

Interaction of oxygen with nanocomposites made of *n*-type conducting polymers and carbon nanotubes: role of charge transfer complex formation between nanotubes and poly(3-octylthiophene)

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Abstract

Photo-induced conductivity changes in *n*-doped poly(3-octylthiophene) (P3OT)/single-walled carbon nanotube (SWNT) composites have been examined. When exposed simultaneously to ultraviolet (UV) light and oxygen, carbon nanotubes exhibit photo-induced oxidation. An analysis of *n*-doped P3OT/SWNT composite exposed to oxygen/UV shows that conductivity increases and that charge carrier mobility is governed by the formation of a charge transfer complex. Possible sites of oxygen photoadsorption and its implications on the observed electrical properties of nanocomposite are considered.

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1. Introduction

The unique electronic and mechanical properties of nanotubes [1] have shown a lot of potential for a vast range of applications, including quantum wire [2] tips for scanning probe microscopy [3] and molecular diodes [4]. Recently, much attention has been paid to the use of nanotubes in composite materials so as to harness their exceptional mechanical [5] and electronic [6,7] properties. A wide range of host materials has been used, including polymers [8,9], ceramics [10] and metals [11]. Most recently, research [12,13] has focused on composites of electronically active conjugated polymers (CP) and carbon nanotubes, which demonstrate a number of advantages. Conjugated polymers incorporated with carbon nanotubes show potential for electronic device applications [14], promising to enhance the transport properties in these systems [15]. This is

thought to be a key issue for the realization of viable devices such as organic light-emitting diodes [15] and solar cells [16].

Moreover, conjugated polymers, in general, are *p*-type or *n*-type semiconductors. Some heavily *p*-doped polymers are very stable under ambient conditions, e.g., polypyrrole and polyaniline. Stable conjugated undoped or very slightly *p*-doped materials are also known, e.g., polythiophene. Until now, no *n*-type-doped conjugated polymers having similar stability have been found. The difficulty in attaining such materials is related to the well-known instability of organic anions which are easily oxidized in contact with air and water. Thus, *n*-doped CP/single-walled nanotubes (SWNTs) photoconductive response is interesting for a fundamental understanding of the *n*-doped CP/SWNT photo-induced processes and for the development of new photosensitive materials with unique optical and conductivity features. In light of the present need for photodegradation studies as well as for the exploration of such composites as photovoltaic material, we have explored and quantified the fundamental interaction

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between molecular oxygen and thin films of K-doped P3OT/SWNTs, using photoelectrical measurements and Fourier transform infrared spectroscopy (FTIR). Films of SWNTs and K-doped P3OT/SWNTs were exposed to constant ultraviolet (UV)/O₂ dosages at variable O₂ pressures and characterized in situ.

2. Experimental details

SWNTs were obtained from CarboLex and consisted of ≈ 50 –70 vol.% SWNTs produced using the arc discharge method and with a Ni–Y catalyst. This material was purified as reported elsewhere [17]. Furthermore, the presence of defect sites that were likely to occur in the as-grown nanotube sidewall were confirmed with Raman spectroscopy [17].

The poly(3-octylthiophene) (P3OT) was purchased from Sigma-Aldrich. P3OT (60 mg), dissolved in 25 ml of CHCl₃, was introduced to a 100-ml round-bottomed flask. The flask was connected to a rotating evaporator to remove CHCl₃ (the bath temperature was 318 K). Due to the rotation of the flask, P3OT was obtained as a thin film. The P3OT film (60 mg) and 200 mg of K were transferred to a 10-ml 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 added to chloroform, and a high-power ultrasonic probe was used to disperse the nanotubes. Then, they were blended (0.5 wt.-%) with K-doped P3OT and sonicated for 1 h. The K-doped P3OT/SWNT composite film was then deposited by drop and spin-coating onto Si₃N₄/Si substrates provided with platinum interdigital electrodes as reported elsewhere [18].

