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SHORT COMMUNICATION

Surface functionalization of multiwalled carbon nanotubes with poly(3,4-propylenedioxythiophene) and preparation of its random copolymers: new hybrid materials

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Abstract Multiwalled carbon nanotubes (MWNTs) were functionalized with poly(3,4-propylenedioxythiophene) (PProDOT) using a simple “chemical grafting” approach. After the conventional acid oxidation (AO) process, the MWNT-COOH was converted to the acyl chloride functionalized MWNTs (MWNT-COCl) by treating them with thionyl chloride. The MWNT-COCl were further reacted with a functionalized monomer based on 3,4-propylenedioxythiophene (ProDOT-OH), followed by oxidative polymerization to prepare the MWNT-*g*-PProDOT hybrid. The monomer-functionalized MWNTs was further copolymerized with thiophene to prepare conducting copolymers on carbon nanotubes (CNTs). Fourier-transformed infrared spectrophotometry was employed to characterize the change in surface functionalities, which revealed that the PProDOT was covalently grafted to the MWNTs, while TGA was used to study the weight gain due to the functionalization. UV–Vis absorption spectra revealed the functionalization of the conjugated polymer by showing the typical absorption band. The morphology micrographs of the grafted PProDOT on MWNTs as evidenced by field emission scanning electron microscopy and transmission electron microscopy showed apparent effect on the structure and appearance of the MWNTs by growing thicker as expected from surface modification. Using the facile route developed in this study, CNTs can be easily fabricated with other types of polymers for several applications.

Keywords Carbon nanotubes · Conjugated polymer · Grafting · Modification · Nanocomposites

Introduction

Ever since their observation, carbon nanotubes (CNTs) have been widely recognized as quintessential nanomaterials in most areas of science and technology [1]. The prospect of developing novel and new hybrid carbon-based materials and composites has excited immense attention among researchers. CNTs have quickly been proven to possess unique and unusual electronic, structural, and mechanical properties, which make them an ideal reinforcing material for polymer nanocomposites and many other engineering applications [2, 3]. However, a number of challenges must be met before nanotubes can be exploited for most of these envisioned applications. Typically, the poor dispersability and mechanical properties of CNTs in polymer matrices still fall short of their anticipated potential values. Considerable amount of research work is being focused on the interfacial molecular engineering of CNTs, aiming at improving their state of interaction with molecules in order to optimize the final properties of the hybrid nanomaterials [3, 4].

To date, two classes of main routes have been well established, including covalent sidewall grafting (linkage) and noncovalent mixing/adsorption (exohederal interactions), which generally provide access to such CNT–polymer composites [5, 6]. While the noncovalent approach includes surfactant modification, polymer wrapping, or polymer adsorption, the main disadvantage is that the forces between the wrapping molecules and the CNT are very weak due to the slippage of the stacked molecules. On the other hand, covalent functionalization of CNT is most frequently initiated by introducing carboxylic acid group,

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which enhance the compatibility between CNTs and the matrix polymer by directly grafting polymer chains onto the surface of the CNTs [7–12].

It is well recognized that the association of conducting polymers (CPs) with CNTs represents a new strategy to obtain composite materials possessing the properties of each component with a synergistic effect and showing great potential applications as supercapacitors, actuators, biosensors, electromagnetic shielding, and electronic devices [13]. A variety of CPs–CNT composites were also prepared with CPs such as polyaniline and its electrorheological application, polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS), etc., and are reported elsewhere and the references therein [14–18]. Most of these composites were prepared by in situ method, i.e., by simply mixing the monomer and CNTs, followed by usual chemical oxidative polymerization. The main drawback of this method is that most of the conjugated polymers are not compatible with CNTs, and thus the coatings are not always uniform. The formation of excess and unbound polymers during the reaction gives an additional task to separate them from the composites. Very recently, Philip et al. [19] used a different strategy to prepare polythiophene-based CP with CNTs by a covalent graft approach using post-polymerization functionalization method. However, to the best our knowledge, chemical functionalization of monomers with CNTs followed by polymerization to yield CP–CNT composites has not been reported yet. Recently, we reported the functionalization of MWNTs with a biomedically important polymer poly-HEMA [20].

