The reagent-free, microwave-assisted purification of carbon nanotubes†

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We have developed a microwave-assisted, reagent-free method for the efficient primary purification of MW and SW carbon nanotubes that is extremely fast compared to previously reported processes. The treatment dissociates and disperses non-nanotube carbon in an organic solvent to yield very pure carbon nanotubes within a few minutes of heating and a simple filtration, without the involvement of acidic/oxidative reagents. According to thermogravimetric analysis, Raman and IR spectroscopy, as well as scanning and transmission electron microscopy, the process yields pure nanotubes with a low degree of defects.

Introduction

Carbon nanotube science has seen enormous development in the past decade, with some of the initially suggested applications slowly reaching the proof-of-concept stage.[1–5] Access to carbon nanotube (CNT) materials of known quality is a critical factor, and hence reliable methods for the synthesis, purification and further manipulation of the CNTs are of great importance. A variety of processes for the preparation of various forms of this carbon allotrope have been developed. Despite these largely successful synthetic efforts, finding efficient and scaleable processes for the low-cost and environmentally friendly primary purification of as-produced CNT materials is still a challenge.[6–9] The cost of medium-purity SWCNT materials has been quite constant over the past few years, whereas the cost of more extensively purified CNTs remains high, and functionalized materials are hardly available at all. A very important aspect of all processes is the time required for any sub-step. Microwave (MiW) heating has become a standard tool for the efficient execution of organic reactions,[10–14] with often excellent yields being obtained in reaction times considerably shorter than when conventional heating is used and when CNTs are involved.[15,16] In the course of exploring MiW heating for side wall cycloaddition chemistry on MWCNTs, aiming towards efficient functionalization-induced solubilization and subsequent surface-selective deposition,[17,18] we also initiated a study on MiW-assisted CNT functionalizations with organic radicals. The studies lead to our serendipitous discovery of a new reagent-free, MiW-assisted purification method for SWCNT and MWCNT materials, which is the topic of this paper.

MiW-assisted purification processes have been reported, but all, however, at some stage, involve the use of oxidative reagents.[19–31] Hence, the advantage of these methods is only that the reaction times required are shorter than for conventionally heated processes. The strong acid and/or oxidizing reagents will render impurities soluble in aqueous media, and hence allow their removal, together with the excess acid/oxidant, by washing with large quantities of water.[6–9,32] The protocols are, however, not innocent with respect to the CNTs, the remaining CNTs also showing evidence of having reacted with the formation of oxygen-containing defects at the ends and at other sites with increased reactivity.[33] As all the reactions occurring at the CNT carbon sites increase the proportion of sp^3 carbon sites and oxygen-decorated sites, this initial unintentional functionalization may also render certain applications impossible.

Our MiW-assisted, reagent-free method is fast, with the additional advantage of giving cleaned CNT materials with significantly less purification-induced defects compared to that observed from all treatments involving oxidative and/or acidic reagents, and without the need for time-consuming isolation and waste disposal protocols.

Results and discussion

In the initial study, commercial post-synthesis processed SWCNTs were MiW-heated in the presence of solutions of stable radicals such as DPPH. The results were discouraging, except for reactions carried out in CH_2Cl_2, where the expected black solutions appeared after the heating step, together with substantial amounts of recovered CNTs. The soluble material contained only amorphous carbon, and hence indicated CNT decomposition as a source of C, but as the quite substantial amount of insoluble CNT material, according to Raman analysis, was of higher purity than before the treatment, a functionalization-induced solubilization of the non-CNT material seemed a more likely process. However, analysis of the soluble material by infrared (IR) spectroscopy gave no clear evidence of any functionalization. Control experiments revealed, in fact, a more pronounced purification effect in the absence of reagents, hence the originally intended chemical

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reactions most likely did not occur. This unexpected finding turned the focus of our study from functionalization to purification.

