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Novel approaches to developing carbon nanotube based polymer composites: fundamental studies and nanotech applications

Luca Valentini, Josè M. Kenny*

Materials Science and Technology Center, University of Perugia, INSTM, UdR Perugia, Loc. Pentima Bassa 21, 05100 Terni, Italy

Abstract

The adsorption of several types of conducting polymers on carbon nanotubes is investigated by electrical transport measurements. We report the optoelectronic properties occurring in single-walled carbon nanotubes (SWNTs) conjugated polymer, poly(3-octylthiophene), composites. Al/polymer-nanotube composite/indium–tin oxide diodes show photovoltaic behavior proposing that the main reason for this increase is the photoinduced electron transfer at the polymer/nanotube interface. Interesting results were obtained in the case of poly(*o*-anisidine) (POAS)-multi-walled nanotubes (MWNTs) composites where the increment of monolayers results in a significant improvement of the specific conductivity. POAS-coated MWNTs thin films demonstrated their potentiality as a new class of materials for inorganic vapors detection for environmental applications.

Keywords: Polymer composite materials; Polymer physical chemistry

1. Introduction

Compared to various other nanostructures (both organic and inorganic), carbon nanotubes (CNTs) are emerging as novel, very promising materials [1–5] because of their exceptional properties, such as those related to electron transport and superconductivity which, in combination with extraordinary mechanical properties, allow in principle for the development of innovative devices in several applied fields.

However, due to their physico-chemical and geometric characteristics, carbon nanotubes are obviously insoluble in any solvent and hybrid functional materials based on CNTs-polymer matrix for photovoltaic devices based on soluble conducting polymers have attracted a great deal of attention.

Replacing the single layer diodes with a heterojunction consisting of a conductive polymer and CNTs would allow a significant increase of the photogeneration efficiency of charges. In fact CNTs can offer the potential for photovoltaic elements as electron acceptor increasing the charge generation in conjugated polymers. Besides, the CNTs extremely low optical gap should guarantee high levels of electron emission. So CNTs may be embedded in polymer matrices, and used to modify electronic properties of the composite.

On the other hand, molecular adsorption effects to the electrical properties of CNTs are of fundamental interest for nanotube molecular electronics and sensors [6]. It is known how the conductivity of semiconducting nanotubes changes due to charge transfer caused by adsorbed molecules. Charge transfer between nanotubes and adsorbed oxidizing or electron donating molecules can increase or decrease hole carriers in semiconducting tubes, thus significantly affecting the electrical conductance [6]. On the basis of this observation, increasing attention is being focused on the interface between the CNT and surrounding polymer matrix for gas sensing applications.

In the present work, we report the extension of the above methods to various families of conductive polymers (PC) believed suitable for the preparation, characterization and performance evaluation of specific CNT/PC composites for photovoltaic [7–11] and gas sensing applications.

2. Experimental section

Two categories of materials have been used: SWNTs obtained from CarboLex, Inc. and multi-walled carbon nanotubes (MWNTs) obtained by pulsed radio frequency

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* Corresponding author. Tel.: +39 744 492939; fax: +39 744 492925.
E-mail address: kenny@unipg.it (J.M. Kenny).

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plasma enhanced chemical vapor deposition (RF-PECVD) [12].

Conducting polymer (poly(3-octylthiophene) (P3OT)) was doped using a method reported previously [13]. Briefly, P3OT dissolved in $CHCl_3$, was introduced to a round-bottomed flask. The flask was connected to a rotating evaporator to remove $CHCl_3$ in order to obtain P3OT as a thin film. The P3OT film and 200 mg of K were transferred to a round-bottomed flask and several vacuum-Ar cycles were carried out, the last being vacuum. The flask was immersed in a thermostatic oil bath (433 K). After 96 h, it was cooled to room temperature and the film was removed from the flask. The SWNT powder was suspended by sonication in chloroform. Then, they were blended (0.5 wt%) with K-doped P3OT and sonicated for 1 h.

UV–visible spectra were obtained in the light range of 200–1000 nm. Atomic force microscopy (AFM) measurements were performed to evaluate the surface morphology of the films using the contact mode technique.

Organic films were deposited by spin coating from a chloroform solution onto a glass substrate coated with indium–tin oxide (ITO). Aluminium electrodes were thermally evaporated. The devices were tested under dark and illuminated (AM 0) conditions through the glass/ITO side.

Patterned MWNTs film was obtained by pulsed RF-PECVD deposition on Si_3N_4/Si substrates as previously reported [12]. Poly(*o*-anisidine) (POAS)-MWNTs nanocomposite was chemically synthesized by oxidative polymerization of the monomers in the presence of a dispersion of MWNTs in HCl 1 M by using $(NH_4)_2S_2O_8$ under controlled conditions as reported elsewhere [14].