To characterize the temperature dependence of the electrical transport properties, SWNTs and an *n*-doped P3OT/SWNT composite deposited onto the electrodes were held in a LEYBOLD COLD-HEAD cryodyne refrigerator with the temperature that was controlled by a 1901 temperature controller. To check whether the presence of UV light and oxygen led to photo-induced conductivity changes in the SWNT and *n*-doped P3OT/SWNT composite, the electrical resistance was monitored for several on/off light illumination cycles as a function of exposure to oxygen/UV radiation with oxygen molecules that were injected in the resistance measurements system with a variable pressure ranging from 2×10^4 to 4×10^4 Pa. The electrical measurements were performed by fixing the temperature of the samples at 298 K.

Infrared transmission spectroscopy (IR) was performed in the air using an FTIR spectrophotometer in the 500–4000-cm⁻¹ range.

3. Results

Fig. 1a shows the time dependence of the electrical resistance of the SWNT sample maintained at 298 K and a pressure of 10^{-1} Pa. From the figure, it is clear that the resistance slightly increases when air is removed from the sample. After 200 min, the value of the resistance stabilizes. Starting from the outgassed sample, 2×10^4 Pa of oxygen was injected into the resistance measurement system. After oxygen injection, no resistance change occurred.

The electrical resistance of the SWNTs were then monitored as a function of exposure to UV radiation in oxygen. In Fig. 1b, electrical resistances for vacuum/UV-exposed and oxygen/UV-exposed SWNTs are plotted. When carrying out photoelectrical measurements in a 10^{-1} Pa vacuum, we observed that the conductance of the nanotubes dramatically decreased upon UV illumination and exhibited no appreciable recovery when the light was switched off (data not shown). These results are consistent with UV-light-inducing desorption of molecular oxygen from SWNTs [19]. However, the electrical resistance sign reverses when films were exposed to oxygen/UV light (Fig. 1b). The motivation for this part of the work was to determine whether the

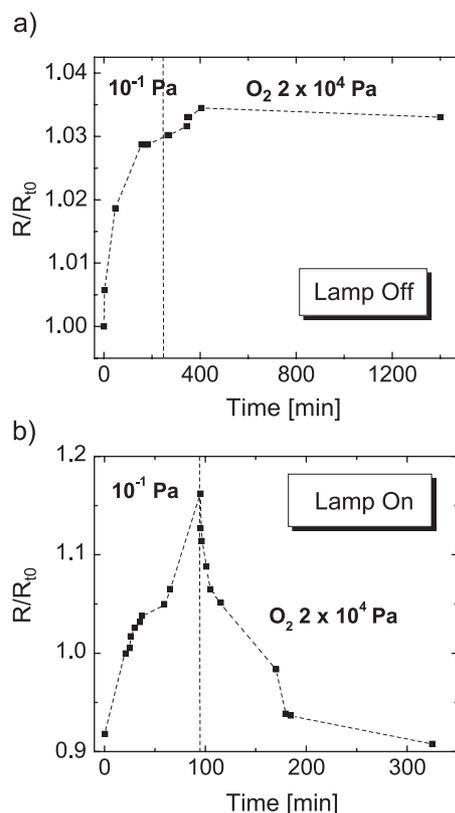


Fig. 1. (a) Evolution of the SWNT sample normalized resistance (R_{10} is the initial resistance of the sample) under exposure to 10^{-1} and 2×10^4 Pa of oxygen. (b) Evolution of the same sample normalized resistance (R_{10} is the initial resistance of the sample) under exposure to vacuum (10^{-1} Pa) and 2×10^4 Pa of oxygen in UV light. At the time, marked by the dashed vertical line, the sample was exposed to oxygen.

presence of UV light leads to photo-induced diffusion of oxygen in the SWNT films.

After this, the photoelectrical measurements were monitored as functions of vacuum and oxygen pressure in the K-doped P3OT sample (Fig. 2a). From the figure, it is clear that, when outgassing the sample, the resistance decreases. Starting from the outgassed sample, 2×10^4 and 4×10^4 Pa of oxygen was subsequently injected into the resistance measurement system, and, after injection, no resistance change was observed.

