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Electrical and morphological study of carbon nanotubes/polyaniline composite films: A model to explain different tunneling regimes induced by a vertical electric field

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ABSTRACT

The way carbon nanotubes can modify the charge transport of organic materials may open opportunities for new uses. However, the understandings of many intrinsic physical properties associated to those changes are still poor. Here, we report our investigation on the properties of (PAni) and PAni/carbon nanotubes (CNTs) composites obtained by innovative interfacial polymerization method at room temperature. We have used spectroscopic methods (XPS, Raman) and microscopy (SEM) to obtain relevant parameters to combine with our electrical modeling and describe properly the transport characteristics of neat polymer and its composites with carbon nanotubes in different ratios. The devices were prepared in planar field effect transistor (FET) geometry to study the tunneling injection of charge carriers under the influence of the vertical component of a crossed electric field. We found that the tunneling injection is significantly improved using the PAni/CNT composite. This effect is related to morphological changes of the PAni film synthesized in the presence of CNTs, where the PAni polymerization on CNT's surface produces tubular structures covering them. Due to the CNT's high aspect-ratio, there is electric field amplification near to their tips that enhances the tunneling injection from the metallic contacts under the influence of the vertical field. We propose a theoretical model that can predict the electric field intensity of the transition. The number of tube's tips with different amplification factors (β) produces different regimes of tunneling injection in samples with moderate CNT concentration. We then propose a theoretical model that can predict the electric field intensity of the transition between those regimes: essentially it happens when the tunneling current produced by a few junctions with strong β is greater than the current produced by the higher number of junctions with low β. However, as the CNT density increases, the enhancement of the tunneling injection decreases due to electric field screening.

1. Introduction

Conjugated polymers and Carbon nanotubes (CNT) can be combined in the active layer of electronic devices to form composites with enhanced properties compared to the isolated polymer. Since CNTs can reach a current densities as high as 10^9 A·cm^{-2} and as it interacts with the polymer by weak van der Waals forces, there is no decrease on stability in the composite [1–4] with a gain in the electronic transport due to the creation of conductive pathways through the polymer [3,5,6]. The main methods of those nanocomposites synthesis include direct mixing materials, in situ polymerization and electrochemical polymerization [5,7,8]. The idea of using CNT in composites, came from their large potential applications [9–11] exploring its novel properties like high hardness and strength, large length-to-diameter ratio (aspect ratio), and good electrical conductivity [12–15]. Many researches have been developed using individual single-wall carbon nanotubes (SWCNT) or multi-wall carbon nanotubes (MWCNT) or films of those materials to be used in nanocells for hydrogen storage [16,17], sensors for gases [18,19], nanofibers [7,20], photodetectors [15], Organic Field Effect Transistors (OFETs) [21], logic circuit and memories [22], supercapacitors [23,24], etc. Combination of the nanotube's chirality and radius can produce either metallic or semiconductor SWCNTs. The standard metallic to semiconductor ratio within the raw, non-separated

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sample of single wall nanotubes is around one third to two thirds [25,26]. Due to the CNTs large aspect-ratio, metallic CNTs have excellent electric field amplification properties which can be applied in field emission devices [27,28].

Among the conjugated polymers, one has been extensively studied, polyaniline (PAni), mainly due to their physical, chemical and electrical characteristics, showing good stability, easiness of polymerization, feasibility of processing into fibers [29], low cost, and wide range of electrical conductivity upon doping [8,30–32]. In this characteristic, PAni conductivity varies from 10^{-10} S·cm^{-1} to about 10^{1} S·cm^{-1} by protonation in acid aqueous solution [8,31–34]. The polymer can reach its conducting state either through the protonation of the imine nitrogens (—N═) of the emeraldine (EM) oxidation state, or through the oxidation of the amine nitrogens (—NH—) of the fully reduced leucoemeraldine (LM) state [29].

Polyaniline is an extremely versatile conducting polymer since it can be easily synthesized adopting classical oxidation method or by electrochemical oxidation of the monomer. In former case, the aniline is oxidized using an oxidant (generally ammonium peroxydisulfate) in an acidic aqueous media. In the second one, the electropolymerization is proceed which results in the conducting polymer covering the surface of the working electrode [11]. Despite the aforementioned properties of the polyaniline, some drawbacks intrinsically linked to this conducting polymer like low electrochemical stability and low mechanical strength makes it harder for further application in the desirable fields of science [35]. CNT/PAni composites have been a clever way to overcome the issues related to the polyaniline, once the CNT acts as a template for the conducting polymer growing. At the same time, the formation of the composite enhances the electrochemical stability and allows the application in flexible devices. The electrical properties of the CNT/PAni composites are then improved compared to the raw polyaniline due to the charge transfer from the conducting polymer to the CNT through a π-π aromatic interaction [7]. Furthermore, the way how to process the final composite using a reduced number of steps shall accredit such material for technological applications. Herein, the interfacial method to obtain thin and transparent films at the interface of two immiscible liquids is an outstanding way to process CNT/PAni composites. Its easily synthesized over environmental conditions and the final material can be simply removed over several kinds of substrates, and all this process is proceeded in one single step [7,24].

