

Scalable Single Walled Carbon Nanotube Separation: From Process to Product.

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ABSTRACT

The extraordinary electronic and optical properties of single walled carbon nanotubes (SWNTs) are determined by their structure; SWNTs are either metallic or semiconducting depending on their diameter and chirality. Current techniques for the separation of SWNTs are only partially successful due to the difficulties in dispersion and scalability. Here, using technology exclusively licensed from University College London Business (UCLB), we detail a fully scalable method of SWNT purification and separation based on the different susceptibilities of impurities, metallic SWNTs and semiconducting SWNTs to chemical reduction. By carefully controlling the metal to carbon ratio in an initial liquid ammonia reduction, followed by spontaneous dissolution of the most easily reduced fraction in an organic solvent, powders of purified SWNTs, metallic SWNTs and semiconducting SWNTs, can be easily, quickly and scalably produced.

Keywords: Carbon, Nanotubes, Separation, Ammonia, Scalable

1 INTRODUCTION

The extraordinary electronic and optical properties of single walled carbon nanotubes (SWNTs) are determined by their structure; SWNTs are either metallic or semiconducting depending on their diameter and chirality [1]. Many valuable applications in, for example, transparent conductors [2], solar cells [3], biosensors [4] and nanoelectronics [5], require nanotubes of specific electronic character and purity [6].

SWNT synthesis techniques produce samples containing a mix of different SWNT types along with a range of different impurities such as graphitic nanoparticles and amorphous carbon [7]. Current techniques for the separation of SWNTs from their impurities and into semiconducting and metallic species are only partially successful due to the difficulties in dispersion [8] and scalability. Before SWNTs can be separated the van der Waals forces that hold them together must be overcome; currently high power sonication is used in all cases to perform this separation. Sonication is known to damage the nanotubes and can destroy their unique properties [9]. Here, using technology exclusively licensed from University

College London Business (UCLB)¹, we detail a fully scalable method of SWNT purification and separation based on the different susceptibilities of impurities, metallic SWNTs and semiconducting SWNTs to chemical reduction; a technique that uses no sonication or centrifugation.

Transferral of these reduced tubes as a dry powder to an organic solvent allows for the spontaneous dissolution of the most easily reduced fraction. By carefully controlling the metal to carbon ratio in the initial liquid ammonia reduction the spontaneously dissolved fraction can be tailored to contain predominantly metallic SWNTs, predominantly carbonaceous impurities or a representative sample of the raw SWNTs. In cases where the metal to carbon ratio is designed to selectively reduce metallic SWNTs, the remaining, undissolved fraction contains predominantly semiconducting SWNTs.

Hence, using this method, powders of purified SWNTs, metallic SWNTs and semiconducting SWNTs can be easily, quickly and scalably produced with no sonication or centrifugation.

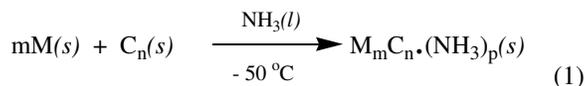
¹ Process technology developed by Milo Shaffer and Siân Fogden of Imperial College London and Neal Skipper and Christopher Howard of University College London.

2 OVERVIEW OF THE PROCESS

2.1 Liquid ammonia Reduction

The critical step in this SWNT separation technology is an initial reduction of SWNTs in liquid ammonia. Alkali metals dissolved in liquid ammonia produce strongly reducing solutions as they readily give up their outer shell electron to form solutions of unpaired (solvated) electrons [10]. These unpaired electrons can be seen as an intense blue colour within the solution. When SWNTs are added to this reaction mixture the blue colour is seen to disappear over the course of a few hours as the electrons are transferred to the SWNTs which are seen to swell greatly in volume within the liquid ammonia. This swelling is thought to be the result of a joint mechanism where the reduction of the SWNT causes intertube repulsions and the

alkali metal counter ion intercalates within the tube network (Equation 1) [11, 12].