The typical photoelectrical responses of a K-doped P3OT sample for the on/off light illumination cycles in air, vacuum and oxygen are shown in Fig. 2b. Two features in the photoelectrical temporal behaviour are of interest: a high rise/decay of the photocurrent in response to the on/off illumination step and photodegradation when the sample was exposed to oxygen and air.

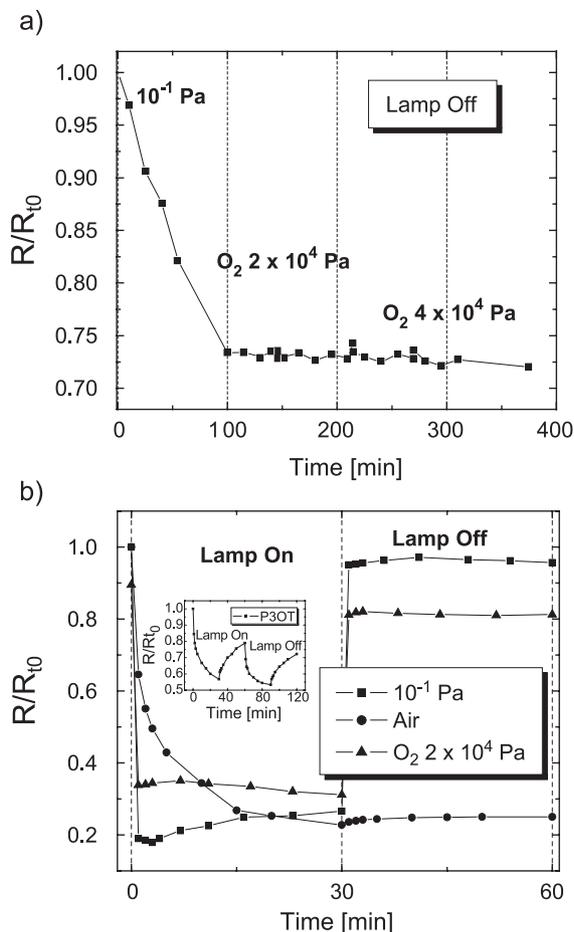


Fig. 2. (a) Evolution of the K-doped P3OT sample normalized resistance (R_{10} is the initial resistance of the sample) during exposure to vacuum (10^{-1} Pa), 2×10^4 and 4×10^4 Pa of oxygen. At the time, marked by the dashed vertical line, the sample was exposed to oxygen. (b) Temporal photoelectrical resistance response of the K-doped P3OT sample with on/off illumination steps in vacuum (10^{-1} Pa), air and 2×10^4 Pa of oxygen. The inset shows the temporal photoelectrical resistance response of the P3OT sample with on/off illumination steps in 2×10^4 Pa of oxygen.

