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Optical Absorption and Raman Spectroscopy Study of the Fluorinated Double-Wall Carbon Nanotubes

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Abstract: Double-wall carbon nanotube (DWNT) samples have been fluorinated at room temperature with varied concentration of a fluorinating agent BrF_3 . Content of the products estimated from X-ray photoelectron data was equal to $\text{CF}_{0.20}$ and $\text{CF}_{0.29}$ in the case of deficit and excess of BrF_3 . Raman spectroscopy showed considerable decrease of carbon nanotube amount in the fluorinated samples. Analysis of optical absorption spectra measured for pristine and fluorinated DWNT samples revealed a selectivity of carbon nanotube fluorination. Nanotubes with large chiral angle are more inert to the fluorinating agent used.

Keywords: Fluorination, carbon nanotubes, optical spectroscopy

INTRODUCTION

One of the attractive applications of double-wall carbon nanotubes (DWNTs) can consist in capacitor development. Actually, a study of

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bromine- and iodine-doped DWNTs using Raman spectroscopy has demonstrated charge transfer from the adsorbed halogen ions onto the outer tube shells (1, 2). Fluorine being the most reactive halogen has been found to attach covalently to carbon nanotube surface (3, 4). Fluorinated single-wall carbon nanotubes (SWNTs) are easily dissolved in alcohols that allow conducting new reactions for tube functionalization (5). The aim of the present work is investigation of DWNTs reactivity toward a fluorinating agent BrF_3 . Application of this reagent to the HiPCO-produced SWNTs has been found with Raman spectroscopy to result in fluorination of thinner nanotubes mainly (6). In DWNT samples, the thin tubes are usually protected by the outer shells. To reveal structural changes of DWNT with fluorination we use optical absorption and Raman spectroscopy.

EXPERIMENTAL

DWNTs were produced by decomposition of CH_4 over $\text{Mg}_{1-x}\text{Co}_x\text{O}$ solid solution with small addition of molybdenum (7). Metal oxides were removed by treatment of the sample with concentrated aqueous HCl solution. High-resolution transmission electron microscopy showed the sample contains 77% DWNTs, 18% SWNTs, and 5% triple-wall nanotubes. The diameter distribution of the DWNTs ranged from 0.53 to 2.53 nm for inner shells and from 1.2 to 3.23 nm for outer shells.

Two fluorinated DWNTs samples were prepared. Sample I was fluorinated with unsaturated BrF_3 vapor, sample II was fluorinated with saturated vapor of BrF_3 and Br_2 mixture. A sample placed in a Teflon flask was held in a vapor for 7 days. Content of the samples I and II was estimated using X-ray photoelectron spectroscopy (XPS) data recorded on VG ESCALAB HP spectrometer with Al $K\alpha$ radiation to be $\text{CF}_{0.20}$ and $\text{CF}_{0.29}$, respectively. The micrographs of the products were obtained with a JEM-2010 transmission electron microscope (TEM).

To measure optical spectra a tube-contained powder was mixed with heptanes and then sonicated for about 1 hour. Suspension produced was deposited on a sapphire substrate (for optical absorption recording) or a silicon substrate (for Raman spectra recording) using an airbrush. Evaporation of the solvent was aided by heating substrate during airbrushing at about 40°C . The width and homogeneity of film obtained were controlled visually. The absorption spectra were acquired using Shimadzu UV 3101 PC instrument in a wavelength range of 190–3200 nm with a resolution of 3 nm. A sample was probed at three different points and the data obtained were summed. The optical spectra were background corrected and normalized at the maximal value. Raman spectra were measured using triple monochromator “TriVista 777.” Scattering was excited by $\lambda = 532.1$ nm.

RESULTS AND DISCUSSION

Raman spectra of the pristine and fluorinated samples are compared in Figure 1. Fluorination results in broadening of the tangential stretching G mode and increase of the disorder D mode intensity (Raman spectra was normalized to G-mode). The most changes are characteristics for the sample II having larger fluorine content. Raman spectroscopy indicates a broadening of the G band with increasing the fluorination degree of DWNTs. The spectra of the fluorinated samples exhibit considerable reduction (in ~ 10 times) of intensity of the radial breathing mode RBM ($100\text{--}400\text{ cm}^{-1}$). Disappearance of peaks over the $100\text{--}200\text{ cm}^{-1}$ Raman spectral region for the sample II indicates fluorination of almost all outer shells of DWNTs.