Removal of the liquid ammonia leaves behind a stable nanotubide (where nanotubide is the term used for a nanotube anion).

2.2 Addition of Organic Solvent

Transferral of the nanotubide as a dry powder to an organic solvent, dimethylformamide (DMF) is used here, allows for the spontaneous dissolution of the most easily reduced fraction (Figure 1).



Figure 1 Spontaneous dissolution of the most easily reduced fraction of the nanotubide salt in DMF

It is important to note that, as has been demonstrated elsewhere [13], no stirring and more importantly no sonication were used to aid this dispersion. This spontaneous dissolution is thought to occur for two reasons: the intertube repulsion between the nanotubides, and superior solvation of the alkali metal cations by DMF. Importantly, for this spontaneous dissolution to occur and be maintained the solvent and atmosphere that the reaction is undertaken within must be kept stringently air and water free. Any oxygen contamination will quench the charge on the nanotubes, leading to nanotube aggregation and sodium hydroxide formation.

By carefully controlling the metal to carbon ratio in the initial liquid ammonia reduction the spontaneously dissolved fraction can be tailored to contain predominantly metallic SWNTs, predominantly carbonaceous impurities or a representative sample of the raw SWNTs.

Using a very low metal to carbon ratio, primarily carbonaceous impurities can be seen to spontaneously dissolve. A high metal to carbon ratio leads to spontaneous dissolution of a sample representative of the initial SWNTs metallicity whereas by using a metal to carbon ratio between these two extremes only metallic SWNT are seen to spontaneously dissolve.

Thus, a process for the purification and separation of SWNTs is described. Please see the upcoming paper by Fogden et. al. [14] for complete technical details and further information.

3 EXPERIMENTAL

SWNTs were purchased from Southwestern Nanotechnologies (CVD grown); all nanotube samples were outgassed for 24 hours at 220 °C before use to remove any adsorbed oxygen and moisture. Both the nanotubes and the sodium were accurately weighed in a nitrogen glovebox and placed in a reaction tube which was cooled to -50°C using a propanol bath and a chiller unit. Ammonia was then condensed onto the reaction mixture; after 12 hours it was removed using a nitrogen flow. In a nitrogen containing glovebox dry DMF was then added to the nanotubide sample which was left to spontaneously dissolve.

Raman spectra of the dry samples were collected with a red (633nm) and green (532nm) laser using a Thermo Fisher DXR Micro Raman instrument.

SEM images were collected using a FEI SFEG Ultra High Resolution instrument.

4 CHARACTERIZATION

Raman spectroscopy is one of the most powerful tools for the characterisation of SWNTs; it originates from the inelastic scattering of light and is used to look at the vibrations and rotations of the carbon atoms contained within an individual nanotube [15]. For carbon nanotubes there are three main peak areas in any given spectra. At approximately 1580 cm⁻¹ is the G-band which is associated with the in plane vibrations in the SWNTs. At approximately 1350 cm⁻¹ is the D-band which is associated with symmetry breaking perturbation on the hexagonal sp² bonded lattices for graphite and nanotubes and is therefore associated with both defects within the tubes themselves and graphitic/amorphous impurities within the sample as a whole. The ratio of the G/D bands gives an indication of the purity of the sample. At 100-500 cm⁻¹ the radial breathing modes (RBMs) can be seen, they occur due to the symmetric in-phase displacement of the carbon atoms in the radial direction. From the position of these peaks the size and specific nanotube type can be determined. Therefore, they can be used to assess the relative metallicity of the SWNT sample. It is important to note that only a small fraction of a polydispersed SWNT sample will be excited at a given wavelength [16]. However, conveniently the Red (633nm) and Green (532nm) lasers used in this study excited both the metallic and semiconducting SWNTs so the change in relative intensity of these two peaks can be used to assess the relative concentrations on SWNTs in the sample.