A survey of a range of solvents of varying polarity[34] revealed that the best purification results were obtained for CH_2Cl_2 and toluene. Neither the less polar solvent n-pentane nor the normally very efficient MiW solvents H_2O, CH_3OH or acetone resulted in any significant purification. A short (5 min) heating step in sealed tube conditions with temperatures well above 100 °C is crucial; treatment of the CNTs with CH_2Cl_2 at RT or reflux for several hours at ambient pressure did not dissolve non-CNT carbon to any significant extent.

The procedure was applied both to post-synthesis processed HiPCO materials as well as to as-produced SWCNT materials. Fig. 1 shows an expansion of the RBM region of the Raman spectra of HiPCO SWCNTs treated several times by the MiW method. While these Raman spectra (see also the ESI†) show only modest differences, it is evident that the procedure is non-destructive, even for small SWCNTs, as the radial breathing modes for these CNTs (at the highest frequencies) remain practically unchanged, even after three cycles of the purification protocol. While HiPCO SWCNTs contain only minor amounts of amorphous carbon, they contain a substantial amount of residual metal catalyst particles. Interestingly, most experiments resulted in the formation of large (up to several mm) brittle iron-containing structures that could be easily removed from the purified CNT material using tweezers or filtration through a glass sinter funnel with a large pore size. Metal residues within the carbon structures will absorb MiW energy very efficiently, resulting in increased mobility, aggregation and eventual escape of the metal particles by cutting of the carbon structures.[26,35] The MiW process thus also decreases the amount of residual metal catalyst content in the material. This is clear from the thermogravimetric analysis (Fig. 2), which shows a decrease in residual mass from 12% for the as-received HiPCO SWCNT material to 2% for the MiW purified material (after one cycle). This substantial decrease of metal residues from the material is further supported by a TEM analysis (see the ESI†).

In contrast to SWCNTs produced by the HiPCO method, as-produced SWCNTs from other sources, such as the arc discharge and CVD methods, may contain large amounts of amorphous carbon. When our MiW method was applied to an as-produced CVD material, a large amount of amorphous carbon was removed. Fig. 3 shows TGA curves of the as-produced and purified materials. The amount of "volatile" carbon impurities dropped from 90 wt% for the as-produced (CVD) SWCNT material to 28 wt% after one cycle of MiW purification. This approximately 60% difference in residual mass after 800 °C is related to an efficient removal of amorphous carbon in the MiW-purified sample.

The mass yield of the purified material varied in this study between 50–90% and was strongly dependent on the quality (CNT content *vs.* amorphous carbon and residual catalyst metal) of the as-received or as-produced material.

Additional information concerning possible damage of the CNTs is provided by IR spectroscopy, which gives a relative measure of the amount of polar bonds in a CNT sample. The IR spectra of MiW-treated SWCNTs are without prominent features, an observation that should not be over-interpreted. For a better comparison, a SWCNT material from a commercial batch was treated by the MiW method and according to reported procedures.[32,36] IR analyses (Fig. 4) of the purified SWCNT samples and as-received material were carried out during one single instrument session in order to minimize the risk of non-comparability due to differences in sample preparation and instrument conditions.

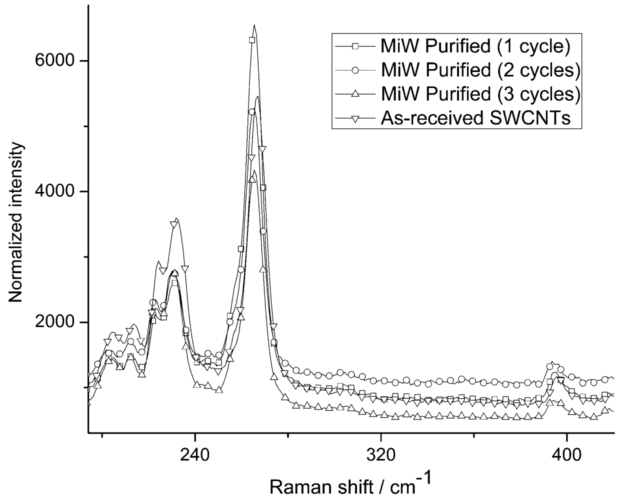

Fig. 1 Expansion of the RBM region (783 nm excitation) from a MiW-assisted cleaning of a commercial post-synthesis treated HiPCO SWCNT material using CH_2Cl_2, normalized to the G-band.

