Photoconductivity Study of Modified Carbon Nanotube/Oxotitanium Phthalocyanine Composites

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Carbon nanotubes (CNTs) bonded to dodecylamine groups were obtained by chemical modification. The modified CNTs showed improved solubility in organic solvents and miscibility with polymer matrix. The photoconductivity of oxotitanium phthalocyanine (TiOPc) doped with modified CNTs was investigated by the xerographic photoinduced discharge method. The results showed that the photosensitivity of the dual-layer photoreceptor (P/R) with modified CNT/TiOPc composite as charge generation material was higher than that with pristine TiOPc and increased with increasing the content of modified CNTs in the composites. It was explained that, as demonstrated by X-ray photoelectron spectroscopy (XPS), after doping with modified CNTs, the intramolecular charge transfer occurred in TiOPc and the charge-transfer exciton was prone to be produced, which was favorable to charge carrier generation. The efficiency of charge carrier separation increased as well because of the photoinduced charge transfer between TiOPc and CNTs, which might also contribute to the improved photosensitivity of the modified CNT/TiOPc composites.

1. Introduction

Since the discovery in 1991,[1] carbon nanotubes (CNTs) have inspired considerable research interests in the past decade because of their unique optic, electric, magnetic, and mechanical properties.[2−5] Scientists regard CNTs as promising candidates for field-effect transistor, full-color display, chemical actuator, tip of scanning-probe microscope, and molecular computer.[6−10] However, CNTs also have some disadvantages, for example, insolubility in any organic solvent, which is the obstacle for scientists to investigate them at the molecular level and to fabricate devices by spin coating.

Oxotitanium phthalocyanine (TiOPc) has been widely used in the area of photoconductive devices and photovoltaic cells for its excellent optic and electronic features.[11,12] Photoconductivity involves the generation of free electron−hole pairs and their subsequent transportation. In inorganic semiconductors, the photon absorption produces free carriers directly. The efficiency of charge carrier generation may approach unity. In organic semiconductors, charge carrier generation proceeds via an intermediate state. The photon absorption produces bound electron−hole pairs first, and then the bound pairs dissociate into free carriers with the aid of an external electric field. Therefore, the key in designing organic photoconductive devices is to promote the efficiency of charge carrier generation and separation. Recent research on the charge carrier generation in TiOPc demonstrated that the charge-transfer exciton (CTE) was important to the charge carrier quantum yield.[13] Our previous work indicated that intramolecular charge transfer in phthalocyanine composites favored producing the CTE.[14] Yu revealed

that photoinduced charge transfer could increase the efficiency of charge carrier separation in poly(*p*-phenylene vinylene) (PPV) sensitized with C_{60} because early time recombination of carriers was inhibited by the spatial separation of electron and hole on C_{60} and PPV, respectively.[15] The implication of high quantum efficiency facilitated by charge-transfer stimulated the fabrication of donor−acceptor heterojunction diodes and photovoltaic cells. In addition to C_{60}, CNTs have also been used to prepare a rectifying heterojunction device with PPV.[16] Evidences for photoinduced charge transfer and energy transfer between PPV and CNTs have been reported.[17,18]

In this paper, CNTs were modified by chemical reaction, aiming at improving their solubility in organic solvents and miscibility with polymer matrix. Another objective is to obtain the modified CNT/TiOPc composites with high photogeneration efficiency by doping TiOPc with modified CNTs. The electronic interactions between modified CNTs and TiOPc were investigated as well.

2. Experimental Section

2.1. Materials and Equipment. The multiwall carbon nanotubes (MWCNTs) were produced by catalytic pyrolysis of ethylene and purified as reported by Smalley.[19] Dodecylamine was purchased from Aldrich. Polyvinylbutyral (PVB), polyamide (PA), polycarbonate (PC), and *N*,*N*′-diethyl-4-aminobenzaldehyde-1-phenyl-1′-(α-naphthyl)-hydrazone (BAH) were commercially available and used without further purification. TiOPc was prepared and purified according to the literature.[20] Pyridine and thionyl chloride were distilled before use.

FTIR measurement was carried out on a VECTOR 22 Fourier transform infrared spectrometer. UV−vis absorption was re-

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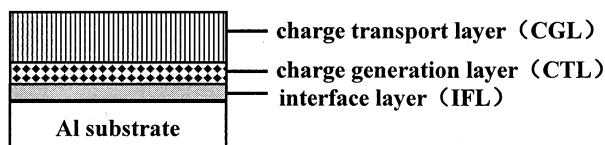
Figure 1. Configuration of dual-layer photoreceptor.

