Highly Enhanced Electrical Conductivity and Thermal Stability of Polythiophene/Single-walled Carbon Nanotubes Nanocomposite

Gholamreza Kiani1*, Hossein Sheikhloie2, and Ali Rostami1

(1) School of Engineering-Emerging Technologies, University of Tabriz, Tabriz, Iran
(2) Department of Chemistry, Islamic Azad University, Maragheh Branch, Maragheh, Iran

Received 14 March 2011; accepted 6 July 2011

ABSTRACT

Herein, we synthesized and characterized polythiophene/single-walled carbon nanotubes nanocomposite. Thiophene (Th) and 2-(2-thienyl) pyrrole (TP) were selected as interfacial modifiers for a SWNT-poly(Th-TP) nanocomposite. The electrical conductivity and thermal stability can be dramatically improved by in-situ polymerization of a thin layer of self-doped conducting polymer around and along the single-walled carbon nanotubes (SWNTs) beside the bulk polymer. The resulting cable-like morphology of the SWNT-poly(Th-TP) composite structure was characterized with Fourier transform infrared (FTIR), ultraviolet-visible spectroscopy (UV-Vis), field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM) and Raman spectroscopy. Also, the morphology of the film was investigated using a scanning tunneling microscopy (STM). The characterization of the molecular structure has indicated that thiophene and TP molecules are adsorbed onto the surface of SWNTs to polymerize and SWNTs have been used as the core in the formation of a hybrid SWNT-poly(Th-TP) composite. Transmission electron microscopy analysis revealed that in the SWNT-poly(Th-TP) composite, SWNT constitutes the core and poly(Th-TP) acts as the shell. TGA data confirm that the presence of SWNT in the composite is responsible for the high thermal stability of the whole material in comparison with pure poly(Th-TP). The standard four-point-probe method was utilized to measure the conductivity of the samples. The conductivity through SWNT-poly(Th-TP) is as high as 38 S cm⁻¹, well above the normal conductivity value of bulk poly(Th-TP) films (~1.67 × 10⁻¹ S cm⁻¹). In addition numerous physical properties of the nanocomposite were measured and the obtained results are discussed.

INTRODUCTION

Carbon nanotubes (CNTs) [1] are the focus of considerable research interest due to their potential applications. Their unique properties include splendid mechanical, thermal and electrical conductivity performances. They offer tremendous opportunities for the development of fundamentally new material systems for application in nanoelectronic devices [2], scanning probe microscopy [3], field emitters [4] and so forth. Similarly, composites based on polymers and nanotubes have ability to make impacts on variety of applications...
ranging from general low-cost circuits and displays to power devices, micro-electromechanical systems, super capacitors and solar cell sensors [5,6].

Alternatively, π-conjugated conducting polymers such as polypyrrole (PPy), polyaniline (PANI), and polythiophene (PTh) or their derivatives have attracted a great deal of attention because of their unique properties, such as environmental stability and ease of preparation [7,8].

Dispersion of carbon nanotubes into polymers can be improved by either using surfactants as processing aids [9], functionalization [10] or in-situ polymerization [11]. The ability to combine CNTs with conducting matrices such as poly(3-octylthiophene) [12] poly(3,4-ethylenedioxythiophene) [13] to produce nanocomposite materials has stimulated much research interest, specifically in organic electronics.

The novel one-dimensional structures of single-walled carbon nanotubes (SWNTs) lead to excellent electrical properties as well as extremely high mechanical and chemical stability, but they are hard to be shaped into film. Meanwhile, conducting polymers show high transparency and flexibility and can be easily processed into films. By combination of these two materials, we can obtain high performance SWNTs/conducting polymer composite films.

Recently, a variety of methods have been reported for producing composites from CNTs and conducting polymers [14-17].

The idea of using carbon nanotubes (CNT) as conductive filler to improve the electrical properties of polymer composites has drawn great attention both from industrial and academic aspects. In our previous work, 1-(2-pyrrolyl)-2(2-thienyl) ethylene (PTE) and 2-(2-thienyl) pyrrole (TP) showed a considerable increment in the electroactivity and redoxability of pyrrole, N-methyl pyrrole and thiophene [18-20].

In our present work, considering the suitable effects of TP on the polymerization of thiophene and the corresponding effects of SWNTs on nanocomposite, modified SWNTs coated with conducting poly(Th-TP) can form complex SWNT-poly(Th-TP) composites. It was assumed to be able to observe various enhancements in nanocomposite properties including electrical conductivity and thermal stability. The molecular structure of the resulting SWNT-poly(Th-TP) composite has been characterized.

