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Direct observation of excitons in polymer/carbon nanotube composites at room temperature: The influence of nanotube concentration

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Abstract

In this work, we have employed spectroscopic ellipsometry technique to study the optical properties of polymer/carbon nanotube (CN) composites as a function of nanotube concentration. Using a two-layer structural model based on Airy rigorous equations, the optical constants in various CN concentrations have been extracted. In the optical absorption spectra, we have observed a tuning of the excitonic transitions with the addition of single wall CN concentration. Based on theoretical calculations for the interaction of CNs with the surrounding effective media, the spectral evolution of the binding energy of optically active excitonic transitions with the addition of CNs suggests that the effective dielectric function of surrounding media decreases. Furthermore, using an oscillator Lorentz model, the absorption peaks, oscillator strengths and energy broadenings of the excitonic transitions have been extracted.

Keywords: Spectroscopic ellipsometry; Carbon nanotubes; Excitonic transitions; Composites

1. Introduction

During the last few years, the excitonic effects in Single-Walled Carbon Nanotubes (SWNTs) and in conjugated polymers have been extensively studied [1,2]. Observations of excitons in SWNTs due to the large binding energies (at room temperature) in semiconducting tubes give an important insight to the optical properties of this material. Recently, theoretical calculations have reported [3] an observable tuning of excitonic transitions of SWNTs in smaller energies decreasing the dielectric function of embedded material. A strong candidate for this matrix due to its promising electrical and optical properties is the conjugated polymers [4]. In these embedded nanotubes in polymer matrix, the electron-hole interactions give rise to large exciton binding energies at room temperature dramatically altering their optical spectra [5]. Furthermore, this material has already been employed in novel devices and photovoltaic applications due to the large absorption spectra as well as due to the increased photo-dissociation efficiency [6] since with the addition of NTs many dissociation centers exist.

In this paper, we examine the absorption properties of nanotube-poly(3-hexylthiophene) composites as a function of SWNT concentration using ellipsometric technique. The recorded data (ellipsometric parameters) have been analyzed using a two-layer structural model based on the Airy rigorous equations [7] and the optical constants of these composites have been extracted. Furthermore, using a Lorentz oscillator model [8] a more qualitative picture for the oscillator strengths and energy broadening of each optical active transition is studied.

2. Experimental

P3HT (5 mg) was dissolved in 10 ml of Xylene inside a quartz pot which was kept over a hot plate at medium temperature. The initial volume of Xylene was noted and solvent was added regularly to replenish the evaporated amount. The P3HT solution was gently steered until all solid P3HT was dissolved. 1 mg of CNI SWNTs was separately dispersed in 40 ml of Xylene. Appropriate amounts of P3HT and SWNTs were mixed from solution and the composites were ultrasonically agitated so long as to reach a uniform solution. Thin layers of the materials were deposited on Aluminium (Al) substrates by drop casting. The total mass of the deposited materials and the surface of the

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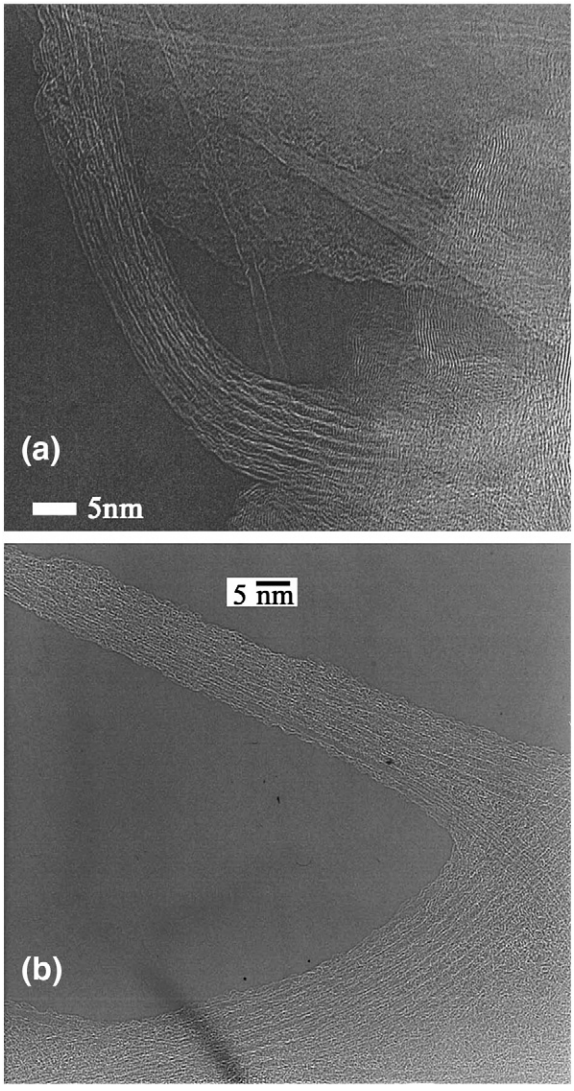

