

Methods of purification and characterization of carbon nanotubes

V. DJORDJEVIĆ^{a*}, J. DJUSTEBEK^a, J. CVETIČANIN^a, S. VELIČKNOVIĆ^a, M. VELJKOVIĆ^a,
M. BOKOROV^b, B. BABIĆ STOJIC^a, O. NEŠKOVIĆ^a

^aVINČA Institute of Nuclear Sciences, P.O. BOX 522, 11001 Belgrade, Serbia

^bFaculty of Natural Sciences, Department of Biology, 21000 Novi Sad, Serbia

In an attempt to purify MWNT in mild conditions, we have applied two different methods of purification. The first method of purifying the material was a combination of relatively often used methods, such as etching and acid treatment, and the second method was a relatively new one, using an organic polymer PmPV. Sample purity was obtained with SEM and ESR techniques.

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1. Introduction

In the late 20th century, fullerenes and carbon nanotubes (CNT) were discovered as new allotropic modifications of carbon [1,2]. Since then, the knowledge of new carbon structures and its derivatives grows. The variety of new species is diverse, such as endo- [3], exo- [4] and heterohedral [5] fullerenes, functionalized [6] or filled single-walled (SWNT) [7] and multi-walled (MWNT) [8] carbon nanotubes, leaving a vast field of diverse new applications to be developed [9]. SWNT are considered to be one-dimensional molecules due to their high length to diameter ratio [10], while MWNT are a collection of concentric SWNT, and as such, it is of great importance to comprehend and explore the possibilities of purifying the material on nanoscale level, with a special curiosity in size of tubes.

Oxidation in oven using various oxygenated species such as air or oxygen was one of the first attempts to purify carbon nanotubes, while separation of desired diameter of CNT is yet to be accomplished. It is generally believed that by selective oxidation, the content of nanotubes could be increased, based on the fact that the etching rate of amorphous carbons is faster than that of nanotubes [11]. Also, acid treatment purification was widely used, often as complementary method to oxidation. It could cause defect of sidewalls [12] but it could also be used for selective burning and narrowing the diameter or length of nanotubes [13,14]. Also, the ends and sidewalls of the acid-treated nanotubes become functionalized with carboxylic groups [15], which lead to manufacturing new derivatives of nanotubes via covalent functionalization [16]. That effect changes electrical properties of nanotubes but it could also be used for some applications of the material, especially with application in analytical chemistry [17]. In attempt for gaining greater yields, combination of different oxidizing agents with or without the use of acids were

used in liquid-phase oxidations, such as KMnO_4 [18], H_2O_2 [19] or bromine water [20] etc. Ultrasonication was combined with almost every technique because treating the sample in ultrasonic bath can free many tubes from the particles which are originally stuck together [21]. A considerable progress in purifying SWNT was made but this has not been the case for MWNT because of difficulties in obtaining larger quantities of pure sample material [22]. It is considered that low yield of MWNT sample has been caused by vigorous burning carried out to remove the graphite pieces. Therefore, the choice of acid, the immersing time, and temperature are the key factors for high yield, while maintaining the least damage of walls as possible.

In attempt to isolate a better product, several nondestructive methods were developed. Purification via organic functionalization [23] is based on making CNT more soluble than impurities by attaching other groups to the tubes, then separating nanotubes from impurities by filtration or chromatography [24]. Even though such methods could be scaled up to high yields, an additional step for removing functional group must be applied. Purification with polymers has a completely different approach. This method is based on the difference in van der Waals potential between CNT and the chemical environment. Due to van der Waals interactions, organic polymers with benzene rings have a tendency to form polymer-nanotube composite solutions. This way, graphitic impurities tend to sediment out of solution, leaving stable polymer-nanotube suspension above. There have been experimental and theoretical studies of interactions of different organic polymers and carbon nanotubes. A recent molecular dynamic study on interaction between polymers and carbon nanotubes shows that CNT-polymer interactions are the strongest for conjugated polymers with aromatic rings on the polymer backbone, as these rings are able to align parallel to the

nanotube surface and thereby provide strong interfacial adhesion [25]. Between PS, PPA, PmPV and PPV polymers, PmPV has the most pronounced effect of interaction due to combined flexibility in the backbone structure and flexible side chains. The intensity of the interaction is also supported by the fact that binding of conjugated polymers is both van der Waals and electrostatic in nature and thus stronger than the van der Waals binding for nonconjugated polymers [26].

2. Experimental

The arc discharge method with graphite anode which was evaporated in inert gas at near-atmospheric pressure was used for the production of MWNT [27]. Row material, gray powder, contains 20-40% MWNT and other carbonaceous particles such as amorphous carbon and crystalline carbon.

