November 2001

Processing of single wall carbon nanotubes and implications for filling experiments

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Recommended Citation

Chikkannanavar, S. B., Smith, B. W., Russo, R. M., Stercel, F., & Luzzi, D. E. (2001). Processing of single wall carbon nanotubes and implications for filling experiments. Retrieved from https://repository.upenn.edu/mse_papers/20

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2001 Fall Meeting Symposium Z
Making Functional Materials with Nanotubes
Publisher URL:http://www.mrs.org/members/proceedings/fall2001/z/Z2_7.pdf

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Abstract

Single wall carbon nanotubes (SWNTs) have been processed in different schemes to get clean material for use in various filling experiments. The SWNTs synthesized by different methods require different processing schemes, and this is presumably due to heterogeneous nature of the various contaminants present along with the carbon nanotubes. For the pulsed laser synthesized SWNTs, a combination of nitric acid, hydrogen peroxide and hydrochloric acid treatment gives best results and the purified SWNTs give best ever filling fraction for fullerene, C₆₀ of ~90%. The processing improves the surface cleanliness of SWNTs, in turn giving greater access for the target molecules, and hence the higher filling fraction. For the carbon arc produced SWNTs, air oxidation followed by treatment with nitric acid has been found to work best and the processed SWNTs have been used for filling experiments with metal chlorides. Both these processing schemes still leave a small fraction of catalyst impurities in the final material, thus the material quality of filled material and hence its properties depend on the processed material used for the filling experiments.

Comments

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Processing of single wall carbon nanotubes and implications for filling experiments

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ABSTRACT

Single wall carbon nanotubes (SWNTs) have been processed in different schemes to get clean material for use in various filling experiments. The SWNTs synthesized by different methods require different processing schemes, and this is presumably due to heterogeneous nature of the various contaminants present along with the carbon nanotubes. For the pulsed laser synthesized SWNTs, a combination of nitric acid, hydrogen peroxide and hydrochloric acid treatment gives best results and the purified SWNTs give best ever filling fraction for fullerene, C₆₀ of ~90%. The processing improves the surface cleanliness of SWNTs, in turn giving greater access for the target molecules, and hence the higher filling fraction. For the carbon arc produced SWNTs, air oxidation followed by treatment with nitric acid has been found to work best and the processed SWNTs have been used for filling experiments with metal chlorides. Both these processing schemes still leave a small fraction of catalyst impurities in the final material, thus the material quality of filled material and hence its properties depend on the processed material used for the filling experiments.

INTRODUCTION

Ever since the discovery of single wall carbon nanotubes (SWNTs) [1-3], there has been an intense research effort focused towards the processing, characterization and property modification, apart from means to produce them by alternate synthesis methods. In order for the well-characterized carbon nanotubes to be available for various studies, one needs to develop methods to process or purify them. This is in order to remove the impurities, which accompany the carbon nanotubes during the formation process. The heterogeneous nature of the impurities has made the processing methods more elaborate and involved in terms of the details of chemical or physical processes involved. Various schemes of processing have been reported over the years for SWNTs synthesized by different methods [4-7]. In this paper we discuss the processing of SWNTs and implications for the various filling experiments.

EXPERIMENTAL

We have carried out the processing of SWNTs obtained by pulsed laser vaporization (PLV-SWNTs) and carbon arc (CA-SWNTs) methods. The laser synthesized material, Tubes@Rice was obtained from Rice University, which was synthesized in a pulsed-laser vaporization technique using Co/Ni catalysts [2]. The carbon arc produced SWNTs were provided by Prof. P. Bernier, CNRS, France and synthesized using Y and Ni as catalysts [3].

The collarette portion of the carbon arc process was subjected to a combination of static air oxidation and acid treatment. In a typical processing experiment ~ 20 mg of collarette (CA-SWNTs) was annealed in static air at 360°C for 3 h. Later the sample was subjected to acid treatment, wherein, refluxing was carried out using ~ 20 ml of 5.3 M HNO₃ for 40 min. The acid treatment was followed by the neutralization with NaOH till a basic pH (~10) is achieved. This was in order to solubilize the acid reaction products, which can be removed by washing with de-ionized water. The basic solution was filtered using a 0.5 µm Nylon filter paper in a filtration setup, followed by continuous washing with de-ionized water. In the final step the sample was re-suspended in toluene with sonicated for 40 min and filtered using 1 µm Teflon filter paper, to get a buckypaper.

