

Purification of carbon nanotubes by dynamic oxidation in air

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We describe a new approach to the purification of single-walled carbon nanotubes (SWCNTs), based on the selective oxidation of carbonaceous impurities by heating at a constantly increasing temperature (*i.e.* dynamic oxidation) in air. Using UV-VIS-NIR spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM) we demonstrate the superior purity of dynamically oxidized SWCNTs. In addition to being faster than other methods, dynamic oxidation allows for an efficient removal of carbonaceous impurities without significant loss of nanotubes. It is hypothesized that the advantages of dynamic oxidation arise from the exposure of the raw material to a wider range of temperatures than in conventional isothermal oxidation.

Introduction

Single-walled carbon nanotubes (SWCNTs) are nanometre-wide hollow carbon structures with exceptional mechanical and electronic properties.¹ For example, metallic SWCNTs can carry current densities at least one thousand times higher than conventional materials, such as copper, silver, or gold.² On the other hand, semiconducting SWCNTs have been used to design the smallest transistors, allowing for further improvements in minimizing and arranging integrated circuits and arrays.³ Applications range from electronic devices and sensors to nanopipettes and composite materials.⁴ In most cases a successful application depends on the availability of large quantities of high-purity SWCNTs.⁴ However, scaling up the production of carbon nanomaterials typically leads to a decrease in quality and thus furthers the need for efficient, environment-friendly and economic purification techniques.

The major impurities present in as-produced CNTs can be divided into (1) metallic catalyst particles (*e.g.* iron, nickel, yttrium) remaining from the synthesis and (2) non-tubular carbonaceous impurities (C-impurities), such as amorphous and graphitic carbon, fullerenes and carbon onions.⁵ Common purification techniques are either based on oxidizing liquids (*e.g.* acids, bases) or utilize gaseous oxidants such as oxygen, carbon dioxide, water vapor or ozone. A detailed overview of existing purification techniques was recently given by Hou *et al.*⁶ While methods using nitric or sulfuric acid remove both residual catalyst and C-impurities, such treatments typically lead to SWCNTs that are highly defective and rich in oxygen-containing functional groups.^{1,7,8}

Gas phase oxidation is a milder purification technique.^{6,9–11} In this treatment, carbon impurities are selectively burnt out during heating at elevated temperature (250–500 °C, depending on the

material and oxidation conditions) in the presence of an oxidant such as oxygen or air.^{9,10,12–14} The major drawback of gas phase oxidation is the likelihood of SWCNT damage and high sample loss under non-optimized purification conditions. Gas phase oxidation is based on the assumption that SWCNTs are more resistant to oxidation than C-impurities. Thus, C-impurities (mainly amorphous carbon) can be selectively removed by purifying the sample at a temperature below the oxidation temperature of SWCNTs, without damaging or destroying valuable nanotubes. However, a very precise control over the temperature is needed. The presence of the metallic particles, which catalyze the carbon–oxygen reaction, further complicates the oxidation process.

During dynamic oxidation SWCNTs are subject to a constantly increasing temperature (*e.g.*, 10 °C min⁻¹) in the presence of air (Fig. 1). The required oxidation times (<1.5 h) are significantly smaller compared to isothermal processes (typically >5 h), thus minimizing contributions of catalytic effects. The purity of dynamically oxidized SWCNTs exceeds that of conventional oxidation methods including that of most isothermal oxidation protocols.¹⁵

Experimental section

Materials

As-received, arc-produced SWCNTs were purchased from Carbon Solutions, Inc. Prior to dynamic oxidation, in order to facilitate sample handling, as-received SWCNTs (~240 mg) were mixed in acetone (~15 ml), so that after drying for two days at

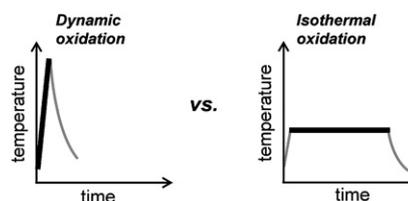


Fig. 1 Comparison of the dynamic oxidation (left panel) with conventional isothermal (“static”) oxidation (right panel).

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~80 °C the sample was compressed by a factor of ~10. Thermogravimetric analysis (TGA) did not show any significant changes in the thermal behavior between the raw and acetone-processed materials (data not shown).