Purification process was started by etching. It is general believe that by selective oxidation, the content of nanotubes could be increased, based on the fact that the etching rate of amorphous carbons is faster than that of nanotubes [11]. A batch of row material was etched on 480 °C in air for one hour. Loss of mass was insignificant. The temperature was raised on 600°C for three hours and the loss of mass was 10.2%. The material was then separated in two. The first part of this material was treated with 12M HCl (approximately 15mg of row material per 1 ml of acid). The mixture was vortex for a short time and left to stand, with occasional shake, for 24 hours. Later it was centrifuged and rinsed with water for several times until mild acid reaction, dried in air and weight. Loss of mass was 2.6%. The second part of same etched material was treated with 6M HCl (with the same concentration of MWNT like the previous sample) in ultrasonic bath for two hours. After that, it was also centrifuged and rinsed with water for several times and dried in air. Loss of mass was slightly greater, 4.6%. The residue acid was used for ICP determination of metal impurities. The content of metals (Co, Fe, Ni, Cu and Cr) in both acid residues was found to be less than 0,001%.

One step purification was applied to the same row sooth material in attempt for "softer", nondestructive purification with greater yield. The principle was to disperse nanotubes in suitable organic polymer solution. Solution of *poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)* (PmPV) [28] in toluene was used in this experiment.

Polymers to nanotube mass range, in which the saturation of MWNTs in suspension will occur, vary with different sooth and it is greatly dependable on purity of nanotubes [29]. We experimented with 12.5 ml of 18g/l PmPV in toluene that was mixed with 0.0840 g row nanotube sooth. This mixture was vortex for a short time, sonicated in ultrasound bath for two hours, and then was left to stand for 48 hours. Three layers were distinguished. The bottom layer was made of black carbonaceous impurities that were sediment out. In the middle of vessel, the green-black suspension layer was made of MWNTs and polymer. The top layer was a clear yellow solution of

residue polymer in solvent, which indicate that no saturation of MWNTs in polymer occurred, but less concentrated polymer solution could have been used.

Middle layer, the green-yellow suspension, was pipetted out of bottom black layer of carbonaceous impurities. To separate MWNTs from polymer it was necessary to weaken van der Waals interactions between carbon hexagons in MWNT and benzene rings from PmPV. To achieve so, we diluted suspension with toluene (10 ml suspension to 250 ml toluene) and sonicated it for a short time. Nanotubes were retrieved from diluted PmPV solution using Buchner filtration. PTFE on polyethylene Millipore FGLP filter with 0.2 µm pore diameter was used to filter MWNTs from polymer solution. MWNTs remained on the filter as black residue, while filtrate was bright yellow, indicating the presence of PmPV but not MWNTs. Nanotubes on the filter were washed out with toluene for several times, until the filtrate emerged colorless, indicating the absence of PmPV. Filter was left to stand in air for toluene to evaporate, then weight. The loss in mass from the row sooth was about 90%. MWNTs were stick to filter with a slight difficulty to scrape it off. In attempt to separate nanotubes from filter with a short sonication in toluene, some dissolving of filter was observed.

Characterization of MWNT was made on SEM (JEOL JSM 6460 LV Japan, 2003) and ESR measurements were performed on a Varian X-band spectrometer with 100 kHz modulation at room temperature.

3. Results and discussion

Small loss in mass and low metal content indicates that nanotubes purified via etching followed by acid treatment are purified in a small extent. SAM images of both samples treated with acid are presented in Fig. 1 and Fig. 2, while Fig. 3 represents MWNT purified by PmPV.

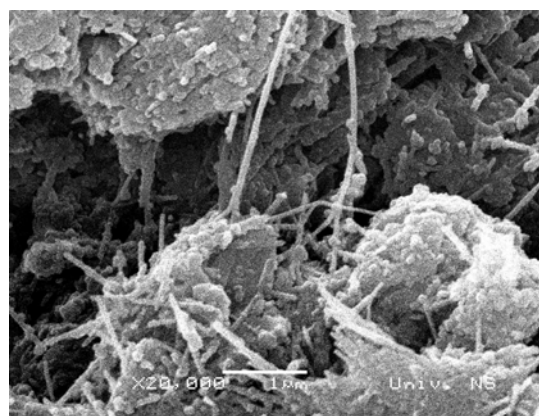


Fig 1. MWNT after acid treatment with 12 M HCl. Large bundles of MWNTs and carbonaceous impurities are obvious.

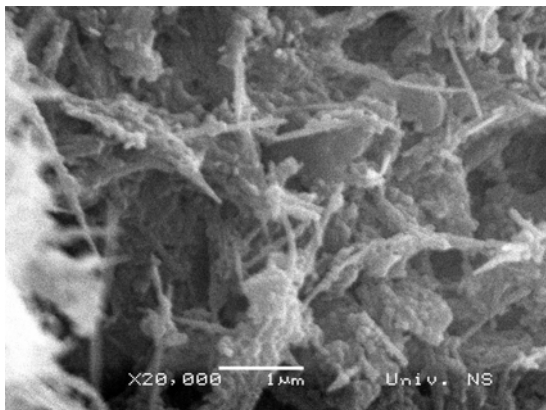


Fig. 2. MWNT after acid treatment with 6 M HCl in ultrasonic bath. The influence of ultrasound is proven to be the cause of dispersing of bundles.