EXPERIMENTAL

Materials and Methods
SWNTs (AP-grade, diameter 1-1.2 nm and length 2-20 μm) were supplied by Iljin Nanotech Co. Ltd., South Korea). The thiophene monomer, chloroform, anhydrous iron (III) chloride (FeCl₃, oxidant) and other organic solvents were bought from Aldrich (reagent-grade) and used without further purification. 2-(2-thienyl) pyrrole (TP) was prepared by the method of Engle and Steglich [18].

A typical in situ chemical oxidative polymerization of thiophene and TP was carried out in the presence of SWNT. The routine synthesis of the SWNT-poly(Th-TP) composite was as follows: 100 mL of chloroform containing SWNTs (0.2 g) was added to a 500-mL, double-necked, round-bottom flask equipped with a magnetic Teflon-coated stirrer. The mixture was sonicated for 30 min at room temperature to disperse the SWNTs. FeCl₃ of 0.1 g dissolved in 100 mL chloroform was added to the solution, and sonicated further for 30 min at room temperature.

The thiophene monomer (1 mL, 0.25 M) and TP (0.186 g, 0.025 M) with 50 mL chloroform were placed in a small portion line of the double necked flask and added gradually (dropwise) to the suspension solution with constant stirring. The reaction mixture was stirred for an additional 24 h under the same conditions.

The resultant SWNT-poly(Th-TP) powder was precipitated in methanol, filtered with a Buchner funnel, and then carefully washed with methanol, hydrochloric acid (0.1 M), distilled water, and acetone. The obtained black powder was dried under a vacuum dryer at room temperature for 24 h. Poly(Th-TP) was synthesized with a similar method, and the same molar ratios of monomer to dopant were incorporated into the polymerization.

Infrared spectra were recorded on a Shimadzu FTIR-8400S, Japan. We also performed X-ray diffraction (XRD) experiments (Rigaku X-Ray diffractometer, Japan). SEM and TEM images were obtained with a field emission scanning electron microscope (FE-SEM) (Hitachi model S-4700, Japan, operating voltage; 15 kV) and Jeol JEM-2100, Japan, respectively. TGA curves were obtained with a
Perkin Elmer Pyris Diamond, USA under nitrogen atmosphere with a heating rate of 10°C/min and temperature range of 25-800°C. Also a laser Raman spectrometer (model HR800, Jobin-Yvon Horiba, Japan) equipped with a Coherent Innova 90C Fred argon ion (Ar+) laser source and an ultraviolet-visible (UV-Vis) spectrophotometer (Cary 50, Varian, USA) were used.

The morphology of the films was investigated using a scanning tunneling microscopy (STM) Nano system Pars (SS-1), Iran. STM images were obtained in constant current mode using Pt/Ir tips, previously tested on an HOPG (highly ordered pyrolytic graphite) standard sample in order to verify their suitability for topographic performances. The STM measurements were performed at a tunneling current of 0.1 nA and at bias of +0.1 V relative to the tip and characterization was performed in air and at room temperature. The room-temperature conductivity of the pressed pellets was measured with the standard four point-probe method with a Jandel Engineering model CMT-SR1060N instrument, Japan.

RESULTS AND DISCUSSION

Structural Characterization

Figure 1a shows SEM image of SWNTs. In Figure 1b, it is evident that pure poly(Th-TP), synthesized without SWNTs, shows a bulk morphology. Also the field emission scanning electron microscopy image in Figure 1c shows a morphological view of the SWNT-poly(Th-TP) composite. The tubular morphology of the SWNT-poly(Th-TP) composite

Figure 1. SEM Images of: (a) SWNTs, (b) poly(Th-TP), and (c) SWNT-poly(Th-TP) composite samples.
has been imaged with TEM, as shown in Figure 2.

Structural characterizations have shown that the SWNTs are used as self-assembly hard templates for the formation of one-dimensional, coaxial SWNT-poly(Th-TP) nanostructures, and the polymer is tightly coated on the surface of the SWNTs. Also, this suggests that the interaction between polymer molecules and SWCNTs overcomes the Van der Waals interaction between SWCNTs, which generally would result in separate growth or aggregates of poly(Th-TP).