Characterization

TGA and dynamic oxidation were performed in a Pyris 6 PerkinElmer thermogravimetric analyzer, using a heating rate of 10 °C min⁻¹ and a constant air flow of 20 ml min⁻¹. Sample loads of ~10 mg were used in each run. Absorption spectra were recorded in a UV-VIS-NIR Spectrophotometer JASCO, V-570 with 10 mm path rectangular quartz cuvettes. Raman spectra were recorded using a Renishaw Raman micro spectrometer (1000) equipped with a 514.5 nm Ar ion laser. Transmission electron microscopy (TEM) was performed on Hitachi H-7600 instrument at an acceleration voltage of 100 kV.

Results and discussion

Determination of final temperature of oxidation

In order to determine the optimal final temperature of oxidation (FTO) for purification of SWCNTs by dynamic oxidation at a given heating rate, as-produced SWCNTs from the same batch were divided into 7 groups. Each group was subjected to dynamic oxidation using similar conditions (*i.e.* same air flow, same heating rate), while the FTO was set to different temperatures in the range 400–770 °C. The selected FTO corresponds to temperatures at which the differential weight loss (dW/dT) of as-produced SWCNTs exhibits a change in slope: 400, 520, 620, 700, 730, 750, and 770 °C (see Fig. 2). After cooling to room temperature, the samples were analyzed using UV-VIS-NIR, Raman and TEM.

UV-VIS-NIR spectra of as-produced SWCNTs, dynamically oxidized to different FTOs (and dispersed in 1 wt% SDS in water solution), are presented in Fig. 3. The absorption features labeled as M₁₁ and S₂₂ arise from metallic and semiconducting carbon nanotubes, respectively.¹² The integrated intensities (peak area) of M₁₁ and S₂₂ are in direct relation with the amount of metallic and semiconducting SWCNTs, respectively. The content of C-impurities can be estimated from the slope of each spectrum

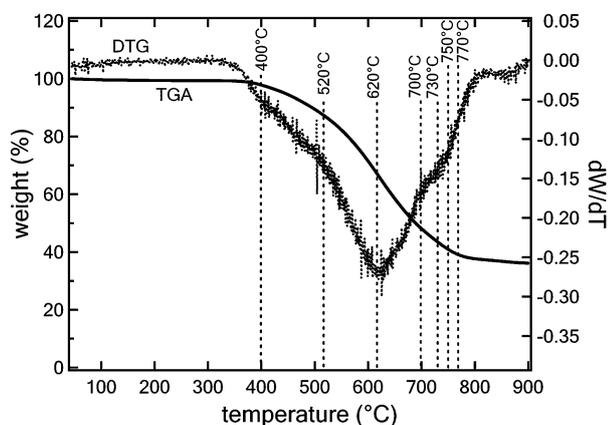


Fig. 2 Thermogravimetric (TGA, solid line) and differential TGA curve (DTG, dotted line) for SWCNTs after compression with acetone.

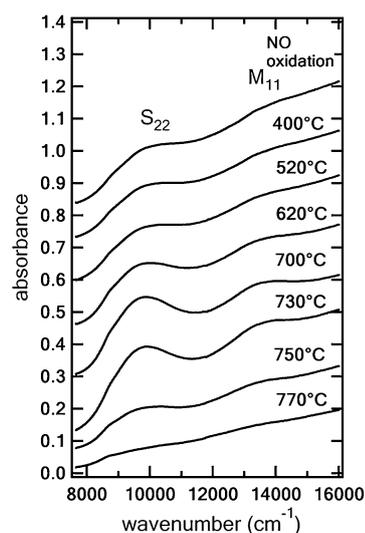


Fig. 3 UV-VIS-NIR spectra of SWCNTs dynamically oxidized to different FTOs (spectra y-offset).

(the greater the slope, the more C-impurities the sample has).^{12,16} The concentration of each of the samples was adjusted (by dilution in SDS solution) in order to get the same slope, *i.e.* C-impurity concentration, as a non-oxidized sample in the UV-VIS-NIR spectra.

The areas under the S₂₂ peaks were calculated using IGOR software (WaveMetrics, Inc.). As seen from Fig. 3, the intensity of the absorption peaks increases when increasing the FTO from room temperature to 730 °C, suggesting that the relative amount of SWCNTs in the samples increases due to the burning of C-impurities. The highest purity was observed for SWCNTs dynamically oxidized to 730 °C. Higher FTOs lead to burning of SWCNTs as indicated by a decrease in M₁₁ and S₂₂.