Even though images in Fig. 1 and Fig. 2 confirm low purity of samples, they also clearly present the influence of ultrasound on the MWNT material. The dispersion of MWNT in acid is greater in the sample treated with milder acid in ultrasonic bath, which enables acid to “wash out” sample in greater extent, regardless to the acid concentration.

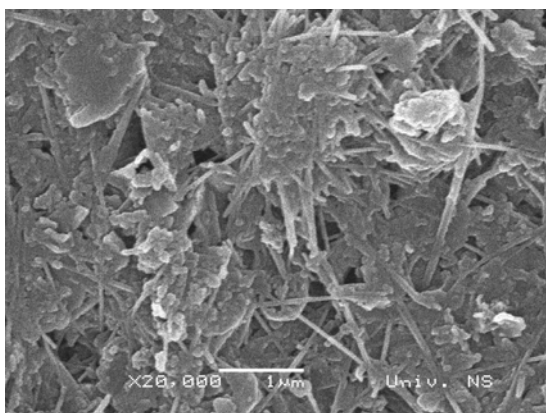


Fig. 3. MWNT purified with PmPV. The morphology of MWNT is different.

Softer, non destructive way of purification with organic polymer PmPV gave greater yield of purification than those MWNT treated with acid. Crude (non-purified) MWNT and purified by polymer SAM images with higher magnification are presented in Fig. 4 and Fig. 5.

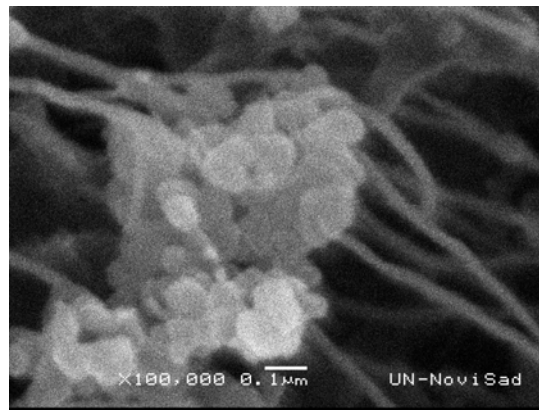


Fig. 4. Crude MWNT. A large bundle of MWNTs with carbonaceous impurities is shown in the center.

The ESR spectrums of crude and purified by polymer carbon nanotubes are shown in Fig. 6 and Fig. 7. The ESR spectrum of purified nanotubes consists of a single line which can be well described by Lorentzian line shape with the g -factor = 2.012 ± 0.002 , and with the linewidth (the half width at half maximum) $\Delta B = (10 \pm 1)$ G (Fig. 7). The ESR spectrum of the crude (non-purified) nanotubes can be roughly described also by Lorentzian line shape with $g = 2.014 \pm 0.002$, and with $\Delta B = (50 \pm 5)$ G (Fig. 6). Since g -factor determines the value of the magnetic field at which the resonance will be observed for a given operating frequency, very close values of the resonance g -factor for the purified MWNT and for the crude MWNT samples indicates that the two resonances arise from the same origin.



Fig. 5. MWNT after PmPV purification. The content of nanotubes to impurities comparing to acid treated ones is higher. The diameter of MWNT appears to be uniform.

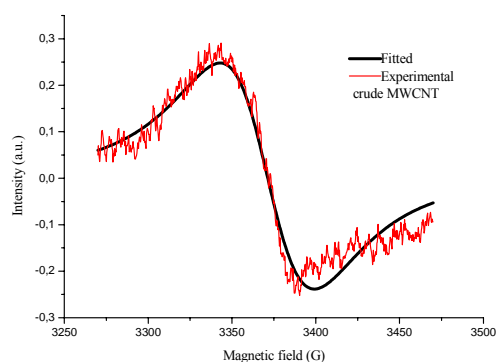


Fig. 6. The ESR spectrum for non-purified (crude) nanotubes.

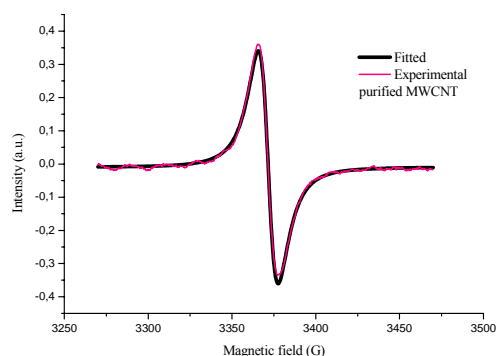


Fig. 7. The ESR spectrum for purified nanotubes.

4. Conclusion

In this work, we have shown that MWCNTs can be effectively purified by a nondestructive method using a conjugated organic polymer. SAM images show a different morphology of such gained product than the one purified by etching followed by acid treatment.

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* Corresponding author: vesipka@vin.bg.ac.yu