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Potential application of carbon nanotube core as nanocontainer and nanoreactor for the encapsulated nanomaterial

Pawan K. Tyagi [a,*], Reetu Kumari [a], Umananda M. Bhatta [b], Raghavendra Rao Juluri [c], Ashutosh Rath [c], Sanjeev Kumar [d], P.V. Satyam [c], Subodh K. Gautam [e], Fouran Singh [e]

[a] Department of Applied Physics, Delhi Technological University, Delhi 110042, India
[b] Centre for Emerging Technologies, Jain University, Jakkasandra, Kanakapura Taluk, Ramanagaram Dist, Karnataka 562 112, India
[c] Institute of Physics, Sachivalaya Marg, Bhubaneswar 751005, India
[d] Department of Physics, Rajiv Gandhi University, Itanagar, Arunachal Pradesh 791112, India
[e] Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India

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ABSTRACT

Fe_3C nanorod filled inside carbon nanotube has been irradiated inside transmission electron microscope at both room and high temperature. *In-situ* response of Fe_3C nanorod as well as CNT walls has been studied. It has been found that when electron irradiation is performed at room temperature (RT), nanorod first bends and then tip makes at the end whereas at high temperature (~490 °C) nanorod slides along the tube axis and then transforms into a faceting particle. Extrusion of solid particle filled in the core of CNT has also been demonstrated. It is suggested that these morphological changes in nanorod may have happened due to the compression which was generated either by shrinkage of tube or by local electron beam heating. Presented results demonstrate that CNT core could be used as nano-container or reactor.

1. Introduction

Concave geometry of hollow core of carbon nanotube (CNT) with confined space offers the tremendous possibility to generate the nanomaterial of superior physical, chemical or electronic properties [1]. In previous reports [2–15], CNT filled with ferromagnetic material has been proposed as a novel material and their myriad potential applications such as magnetic recording media [16], magnetic force microscopy (MFM) [17], biomedicine [18,19] and spintronics [20] have been demonstrated. This has been attributed to the fact that in filled-CNT, tube-walls not only protect the filled nanomagnets against harsh environment but also prohibit coalescence. Filling of CNT core with different materials have facilitated the fabrication of nanostructures in a controlled fashion and has introduced the interesting applications of CNT such as containers, conduits, pipettes, and coaxial cables. In order to further expand the applications of filled-CNT key aspect will be post-growth modification techniques which can modify shape as well as position of the filled materials in a controlled manner. In recent reports, electron irradiation performed inside high-resolution transmission electron microscopy (HRTEM) demonstrated that when post-growth modification is performed in a controlled manner, it is possible to control the shape, size and properties of the CNTs as well as encapsulated metal by producing defects, at both room [21,22] and high [23] temperatures. Under the energetic electron beam, extrusion of filled material has been demonstrated [24,25]. This evidenced that electron beam might be a tool which has post-synthesis alteration capability on CNT [23,26–30]. Hence, we envision that CNTs either fully or partially filled have many prospective applications. Some of them have been already demonstrated where CNT was used as nanopipette [31], high pressure nanoextruder [24], diagnostic tool [18] and preservative nanocell [18].

Another interesting applications of ferromagnetic nanoparticles, and nanorod of sharp tip filled inside CNT has been reported in the area of high-density magnetic recording media and medicinal imaging [32–34]. Hence, being motivated with the approach adopted in references, [24,25] we performed electron irradiation on Fe_3C-filled CNT at both room and high temperature. *In-situ* response of Fe_3C nanorod as well as CNT was monitored and irradiation induced structure related phenomena such as: shrinkage, thinning, sharpening of tip and shape transformation of nanorod were studied.

* Corresponding author.
E-mail addresses: pawan.phy@dce.edu, pawankumartyagi@gmail.com (P.K. Tyagi).

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2. Experimental details

Fe_3C-filled MWCNTs were grown by modified thermal chemical vapor deposition (Thermal CVD) technique. More details are described previously [35]. The as-grown CNTs were scratched from the quartz tube and a very small amount of the sample was dispersed in isopropyl alcohol. Few drops of the sample were casted on Cu-substrate and glass substrate for XRD and Raman measurement, respectively. As-grown filled-CNTs sample was characterized by using Bruker D8 Advance X-ray diffractometer, Hitachi S3100 Scanning Electron Microscope and Raman spectrometer (Renishaw, model Invia) with 514 nm Ar ion laser operated at power 5 mW.

For TEM measurement dispersed sample was sonicated for 10 min and then one drop of the dispersion was casted onto uncoated copper grid of 1000 mesh for high resolution TEM imaging (JEOL JEM 2010 operated at 200 kV) for carrying out *in-situ* electron irradiation experiments as well as imaging. The grid was then transferred to the specimen holder for electron irradiation and microscopy measurement. Electron beam of energy 200 keV was used. Irradiation at both room and high temperature (~490 °C) was carried out at current density of 100–300 A/cm^2 which corresponds to electron concentration 6×10^{21}–19×10^{21} per cm^2 per second.