Figure 3 is a STM topographic image of SWNT-poly(Th-TP) composite showing a boundary region between nanotubes and polymer. However, no exact information about the relative location of two materials can be extracted from this 3-dimensional image. STM topographic images show the composite nanostructure in which all the individual aligned nanotubes were fully or partially coated with a concentric layer of conducting polymers. The STM topographic image also indicates that the nanotubes have not been damaged during the chemical polymerization process.

To examine the mixing-induced interaction between SWNTs and poly(Th-TP), FTIR and Raman spectroscopic analyses were carried out. The FTIR spectra of poly(Th-TP), SWNTs, and SWNT-poly(Th-TP) composite are shown in Figures 4, spectra a-c, respectively. There are several low-intensity peaks in the range of 2800-3100 cm\(^{-1}\) that can be attributed to the aromatic C-H stretching vibrations and C=C characteristic band (1637 cm\(^{-1}\)) [21,22]. The absorption in this region is obscured by the bipolaron absorption of the doped poly(Th-TP).

The range of 600-1500 cm\(^{-1}\) is the fingerprint region of poly(Th-TP). The peak at 786 cm\(^{-1}\) is usually ascribed to the C-H out-of-plane deformation mode, whereas other peaks in this region are attributed to the ring stretching, and C-H in-plane deformation modes [23,24]. The C-S bending mode has been identified at approximately 690 cm\(^{-1}\) and indicates the presence of a thiophene and TP monomer [25]. The SWNT-poly(Th-TP) composite shows nearly identical numbers and positions of the main FTIR bands in the range of 600-3200 cm\(^{-1}\).
C-H stretching vibrations and C=C characteristic peaks can be identified almost in the same range at 2800-3100 cm\(^{-1}\) and 1637 cm\(^{-1}\), respectively. Only peaks of ring-deformation modes are shifted because of the probable polaron/π-transition interaction between the planar poly(Th-TP) backbone and SWNTs surface, indicating that some of the SWNTs do not fully interact with the poly(Th-TP) molecules. Also, Table 1 shows some FTIR characteristic peak positions (cm\(^{-1}\)) in detail.

To detect the structure of nanocomposites of carbon nanotubes and conducting polymers Raman scattering was employed. The Raman analysis of nanotubes samples, pure and composite polymer films have been performed in the 150-2000 cm\(^{-1}\) spectral region, where one can observe the peaks produced by the tangential modes of carbon nanotubes as well as the peaks ascribed to different forms of conducting polymers. For Raman spectrum, the strong peak at 1583 cm\(^{-1}\) represents the backbone stretching mode of C=C bonds and the peaks at ~1377 and 1083 cm\(^{-1}\) belong to the ring stretching and the N-H in-plane deformation of the oxidized (doped) species of the poly(TP), respectively.

In Figure 5, the typical Raman spectra of SWNTs, SWNT-poly(Th-TP) composite, and Poly(Th-TP) are presented. In general, the Raman spectra of the polythiophene family show three main lines coupled to the electronic transition. The main dominant lines of the poly(Th) powder (spectrum c in Figure 5) are around 1500 and 1450 cm\(^{-1}\) (C-C stretching region) which are totally symmetric, in-phase vibrations of the thiophene rings that spread over the whole polymer chain [25]. A weaker feature can be seen within the range of 1070-1040 cm\(^{-1}\) (C-C stretching plus a C-H wagging component) and at 697 cm\(^{-1}\) for C-S-C ring deformation [26,27].

This behaviour is a vibrational signature that proves that in PTh, π electrons are mostly confined within each thiophene ring or within a very restricted domain of the chain [28,29]. The bands located at about 970 and 930 cm\(^{-1}\) are belonged to ring deformations associated with dication (bipolaron) and radical cation (polaron), respectively [30,31].

We have observed two phonon modes for the SWNTs (spectrum a in Figure 5) that give strong Raman scattering including low-energy peaks which are attributed to a radial breathing mode (R band) at approximately 163 cm\(^{-1}\) and 177 cm\(^{-1}\), and the higher energy peaks, with neighboring C atoms, vibrating

<table>
<thead>
<tr>
<th>Band assignments</th>
<th>SWNTs</th>
<th>Poly(Th-TP)</th>
<th>SWNT-poly(Th-TP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring deformation</td>
<td>791</td>
<td>779</td>
<td>785</td>
</tr>
<tr>
<td>C-H in-plane bend</td>
<td>1026</td>
<td>1036</td>
<td>1023</td>
</tr>
<tr>
<td>Ring breathing</td>
<td>1203</td>
<td>1210</td>
<td>1198</td>
</tr>
<tr>
<td>C-H in-plane bend</td>
<td>1296</td>
<td>1298</td>
<td>1300</td>
</tr>
<tr>
<td>Ring breathing with contribution from C=C/C-C and C-N</td>
<td>1419</td>
<td>1430</td>
<td>1427</td>
</tr>
<tr>
<td>C=C/C-C stretching</td>
<td>1542</td>
<td>1550</td>
<td>1446</td>
</tr>
</tbody>
</table>

Table 1. Peak positions (cm\(^{-1}\)) of FTIR absorption bands for poly(Th-TP), SWNTs and SWNT-poly(Th-TP) composite.