As for the electrical conductivity in PAni films, CNT films and PAni/CNT composites, there are works that shows the increase of the electrical conductivity in the PAni film as a function of the protonation degree [33,36,37] and as a function of both the protonation degree and the increase of CNT concentration in the composite [8,38–40]. In application as filed effect transistors (FET) to study the device performance, there are works applying PAni only [41–43], CNT only [44–47] and PAni/CNT composites [48,49]. Nevertheless, there are few studies in the literature that investigate the electrical properties of PAni/CNT composites submitted to cross electric field.

From a technological perspective, OFETs are candidates to be employed as cheap disposable electronic devices in many applications [50–52]. Likewise, the planar geometry of OFET is a powerful tool to study the charge carrier injection and transport in organic conducting or semiconducting polymeric materials [53]. In this work, we analyze (using OFET geometry) the electrical properties of emeraldine (EM) PAni films and composites of EM PAni films with different concentrations of SWCNT. Those films were obtained through the liquid-liquid interfacial polymerization method at room temperature [7,24]. The preliminary step of our study involves the use of different experimental techniques to characterize some physicochemical and morphological properties of the films and their variation with increasing CNT concentration. The OFETs are then fabricated in a second step. The scheme of voltage polarizations of those devices produce a region (sandwiched between the source electrode and the gate dielectric) where the PAni/CNT layer is submitted to high electric fields. Applying a simple model based on the tunneling injection of charge carrier in the active layer, we are able to correlate the OFETs field effect response with the properties of the PAni/CNT films measured in the characterization step.

Following this two-step approach, we show that the enhanced field effect modulation of the drain current in OFET based on the PAni/CNT composites is due to the tunneling injection produced by the amplification of the local electric field in tips of PAni-covered metallic nanotubes (that are always present in unpurified samples of SWCNTs [25,26]). The enhancement of the local electric filed modeled using an amplification factor (β) that is related to the large aspect-ratio of those tubular structures [54,55]. At low applied vertical electric fields and moderate CNT concentrations, the high number of tips with low β dominates the tunneling current. With increasing vertical field, however, the charge carriers injected near tips with stronger β start to dominate the tunneling process which induces a transition in the current dependence on the applied voltages. Therefore, one can observe two different regimes of tunneling injection at low and high vertical fields. It is then possible to determine the threshold voltage necessary to promote this regime transition with the application of a simple tunneling model. As the CNT concentration increases, however, the field enhancement factor decreases due to the lower penetration of the electric field in the region between the tubular structures (electric field shielding effects). This phenomena suppresses the observation of the transition between the regimes of tunneling injection. Those results suggest that the field effect modulation of the drain current can be optimized by tuning the CNT density. In fact, we show that OFETs with a lower concentration of CNT can reach the highest drain current with increasing gate voltage.

2. Experimental methods

SWCNT's (HiPCO/Unydim) with a length range of 100–1000 nm and individual diameter of 0.8 to 1.2 nm were used as received. There are works that shows efficient ways to separate of metallic SWCNT and semiconductor SWCNT [56–59], but our intention was to test the electric field amplification effects in a device assembled with commercial SWCNT composed by both, metallic and semiconductor SWCNTs. If there was only metallic SWNT in the composite film, it should be very conductive [8] that would shield the applied electric fields [27,28]. If there was only semiconductor SWCNT in the composite film, probably we would not see the significant variations in the amplification factors β.

The aniline was bi distilled under vacuum before use and ammonium persulfate (APS) was used as received. The synthesis of the PAni/CNT composites, neat PAni and SWCNT films were carried out following the interfacial polymerization for production of thin films [7,24]. For the composites, 0.01 mg of SWCNT was added to 20 mL of toluene in a beaker. Then, this mixture was dispersed maintaining it in an ultrasonic bath (154 W, 37 kHz) for 30 min, followed by 10 min using an ultrasonic probe system (Cole-Palmer ultrasonic processor) and finally repeating the first procedure using the ultrasonic bath. All the dispersions steps were performed using an ice bath to avoid the toluene evaporation. Afterwards, the aniline was added (10 or 20 μL) to the CNT dispersion and this mixture was poured into a 50 mL round bottom flask containing APS (6.35 mg and 12.7 mg for the composite with 10 μL and 20 μL, respectively) previously dissolved in 30 mL of an aqueous solution of H_2SO_4 1 mol L^{-1}. This system was maintained under magnetic stirring (1500 rpm) for 22 h. After this time the magnetic stirring was interrupted and a green and freestanding film could be seen assembled at the liquid-liquid interface. The organic phase was removed using a pipette and fresh toluene was added to the system, which was stirred by 5 min. After this time the system was kept to stand and the green film spontaneously self-organize again at the liquid-liquid interface. This procedure of exchanging the organic phase was repeated 5 times in order to remove any soluble side product, as aniline oligomers. The same procedure was afterwards done with the aqueous phase, which was firstly replaced by an aqueous solution of H_2O milli-Q five times,