Figure 2 presents optical absorption spectra obtained for the investigated samples. Compared to the spectrum of pristine DWNTs, the spectra of fluorinated samples show larger number of features those are shifted toward high energies. Better resolution and red shift of optical absorption features are usually achieved in the result of carbon nanotubes dispersion using an appropriate surfactant (8). In our case, fluorine attachment to the tube surface results in increase of the tube spacing and thus appearance of the fine structure of spectrum. The largest number of features are exhibited in the sample I spectrum; their assignment to the electron transitions between singularities

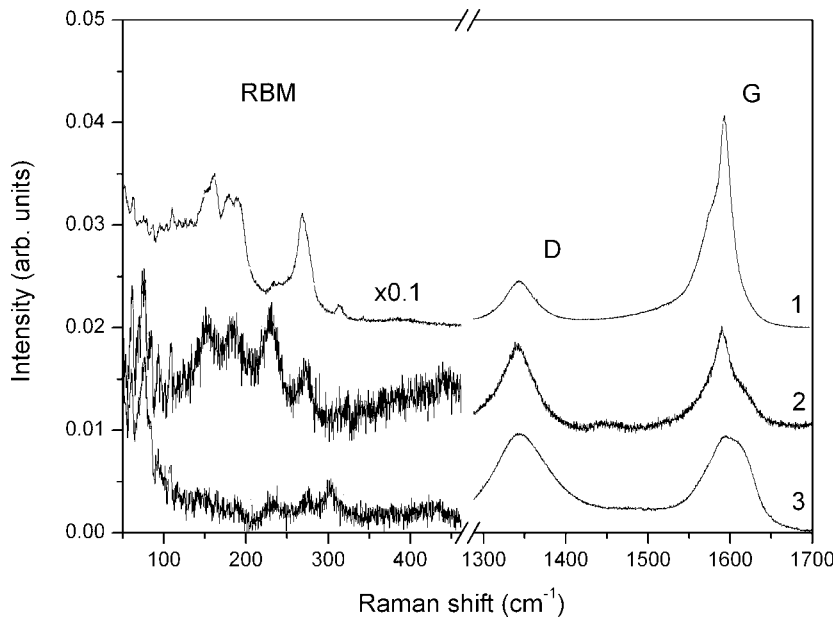


Figure 1. Raman spectra of pristine DWNT sample (1), fluorinated sample I (2), and fluorinated sample II (3).

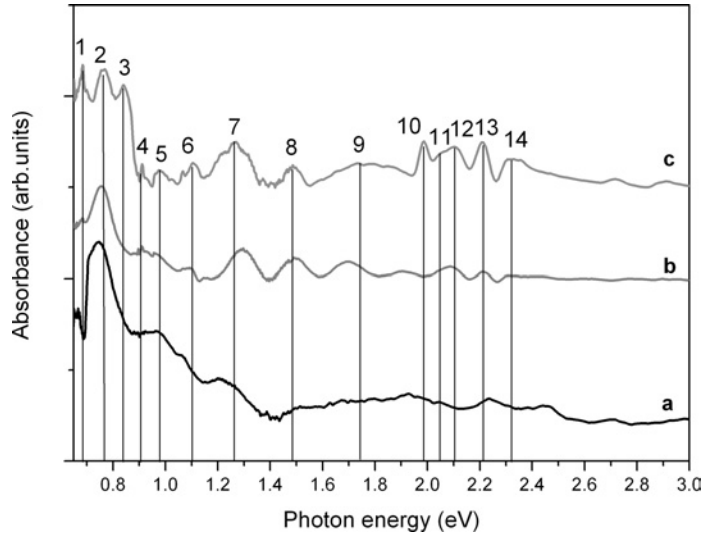


Figure 2. Optical absorption spectra of pristine DWNT sample (a), fluorinated sample II (b), and fluorinated sample I (c).

in density of states of carbon nanotubes (see Table 1) was made based on Bachilo *et al.* data (9). E_{11} and E_{22} indicate transitions between the first and second singularities specularly located around the Fermi level. The first two features in the spectra of fluorinated DWNTs have lower energies than the values collected in (9) that prevent their assignment. The features exhibited in the low-energy spectral region (up to ~ 1.4 eV) mainly correspond to E_{11} transitions in semiconducting tubes. The next features, having energy less than 2.4 eV, are formed due to E_{22} transitions in the selected tubes and E_{11} transitions in metallic tubes (10). Some of the features can be attributed to

