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Optical properties of single-walled carbon nanotubes functionalized with copolymer poly(3,4-ethylenedioxythiophene-co-pyrene)

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ABSTRACT

Optical properties are reported for composites based on single-walled carbon nanotubes (SWNTs) and copolymer poly(3,4-ethylenedioxythiophene-co-pyrene) (PEDOT-Py) prepared by chemical polymerization of two monomers in the presence of carbon nanotubes. A charge transfer between SWNTs and the PEDOT-Py copolymer was demonstrated by Raman scattering. The increase in the relative intensity of the Raman lines peaked at 440–577 cm^{-1}, which were assigned to the ethylenedioxy ring vibrational modes, indicated a significant hindrance steric in the case of the composites based on the PEDOT-Py copolymer and metallic SWNTs. The increase in the absorbance of IR band peaked at 984 cm^{-1} occurred simultaneously with the disappearance of the IR band at 1639 cm^{-1}. This finding was a consequence of the formation of new covalent bonds between SWNTs and the thiophene and benzene rings of the repeating units of the PEDOT-Py copolymer. The photoluminescence (PL) quenching process of the PEDOT-Py copolymer was induced by semiconducting SWNTs. The PL quenching of PEDOT-Py copolymer in the presence of SWNTs was demonstrated based on the energy level diagrams of the two constituents of the PEDOT-Py/SWNTs composite material.

1. Introduction

The use of copolymers having repeating units based on monomers carbazole –pyrene [1], fluorine-pyrene [2], 3,4-ethylenedioxythiophene – pyrene [3], 2, 2'-bithiophene – pyrene [4,5] and benzothiadiazole – pyrene [5,6] as light-emitting materials has been developed since 2006. The synthesis methods often used for these copolymers consist of chemical [1,2,7] and electrochemical polymerization [3–6,8]. Recently, a sustained effort was focused on the functionalization of single-walled carbon nanotubes (SWNTs) with such copolymers as poly(3,4-ethylenedioxythiophene)-block-poly(ethyleneoxide) (P-PEDOT-b-PEO) [9] and poly (2, 2'-bithiophene-co-pyrene) (PBTh-Py) [7,8] in order to develop new applications in flexible transparent conductive devices, biological sensors and energy storage. To determine the interfacial interactions, experimental techniques such as resonant Raman scattering, surface-enhanced Raman scattering, UV-VIS-NIR and FTIR absorption spectroscopy, surface enhanced infrared absorption spectroscopy, photoluminescence (PL), high resolution transmission electronic microscopy, and so on were used [7–9]. Previous studies considering composite materials based on the above copolymers and carbon nanotubes have led to the following conclusions: i) spectroscopic analyses are valuable tools to explain the interfacial interactions between carbon nanotubes and copolymers when the formation of three-dimensional interpenetrated networks occur [9]; ii) the percolated electron transport in the case of the SWNTs/P-PEDOT-b-PEO composite makes this material a good candidate for flexible electronics [9]; iii) the surface-enhanced infrared absorption (SEIRA) spectroscopy shows significant information concerning different orientations of the composite material functional groups with respect to the metallic supports, allowing the improved monitoring of the interface processes [7,8]; and iv) the PL quenching of the macromolecular compound in the presence of SWNTs results from the two mechanisms, energy transfer and charge collecting processes [7]. The role of the metallic and semiconducting carbon nanotubes in the PL quenching process is dependent on the electronic energy level diagrams of the constituents of the composite material [7,10,11].

In this paper, chemical synthesis and optical properties are

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reported for the poly(3, 4-ethylenedioxythiophene-co-pyrene) (PEDOT-Py) copolymer and the PEDOT-Py/SWNTs composite materials. The targets of this work are many fold: i) to report on the vibrational properties of the composite materials in order to establish the physical and/or chemical interactions at the interface of the two constituents and ii) to describe the de-excitation pathway involved for the understanding of PL quenching process of copolymer in the presence of SWNTs. At present it is well known that i) the electrochemical and chemical polymerization of 3,4-ethylenedioxythiophene in the presence of SWNTs, as well as the chemical interaction of PEDOT with SWNTs, involves a charge transfer between the two constituents, which leads to the synthesizing of composites of the type SWNTs covalently functionalized with PEDOT in doped and un-doped state [12], PEDOT non-covalently functionalized SWNTs [13] and PEDOT doped with SWNTs [14]; and ii) the chemical interaction of pyrene with SWNTs involves a non-covalent functionalization of carbon nanotubes with pyrene molecules when new physical bonds π - π^* appear between pyrene and the basal plane of SWNTs graphitic structure [15]. Taking into account this background and the different interactions encountered, we will demonstrate in this work that the chemical polymerization of 3,4-ethylenedioxythiophene and pyrene in the presence of carbon nanotubes lead to the composites of the type PEDOT-Py copolymer doped with SWNTs as a result of the charge transfer between SWNTs and repeating units both of PEDOT and Py.

Among applications of the carbon nanotubes-based composite materials, synthetized by electrochemical methods, the field of sensors for sensing volatile organic compounds is of primary importance [16]. In order to optimize sensing performance, knowing the adsorption of composite materials onto metallic supports is necessary. Therefore, in the present manuscript, a special attention is given to the assessment of the composite materials orientation on the metallic supports surface using the IR spectroscopy in the grazing-incidence angle reflection geometry under ***s*** and ***p*** − polarization.