Thus, different numbers of monolayers (1, 10, and 30) of both the material were deposited onto glass substrates by using the LS technique [14,15]. For gas sensing measurements a POAS film (30 monolayers) was then deposited onto the planar resistor coated with CNTs.

3. Results and discussion

The absorption spectra of K-doped P3OT and K-doped P3OT/SWNT 80 nm thick films are shown in Fig. 1. Both films were 80 nm thick. An absorption maximum at 520 nm was observed for K-doped P3OT. Upon nanotube incorporation, the intensity of this band decreased and a new band appeared at 470 nm. Given that K-doped P3OT/SWNT show a blue shift, it might be reasonable to assume that a significant ground state interaction is taking place between the two materials. These results could be explained by a gradual increase in the lattice spacing of the π-stacked polymer chains, as reported elsewhere [16].

Fig. 2 shows the AFM images of K-doped P3OT and K-doped P3OT/SWNT films on ITO. For the blend device (Fig. 2(b)) we can see an aggregate in which we observe a large amount of SWNTs organized in bundles. If we compare Fig. 2(a) and (b), these micrographs show evidence that the polymer was adsorbed on the nanotube bundles.

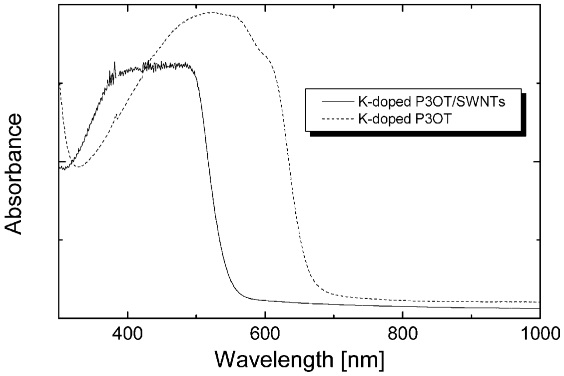

Fig. 1. UV–vis absorption spectra of K-doped P3OT and K-doped P3OT/SWNTs films.

The photovoltaic behavior of the fabricated device is reported in Fig. 3. From this figure, it is clear that K-doped P3OT sample is not sensitive to light and thus no photovoltaic behavior was detected. On the contrary, when

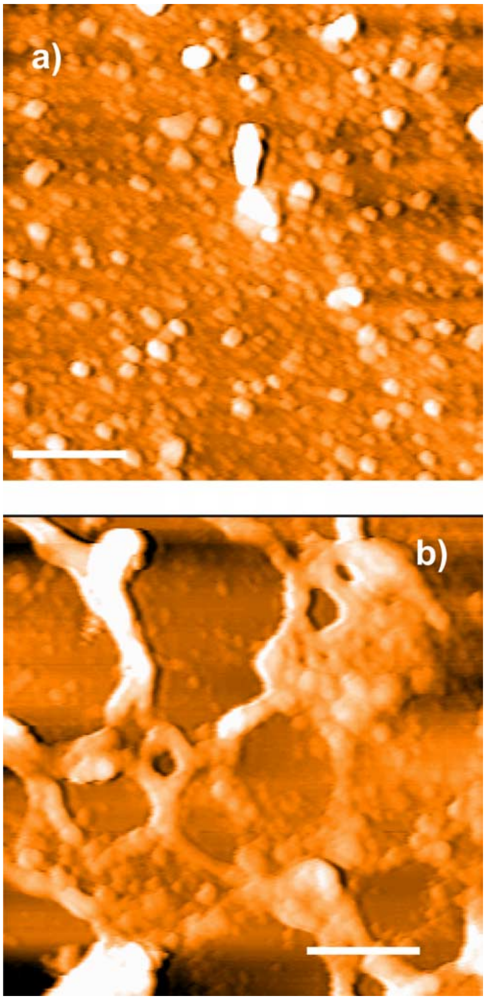

Fig. 2. AFM images of K-doped P3OT and K-doped P3OT/SWNTs films. Scale bar: 8 μm.

K-doped P3OT/SWNTs sample is exposed to the light, the reverse bias current increases. The photovoltaic parameters, such as the open circuit voltage (V_{OC}), short circuit current (I_{SC}) have been obtained from the *I–V* curves. The V_{OC} and I_{SC} of the K-doped P3OT/SWNTs sample when exposed to light is about 0.25 V and 1.3×10^{-9} A cm^{-2} with the fill factor of 0.26. These findings together with the AFM analysis (see Fig. 2b) propose that the photovoltaic effect could be attributed to the formation of internal polymer/nanotube junctions, which act as an interface creating a continuous pathway for the electrons to be efficiently transported to the negative electrode.