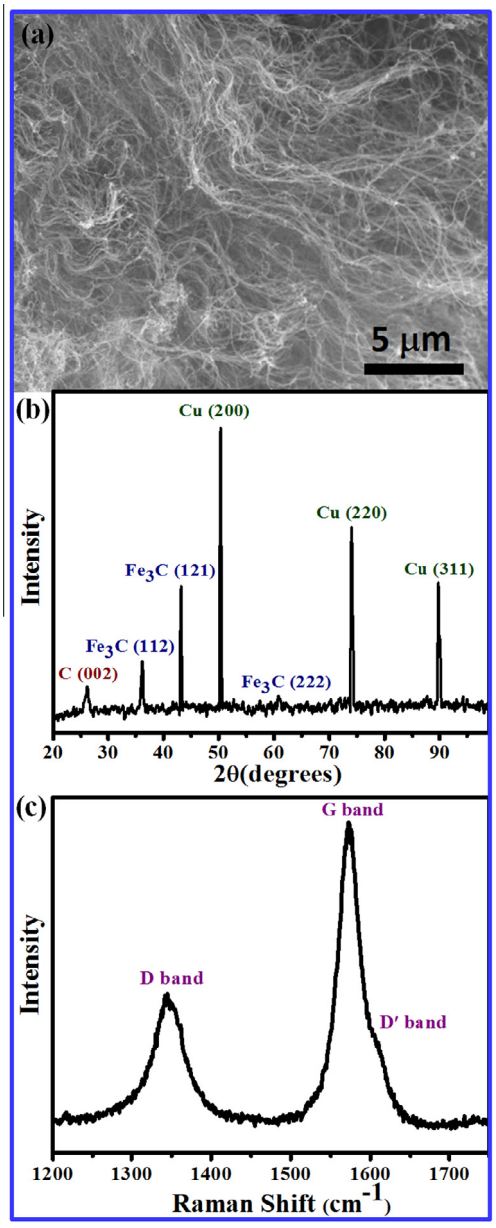

Fig. 1. (a) SEM micrograph, (b) XRD pattern and (c) Raman spectrum of Fe_3C-filled MWCNTs.

3. Results and discussion

SEM image of as-grown MWCNTs is shown in Fig. 1(a). In order to confirm that wire type structures shown in Fig. 1(a) are filled-MWCNT, the sample was further characterized by using XRD measurement as well as Raman measurement. The observed diffraction pattern of filled-MWCNT is shown in Fig. 1(b). The diffraction peak observed at $2\theta = 26.4°$ is indexed as a characteristic peak of MWCNT, representing the inter-wall spacing. The observed value of average d_0 is 3.3529 ± 0.0005 Å (PCPD file no: 89-8487). The diffraction peaks at $2\theta = 36.82°$, 43.38° and 61.45° assigned to (112), (121) and (222) planes of orthorhombic crystal structure (cementite phase) of Fe_3C. These reported values are in accordance with 37.6°, 43.7° and 61.3° (PCPD file no: 89-2722) for same planes. Remaining peaks are indentified and found to correspond to Cu substrate.

Raman spectrum of as-grown sample is shown in Fig. 1(c). Main Raman features have observed at position around 1345 cm^{-1}, 1573 cm^{-1} and 1606 cm^{-1}. D peak at 1347 cm^{-1} assigned to K-point phonons of A_{1g} symmetry associated with breathing vibration of a 6-fold aromatic ring. This mode activates by disorder in graphitic structures. G peak position at 1575 cm^{-1} assigned to zone center phonons of E_{2g} symmetry or sp^2 stretch vibration in benzene or condensed benzene rings. D′ peak at 1611 cm^{-1} originates when phonons in defected graphite with a small q activates.

Fig. 2(a) is the TEM image of cementite nanorod encapsulated inside the CNT. The diameter of the metal nanorod is 10.2 nm. Lattice fringes (Fig. 2b) of cementite crystal encapsulated inside the core of CNT reveal that cementite is a single crystal. The image in Fig. 2(b) demonstrates that the lattice fringe with a periodicity of

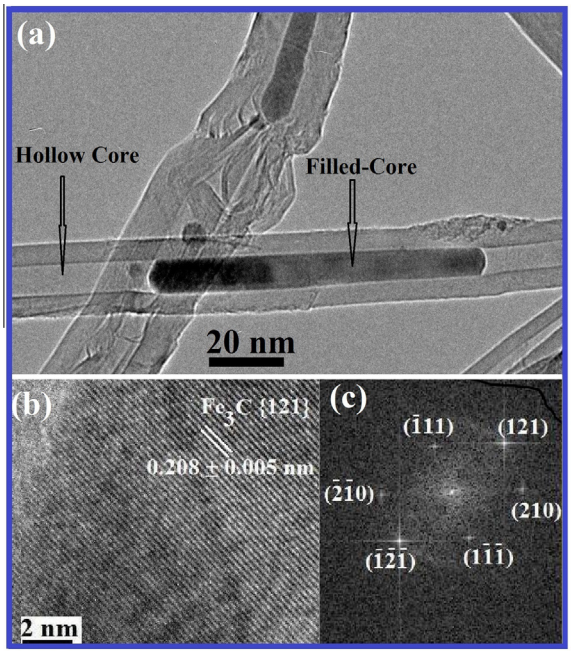

Fig. 2. Panel (a) TEM image of nanorods encapsulated inside the MWCNT. Panel (b) and (c) is the lattice image of nanorod and their corresponding Fast Fourier Transforms (FFT) pattern, respectively. The encapsulated crystal was identified as iron carbide (cementite, Fe_3C).