Optical Materials 72 (2017) 612–617

Contents lists available at ScienceDirect

Optical Materials

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

Size dependent Raman and absorption studies of single walled carbon nanotubes synthesized by pulse laser deposition at room temperature

Saurabh Dixit, Sonal Singhal, V.D. Vankar, A.K. Shukla*

Laser Assisted Material Processing and Raman Spectroscopy Laboratory, Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

ARTICLE INFO

Article history:
Received 25 May 2017
Received in revised form
30 June 2017
Accepted 3 July 2017

Keywords:
Pulse laser deposition
SWCNTs growth at room temperature
Raman-active acoustic modes
NIR absorption spectroscopy

ABSTRACT

In this article, size dependent correlation of acoustic states is established for radial breathing mode (RBM). Single walled carbon nanotubes (SWCNTs) are synthesized along with carbon encapsulated iron nanoparticles by pulse laser deposition at room temperature. Ferrocene is used as a catalyst for growth of SWCNTs. Various studies such as HR-TEM, X-Ray Diffraction (XRD), Raman spectroscopy and NIR-Absorption spectroscopy are utilized to confirm the presence of SWCNTs in the as-synthesized and purified samples. RBM of SWCNTs can be differentiated here from Raman modes of carbon encapsulated iron nanoparticles by comparing their line shape asymmetry as well as oscillator strength. Furthermore, a quantum confinement model is proposed for RBM. It is invoked here that RBM is manifestation of quantum confinement of acoustic phonons. Well reported analytical relation of RBM is utilized to explore the nature of phonons responsible for RBM on the basis of quantum confinement model. Diameters of SWCNTs estimated by Raman studies are found to be in reasonably good agreement with that of NIR-absorption studies.

1. Introduction

An intensive research has been carried out on carbon nanotubes (CNTs) to study the growth mechanism and optimization of electrical properties [1,2]. Single walled carbon nanotubes (SWCNTs), which have cylindrical carbon molecules, have novel electrical and vibrational properties for wide variety of applications in the nanotechnology [3–7]. However, the critical problem, which still persists for development of SWCNT based applications (such as sensors and field emitters etc.), is mass production of SWCNTs. Thermal chemical vapor deposition (TCVD) technique is used for mass production of CNTs. Most often used catalyst precursor in TCVD is organometallic compounds (e.g. ferrocene and chromocene etc.). In TCVD, carbon and catalyst precursors are decomposed and CNTs are deposited over substrate at temperature in the range of 800–1000 K [8,9]. Generally, TCVD produces multi walled CNTs [9]. Therefore, laser ablation technique is preferred over TCVD for growth of SWCNTs.

In laser ablation, metallic powder is used as a catalyst in the graphite powder for the production of SWCNTs [10]. Target is usually ablated at the temperature of 1200 K. Yudasaka et al. [11] have explained the role of atmospheric temperature in the formation of SWCNTs. At ambient temperature of 1200 K, carbon can melt easily and makes a mixture with metallic catalyst [12]. The temperature of target graphite within the laser irradiated area is increased in the range of 3000–4000 K. The sudden increase in localize temperature at graphitic target results emission of melted carbon along with catalyst in the form of droplets [12]. Therefore, initial high temperature of target is required to make a mixture of molten carbon and metallic catalyst. Otherwise, the laser energy vaporizes carbon and expels them from the surface of target leaving behind the metallic catalyst in the target. The droplets of homogeneous mixture of carbon-catalyst are condensed on moving away from the target. During condensation, the metal atoms aggregate and form metal cluster which acts like a catalyst for the formation of SWCNTs [13,14]. Synthesis of SWCNTs at high ambient temperature limits the per day production rate of SWCNTs. Since ferrocene has low sublimation temperature, ferrocene can be used as a catalyst during laser ablation technique at room temperature. In this article, we focus on the laser ablation technique which can synthesize SWCNTs at room temperature.

Raman spectroscopy is vital tool for characterization of SWCNTs and graphene [15,16]. Ability of Raman spectroscopy to

* Corresponding author.
E-mail address: akshukla@physics.iitd.ac.in (A.K. Shukla).

http://dx.doi.org/10.1016/j.optmat.2017.07.008
0925-3467/

differentiate among single-walled, double-walled and multi-walled structure makes it a versatile technique. SWCNTs have RBM in the low frequency of Raman spectrum [10]' [15]. RBM appears due to vibration of carbon atoms in the radial direction. An analytical relation between frequency of RBM and diameter of SWCNTs has been reported [15]. Nature of phonons responsible for RBM has not been described in the literature to best of our knowledge. Therefore, a physically based model is required to predict the nature of fundamental phonons associated with RBM. Low frequency acoustic phonons of nanostructure can also contribute in the first-order Raman scattering due to quantum confinement effect. In this article, laser ablation technique is proposed for synthesis of SWCNTs at room temperature. Furthermore, a theoretical quantum confinement model for Raman line-shape of RBM is proposed for SWCNTs and is verified with experimental data of Raman studies and NIR absorption studies.

SWCNTs are synthesized by laser ablation using organometallic compound (ferrocene) as precursor of catalyst in the graphite target. Presence of the SWCNTs is confirmed by HRTEM, Raman spectroscopy and NIR- absorption spectroscopy. All the measurements reveal the presence of iron nanoparticles along with SWCNTs in the as-synthesized sample and removal of iron nanoparticles after purification leaving behind SWCNTs only. Raman line-shape analysis of RBM is conducted here on the basis of quantum confinement model for purified sample. It is invoked that RBM is manifestation of quantum confinement of acoustic phonons. Size-dependent correlation of acoustic states is established for RBM. It is found that diameters of SWCNTs estimated by proposed theoretical quantum confinement model are in agreement with analytical relation [15] available in literature as well as absorption studies. To best of our knowledge, this is the first Raman study of size dependent correlation of acoustic states with RBM in the SWCNTs at length.

