Removal of oxidation debris from multi-walled carbon nanotubes†

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Conventional liquid phase oxidation of multiwall carbon nanotubes (MWCNTs) using concentrated acids generates contaminating debris that should be removed using aqueous base before further reaction.

Carbon nanotubes are currently receiving enormous attention, due to their remarkable intrinsic properties and wide range of potential applications.[1] Unfortunately, as-synthesised, carbon nanotubes are generally impure and have very low solubility/dispersibility in either organic solvents or aqueous solutions. Chemical treatments are widely studied for both purification and improved solubility.[2] In addition, covalent strategies have been used to introduce functional groups,[3] proteins,[4] and nanoparticles,[5] to guide structural assembly,[6] and to improve the performance of polymer nanocomposites.[7] Initially, purification was pursued using competitive oxidations in the gas phase,[8] but due to limited yields, attention quickly switched to aqueous oxidations, most frequently with acid(s).[9–11] These treatments can cut nanotubes, reduce their length,[10] and decrease the diameter of multi-walled nanotubes,[11] as well as removing amorphous carbon and contaminating metals. Perhaps most importantly, they introduce oxygen-containing groups, especially hydroxyl, carbonyl and carboxylic functionalities. These groups provide electrostatic stabilisation when the CNT are dispersed in water[12] and are widely used for further functionalisation, for example, by the formation of amides.[13] The presence of these groups has been demonstrated by FTIR, XPS, titrations, elemental analysis, and other methods, and it is usually simply assumed that these groups are somehow covalently-bound to the outer shell of the nanotube, representing a direct method of functionalisation. Here we report that, in reality, the majority of these groups are associated with molecular debris that is not removed from the sample in conventional treatments; however, the addition of aqueous base successfully cleans the oxidised material.

Multi-walled carbon nanotubes (MWNT) used in this study were synthesized in-house by a chemical vapour deposition (CVD) technique[14] (sample U). These nanotubes were refluxed in 3 : 1 concentrated H_2SO_4/HNO_3 mixture at around 120 °C for 30 min, and then thoroughly washed with distilled water, until the filtrate was colourless and neutral; the product was a stable dispersion in water (sample A). This procedure has been used frequently in the literature.[10,15] Further treatment with 0.01 M NaOH initially produced a yellow/brown filtrate and was continued until colourless. The resulting nanotube dispersion was then washed with distilled water until neutral. Finally, the product was washed with 0.01 M HCl, and again returned to neutral with distilled water (sample B). All washes were carried out using standard vacuum filtration on a 0.2 μm pore PTFE membrane. The various products were analysed with infrared and Raman spectroscopy, transmission electron microscopy (TEM) (JEOL 2010, operated at 200 kV), X-ray Photoelectron Spectroscopy (XPS) (ESCA300) and thermogravimetric analysis (TGA) (Perkin Elmer Pyris 1).

High resolution TEM images (Fig. 1) show that the nanotubes are well-graphitised, with 10–20 concentric layers, although, as frequently observed with CVD-grown materials,[16,17] the outer surface is not completely smooth. After the acid treatment, there is a clear increase in thickness of the disordered region consistent with significant adsorption of molecular debris. After treatment with aqueous base, a very clean surface is regenerated, though some defect features remain. Raman spectroscopy[18] is frequently used to indicate the graphitic quality of carbon samples, by comparing the intensity of the disorder (D) peak at around 1350 cm^{-1} and the graphitic (G) peak at 1580 cm^{-1}. The Raman data (see ESI†) indicates a significant increase in disorder on comparing the acid-treated (G/D = 0.79) to the raw material (G/D = 1.54), and an improvement on washing with base (G/D = 1.08) although some functionalisation remains. This reduction in the G/D intensity ratio has often been observed on treating nanotubes with acid,[16,19] and is usually attributed to direct damage/functionalisation of the nanotubes. Recovery observed on heating in vacuum is usually attributed to annealing of the carbon lattice,[20] but may, in fact, relate to desorption, sublimation, or decomposition of oxidation debris.

FTIR spectroscopy (Fig. 2) was used to qualitatively establish the nature of the surface groups and waste by-products,[21] although analysis is hindered by the high absorbance of the material, the low concentration of groups, and the variety of local environments. In all the MWCNT spectra (Fig. 2a), there are O–H stretching vibrations in the 3600–3200 cm^{-1} range, due to, surface hydroxyl groups and water. The intensity of this peak is much stronger, as expected after oxidation, but partly disappears again after base treatment as hydrophilic, oxidised debris is removed. All three samples show weak bands characteristic of aliphatic hydrogen in the range 2850–2950 cm^{-1}, which may relate to a low concentration of H-terminations on the nanotube surface, or explicit amorphous carbon. Note that the intensities cannot be readily compared between spectra, due to the difficulties of sample preparation. Below 2000 cm^{-1}, the most obvious features in the untreated material are at 1400 cm^{-1} and 1090 cm^{-1}, and can be attributed to CO–H bending and C–OH stretching, respectively, (note that the presence of oxygen-containing groups is confirmed

