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Physical Interactions of Carbon Nanotubes and Conjugated Polymers

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ABSTRACT

Single walled carbon nanotubes are shown to interact with a conjugated polymer in a periodic manner. Here this interaction is probed using electron microscopy, scanning tunneling microscopy optical and vibrational spectroscopy. The spectroscopic behaviour of the polymer is seen to be dramatically affected, which is attributed to conformational changes due to the effect of the nanotubes.

INTRODUCTION

Since the discovery of carbon nanotubes in 1991[1], researchers have envisaged potential applications such as nanoscale electronic circuits and the construction of complex carbon-based nano-machines. Thus, the assembly of basic building blocks of complex nano-architectures, such as conjugated polymers and nanotubes, has been a driving goal of much of the nano-science community. A first step toward realizing this goal may be the attachment to, or modification by carbon nanotubes of structures such as polymers. This leads to the possibility of assembling individual polymer molecules onto carbon nanotubes with the net effect being the modification of the polymer's electronic properties and structure in a predictable way. To accomplish this, clearly, a more detailed understanding of the interactions between conjugated polymers and carbon nanotubes must be sought. In this work, we describe the assembly of the polymer, poly(m-phenylenevinylene-co-2,5-diethoxy-p-phenylenevinylene), (PmPV), into a coating around single walled carbon nanotubes, (SWNT). Electron microscopy, scanning tunneling microscopy and Raman spectroscopy indicate that the polymer backbone interacts with the lattice of the nanotubes. This results in pronounced alterations to the fluorescence and absorption characteristics. This is explained as a reduction in electron delocalisation due to the affected polymer conformation, and also a dilution of aggregation effects.

EXPERIMENTAL

Synthesis of the polymer has been described previously[2]. Notable about this polymer are the diethoxy sidegroups, which impose a linear, exposed structure onto the PmPV backbone thus allowing significant interaction with the lattice of nanotubes. SWNT were produced in a generator using the arc discharge technique[3]. Composite preparation is relatively simple; SWNT are added to a solution (typically in this case 1g/L) of PmPV in toluene. Nanotube aggregates are broken up by briefly exposing the composite solution to a high power sonic tip (3 minutes), and then sonicating for several hours in a low power sonic bath. Due to the strong tendency of SWNT to aggregate, relatively low mass fractions of SWNT to PmPV can be

achieved (typically 2-3%). In this case, to achieve as high a SWNT concentration as possible, a greater than saturation (~20% SWNT) solution was prepared. After sonication, this was allowed to stand for several days, after which the majority of the SWNT had aggregated. The unaggregated PmPV/SWNT supernatant was pipetted off, and this was used in spectroscopic measurements. Absorption measurements were performed with films spuncoat onto Spectrosil B disks. Fluorescence measurements were performed in solution. TEM (Hitachi H7000) samples were prepared by dipping copper grids into this solution.

RESULTS

Figure 1 shows a TEM micrograph of the composite. It should be noted that there is very little free polymer present, as it is mostly bound to the SWNTs. It is also evident that the SWNTs are well dispersed within the system. Figure 1b shows a magnified view of figure 1a (contrast has been enhanced for clarity). A SWNT rope can clearly be seen at the centre of the large strands present. The diameter of these strands is approximately 120 nm with the central core being approximately 4nm. This suggests a reasonably strong interaction between the SWNTs and the PmPV, given the large relative weight of PmPV that each SWNT supports. This may be beneficial for mechanical reinforcement of polymeric materials. Given the diameter of the central region, these cannot be individual coated SWNT, but are small ropes. Figure 1c shows a magnified view of nanotube with an apparent ordered cylindrical coating of the polymer. This has been previously attributed to an individual SWNT with the PmPV mapping on the tube lattice in a structured way.



Figure 1. shows a wide area view of the composite. Note the absence of free polymer, which differs from other composites of lower mass fraction. Top right micrograph is a contrast enhanced magnified view, so the SWNT ropes within can be clearly seen. (arrows point to these SWNT cores). Lower left micrograph shows the structured periodic wrapping visible in some cases.

Raman scattering is a powerful technique to probe the structure-property relationship in both carbon nanotubes and conjugated polymers. In figure 2, the high frequency region of the PmPV spectrum is compared to that of the composite for an excitation wavelength of 676 nm.

For completeness, the spectrum of nanotube powder is also shown. In this region, the so-called G-line feature centered at 1580 cm^{-1} dominates the nanotube spectrum. This group of modes corresponds to splitting of the optical phonon, the E_{2g} mode in graphite, into longitudinal components at high energies and transverse ones at lower energies. The apparent broadening on the low frequency side has been attributed to both metallic and semiconducting nanotubes being resonant at this excitation energy[4].

