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Coexistence of positive and negative photoconductivity in nickel oxide decorated multiwall carbon nanotubes

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ABSTRACT

Within this work was explored the influence of nickel oxide decoration on the photoconductive effects exhibited by multiwall carbon nanotubes. Samples in thin film form were prepared by a chemical vapor deposition method. Experiments for evaluating the photo-response of the nanomaterials at 532 nanometers wavelength were undertaken. A contrasting behavior in the photoelectrical characteristics of the decorated nanostructures was analyzed. The decoration technique allowed us to control a decrease in photoconduction of the sample from approximately 100 μmhos/cm to −600 μmhos/cm. Two-wave mixing experiments confirmed an enhancement in nanosecond nonlinearities derived by nickel oxide contributions. It was considered that metallic nanoparticles present a strong responsibility for the evolution of the optoelectronic phenomena in metal/carbon nanohybrids. Impedance spectroscopy explorations indicated that a capacitive behavior correspond to the samples. A potential development of high-sensitive Wheatstone bridge sensors based on the optoelectrical performance of the studied samples was proposed.

1. Introduction

The control of specific quantum levels in carbon nanotubes decorated with metallic nanoparticles can be possible from photoconductive interactions between these and light [1]. The electronic states exhibited by CNTs depend on morphology, structure and chiralities [2]; but the purity in the tubes, their geometric form and the resulting interparticle interactions by doping or decorating processes, may play a fascinating role in their physical characteristics [3]. For this reason, numerous efforts have been devoted to incorporate metallic nanoparticles (NPs) on CNTs in order to improve their integrated electronic, magnetic and optical properties [4]. Wet impregnation, precipitation, sputtering and chemical vapor deposition techniques have been widely employed for designing and developing nanohybrid samples constituted by NPs and CNTs [5–7]. Particularly, the chemical vapor deposition method (CVD) has shown good control of particle size and homogeneous distribution of metallic NPs (in a fast and low cost process). However, it is well known that the procedure to include metallic NPs in CNTs functionalizes the surface producing carboxylic and hydroxyl groups [8]. Functional groups produced mainly by oxidation with acid treatments [11] (used to clean CNTs), remain as active sites on the surface [9,10], affecting its properties.

Metallic NPs or metal oxides derived from Pd, Cu and Ni display excellent conductivity parameters reliable as those obtained from expensive Pt, Ag and Au elements. In particular, Ni NPs show a high level of surface energy, high magnetism, low melting point, high surface area and low burning point [12,13]. Furthermore, NiO has potential applications in electrochromic materials [14], light-emitting devices [15] and electrochemical capacitors [16]. It is valuable to comment, that these kinds of materials are unstable for extended periods of time [17]. For this reason, NiO NPs were supported onto CNTs in this work.

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From the combination of CNTs and metallic NPs can be obtained unique properties which are different from those that correspond to their individual components [18]. As an example, multiwall CNTs (MWCNTs) decorated with metallic NPs exhibit major strength, stiffness and toughness [19], and also they modify their conductivity by a few orders of magnitude [20]. Then it is attractive to consider the preparation of MWCNTs decorated with metallic NPs for developing sensors, instrumentation mechanisms and nanoelectronic systems [21–23].

Accordingly, in this paper NiO decoration on MWCNTs was explored by the *in-situ* CVD method. The samples were structurally and morphologically characterized by Scanning Electron Microscopy (SEM) studies, Transmission Electron Microscopy (TEM) observations, X-ray diffraction evaluations and Raman spectroscopy analysis. Here is reported, the modulation of conductive properties induced by light from negative to positive behavior in the sample studied.

2. Experimental

2.1. Sample preparation

The MWCNTs were synthetized by a CVD using a toluene/ferrocene solution at 850 °C and an Argon gas carrier with flow rate of 2 l/min. Full experiment details can be found elsewhere [24].

To generate functional groups (carboxylic) and eliminate some traces of Fe from the synthesis, MWCNTs were mixed in HNO_3 (40% v/v) in a reflux in an interval of 90–100 °C for 24 h [8,9]. Functionalized MWCNTs (*f*-MWCNTs) were filtered and dried to exclude the remaining of HNO_3.

Samples containing NiO NPs incorporated onto *f*-MWCNTs (NiO/*f*-MWCNTs) were prepared by an *in-situ* CVD method; which has been described elsewhere [25]. This method basically consists in two steps. In the first step, the NiO precursor ($C_{10}H_{14}NiO_4$, 98% of purity, EMD Millipore) was mixed with *f*-MWCNTs and then was treated at 180 °C for 10 minutes in a quartz tube reactor, so the organic part of the precursor was evaporated. In the second step, the crystallization of NiO has been made at 400 °C for 10 minutes inside the reactor under Ar gas flow (100 cm^3/min).

