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Electronic interaction between photoexcited poly(*p*-phenylene vinylene) and carbon nanotubes

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We have studied the electronic interaction between photoexcited poly(*p*-phenylene vinylene) (PPV) and multiwall carbon nanotubes (MWNT's) using photoluminescence (PL) and photoinduced absorption (PIA) spectroscopy. We have found that the MWNT's strongly interact with the photoexcited PPV, while there is no significant interaction in the ground state. The π conjugation of PPV was slightly reduced in the composite, reflecting the nanoscopic structural influence of the MWNT's. On the basis of its temperature and frequency dependence, the PIA spectrum was found to originate from the same species as the pure PPV film, namely, triplet excitons formed in PPV via intersystem crossing. We have concluded that the predominant electronic interaction is the nonradiative energy transfer of singlet excitons from the PPV to the MWNT's.

I. INTRODUCTION

Composites of polymers and carbon nanotubes for the purposes of mechanical reinforcement have been attracting increased interest recently.[1] Several studies on the composites would appear to provide some support for this application.[2,3] In addition to their mechanical properties, unique electronic properties are expected due to electronic interactions between polymers and nanotubes, or due to nanoscopic structural modifications of the polymer chains. In these respects, the combination of carbon nanotubes with π-conjugated polymers is of particular interest because the latter are potential materials for several macroscopic device applications, such as light-emitting diodes (LED's),[4] field-effect transistors (FET's),[5] and photovoltaic devices.[6]

Diodes comprised of multiwall carbon nanotubes (MWNT's) and a derivative of poly(*p*-phenylene vinylene) (PPV) were fabricated by Romero *et al.*, where the MWNT layer was used as a hole injecting layer.[7] It has been suggested that a heterojunction formed at the interface between the MWNT and PPV layers significantly improved the diode characteristics. This improvement was attributed to the enhanced local field at the tip of the MWNT's. Curran *et al.* dispersed MWNT's into a metalinked PPV derivative and fabricated LED's.[8] This metalinked PPV was claimed to possess a helically coiled structure which wraps around a MWNT and thus aids its dispersion in the PPV solution. Composite LED's fabricated from such solutions are reported to show lifetimes in air up to 5 times longer than LED's without MWNT's. The authors suggested that the MWNT acts as a heat sink in the polymer matrix, dissipating the heat generated in the PPV during operation.

In our previous paper, we fabricated photovoltaic devices using a composite of MWNT's and PPV.[9] The surfaces of the MWNT's were chemically oxidized to disperse them in water at high concentration, which enabled us to spin-coat thin and relatively flat films of the MWNT's on glass substrates. Conversion of the sulphonium salt precursor of PPV on the MWNT layer at high temperature yielded a highly interpenetrating network.[9] We found that the MWNT layer acts as a hole-collecting electrode and obtained about twice the external quantum efficiency compared to the standard indium-tin oxide (ITO)-based devices. This enhanced efficiency was explained in terms of the high surface area of the MWNT film and a stronger built-in field than ITO.[9,10] Although the MWNT layer was found to collect holes from the PPV layer effectively, it is still unclear whether this property originates from an intrinsic interaction between the PPV and MWNT's or only from the built-in field. Conjugated polymer/nanotubes composite devices are very intriguing. However, further development of composite devices requires a better understanding of the interfacial interaction between π-conjugated polymers and carbon nanotubes in both the ground and excited states. As far as we know, no study has reported on the electronic interaction between these two elements.

In this paper, we have prepared PPV-MWNT composites and studied their interface interaction based on absorption,

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photoluminescence (PL), and photoinduced absorption (PIA) spectroscopy. It will be shown that the present catalytically grown MWNT's are intrinsically semiconducting on the basis of the temperature dependence of the electrical conductivity. We will show that a significant degree of energy transfer occurs from photo-excited PPV to the semiconducting MWNT's, while there is no electronic interaction in their ground state.

II. EXPERIMENT

Catalytically grown MWNT's were chemically oxidized to disperse them in distilled water.[11] For optical measurements, a very thin MWNT layer (ca 20 nm) was deposited on a quartz substrate from a 0.5 wt.% dispersion by spin-coating; this approach maintained optical transparency. The precursor PPV solution was spin-coated onto the MWNT layer and converted at 200 °C for 10 h in vacuum. The thickness of the PPV layer was around 40 nm. The film thickness of PPV and MWNT layers was measured separately on a glass substrate. Electrical conductivity was measured using a standard dc four-points contact method down to liquid He temperature. For conductivity measurements, we used a relatively thick MWNT film (ca 150 nm) in order to avoid effects due to the polyimide substrate.