When a very low metal to carbon ratio is used in the initial liquid ammonia reduction, primarily amorphous carbon is seen to spontaneously dissolve into the DMF. This can be seen in the Raman spectra by the lack of RBMs (therefore the lack of SWNTs) and an increase in the size on the D-band relative to the size of the G-band. Dissolution of the amorphous carbon results in a purified SWNT sample as demonstrated by the G/D ratio – the ratio increased from 8.4 for the as-received nanotubes to 9.8 for the purified sample.

When a high metal to carbon ratio is used in the initial liquid ammonia reduction, all of the nanotubes are charged and the spontaneously dissolved fraction is seen to contain a metallicity proportionally equal to the initial sample (as seen by Raman spectroscopy). Therefore, this gives a solution of individually, reduced SWNTs or carbon nanotubide salts.

However, when a metal to carbon ratio between these two extremes is used in the initial liquid ammonia reduction, primarily metallic SWNTs are seen to spontaneously dissolve. This can be seen clearly with both the red and the green Raman lasers. The red laser (Figure 2a) shows that in the spontaneously dissolved fraction the intensity of the metallic peaks between 160 cm^{-1} and 220 cm^{-1} greatly increase where as the intensity of the semiconducting peaks between 240 cm^{-1} and 340 cm^{-1} greatly decrease. This spontaneous dissolution of primarily the metallic SWNT can also be seen using the green Raman laser (Figure 2b) where the intensity of the metallic peaks in the two regions 140 cm^{-1} to 165 cm^{-1} and 205 cm^{-1} to 265 cm^{-1} can be seen to greatly increase where as the intensity of the semiconducting peaks in the 300 cm^{-1} to 350 cm^{-1} region can be seen to greatly decrease.

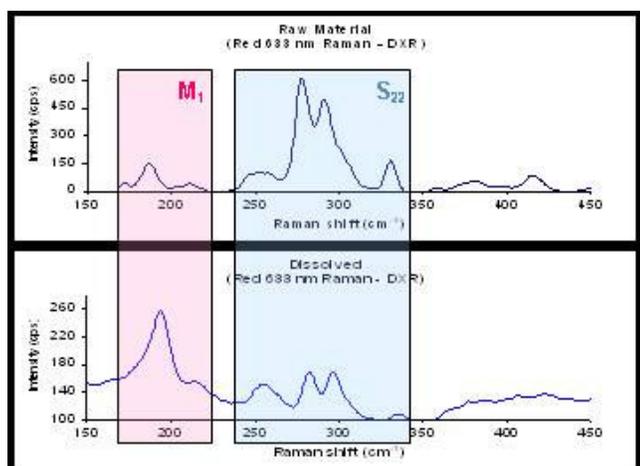


Figure 2a Red RBMs

During the spontaneous dissolution of the metallic fraction the amorphous carbon impurities also spontaneously dissolve. This can be seen as a decrease in the G/D ratio

from 8.4 for the as-received material to 3.2 for the metallic spontaneously dissolved sample. Therefore, when this metallic fraction is removed the remaining, undissolved fraction contains purified, primarily semiconducting SWNTs. The purification of the semiconducting fraction can be seen by the increase in the G/D ratio from 8.4 for the as-received sample to 14.8 for the undissolved, semiconducting sample.