Evaluation of the purity of SWCNTs by UV-VIS-NIR spectroscopy

The purity of the samples was determined following the method of Haddon *et al.*^{12,16} In this method, the purity of SWCNTs is defined as:

$$P_{\text{sample}} = \frac{\text{Content (SWCNTs)}}{\text{Content (SWCNTs + C-impurities)}} = \frac{\text{AA(S)}}{\text{AA(T)}} \quad (1)$$

where P_{sample} is the purity of the sample; AA(S) is the area under S₂₂ minus the area under the baseline, associated with the SWCNTs content (Fig. 4a), and AA(T) is the total area under the S₂₂ absorption peak (Fig. 4b) resulting from both the SWCNTs and the C-impurities. A straight line, intersecting UV-VIS-NIR spectra of SWCNTs at 8000 and 11 765 cm⁻¹ was chosen as a baseline.

In order to standardize the method, the relative purity (RP) of the sample was defined as:

$$\text{RP}_{\text{sample}} = \frac{P_{\text{sample}}}{P_{\text{reference}}} = \frac{P_{\text{sample}}}{0.141} \times 100\% \quad (2)$$

where $\text{RP}_{\text{sample}}$ is the relative purity of the sample and $P_{\text{reference}} = 0.141$ is the purity (determined based on eqn (1)) of “an arbitrary high-purity reference sample”.¹⁶

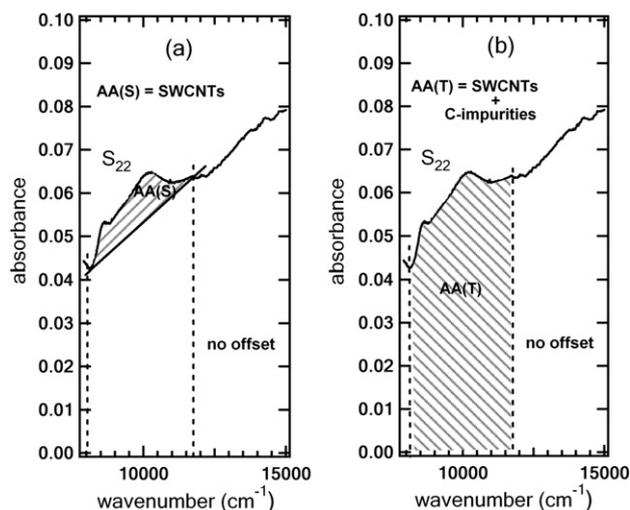


Fig. 4 UV-VIS-NIR spectrum of SWCNTs dispersed in dimethylformamide. (a) AA(S) (dashed area) is associated with SWCNTs content and (b) AA(T) (dashed area) is associated with both the SWCNTs and the C-impurities content.

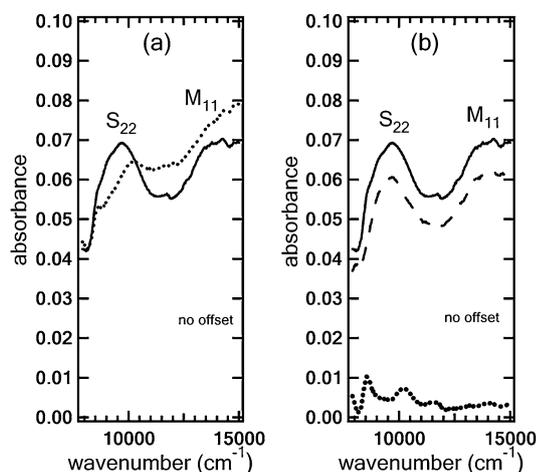


Fig. 5 UV-VIS-NIR spectra of SWCNTs (a) dispersed in dimethylformamide before (dotted line) and after (solid line) the dynamic oxidation to 730 °C and (b) dispersed in dimethylformamide after dynamic oxidation to 730 °C before (solid line) and after centrifuging (sediment—dashed line; supernatant—dotted line).

Samples of SWCNTs before (dotted line in Fig. 5a) and after the dynamic oxidation to 730 °C (solid line in Fig. 5a) were dispersed in dimethylformamide (DMF) (Fisher Scientific) and their purity was evaluated (Table 1).

