

# New developments in the purification, filling and functionalization of carbon nanotubes

Russell Clarke\*

\*Thomas Swan & Co Ltd., Consett, County Durham, DH8 7ND, United Kingdom  
[rclarke@thomas-swan.co.uk](mailto:rclarke@thomas-swan.co.uk)

## ABSTRACT

A vast amount of research is currently being done on the purification, filling and functionalization of carbon nanotubes (CNTs) due to the potential applications of these materials. Here we report on the use of steam for the purification and opening of CNTs, which allows the removal of the amorphous carbon and the graphitic layers surrounding the metal particles.

The steam purified CNTs can be filled by solutions of the desired compounds. Fullerenes can be used as corks for the containment of the encapsulated materials inside the open-ended CNTs.

The removal of amorphous carbon is proven to be a key step for the sidewall functionalization of CNTs. Finally, we show that the direct visualization of organic molecules covalently bonded to the carbon nanotubes by electron microscopy techniques can be achieved by first labelling them with a high scattering element.

SWAN CNTs were used in all the reported experiments.

**Keywords:** carbon nanotubes, purification, filling, functionalization, corking

## 1 CARBON NANOTUBE PURIFICATION BY STEAM TREATMENT

The main impurities in as-made CNTs are typically amorphous carbon, graphitic particles and metal particles. Although several procedures have been used to remove them off, the nitric acid has become the standard reagent for purification of CNTs and constitutes one of the steps in many different purification schemes [1]. Recent studies have shown that acid purification also leads to partial oxidation of CNT themselves and sometimes to an extensive disruption of the tubular structure, especially in the case of single-walled carbon nanotubes (SWCNTs) [2, 3]. On the contrary, the use of the mild oxidising agent steam can remove the amorphous carbon present in samples of as-made CNTs without introducing defects and functional groups, as confirmed by IR and Raman spectroscopies [4]. Raman spectra (Figure 1) show a decrease in the ratio of D/G band intensity ( $I_D/I_G$ ) from  $8.2 \pm 1.4\%$  for the as-made SWCNTs to  $4.6 \pm 0.4\%$  after steam treatment at  $900\text{ }^\circ\text{C}$  for 4 h. On the contrary, when refluxing the as-made SWCNTs in 3 M nitric acid for 45 h, which is the most commonly used method reported in the literature, the D/G band ratio increases from  $8.2 \pm 1.4\%$  to  $44.7 \pm 0.5\%$

0.5%. Both,  $sp^3$ -hybridized carbon present as impurities and SWCNT defects contribute to the intensity of the D-band [5]. If compared to the as-made SWCNTs, the increase in D/G band ratio for the nitric acid treated SWCNTs indicates a large amount of defects, which is consistent with the studies showing that nitric acid purification alters the SWCNT structure. In the case of steam treated samples, the observed decrease in  $I_D/I_G$  can be attributed to the removal of carbonaceous impurities during purification and to a self-healing process of the defect sites resulting in an enhanced graphitization. The preferential removal of the more defective SWCNTs could also play a role in the decrease of the D-band intensity. There is no significant change in  $I_D/I_G$  when a sample of as-made SWCNTs is heated at  $900\text{ }^\circ\text{C}$  for 4 h under argon ( $I_D/I_G = 7.7 \pm 1.3\%$ ; spectrum not shown). The radial breathing modes (RBM) show the same features before and after the steam purification, which indicates that the tubular structures of the SWCNTs are preserved during the steam treatment.

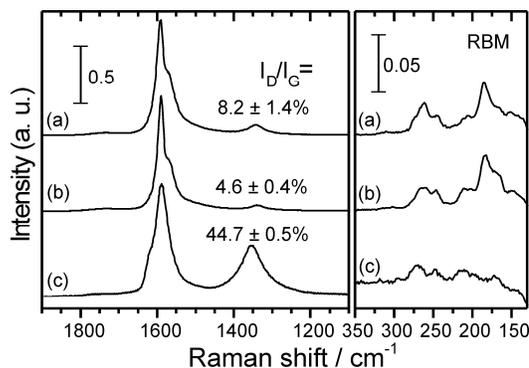


Figure 1. Raman spectra of (a) as-made SWCNTs, (b) steam-purified SWCNTs at  $900\text{ }^\circ\text{C}$  for 4 h, (c) as-made SWCNTs after treatment with 3 M  $\text{HNO}_3$  for 45 h.