Table 1. Energy (eV) and assignment for features of the sample I optical absorption spectrum

Feature	Energy	Assignment	Feature	Energy	Assignment
1	0.68	—	8	1.49	E_{22} (9, 8)
2	0.76	—	9	1.75	E_{22} (9, 4), E_{22} (8, 7), E_{22} (7, 6)
3	0.84	E_{11} (13, 5)	10	1.99	E_{22} (10, 3)
4	0.92	E_{11} (9, 8), E_{11} (9, 4)	11	2.06	E_{11} (13, 1)
5	0.98	E_{11} (8, 7)	12	2.10	E_{11} (11, 5)
6	1.10	E_{11} (7, 6), E_{11} (10, 3)	13	2.20	E_{22} (6, 5)
7	1.26	E_{11} (6,5), E_{22} (13,5)	14	2.32	E_{11} (10, 1)

the electron transitions in two (4, 6, 7, and 11 features) and even in three (9 features) carbon nanotubes. The low-intensity features in the high-energy spectral region are not possible indexing for lack of data.

Appearance of the resolved features in the optical absorption spectra of the fluorinated DWNTs indicates that certain tubes remain non-fluorinated. Because these tubes have diameter less than 1.3 \AA , they are probably the inner shells of DWNTs. It is surprise that most of intact nanotubes correspond to the $(n, n - 1)$ branch being near-armchair one. Probably, the synthesis peculiarities cause enriching the DWNT sample in such a type of tubes. The optical absorption spectrum of the sample II slightly differs from the sample I spectrum. Thus, features 3 and 10 assigned to $(13, 5)$ and $(10, 3)$ nanotubes are absent in the former spectrum and intensity of features 6, 7, 12, and 14, which are formed with the tubes unrelated to the $(n, n-1)$ series, are reduced. Hence, increase in the fluorinating agent concentration results in fluorination of these tubes while the near-armchair carbon nanotubes still remain intact. This result suggests selectivity of carbon nanotube fluorination depending on tube chirality. Transmission electron microscopy picture of the sample II demonstrates disruption of the inner shells of some tubes and retention of double-walled structure for other tubes (Figure 3).

Q2

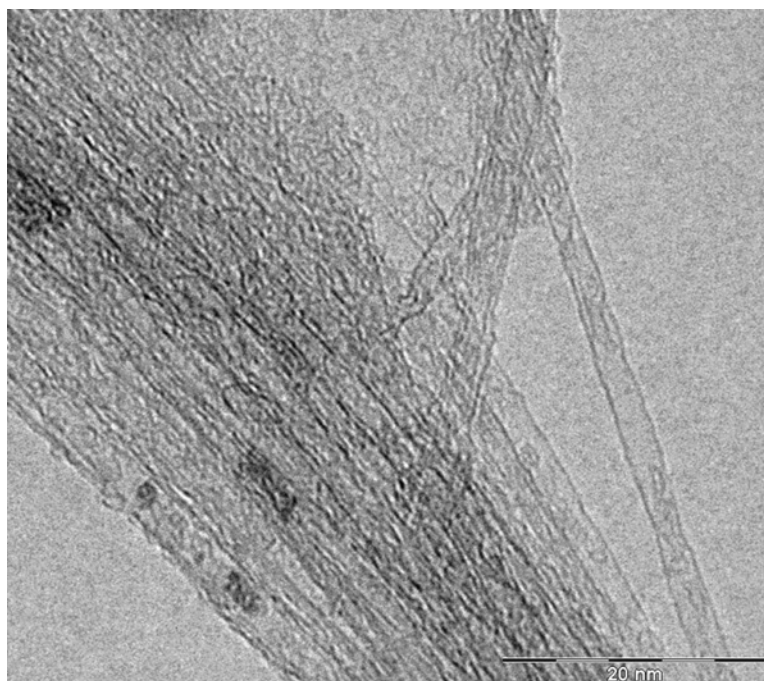


Figure 3. TEM image of nanotubes occurred in fluorinated sample II.

In summary, optical absorption and Raman spectroscopy showed retention of the intact carbon nanotubes in the fluorinated DWNTs sample, which could be the inner tube shells. Increase of the fluorinating agent concentration results in etching some of these tubes while the near-armchair carbon nanotubes are inert to the fluorination.

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