MWCNTs, *f*-MWCNTs and NiO/*f*-MWCNTs were made available for measurements in an ethanol suspension and in film form. A quartz cuvette with 1 mm width was employed to contain the separated dispersed samples for observing their optical absorption. Consecutively, different SiO_2 substrates were used to support the nanostructured films by dripping on the samples in liquid solution. This coating method for preparing nanostructures in thin film form is simple and may be strongly useful for tailoring physical properties of the resulting sample. The film geometry, morphology and structure are critical parameters for electrochemical, photoconductive and nonlinear optical experiments, and the film quality has potential for designing particular functions exhibited by the samples. The approximate thickness of the selected films was estimated by spectroscopy in about 1 μm. Electrochemical measurements, photoconductive experiments and the evaluation of nonlinear optical effects were carried out with the film samples.

2.2. Structure and morphology characterization

In order to analyze the particle size and homogeneity of dispersed NiO onto *f*-MWCNTs, Scanning Electron Microscopy (SEM; JEOL JSM-6701F) coupled with a microanalysis detector for Energy-Dispersive X-ray Spectroscopy (EDX) was employed. Transmission Electronic Microscopy (TEM; JEOL JEM-2200FS) evaluations were employed to confirm the multiwall nature of the tubes studied. The NiO incorporation was analyzed by a X-Ray diffraction system (XRD; Bruker D8 Focus).

2.3. Electrochemical impedance spectroscopy studies

Electrical measurements of the samples in film form were undertaken by using an Autolab/PGSTAT302N high power potentiostat/galvanostat. A low-voltage signal with 10 mV was employed to evaluate the impedance spectrum in an integration time of 1 s. Carbon electrodes were in direct contact with the film to be electrically connected with the system for recording conductivity. A 5 mm distance between electrodes was defined to examine the observed samples.

2.4. Photoconductive measurements

Electrical measurements were monitored under the irradiation of a 532 nm wavelength provided by a continuous wave (CW) laser (Wickedlasers, Kripton) emitting 100 mW of average power. A calcite polarizer allowed us guarantee the illumination by linear polarization by direct irradiation to the sample by normal incidence. The path in measurement was aligned to be parallel to the incident polarization of the optical beam. The electrodes were located in the vicinity of the 3 mm diameter of the incident beam. A metallic diaphragm and a quartz lens were employed to focusing the beam in the sample.

2.5. UV–VIS spectroscopy evaluations

A Perkin Elmer XLS spectrophotometer with range of measurement from 200 nm to 900 nanometers wavelength allowed us to conduct the optical absorbance studies related to the samples suspended in a liquid solution. The content of the samples in the ethanol was heuristically chosen to better observe the characteristic ultraviolet absorption band exhibited by the MWCNTs.

2.6. Nanosecond two-wave mixing experiments

The influence of the NiO decoration on the third order nonlinear optical behavior exhibited the NiO/*f*-MWCNTs was experimentally distinguished. The transmittance in two-wave mixing experiment as a standard optical Kerr gate was registered at 532 nm wavelength, 4 ns pulse duration and a single-shot mode (Nd:YAG laser source Continuum Model SL II-10) [26]. The modification of the linear polarization of the probe beam in interaction with the pump beam was recorded by a PIN photodetector. We employed 30 mJ of pulse energy provided by the output of the laser system during the experiments, and the diameter of the beams in the sample was approximately 6 mm. The geometrical angle of the rays in the two-wave mixing was 30°.

In order to describe the transmitted beams through the nonlinear optical sample we employed the finite-differences method for numerically solving the wave-equation [27]:

$$\nabla^2 E_{\pm} = -\frac{n_{\pm}^2 \omega^2}{c^2} E_{\pm} \tag{1}$$

where E_+ and E_- represent the right and left circular components of the electric field; respectively. The optical frequency is ω and we considered that the index of refraction can be approximated as [27]:

$$n_{\pm}^2 = n_0^2 + 4\pi\left(A|E_{\pm}|^2 + (A+B)|E_{\mp}|^2\right) \tag{2}$$

where $A = \chi^{(3)}_{1122}$ and $B = \chi^{(3)}_{1212}$ correspond to the components of the third order susceptibility tensor and n_0 is the weak-field refractive index.