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Fullerene-Clad Ultra-Long Carbon Nanotubes

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Abstract

Fullerene-clad double-walled carbon nanotubes were synthesized by impregnation of the nanotubes with organic solution of fullerene C₆₀ and consequent immobilization by laser irradiation. The resulting fullerene- nanotube composites were characterized by both electron microscopy and X-ray photoemission spectroscopy. The formation of densely packed layer of polymerized fullerene bonded to the nanotube surface was shown.

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1. Introduction

Both double-walled carbon nanotubes (DWNT) and fullerenes C₆₀ attract researchers' attention since the moment of relatively recent discovery of these carbon nanostructures due to novel properties predicted for these nanostructures. Although DWNT and C₆₀ both represent giant closed structures of aromatic carbon sheets and thus resemble each other, their properties differ dramatically. In particular, C₆₀ is characterized by extremely high elastic modulus up to 900 GPa [1, 2], while carbon nanotubes show even high elastic modulus of up to 1,200 GPa in axial direction only [3, 4]. Another important distinction is in hardness, which can be comparable with that of diamond for polymerized C₆₀, while DWNT is a soft matter [5].

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It is suggested that composite materials based on combination of DWNT and C_{60} can possess unique and valuable properties..

A weak bonding between a C_{60} binder and carbon nanotubes serves an obstacle for development of any DWNT-based composite material. However literature suggests that modification of graphene-based structures such as nanotubes with fullerenes is possible [6-8].

According to [5] additional C-C bonding can be provided by laser treatment. The laser processing induces polymerization in an inert atmosphere if irradiation intensity is higher than 1 W/cm^2 [9]. The authors [9] show that accumulated irradiation should be at least 20 kJ/cm^2 .

The purpose of this work was to synthesize fullerene-clad DWNT and find experimental XPS confirmation of bonding between DWNT and C_{60} .

2. Experimental

DWNT were synthesized by catalytic decomposition of ethanol as disclosed in [10] in detail. The as-synthesized DWNT (designated as CNT1) comprised nanotubes with diameter varying from 3 to 6 nm, catalyst residue particles and lateral amorphous carbon formations. The DWNT in as-synthesized form were deep-black, light-weight (density of 0.1 to 0.2 g/cm^3 only) unwoven threads cut to 10-cm pieces. The CNT1 were subjected to oxidative treatment by annealing in air at 380°C for 3 hours and consequent treatment in 65 % nitric acid. The treated material is designated CNT2 further in this paper.

The fullerene-clad nanotubes (composites) were prepared using both as-synthesized and oxidized DWNT. The composites were prepared in the following way: DWNT were impregnated with saturated solution of C_{60} in carbon disulfide at 25°C ; then the solution was decanted and the solid phase was dried in argon gas at 100°C thus forming Van der Waals-bonded composites CM1 (with CNT1) and CM2 (with CNT2).

The CM1/CM2 were further subjected to laser processing using continuous-wave green laser (wavelength 514 nm; irradiation intensity 10.3 W/cm^2 ; accumulated irradiation dose 9.6 J/mm^2). The laser treatment resulted in formation of covalent-bonded composites CM1-p and CM2-p.

Both as-synthesized and oxidized nanotubes were characterized by scanning electron microscopy (SEM) using JSM-6700F microscope by JEOL with acceleration voltage of 15 kV and by transmission electron microscopy (TEM) using JEM-2010 microscope by JEOL.

X-ray photoelectron spectroscopy (XPS) investigation was performed with PHI 5000 VersaProbe II, ULVAC-PHI. $\text{Al } K\alpha$ irradiation with power 50 W was used for excitation, an analysis area had diameter 100 to 200 μm . Samples were fixed in a stainless steel platen with a recessed slot so a low background signal was insured. The C_{60} powders were pressed into Indium foil.

Elemental composition of the samples was determined from review spectra taken in the range from 0 up to 1,100 eV at the analyzer pass energy 93.9 eV and 0.8 eV step size. The high resolution spectra were taken at the analyzer pass energy 11.75 eV and 0.1 eV step size. Data approximation was done by non-linear least squares method. Complete XPS analysis including both survey spectra and high resolution spectra was done for 3 to 5 analysis points for every sample.