The absorption spectrum was measured with a Hewlett Packard HP-8453 UV/Vis spectrometer in air at room temperature. The PL spectra were measured using excitation from an argon ion laser at a wavelength of 458 nm in an integrated sphere connected to an Oriel intraspec IV spectrophotometer through a liquid light guide.[12] The measurement was carried out under nitrogen flow at room temperature.

The PIA measurements were performed in a cryostat under either a helium atmosphere or dynamic vacuum. A mechanically chopped Ar ion laser (458 nm) with an intensity of approximately 25 $\mathrm{mW/cm^2}$ was employed as the excitation source. Monochromatic light was used to monitor the fractional photoinduced changes in the sample transmittance using a lock-in amplifier. Detection was provided by either a silicon photodiode or an InAs photodiode, depending on the wavelength range (500–1000 nm and above 1000 nm, respectively). The details of the measurement are described elsewhere.[13]

III. RESULTS AND DISCUSSION

Figure 1 shows an SEM micrograph of a very thin MWNT film spin-coated on a quartz substrate. Because the present catalytically grown MWNT's suffer from a larger number of structural defects than arc-evaporated MWNT's,[11] almost all the MWNT's showed a curved structure. One can also see the present MWNT film is free from impurities, such as carbon nanoparticles, fullerenes, and graphite fragments. This SEM image indicates that the film is very thin with only two or three MWNT's stacking on the substrate. Although the substrate is seen in some areas, the film is relatively homogeneous. Considering the average diameter of the MWNT's (10 nm), the average film thickness is estimated to be around 20 nm. As shown below, the present MWNT film possesses sufficiently high transparency to allow optical measurements.

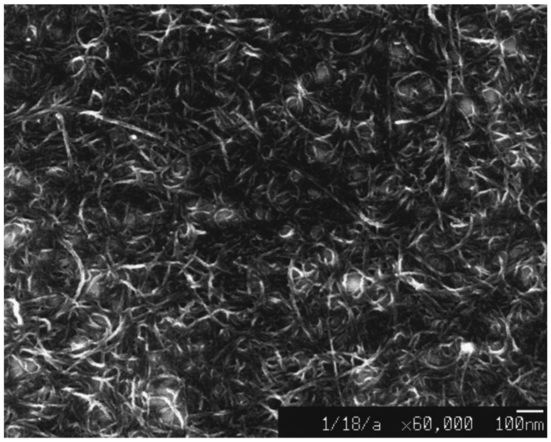

FIG. 1. SEM micrograph of a thin MWNT film prepared by spin coating the dispersion onto a quartz substrate.

To investigate the intrinsic electronic structure of the MWNT's, we have studied temperature dependence of the conductivity of a MWNT film. As shown in Fig. 2, the MWNT film showed semiconducting behavior with relatively weak temperature dependence down to 50 K. This semiconducting behavior has been reported for bundles of arc-grown MWNT's and has been attributed to the dominating intertube contact resistance.[14] However, the conductivity at room temperature was determined to be 8.3 s/cm for the present MWNT's which is much smaller than the conductivity of bundles (10^2 S/cm) (Ref. 15) and individual (10^3-10^4 S/cm) (Ref. 16) arc-evaporated MWNT's. We consider that this relatively low conductivity arises from the structural defects (see Fig. 1) as well as the surface oxidized groups.[10] On the other hand, the certain conductivity of the present MWNT in spite of potential barriers suggests the formation of percolation paths throughout the film.

The inset of Fig. 2 indicates the conductivity normalized to the data at 286 K. It is found that the normalized conductivity becomes zero when extrapolated to 0 K. Arc-evaporated MWNT's, which possess a more perfect one-dimensional structure, show a finite conductivity even at 0 K (0.3–0.4).[14] These facts suggest that the present catalytically

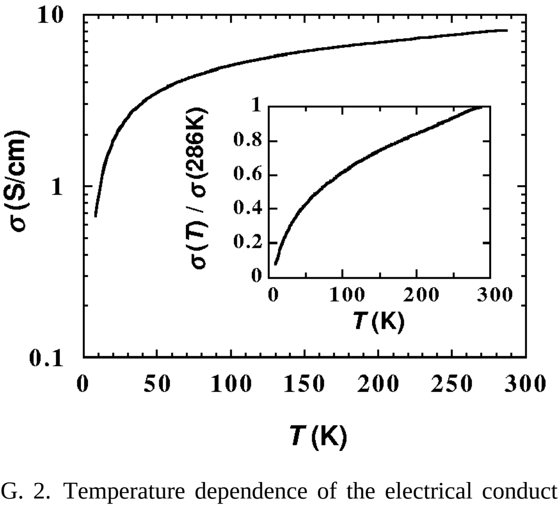

FIG. 2. Temperature dependence of the electrical conductivity of a MWNT film. Inset shows the conductivity normalized to the data at 286 K.