In this region, the spectrum of the polymer is dominated by a multiplet of modes centered on 1600 cm^{-1} . The spectrum is fitted by searching the minimum number of frequencies that fitted the different Raman bands equally well without fixing the positions and the widths of the individual peaks. The band at 1627 cm^{-1} can be attributed mainly to the vinyl group A_g mode (stretching of C=C bond)[5, 6]. The other bands may be attributed mainly to the phenyl group A_g mode (stretching of C-C bond). There is also a number of features centred at 1300 cm^{-1} . In PPV, the main band at 1330 cm^{-1} has been assigned to a vibration associated with the vinyl bond. In the composite, the introduction of nanotubes causes a number of modifications to the spectrum. The broad band at 1627 cm^{-1} appears to evolve into two well-defined features. There also appear to be modifications to the relative intensities of the modes at 1610 cm^{-1} and 1590 cm^{-1} . This change manifests itself as the 1590 cm^{-1} band becoming dominant. These changes are more than just a superposition of modes due to the different species, indicating that the vibrational structure of the polymer is being altered. These observations agree well with the observations of polymer wrapping witnessed in the micrographs of figure 1.

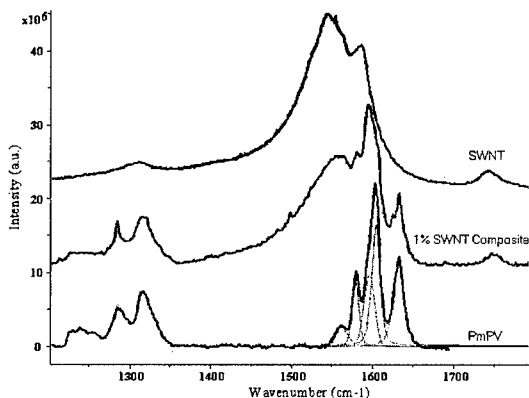


Figure 2. Raman Spectra of the high frequency region of the PmPV spectrum compared to the composite. (Excitation wavelength of 676 nm).

Scanning Tunneling Microscopy (STM) images give strong evidence for such an interaction. When the PmPV-SWNT solution is cast on highly oriented pyrolytic graphite (HOPG) an array of these wrapped structures can be observed using tunneling microscopy. The wrapped nature of two of the tubes can clearly be seen in the STM micrograph of Figure 3. Notice that again, the SWNT on the right appears to have an order to its wrapping while the SWNT on the left has no apparent structure to it. Generally, both types of coatings are found with the ordered being less common. Cross-sections of the STM image suggest that the height/width of these objects is in

agreement with that expected from a 1.2 nm – 1.4 nm SWNT coated with this coiled polymer. To confirm that a SWNT is inside the polymer coating, the tunneling spectra from the tubes is also shown and compares them with the spectra of an amorphous PmPV film on HOPG and pure HOPG itself. The tunneling spectra are collected by placing the STM tip over the object, disengaging the feedback, ramping the voltage and collecting the current. The resulting I-V spectrum reflects the electronic structure of the object. These tunneling spectra are presented as differential conductivity dI/dV (nA/V) and represent the local electronic density of states (LDOS) of the material. In the -1.0 eV to 1.0 eV energy range, the clean HOPG surface yields a parabolic LDOS as expected. The amorphous film of PmPV also exhibits a relatively featureless LDOS in this energy range [7], bar a noticeable feature at 0.8 eV, believed to be due to tunneling via a localized polaronic state [8]. This is because the band-gap of this polymer is approximately 3.1 eV and electrons tunnel across the polymer region into the HOPG substrate below with little scattering. The LDOS of the wrapped nanotubes, however, are quite different showing sharp, regularly spaced features. These features appear to be the van Hove singularities of the underlying SWNT as reported for clean SWNT by several groups [9,10].

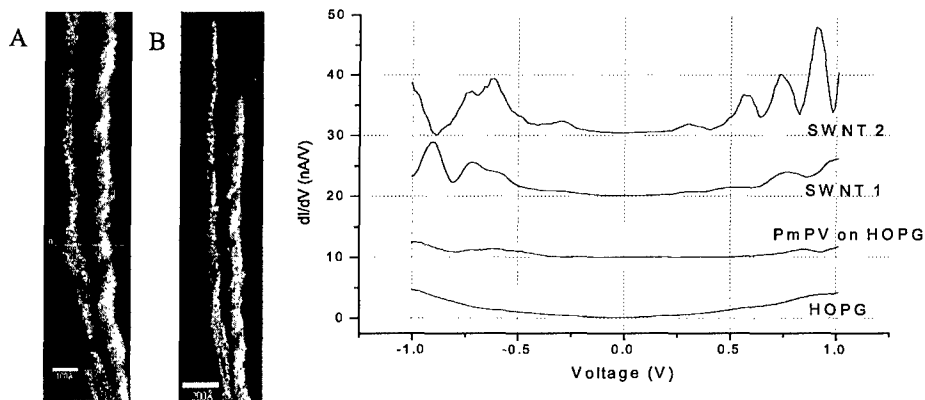


Figure 3. (Left) STM image of two polymer wrapped SWNT lying on HOPG. STM parameters were an applied voltage of 200 meV, and a tunneling current of 10s of picoAmps. Line marked A denotes position at which cross-section is taken. STM used was an RHK Technologies operating in UHV ($<10^{-9}$ Torr). Films were imaged using mechanically formed Pt-Ir tips. B) The tips of the two nanotubes shown in A). (Right) Electronic Structure of the nanotubes shown in A). Curves are each offset by 10 nA/V from previous for clarity. For comparison the electronic structure of the HOPG substrate and a PmPV film lying on HOPG are shown

