

Removal of amorphous carbon for the efficient sidewall functionalisation of single-walled carbon nanotubes†

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Received (in Cambridge, UK) 16th August 2007, Accepted 28th September 2007

First published as an Advance Article on the web 5th October 2007

DOI: 10.1039/b712614j

The sidewall functionalisation of carbon nanotubes using the standard nitric acid treatment can be greatly enhanced by first removing the amorphous carbon present in the sample.

The functionalisation of carbon nanotubes (CNTs) is an increasing area of research since it leads to a higher solubility, processability and biocompatibility of the CNTs,¹ enabling their use in a wide range of applications, from composites to medical applications. The most common functional group that has been discussed in the literature is the covalently bonded COOH group, by treatment of CNT samples with nitric acid or a mixture of sulfuric and nitric acids.² The presence of carboxylic acid groups increases the solubility of the CNTs in water and organic solvents,³ opening the possibility of further modifications and coupling of molecules through subsequent solution-based chemistry.⁴ Rinzler *et al.*⁵ and Dillon *et al.*⁶ observed that treatment of a sample of as-made single-walled carbon nanotubes (SWNTs) with nitric acid produces a uniform functionalised coating of disordered carbon on the SWNTs. Recently it has been shown on both multi-walled carbon nanotubes⁷ (MWNTs) and SWNTs⁸ that this functionalised coating, also called “oxidation debris”⁷ or “carboxylated carbonaceous fragments (CCFs)”⁸, is in fact the carrier of the majority of the COOH groups present in the sample† and can be easily removed by an aqueous base washing. Therefore at the outset of the work described below there was no evidence as to whether nitric acid treatment of MWNTs or SWNTs could introduce carboxylation of the hexagonal rings which form the body of the CNTs. We now provide such evidence for the first time.

SWNTs were prepared using a high yield metal catalysed arc synthesis method.⁹ Following the sequence of reactions recently reported,^{7,8} as-made SWNTs (sample A) were refluxed in 3 M nitric acid for 24 h, followed by filtration and rinsing with water. The remaining solid (sample B) was treated with 4 M NaOH, filtered and rinsed with water leading to a dark filtrate (sample F) due to the presence of oxidation debris.^{7,8} The solid sample on the

filter membrane was further washed with water (sample C). The Raman and IR spectra of the samples obtained after each step are shown in Fig. 1, and are in good agreement§ with those previously reported.^{7,8} The IR spectrum of sample A shows an absence (low degree) of functional groups. After nitric acid treatment (sample B) strong peaks appear at $\sim 1735\text{ cm}^{-1}$, $\sim 1585\text{ cm}^{-1}$ and $\sim 1200\text{ cm}^{-1}$, due to the C=O, C=C and C–O stretching transitions respectively, most likely due to formation of carboxylic acid groups.¹⁰ The peak at $\sim 1200\text{ cm}^{-1}$ could also be assigned to O–H bending.¹⁰ A small broad peak can also be seen at $\sim 1400\text{ cm}^{-1}$ corresponding to CO–H bending or C–H deformations.⁷ The peaks at $\sim 1735\text{ cm}^{-1}$ and $\sim 1200\text{ cm}^{-1}$ vanish after NaOH wash (sample C) due to the removal of the oxidation debris, which contains the majority of COOH functionality created by the acid treatment. The Raman spectrum of sample B shows an increase in the ratio of D/G band intensity (I_D/I_G) compared to sample A, which has long been attributed to the functionalisation of the sample due to its oxidation by nitric acid. The NaOH treatment leads to a dramatic decrease of the I_D/I_G from 47.5% (sample B) to 20.5% (sample C) due to the removal of the oxidation debris.

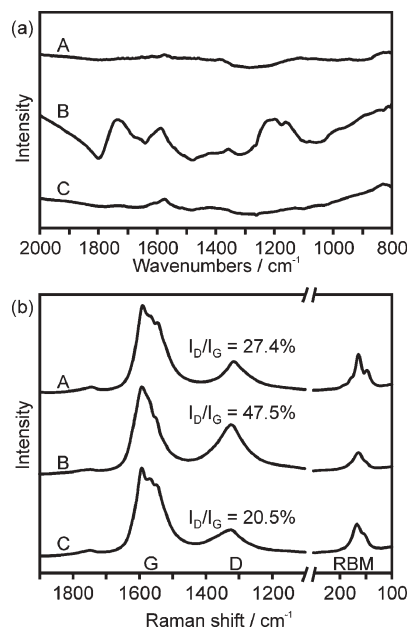


Fig. 1 (a) FTIR and (b) Raman spectra of as-made arc SWNTs (sample A), after acid treatment (sample B) and base wash (sample C).

