



The photoconductivity of PVK-carbon nanotube blends

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Abstract

Using both purified multi-walled carbon nanotubes (*p*-MWNTs) and didecylamine-solubilized carbon nanotubes (MDDA), we have prepared PVK/carbon nanotube blends. The PVK/MDDA blend shows good photoconductivity. Their fluorescence spectra indicated that MDDA could act as electron acceptors either in the ground or excited state. In contrast, *p*-MWNTs could hardly improve the photoconductivity of PVK, largely due to its immiscibility with PVK. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Since being discovered in 1991 [1], carbon nanotubes (CNTs) have attracted much attention [2,3]. Depending on their chirality and diameter, CNTs can act either as a semiconductor or metallic conductor [4–7]. Furthermore, Raman spectroscopy and resistivity measurements indicated that single-walled carbon nanotube (SWNT) bundles could exhibit amphoteric behavior by exchanging electrons with electron acceptors or donors to form the corresponding positively or negatively charged counterions [8,9]. However, the mechanism underpinning these charge-transfer processes has not been well understood. Using both insoluble pure

MWNTs (*p*-MWNTs) and didecylamine-modified MWNTs (MDDA) as dopants, we investigated the nanotube-induced charge-transfer with polyvinylcarbazole (PVK). Our photoluminescence and photoconductivity measurements indicated that the MDDA could act as electron acceptors, in both ground and excited states, for PVK. Comparing with the PVK/*p*-MWNTs blend, the PVK/MDDA counterpart shows better photoconductive performance due to a better compatibility, as confirmed by scanning electron microscopic (SEM) imaging. In this Letter, we present some of our recent results on the photoconductivity of PVK/carbon nanotube blends.

2. Experimental

PVK (molecular weight ~1,100,000) was purchased from Aldrich. The MWNTs were pur-

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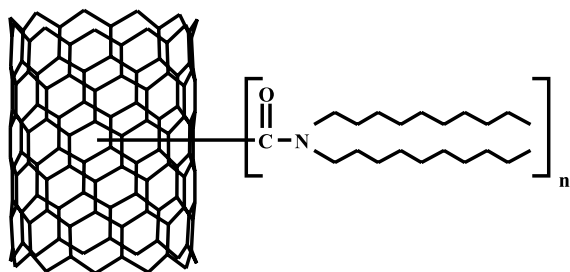
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chased from Sun Nanotech (Nanchang, China) and were purified according to the literature method [10]. MDDA (Scheme 1) was prepared following the procedure we reported elsewhere [11].

To prepare PVK (1.6 wt%) blends with *p*-MWNTs or MDDA for the photoconductivity measurements, a predetermined amount of *p*-MWNTs or MDDA was added into a chloroform solution of PVK (25 mg/ml) and sonicated for 3 h. The resulting mixture was spin-coated onto aluminum substrates covered with a thin layer of nylon film to ensure a full charge for the sample film. A series of samples with a uniform thickness were prepared under the same experimental conditions and dried in vacuum at 60 °C overnight.

The standard photo-induced discharge method [12,13] was used to measure the photoconductivity. Sample films supported by the electrically grounded aluminum substrate were corona-charged (either positively or negatively) in the dark. The amount of surface charge was detected by an electrostatic voltmeter, while the photo-induced discharge curve was recorded on an Electrostatic Paper Analyzer (Model sp-428). A tungsten lamp (30 W, 400 lx) was used as the light source.

SEM images were obtained on JEOL JSM-6700F. Photoluminescence spectra were recorded on a Spex Fluorolog-3 photon-counting emission spectrometer equipped with a 450 W xenon lamp, a Spex 600 grooves/mm dual-grating (blazed at 1000 nm) as the emission monochromator, and 1200 grooves/mm grating (blazed at 600 nm) as the excitation monochromator. A thermoelectronically cooled detector consisting of a near-infrared-



Scheme 1.

sensitive Hamamatsu R2658P photomultiplier tube operated at -1500 V was used.

3. Results and discussion

Fig. 1 shows the photo-induced discharge curves for the blends of PVK/MDDA and PVK/*p*-MWNT obtained under the same conditions. As seen in Fig. 1a, a clear photo-induced discharge effect was observed, though the photo-induced discharge is incomplete due to the presence of the thin layer of nylon underneath the sample film. In contrast, PVK doped with 1.6 wt% *p*-MWNTs does not show any photo-induced surface discharge upon the same photo-illumination. However, both of the samples show significant dark discharges, indicating a good dark conductivity for both of them.

In order to gain a better understanding of the interaction between PVK and MDDA at molecular level, we measured photoluminescence emission spectra of the PVK/MDDA mixture in tetrahydrofuran solution at different content of MDDA (Fig. 2). Although the addition of MDDA did not cause any new spectroscopic feature, it did lead to a continuous decrease in the photoluminescence intensity at the peak position. By plotting the ratio of the photoluminescence peak intensity

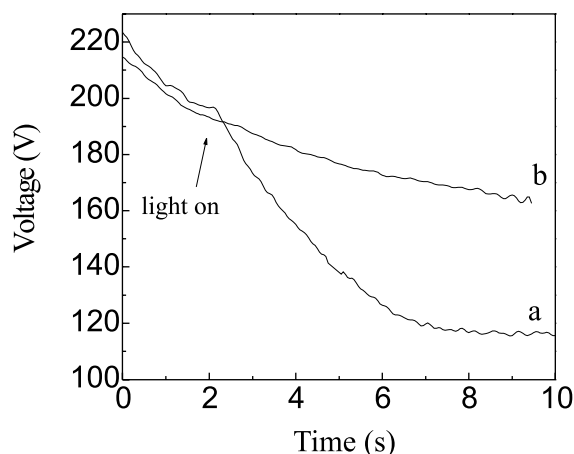


Fig. 1. A qualitative comparison of the photo-induced discharge curves for PVK/MDDA blend (a) and PVK/*p*-MWNTs blend (b).