In this study, we exploited the opportunity to graft a functionalized monomer based on 3,4-propylenedioxythiophene, namely, ProDOT-OH, with that of MWNTs, followed by polymerization to prepare MWNT-*g*-PProDOT nanocomposites. The presence of the free hydroxyl group makes ProDOT-OH the material of choice due to ease of derivatization. Furthermore, ProDOT-OH can be controllably synthesized in a single step [21]. Dietrich et al. [22] first reported that the conjugated polymers from ProDOT exhibit higher contrast in comparison to polymers from EDOT. The difference between ProDOT and EDOT is one extra methylene group in the cyclic structure. Based on this finding, very recently, Kumar and coworkers [23] have shown that polymers based on ProDOT are processable and highly efficient electrochromic materials. These materials are shown to have promising applications in optical materials, smart windows, and electrochromic displays. In addition, the monomer functionalized MWNTs were further copolymerized with thiophene to prepare tubular nanostructures coated with conducting copolymers on CNTs (MWNT-*g*-PProDOT-*co*-PTh).

Experimental section

Materials MWNTs with an average diameter and length of about 10–20 nm and 20 µm, respectively, were provided by Iljin Nanotech, Korea. 3,4-Dimethoxythiophene, thiophene and 1,1,1-tris(hydroxymethyl)ethane were purchased from Aldrich and used as received. Dry tetrahydrofuran (THF), toluene, and freshly distilled thionyl chloride (Duksan Pure Chemical, Korea) were used.

Purification and acid oxidation of MWNTs The as-purchased MWNTs were further purified in-house to remove impurities such as metallic catalysts present in it by exposing them to thermal treatment. Briefly, the raw soot was heated in air at 600 °C for 2 h, cooled, and soaked in hydrochloric acid for 2 h. Short-time acid treatment is not expected to cause severe structural damage or surface functionalization on MWNTs [15]. In order to remove the residues of the acid treatment, the mixture was diluted with distilled water and centrifuged. Upon centrifuging the suspension (4,000 rpm), the obtained precipitate was then rinsed repeatedly with deionized water until a neutral pH was achieved. Using a membrane filter system and a vacuum pump, the nanotubes mixture was filtered, washed, and completely dried in the vacuum oven for around 12 h at 40 °C. A flask charged with 1 g of the purified MWNTs was chemically functionalized by ultrasonification in a mixture of 3 M of concentrated sulfuric acid and 1 M of concentrated nitric acid (3:1) for 8 h. The acid-oxidized MWNTs were washed with deionized water, separated by centrifuging thrice, and further vacuum-filtered thoroughly using a filter paper until the pH of the filtrate became neutral. The solid was then dried under vacuum for 12 h at 40 °C to yield 0.8 g (~80%) of the carboxylic-acid-functionalized MWNT (MWNT-COOH). These acid treatments may shorten the length of the MWNT and introduce carboxylic acid and hydroxyl groups [24].

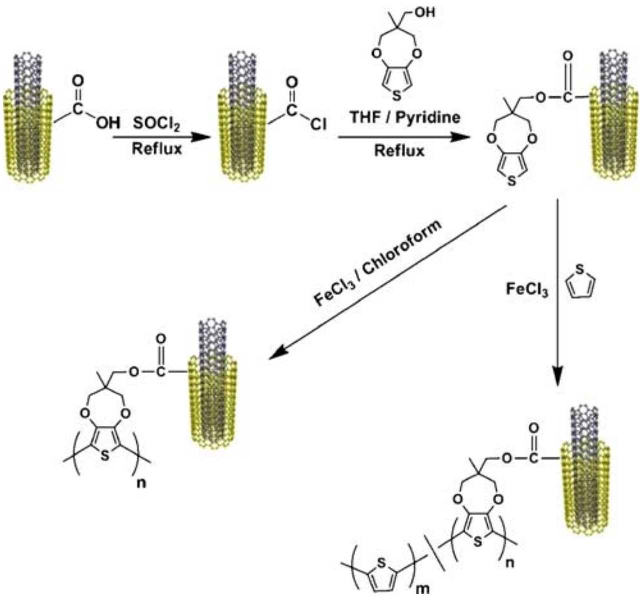
Synthesis of 3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4] dioxepin-3-yl)-methanol (ProDOT-OH) monomer In the presence of catalytic amount of *p*-tolylsulfonic acid in dry toluene, ProDOT-OH monomer was synthesized from 3,4-dimethoxythiophene and 1,1,1-tris(hydroxymethyl)ethane by a transesterification route by previously established method [21].

