Carbon 124 (2017) 348–356

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Multiwall carbon nanotubes filled with Al_4C_3: Spectroscopic signatures for electron-phonon coupling due to doping process

P.T. Araujo [a, b, *], N.M. Barbosa Neto [c, **], M.E.S. Sousa [c], R.S. Angélica [d], S. Simões [e], M.F.G. Vieira [e], M.S. Dresselhaus [f, g], M.A. Leite dos Reis [h, ***]

[a] Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL, 35401, USA
[b] Center for Materials for Information Technology (MINT Center), University of Alabama, Tuscaloosa, AL, 35401, USA
[c] Programa de Pós-graduação em Física, Instituto de Ciências Exatas e Naturais, Universidade Federal do Pará, 66075-110, Belém, PA, Brazil
[d] Instituto de Geociências, Programa de Pós-graduação em Geologia e Geoquímica, Universidade Federal do Pará, 66075-110, Belém, PA, Brazil
[e] Faculdade de Engenharia da Universidade do Porto, Universidade do Porto, 4200-465, Porto, Portugal
[f] Department of Electrical Engineering and Computer Sciences, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA
[g] Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA
[h] Programa de Pós-graduação em Engenharia de Recursos Naturais da Amazônia, Universidade Federal do Pará, 66075-110, Belém, PA, Brazil

ARTICLE INFO

Article history:
Received 9 April 2017
Received in revised form
15 August 2017
Accepted 20 August 2017
Available online 23 August 2017

Keywords:
Al_4C_3-MWCNTs
Density of states
Scanning electron microscopy
Transmission electron microscopy
Raman spectroscopy
Electron-phonon coupling

ABSTRACT

The spectroscopic signatures related to doping mechanisms in multiwall carbon nanotubes filled with aluminum carbide (Al_4C_3@MWCNTs) were studied and interpreted relative to changes in their electronic and phononic structures. Unfilled MWCNTs were used as standard samples to help interpreting the filling and the doping processes. The samples were characterized via scanning electron microscopy, transmission electron microscopy, X-ray diffraction and resonant Raman spectroscopy. The electron-phonon coupling mechanisms associated to the Raman intensities, frequencies and linewidths of the G- and G'-band Raman modes were analyzed and connected to the doping mechanism in these multi-walled systems. Our results indicate that the Al_4C_3 particles transfer electrons to the MWCNTs. In order to shed light into the experimental findings, theoretical calculations were performed using two examples of filled and unfilled achiral MWCNTs and the results for the density of electronic states indicate that the two systems under consideration, exhibit metallic behavior, with aluminum carbide doping the carbon nanotubes, thereby supporting our experimental observations.

1. Introduction

Synthesis of nanocomposites has been widely used by researchers worldwide as alternative solutions for advancing, among others, the aerospace, the automotive, and the aeronautic industry. Metal matrix nanocomposites (MMC) based on multiwall carbon nanotubes (MWCNT) have historically been one of the leading composites in this field of study [1–3]. Indeed, due to their outstanding mechanical properties (including high Young modulus values of about 1200.00 GPa), these MWCNT-based nanocomposites have been applied as reinforcing materials [1–3].

In 2007, Cava and collaborators [4] developed a synthesis path capable of producing nanocomposites based on MWCNTs filled with metal oxides, such as iron oxides. Posteriorly, Reis et al. [5] presented results of a hybrid process based on the DC arc discharge and the Chemical Vapor Deposition (CVD) techniques, in which nanocomposites of MWCNTs filled with aluminum carbide (Al_4C_3) were successfully synthesized. The results further suggested that the formation of Al_4C_3 occurs through chemical reactions between the carbon nanotubes and the aluminum matrix. In their synthesis process [5], the nanotubes are directly extruded from the aluminum matrix via the vapor-liquid-solid (VLS) growth process while the sintering of the nanocomposite occurs. Carbon nanotube-based nanocomposites have a great technological appeal due to their potential applications which involve reinforcement of materials [6], electronic device fabrication [7] and other applications [8]. Dresselhaus et al. [9] proposed that an increased charge density

* Corresponding author. Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL, 35401, USA.
** Corresponding author.
*** Corresponding author.
E-mail addresses: paulo.t.araujo@ua.edu (P.T. Araujo), newtonfisico@gmail.com (N.M. Barbosa Neto), marcosallan@ufpa.br (M.A. Leite dos Reis).

http://dx.doi.org/10.1016/j.carbon.2017.08.041
0008-6223/

distribution can be attained by filling carbon nanotubes with metal nanoparticles. In their report [9] they explain that the increase in the charge density is mediated by electron-phonon coupling mechanisms available in such systems. It is also interesting to note that the strong many-body interactions observed in these nanotube-based composites provide an additional route for exploring superconductivity phenomena [10].

The mutual interactions between Al_4C_3 and MWCNTs could be observed through the electronic and vibrational structure of the MWCNT systems. Resonant Raman spectroscopy (RRS) is a suitable technique to study the behavior of electron and phonons through the analysis of photons inelastically scattered by the materials. These inelastically scattered photons most always carry important information about the interactions between the electrons and phonons in or associated with these materials [11]. These electron-phonon (*e-ph*) interactions carry, among other things, valuable information related to the charge transfer mechanisms in doped systems [12–16]. The *e-ph* coupling mechanism can also be responsible for generating electron-hole (*e-h*) pairs which leads to the phenomena of phonon self-energy renormalizations, first explained by Walter Kohn [17]. Nowadays, these self-energy renormalizations, which are often observed as a phonon frequency softening, are baptized as Kohn anomalies and these anomalies have been observed in several different situations [12–16,18–21]. In the present work, we provide an analysis of multiwall carbon nanotubes (MWCNTs) filled with aluminum carbide (Al_4C_3) particles. Our experiments, which are supported by theoretical calculations, demonstrate that the innermost tubes in the MWCNT systems host the Al_4C_3 nanoparticles and that these nanoparticles are efficient electron donors to the MWCNTs. Our analysis also allow for the identification of Raman scattering spectroscopic signatures which are valuable to recognize the successful filling and doping of these complex multiwall carbon nanotube systems.