Fig. 1. High resolution electron microscopy images of (a) pure SWNTs and (b) SWNTs dispersed in polymer (SWNT concentration 50 wt.%).

Al substrates were kept the same to insure that the resulting films had similar thicknesses. Processing and measurements were performed under ambient conditions.

The pure SWNTs and the SWNT-polymer composites were examined by high resolution electron microscopy (HREM) using the JEOL 2000EX II microscope. In both cases, samples were drop cast onto holey carbon grids directly from solution. The images presented in Fig. 1 were taken from areas over the edge of holes in the grid. In order to increase the chances of locating the SWNTs we drop cast from solutions with high SWNT concentration. The SWNT concentration in the composite was 50 wt.%. It is therefore reasonable that the SWNTs have formed ropes and bundles both in the pure SWNTs sample (Fig. 1a) and in the composite (Fig. 1b). From these HREM images, we have predominantly measured SWNT diameters of 1.4±0.1 nm [9]. The HREM data does not exclude the possibility that SWNTs with diameters outside the measured region exist in our samples, but if they do exist they are a small fraction.

3. Results and discussion

In this work, using spectroscopic ellipsometry technique [10], the optical properties of polymer/carbon nanotubes composites are studied. All ellipsometric spectra were acquired using a GES5-SOPRA multiwavelength spectroscopic ellipsometer within the energy range of 1.4–5 eV and at an optimum incident angle of 75°. Typical results for the ellipsometric spectra are presented in Fig. 2 for SWNT concentration 0.2, 0.4 and 1 wt.%. For energies above 2 eV, we observed a similar ellipsometric behavior for all samples in contrary to the low energy region where an oscillatory behavior appeared. Furthermore, a tuning in smaller energies of the observable two peaks in the ellipsometric spectra with increasing SWNT concentration is observed. We should point out that in the ellipsometric spectrum of the material where the SWNT concentration is 1 wt.%, the two peaks smooth out.

In order to investigate the optical properties of polymer/carbon nanotube composites from the ellipsometric spectra, we utilized a two-layer structural model. In this model the first layer was the substrate Al film. The optical constants of the substrate were extracted by bulk calculations [11]. The second layer represented the unknown composite material in which its optical constants extracted using the Airy model [7]. This model takes

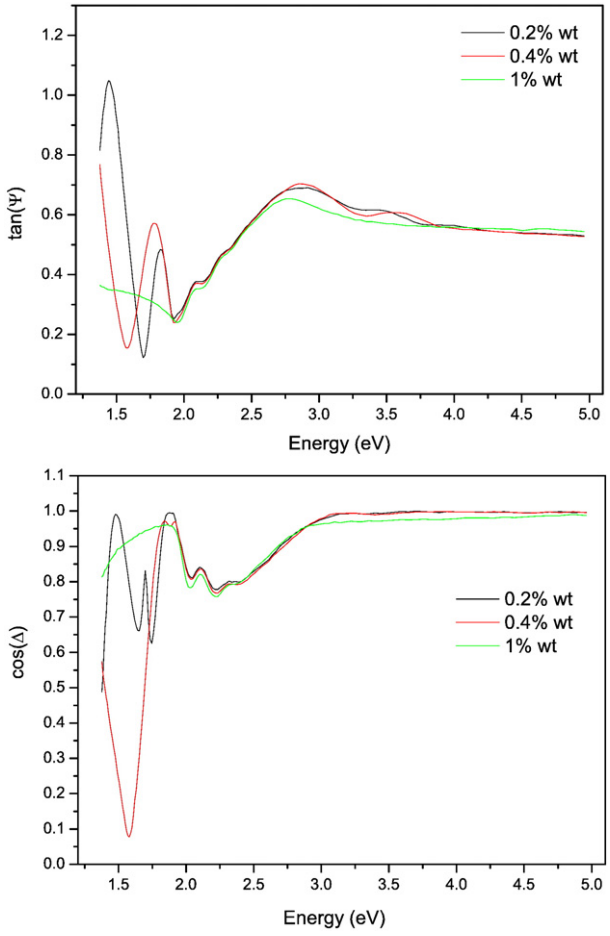

Fig. 2. Typical ellipsometric spectrum of polymer/carbon nanotube composites for SWNT concentration 0.2, 0.4 and 1 wt.%.