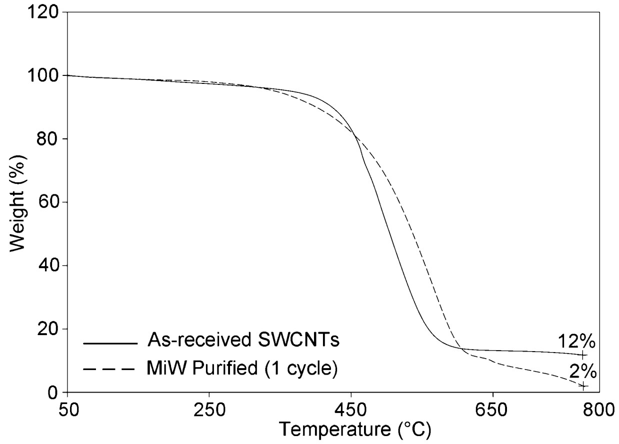

Fig. 2 TGA analysis (in an air atmosphere) monitoring the cleaning of HiPCO SWCNTs in CH_2Cl_2. The residual mass decreased from 12% for the as-received material to 2% for the MiW-purified material after one cycle.

In accordance with the literature,[32] the HCl-treated SWCNTs exhibited a prominent C–O stretch, whereas the C=C and C=O bands were quite weak, whereas SWCNTs treated with HNO_3 gave IR spectra with more dominant C=C and C=O features, a result of the oxidative conditions that produce a large number of IR-active bonds. In contrast, the MiW-treated SWCNTs display as few features as the as-received commercial material. This implies that the MiW treatment does not to any great extent involve an *in situ*-formed strong acid,[37] and provides further support

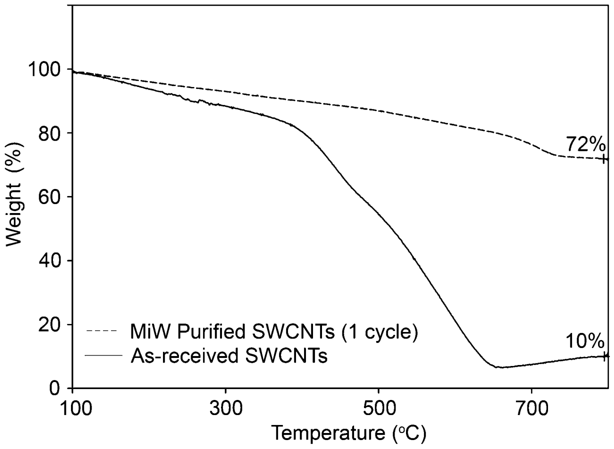

Fig. 3 TGA analysis (in a nitrogen atmosphere) monitoring the cleaning of a SWCNT material in CH_2Cl_2. The amount of "volatile" carbon impurities dropped from 90 wt% in the as-produced SWCNT material to 28 wt% after one cycle.