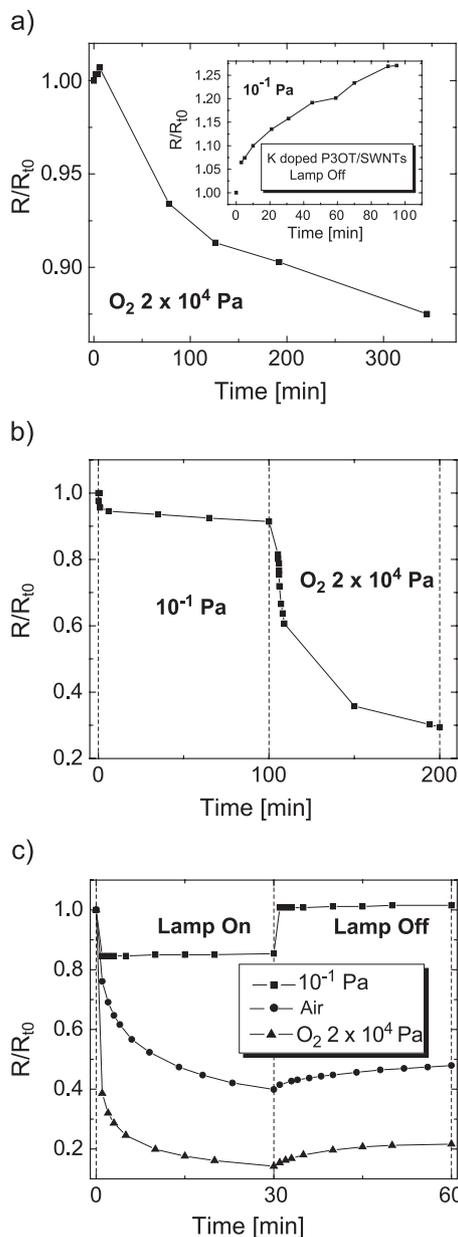
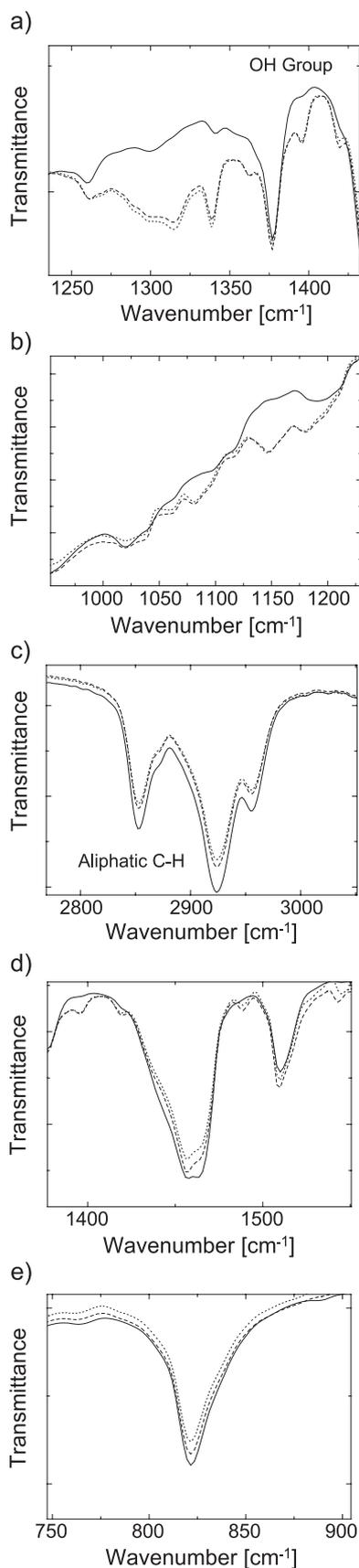


Fig. 3. (a) Evolution of the K-doped P3OT/SWNT sample normalized resistance (R_{10} is the initial resistance of the sample) during exposure to 2×10^4 Pa of oxygen in room light. The inset shows the evolution of the K-doped P3OT/SWNT sample normalized resistance during exposure to vacuum (10^{-1} Pa). (b) Evolution of the K-doped P3OT/SWNT sample normalized resistance during exposure to vacuum (10^{-1} Pa) and 2×10^4 Pa of oxygen in UV light. At the time, marked by the dashed vertical line, the sample was exposed to oxygen. (c) Temporal photoelectrical resistance response of the K-doped P3OT/SWNT sample with on/off illumination steps in vacuum (10^{-1} Pa), air and 2×10^4 Pa of oxygen.

Starting from the outgassed condition, we monitored the evolution of the K-doped P3OT/SWNT sample resistance while being exposed to oxygen. Fig. 3a depicts the resistance decrease from the beginning of the oxygen injection. In Fig. 3b, electrical resistances for the vacuum/UV-exposed and oxygen/UV-exposed K-doped P3OT/SWNT samples are plotted. From Fig. 3b, it turns out that



the composite's resistance decreases when the K-doped P3OT/SWNT sample is under vacuum (i.e., 10^{-1} Pa), with the amplitude of resistance variation similar to that observed in room light. On the contrary, for the oxygen/UV-exposed sample, the resistance rate decrease is markedly accelerated.

