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Photoinduced anisotropic response of azobenzene chromophore functionalized multiwalled carbon nanotubes

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Azobenzene chromophore covalently functionalized multiwalled carbon nanotubes (AZO-MWCNT) were synthesized and their optical properties were investigated by ultraviolet-visible absorption and photoluminescence spectroscopy. The polarized absorption of the AZO-MWCNT film was measured by cross-polarized light along the directions parallel and perpendicular to the incident light under the irradiation of polarized ultraviolet light. Photoinduced optical anisotropy of the AZO-MWCNT film was dominated by the enhanced dipole transition of the nanotube axis parallel to the incident light and the decreased transition perpendicular to light. The unique anisotropy induced by the photo-orientation of azobenzene chromophore provides insight into the polarized optical properties of carbon nanotubes. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2776220]

I. INTRODUCTION

Carbon nanotubes (CNTs) structurally feature the closed-cage delocalized π-electrons clouds along the tube axis. They are studied as the ideal one-dimensional material for optical nanodevice architectures[1–3] due to their unique electrical and photoconductive performances. Recent studies have been directed to their optical polarization from their outstanding cylindrical nanostructure of CNTs because of their significance in polarization-sensitive optical devices. Islam *et al.*[4] reported that single-walled carbon nanotubes (SWCNT) had a weak optical absorption for the cross-polarized light parallel and perpendicular to the tube axis in the intersubband energy region below 3.3 eV, but the mechanism for the effects were not clarified and the absorption baseline from the parallel-polarized light was not given. Previous works led to the assumption that polarized light perpendicular to the CNT axis was not absorbed.[5,6] However, this assumption appears incorrect for intersubband absorption and baseline absorption.[7,8] Understanding the fundamental anisotropic polarized optical properties of CNTs is important to their application in advanced polarization-sensitive optical nanodevices.

In the past few years, optical polarization of azobenzene chromophore (AZO) based on polymers were extensively studied for their applications in optical data storage and liquid crystals.[9,10] However, less experimental evidence was provided to elucidate the correlation of the polarization and nanostructure of CNTs and to the polarized absorption of CNT photoresponsive chromophores.[4,5,11] We recently studied the photophysical process of AZO attached to polymers[12] and organic molecules.[13] In the previous studies, we reported the synthesis of azobenzene chromophore covalently functionalized multiwalled carbon nanotubes (AZO-MWCNT) by amidiation reaction.[14] In this paper, the optical properties of AZO-MWCNT composites were characterized by ultraviolet-visible (UV-VIS) absorption and photoluminescence (PL) spectroscopy. The polarized absorption of AZO-MWCNT composites induced by the photo-orientation of AZO under polarized ultraviolet (UV) light was studied.

II. EXPERIMENTAL SECTION

Raw multiwalled carbon nanotubes (MWCNT) were oxidized and purified by the method described in Ref. 15. AZO-MWCNT was synthesized by functionalizing AZO on the sidewalls of MWCNT via covalent bonding. The synthesis and characterization of AZO-MWCNT composites have been published elsewhere.[14] The preparation process is outlined in Fig. 1. All the solvents and chemicals were in analytical grade.

The microstructures of the AZO-MWCNT film were observed by a Hitachi 8000 transmission electron microscope (TEM). The UV-VIS absorption studies were measured by a Hitachi 330 UV-VIS spectrophotometer. The PL spectra were characterized by a Hitachi f-4500 fluorescence spectrophotometer. The polarized absorption of the diaminoazobenzene (DAZO) film and the AZO-MWCNT film was analyzed under the irradiation of polarized UV light of 265–400 nm. The cross-polarized light was generated via a polarizer