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† Electronic supplementary information (ESI) available: Scheme summarising treatments and sample names. AFM data including blank experiments. Characterisation of CVD SWNTs (FTIR, Raman and HRTEM). Experimental procedures and characterisation techniques. See DOI: 10.1039/b712614j

In another set of experiments, as-made SWNTs were treated with steam in order to remove the amorphous carbon.¹¹ The same reactions performed on sample A were then carried out on this purified material (sample A'), namely treatment with nitric acid and washing with NaOH. The IR and Raman spectra acquired after each step are shown in Fig. 2. Only a small peak at 1575 cm⁻¹ due to C=C bonds¹⁰ can be observed in the IR spectrum after steam purification (sample A', Fig. 2a), confirming that this treatment does not introduce functional groups.¹¹ The Raman spectrum shows a decrease in the I_D/I_G, from 27.4% (sample A) to 5.8% (sample A'), which has been attributed to the removal of the amorphous carbon without changing the SWNT structure.¹¹ The D-band is associated with disordered, sp³-hybridized carbon present as impurities and SWNT defects.¹² The lower degree of disorder in sample A' compared to sample A is also reflected by the increase in the intensity of the radial breathing modes (RBM) with respect to that of the G-band (I_R/I_G).¹⁰ Sample A' was next treated with 3 M nitric acid for 24 h. After this treatment, the IR spectrum of the product (sample B') shows the appearance of the C=O band corresponding to the formation of carboxylic acid groups in the sample. An increase of the I_D/I_G in the Raman spectrum is also clearly visible with respect to sample A'. Sample B' was then treated with 4 M NaOH, filtered and rinsed with water. To our surprise, the filtrate (sample F') was almost colourless, indicating that the amount of oxidation debris had been dramatically reduced compared to sample F (Fig. 3). The remaining solid on the filter membrane was further washed with extra water until the filtrate was neutral and no change was observed by Raman and IR spectroscopy on the remaining powder (sample C'). In contrast to the as-made arc SWNTs, where a decrease of the I_D/I_G is observed after the acid and base treatments, from I_D/I_G = 27.4% (sample A) to 20.5% (sample C), the opposite trend is observed for the purified sample. The I_D/I_G increases from 5.8% (sample A') up to 19.3% after the nitric acid and base wash (sample C'), indicating that treatment with nitric

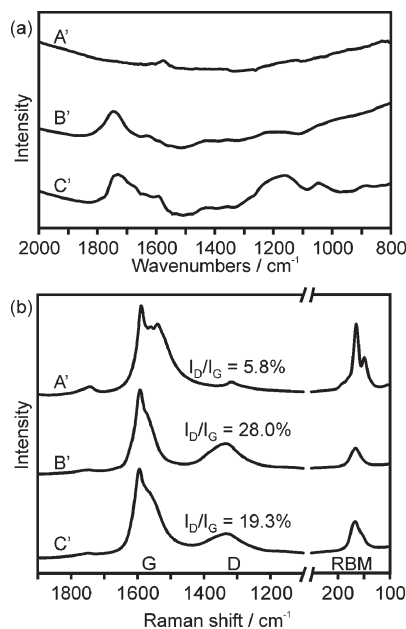


Fig. 2 (a) FTIR and (b) Raman spectra of steam purified arc SWNTs (sample A'), after acid treatment (sample B') and base wash (sample C').

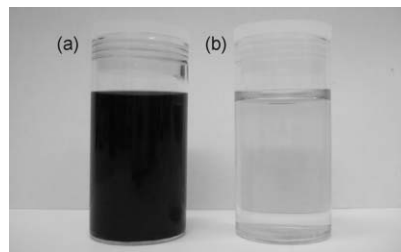


Fig. 3 Samples of filtrates containing oxidation debris: (a) sample F and (b) sample F'.

acid has successfully altered the SWNTs structure. Furthermore, in the IR spectrum of sample C', the C=O stretching transition is clearly visible (Fig. 2a), confirming that for the purified sample the majority of the carboxylic acid groups are present on the SWNT walls rather than on oxidation debris. The band around 1200 cm⁻¹ due to C–O stretching becomes more visible after the NaOH wash.

The main difference between sample A and sample A' is the amount of amorphous carbon, which is the more reactive form of carbon present in as-made CNTs. We suggest that when a sample of as-made CNTs is treated with nitric acid, oxidation debris (CCFs) is formed due to the functionalisation of the amorphous carbon. The oxidation debris creates a continuous coating on the carbon nanotube walls, preventing the attack of the carbon nanotubes themselves. In contrast, when a sample free of amorphous carbon (steam purified) is treated with nitric acid, the formation of oxidation debris is dramatically reduced and most of the functional groups are present on the carbon nanotube walls.

The changes on the G-band observed in Raman spectroscopy are also in agreement with these observations. This band is composed of several tangential modes due to stretching vibrations of the SWNT sidewall carbon–carbon bonds.¹² Although after nitric acid treatment the features of this band become less resolved for both samples B and B', compared to samples A and A' respectively, they are recovered after the NaOH wash in the case of the as-made SWNTs (sample C, Fig. 1b) but remain permanently altered in the steam purified sample (sample C', Fig. 2b). This provides further evidence that nitric acid is able to functionalise the carbon nanotube walls to a much greater extent when the amorphous carbon has been previously removed.