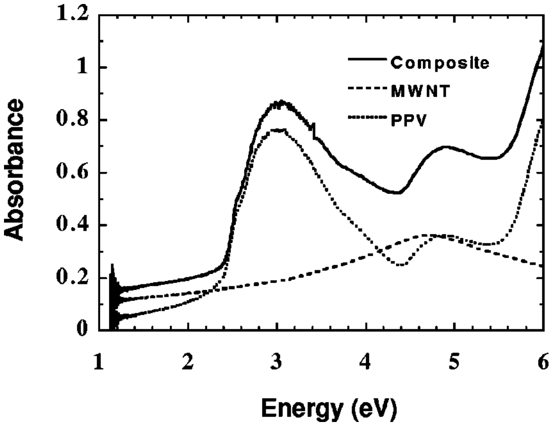

FIG. 3. Absorption spectra of the PPV-MWNT composite (real line), MWNT (broken line), and PPV (dashed line) films measured at room temperature. The thicknesses of MWNT and PPV layers are around 20 and 40 nm, respectively.

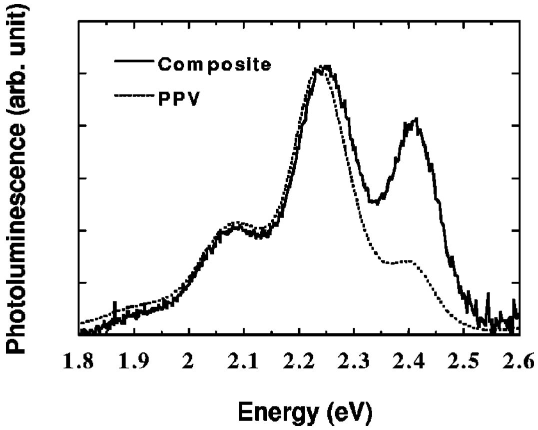

FIG. 4. PL spectra of the PPV-MWNT composite (real line) and PPV (dashed line) films measured at room temperature. The 458 nm Ar ion line was used as an excitation source.

grown MWNT's are intrinsically semiconductors. Based on the observed temperature dependence, we have estimated the activation energy to be 3–14 meV. Although we cannot simply attribute this value to the real band gap due to the effects of intertube resistance on the conductivity, the present MWNT's are considered to be semiconductors with a very small band gap.

The absorption spectra of the composite, PPV, and MWNT films are shown in Fig. 3. The MWNT film showed a very broad and featureless spectrum. We note that the MWNT film showed high optical transparency of 70% at the PL wavelength of PPV (2.24 eV) due to the very thin film. Because the plasma frequency (ω_p) of carbon nanotubes is very high (ω_p has been estimated to be 22.6 eV for arc-evaporated MWNT's),[17] reflection by the MWNT's affects the absorption spectrum in the whole measured energy range. The broad peak at 4.7 eV is assigned to the π-π^* optical transition from the DOS that was previously identified by the UPS measurements.[10] The absorption spectrum of the composite was found to be sum of the spectra of each components, except for a slight blueshift [6 nm (40 meV)] of the main peak of PPV for the composite. This blueshift signifies that the effective π-conjugation length of PPV is shortened in the composite. We speculate that the MWNT's modify the local nanoscopic structure of PPV leading to more intrachain disorder. Apart from the small change of the peak position, there was no significant change in the absorption spectrum of the composite, indicating the absence of electronic interaction in the ground state of PPV and MWNT's.

The electronic interaction in the excited state was studied by means of PL and PIA spectroscopy. The PL spectra are shown in Fig. 4. The MWNT film gave no PL signal. As was reported for a composite with a thicker MWNT layer,[9] a change in the vibronic structure of the composite was observed, namely that the peak at the highest energy (2.41 eV) became intense. We speculate that this change stems from an interference effect because the more intense peak came from the thicker MWNT layer which has higher reflectivity and no transmissivity.[9] As is the case of the absorption spectra, we find a slight blueshift for the PL spectrum of the composite. It should be noted that this blueshift was not observed for the composite with a thicker PPV layer (210 nm),[9] probably because the PPV film is too thick to be influenced structurally by the MWNT's. The PL efficiency measured with the excitation wavelength of 458 nm decreased from 24% for the pure PPV film to 1% for the composite. This observed PL quenching indicates singlet excitons generated in PPV are diminished before radiative recombination by the presence of the MWNT's in addition to absorption and scattering by the MWNT's. We will discuss this mechanism later by referring to the PIA results.