Functionalization of MWNT with ProDOT-OH (MWNT-f-ProDOT-OH) The acid-treated MWNT (MWNT-COOH; 0.5 g) was reacted with excess $SOCl_2$ (20 mL) for 24 h under reflux, and then the residual $SOCl_2$ was removed by reduced pressure distillation, subsequently dried under vacuum to yield the acyl chloride-functionalized MWNT

(MWNT-COCl). The prepared MWNT-COCl was added to 10 mL of anhydrous THF, and the mixture was sonicated for 20 min in order to create a homogeneous dispersion. The dispersed MWNT-COCl was immediately reacted in reflux with 0.170 g of ProDOT-OH dissolved in 5 mL of THF in the presence of catalytic amount of pyridine for 12 h under nitrogen atmosphere. The resulting reaction medium was dissolved in excess THF and vacuum filtered through a polytetrafluoroethylene membrane to yield MWNT-*f*-ProDOT-OH, which was subsequently dried overnight under vacuum.

Polymerization of MWNT-f-ProDOT-OH (MWNT-g-PProDOT) In a typical chemical oxidative polymerization process, 150 mg of the monomer functionalized MWNT (MWNT-*f*-ProDOT-OH) and 50 mg of the oxidant ($FeCl_3$) in 10 mL chloroform were reacted with stirring in argon atmosphere for 24 h. The reaction medium was then dissolved in excess chloroform and vacuum filtered to yield the MWNT-*g*-PProDOT hybrid.

Preparation of copolymers of MWNT-f-ProDOT-OH with thiophene (MWNT-g-PProDOT-co-PTh) Oxidative polymerization to form the copolymers of MWNT-*f*-ProDOT-OH was carried out as follows: 10 mL of a $CHCl_3$ solution containing 150 mg of the monomer functionalized MWNTs was sonicated for 30 min. $FeCl_3$ (50 mg) in 10 mL of $CHCl_3$ was added to the solution. Then, thiophene monomer (1 mL) with 10 mL of $CHCl_3$ solution was added dropwise to the suspension solution and stirred for 24 h. The resultant mixture was washed several times with methanol in order to remove the homopolymers, if any, vacuum filtered, and dried to yield MWNT-*g*-PProDOT-*co*-PTh.



Scheme 1 Strategy for the grafting of PProDOT and its copolymers with MWNT

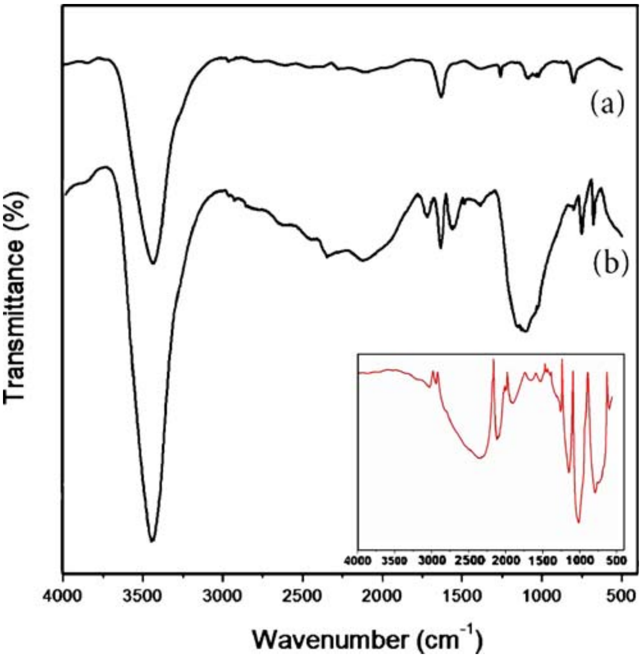


Fig. 1 FT-IR spectra of **a** pristine MWNT and **b** MWNT-*g*-PProDOT-*co*-PTh. *Inset* shows the spectrum of MWNT-*g*-PProDOT