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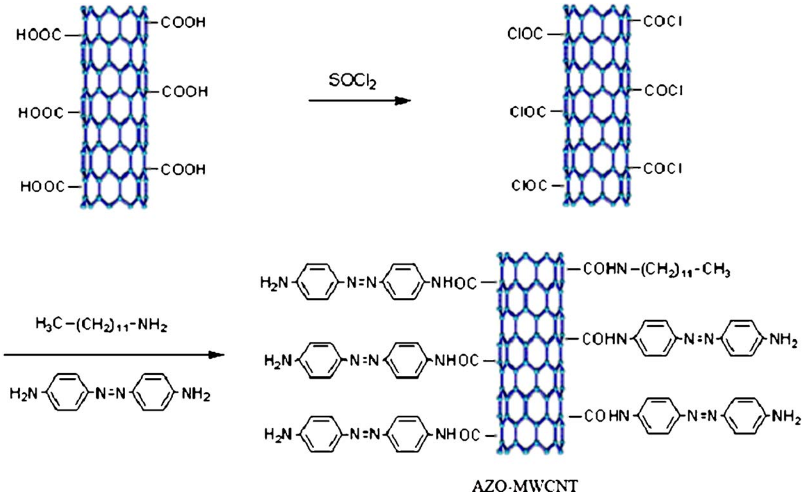

FIG. 1. (Color online) Preparation process of AZO-MWCNT.

placed in the front of UV light source illuminated by UV-GUN (ELC-403, ELECTRO-LITE CORPORATION). The experimental setup is schematically illustrated in Fig. 2.

III. RESULTS AND DISCUSSION

A. Morphology

The morphology of individual AZO-MWCNTs in the film was observed by TEM (Fig. 3), which showed the core–shell nanostructure of the MWCNT core encapsulated in AZO in the nanocomposites. The nanotubes were wrapped by a stable organic layer (as arrowed). Such a core–shell structure is essentially a molecular nanocomposite of the covalent bonding between the core and the shell. The enwrapped organic layers of the shell on the sidewalls of the MWCNT are clearly seen in the TEM images. The dense organic molecules on the sidewalls of the MWCNT reduced attraction among the nanotubes, and hence, avoided their aggregation. As a result, the individual nanotube was well dispersed, as seen from the inset in Fig. 3.

B. UV-VIS absorption spectra

Figure 4 shows the UV-VIS absorption spectra of DAZO [Fig. 4(a)] and AZO-MWCNT [Fig. 4(b)] in tetrahydrofuran (THF). The AZO-MWCNT solution exhibited two strong bands centered at 297 and 406 nm. The band at 297 nm assigned to the π-plasmon transition of MWCNT showed a redshift of 17 nm from that of MWCNT-CONH-$C_{12}H_{25}$,[16] indicating an increase in particle size. This was due to a substantial increase in electron delocalization from the covalent bonding of the functionalized groups around the nanotube lattices.[16] A previous study on the symmetrically aminoazobenzene derivatives[17] showed a characteristic band of DAZO solution at 394 nm. Therefore, the band at 406 nm in the AZO-MWCNT solution can be assigned to the $\pi-\pi^*$ electronic transition of the *trans*-azobenzene chromophore on the surface of the MWCNT. This band displayed a redshift of 12 nm, differing from that of DAZO, which indicates the occurrence of a partial overlapping of π-electron conjugation from the electronic interaction between AZO and the MWCNT. Similar phenomena were found in the nanocomposites of PV-MWCNT and NaPc-MWCNT.[18,19]

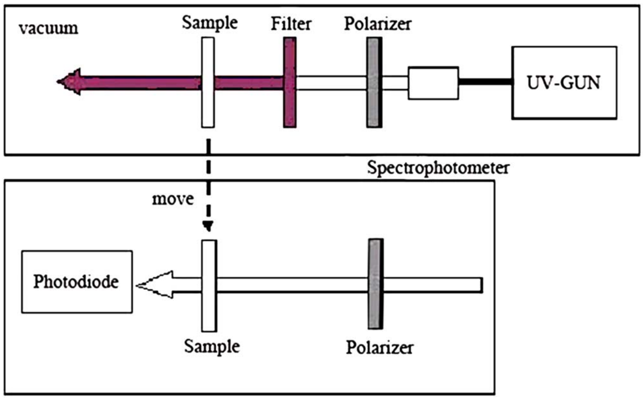

FIG. 2. (Color online) Experimental setup for polarized UV light irradiation and absorption measurements.