We observed that amorphous carbon was much more reactive with the steam than carbon nanotubes and graphitic particles. No amorphous carbon was present after 2 h treatment. Although graphitic particles cannot be removed from the sample without consuming SWCNTs, we found that 4 h treatment was a good compromise for purifying the as-made SWCNTs. Figure 2 shows HRTEM pictures of as-made SWCNTs and after steam treatment at  $900\text{ }^\circ\text{C}$  for 4 h. The purification of the sample with steam clearly removes amorphous carbon and some graphitic particles entangling the as-made SWCNTs (Figure 2a) leaving behind cleaner SWCNTs (Figure 2b).

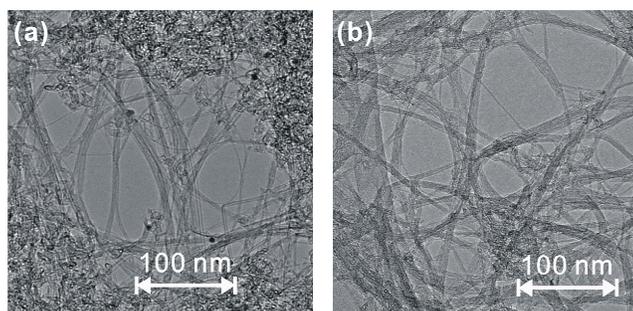


Figure 2. HRTEM images of (a) as-made SWCNTs and (b) SWCNTs after steam treatment at 900°C for 4h

Recently we have proved that steam can also remove the graphitic shells coating the metal particles present in samples of as-made SWCNTs [6]. These now exposed catalytic particles can be easily dissolved by hydrochloric acid treatment.

In order to get the minimum amount of metal catalyst particles, the steam treatment time needs to be optimized. Therefore we treated SWCNTs for different times with steam at 900°C and we subsequently washed the steam treated samples with HCl. Figure 3 summarises the metal content (% of Fe) in each steam and acid washed sample. The values were obtained by carrying out TGA experiments under flowing air.

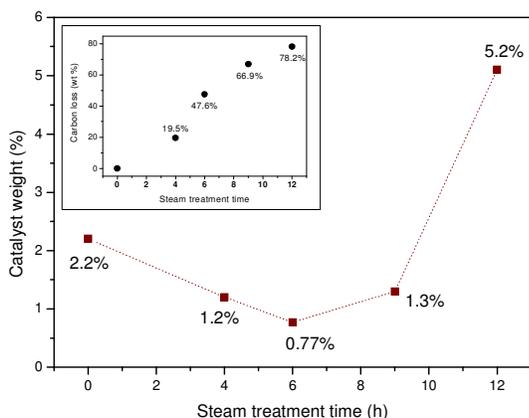


Figure 3. Summary of the amount of iron present in the as-made SWCNTs and the different steam treated samples after the HCl wash. *Inset*: Weight percentage of carbon loss with respect to the amount of carbon in the starting material after different steam treatment times.

The as-prepared sample has a metal content of 2.2 %wt. Lower metal contents with respect to the starting material can be obtained after 4 h, 6 h and 9 h steam treatment. However, the lowest percentage of catalytic particles is observed after 6 h treatment (0.77%). Longer treatments result in a relative increase of the metal content (1.3% after 9 h and 5.2% after 12 h) and therefore are not recommended. The carbon loss in weight % with respect to the initial amount of carbon present in the sample is

depicted in the inset in Figure 3. As expected, the longer the steam treatment the more carbon in its different forms (amorphous carbon, graphitic particles or SWCNTs) is removed from the sample. Therefore there is a clear compromise between the quality of the sample and the weight loss.

Steam purification has the advantages of being an economic, easily scalable and non-toxic process. The purification time needs to be adjusted depending on the carbon nanotube source. For instance, arc-discharged SWCNTs are more reactive towards steam compared to SWAN CVD SWCNTs [7].

## 2 FILLING AND CORKING OF CARBON NANOTUBES

As-made SWCNTs, normally closed at both ends, may be readily filled by direct heating to about 700-900 °C in the presence of any material which is liquid at that temperature and of suitable surface tension [8]. On cooling the reaction mixture, the ends of the filled SWCNTs are still closed [9]. Therefore, the excess of material external to the SWCNTs may be dissolved away by choice of a suitable solvent. This high temperature filling method is limited mainly by the requirement that the chosen filling material is thermally stable as a melt. For example, organic molecules can not be filled using this approach.