Figure 2. FTIR spectra of CNTs before and after modification: (a) CNTs before modification; (b) CNT−COOH; (c) CNT−CONH(CH$_2$)$_{11}$-CH$_3$.

corded by a CARY Bio100 spectrophotometer. Morphology of CNTs in polymer matrix was observed on a JEM-200CX II electron microscope. Angle-dependent X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB MK II X-ray photoelectron spectrometer. Film thickness was measured on an Elektko-Physik minitest 2000 thin film measuring apparatus.

2.2. Modification of CNTs and Preparation of Modified CNT/TiOPc Composites. MWCNTs were sonicated in a mixture of concentrated sulfuric and nitric acid for 16 h at 40 °C. The obtained carboxyl-terminated CNTs (0.5 g) were then refluxed in excess SOCl$_2$ (50 mL) at 70 °C for 24 h. The excess SOCl$_2$ was removed by distillation and the remaining solid was dried in the vacuum. The solid (0.1 g) reacted with dodecylamine (0.6 g) at 90 °C for 5 days. The excess amine was removed by washing with anhydrous ethanol, giving a black solid.[21]

TiOPc was dispersed in PVB homogeneously by ball milling in dichloroethane for 8 h. Modified CNTs were also suspended in dichloroethane. These two slurries were blended together and sonicated for 2 h. The obtained modified CNT/TiOPc composites were used to fabricate photoreceptors by dip coating.

2.3. Fabrication of Photoreceptor and Measurement of Photoconductivity. The photoconductivity of modified CNT/TiOPc composites was studied in dual-layer photoreceptors. A schematic diagram of the typical device structure is shown in Figure 1. The photoreceptor was made by coating the interface layer (IFL), the charge generation layer (CGL), and the charge transport layer (CTL) in that order on an aluminum substrate.[22] The IFL contained PA with 1 μm thickness. The CGL was formed with 1 μm thickness from the dichloroethane slurry containing 50 wt % TiOPc or modified CNT/TiOPc composites in PVB matrix. The CTL consisted of 50 wt % BAH in PC matrix, and the thickness was 25 μm.

Photoconductivity measurements were carried out on a GDT-II model photoconductivity measuring device by the photo-induced xerographic discharge technique, which included charging, dark decaying, and illuminating steps. The intensity of exposure light (I) was tuned at 10 μJ/cm^2 during measurement, where a halogen lamp (5 W, 24 V) was used as light source. The monochromatic wavelengths of 454, 500, 570, 605, 678, 703, and 762 nm were obtained by optical filters. In the measurement, the surface of the dual-layer photoreceptor was negatively charged in the dark with initial surface potential (V_0). As soon as the lamp was lit, charge carriers were generated in the CGL and injected into the CTL. The surface voltage decreased sharply because of photoinduced carriers recombining with the surface charge. The photoinduced discharge curve was output by a computer, from which we can obtain V_0, residual potential (V_r), dark decaying rate (R_d), and time from original surface potential to half under illumination ($t_{1/2}$). The photosensitivity was characterized by half decaying exposure energy ($E_{1/2}$), which is defined as the product of half decaying time ($t_{1/2}$) and the intensity of exposure light (I), that is, $E_{1/2} = It_{1/2}$. A desired photoreceptor should have a large V_0 and a small V_R, R_d, and $t_{1/2}$. The smaller the $E_{1/2}$ is, the higher the photosensitivity of the photoreceptor is.
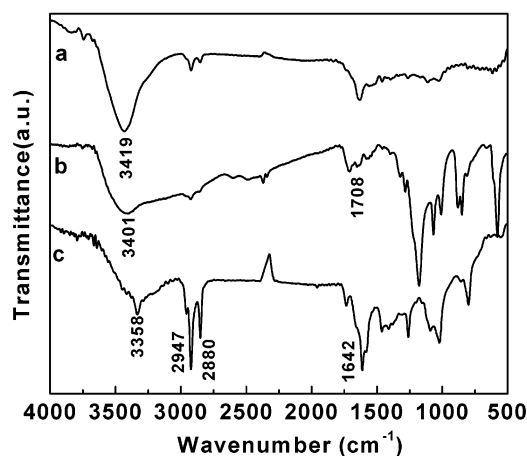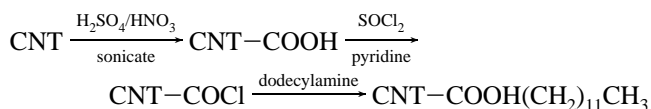
3. Results and Discussion