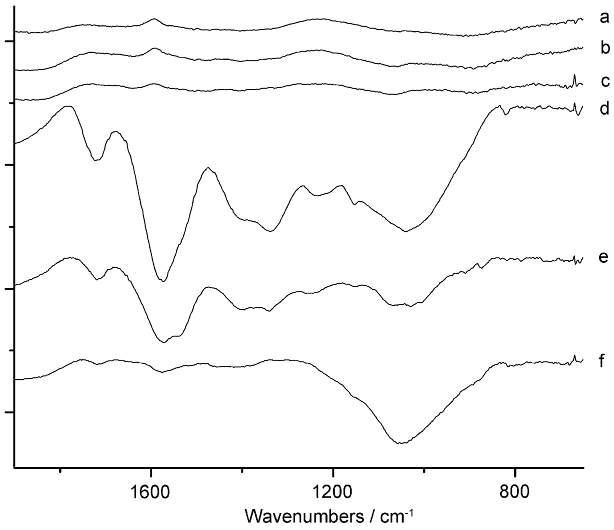

Fig. 4 FT-IR (neat) of (a) a commercial, post-synthesis-treated HiPCO SWCNT material, (b) MiW-purified SWCNTs (one cycle), (c) MiW-purified SWCNTs (two cycles), (d) SWCNTs treated with HNO_3 (2.6 M, reflux, 4 d), (e) SWCNTs treated with fuming HNO_3 (reflux, 5 d) and (f) SWCNTs treated with HCl (12 M, 80 °C, 5 d).

for a thermally assisted dissociation–solubilization of the adsorbed non-CNT carbon.

In order to explore the scope of the method, we also applied the purification protocol to MWCNTs. The left panel of Fig. 5 shows the Raman spectra of the as-received MWCNTs (CNI, (∅: 60–100 nm), MWCNTs purified by the MiW method (one cycle) and of the filtrate containing the impurities. The D-band was found at 1352 cm^{-1}, the G-band at 1578 cm^{-1} and the G′-band at 2708 cm^{-1}. The only significant difference between the untreated MWCNT sample and the MiW-purified sample was a decrease in the intensity of the D-band. The D/G ratio was ~0.8 for the as-received sample and ~0.7 for the sample treated once. This is consistent with a decrease in the amount of amorphous carbon in the purified sample. The composition of the material in the filtrate was significantly different, reflected by broader D- and G-bands, a G-band frequency of 1589 cm^{-1}, and no distinguishable G′-band; features typical for amorphous carbon.[38] A scanning electron microscopy (SEM) survey (Fig. 6) confirmed the conclusions formed from the Raman study. The non-CNT matrix that surrounds the as-received CNTs (panel a) is transformed into irregularly-shaped amorphous carbon recovered from the filtrate (panels c and d), and the MWCNTs become more individualized (panel b).

The purification protocol could be repeated several times with fresh solvent, resulting in an increasing purity of the CNT material, as seen by Raman and SEM analyses. However, repeating the purification protocol more than twice resulted in some damage to the MWCNTs, as was evident by the small relative increase of the D band intensity (Fig. 5, right panel), but to a very low degree compared to conventional oxidative processes.

As for the experiments carried out with SWCNTs, we observed the formation of large metal-containing structures in the MiW-treated MWCNT material (see the ESI†). These structures could be easily removed by hand, leaving a MWCNT material with a lower metal content than the as-received material. This was also confirmed by thermogravimetric analysis (carried out in air, Fig. 7), which showed a lower residual mass after 750 °C for the purified MWCNTs (1.2%) as compared to the as-received material (3.3%).

Overall, the results suggest an interplay between the ability of the solvent to dissolve the relatively non-polar impurities and the MiW energy absorption of the solvent–CNT mixture. The solubility of non-polar compounds in solvents of intermediate to low polarity is higher than in more polar solvents. The components of the CNT samples are non-polar and thus not soluble in water or methanol, solvents that would also, by absorption of the MiW radiation energy, shield the CNT material. In contrast, the non-polar solvents absorb less of the MiW energy, which instead is absorbed by the CNT-containing material to such an extent that significant dissociation of the non-CNT material takes place. Encapsulated metal particles absorb even more strongly.[26,35] The ability of the solvent to accommodate the carbon impurities then determines if re-aggregation or dispersion/solubilization dominates. The initially puzzling results using less polar solvents is explained by the fact that toluene, but not pentane, has the ability dissolve large PAH systems by π–π interactions. CH_2Cl_2 dissolves a wide range of organic compounds of different sizes and polarities; hence, it is not too surprising that treatments in this solvent gave the best results.