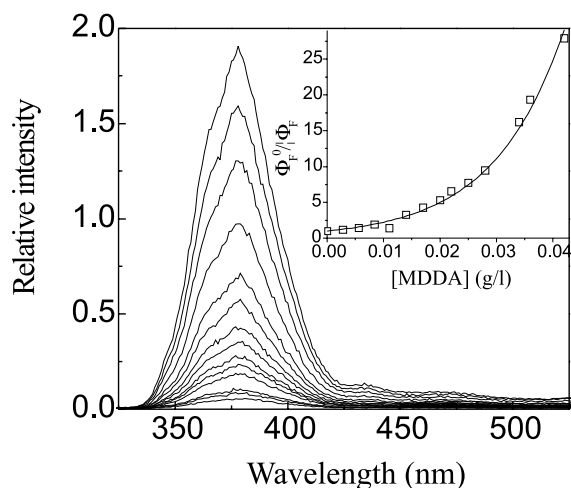


Fig. 2. Photoluminescence spectra of PVK doped with various proportions of MDDA. From top to bottom, the weight proportion of MDDA to PVK are 0%, 20%, 40%, 60%, 80%, 100%, 120%, 140%, 160%, 180%, 200%, 240%, 260%, 300%, successively. Solvent: THF. Inset shows the Stern–Volmer plot for the quenching of photoluminescent intensities of PVK by MDDA in THF at room temperature (\square). The line represents least squares fit.

without and with quencher, Φ_F^0/Φ_F , against the concentration of MDDA, $[MDDA]$, a quenching curve with an upward curvature was obtained (Inset of Fig. 2). As the curve shown in the inset of Fig. 2 fits well to Eq. (1) [14], the observed photoluminescence quenching may be attributed to static quenching due to the formation of the ground state complexes and the excited state exciplexes [14,15]

$$\Phi_F^0/\Phi_F = (1 + k_q \tau_F^0 [MDDA]) \times \exp(Nv[MDDA]), \quad (1)$$

where N is Avogadro's number, v is the static quenching volume, k_q is the bimolecular quenching rate constant, and τ_F^0 is the fluorescence lifetime in the absence of quencher.

The exciplexes formed in the system are apparently not photoluminescent. Our photoconductivity measurements, coupled with the photoluminescence quenching results, suggested the formation of charge-transfer exciplexes under light, which subsequently dissociated into electron–hole pairs. The newly generated electron–

hole pairs either recombine or separate into free electrons and holes, leading to an increase in photoconductivity. The MDDA and PVK may also form the charge-transfer complex in the ground state, which is responsible for the relatively high value of the dark conductivity. Therefore, it may be concluded that the soluble MDDA can act as an electron acceptor to form charge-transfer complexes with PVK.

The difference in the effects of MDDA and *p*-MWNTs on the photoconductivity of PVK is, most probably, resulted from the different morphologies of the PVK/*p*-MWNTs and PVK/MDDA blends (Fig. 3), though chemical grafting of the didecylamine chains onto the carbon nanotubes may also change their work function (i.e., electron affinity). The well-dispersed MDDA in the PVK/MDDA blend (Fig. 3a) provide a large interface area for the charge separation to occur. Morphological structure has been previously

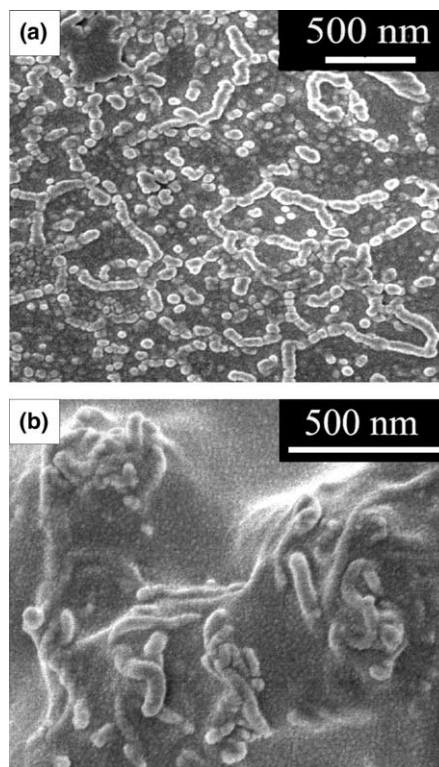


Fig. 3. SEM images of PVK/MDDA (a) and PVK/*p*-MWNTs (b) blends.

demonstrated to have a strong effect on physico-chemical properties of composites based on carbon nanotubes and polymers [16].

In conclusion, we have prepared composite materials by blending PVK with multi-walled carbon nanotubes and measured the photo-induced discharge curves for them. The blends of PVK and didecylamine-solubilized carbon nanotubes (MDDA) show a good photoconductivity with MDDA acting as electron acceptors in both the ground and excited states. In contrast, pure carbon nanotubes (*p*-MWNTs) do not improve the photoconductivity of PVK because the polymer and carbon nanotubes are hardly miscible in this case.

Acknowledgements

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