3.1. Chemical Modification of CNTs. MWCNTs bonded to dodecylamine groups were prepared by attaching functional groups onto the inert molecules. The reactions were carried out in the following way:

$$CNT \xrightarrow[\text{sonicate}]{H_2SO_4/HNO_3} CNT-COOH \xrightarrow[\text{pyridine}]{SOCl_2}$$
$$CNT-COCl \xrightarrow{\text{dodecylamine}} CNT-COOH(CH_2)_{11}CH_3$$

The nature of the chemical groups on surface of CNTs was investigated by FTIR spectra shown in Figure 2. CNTs before modification exhibited an O−H stretching band at 3419 cm^{-1}, which was induced by the carboxyl and hydroxyl attached to the open ends of CNTs when purified in refluxing nitric acid. After being sonicated and refluxed in the H$_2$SO$_4$/HNO$_3$ (3:1 by volume) mixture solvent, CNTs showed two absorption bands at 3401 and 1708 cm^{-1}, associating with O−H stretching and C=O stretching in carboxyl, respectively. Another strong band at 1200 cm^{-1} was assigned to the C−O stretching in carboxylic and phenolic groups. The results indicated that CNTs bonded to −COOH groups were obtained. Carboxyl-terminated CNTs were further reacted with dodecylamine. The end product exhibited a peak at 3358 cm^{-1} due to N−H stretching in −CONH− group. The C=O stretching band in −COOH at 1708 cm^{-1} converted to the C=O stretching in −CONH− at 1642 cm^{-1}. Another feature that should be given attention was that the peaks at 2947 and 2880 cm^{-1} due to C−H stretching in the long dodecylamine chain were obviously strong, indicating that the amine had been attached onto CNTs successfully. Therefore, it was believed that CNTs bonded to dodecylamine groups were finally obtained.

3.2. Miscibility with Polymer Matrix. Figure 3 shows the TEM images of CNT films before and after modification. The unmodified CNTs are immiscible with PVB because they separated from PVB on the film surface when dried in the oven. That is why we only take TEM images of unmodified CNTs without polymer matrix. We can see clearly that CNTs before modification are nearly endless tangled ropes (Figure 3a). After sonicating in concentrated acid, CNTs are cut into short pipes. Holes can be observed in the film where carboxyl-terminated CNTs dispersed in PVB matrix (Figure 3b), indicating immiscibility with PVB. From Figure 3c,d, we can find that each threadlike feature of dodecylamine-functionalized CNTs was
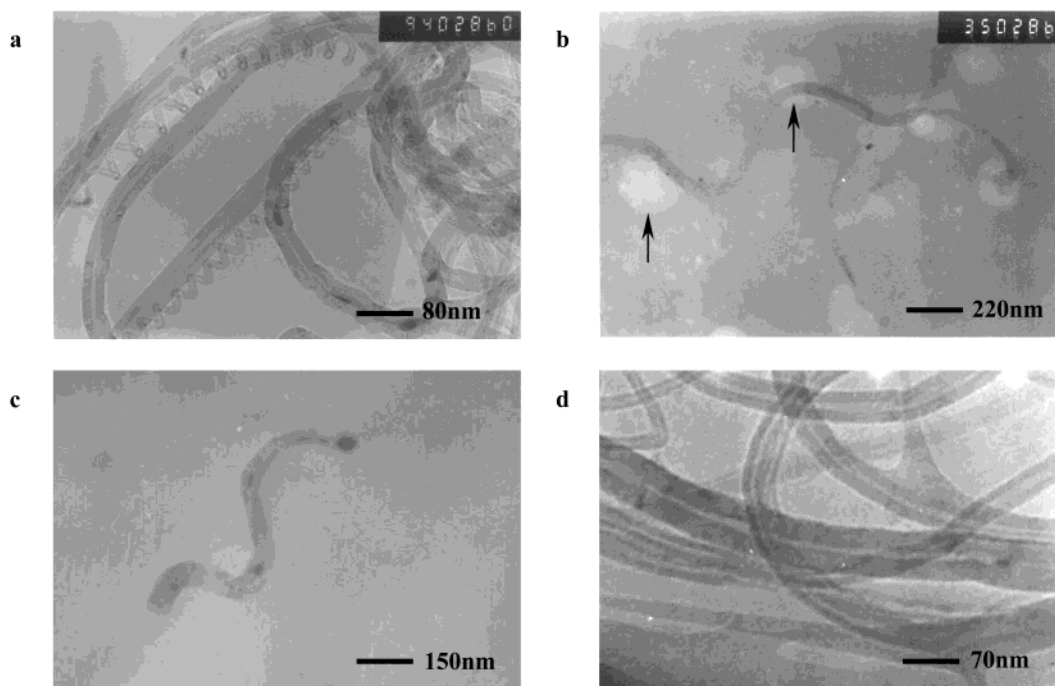
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Figure 3. TEM image of CNTs films before and after modification: (a) CNTs before modification; (b) carboxyl-terminated CNTs in PVB matrix; (c) and (d) dodecylamine-functionalized CNTs in PVB matrix.