Two processing schemes have been applied to the PLV material. In the first scheme, as synthesized laser material has been subjected to reflux with ~3 M HNO₃ for 12 h, followed by neutralization with NaOH and final re-suspension in toluene [4,5]. This formed the stock of Tubes@Rice. In the second scheme, ~30 mg of Tubes@Rice were refluxed with 30 ml of 15 vol% H₂O₂ for 2 h. The resulting suspension was filtered using Teflon filter paper, with repeated washing with de-ionized water. In the next stage of acid treatment, sample was sonicated in 12 M HCl (30 ml) for 20 min, following which neutralization with NaOH and filtration was carried out. In the final step of processing, sample was resuspended in toluene and filtered to get a robust buckypaper.

In order to disperse peapods (C₆₀@SWNTs), ~ 1 mg of peapod sample was sonicated in 15.8 M HNO₃ for 1 h, 6 h, 12 h and 15 h. Following the sonication, sample was washed with de-ionized water repeatedly (8-10 times) and centrifuged for 5 min. The solution was decanted/pipetted out, and after the final wash sample was re-dispersed in N, N-dimethylformamide (DMF) with sonication for 1 h. This resulted in a stable light black color suspension of C₆₀@SWNTs, which is stable for months. Later the sample was deposited on silicon substrates and atomic force microscope measurements (using Digital Instrument AFM) were carried out in order to study the dispersions.

The samples of as synthesized and processed CA-SWNTs, PLV-SWNTs have been characterized by techniques such as transmission electron microscopy (TEM, using JEOL 2010F), scanning electron microscopy (SEM, using JEOL 6400F), Raman spectroscopy in a Renishaw micro Raman spectrometer, and thermo gravimetric analysis (TGA) using TA Analyzer.

RESULTS AND DISCUSSION

As synthesized SWNTs consist of contaminants like metal catalyst, amorphous carbon and graphitic nanoparticles which encapsulate the metal. Generally acid treatment is supposed to oxidize amorphous carbon and metal catalyst. The graphitic nanoparticles

formed along with the SWNTs are generally multi-shelled and they can't be effectively oxidized by treatment with acid alone. The oxidation carried out by heat-treatment in air is found to be more effective in oxidizing the graphitic particles, thus allowing the access to the metal inside to be oxidized in the following step of acid treatment. Thus a combination of air oxidation and acid treatment seems to be a logical way for processing the SWNTs. This treatment has been applied to CA-SWNTs and it seems to get rid of most of the catalyst and amorphous carbon. The TEM images of as-synthesized and processed samples are shown in Figure 1.(a) and (b) respectively. It can be clearly seen that the catalyst and amorphous carbon have been effectively removed after the purification process. The Raman spectroscopic measurements also justify this argument in terms of the disorder induced D-band peak intensity.

Figure 1. TEM image of SWNTs from CA/Collarette (a) before processing and (b) after processing by air oxidation/acid treatment.

In the case of PLV-SWNTs, the solution after the reflux with 3 M HNO_3 exhibits a dark brown color, due to the desolution of catalyst Co/Ni. After the neutralization with base and filtration, a dark brown colored solution (which is nothing but solubilized reaction products) collects in the filtration jar. In the next step, involving treatment with peroxide, amorphous carbon is oxidized. It is well known that, peroxide is a good oxidant in order to remove amorphous carbon [8]. The final procedure of sonication with HCl serves the same purpose of catalyst desolution, and is an optional step in the processing.

The as-received Tubes@Rice have been subjected to additional purification procedure, as the material doesn't seem to be clean, in terms of surface covering. This is borne out from the TEM observations as well as filling experiments. TEM image of as received Tubes@Rice is shown in Figure 2.(a). In contrast, the material after the peroxide and hydrochloric acid treatment shows a much clean surface of SWNTs and free from amorphous impurities on the surface (Figure 2.(b)). Few catalyst particles are seen, which survive the oxidation, due to thick protective graphene layers. Various molecular filling experiments have been carried out using the Tubes@Rice as well with the processed batch, and in terms of good access to the ends and walls of the nanotubes for the target molecules, the peroxide processed batch is found to be the best [9]. A calibrated weight uptake procedure for high yield filling of C_{60} in SWNTs has shown that