The alternative methods of filling SWCNTs require opened ends. This can readily be accomplished by use of an oxidising agent such as steam [4]. The resulting open-ended SWCNTs may then be filled by solution, vapour or melt of the chosen materials [10]. A high resolution transmission electron microscopy (HRTEM) image of uranyl acetate solution-filled carbon nanotubes is shown in Figure 4. The encapsulated uranium compound is presented in the form of short crystals along the SWCNTs, characteristic of the solution filling method.

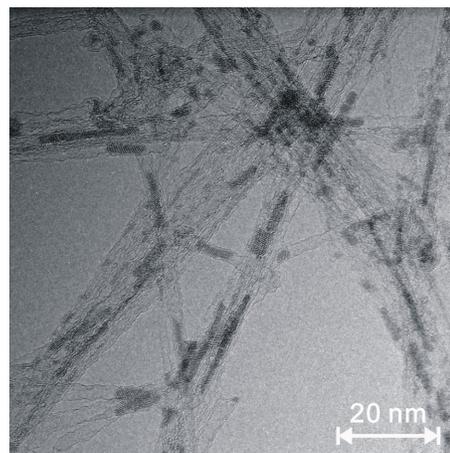


Figure 4. HRTEM image of an uranium compound encapsulated inside steam opened SWCNTs

The solution filling experiment was carried out by stirring 10 mg of steam-purified carbon nanotubes at 70 °C for 2 days in a saturated solution of uranyl acetate  $\{UO_2(CH_3CO_2)_2(H_2O)_2\}$ . Uranyl acetate was chosen since the heavy element component uranium can be easily observed by HRTEM.

Bulk filling of carbon nanotubes always results in a large amount of unwanted external material. However, when using solution filling it is not possible to remove the material external to the filled SWCNT by washing, as this also removes the material encapsulated in the open-ended SWCNTs. To solve this problem, fullerenes have been used as corks (plugs) to block the opened ends of filled SWCNTs. The resulting “nanocapsules” can then be readily purified from the external material by washing in a suitable solvent.

Following the procedure described by Iijima *et al.* for filling  $C_{60}$  into the SWCNTs ( $C_{60}@SWCNTs$ ) [12], the fullerene  $C_{60}$  in ethanol was added to the uranyl acetate filled SWCNTs (prepared as described above). The mixture was then stirred in aqueous hydrochloric acid, in which uranyl acetate is very soluble. After filtering and drying, the sample was examined by HRTEM and the continuing presence of uranyl acetate inside the SWCNTs was confirmed whilst the uranium material outside the SWCNTs had been removed. Also, the presence of both  $C_{60}$  molecules and uranyl acetate crystals could be observed along individual SWCNTs (Figure 5). A blank experiment with uranyl acetate was made by repeating all the experimental procedures but without addition of  $C_{60}$ . After the final washing step with hydrochloric acid, no uranyl acetate could be detected neither inside nor outside the SWCNTs and only empty SWCNTs were observed by HRTEM. The fact that filled tubes with uranyl acetate after the HCl wash can only be seen when  $C_{60}$  are also present, confirms the ability of  $C_{60}$  to seal materials inside the SWCNTs.

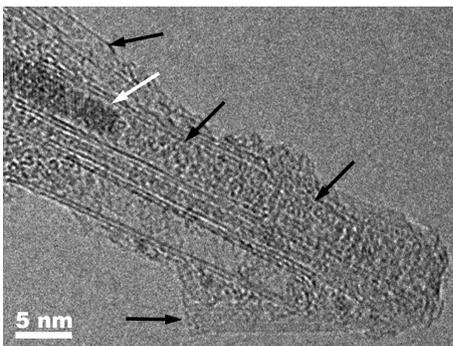


Figure 5. HRTEM images of  $C_{60}$  corked uranyl acetate filled SWCNTs after being washed in HCl. As guides to the eye, white arrows point the uranium compound, and black arrows point some of the encapsulated  $C_{60}$ .

The methodology described here is simple and effective way to seal soluble materials inside open-ended SWCNTs,

using  $C_{60}$  molecules, and allow the washing of the external undesired material. Samples free of material outside the SWCNTs are of great interest for the bulk characterization and application of filled SWCNTs.