Figure 5 shows the PIA spectra of the composite and PPV films measured at 10 K. It is seen that the PIA signal is almost identical for the composite and the pure PPV, but that the intensity of the signal is smaller for the composite. The peak at around 1.47 eV was observed only at low temperatures (10–90 K) and the positive $\Delta T/T$ observed above 2.3 eV is due to the unsubstracted PL signal. In order to confirm that the PIA spectra come from identical species, we have measured their frequency and temperature dependence. Figure 6(a) shows the change of PIA signal intensity as a function of the chopping frequency of the excitation light. We have calculated the lifetime (τ) of the excited state based on the following equation for the signal intensity $S(\omega,\tau)$ assuming monomolecular decay:

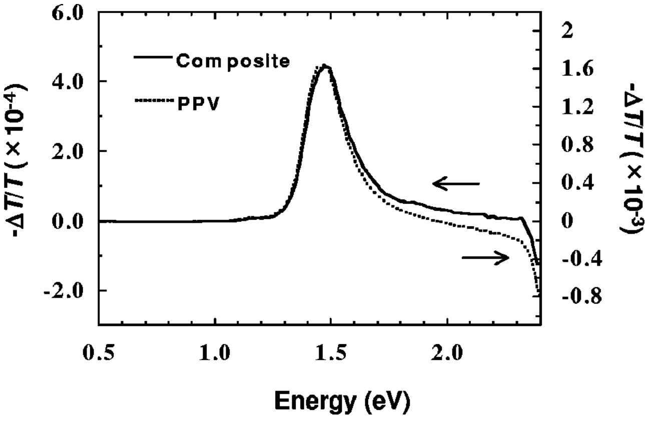

FIG. 5. PIA spectra of the PPV-MWNT composite (real line) and PPV (dashed line) films measured at 10 K with a chopping frequency of 898 Hz.

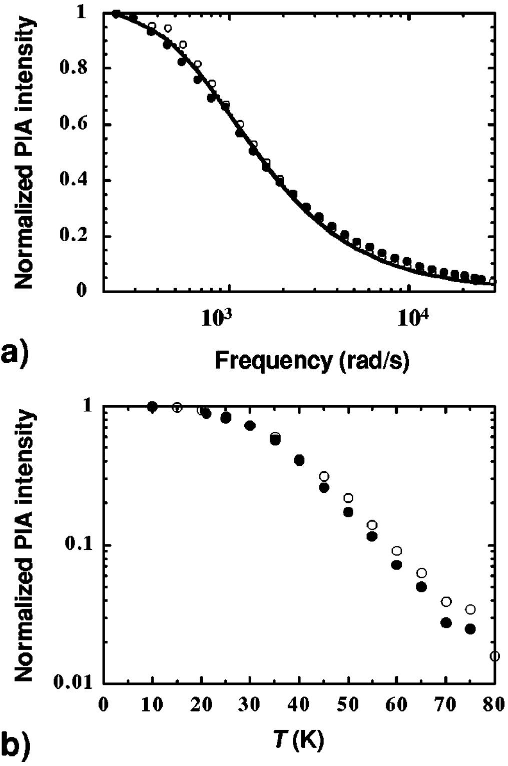

FIG. 6. (a) Chopping frequency dependence of PIA signal at 1.47 eV of the PPV-MWNT composite (closed circles) and PPV (open circles) films measured at 10 K. The solid and dashed curves are fitted to the data for the composite and PPV, respectively, (see text). (b) Temperature dependence of the PIA signal at 1.47 eV with the chopping frequency of 898 Hz, using the same symbols as (a).

$$S(\omega,\tau)=\frac{kI_\tau}{\sqrt{1+\omega^2\tau^2}}, \qquad (1)$$

where ω is the angular chopping frequency, I the pump intensity, and k a constant proportional to the absorption cross section of the species. The solid and dashed lines indicate the fits obtained for the composite and PPV films, respectively. The spectra of both the composite and PPV films were well fitted by Eq. (1) with nearly the same lifetime of 1.3 msec at 10 K. We have also obtained similar strong temperature dependences with no signal being observable above 90 K for either the composite or the pure PPV films [Fig. 6(b)]. Therefore, we find that the nature of the PIA in the composite is essentially same as that in the pure PPV film.