Fig. 4 shows the results obtained from the specific conductivity measurements of POAS and POAS-MWNTs nanocomposite in the undoped (in air) and doped (exposed to HCl) forms, respectively. When the thickness of the POAS undoped film increases, the electrical conductance decreases as expected for an insulating layer in the undoped form. The presence of MWNTs in the polymeric matrix increases the conductivity. In the case of POAS doped no changes of the conductivity was detected. On the contrary the increment of POAS-MWNTs monolayers results in a significant improvement of the specific conductivity. In this case, the MWNTs seems to have close interactions with the conducting mechanism of the polymer demonstrating that the polymeric chains are not only physically wrapped around the MWNTs.

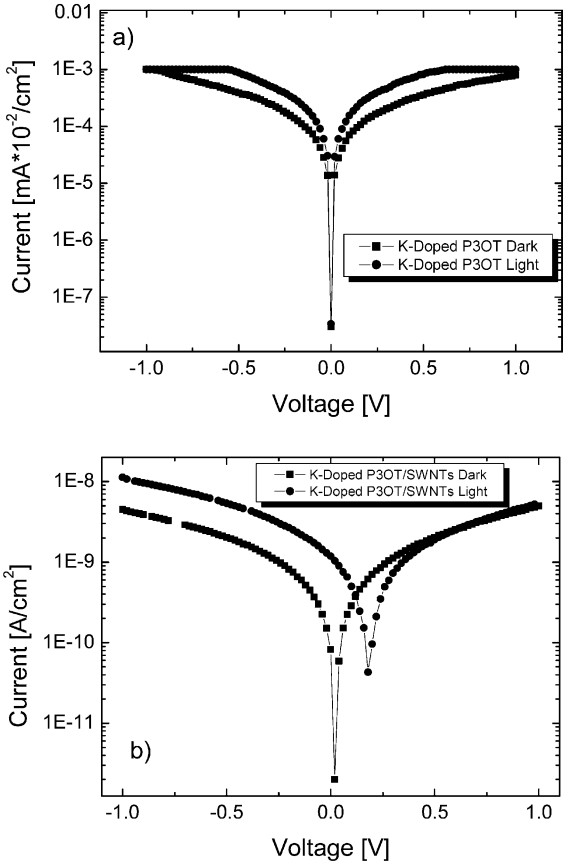

Fig. 3. (a) *I–V* characteristics of an ITO/K-doped P3OT/Al device in dark and under illumination. (b) The same data for an ITO/K-doped P3OT/SWNTs/Al device.

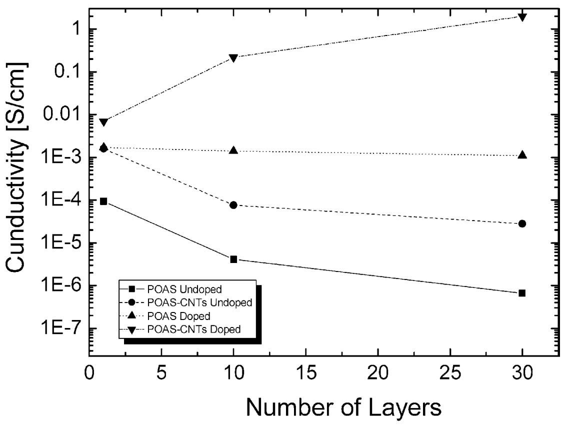

Fig. 4. Specific conductivity parameters of POAS and POAS-CNTs composite LS films as a function of different numbers of layers.

It was observed [14] that the conductivity varies for the device when exposed to HCl. In particular, the gas sensitivity increases from 3.0% for bare MWNTs to 27.9% for POAS coated MWNTs [14]. Regarding the reversibility of the conductivity variation, it should be mentioned that sensing process is not completely reversible due to the hysteresis effect known as secondary doping. This issue will be object of further investigation. Nevertheless, as preliminary investigation the obtained results reveal that by selecting proper polymer functionalization sensor sensitivity to molecular species and their recognition in gases or in solutions may be improved.

4. Conclusion

The nanostructured functional carbon nanotubes-based materials will allow to develop miniaturized devices and intelligent materials. The results show that the conjugated polymer-SWNTs composite represents an alternative class of organic semiconducting material that can be used to manufacture organic photovoltaic cells and gas sensing devices with improved performance.

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