Characterization and instrumentation Transmission electron microscopic (TEM) images were recorded using Joel Japan JEM 2010 instrument to observe the nanoscale structures of the MWNT-*g*-PProDOT hybrids. The morphology and elemental analysis of the polymer–CNT hybrids were carried out by using field emission scanning electron microscopy (FESEM) equipped with in situ energy dispersive X-ray (EDX) spectra (Hitachi, S-2700 model microscope, Japan). The changes in the surface chemical bondings of the MWNTs and the grafting behavior of the hybrid were recorded by Fourier-transformed infrared spectrophotometry (FT-IR, Perkin-Elmer Spectrum GX, USA). The absorption spectra of the hybrid randomly dispersed in ethanol were obtained using a Perkin Elmer Lambda 40 ultraviolet—visible (UV–Vis) spectrometer. Thermogravimetric analysis (TGA) was performed using Perkin-Elmer, Pyris 1TGA analyzer at a ramp rate of 10 °C min^{-1} under continuous nitrogen flow.

Results and discussion

The schematic illustration of the experimental procedure involving the grafting of PProDOT onto MWNT and the

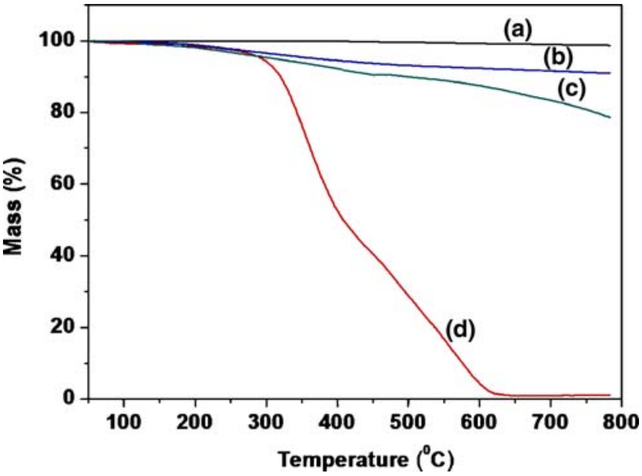


Fig. 2 TGA thermograms of **a** pristine MWNTs, **b** MWNT-*g*-PProDOT, **c** MWNT-*g*-PProDOT-*co*-PTh and **d** pure PProDOT-OH

copolymer formation is presented in Scheme 1. The changes in surface functionalities were obtained from FT-IR spectroscopy and presented in Fig. 1. A distinct difference between the pristine MWNT and the hybrid can be observed. Figure 1a shows the characteristic vibration bands of MWNTs, wherein a strong peak at 3,440 and 1,258 cm^{-1} can be attributed to the presence of hydroxyl groups (–OH stretching) on the surface of MWNTs, which could appear from ambient temperature moisture. Apart from the usual peak ascertained to the MWNTs, the hybrid showed characteristic peaks belonging to the thiophene present as seen in Fig. 1b. The vibrational peaks arising from the PProDOT at around 1,520 and 1,116 cm^{-1} correspond to the stretching of C=C and C–S in the thiophene ring. A sharp peak at around 1,630 cm^{-1} in both Fig. 1a and b can be attributed to the C=C stretch mode in the MWNTs, while the peak at 1,720 cm^{-1} in Fig. 1b corresponds to the C=O stretching mode of the ester linkage of the MWNT-*g*-PProDOT-*co*-PTh hybrids. Further vibrations from the C–S bond in the thiophene ring can be seen at around 797 and 674 cm^{-1}, respectively. Inset figure shows the IR spectrum of MWNT-*g*-PProDOT hybrid with all the characteristic peaks of polythiophene and the peaks attributable to MWNTs. Consequently, it can be confirmed that PProDOT is well coated on the MWNTs.