Fig. 3c shows the photoelectrical response of the composite for the on/off light illumination cycles in vacuum, air and oxygen. Two general observations can be made: the "on" current is increased upon oxygen exposure, and the photoelectrical response shows a relaxation time.

FTIR spectra of the K-doped P3OT and K-doped P3OT/SWNTs are reported in Fig. 4. The FTIR of the samples was monitored over a 60-min period of air/UV irradiation. Several features concerning the FTIR spectra of the K-doped P3OT sample should be noted: (I) The formation of relatively strong absorption bands at 1395 and 1370 cm^{-1} relating to the symmetric and asymmetric bending of the OH group [20] (Fig. 4a). (II) The formation of strong bands in the region 1260–1000 cm^{-1} , which indicate sulfine residues of the structure $\text{C}=\text{S}^+\text{O}^-$ or $\text{C}=\text{S}=\text{O}$. The 1090 and 1020 cm^{-1} bands are attributed to C=S stretching and S=O vibrations, respectively, of $\text{C}=\text{S}^+\text{O}^-$ [21–26]. Absorptions at 1226 cm^{-1} are characteristic vibrational modes of the alternate resonance structure, $\text{C}=\text{S}=\text{O}$ (Fig. 4b). (III) A decrease in the aliphatic C–H stretching peak in the region of 2900 cm^{-1} due to a loss in the alkyl side chain. This is considered to be direct evidence of the participation of the alkyl chain in the photochemistry of poly(3-alkylthiophenes) [20] (Fig. 4c). (IV) A decrease in the absorption bands, characteristic of interannular stretching modes (1460 cm^{-1}) and a decrease in the aromatic C–H out of plane deformation at 823 cm^{-1} (Fig. 4d–e). This is attributed to the disruption of the conjugated system [20].

The IR spectra of the K-doped P3OT/SWNT sample are reported in Fig. 5. In these spectra (Fig. 5a–b), we note that signals relating to new species on the composite's surface are not present, that is, the air-exposed composite has a spectrum similar to that of the sample under air/UV irradiation.

4. Discussion

The photo-induced oxygen adsorption on SWNTs may be explained in terms of changes in the surface electronic structure upon UV illumination, which are associated to the characteristic charge transfer properties of nanoscale carbon materials. The effect of O_2 adsorbed on the electrical resistance of SWNTs presented in Fig. 1 is fully consistent

Fig. 4. FTIR of a K-doped P3OT sample on KBr disks as a function of time of irradiation: (a) bending of the OH group; (b) C=S stretching and S=O vibrations of $\text{C}=\text{S}^+\text{O}^-$; (c) C–H stretching; (d) interannular stretching modes; (e) aromatic C–H out of plane deformation. Solid line: K-doped P3OT sample in air; dashed line: K-doped P3OT sample over a 30-min period of air/UV irradiation, Dotted line: K-doped P3OT sample over a 60-min period of air/UV irradiation.