The same set of experiments were done on commercial SWNTs prepared by chemical vapour deposition (Thomas Swan & Co. Ltd.) for as-received and steam purified samples, leading us to the same conclusions (see ESI†).

High resolution transmission electron microscopy (HRTEM) of sample B confirms the presence of amorphous material, as previously reported.^{5–7} In contrast, the absence of an amorphous coating was observed for sample B'.

Atomic force microscopy (AFM) in conjunction with chemical tagging techniques has been shown to be a reliable method for locating functional groups and determining their distribution.¹³ The carboxylic acid groups present on sample C' were chemically modified by reaction with thionyl chloride followed by cysteamine. The resulting thiol groups were then tagged with gold nanoparticles. Fig. 4 shows a typical AFM image of the same individual nanotube before and after exposure to gold colloids, providing direct evidence that the functional groups of the sample C' are present along the carbon nanotubes by unambiguous

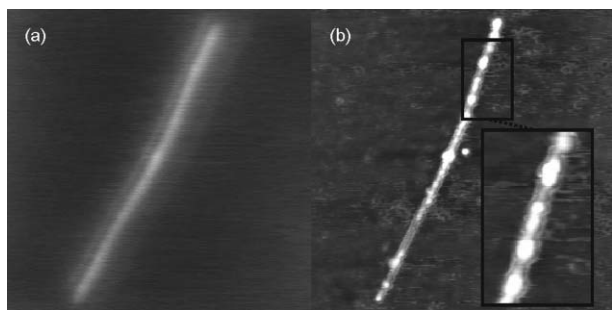


Fig. 4 AFM (a) before and (b) after exposure of gold colloids on a nitric acid treated and base washed sample of steam purified SWNTs (sample C') which has been chemically modified with thiol groups. Images are 850×850 nm, z scale 0–5 nm.

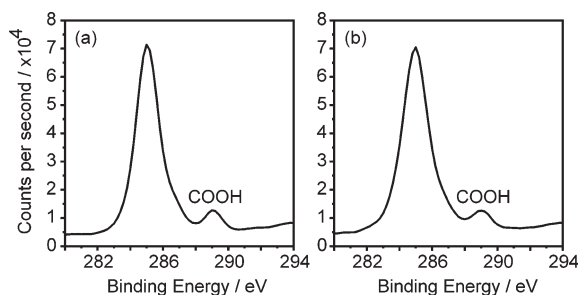


Fig. 5 XPS data of C1s for steam purified SWNTs after (a) nitric acid treatment (sample B') and (b) base wash (sample C').

differentiation of the attached gold nanoparticles.¶ Blank experiments conducted on samples A' and C showed an absence of gold nanoparticles along the SWNT walls (see ESI†). The lack of gold nanoparticles after thionyl chloride and cysteamine treatments on sample C confirms a much lower concentration of COOH groups on the SWNTs with respect to sample C'. The absence of carboxylic acid groups in sample C cannot be inferred from this experiment since several neighbouring functional groups can be needed to attach one gold nanoparticle.

The amount of COOH functionality present in sample B' and sample C' was estimated by X-ray photoelectronic spectroscopy (XPS). Two main components are observed in the C1s peak (Fig. 5) which can be attributed to unfunctionalised graphitic carbon and to carboxylic acid groups (at higher binding energy).¹⁵ The concentration of carboxylic acid groups can be determined by the ratio of peak intensities, being 9.2% for sample B' and 8.5% for sample C', confirming that the large majority of functionality is still present in the sample of SWNTs after base wash.

In summary, we have demonstrated that the removal of amorphous carbon from the as-made carbon nanotube sample is a key step for the successful sidewall functionalisation of carbon nanotubes using nitric acid. When amorphous carbon is present, oxidation debris (CCFs) is formed, shielding the nanotube walls from further functionalisation. Since the amorphous carbon is the most reactive carbon form present in a sample of as-made carbon

nanotubes, its removal should be considered before doing any chemical treatment, as it can dominate the features of bulk measurements done on carbon nanotube samples and prevent the sidewall functionalisation of the CNTs.

We thank Dr Robert Jacobs for advice on AFM and Dr Gregory G. Wildgoose for discussions. This research was supported in part by a Marie Curie Intra-European Fellowship within the 6th European Community Framework Programme (MEIF-CT-2006-024542) (G.T.). We are grateful to the Austrian Academy of Sciences (APART programme) (C.G.S.), to Samsung Corporation for a scholarship (S.Y.H.) and to Thomas Swan & Co. Ltd. for SWNTs and funding.

Notes and references

‡ Although carboxylic acid groups are the main feature of this oxidation debris, other oxygen-containing functional groups may also be present.^{6,7}
§ For comparison with other work, it has to be taken into account that the I_D/I_G ratio on the Raman spectra is dependent on the laser excitation frequency.¹⁴

¶ The exact location of individual functional groups and defects on the CNT structure in the atomic scale resolution is challenging. State-of-the-art high resolution microscopy would be needed.

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