TAILORING DEFECTS IN NANOCARBONS: SINGLE-WALLED CARBON NANOTUBES AND COMPOSITES WITH NANODIAMOND BY IRRADIATION

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Introduction

Carbon is a unique element because a simple variation in its local bonding configuration (sp^3 *versus* sp^2) gives rise to a variety of materials as diverse as diamond, graphite, fullerenes, disordered and nanostructured carbons including nanocrystalline diamond and carbon nanotubes [1]. For over a decade, advanced multifunctional carbon-based nanomaterials excited a great interest both in view of the obvious academic importance and technological relevance [2]. In this family, carbon nanotubes (CNTs) continue to attract a great deal of attention attributed to several unique physical (mechanical, electrical, thermal, chemical and biological) properties [3, 4]. Likewise, nanoscale diamond shows great promise due to similar range of unsurpassable physical properties. In addition to their technologically interesting electrical/electronic properties, these materials have many other attractive physical and chemical properties, such as chemical inertness and resilience to harsh environments [3]. Diamond is reputed for being radiation hard and hence preferable over the other existing semiconductors [5].The above mentioned promises incite fundamental understanding the way in which these nanoscale carbon material interacts with the radiation field. Moreover, for space applications that they are physically stable and structurally unaltered when subjected to irradiation is indispensable. The present work investigates single-walled carbon nanotubes (SWCNT) and their hybrids with ultradispersed nanodiamond (UDD) forming truly *tetragonal-trigonal* nanocomposite ensembles.

Experiments show that irradiation display various local structural instabilities due to nanoscopic defects in the lattice. Resonance Raman spectroscopy revealed that irradiation generated defects elucidated through the variation in the intensity and position of some of the important Raman bands include radial breathing mode (RBM), D and G and the first overtone of the D band (2D) band. The increase in the defect-induced D band intensity, a slight change in the position and intensity of G and 2D bands are some of the implications for both the SWCNT and nanocomposites. Compared with electron beam effects which introduces dramatic modification in SWCNT [6], the gamma irradiation is much softer and the nanocomposites are quite resilient towards electromagnetic irradiation. The results are discussed in terms of critical role of defects.

Experimental

The SWCNT with average diameter ~ 1.35 nm were produced using well-known HipCO process developed at CNI Technologies Inc. [7].Briefly, these materials were spin coated on SiO_2/Si wafers forming thin films and subjected to gamma ray (E = 1 MeV) doses of 50, 100 and 10^3 kGy at the rate of 12 kGy/h from ^{60}Co nuclide from a ^{60}Co source at the MURR Reactor of the University of Missouri, Columbia. The nanodiamond with individual grain size of ~ 2-5 nm and of aggregate ~ 20-30 nm was supplied by Dr. V. Padalko (Alit Co.). To assess structural modification and probing defects, they were analyzed prior to and post-irradiation using SEM, TEM, XRD, resonance micro-Raman spectroscopy (RS) and *I-V* analytical techniques in terms of morphology, microscopic structure and physical properties.

Results and Discussion

Figure 1 shows the SEM and TEM images of dispersed diamond, SWCNT and composites thereof revealing surface morphology. The images are colored for the sake of clarity only. The pristine UDD showed an agglomerate of nanoparticles and the average cluster size is estimated to be around 5-10 nm. Since SWCNT satisfies the weak phase object approximation, its TEM image is a direct projection of the specimen in the direction of the electron beam. Maximum contrast is produced where the beam encounters the most carbon atoms, which occurs when it is tangent to the tubes' walls. SWCNT tend to form typical 'spaghetti-like' bundles of nearly parallel tubules (appeared as a regular two-dimensional hexagonal lattice structure. Apparent from TEM images, the diameter of the tube and bundle is estimated to be around 1-2 nm and 10-20 nm, respectively. Both the UDD and SWCNT contain quite small amount of undesired carbonaceous and catalyst particles implying that these materials had much less impurities. As far as the SWCNT and UDD nanocomposite is concerned, SEM/TEM images show the sticking of UDD nanoparticles on the walls of the SWCNT bundles that is spread uniformly across the films. No apparent change has been observed in the SEM and TEM images on gamma irradiated SWCNT and nanocomposites. This observation is in contrast to the ones made using electron-beam irradiation wherein SWCNT showed an apparent "synapse" or interlinking of an occasional found bundle containing a few tubes in the irradiated area, graphitization and aggregation of amorphous carbon; *a-C* [6].

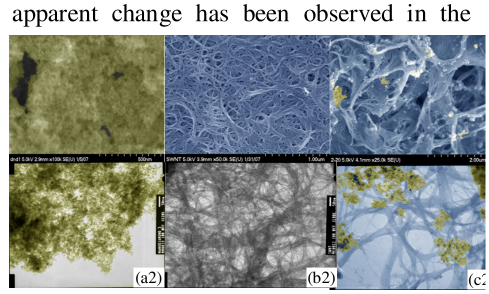

Fig. 1 Shown are (top) SEM and (bottom) TEM images of pristine UDD, SWCNT and nanocomposite.