The amount of PProDOT attached to the MWNTs and the comparison of mass losses of MWNT, MWNT-*g*-PProDOT, and MWNT-*g*-PProDOT-*co*-PTh upon heating in nitrogen atmosphere is determined by TGA as shown in Fig. 2. The degree of functionalization from the gradual mass loss of the MWNT-*g*-PProDOT suggest that around 11 mass percent has been functionalized. Pristine MWNTs were more stable and did not show any dramatic decomposition in the temperature range of 70–800 °C. Upon functionalization, a gradual mass loss starting from 200 °C, with a major loss at around 450 °C, was noticed (Fig. 2b). This decomposition is ascertained to the PProDOT wrapped around the nanotube. In the case of the copolymer hybrid, MWNT-*g*-PProDOT-

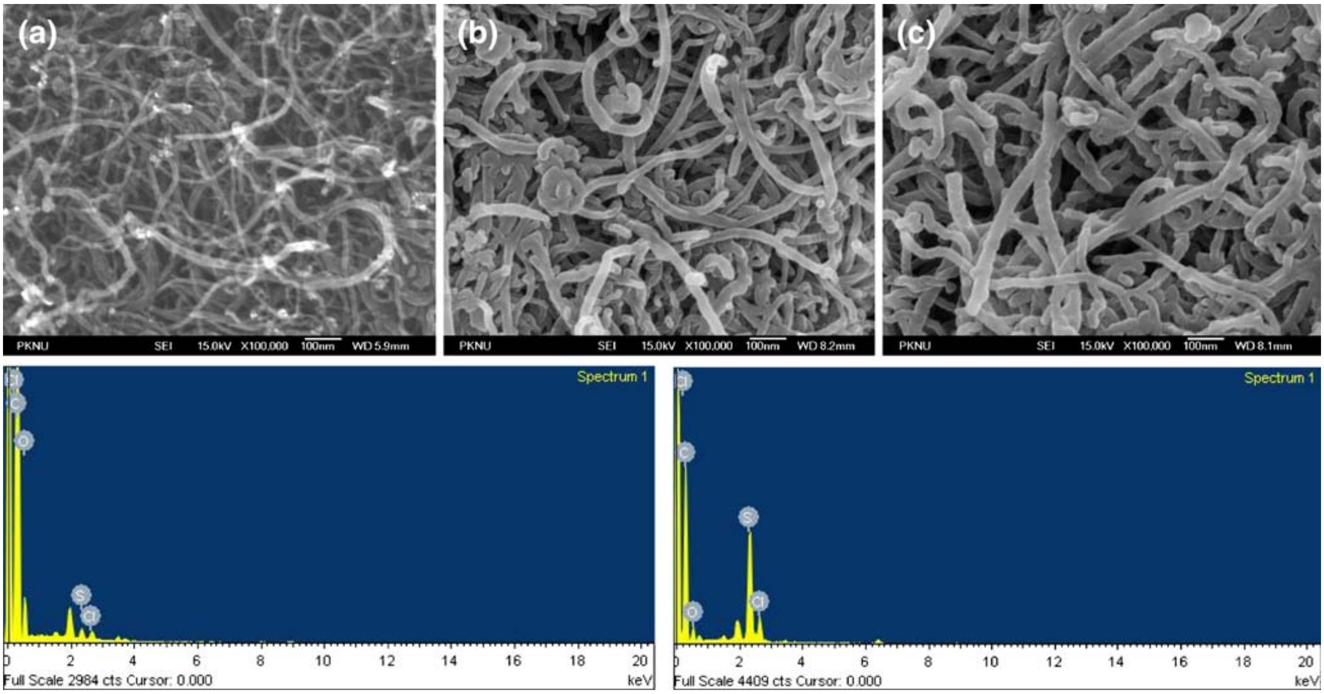


Fig. 3 FESEM images of **a** purified MWNTs and **b** MWNT-*g*-PProDOT and **c** MWNT-*g*-PProDOT-*co*-PTh. EDX images corresponding to **b** and **c** are shown