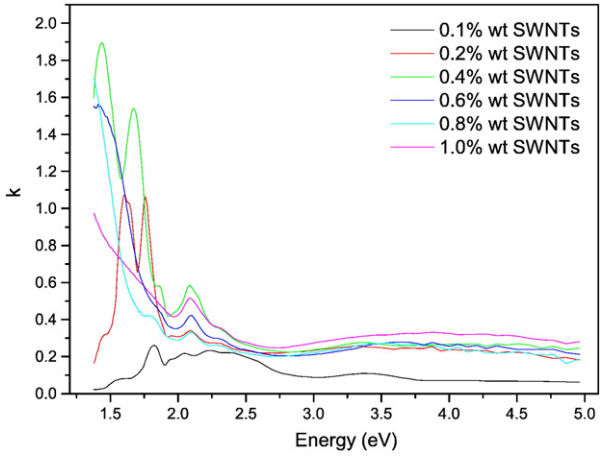

Fig. 3. Extinction coefficient (k) of polymer/carbon nanotube composites for SWNT concentration between 0.1 wt.% and 1 wt.%.

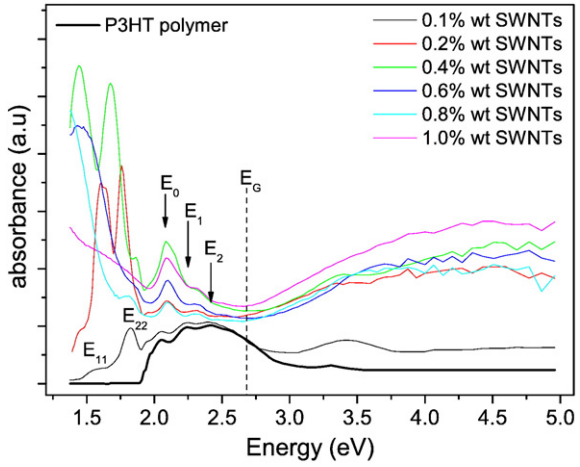

Fig. 4. Optical absorption of polymer/carbon nanotube composites for SWNTs concentration between 0.1 wt.% and 1 wt.%. The reference spectrum of pure P3HT polymer is shown by the thick line.

into account the multiple Fabry–Perot reflections from the front and back interfaces of unknown layer using Fresnel coefficients. The convergence process in this model was achieved using the error function:

$$X^2 = \left(\tan \Psi_{\text{cal}} - \tan \Psi_{\text{exp}}\right)^2 + \left(\cos \Delta_{\text{cal}} - \cos \Delta_{\text{exp}}\right)^2.$$

Fig. 3 shows the extracted extinction coefficient (k) of the composites for SWNT concentration between 0.1 wt.% and 1 wt.%. As shown in these results, two exciton peaks appear with energies below 2 eV [12]. With increasing the SWNT concentration, these optically active exciton transitions are shifted to smaller energies. Furthermore, in the SWNT concentration of 1 wt.% the extinction coefficient appears to have a continuum absorption for energies smaller than 2 eV. This is attributed to the formed nanotube network and agrees well with the enhancement of electrical conductivity of composite in this concentration [13]. In Fig. 4 we present the extracted optical absorption for all composites as a function of the photon energy. For comparison purposes we have included the optical absorption spectrum of the pure P3HT polymer with the solid black line. It is clearly evident from our results that the observable peaks E_0, E_1 and E_2 in the absorption spectrum of P3HT remain at the same energies with the addition of SWNT concentration. These peaks have been reported in the literature as the single exciton peak and vibronic sidebands of P3HT polymer [14] and are not dependent on the interactions of nanotubes with the embedded media.