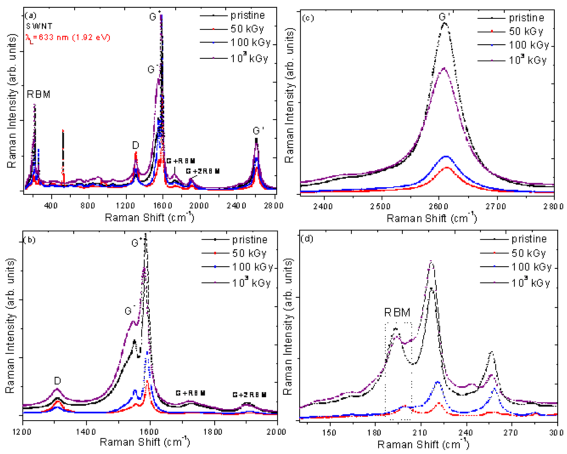

Fig. 2. (a) Shown are the first- and second-order micro-Raman spectra of SWNT with varying gamma irradiation dose demonstrating the characteristic (b) D and G bands, (c) first overtone of the D band (G' band) and (d) radial breathing mode (RBM).

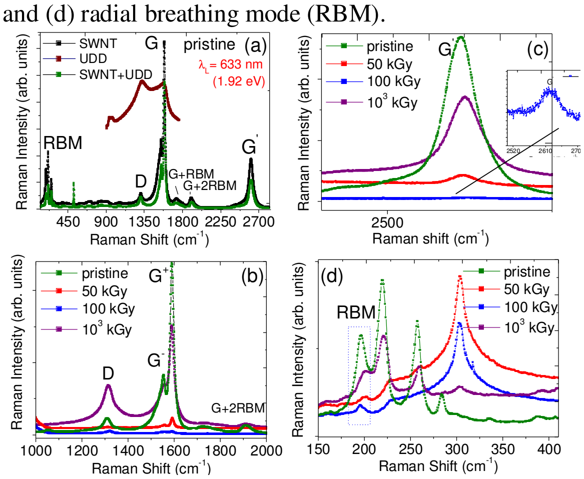

Fig. 3. Shown are the first- and second-order micro-Raman spectra of (a) pristine and (b, c, d) gamma irradiated nanocomposites with varying dose demonstrating the characteristic D and G band, G' band and radial breathing mode (RBM). The spectrum for UDD is also shown in (a).

To further analyze the modification induced by gamma irradiation, we used resonance Raman spectroscopy technique. Figs. 2 and 3 display Raman spectra for both the SWCNT and composites with nanodiamond in different regions of the Raman spectra *i.e.* first- and second- order spectra. Experiments showed that with irradiation, SWCNT display various local structural instabilities due to nanoscopic defects in the lattice. Since the irradiation conditions may resemble increased pressure regime enabling a degree of structural fluidity at nanoscale, a microscopic stress/strain may also result in the films. These effects exert a significant influence on their physical (optical and electrical) properties. Resonance Raman spectroscopy revealed that irradiation generated defects elucidated through the variation in the intensity and position of radial breathing mode (RBM), intensity ratio of D to G band (I_D/I_G), D and G band position and widths and the position of the first overtone of the D band (G'). The increase in the defect-induced D band intensity, partial quenching of RBM intensity and a slight change in the position and intensity of G band are some of the implications for both the SWCNT and nanocomposites. In the interpretation of various findings, we suggested the following: 1) a minimal change in G band intensity is not explained by the defect-mediated double-resonance mechanism 2) a concomitant electronic charge transfer arising due to the difference in the electronegativity of C-sp^3 and C-sp^2 and mis-orientation of C-sp^2 resulting in structural disorder and 3) softening of the $q = 0$ selection rule. To further gain an insight into the nature of the defects (charged *versus* residual), the in-plane correlation length (L_a) was determined following TK relation. It was found that gamma irradiation increases L_a for SWCNT thus passivating residual defects, but a decreasing trend implies charged defects which is described in terms of dangling bonds for the hybrids. The SWCNT combined with nanodiamond in most part retain their semiconducting behavior unlike those found with SWCNT being exposed to electron-beam which seems appropriate and needs attention. Moreover, these irradiated material systems with artificial defects may serve as electrochemical sensors with faster response time.

Conclusion

In summary, we have investigated the influence of gamma irradiation on SWCNT and composites with nanodiamond. The accumulated evidence point at the radiation tolerance of SWCNT towards gamma rays especially when combined with nanodiamond and existence of an insensitive radiation microstructural state ascribed to saturation damage. These findings provided a contrasting comparison between gamma rays and E-beam effects on SWCNTs. The authors wish to acknowledge M. Muralikiran for technical assistance in preparing nanocomposite films and electron microscopy and X. Han (Brewer Science Inc. Rolla, MO) for using micro-Raman spectrometer. This work was financially supported in parts by internal MU Research Council funds.

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