Conclusion

We have found a new MiW-assisted process for the purification of carbon nanotubes that does not require oxidative reagents, only a relatively non-polar solvent, with the best results being obtained for toluene and CH_2Cl_2. The cleaning is efficient both for as-produced and post-synthesis treated CNTs, and has been demonstrated for both SWCNTs and MWCNTs. The featureless IR spectrum of the MiW-treated CNTs compared to CNTs treated under conventional purification conditions, and the morphology of the removed material, suggests that

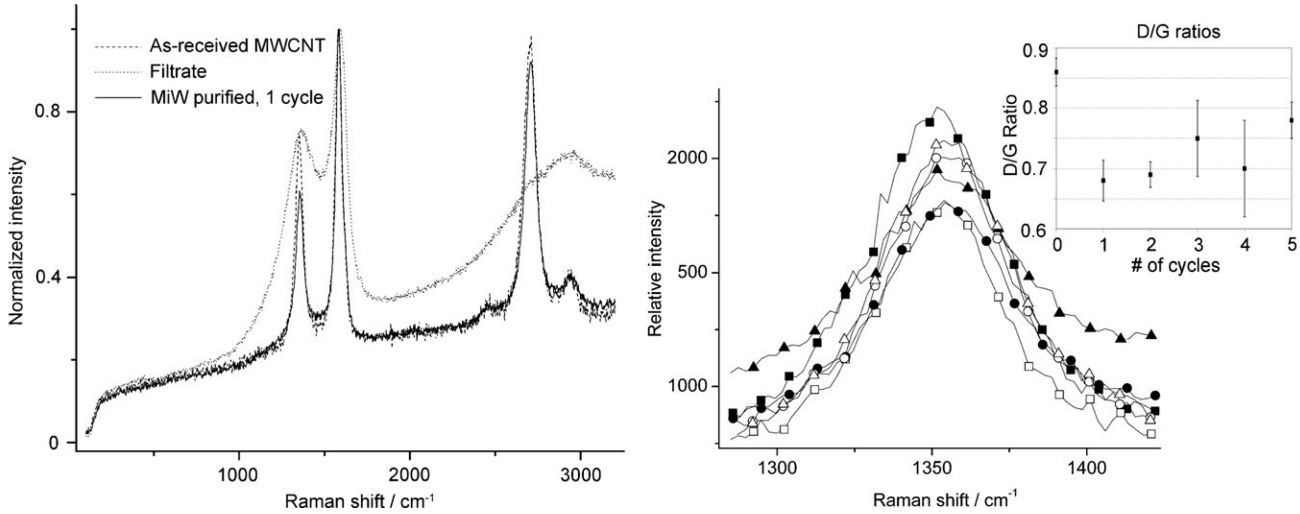

Fig. 5 Raman spectra of the MWCNTs (normalized to the G-band). Left panel: as-received MWCNTs (dashed line), MiW-purified MWCNTs (one cycle in CH_2Cl_2) (—), filtrate (---). Right panel: expansion of the D-band region of MWCNTs treated for 1–5 cycles in CH_2Cl_2: ■ As-received MWCNTs, □ MiW purified (one cycle), ● MiW purified (two cycles), ○ MiW purified (three cycles), ▲ MiW purified (four cycles) and △ MiW purified (five cycles) (spectra are normalized to the G-band). The inset shows the D/G ratio for the material treated 1–5 times (based on three measurements per sample). Error bars indicate standard deviations.