In order to exclude the possible effects of the catalyst (Ni,Y) oxides (~ 70 wt% in dynamically oxidized sample (Fig. 3)) on the evaluation of the purity of the dynamically oxidized sample by UV-VIS-NIR spectroscopy (oxides have a non-zero absorbance), 10 ml of the solution of the dynamically oxidized sample in DMF (solid line in Fig. 5b) were centrifuged at $\sim 3000g$ (Sorvall) for 30 min. After centrifuging, 8 ml of the supernatant, which was expected to have a lower content of heavy metal oxides, were mixed with 2 ml of neat DMF (to make original volume of 10 ml), sonicated for 20 min and the UV-VIS-NIR spectrum was

Table 1 Purity of the samples before and after dynamic oxidation

Sample	AA(S)	AA(T)	Purity	Relative purity
As-received	18.256	220.327	0.083	59%
Dynamically oxidized to 730 °C (before centrifuging)	40.002	225.338	0.178	126%
Dynamically oxidized to 730 °C (sediment after centrifuging)	30.461	194.677	0.156	111%
Dynamically oxidized to 730 °C (supernatant after centrifuging)	9.444	18.861	0.501	355%
Analytically pure ^a			0.325 ^a	230% ^a

^a Estimated by Haddon *et al.* (see ref. 16).

taken (dotted line, Fig. 5b). The evaluation of the relative purity of the dynamically oxidized sample with decreased amount of the metal oxides, based on the method suggested by Haddon *et al.*, gave a relative purity of 355%, which is higher than the previously achieved relative purity of 230% for analytically pure SWCNTs according to the same classification by Haddon *et al.* (Table 1).¹⁴ This result suggests that nanotubes, dynamically oxidized in air, are almost totally free from carbonaceous impurities. It should be stressed here that purity of the SWCNTs determined by NIR spectroscopy in this work is the relative purity.

Purity of dynamically oxidized SWCNTs was compared to the purity of SWCNTs, oxidized *via* the isothermal oxidation protocol, described elsewhere.^{13,17,18} In comparison to as-received samples, the dynamically oxidized material is a factor of 6 purer. However, isothermal oxidation yields SWCNTs which are only ~ 2 times purer than a raw material.

It should be mentioned that the application of UV-VIS-NIR spectroscopy for purity evaluation of SWCNTs has its limitations and that such analysis should be used only in combination with other characterization techniques, such as Raman spectroscopy, TEM, and TGA. Special attention must be paid to the preparation process of the samples. Dispersions of SWCNTs have to remain stable during the time of the measurements. While this is usually achieved by a series of sonication–dilution cycles using dimethylformamide as a solvent, slight variation in the concentration of SWCNTs may still occur. To further minimize bundling and sedimentation of SWCNTs, concentrations as low as ~ 0.01 mg ml⁻¹ for 10 mm path cuvettes should be used.¹⁶

UV-VIS-NIR-based purity evaluation is limited to SWCNTs whose S₂₂ electronic transitions do not overlap with other transitions. Moreover, such analysis can only provide semi-quantitative information about the content of SWCNTs and amorphous carbon. The effect of other impurities such as metal particles present in the samples is not taken into consideration.

Evaluation of the purity of SWCNTs by Raman spectroscopy

Raman spectra of as-received, air–HCl purified (purification by Carbon Solutions, Inc.) and dynamically oxidized SWCNTs are presented in Fig. 6(a,b). All samples show the typical Raman features of SWCNTs: the disorder-induced D band (1300–1400 cm⁻¹) (Fig. 6b) resulting from amorphous carbon and structural defects in SWCNTs; the G band (~ 1590 cm⁻¹) (Fig. 6b) originating from

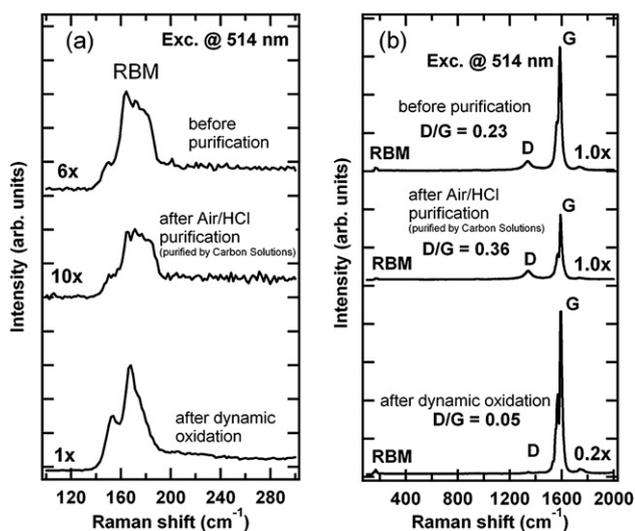


Fig. 6 Raman spectra of SWCNTs showing D band (b), G band (b) and RBM peaks (a,b) before purification (top line), after air–HCl purification (middle line) and after dynamic oxidation (bottom line). Spectra were recorded using a 514 nm excitation wavelength.