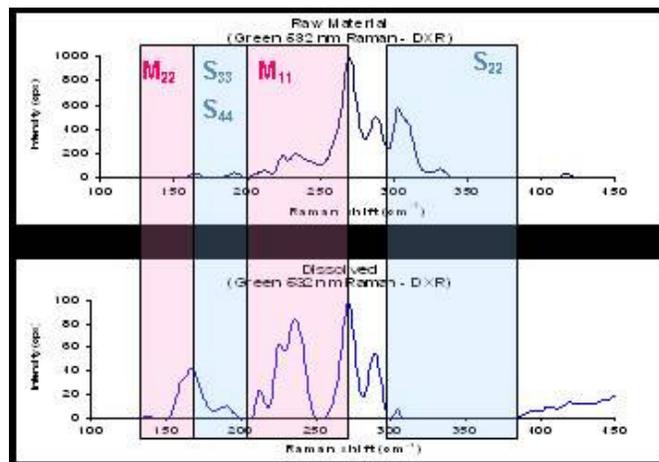


Figure 2b Green RBMs

	G/D ratio
As-received	8.4
Purified Fraction	9.8
Metallic Spontaneously dissolved fraction	3.2
Amorphous carbon spontaneously dissolved fraction	1
Semiconducting fraction	14.8

Table 1: G/D ratio of CoMoCAT SWNTs using Red (633nm) Raman laser line.

Scanning Electron Microscopy (SEM) images of this, undissolved, primarily semiconducting fraction show, small bundles of long tubes with low amorphous carbon content (Figure 3).

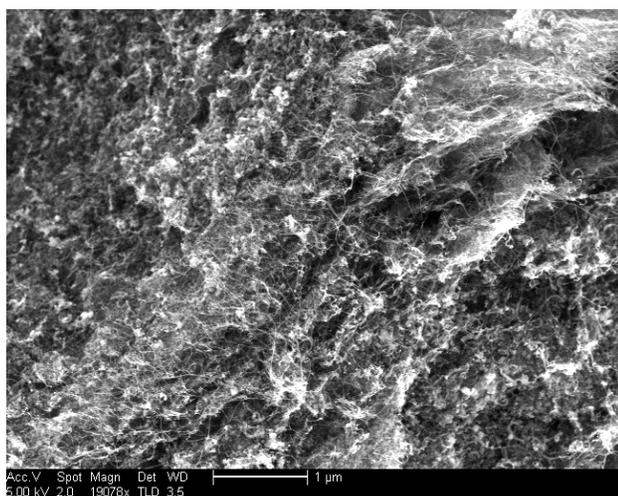
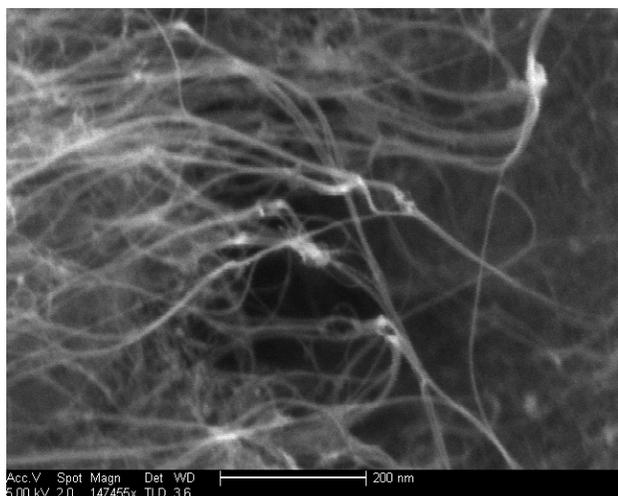


Figure 3 SEM images of semiconducting fraction.

5 SCALABILITY

As discussed in the introduction, it is the dispersion step that limits the scalability of current separation methods. No such limit exists for the technology described here. The liquid ammonia reduction step is only limited by the size of the apparatus in use. A one hundred fold increase in scale has been realized at Linde's pilot facility. Indeed, a compressed gas company such as Linde is well-placed to practice this technology at scale due to its core capabilities in the bulk, cryogenic handling of high purity liquid ammonia. Similarly, the spontaneous dissolution process is also limited only by the scale of the apparatus in use.

The scaled process offers the prospects for high volume manufacture of powders of purified SWNTs, and powders or solutions of SWNTs of defined metallicity

Importantly it should be noted that no sonication and no centrifugation was used in the process meaning that the SWNTs contained within the samples are long and defect free.

6 REFERENCES

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