

## Single-walled carbon nanotubes as nanotest tubes

E. Borowiak-Palen\*

Szczecin University of Technology, Centre of Knowledge Based Technologies and Nanomaterials,  
Institute of Chemical and Environment Engineering, Poland

Received 9 August 2007, revised 20 September 2007, accepted 28 September 2007  
Published online 8 November 2007

PACS 61.46.Fg, 68.37.Lp, 79.20.Kv, 81.07.De, 81.15.Fg

In this study a wet-chemistry procedure to perform a metathesis reaction in the interior of single-walled carbon nanotube (SWCNT) is shown. Initially,  $\text{AgNO}_3$  was placed into the tube interior. The  $\text{AgNO}_3$  filling was then transformed into  $\text{AgCl}$  through a metathesis reaction involving a treatment step with  $\text{HCl}$ . The reaction highlights the potential application of SWCNT as nanotest tubes. This was further demonstrated by the successful development of a facile and efficient wet-chemistry route to purge the  $\text{AgCl}$  filling from the interior of the SWCNT.

© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

### 1 Introduction

Since the identification of SWCNT in 1993, they have attracted significant attention from scientists due to their outstanding optical, electronic and mechanical properties [1, 2]. A more recent area of research within the carbon nanotube field is that in which the tubes are filled with material. This is attractive in that the carbon coating can protect the optical, magnetic and electronic properties of the filler material, e.g. protection against oxidation [3]. Filling of nanotubes is particularly relevant for SWCNT, as opposed to multiwalled carbon nanotubes (MWCNT), because the narrow diameter afforded by SWCNT is expected to allow peculiar physical phenomena to occur and/or peculiar properties to be obtained [4]. However, the narrower diameter of SWCNT, as compared to MWCNT, makes filling them more difficult. By far, most successful filling routes for SWCNT employ wet-chemistry techniques.

The number of groups actively involved in the filling of SWCNT is somewhat limited, and, in terms of published works, the two most active groups are based at the universities of Oxford and Pennsylvania. Details of the numerous studies from these laboratories can be found in Ref. [4]. In most cases the filling occurs in a single step, in that the final filling is obtained directly from the filling procedure. However, SWCNT also offer the unique potential to serve as a nanoreactor in which the filling can react to form a new product within the interior. Such examples are very limited and perhaps the best known example is that where  $\text{C}_{60}$  are encapsulated within the SWCNT, forming so-called peapods. The peapods can be annealed in ultrahigh vacuum (UHV), which leads to the fullerenes decomposing and a new SWCNT forming in the interior of the initial SWCNT. The result is a double-walled carbon nanotube (DWCNT) [5]. The use of single-walled carbon nanotubes as a nanoreactor for reduction reactions has been shown previously [6, 7].

In this contribution a study is presented in which SWCNT are used as a nanotest probe for a metathesis reaction. In the metathesis reaction, the  $\text{NO}_3^-$  anions from  $\text{AgNO}_3$  are successfully replaced by  $\text{Cl}^-$  forming  $\text{AgCl}$ . In addition, a post-filling treatment of the  $\text{AgCl}$  filled SWCNT with  $\text{NH}_4\text{OH}$  is shown to

\* e-mail: eborowiak@ps.pl

efficiently purge the nanotubes, leaving pure empty tubes. All the chemical procedures were performed at room temperature.

