

# Separation of carbon nanotubes by size exclusion chromatography

G. S. Duesberg,\* M. Burghard, J. Muster, G. Philipp and S. Roth

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart and EU TMR network Namitech, Germany and University of Dublin, Trinity College, Physics Department, Dublin 2, Ireland

**Size exclusion chromatography has been performed on micellar aqueous dispersions of soot from an arc discharge experiment to yield chemically unmodified, almost impurity free and size separated multiwall nanotubes.**

Several large-scale synthesis routes for carbon nanotubes (NTs) have been reported,<sup>1-3</sup> however, they lead to by-products of other carbon species. In addition to multiwall NTs the soot of a conventional arc discharge experiment contains fullerenes, carbon polyhedra, and amorphous carbon, which are interconnected in a dense network. For a number of proposed applications of NTs, which include field emission<sup>4</sup> and electronic devices,<sup>5,6</sup> their purification and size separation is of great importance.

In destructive methods, like oxidation, the soot material is purified by decomposition of the small particles while some tubes remain. However, the caps of the tubes are opened and chemical functionalities are introduced on the tube surface.<sup>7,8</sup> In

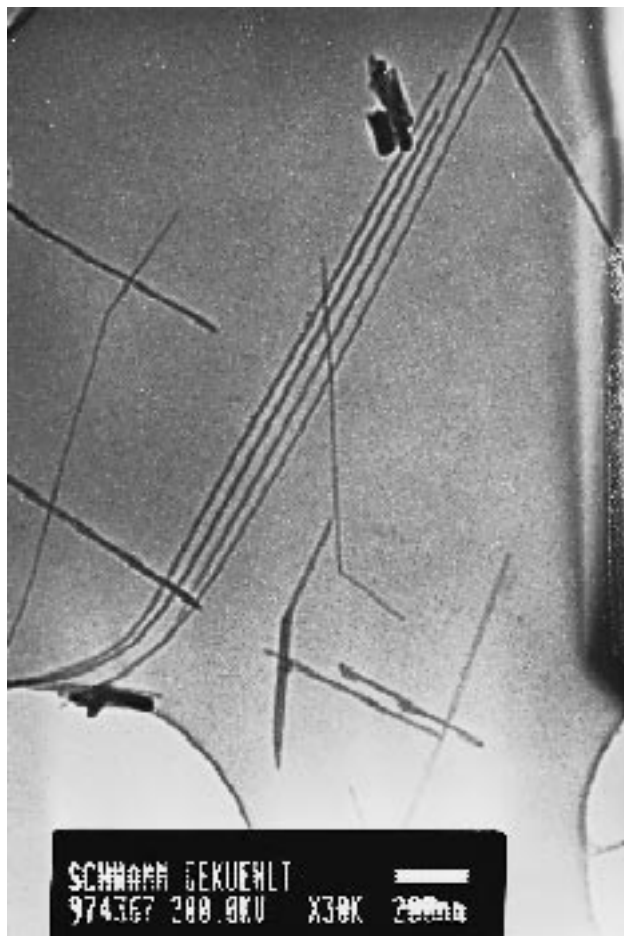
addition, no size separation of the tubes can be accomplished by these methods.

Non-destructive methods like filtering or flocculation have been reported but their efficiency is limited,<sup>9,10</sup> and especially in filtration techniques blocking of pores is a severe problem.

Here, we report the purification and size separation of multiwall NTs by size exclusion chromatography (SEC), which is a multistep process using a stationary phase with defined pore sizes. SEC is a powerful tool for the separation of large molecules, e.g. biological macromolecules or virus particles.<sup>11</sup>

A dispersion of multiwall NTs in water was prepared with the aid of sodium dodecyl sulfate (SDS). Through the action of the surfactant the carbon particles were incorporated into micelles.<sup>10</sup> 10 mg of the raw soot from a conventional arc discharge experiment was added to 2 ml of a 1 mass% aqueous SDS solution and sonicated for 5 min with an ultrasonic tip. After a settling time of 15 min a black supernatant was obtained, leaving a sediment of some undispersed aggregates. The colloidal dispersion was stable for days and was used directly for chromatography.

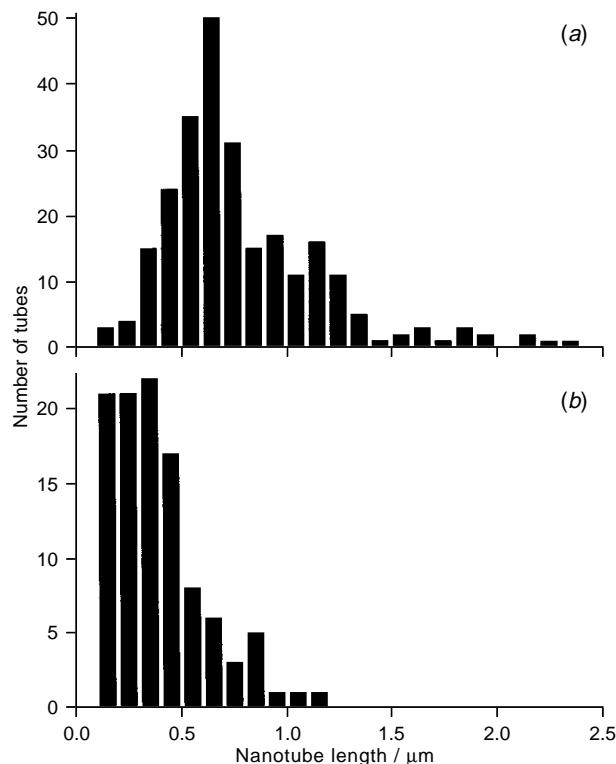
Two successive columns were used for the fractionation. The purpose of the first column was to remove the gross of small particles and fullerenes. The packing ( $7 \times 2$  cm) consisted of controlled pore glass (CPG) with an average pore size of 140 nm (CPG 1400 Å, Fluka). This material is characterized by a narrow pore size distribution and is chemically inert. The column was loaded with 1.5 ml of the supernatant and eluted with a 0.25 mass% aqueous SDS solution buffered at pH 7. The flow rate was adjusted to  $9 \text{ ml h}^{-1}$ . After a void volume of 16 ml, two fractions of 6 ml were collected. The first fraction was concentrated to 1.5 ml by addition of 100 mg of polyacrylamide adsorbent gel (Fluka) followed by continuous shaking for 30 min. No darkening of the gel was observed, indicating that this technique allows the concentration of aqueous NT dispersions without an apparent loss of material.