the in-plane vibrations of carbon–carbon bonds; and the radial breathing modes (RBMs) between ~ 100 and 500 cm^{-1} (Fig. 6a,b) attributed to the collective breathing vibration of the entire SWCNT.^{13,17,18} The integrated intensity ratio (peak area) between D and G bands (D–G) is conventionally used to evaluate the purity of CNT samples.¹⁹

The Raman spectrum of dynamically oxidized SWCNTs revealed a low D band and a high G band intensity with well separated G^- and G^+ sub-bands (Fig. 6b). The D–G ratio of dynamically oxidized SWCNTs (0.05) is much smaller than that of as-received (0.23) or air–HCl purified (0.36) SWCNTs, indicating higher purity (and lower level of structural defects) of the dynamically oxidized sample (Fig. 6b). The RBM range does not show significant changes, indicating little or no tube damage.²⁰

The relative increase of the RBM Raman intensity, with respect to D and G bands, of dynamically oxidized SWCNTs further supports this idea (Fig. 6a). It should be mentioned that the intensity distribution in the RBM frequency range slightly changes during dynamic oxidation. The maximum in the RBM intensity is shifted to lower frequencies, probably because of the oxidation of small-diameter SWCNTs which exhibit larger RBM frequencies. However, narrower diameter distributions are often more favorable for SWCNT applications due to the strong diameter-dependence of SWCNT properties.

Evaluation of the purity of SWCNTs by transmission electron microscopy

Transmission electron microscopy (TEM) clearly shows that the sample of as-produced non-purified SWCNTs contains an abundance of impurities either deposited on the bundles of SWCNTs (making the surface of the bundles unsmooth and not well distinctive) or in the form of “clumpy” aggregates (Fig. 7a). Bright regions in TEM images of SWCNTs correspond to C-impurities. The dark spots are associated with catalytic metallic particles and their oxides (Fig. 7a).

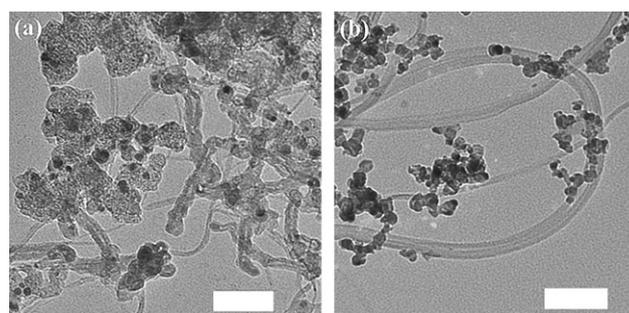


Fig. 7 Transmission electron microscopy images of SWCNTs (powder) before purification (a) and after dynamic oxidation (b). Scale bar is 100 nm on both of the images.

In contrast to TEM images of as-produced non-purified SWCNTs, TEM images of dynamically oxidized SWCNTs show no amorphous carbon, indicating an efficient elimination of C-impurities from the sample (Fig. 7b). Dark regions in the TEM images of dynamically oxidized SWCNTs are tentatively associated with oxides of the catalytic metals (Fig. 7b).

It should be mentioned that results obtained by TEM analysis provide only low statistical reliability. Therefore, TEM analysis should be used only as a complementary technique in purity evaluation of SWCNTs.¹⁶

Conclusions

Dynamic oxidation in air, *i.e.* oxidizing SWCNT containing samples at a constant heating rate in air, was shown to be a fast and effective method of purification of SWCNTs from C-impurities (mainly amorphous carbon), leaving residual metal and metal oxide particles as the only major impurities in the sample. UV-VIS-NIR, Raman, and TEM revealed a much higher degree of purity of dynamically oxidized SWCNTs in comparison with the conventionally purified samples. UV-VIS-NIR spectroscopy showed that dynamically oxidized SWCNTs have a lower content of C-impurities than previously reported for “analytically” pure SWCNTs. Short operation times (<1.5 h), along with ~ 6 times improvement in purity of SWCNTs, make dynamic oxidation an excellent alternative to other purification methods. In our opinion, the advantages of dynamic oxidation in air arise from the fact that raw material in this treatment is subject to oxidation in the widest possible range of temperatures (up to the threshold temperature of burning of SWCNTs), providing access to all thermodynamically allowed conditions for burning various fractions of C-impurities.

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