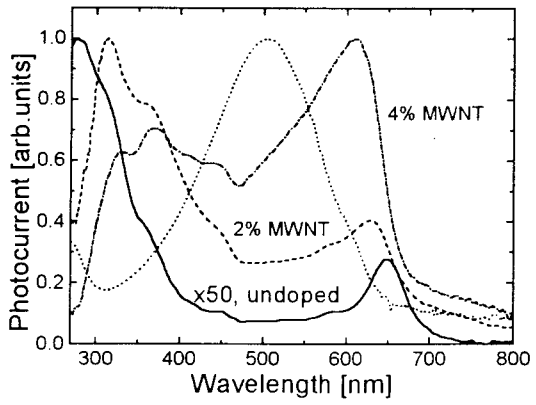

Fig. 6 Spectral dependence of photoconductivity of C_{60}-sensibilized (5 mol%) P3HT + MWNT composite film.

The experimental results are shown is shown in Fig. 6. The enhanced UV photoresponse was observed due to efficient charge separation and reduced recombination in C_{60}-doped P3HT + MWNT composite film. Absorption spectra of the P3HT film doesn't change after MWNT-doping (dotted line). The decreased photoconductivity in the spectral range of maximum absorption was observed in undoped polymer film (solid line) because of surface recombination of photogenerated charge carriers. The enhanced photoconductivity in this spectral range was observed with increase of concentration of MWNTs (dashed line - 2 wt.%, dash-dotted line - 4 wt.%).

We would like to note in conclusion that the recently developed method of the end-group functionalization of single-wall nanotube (SWNT) for preparation of soluble SWNT[10] can also be applied to MWNTs and should further decrease the percolation threshold. Moreover, this method could provide the way for drastic improvement of photoconductivity of MWNT-polymer composite system by chemical bonding of photoactive molecule like C_{60} to the end of nanotubular conductor.

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