dispersed uniformly in PVB film, showing good miscibility with PVB.

Therefore, CNTs before modification are insoluble in any organic solvent and exhibit poor miscibility with polymers. However, modified CNTs show enhanced solubility in solvents and miscibility with polymer matrix as well. The homogeneous suspension of CNTs bonded to dodecylamine groups in chloroform without surfactant can be formed by stirring and remains very stable. No precipitation can be found after a month. The good miscibility with host polymer might be due to the interaction between functional groups in polymer and long dodecylamine chains attached to the end of CNTs. A detailed investigation is in progress.

3.3. Photoconductivity of Modified CNT/TiOPc Composites. Table 1 presents the photoconductive properties of P/Rs from TiOPc and modified CNT/TiOPc composites. The effect of illumination wavelength on photosensitivity of modified CNT/TiOPc composites with various CNT-doping content is given in Figure 4. We can find that at the same exposure wavelength, for example, at 570 nm, the photoreceptor of pure TiOPc shows a half-discharge time ($t_{1/2}$) of 0.04 s, a residual potential (V_r) of 53 V, and a photosensitivity (($E_{1/2})^{-1}$) of 2.50 $\mu J^{-1} cm^2$. When doped with a small amount of CNTs, with 1 wt %, both V_r and $t_{1/2}$ decrease to 45 V and 0.03 s, respectively. The photosensitivity increases substantially with increasing the content of CNTs in the composites and reaches the maximum in the composite doped with 6 wt % CNTs, 5 times higher when compared to that of undoped TiOPc. When the photoreceptor is exposed to other monochromatic wavelengths of 500, 605, 678, or 703 nm, the similar results are obtained. It can be concluded that, in almost the entire spectral region investigated, the photosensitivity of TiOPc doped with CNTs is consistently higher than that of undoped TiOPc. Another feature observed from Figure 4 is that the dependence of the photosensitivity of the composites on the wavelength is in accordance with that of pristine TiOPc, implying that TiOPc serves as the predominate component for charge carrier generation, while CNTs take the synergetic role.

TABLE 1: Photoconductive Properties of P/Rs from TiOPc and Modified CNT/TiOPc Composites[a]

	wavelength (nm)	V_0 (V)	V_r (V)	R_d (V/s)	$t_{1/2}$ (s)	$(E_{1/2})^{-1}$ $(\mu J^{-1} cm^2)$
TiOPc	454	832	62	41	0.14	0.71
	500	806	67	35	0.12	0.83
	570	845	53	39	0.04	2.50
	605	813	62	40	0.09	1.11
	678	827	57	34	0.08	1.25
	703	792	53	39	0.05	2.00
	762	823	46	42	0.02	5.00
TiOPc /CNT (100/1)	454	827	53	43	0.16	0.63
	500	816	49	39	0.12	0.83
	570	830	45	41	0.03	3.33
	605	781	47	32	0.10	1.00
	678	816	47	37	0.06	1.67
	703	776	44	36	0.04	2.50
	762	792	39	40	0.01	10.00
TiOPc /CNT (100/3)	454	803	47	39	0.12	0.83
	500	796	42	37	0.05	2.00
	570	782	37	40	0.02	5.00
	605	790	40	34	0.05	2.00
	678	810	41	37	0.04	2.50
	703	773	35	32	0.03	3.33
	762	780	33	41	0.01	10.00
TiOPc /CNT (100/6)	454	764	31	35	0.09	1.11
	500	792	33	40	0.04	2.50
	570	773	30	37	0.01	10.0
	605	803	27	31	0.04	2.50
	678	784	31	34	0.03	3.33
	703	758	24	29	0.02	5.00
	762	769	28	33	0.01	10.00

[a] V_0, initial surface potential; V_r, residual potential; R_d, dark decaying rate; $t_{1/2}$, half-decaying time; $E_{1/2}$, half-decaying exposure energy; $(E_{1/2})^{-1}$, reciprocal of $E_{1/2}$.