## 2 Experimental

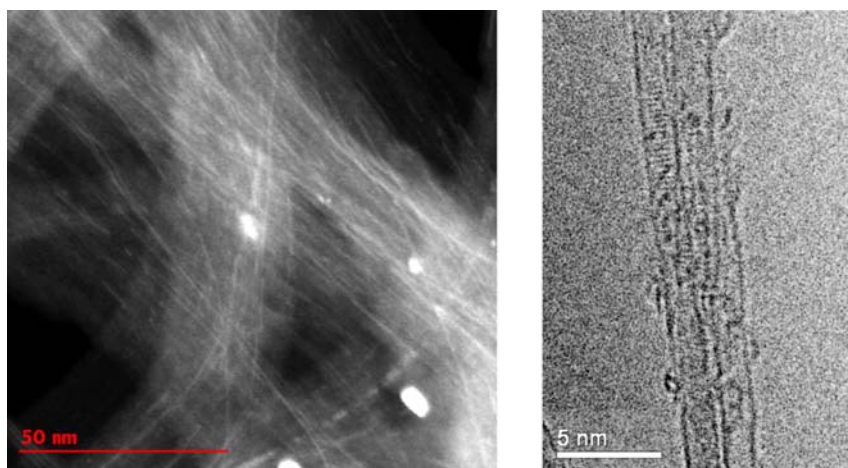
The pristine SWCNT material was produced by a standard laser ablation technique [8] with Pt/Rh/Re as catalysts. The mean diameter of the sample SWCNT is 1.5 nm. In order to perform the replacement reaction the as-grown material was purified. More details of the experimental aspects are described elsewhere [9]. In brief, the purified tubes were transferred to a concentrated silver nitrate ( $\text{AgNO}_3$ ) solution and sonicated for ca. 15 min, followed by a stirring process for 48 h at room temperature. In the next step, the sample was transferred to a 2M HCl solution and stirred for 24 h. The metathesis reaction takes place during this latter step. To thoroughly wash out any excess AgCl, the sample was thoroughly rinsed through multiple centrifuge treatments in distilled water.

Purging the AgCl-filled carbon nanotubes was accomplished by sonicating the filled nanotubes in a  $\text{NH}_4\text{OH}$  solution for 1 h at room temperature.

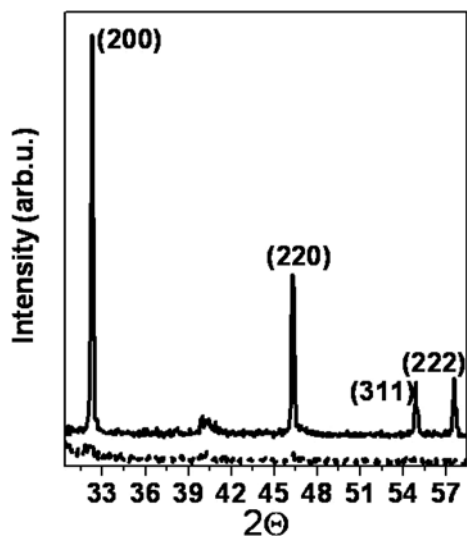
The morphology and chemical composition of the sample were studied using high-resolution transmission electron microscopy (HR-TEM, Tecnai F30 from FEI) and its energy-dispersive X-ray spectroscopy (EDX) mode. The specimens for the microscopic studies were prepared on the standard TEM copper grids. X-ray diffraction (XRD) studies were performed on a Philips X'Pert Pro. Resonance Raman measurements were conducted using a Renishaw InVia Raman Microscope spectrometer (excitation laser wavelength = 514 nm). The Raman and XRD measurements achieved using the sample in powdered form.

## 3 Results

To check that the SWCNT were actually filled after the filling and reaction procedures, the samples were subjected to TEM studies, namely high-angle annular dark-field (HAADF) and bright-field imaging. The HAADF studies are particularly useful for highlighting the efficiency of the filling process due to the relatively better contrast between the tubes and filling as compared to bright-field imaging. The left panel of Fig. 1 shows a typical HAADF image of the product. Many long strands within SWCNT are visible. These correspond to the AgCl filling within bundles of SWCNT. The lengths of these strands range from 10 nm to several hundred nm. However, such HAADF images do not confirm filling within the tubes



**Fig. 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) HAADF image of AgCl-SWCNT (left panel) and the bright-field image of AgCl-SWCNT (right panel).



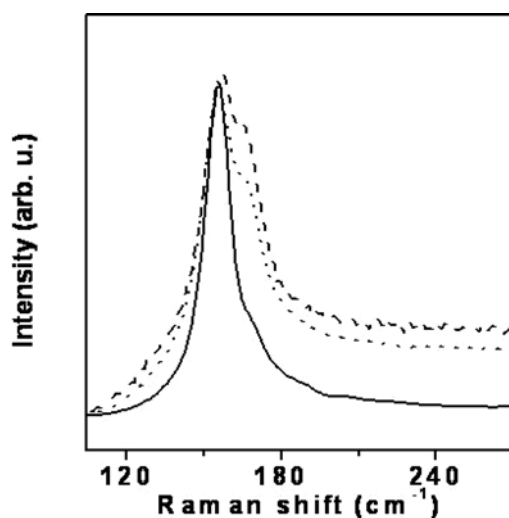
**Fig. 2** XRD patterns of AgCl-SWCNT (solid line) and AgCl-SWCNT after  $\text{NH}_4\text{OH}$  treatment (dashed line).

themselves, since, for example, they may form in between tubes within a bundle. High magnification bright-field images of individual tubes as shown in the right panel of Fig. 1 confirm the filling actually lies *within* the SWCNT.