2. Materials and methods

The Al_4C_3@MWCNTs were synthesized through a hybrid process which combines the DC arc discharge method with the chemical vapor deposition (CVD) method as described in Ref. [5]. The unfilled MWCNTs were synthesized via the CVD method. A Jobin Yvon T64000 spectrometer with a charge coupled device (CCD) for signal detection was used to acquire the Raman spectra. All the spectra were obtained at room temperature in a backscattering geometry. The samples were excited at 514.5 nm (2.41 eV) and the power density measured from the objective was kept low enough to avoid heating of the samples. A 20× objective lens with a focal distance $f = 20.5$ mm and numerical aperture NA = 0.35 was used to focus the laser beam on the sample surface and also to collect the backscattered signals. The morphologies of the MWCNTs and of the Al_4C_3@MWCNT samples were characterized with a Scanning Electron Microscopy (SEM) model VEGA3 SB − TESCAN tuned at 20 kV and with a Transmission Electron Microscopy (TEM) model TECNAI G2 20 S-TWIN tuned at 100 kV.

XRD analysis were carried out in a divergent beam diffractometer (Empyrean, PANalytical) equipped with a PW3050/60 (θ/θ) goniometer, a PIXel^{3D} 2 × 2 area detector, a Co-sealed X-ray tube ($K\alpha_1 = 0.178901$ nm), and a kβ iron metallic filter. The instrument conditions were as follows: 40 kV and 40 mA; 0.02° 2θ step size and an acquisition time of 20 s per step in a step-scan mode; 1/2° divergent slit and 1° anti-scattering slit. The instrument resolution was obtained by using the LaB6 NIST/SRM 660b standard.

The sample preparation included deposition of the materials on a silicon plate (zero background sample holder) with a few drops of ethyl alcohol. The samples were scanned in two main 2θ ranges: from 1 to 10° (in order to detect the nanotubes alignment/orientation) and the normal 5 to 70° range.

The simulations were performed with two types of triple wall carbon nanotubes (TWCNT), which are simpler versions of MWCNT systems, *i.e.*, armchair (chirality 3.3@6.6@9.9) and zigzag TWCNTs (chirality 6.0@11.0@16.0), in which the innermost tube of each system exhibits electronic properties of a metallic and semiconductor CNT, respectively. The MWCNT systems were designed with three walls each in order to shorten the time spend in the calculation, and they were filled with Al_4C_3 so that the electronic density of states of the MWCNTs filled with Al_4C_3 could be compared with the equivalent unfilled MWCNT systems. In order to calculate the density of states (DOS), the model systems were separated into three regions: right and left electrodes (*semi-infinite*); a sequence of the unit cell of tube equivalent to an aromatic ring; and a central region (*scattering center for the transport calculations*). The systems were optimized via the MM+ (*Molecular mechanics*) force field, and then the DOS calculations were performed within the Extended Hückel Theory (ETH), which is a semi-empirical method to describe the wave function of the electron that has very good agreement with experimental results. This method has been successfully employed in many other problems [22–24]. The Hamiltonian of these systems were constructed via the *H*-matrix method in which the Hamiltonian is formed by the energy of the molecule's ionized valence orbital and by the coating matrix *S* [25], which is a correction accounting for any loss coming from the approximations made by using the semi-empirical method.

Additionally, ETH utilizes a self-consistent Hamiltonian formalism of matrix Green functions out of balance *(NEGF)*, so that the electric currents simulated can give important information about electronic transport. Also, the external potential applied gives us information about the interactions between electrons and phonons. Moreover, the Green's function formalism uses the spectral transmission method to describe the electronic distribution of the system as well as to characterize the electronic properties of the target systems, *i.e.*, density of states (*DOS*), MPSH (*Molecular Projected Self-consistent Hamiltonian*) states, differential conductance, among others [26]. In the present work the same isovalue (~0.03) was used to all the plots and visual grid sampling was set to 1.

3. Results and discussion

Fig. 1(a) and (b) show the morphology of the unfilled CNTs used in this work as control samples. The SEM image (Fig. 1(a)) shows a dense agglomerate of MWCNTs while the TEM image (Fig. 1(b)) reveals CNTs with several walls with the diameters of the outermost tubes ranging from approximately 10 nm–60 nm. For the MWCNTs filled with Al_4C_3, the SEM images show MWCNTs with diameters of at most 90 nm, as shown in Fig. 2(a) and (b). Also from TEM image, we are able to estimate that for both samples the majority of the tubes have external diameters around 10 nm and that most of the filled MWCNTs present closed tips, as shown in Fig. 2(c) and Fig. S2 (supplementary information), where the main morphological difference between the two samples (filled and unfilled MWCNTs) was the presence of Al_4C_3 inside the filled MWCNTs (Fig. 2(d)). As previously shown by Colbert et al. [27], open-tip CNTs are expected under applied voltages of about −75 V and high temperatures (around 1200 °C). However, when the voltage is turned-off, the tip is closed again. These observations imply that dome-closed tip is much easier to be found in the arc discharge synthesis method since higher voltages are applied and at the end of the synthesis procedure the voltage is also turned off at high temperatures. In our case, the Al_4C_3-filled nanotubes were synthesized by the arc discharge apparatus [5] and nucleated by the