### 3 FUNCTIONALIZATION OF CARBON NANOTUBES

The use of CNTs for materials science and biomedical applications is limited by their poor solubility and processability. An approach to overcome these problems consists in the chemical functionalization of the sidewalls of the carbon nanotubes. 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 [13].

The nitric acid treatment of as-produced SWCNTs generates contaminating debris, which can be easily removed by base wash leaving behind CNT samples with low degree of functionalization. The sidewall functionalization of carbon nanotubes using nitric acid treatment can be greatly enhanced by first removing the amorphous carbon present in the sample [7].

As-made SWCNTs (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 due to the presence of oxidation debris. The solid sample on the filter membrane was further washed with water (sample C). The IR spectrum of sample A (Figure 6a) shows an absence (low degree) of functional groups. After nitric acid treatment (sample B) strong peaks appear at  $1735\text{ cm}^{-1}$ ,  $1585\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ , due to the C=O, C=C and C–O stretching transitions respectively, most likely due to formation of carboxylic acid groups. The peak at  $1200\text{ cm}^{-1}$  could also be assigned to O–H bending. The peaks at  $1735\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  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.

In another set of experiments, as-made SWCNTs were treated with steam in order to remove the amorphous carbon [4]. The same reactions performed on sample A were then carried out on this purified material (sample A'), namely treatment with nitric acid (sample B') and washing with NaOH (sample C'). Only a small peak at  $1575\text{ cm}^{-1}$  due to C=C bonds can be observed in the IR spectrum after steam purification (sample A', Figure 6b), confirming that this treatment does not introduce functional groups. The IR spectrum of sample B' shows the appearance of the C=O band corresponding to the formation of carboxylic acid groups in the sample. This peak remains unchanged on the IR spectrum of the powder (sample C') obtained after washing the sample with NaOH, confirming that for the

purified sample the majority of the carboxylic acid groups are present on the SWCNT walls rather than on oxidation debris. The band around  $1200\text{ cm}^{-1}$  due to C–O stretching becomes more visible after the NaOH wash.

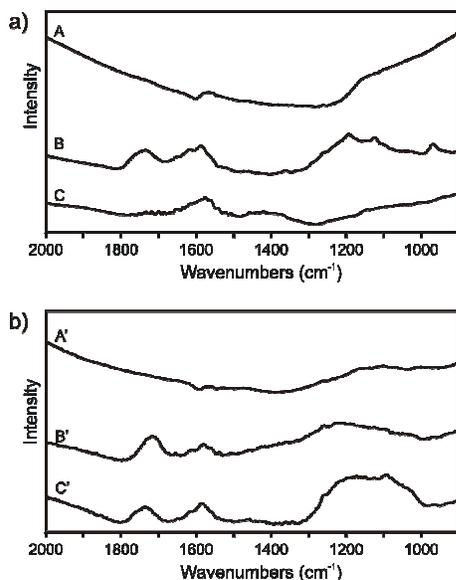


Figure 6. FTIR spectra of (a) as-made SWCNTs (sample A), after acid treatment (sample B) and base wash (sample C) and (b) steam purified SWCNTs (sample A'), after acid treatment (sample B') and base wash (sample C').

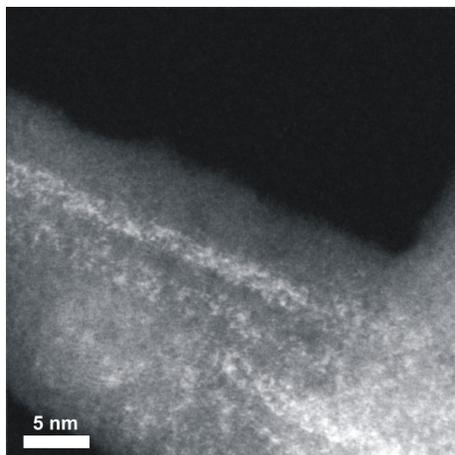


Figure 7. Z-contrast dark field STEM images of SWCNTs functionalized with iodide labelled carbohydrates. Individual iodides (white dots) can be clearly seen.

However, these do not provide direct evidence of the attachment of individual molecules. The use of electron microscopy techniques such as HRTEM and scanning transmission electron microscopy (STEM) for characterization of organic compounds is typically limited

by the lack of structural periodicity and the presence of low scattering elements (H, C, N, O). We have been able to directly visualise organic molecules covalently bonded to the carbon nanotubes by first labelling them with a high scattering element, such as iodine [14] (Figure 7).

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