C. Photoluminescence spectra

Figure 5 shows the normalized photoluminescence (PL) spectra of DAZO [Fig. 5(a)] and AZO-MWCNT [Fig. 5(b)] of fixed concentration (0.025 mg/mL) in THF under excita-

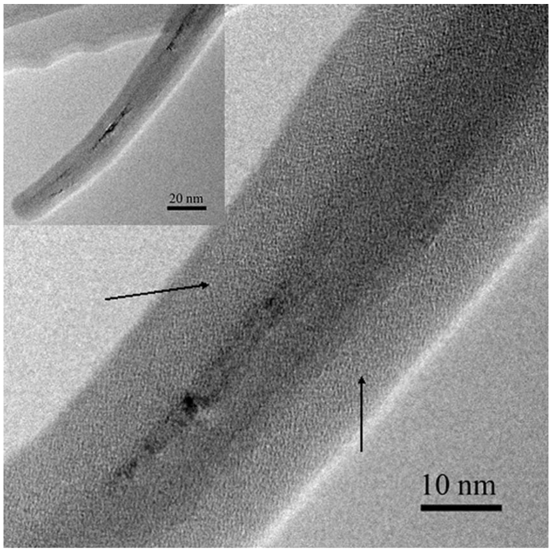

FIG. 3. TEM images of individual AZO-MWCNT in the film. Inset shows a lower-magnification micrograph.

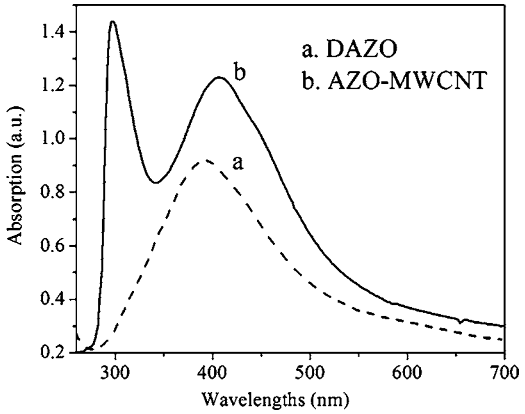

FIG. 4. The UV-VIS absorption spectra of (a) DAZO and (b) AZO-MWCNT in THF.

tion light at 480 nm. The DAZO solution emitted a weak luminescence at 523 nm with a shoulder at 563 nm, which was due to the vibronic transition in the photoexcited state of the conjugated structure. In contrast, the intensity of the PL was enhanced dramatically [Fig. 5(b)] as there was AZO attached to the surface of the MWCNT. The AZO-MWCNT solution exhibited a strong PL centered at 527 nm of a shoulder at 568 nm with a high baseline. Compared to the DAZO solution, the normalized PL intensity of the AZO-MWCNT solution at 527 nm and 568 nm increased remarkably by 96.79% and 334.32%, respectively. It is well known that MWCNT shows broad and weak PL emission. However, through the chemical modification, different types of chemical defects could be generated in the nanotubes.[20] Thus, the enhanced luminescence of the AZO-MWCNT arose from excitation trapping in association with the defects in the conjugated structures of the nanotubes.[21,22] Moreover, the luminescent bands in the AZO-MWCNT solution redshifted by 4–5 nm from that of the DAZO solution due to partial overlapping of the π-electron conjugation, which was consistent with the redshifted band in the UV-VIS absorption spectra.

D. Polarized absorption spectra

The cross-polarized absorption of the DAZO film and the AZO-MWCNT film was investigated using polarized UV light of 265–400 nm. Figure 6 shows the evolution of the polarized absorption spectra of the AZO-MWCNT film with time measured by the cross-polarized light along the directions parallel [Fig. 6(a)] and perpendicular [Fig. 6(b)] to the incident light. Both spectra exhibited two distinct bands at 302 nm and 408 nm assigned to the π-plasmon transition of the MWCNT and the $\pi-\pi^*$ electron transition of *trans*-azobenzene chromophore, respectively. Interestingly, the photoinduced polarized anisotropic response of the AZO-MWCNT film was obtained. A continuous increase in polarized absorption for measured light parallel to the polarization of the incident light and a successive decrease in the absorption perpendicular to the incident light are observed in Fig. 6. This photoinduced polarized anisotropy was different from that of many azobenzene derivatives as side groups of polymers under the irradiation of polarized light.[23,24]