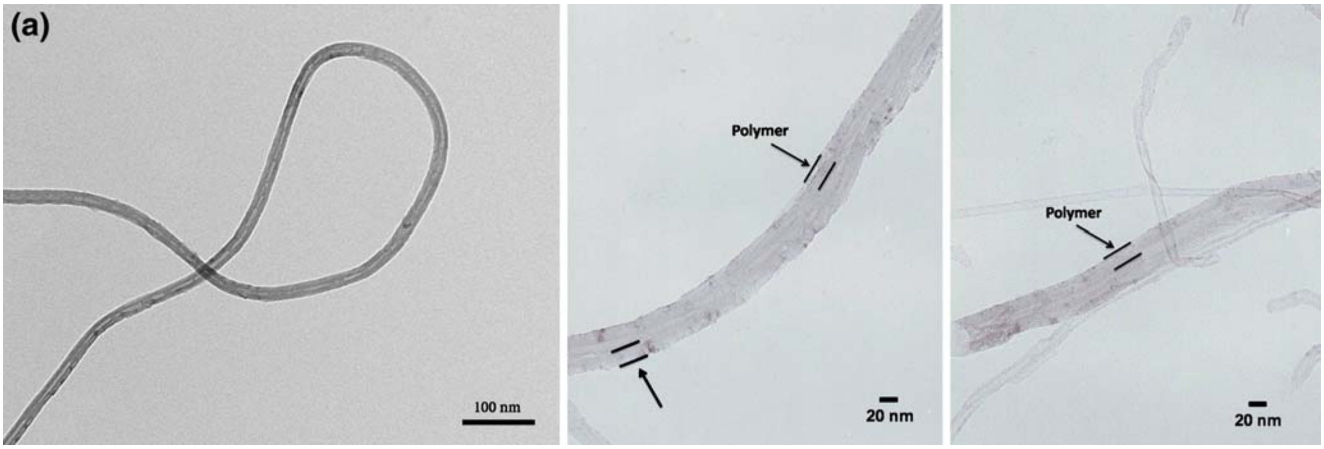


Fig. 4 TEM images of **a** MWNT-*g*-PProDOT (images at higher magnifications are shown below)

co-PTh, a stable and uniform decomposition is noticed at around 300 °C; thereafter, they decompose sharply when compared to the MWNT-*g*-PProDOT. The total mass loss is estimated to be around 24%, which is nearly more than double to that of MWNT-*g*-PProDOT. As a result, this decomposition behavior confirms the formation of copolymer hybrid, MWNT-*g*-PProDOT-*co*-PTh as seen in Fig. 2c. The decomposition curve of pure PProDOT is given in Fig. 2d, which shows an unsteady mass decrease up to 600 °C. This also suggests that the thermal stability of the hybrid material was better improved.

More evidence on the grafting has been collected from the morphologies by SEM and TEM images. The FESEM image in Fig. 3a shows well-dispersed oxidized tubes with little or no aggregation, and the tubes are loosely entangled. It is well known that HNO_3/H_2SO_4 mixture, as an oxidizing agent, creates open-end termini in the structure that are stabilized by –COOH and –OH groups left bonded to the nanotubes at the end termini and/or the sidewall defect sites. As seen, after the oxidation process, the tubes are open-ended to some extent due to the end cap cutting [25, 26]. However, after the polymerization process, the thickness of the tubes increased with an increase in surface roughness. Clearly, the polymer and copolymer formation is visible, thus covering the tube walls as seen in Fig. 3c and d, respectively. In order to understand the chemical composition of the hybrids viz., MWNT-*g*-PProDOT and MWNT-*g*-PProDOT-*co*-PTh, EDX analysis was done. The results confirmed the presence of sulfur, which can be attributed to the presence of thiophene. The only significant difference from the hybrid and its copolymer is the amount of sulfur, which was high in the latter compound, thus