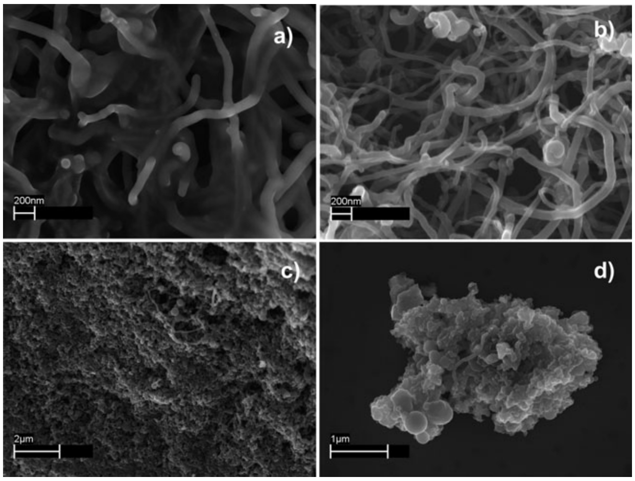

Fig. 6 SEM images of (a) as-received MWCNTs (120.000×; the MWCNTs are covered with amorphous carbon), (b) purified MWCNTs (two cycles) (120.000×; the MWCNTs are no longer covered with amorphous carbon and appear as individual tubes), (c) filtrate (40.000×; the image shows amorphous carbon and a few MWCNTs) and (d) filtrate with aggregates of amorphous carbon.

thermal delamination of non-CNT carbon from CNTs is the key step, which is attenuated by solubilization of the amorphous carbon, preventing re-aggregation. In addition, the thermally-induced increased mobility of the residual metal within the CNTs eventually leads to large overheated aggregates that escape from the carbon structure, forming precipitating tree-like structures that could be removed manually from the suspended CNTs and dissolved amorphous carbon in the heat-treated sample prior to the filtration step.

The use of MiW heating in sealed tube conditions is a process that is substantially faster, minutes instead of days, than any conventional heating process. Additional benefits arising from the reagent-free conditions are (i) significantly less damage to the CNTs, (ii) significantly faster isolation of the CNTs from the impurities after the treatment step and (iii) significantly less waste to dispose of. The resulting increased productivity could also be economically beneficial as, for small to medium-scale purifications, less time-demanding handling by skilled staff is required.

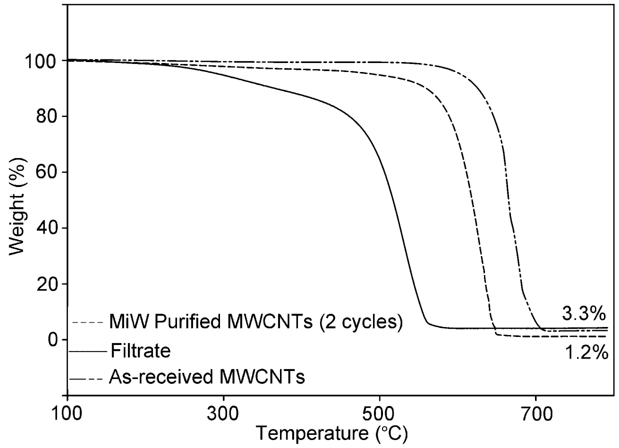

Fig. 7 TGA curves recorded in air for the as-received MWCNT (——--), MiW-purified MWCNT (---) and filtrate (—). The residual metal oxide content decreases from 3.3% in the as-received material to 1.2% in the MiW-purified material (two cycles).

Experimental

Materials and instrumentation

MWCNTs (∅: 60–100 nm) were purchased from Shenzhen Nanotech Port Co., Ltd. (claimed purity: >95%, <3% amorphous carbon, <0.2 wt% ash content). SWCNTs were either post-synthesis treated HiPCO CNTs from Carbon