Figure 4 shows a comparison of the absorption spectrum for PmPV and the composite. For comparison, the spectrum of raw SWNT powder is also shown. The pristine polymer and composite spectra are normalized to the lowest energy peak near 3 eV. For the polymer, this has been assigned to a transition associated with a state delocalised along the polymer backbone [11] (B_u exciton). The feature at 3.7 eV may be due to the effects of broken charge conjugation symmetry similar to that seen in other PPV derivatives [12]. There are three poorly resolved

features in the higher energy region (4.5 eV). These are due to localized excitations on the phenyl rings.

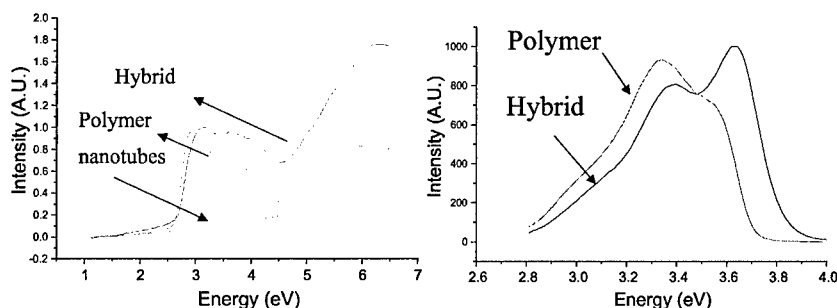


Figure 4. (Left) Absorption Spectrum of the SWNT/PmPV Composite, with PmPV and SWNT for reference. (right) Fluorescence Spectrum (Excitation wavelength of 340nm) of the SWNT/PmPV Composite and PmPV.

When comparing the absorption of the composite to the pristine polymer, it is immediately noticeable that there are many dramatic differences. The low energy peak has blue-shifted from 3 eV in the polymer to 3.15 eV in the composite. One possible explanation for this is that there is a substantial reduction in electron delocalisation along the backbone due to the conformational relaxation of the polymer around the nanotube lattice. This has previously been hypothesized by Ago *et al* [13]. Another explanation for this apparent blue-shift may be that the presence of the nanotubes are hindering the formation of inter-strand species such as aggregates which have been shown to play a large role in the photophysics of this polymer [14]. Aggregation is a result of weak inter-chain interactions. In dilute solutions, the individual strands are isolated and these interactions can therefore be neglected. In the solid, the distances between the polymer chains become appreciably smaller and these inter-chain forces become more significant. In the absorption spectrum, this manifests with the emergence of a markedly red-shifted feature in the solid state compared to the solution. Upon introduction of nanotubes, the peak at 3.7 eV broadens with the evolution of two features at 3.64 eV and 4.0 eV respectively. The relative absorbance of these features has also increased markedly becoming as intense as the peak at 3 eV, unlike PmPV where the corresponding peak is approximately 75 % of the main peak intensity. As this is due to broken charge conjugation symmetry in PmPV, it suggests that the symmetry is further broken due to the presence of SWNTs and the associated effects this has on the conformation of the polymer. There is also less noticeable structure in the high-energy region, but relatively stronger absorption. This suggests that the dominant absorption in the composite shifts to the phenyl ring of the PmPV.

Also shown in figure 4 is the fluorescence spectrum of the composite compared to the pristine polymer for an excitation energy of 3.63 eV (340 nm). Similar to absorption, the presence of nanotubes dramatically effects the polymers emission spectrum. The polymer has broad emission centered in the green with a main vibronic feature at 2.58 eV (480 nm) and a strong shoulder at 2.75 eV (450 nm). In the composite, there is an overall red shift in the spectrum with the dominant feature centered at 2.78 eV (445 nm) and a second peak at 2.61 eV (475 nm). These

effects agree well with the modifications to the absorption spectra with the nanotubes acting to reduce electron delocalisation. Additionally, the aggregation effects are also diluted.

CONCLUSIONS

Our results show that it is possible to assemble polymer strands onto single walled carbon nanotubes using mechanical agitation and constitutes the first visual confirmation of such assembly. Further, we suggest that such wrapping results in the alteration of the polymer's electronic structure, as evidenced in the modified optical spectra of the bound polymer. This may well represent a previously unconsidered route to polymer-nanotube assembly for molecular scale electronics.

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