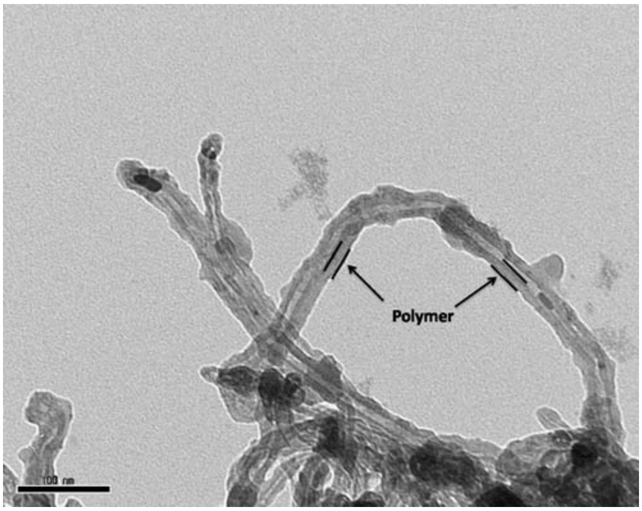


Fig. 5 TEM image of MWNT-*g*-PProDOT-*co*-PTh

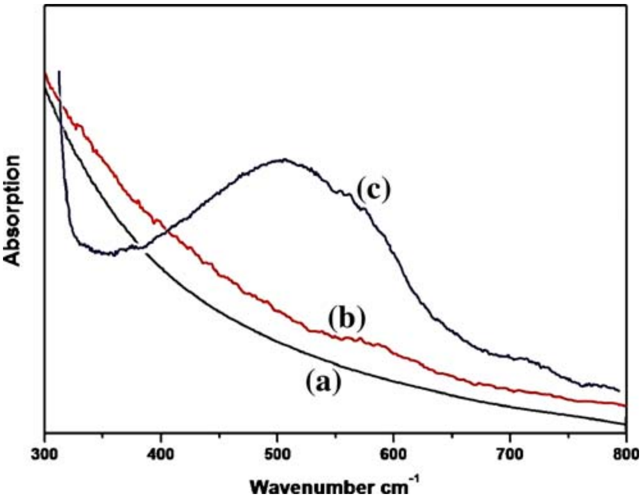


Fig. 6 UV–Vis absorption spectra for **a** crude MWNTs **b** MWNT-*g*-PProDOT and **c** MWNT-*g*-PProDOT-*co*-PTh

suggesting the copolymer formation as shown in the corresponding EDX graphs to SEM images. To give a further insight on the tubes morphology, typical TEM images of PProDOT-grafted MWNTs obtained are shown in Fig. 4. The images reveal the coaxial structure of the resulting hybrid in which the MWNT is encapsulated by a few-nanometer-thick layer of PProDOT. The surface of the tube appears to be grown well with increased thickness. There is a clear vicinity of MWNT core with a crystalline lattice structure and a fine discontinuous coating of an amorphous polymer layer around the tubes. Figure 5 represents the image of the copolymer hybrid, MWNT-*g*-PProDOT-*co*-PTh. These images well correlate with the FESEM results obtained, thus proving the grafting of PProDOT onto the MWNTs. In addition, the UV–Vis spectroscopy supports a significant interfacial interaction between the copolymer hybrid and MWNTs as shown in Fig. 6. The UV–Vis spectrum of copolymer hybrid randomly dispersed in ethanol shows that an absorption maximum at around 440–500 nm is attributable to the characteristic absorption band of polythiophene, also suggesting the formation of copolymer on the tube walls. Weak absorption is seen in the case of MWNT-*g*-PProDOT. This behavior can be attributed to the less composition of the sulfur content on the surface, which is also explained by the EDX results.

Conclusions

In conclusion, a facile way to graft ProDOT-OH monomer onto functionalized MWNTs followed by oxidative polymerization is demonstrated. FT-IR and TGA data verify that the surface modification of MWNT by a “chemical grafting” approach was indeed successful. The characterization of the CNT/polymer hybrid by microscopic images revealed the fine polymer grafted to the tubes. These hybrids showed improved thermal stability. This strategy is versatile and can be applied to a number of other polymers. Due to the wide role and importance of PProDOT in electrochromic devices and semiconductor industries, these hybrids are expected to have practical and great potential applications for high-performance devices. Further improvements in making block copolymer nanostructures are in progress.

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