2. Experimental method

2.1. Synthesis of SWCNTs using laser ablation

Samples were synthesized by pulse laser deposition of graphitic target which contained ferrocene as catalyst with optimized parameters (conc. of ferrocene and laser power). Litron Nd: YAG pulsed laser with pulse duration of 6 ns and wavelength of 1064 nm was used for ablation of target. Initially, 3 mM of ferrocene was mixed with 1.6 g of graphite powder uniformly and was converted into cylindrical target of diameter of 10 mm and height of 10 mm. An inert ambient was created in the ablation system by purging nitrogen gas. A constant flow of nitrogen was maintained in the ablation system during ablation. Nd: YAG pulsed laser beam was irradiated on target with power density around 2 GW/cm^2 for 20 min. A thin film of CNTs was deposited over quartz substrate. The collected sample was named as-synthesized sample. Purification of the as-synthesized sample was carried in two steps which were liquid phase purification and gas phase purification. Firstly, as-synthesized sample was treated with chemical solution of HNO_3 (70% solution) and H_2O_2 (30% solution) in the ratio of 1:2 v/v. Solution was then heated at 100° C for 1 h. The color of solution was first turned from black to grey and then again black. It was cooled down to room temperature and was filtered to get powder soot. The filtered soot was dried and was annealed at 500° C for half an hour. The collected sample was named as purified sample.

2.2. Characterization

The as-synthesized and purified samples were characterized by HRTEM, X-ray diffraction (XRD), Absorption spectroscopy and Raman spectroscopy. Electronic microscopic images were observed by using High Resolution-TEM (Technai G^{2}20S-Twin model) operated at accelerating voltage of 200 kV. XRD patterns of samples were recorded using a Phillips X'pert PRO X-ray diffractometer with Cu-Kα radiation (λ = 1.54 Å) operated at accelerating voltage of 45 kV and filament current of 40 mA. NIR absorption spectra of as-synthesized and purified samples were recorded by Perkin-Elmer LAMBDA 1050/UV/Vis/NIR absorption spectrometer. Micro Raman experiments were performed by excitation wavelength of λ = 514.5 nm of an argon ion laser using double monochromator Jobin Yvon Lab-Ram 800. Micro-Raman studies of carbon nanostructures were carried out in the backscattering geometry at room temperature. The laser was focused on sample using 100× objective lens and the diameter of laser spot was around 2 μm. Spectral resolution of the Raman spectrometer was 0.5 cm^{-1}.

3. Results and discussion

Fig. 1(a)-(d) shows the representative HR-TEM images of the as-synthesized and purified samples. Presence of the carbon encapsulated iron nanoparticles is clearly visible in Fig. 1(a)-(b). The size of iron nanoparticles are found around few tens of nanometer as shown in Fig. 1(b). Fig. 1(c) display representative HRTEM image of the purified sample. Iron nanoparticles are removed up to very large extent leaving behind the encapsulation of carbon. It is clearly visible in Fig. 1(c) Furthermore, entangled SWCNTs are observed in purified sample and are shown in Fig. 1(d). HR-TEM images justifies the formation of SWCNTs from laser ablation of ferrocene doped graphitic target at room temperature.

XRD patterns of the as-synthesized and purified samples are shown in Fig. 2. The diffraction patterns of the as-synthesized and purified samples exhibit diffraction sharp peaks at 2Θ of 27.7° and 26.6° respectively. It corresponds to hexagonal structure of carbon nanotubes with plane (002) [17]. Diffraction peaks observed at 2Θ of 54.08° and 54.73 in the XRD patterns of as-synthesized and purified samples respectively are due to hexagonal carbon plane (004) [17]. The d-spacing between two planes is estimated around 0.32 nm and 0.34 nm for as-synthesized and purified samples respectively. Few diminished diffraction peaks due to hematite (Fe_2O_3) nanoparticles crystalized in the rhombohedral structures [18] are also observed in the diffraction pattern of as-synthesized sample. These diffraction peaks of Fe_2O_3 are shown as "*" in Fig. 2. It reveals that concentration of hematite is very less in comparison with that of carbon. Diffraction peaks of Fe_2O_3 are missing in Fig. 2 for purified sample which confirms the removal of iron nanoparticles after purification.

Near-IR (NIR) absorption spectra of the as-synthesized and purified samples are shown in Fig. 3(a)-(b). Multiple absorption bands are observed at 0.62 eV, 0.67 eV and 0.75 eV for the as-synthesized sample as well as the purified sample. These bands are tabulated in Table 1. SWCNT exhibits sharp peaks in the absorption spectra for NIR region [19,20]. This is due to Van Hove singularities in the electronic density of states for quasi-one dimensional structure of SWCNTs [20]. Optical excitation by suitable energy results transition between first and second Van Hove singularities of the density of states. It has been reported that the allowed transition between first Van Hove singularities (E_{11}) lies in the range of 0.6 eV–0.8 eV [19]. It corresponds to band gap of semiconductor SWCNTs. This band gap can be estimated by following relation [21].

$$E_g = \frac{0.7}{d_t} \quad (1)$$

where E_g is band gap of semiconducting SWCNT and d_t is diameter of SWCNT. Diameters of different SWCNTs corresponding to