3. Results and discussion

Investigation of fullerene-clad DWNT by transmission electron microscopy showed that the molecules of fullerene formed a shell and covered nanotubes by bimolecular closely-packed polymerized layers. The thickness of such C_{60} layer was 2-3 nm only as shown in Figure 1. It is interesting that immobilization of fullerene was accompanied by visible film self-ordering.

The analysis of review XPS spectra of C_{60} crystals revealed no admixtures except some adsorbed molecular oxygen, which occurred in concentration below 0.3 % at. The measurements of XPS spectra of C_{60} were hindered by strong charge-up due to low electrical conductivity of C_{60} . Low energy electrons were used for neutralization of the charge up. It is necessary to note that C1s spectra of C_{60} are symmetrical and hence very much different from those of DWNT.

The values of C1s binding energies for both pristine and fullerene-clad DWNT were identical and constituted 284.45 eV, however the shift in satellite extra peaks was different and varied from 0.05 eV for CNT1 up to 0.4 – 2.6 eV for CNT2-p. The positive shift in CNT2-p is probably determined by differential charge-up, which is caused, in turn, by the presence of both conductive DWNT and insulator fullerene microphases. Since the numerous oxygen-containing groups block fullerene-nanotube bonding in these composites, the microphases are separate enough. Elemental analysis by XPS showed that as-synthesized DWNT samples contain substantial amounts of iron and oxygen. The purification led to complete removal of iron, while oxygen content increased from ≤ 1.0 % at. up to 3.0 – 5.0 % at. The latter was rather expected because oxidative purification has to result in seeding a lot of hydroxyl and other functional groups at the surface of carbon. These groups were detected by the analysis of C1s peak shape. The C1s spectrum of as-synthesized sample CNT1 has an appearance typical for nanotubes, i.e. consists of a main asymmetric peak at 284.45 eV; and a satellite peak caused by excitation losses in π - π^* transitions and π - plasmon (π – satellite). The oxidation to CNT2 causes appearance of two additional peaks at 286.4 – 286.9 eV and at 287.5 – 288.5 eV. The former peak corresponds to -C-OH (hydroxyl) and -C-O-C- (ether, epoxy group), while the latter peak is typical for -C=O .

The results of instrumental studies of CNT1-p and CNT2-p also showed that fullerene molecules were immobilized with covalent bonds after laser processing effectively decreasing the surface concentration of C-O bonds, the oxygen concentration in general and healing some of the surface defects. XPS study also manifested partial transition of sp^2 -hybridized carbon into sp^3 -hybridized form as a result of immobilization.

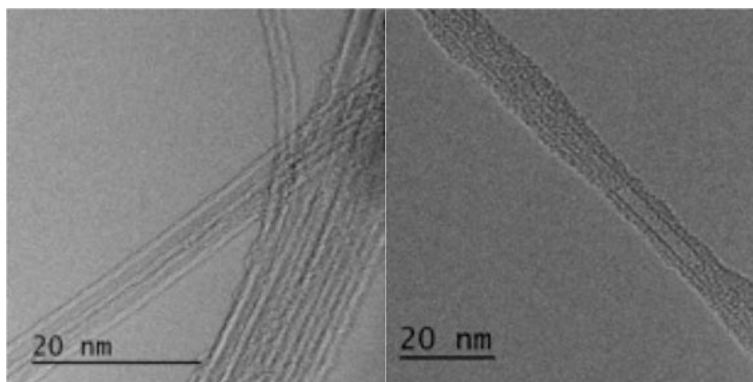


Fig. 1. Double-walled nanotubes: as-synthesized (left); fullerene-clad (right).

The C_{60} content in such nanocomposites may reach 37 % weight. It was also shown that the combination of fullerenes with fibrous carbons in such immobilized composites leads to drastic alteration of mechanical properties as well as of chemical durability. Enhancement of electrical conductivity was registered as well.

(1)

4. Conclusions

Ultra-long double-walled carbon nanotubes (DWNT) were grown in a scaled-up continuous reactor. These nanotubes were transformed into fullerene-clad form by two-step process of impregnation and immobilization. The 2-3 nm thick C_{60} covering was closely-packed and tied strongly by covalent bonds. It has been established that the new properties can be reached in such nano-composites. As a result, the new fullerene-clad centimeter-long nanofibers were synthesized as a basis for novel nanomaterials.

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