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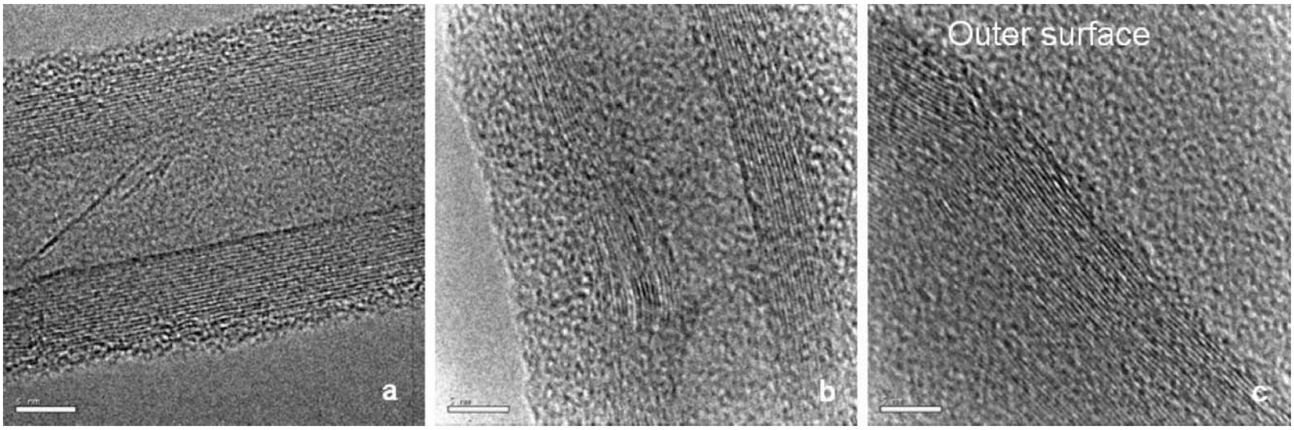

Fig. 1 TEM images of as produced MWCNT (a) and after acid treatment (b) and base wash (c). Scale: 5 nm.

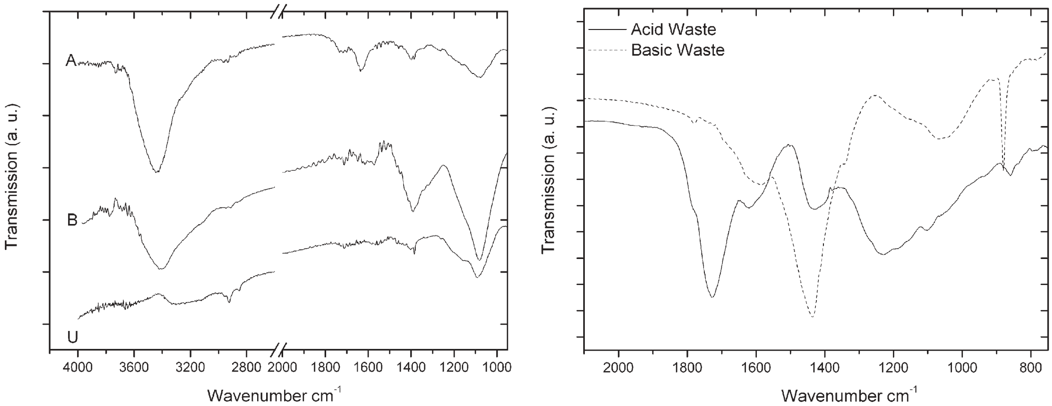

Fig. 2 FTIR spectra of as produced MWCNT, after acid treatment and base wash (left) and the residue from the reflux and the base wash (right).

in the XPS data below); C–H deformations may also make a small contribution in the range 1390–1470 cm^{-1}. In addition, there is a slight suggestion of broad C=C and C=O stretches around 1580 cm^{-1} and 1730 cm^{-1}, respectively. After oxidation, the C=O peak, most likely associated with carboxylic acids, becomes more evident, along with some water at 1630 cm^{-1} associated with increased hydrophilicity. The two features attributed to COH remain or are enhanced after treatment; in particular, the base-washed (and reneutralised) sample shows strong COH signals, consistent with a preferential removal of the most oxidised, carboxyl-rich fragments. The predominantly carboxylic/phenolic character of the surfaces is in broad agreement with previous studies of oxidised nanotubes,[18–24] although the lower carboxylic content is significant, since these groups are the most common target of further functionalisation.