The utility of the carbon nanotubes-based composite materials also in the solar cells field involves a good knowledge of photoluminescence (PL) properties [17]. According to recent progress concerning the PL quenching processes of conjugated polymers [8] and copolymers [7] in the presence of SWNTs, a significant role in this optical process was shown to be played either by metallic tubes or by semiconducting tubes depending on the electronic energy level diagrams of the constituents of the studied composite materials. Taking into account this dependence, we clarify in this work the role of the metallic and semiconducting SWNTs on the PEDOT-Py macromolecular compound PL.

2. Experimental

Compounds used in this work (3, 4-ethylenedioxythiophene (EDOT), pyrene, bis(2-ethylhexyl) sulfosuccinate sodium salt (abbreviated AOT), methanol, $FeCl_3$ and SWNTs) were purchased from Sigma Aldrich.

The synthesis procedure of the PEDOT-Py copolymer was similar with that reported in Ref. [18]. Briefly, an aqueous solution of 1 ml $FeCl_3$ 20×10^{-3} mol was added to a micro-emulsion of AOT 15×10^{-3} mol in 50 ml n-hexane with magnetic stirring time of 10 min, after which an orange solution was obtained. Next, 2×10^{-3} mol EDOT and 10^{-3} mol pyrene were added at the orange solution under magnetic stirring for 3 h when a dark blue filter cake corresponding to the PEDOT-Py copolymer was obtained. The PEDOT-Py copolymer was filtered and subsequently washed with methanol and dried until a constant mass was measured. The synthesis of the PEDOT-Py/SWNTs composites was performed with different SWNTs masses, i.e., 0.01 and 0.1 g, at a micro-emulsion of AOT in n-hexane, and the other steps were made in the same way as in the case of the PEDOT-Py copolymer. The resulting composites were labeled as PEDOT-Py/SWNTs-1 and PEDOT-Py/SWNTs-2, respectively.

Resonant Raman spectra of SWNTs and their composites as well as the PEDOT-Py copolymer were recorded at excitation wavelengths of 514 nm and 676 nm with a resolution of 1 cm^{-1} in backscattering geometry using a Horiba Jobin Yvon spectrophotometer, model T64000.

IR spectra of the PEDOT-Py copolymer and the PEDOT-Py/SWNT composites were recorded with a resolution of 4 cm^{-1} using a Bruker FTIR spectrophotometer, model Vertex 70. IR spectra of the thin films of copolymer and composites deposited onto Au supports were recorded using a Bruker FTIR spectrophotometer equipped with a Hyperion 2000 FTIR microscope and a grazing angle objective.

Photoluminescence (PL) spectra of the PEDOT-Py copolymer and its composites were recorded in a right-angle geometry at room temperature (RT) using a Horiba Jobin Yvon Flurolog-3 spectrometer model FL 3-22.

UV-VIS spectra of the PEDOT-Py copolymer were recorded using a Perkin Elmer spectrometer model Lambda 950.

Cyclic voltammetry studies were carried out on the PEDOT-Py films using a Radiometer Analytical potentiostat/galvanostat model VOLTALAB 80. These studies were performed for the creation of energy level diagrams. An electrochemical cell was used with the working, counter and reference electrodes consisting of a rough Au support, a spiral Pt wire and a commercial Ag/AgCl electrode (3 M KCl), respectively. An electrolyte solution consisting of 2×10^{-3} M EDOT, 10^{-3} M pyrene and 10^{-3} M $LiClO_4$ in CH_3CN was prepared in order to record the cyclic voltammograms of the PEDOT-Py copolymer in the potential range from -1000 to +1500 mV vs. Ag/AgCl with a sweep rate of 100 mV s^{-1}.

The reproducibility of the data shown in this paper was verified by the repetition of all measurements for at least three times for each measurement.

3. Results and discussion

For a better understanding of the vibrational properties of the composites PEDOT-Py/SWNTs-1 and PEDOT-Py/SWNTs-2, a brief overview of the main features of the Raman spectra of SWNTs and the PEDOT-Py copolymer at the excitation wavelengths 514 and 676 nm (Figs. 1 and 2) is given in the following. The Raman spectrum of SWNTs shows in the spectral range: i) 100-350 cm^{-1}, Raman bands peaked at 164 and 174 cm^{-1} when the Raman spectra are recorded using excitation wavelengths of 514 nm (Fig. 1) and 676 nm (Fig. 2), respectively, are assigned to radial breathing modes (RBM) [13] of nanotubes; and ii) 1000-1700 cm^{-1}, there are two Raman bands situated between 1100 and 1400 cm^{-1} and 1500-1700 cm^{-1} assigned to the disorder state or defects in the carbon nanotubes structure (labeled D band) and the tangential vibrational mode (TM), respectively. These bands change in peak positions depending on the excitation wavelength used, i.e., 514 and 676 nm, from 1340 to 1586 cm^{-1} (Fig. 1) at 1316 and 1588 cm^{-1} (Fig. 2) [19]. At the excitation wavelength of 676 nm, the Raman band of SWNTs assigned to TM (Fig. 2) shows an asymmetrical profile in the low energy range with a maximum at 1546 cm^{-1} which originated with the electron-phonon interaction [19]. Raman spectra of the PEDOT-Py copolymer are dominated by an Raman band situated in the spectral range 1400–1500 cm^{-1} with a position that changed with the excitation wavelength. According to Figs. 1(d) and 2(d), the main Raman lines of the PEDOT-Py copolymer are situated at 441-571, 701, 1267, 1367, 1437, 1500-1510 and 1565 cm^{-1}. The bands are attributed to the following vibrational modes: oxyethylene ring