Photoconductivity of the photoreceptor made from TiOPc doped with over 6 wt % modified CNTs is investigated as well. It is found that the initial surface potential (V_0) of the photoreceptor is less than 300 V, too low to be practical. The lower charged V_0 might be induced by the good conductivity due to the high content of CNTs in the composites.[23] For a comparison, photoreceptors with the unmodified CNT/TiOPc
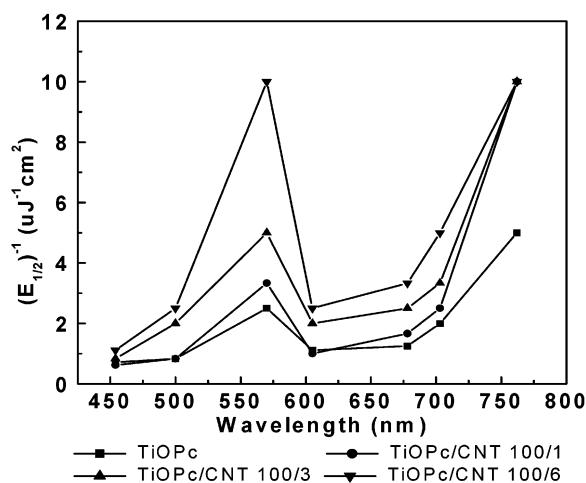
Figure 4. Effect of illumination wavelength on photosensitivity of modified CNT/TiOPc composites with different CNT-doping content.
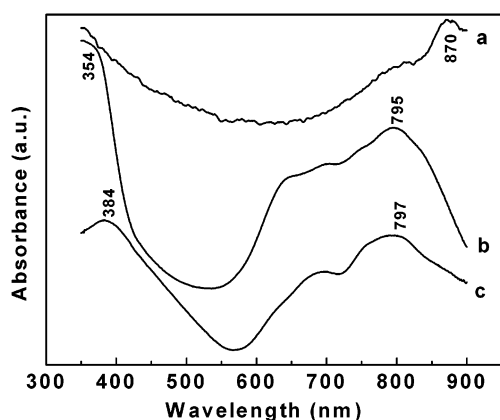

Figure 5. UV−vis absorption spectra of modified CNTs, TiOPc, and modified CNT/TiOPc composite: (a) modified CNTs; (b) modified CNT/TiOPc composite (6/100 by wt %); (c) TiOPc.

TABLE 2: Binding Energy (E_v, eV) of TiOPc and Modified CNT/TiOPc Composite[a]

	C_{1s}	N_{1s}	O_{1s}		$Ti_{2p3/2}$	$Ti_{2p1/2}$
TiOPc	284.6	398.0	533.0		456.6	462.1
TiOPc/CNT (100/6, by wt)	284.6	398.9	531.2	529.8	456.8	463.0

[a] In the composite, all peaks are induced by the binding energy of atoms in TiOPc except for the weak peak at 529.8 eV due to the binding energy of O_{1S} in modified CNTs.

Table 2 lists the binding energy (E_v) of various atoms in TiOPc before and after doping with modified CNTs measured from the X-ray photoelectron spectroscopy. The binding energy was corrected by using E_v of C_{1s} (284.6 eV) in benzene as calibration. From Table 2, we can find that the binding energy of N, O, and Ti atoms in TiOPc changed after doping with CNTs. E_v of N_{1s} increased by 0.9 eV, and E_v of $Ti_{2p3/2}$ and $Ti_{2p1/2}$ increased by 0.2 and 0.9 eV, respectively. E_v of O_{1S}, on the other hand, decreased by 1.8 eV. As we know, the binding energy is correlated with the electronic density around nuclear. The higher the electronic density is, the lower the binding energy is. Therefore, to TiOPc doped with modified CNTs, the electronic density around N and Ti atoms decreases, while electronic density around O atom increases, indicating that intramolecular charge transfer occurs in TiOPc.