The spectrum of the initial acid waste shows strong carboxylic acid signal at 1725 cm^{-1}; its subsequent disappearance in the basic waste, suggests that the contribution of other carbonyls is minimal; the band just above 1600 cm^{-1} may be water or C=C conjugated to the carbonyl. The other broad absorptions are associated with COH as discussed above, possibly with small features from sulfate and nitrate ions at around 1100 and 850 & 1390 cm^{-1}, respectively. The waste removed by the basic treatment no longer shows the carboxylic acid peak, instead showing evidence of carboxylate anions at 1600 cm^{-1} and 1420 cm^{-1}; the intensity in the acid waste around 1250 cm^{-1}, attributed to CO–H also disappears; the sharp feature at 880 cm^{-1} may be associated with sodium alkoxide, which has been observed previously.[22] These observations are consistent with a proposed structure for partially oxidised graphitic fragments based on a polyaromatic core terminated by a variety of oxygen-containing groups; the carboxylic acid and phenolic groups are converted to carboxylate and phenoxide functionalities in basic conditions.[23] It seems likely that, apart from the neutralisation, the wastes from the two washes are similar, except that the graphitic core is larger in the second wash, increasing the binding to the nanotubes, and preventing dissolution until the groups are ionised.

In XPS, all of the nanotube samples show C1s and O1s peaks; as-produced CNTs have a small additional Si2p peak which arises from the quartz substrate used during CVD. The oxygen content of the as-produced sample is 0.8 at%, indicating chemisorption of oxygen during or after the original synthesis; the value is typical of a range of CVD nanotubes. After the reflux process, the oxygen content increases dramatically to 8.9 at% due to the accumulation of oxidation products in the sample. After the base wash, the oxygen content decreases significantly to 2.8 at%; clearly much of the oxidised material is only loosely attached to the nanotubes, and can be removed under appropriate conditions. The signal strength is too weak for detailed analysis of O1s in the as-produced material; however, the O1s peaks of the other samples were resolved into components representing COH and COOH functionalities, following previously established methods.[21,24] Before base-washing, the COH and COOH ratio is close to 1 : 1;

afterwards, the COH signal is significantly stronger (4 : 3), suggesting that the loose debris is more strongly oxidised. The C1s peaks can be fitted with a number of components, but due to the strength of the shake-up tail relative to the low concentration of varied oxide groups, the procedure cannot be considered reliable. However, the C1s peaks are broadly consistent with the O1s data, indicating the presence of COH and COOH groups; the XPS results as a whole complement the FTIR spectroscopy discussed above. In addition, Boehm titrations (using NaOH) on the acid-oxidised and base-washed nanotubes[10] gave surface acid concentrations of 2.2 and 1.1 mmol g^{-1}, respectively, again showing the loss of oxidised debris after washing, but the retention of a significant number of surface groups.

Thermogravimetric analysis in air (shown in the ESI†) demonstrates that the as-grown CNTs have a single, sharp combustion peak around 650 °C, a necessary though not sufficient indication of a relatively low external amorphous carbon content. The acid-treated CNTs, in contrast, show a two stage decomposition process, initially losing 17 wt% at 400 °C, followed by the main decomposition at 700 °C, consistent with the loss of the oxidation debris at the lower temperature. After the base wash, there is no clear early peak associated with this debris, but there is an earlier onset to the oxidation of the nanotubes, which is consistent with the partial oxidation of the outer shells. The measured yield of the acid treatment was 46%, dropping to 35% on base washing (determined from the mass isolated by filtration relative to the initial mass of untreated MWCNTs). The implied debris content of the acid treated sample (24%) is consistent with the TGA data (17%) given the filtration losses inherent in the washing process. The debris content is greater than the equivalent carbon fibre experiments[23] due to the greater surface area.

In summary, conventionally applied acid treatments, widely used to purify and functionalise multiwall carbon nanotubes, can leave a residue of oxidation debris on the surface which is not removed by simple water washing. This residue has been reported in carbon fibre science, and consists of a mixture of partially oxidised polyaromatic fragments adhered to the surface,[23] washing with aqueous base, removes much, if not all, of this contamination, improving the quality and purity of the sample. The base converts the acidic groups on the debris (and on the nanotubes) to their conjugate salts, improving their solubility in water. Removing the debris is crucial step for effective covalent functionalisation of the nanotube itself. This observation highlights one of the challenges of nanotube chemistry, in general, since it is difficult to determine precisely where the apparent reaction takes place. In some cases, functionalisation of adsorbed debris molecules may be sufficient (for example for improving dispersibility) but in many cases a direct bond is desired, and the possible removal of grafted groups by, for example, mechanical stress or dissolution, would be a serious disadvantage. A particularly important case is in composite materials, where a strong bond is required to provide stress transfer between nanotube and matrix. Preliminary results suggest that similar effects are observed with single wall nanotubes treated under equivalent conditions.

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