**Fig. 1** Transmission electron micrograph of fraction 3: multiwall nanotubes purified by size exclusion chromatography



**Fig. 2** Scanning electron micrograph of purified carbon nanotubes adsorbed on a chemically modified Si wafer



**Fig. 3** Histograms of nanotube lengths in the third fraction (a) and sixth fraction (b)

The concentrated first fraction was loaded into the second column ( $33 \times 1$  cm) filled with CPG with an average pore size of 300 nm (CPG 3000 Å, Fluka). The same eluent as before was used with a flow rate of  $5 \text{ ml h}^{-1}$ . After a void volume of 16 ml, eight fractions of 1.5 ml were collected.

The fractions were characterised by transmission and scanning electron microscopy (TEM/SEM) as well as atomic force microscopy (AFM). For the TEM investigations, the carbon grids were treated with a fraction for 15 min and then rinsed briefly with water. Fig. 1 shows a typical TEM micrograph of the third fraction. Individual NTs are clearly recognized, demonstrating that the network of the soot was successfully disintegrated by the surfactant. Furthermore, scarcely any small spherical particles were observed in this fraction, revealing successful purification of the NTs.

For the determination of NT sizes in the different fractions, the NTs were adsorbed onto chemically modified Si wafers. The wafers were silanized for 30 min in an aqueous solution of 3-aminopropyltriethoxysilane (2.5 mM), and then treated with

the NT dispersion for 30 min. After drying, they were immersed in water for 1 min to remove the surfactant. The adsorbed NTs were investigated by SEM and AFM, which revealed that the surfactant was removed from the surface by the washing step.

In the first fraction from the second column (fraction 1), aggregates of NTs and other carbon species were found while fractions 7 and 8 contained mainly spherical particles and a few short tubes, both  $< 0.1 \mu\text{m}$ . Fractions 2–6 consisted of individual nanotubes and, for the later fractions, a low content of spherical particles. Fig. 2 presents a representative SEM image of the third fraction. It shows individual NTs, mainly with a length of ca.  $1 \mu\text{m}$ .

A statistical evaluation of the size distribution was performed using the NT lengths determined from a number of SEM and AFM images. The histograms of fraction 3 and 6 are shown in Fig. 3(a) and (b), respectively. There is a significant difference in the length distribution of the NTs: the average NT length in fraction 3 was calculated to be  $0.8 \mu\text{m}$  and in fraction 6 to be  $0.4 \mu\text{m}$ .

In conclusion, the chromatographic technique presented is an effective, non-destructive method for purification and size separation of carbon NTs. This type of chromatography should also be applicable to micellar dispersions of single wall NTs. This work is now in progress. In addition, the method can easily be scaled up and by the use of more sophisticated chromatographic systems, e.g. HPLC, the size separation could be improved.

Supported by EU TMR network Namitech.

## Notes and References

\* E-mail: duesberg@klizix.mpi-stuttgart.mpg.de

- 1 T. W. Ebbesen and P. M. Ajayan, *Nature*, 1992, **358**, 220.
- 2 A. Thess, H. Dai and R. Smalley, *Science*, 1996, **273**, 483.
- 3 K. Hernadi, A. Fonseca, J. B. Nagy, D. Bernaerts, J. Riga and A. Lucas, *Synth. Met.*, 1996, **77**, 31.
- 4 W. A. de Heer, J.-M. Bonard, K. Fauth, A. Chatelain, L. Forro and D. Ugarte, *Adv. Mater.*, 1997, **9**, 87.
- 5 L. Chico, V. H. Crespi, L. X. Benedict, S. G. Louie and M. L. Cohen, *Phys. Rev. Lett.*, 1996, **76**, 971.
- 6 S. Saito, *Science*, 1997, **278**, 77.
- 7 H. Hiura, T. W. Ebbesen and K. Tanigaki, *Adv. Mater.*, 1995, **7**, 275.
- 8 T. W. Ebbesen, P. M. Ajayan, H. Hiura and T. Tanigaki, *Nature*, 1994, **367**, 519.
- 9 W. A. de Heer, W. S. Bacsá, A. Chatelain, T. Gerfin, R. Humphrey-Baker, L. Forro and D. Ugarte, *Science*, 1995, **268**, 845.
- 10 J.-M. Bonard, T. Stora, J.-P. Salvetat, F. Maier, T. Stöckli, C. Duschl, L. Forro, W. A. de Heer and A. Chatelain, *Adv. Mater.*, 1997, **9**, 827.
- 11 *Handbook of Size Exclusion Chromatography*, ed. C.-S. Wu, Marcel Dekker, 1995.

Received in Cambridge, UK, 16th October 1997; 7/07465D