the peroxide and hydrochloric acid processed SWNTs show best results in terms of high yield filling [9]. The results are discussed in the poster session Z 6.21 and the TEM image of filled material is shown in Figure 3. The fullerene target molecules have a good access to the walls and the open ends of the carbon nanotubes, and at high temperature the vapor pressure of fullerene being high, leads to ~90 % of filling efficiency for SWNTs. This is to be compared with the near saturation of filling efficiency for the nitric acid processed material. The role of hydrogen peroxide can be that under the effect of temperature, it decomposes and gives rise to highly reactive hydroxy radicals, which in turn oxidize the amorphous carbon and other impurities and clean off the surfaces of SWNTs.

Figure 2. TEM images of (a) as received Tubes@Rice and (b) after treatment with H_2O_2 and HCl. The SWNT surface is clean and shows defects in the walls due to processing.

Figure 3. TEM image of C_{60} @SWNT which is from the 90% yield sample and shows well filled rope and the rope surface is free from amorphous coverage.

The processed carbon arc SWNTs have been used for filling experiments of metal chlorides and the filling fraction for metal chlorides eg. HoCl_3 and GdCl_3 is in excess of 60%. The results of the chloride filling experiments are discussed in poster session Z 6.23. Metallofullerene filling results are discussed in poster session Z 6.21.

The sonication of peapods, ie C_{60} @SWNT in presence of 15.8 M HNO_3 for various time periods breaks the buckypaper into shorter and thinner bundles. In the case of 2 h, 6 h and 12 h sonication the length of SWNT bundles decreases from several microns to

Figure 4. (a) Atomic Force Microscope image of C_{60} @SWNT showing isolated SWNT ropes after sonication for 6 h in HNO_3 , followed by dispersion in DMF for 1 h ; (b) height profile across the nanotube showing a height of 3.5 nm, referring to a thinner SWNT rope.

Figure 5. (a) Atomic Force Microscope image of C_{60} @SWNT showing isolated nanotubes after sonication for 12 h in HNO_3 , followed by dispersion in DMF for 1 h ; (b) height profile across the nanotube showing a height of 1.4 nm, referring to an isolated single nanotube.

several hundred nanometers. The diameter of the bundles decreases from hundreds of nanometers to tens and/or few nanometers. These measurements have also been confirmed by TEM observations on the dispersions. The acid treatment together with high energy sonication is responsible for breaking the ropes and they disperse into DMF as result of covalent functionalization. The details of functionalization process are being worked out by means of infra-red (IR) spectroscopy measurements on nanotube dispersions.

CONCLUSIONS

Single wall carbon nanotubes have been successfully processed and specific to the synthesis method, different purification schemes have been applied. SWNTs synthesized by PLV process have been purified by a nitric acid followed by peroxide/hydrochloric acid method, while the carbon arc produced SWNTs have been processed using air oxidation and nitric acid treatment procedure. Both the procedures give rise to pure SWNT material and the filling experiments have been quite successful in terms of high yield filling for various molecules as well metal chlorides etc. The surface cleanliness of SWNTs plays a major role in the filling experiments in terms of greater access to target molecules.

ACKNOWLEDGEMENTS

The authors thank Office of Naval Research and National Science Foundation for financial assistance. We acknowledge the help of Mr. Chi Heon Lee for the AFM measurements on peapod dispersions.

REFERENCES

- [1] S. Iijima and T. Ichihashi, *Nature* **363**, 603 (1993) ; D. S. Bethune et al. *Nature* **363**, 605 (1993)
- [2] A. Thess et al., *Science* **273**, 483 (1996)
- [3] C. Journet et al., *Nature* **388**, 756 (1997)
- [4] A. G. Rinzler et al., *Appl. Phys. A* **67**, 29 (1998)
- [5] J. Liu et al., *Science* **280**, 1253 (1998)
- [6] M. Monthieux et al., *Carbon* **39**, 1251 (2001)
- [7] W. Zhou et al., *Chem. Phys. Lett.* submitted (2001).
- [8] H. Kataura et al., *Synth. Metals* **121**, 1195 (2001)
- [9] B. W. Smith et al., in print, *J. Appl. Phys.* (2001)