It is interesting to point out that in the absorption spectrum of the composite with 0.1 wt.%, two peaks at 1.56 eV and 1.82 eV are observed. These peaks are strongly related with the first and second Van-Hove singularities of SWNTs with diameter size 1.4 nm [5]. These results are in good agreement with the diameter

Table 1
Binding energies of the second optically active exciton for SWNT concentration 0.2, 0.4 and 0.6 wt.%, respectively

	0.2%	0.4%	0.6%
E_b	0.05	0.13	0.37

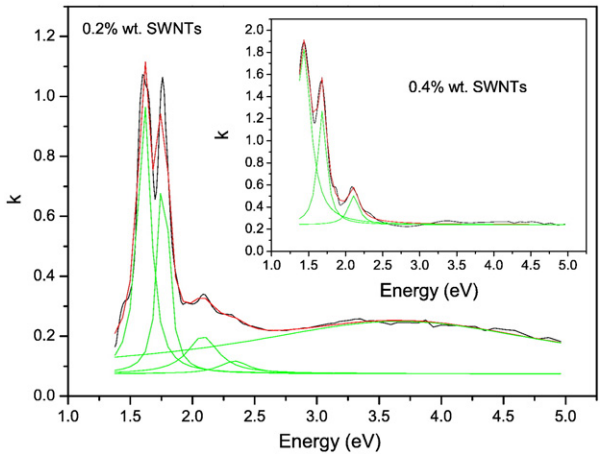

Fig. 5. Typical example of oscillator Lorentz fits (red lines) to the derived data (black lines) of our structural model. The green lines represent the oscillator fit for each optical transition between two molecular orbitals.

Table 2
$K_\infty = 0.05405$ for SWNT concentration 0.1 wt.%

Peak i	E_o	E_P	Γ
1	1.82	0.06	0.10
2	2.03	0.08	0.17
3	2.23	0.10	0.24
4	2.47	0.26	0.52

Table 3
$K_\infty = 0.07467$ for SWNT concentration 0.2 wt.%

Peak i	E_o	E_P	Γ
1	1.61	0.17	0.13
2	1.77	0.12	0.10
3	2.08	0.15	0.30
4	2.34	0.08	0.29
5	3.66	1.84	3.12

Table 4
$K_\infty = 0.24054$ for SWNT concentration 0.4 wt.%

Peak i	E_o	E_P	Γ
1	1.43	0.42	0.24
2	1.68	0.21	0.15
3	2.11	0.13	0.17

size of our HREM observations. With the addition of nanotubes these excitonic peaks are shifted to smaller energies resulting to the enhancement of binding energies. Considerable attention is focused on the binding energy of the second optically active exciton for SWNT concentration 0.2, 0.4 and 0.6 wt.%, respectively. The results are presented in Table 1. As shown in this table, the binding energy increases with increasing the SWNT concentration. Based on theoretical predictions in different surrounding media [3] we have concluded that with the addition of SWNT concentration the effective dielectric function of surrounding material decreases. We believe that this is attributed to the strong electric field interactions at the interface of embedded nanotubes into polymer.

To further explore the excitonic peaks, we utilized the oscillator Lorentz model on the extinction coefficient curves:

$$\kappa = \kappa_\infty + \sum_{i=1}^{n} \frac{E_{pi}^2}{4(E - E_{0i})^2 + \Gamma_i^2}$$

where κ_∞ is the value we obtain for the core extinction coefficient, E_P is the oscillator strength, Γ is the energy broadening in the full width at half maximum and E_{0i} is the energy of the peak i. Fig. 5 shows some typical examples of oscillator Lorentz fits (red lines) to the derived data (black lines) from our model for SWNT concentration 0.2 and 0.4 wt.%. The green lines represent the oscillator fit for each optical transition between two molecular orbitals of composite. The Lorentz oscillator fitting parameters are listed in Tables 2, 3, 4 for SWNT concentration between 0.1 to 0.4%. As shown in these tables, the exciton peaks, the oscillator strengths and the energy broadenings could be extracted. For the rest of the composites it was not feasible to use the oscillator Lorentz approach as the exciton peaks were out of the spectrum range of ellipsometer.

4. Conclusions

In conclusion, using spectroscopic ellipsometry technique, we have studied the optical properties of polymer/carbon nanotube composites. Using a two-layer structural model based on Airy rigorous equations we have extracted the optical constants in various SWNT concentrations. Based on theoretical predictions [3], we have concluded that with the addition of nanotubes the excitonic peaks are shifted to lower energies resulting in the decrease of the effective dielectric function of the surrounding media. Furthermore, absorption peaks, oscillator strengths and energy broadenings of the excitonic transitions have been extracted. All this information of nanocomposite materials could be used to optimize their absorption properties of plastic solar cells.

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