EDX analysis of the sample shows it to be comprised of carbon, silver and chlorine (data not shown here). Copper from the TEM grid was also detected. More detailed studies of the sample were conducted with XRD to confirm the presence of AgCl as well as a means to determine the efficiency of the purging treatment. Figure 2 shows the XRD patterns for the filled SWCNT (solid line) and the purged sample (dashed line). The XRD data for the filled sample shows clear evidence for the presence of AgCl via the labeled peaks that correspond to the  $hkl$  indexes of AgCl. This confirms the filling within the SWCNT is AgCl and that the metathesis reaction inside the tubes was successful.

Turning to the ammonia-treated sample, the XRD spectrum clearly shows the almost complete disappearance of the AgCl signatures. Closer inspections of the signals show a 95% reduction in intensity.

This is clear evidence for the ammonia treatment being an efficient procedure for the removal of AgCl from the interior of the tubes. Again, as with the metathesis reaction, this is further evidence showing the potential for chemical reactions to take place within nanotubes, even multiple times, via externally sup-



**Fig. 3** RBM modes from Raman spectra (514 nm) for starting SWCNT (solid curve), AgCl-filled SWCNT (dashed curve), filled SWCNT after  $\text{NH}_4\text{OH}$  treatment (dotted curve).

plied chemicals. Not only does this purging treatment highlight the potential of SWCNT as nanoreactors, but it also provides a novel wet-chemistry route at room temperature to remove intercalates. Previous experimental work focused on the removal of intercalates from SWCNT using high-temperature annealing in high vacuum [10].

Resonance Raman spectroscopy is a useful tool to investigate SWCNT with. In these studies we focus on the radial breathing mode (RBM) region, which show shifts for the various samples. The solid line in Fig. 3 shows the RBM of the starting SWCNT. The position of the main peak is centered at  $155.4 \text{ cm}^{-1}$ . The resonance conditions are changed for SWCNT upon the AgCl filling (dashed line in Fig. 3) where an upshift of about  $2 \text{ cm}^{-1}$  to the higher Raman shift is detected.

The treatment of AgCl-filled SWCNT in ammonia solution, which removes the filling, leads to upshifted RBM position being reversed and shifting back to the position of the starting SWCNT (Fig. 3 – dotted line). This reversible shift of the RBM highlights the efficiency of the purging process.

## 4 Conclusions

It is clearly shown that a metathesis reaction in the interior of SWCNT can take place. SWCNT were initially filled with  $\text{AgNO}_3$ . Exposing the  $\text{AgNO}_3$ -filled SWCNT to HCl converts the filling to AgCl via a metathesis reaction. Further, a novel wet-chemical purging route, using ammonia, via externally supplied chemicals highlights the potential for chemical reactions to take place within nanotubes. This highlights the potential application of SWCNT as a nanotest tube. In addition, all the steps were performed at room temperature. This is advantageous because the SWCNT are less likely to suffer any damage.

**Acknowledgements** The author is grateful to M. H. Rummeli, T. Gemming for TEM analysis. Research was supported by the European Community through the Marie Curie Research Training Network CARBIO under Contract MRTN-CT-2006-035616.

## References

- [1] S. Iijima et al., *Nature* **363**, 603 (1993).
- [2] B. Yakobson et al., *Am. Sci.* **85**, 324 (1997).
- [3] E. Flahaut et al., *Chem. Mater.* **14**, 2553 (2002).
- [4] M. Monthieux, *Carbon* **40**, 1809 (2002).
- [5] R. Pfeiffer, *Nano Lett.* **7**, 2428 (2007).
- [6] E. Borowiak-Palen et al., *Nanotechnology* **17**, 1 (2006).
- [7] E. Borowiak-Palen et al., *Chem. Phys. Lett.* **421**, 129 (2006).
- [8] M. H. Rummeli et al., *J. Phys. Chem.* **111**, 4094 (2007).
- [9] E. Borowiak-Palen et al., *J. Am. Chem. Soc.*, submitted.
- [10] X. Liu et al., *Phys. Rev. B* **67**, 125403 (2003).