Previous studies of PPV have assigned the peak near 1.45 eV to a triplet-triplet induced absorption;[18] due to the similarity in frequency and temperature dependence of those studies and the feature that we observe at 1.47 eV, we assign the main peak in our samples to be a triplet-triplet absorption. Because this triplet-triplet absorption of the PIA measurement as well as the luminescence is reduced by MWNT's, it is highly plausible that the MWNT's quench the singlet excitons in PPV before intersystem crossing occurs. In addition, the slight blueshift of the composite triplet peak may provide further evidence that the MWNT shorten the effective π-conjugation length of PPV chains in the composite. There are three possibilities for the explanation of the PL and PIA quenching: (i) electron transfer, (ii) hole transfer, and (iii) both electron and hole transfer (i.e., energy transfer) from the photoexcited PPV to MWNT's. In the case of composites of C_{60} and π-conjugated polymers, efficient and ultrafast electron transfer from the polymer to C_{60} has been observed.[19,20] Based on our photovoltaic experiments,[9] we speculated that energy transfer and/or hole transfer may occur at the interface. In the case of (i) and (ii), the absorption due to the resulting polaronic and/or bipolaronic states should be observed. Among charged states, the bipolaronic state is thought to be preferred to the polaronic state and gives two peaks at 0.6 and 1.6 eV.[18] However, no such states are observed in our experiment. Another scenario which could explain the absence of polaronic/bipolaronic bands is fast recombination between charge on the polymer and charge on the MWNT's. However, the recombination process is usually relatively slow. For example, dye-sensitized TiO_2 shows a recombination time of $\sim 10^{-1}$ sec,[21] and recombination between poly(2-methoxy-5-(2-ethyl hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and CdSe nanocrystals can last at least several msec.[13] Therefore, from the absence of such absorption, we believe that mainly energy transfer (iii) occurs at the interface.

It has been suggested that the diffusion length of singlet excitons in PPV is 7 ± 1 nm.[20] This length is not enough to account for the observed decrease of the PL efficiency of the PPV-MWNT composite. We think that the observed PL quenching can be explained in terms of interpenetrating network achieved in the composite, since previous SEM measurements showed that PPV penetrates into a MWNT layer significantly after thermal conversion.[9] The interpenetrating network increased a probability for singlet excitons to find MWNT's within their diffusion length. It should be noted that absorption and multiple scattering by MWNT's is also important for the apparent PL quenching. However, because the transmittance is high at the PL wavelength of PPV (70% at 2.24 eV), we speculate that the observed PL quenching arises not only from absorption and scattering by the MWNT's but also from energy transfer.

Being different from PL spectra, PIA spectra are not highly susceptible to absorption and reflection by MWNT's, because PIA measures fractional change of the optical transmittance after photo-excitation. In this respect, decrease of the PIA intensity (Fig. 5) observed for the PPV-MWNT composite should be interpreted as a consequence of electronic interaction between PPV and MWNT's.

Compared to intersystem crossing and the radiative decay of the singlet excitons, which occur on time scales of 10^{-9} and 10^{-10}–10^{-9} sec, respectively, energy transfer can be much faster than these time scales. Actually, the energy transfer with a time scale of 10^{-11} sec was reported for a polymer blend.[22] Therefore, the triplet excitons observed in the PIA spectrum of the PPV-MWNT composite are supposed to locate far from MWNT's over the diffusion length, because singlet excitons near MWNT's experiences energy transfer before intersystem crossing occurs. This explains why the lifetime of the triplet excitons of the composite is identical to that of a pure PPV film.

We note that the interface interaction between the MWNT's and PPV is similar to the case of a normal metal/semiconductor interface in terms of energy transfer, even though the present MWNT's possess a semiconducting electronic structure. The observed energy transfer could be partially attributable to the quenching by surface oxidized groups of the MWNT's such as carboxylic groups.[10] In the photovoltaic devices previously fabricated using this composite, we conclude that holes are collected by the MWNT layer as a result of the electrostatic field generated between the MWNT's and the Al counter electrode. We also note that the thermal stability of the composite LED (Ref. 8) might originate in the exciton quenching that occurs at the PPV/MWNT interface, which may also reduce the external electroluminescence (EL) quantum efficiency.

IV. CONCLUSIONS

We have investigated the electronic interaction between photoexcited PPV and semiconducting MWNT's based on absorption, PL, and PIA spectroscopy techniques. In the ground state, no significant electronic interaction was observed, except for the slight reduction of the π conjugation of PPV. This suggests the introduction of nanoscopic structural disorder of the PPV chains in the composite. In the excited state, we have observed in the PL and PIA spectra suppression of the absorption of triplet excitons as well as the radiative recombination of the singlet excitons of the original pure PPV. From the analysis of the PIA spectrum, we have concluded that the main electronic interaction is energy transfer from photoexcited PPV to the MWNT's.

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