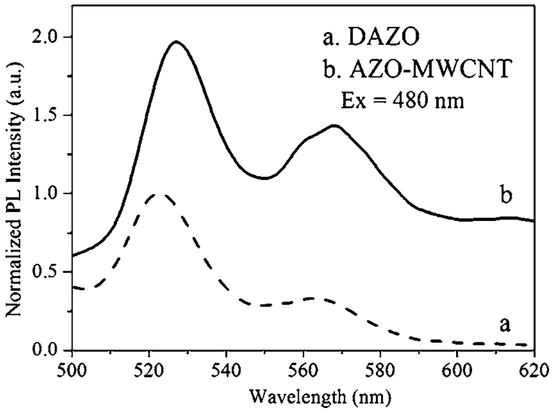

FIG. 5. The potoluminescence spectra of (a) DAZO and (b) AZO-MWCNT in THF under the excitation wavelength of 480 nm light.

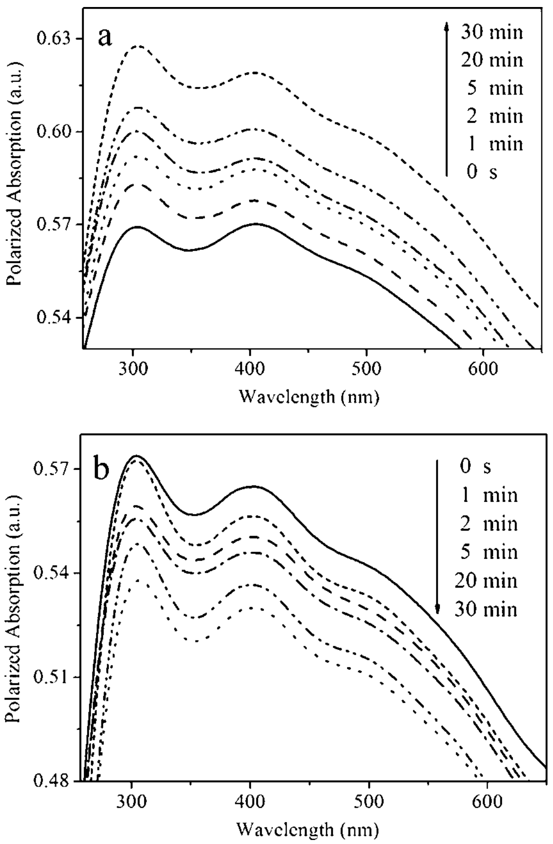

FIG. 6. Time evolution of cross-polarized absorption spectra of the AZO-MWCNT film measured by polarized light along the directions (a) parallel and (b) perpendicular to the incident light.

In Fig. 7, the evolved photoresponses of the DAZO film (dashed line) and the AZO-MWCNT film (solid line) with time at 302 [Fig. 7(a)] and at 406 nm [Fig. 7(b)] were measured by the cross-polarized light. Previous studies indicated that[25–27] *trans*-azobenzene chromophore away from the perpendicular light could induce *trans-cis-trans* isomerization[28] at thermodynamic equilibrium. Keeping irradiation at a fixed intensity led to an increase of the angle between the dipole moment of AZO and the incident light polarization vector as a result of the repeated angle-selective transformations.[29–31] AZO tended to orient perpendicular to the incident light polarization vector under continuous irradiation. Thus, the