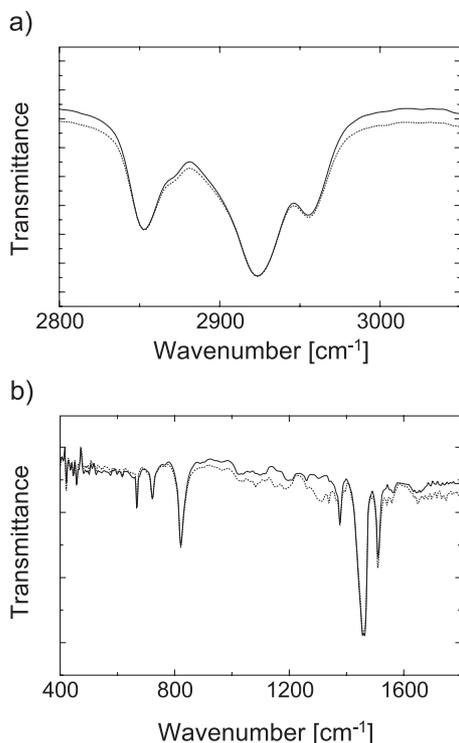


Fig. 5. FTIR of a K-doped P3OT/SWNT sample on KBr disks as a function of the time of irradiation: (a) 2800–3000 cm^{-1} region and (b) 400–1700 cm^{-1} region. Solid line: K-doped P3OT/SWNT sample in air, dotted line: K-doped P3OT/SWNT sample over a 60-min period of air/UV irradiation.

with theoretical calculations reported in Refs. [27,28]. In particular, the band structure and density of states results predict that O_2 molecules interact with nanotube lattice defects, giving rise to a significant charge transfer from the nanotubes to the O_2 molecules and that UV light excitation of the O_2 molecules to its singlet state give rise to a significant reduction of the activation energy for their chemisorption. Accordingly to the results reported in Refs. [27,28], in the case of a physisorbed spin-polarized (triplet) oxygen molecule, the charge transfer is negligible and cannot account for the experimentally observed effects attributed to oxygen absorption in the photoelectrical measurements. A stronger interaction, associated with chemisorption, must be invoked to account for the experimental data reported in Fig. 1. In particular, the existence of a possible chemisorbed activated singlet state for oxygen on nanotubes is confirmed by our experimental findings. Oxygen chemisorbs on the nanotube surface and effectively traps the local charges resulting from UV illumination.

An additional comment should be made on the role of potassium in the photo-induced oxidation process. It was established [29] that potassium dedoping occurs as a consequence of oxygen exposure leading to the formation of K–O species. On this regard, we observed that the photoelectrical response of a P3OT/SWNT sample for the on/off light illumination cycles in oxygen (data not shown) shows a lower rise/decay of the photocurrent in response to

the on/off illumination step. This, explained by a model in which the most important mechanism involved the strong change in the *n*-doped P3OT/SWNT film when the composite is submitted to O_2 and UV light excitation, is the modification of the density of states of the semiconductor nanotube surface during the exposition to O_2 , with the introduction of an impurity-like level near the onset of the valence band of the nanotube. A large number of interacting O_2 molecules act as a temporary *p* doping of the nanotube, and therefore the resistance of both the nanotube body and the intertube tunnelling barrier are lowered with respect to the unexposed nanotubes. Then, potassium donates electrons to the nanotube rope, thus, if this concurs with the oxidation process, electrons are captured by oxygen, and the remaining photoholes become major photocarriers.

Moreover, it is well established that singlet oxygen undergoes addition to polymers that possess double bonds. The product is a hydroperoxide, which, upon photolysis, initiates an autocatalytic chain reaction leading to chain scission [30]. It is postulated that photochain scission of K-doped P3OT occurs via the hydroperoxide route in as much as the number of double bonds in the polymer is large and thiophenes are efficient singlet oxygen photosensitizers. This is supported experimentally by the marked dependence of the photoelectrical yield on the loss of the reversibility of the on/off illumination cycles only in the presence of oxygen.

The observation that, for the K-doped P3OT/SWNT, a photoconductive relaxation time was observed is consistent with the average singlet oxygen diffusion time inside the polymer film reported elsewhere [31].

5. Conclusions

These studies show how oxygen interacts with *n*-doped P3OT/SWNT thin films by inducing a charge transfer complex with SWNTs. Our experimental findings performed on SWNTs suggest that oxygen forms a charge transfer complex with SWNTs. The charge transfer complex is largely responsible for the generation charge carriers in semiconducting *n*-type conjugated polymer/SWNT composite exposed to oxygen; that is, the photoconductivity of the composite increases with oxygen pressure. These composites act as both the amplifying and sensing medium; thin-film transistors using poly(3-alkylthiophenes)/SWNTs might prove to have interesting oxygen-sensor applications.

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