In the study of charge carrier generation in TiOPc via electric-field-modulated picosecond time-resolved fluorescence spectroscopy, Yamaguchi found two components with different fluorescence lifetimes.[13] It was concluded that the shorter lifetime species corresponded to the intramolecular charge transfer (CT) in TiOPc and it was a key intermediate in the carrier generation. Popovic's results also supported the existence of a carrier precursor state with intramolecular CT character.[25] It is believed that the production of a CT exciton is important to carrier quantum yield. In our CNT/TiOPc composite case, as demonstrated by XPS just now, intramolecular charge-transfer happens in TiOPc doped with CNTs. This means that, when exposed to light, a TiOPc CT exciton might be prone to be produced, which favors charge carrier generation, hence resulting in higher photosensitivity in the modified CNT/TiOPc composites.

The charge carriers might be recombined or trapped by impurity in the polymer matrix, which handicaps high sensitivity. So photoconductivity depends heavily on the carrier lifetime. It has been proved that photoinduced CT might occur between excited PPV and CNTs, which can enhance carrier lifetime, hence leading to better photoconductivity.[17] Following this argument and our results, we put forward an assumption as follows. Phthalocyanines are typically weak donors, so charge transfer does not occur in the ground state as has been demonstrated by the UV/vis absorption spectrum. When TiOPc was photoexcited by photoenergy greater than the π(valence)−π*(conduction) gap, electron transfer from TiOPc excitons to CNTs occurs in subpisecond scale. Photoinduced charge transfer was shown to have a strong dependence on the ionization potential of the excited state of the donor and the electron affinity of the acceptor.[15] The barrier for the ionization process of TiOPc can be easily overcome.[13] CNTs have been proven to be electron acceptors in the composites with conjugated polymers.[26] Because of the interfacial potential barrier, as demonstrated by the built-in potential at TiOPc/CNT heterojunctions, both ultrafast photoinduced charge transfer and charge separation take place at the TiOPc/CNT interfaces under strong applied electric field, and the quantum efficiency may approach unity. The interfaces between modified CNTs and TiOPc act

composites as CGM are also studied. The photosensitivity is lower than that of pristine TiOPc because of poor miscibility of CNTs in PVB matrix.

The enhanced photosensitivity might result from interactions between CNTs and TiOPc, such as charge transfer or energy transfer. As shown in Figure 5, the modified CNTs have a broad absorption band in the near-infrared region with the maximum peak at 870 nm, which is similar to the unmodified CNTs suspended in organic solvents reported by Hauge.[24] So it might be concluded that the CNTs got modified without graphitic structure being collapsed. In other words, the original electronic features of CNTs are retained. TiOPc has two strong absorption bands in both ultraviolet and near-infrared regions associated with Soret and Q-band, respectively. Upon introduction of 6 wt % CNTs, the absorption spectrum of the composite was observed to exhibit characteristic energy bands of TiOPc, with little contribution from CNTs. But the Soret band was found to be blue-shifted nearly 30 nm. We speculate that this change might stem from the presence of CNTs, which handicap the formation of aggregate structure of TiOPc and hence heavily affects its absorption. Apart from the little shift of the maximum peak, the Q-band of the composite remained similar with that of pure TiOPc, implying the absence of significant interaction between CNTs and TiOPc in the ground state. However, in the photoexcited state, photoinduced charge transfer or energy transfer was expected to take place as has been revealed in PPV composites doped with CNTs.[17,18]

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as the dissociation centers, where the bound excitons split into free charge carriers. Electrons generated by TiOPc excitons (donor) transfer to CNTs (acceptor), leaving holes on TiOPc. CNTs can sufficiently be conductive with high mobility for electron because of the one-dimensional nature of the conduction electron states, which allows removing the photogenerated electrons out of the recombination ranges. So, early time recombination of carriers are inhibited by the spatial separation of electron (on CNTs) and hole (on TiOPc), which enhances the carrier lifetime. In other words, it is the photoinduced CT between modified CNTs and TiOPc that contributes to higher photosensitivity in the modified CNT/TiOPc composites.

4. Conclusions

MWCNTs were functionalized by grafting dodecylamine chains. The modified CNTs showed enhanced solubility in solvents and miscibility with host polymers. Enhanced photosensitivity was observed in the photoreceptors of TiOPc doped with a small amount of modified CNTs in almost the entire spectral region. The photosensitivity increased with the increase of CNTs content in the composites and reached the maximum in the composite doped with 6 wt % CNTs, 5-fold higher than that of undoped TiOPc when exposed to 570 nm wavelength. It was interpreted in terms of intramolecular charge transfer in TiOPc and photoinduced charge transfer from TiOPc to CNTs. It is a benefit for us to design photoconductive devices with high efficiency of charge carrier generation.

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