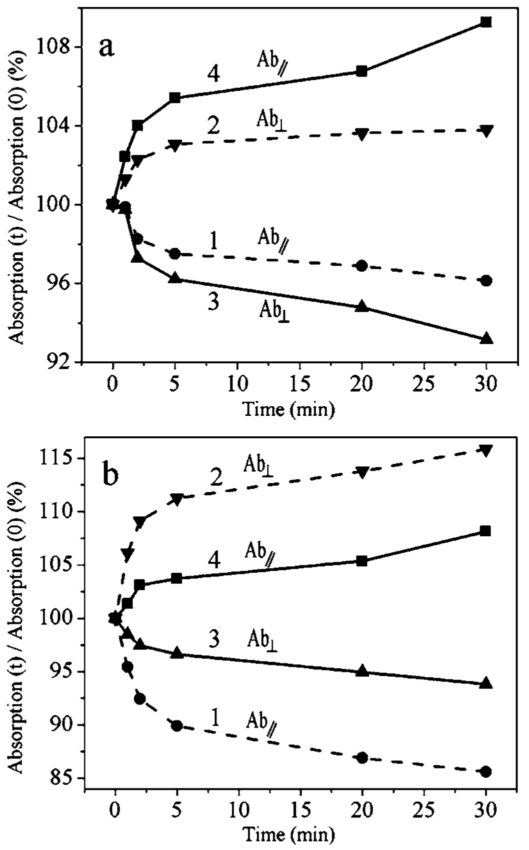

FIG. 7. Time-evolved photoresponses of the DAZO film (dashed line) and the AZO-MWCNT film (solid line) at (a) 302 nm and at (b) 406 nm measured by polarized light along the directions parallel (1, 4) and perpendicular (2, 3) to the incident light.

DAZO film (dashed line) exhibited an anisotropic polarized response. As shown in Fig. 7, the polarized absorption parallel to the incident light decreased, while the intensity perpendicular to the incident light increased due to the photoorientation of AZO. This was in agreement with recent findings of the polarized absorption of AZO.[32,33] In the present case, however, the response of the AZO-MWCNT film (solid line) was opposite to that of the DAZO film (dashed line). The big difference between the DAZO film and the AZO-MWCNT film at 302 nm [Fig. 7(a)] and 406 nm [Fig. 7(b)] indicated large effects of irradiation angles on anisotropy of AZO-MWCNT film (Fig. 6).

In the AZO-MWCNT film, the angle-selective transformations of AZO increased the angle between the dipole moment of AZO and the incident light polarization vector. Meanwhile, the rotation on the MWCNT surface reduced the angle between the nanotube axis and the polarization vector. Murakami[34] observed increasing absorption by continuously decreasing the angle between the SWCNT axis and the electric field vector of polarized light, which was due to enhancement of the dipole transition on the SWCNT axis. Thus, the dipole transition of the nanotubes contributed to the continuous polarized absorption of the AZO-MWCNT film parallel to the incident light, while the absorption perpendicular to the incident light decreased accordingly. The AZO-MWCNT film exhibited polarized absorption opposite to that of the DAZO film. Such optical anisotropy from AZO was found by Cimrova,[23] who reported that the photoinduced transformation of AZO under polarized light induced the long-lasting optical anisotropy of the film. The above behavior was further confirmed by different photoresponses between 302 nm [Fig. 7(a)] and 406 nm [Fig. 7(b)]. The AZO-MWCNT film (solid line) exhibited a stronger anisotropic response at 302 nm than that at 406 nm. In contrast, the response of the DAZO film at 302 nm was weaker than that at 406 nm. These results indicated that the anisotropic response of the AZO-MWCNT film was dominated by the enhanced dipole transition of the nanotube axis parallel to the polarized light and the decreased transition perpendicular to light rather than that of AZO.

IV. CONCLUSION

In summary, we studied the optical polarization of AZO-MWCNT composites prepared by functionalizing AZO onto the sidewalls of MWCNT via covalent bonding. TEM images showed well-dispersed individual AZO-MWCNTs. The redshifted bands of AZO-MWCNT solution in the UV-VIS absorption spectra were ascribed to the overlap of π-electron conjugation. The enhanced luminescent emission with the redshifted band was observed in the PL spectra. The photoinduced anisotropy of the AZO-MWCNT film in cross-polarized absorption spectra was dominated by the enhanced dipole transition of the nanotube axis parallel to the polarized light and the decreased transition perpendicular to the light. The observed polarized optical anisotropy provides an insightful view into the polarized optical properties of CNTs.

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