![Figure 5. Raman spectra of: (a) SWNTs, (b) poly(Th-TP), and (c) SWNT-poly(Th-TP) composite samples measured by 514-nm laser source.](https://www.SID.ir)
out of phase and parallel to the surface of the cylinder (tangential modes, T band) are related to the $E_{2g}$ phonon at about 1555 cm$^{-1}$ and 1581 cm$^{-1}$ in graphite [32-34]. The band at 1336 cm$^{-1}$ appears only in the slightly disordered graphite (D band) [35]. A combination mode has also been observed at 1727 cm$^{-1}$ [36].

The spectrum c in Figure 5, the Raman spectra are shown for the SWNT-poly(Th-TP) composite, and they are clearly identical to those of poly(Th-TP) and SWNTs, demonstrating that the SWNTs serve as the core in the formation of SWNT-poly(Th) nanotubular composites. For instance, the so-called T band centered at 1581 cm$^{-1}$ and R band of low-energy peaks (163 and 177 cm$^{-1}$) dominate the nanotubes spectra. On the other hand, the peaks at 1044 and 697 cm$^{-1}$ demonstrate the effects of poly(Th-TP) spectra. Consequently, this result further confirmed that the poly(Th-TP) layer was deposited within the network of the SWNTs.

XRD patterns of SWNTs, poly(Th-TP) and SWNT-poly(Th-TP) composite were depicted in Figure 6. The pure SWNTs have characteristic peaks at 23.4°, 44.1°, and 51°, which are in good agreement with other reports [37]. In contrast, no peaks (broad pattern) were observed in the spectrum of poly(Th-TP), amorphous diffraction peak at approximately $2\theta = 20-24^\circ$, suggesting an amorphous structure of the polymer prepared by in-situ oxidative polymerization. A peak centered around 22°, corresponding to intermolecular $\pi-\pi$ stacking [38]. For the SWNT-poly(Th-TP) composites, the XRD data show characteristic poly(Th-TP) broad peaks and strong SWNTs peaks. There are, however, no new peaks.

UV-Vis spectroscopy was used to observe the interfacial interaction between poly(Th-TP) and SWNTs. Figure 7 shows the UV-Vis spectra of SWNTs, SWNT-poly(Th-TP) composite, and bulk poly(Th-TP) in tetrahydrofuran (THF) solutions. For the SWNTs, there is no absorption peak in the 350-800 nm range. The characteristic absorption band of poly(Th-TP) at approximately 441 nm is attributed to the transition from the valence bond to the antibonding polaron state ($\pi-\pi^*$ electronic transition), indicating that the resultant poly(Th-TP) is in the doped state [39]. When the tubular nanostructure of SWNT-poly(Th-TP) is formed, the characteristic broad peak is slightly shifted to a higher wavelength (463 nm) as the SWNTs content loads inside close packing by poly(Th-TP), revealing the interaction possibility between the quinoid rings of poly(Th-TP) and the $\pi$ transition of SWNTs [40].

This could be described by the percolation theory...
as the insulator-to-conductor transition in composite made of conductive filler in an insulating matrix [41].

TGA curves of SWNTs, poly(Th-TP) and SWNT-poly(Th-TP) composite has been exhibited in Figure 8 upon heating in a nitrogen atmosphere. The SWNTs are comparatively more stable in the range of 25-800°C. It can be seen that SWNTs were stable and did not show a dramatic decomposition in the tested temperature range. A small amount of weight loss occurred due to water or volatile impurities evaporation.

In the case of poly(Th-TP), the TGA curve shows a weight loss at two stages as shown in curve c of Figure 8. The first stage ranges between room temperature and 100°C, may be attributed to the loss of adsorbed and bound water. The second stage of weight loss starts at about 230°C for poly(Th-TP) that could be due to the large scale thermal degradation of the poly(Th-TP) chains. Addition of SWCNTs to the poly(Th-TP) increased the thermal stability of poly(Th-TP) between 25 and 500°C around 6% mass loss (comparing curves b and c of Figure 8). Also, the remained mass of the composite is higher than that of poly(Th-TP) itself at temperatures higher than 400°C which was obviously related to the existence of thermally stable SWNTs.

As a result, these data confirm that the presence of SWNTs in the SWNT-poly(Th-TP) composite is responsible for the high thermal stability of the composite material in comparison with pure poly(Th-TP). For instance in comparison with TGA data of Karim et al. [42] the thermal stability of our composite in the presence of TP is improved.

It is well-known that the electrical conductivity of any material depends on the carriers’ concentration and mobility. In conducting polymers (CPs) carriers (polaron and bipolaron) concentration is determined by the level of oxidation or doping. Alternatively, the carrier mobility depends on the frequency of interchain hopping. Therefore, it is related to the conjugation length and the interchain distance.

As a consequence, any method of synthesis of CPs that enhances molecular and super molecular order leads to an increase in carrier mobility and enhances electrical conductivity. We believe that increased mobility and conductivity can further improve the performance of the electronic device. Thus, introduction of CNTs into a polymer matrix can improve the electric conductivity as well as the mechanical properties of the original polymer matrix [43-45] while it possibly provides an additional active material for capacitive energy storage.

How CNTs enhance the electrical conductivity of the composite may be attributed to two reasons. One reason is the introduction of effective conducting paths to polymeric matrix [7,28]. The other reason is a good interfacial combination between CNTs and matrix. A powder sample of 0.02 g was loaded and pressed into a pellet of 1.2 cm diameter and at 170 atm of pressure by a manual hydraulic press for 10 min. The electrical conductivity measurements of SWNTs, poly(Th-TP) and SWNT-poly(Th-TP) composite were carried out using a four point-probe apparatus at the room-temperature.

The conductivity of the resulting SWNT-poly(Th-TP) composite, at room temperature, is 38 S cm⁻¹, which is higher than that of the pure poly(Th-TP) (1.67×10⁻¹ S cm⁻¹) synthesized without CNTs under the same conditions. The obtained conductivity of our composite in the presence of TP is approximately 90 times of the one previously reported in the absence of TP [42]. For each of the conductivity values reported, the results are an average of five measurements.

A different behaviour is observed for the SWNT-poly(Th-TP) composite which in any case, exhibits a
higher conductivity than the pure polymer. Moreover it is clear that, whether chemically treated or untreated, SWNTs are found to enhance charge transport and electrical properties of the composite significantly depending on the treatments to which the SWNTs were undergone.

The CNTs may also serve as "conducting bridges" connecting the conducting domains of poly(Th-TP). Such enhanced conductivity of polymeric chains, due to an increased degrees of electron delocalization and CNT bridging, has been reported for macroscopic PAN/CNT [46] and PPy/ CNT [47] films. The one-dimensional structure of CNTs may also induce and promote oriented polymerization, hence yielding an enhanced supramolecular order and higher conductivity.

CONCLUSION

We have developed a new composite of SWNTs and conducting poly(Th-TP). The composite SWNT-poly(Th-TP) has been synthesized successfully by the in situ chemical oxidative polymerization method of the thiophene monomer in the presence of TP onto SWNTs. The characterization of the molecular structure has indicated that thiophene and TP molecules are adsorbed onto the surface of SWNTs, and then polymerized. Thus SWNTs have been used as the core in the formation of hybrid SWNT-poly(Th-TP) composite. The conductivity through SWNT-poly(Th-TP) is as large as 38 S cm⁻¹ which is much larger than the usual value of bulk poly(Th-TP) films (~1.67 ×10⁻¹ S cm⁻¹). The SWNT-poly(Th-TP) composite shows improved thermogravimetric stability in comparison with the poly(Th-TP). Consequently, the improvements made in the various physical properties of SWNT-poly(Th-TP) composite are paving the way for enhancement in the application potential of conducting poly(Th-TP) without hampering its chemical properties. The conductivity and thermal behaviour of composite have been improved in comparison with other similar composite. The method described here may be utilized in developing new applications for SWNT-poly(Th-TP) composite in molecular electronics and other fields.

ACKNOWLEDGEMENT

The authors wish to thank University of Tabriz for all the supports provided. We would like to thank Mr. A. Haddadpour for his kind cooperation.

REFERENCES