Nanotechnologies (claimed purity: 15% ash content), or as-produced CNTs from a Fe-catalyzed CVD process[39] (Chalmers University, Sweden). Reference samples, monitoring the introduction of polar bonds by treatment with acid, were prepared from post-synthesis treated SWCNTs according to reported procedures.[32,36] MiW-assisted purification reactions were carried out with 5 ml or 20 ml process vials sealed with aluminium crimp caps fitted with a silicon septum. The MiW heating was performed with a Biotage initiator 2.0 with a 400 W magnetron. Reaction mixtures were stirred with a magnetic stirring bar during the irradiation. The temperature, pressure and irradiation power were monitored during the course of the reaction to ensure that the pressure did not exceed the limit for the instrument (see the ESI for the relevant temperature/pressure graphs†). After the completed irradiation, the reaction tube was cooled with high pressure air until the temperature was below 47 °C. Centrifugation-assisted filtration was performed using an Eppendorf minispin centrifuge together with Vectaspin microvials equipped with a 0.45 μm polypropylene filter membrane (Whatman Schleicher & Schuell). Raman spectra were recorded on a Renishaw Raman spectrometer using a 514 nm Ar laser or a 783 nm diode laser with a 50× lens and a laser power of 10 mW. IR spectra were recorded on a Perkin-Elmer Spectrum-100 FT-IR spectrometer with an ATR accessory. The samples were analyzed by placing the neat CNT samples directly on the ATR crystal. Thermogravimetric analysis was performed on a Q500 TGA (TA instruments) in air or in an N_2 atmosphere (gas flow = 60 ml min^{-1}). Samples (1.5–2 mg) were placed on a platinum plate and heated in the TGA at a rate of 20 °C min^{-1} up to 600 or 800 °C. SEM analysis was carried out using a Zeiss LEO1550 instrument. Samples were prepared by placing a drop of a chloroform suspension of the carbon nanotubes on a silicon substrate and allowing the solvent to evaporate. TEM images were acquired on a Jeol 2000FXII TEM instrument operated at 200 kV, and the carbon nanotubes were deposited on standard TEM carbon grids.

MiW-assisted purification

Note: maximum volumes for the MiW heating equipment used should never be exceeded, and, for safety reasons, the use of vessels developed for the specific equipment is strongly recommended.

In a typical experiment, 20 mg of CNT material (SWCNTs or MWCNTs) was suspended in 5 ml of CH_2Cl_2 in a MiW vessel. The mixture in the closed MiW vessel was then rapidly heated to 100–150 °C for 5 min. This produced a black organic phase, a black precipitate and, in some runs, precipitated metal-containing particles. After removal of the particles using tweezers or filtration through a glass sinter funnel (pore size G1), the CNTs were collected by centrifugation-assisted filtration and washed on the filter with CH_2Cl_2. The entire procedure could be repeated at least 2–5 times, with increasing purity of the CNT material, as determined by TGA, Raman and SEM analyses with increasingly less dissolved material for each subsequent run. By using larger MiW vessels, it was possible to treat up to 300 mg of CNTs in 20 ml of solvent. The yield of the purified CNT material varied, depending on the quality of the as-received or as-produced material, and was, in this study, generally between 50–90%.

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References

1 S. Bellucci, *Phys. Status Solidi C*, 2005, **2**, 34–47.
2 P. Sharma and P. Ahuja, *Mater. Res. Bull.*, 2008, **43**, 2517–2526.
3 D. Vairavapandian, P. Vichchulada and M. D. Lay, *Anal. Chim. Acta*, 2008, **626**, 119–129.
4 K. Balasubramanian and M. Burghard, *Anal. Bioanal. Chem.*, 2006, **385**, 452–468.
5 M. Prato, K. Kostarelos and A. Bianco, *Acc. Chem. Res.*, 2008, **41**, 60–68.
6 S. R. C. Vivekchand, R. Jayakanth, A. Govindaraj and C. N. R. Rao, *Small*, 2005, **1**, 920–923.
7 P.-X. Hou, C. Liu and H.-M. Cheng, *Carbon*, 2008, **46**, 2003–2025.
8 M. C. Hersam, *Nat. Nanotechnol.*, 2008, **3**, 387–394.
9 T.-J. Park, S. Banerjee, T. Hemraj-Benny and S. S. Wong, *J. Mater. Chem.*, 2006, **16**, 141–154.
10 C. O. Kappe, *Angew. Chem., Int. Ed.*, 2004, **43**, 6250–6284.
11 U. M. Fernández-Paniagua, B. Illescas, N. Martin, C. Seoane, P. de la Cruz, A. de la Hoz and F. Langa, *J. Org. Chem.*, 1997, **62**, 3705–3710.
12 S. Caddick, *Tetrahedron*, 1995, **51**, 10403–10432.
13 A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault and D. Mathé, *Synthesis*, 1998, 1213–1234.
14 W. Zhang, C. H. T. Chen, Y. Lu and T. Nagashima, *Org. Lett.*, 2004, **6**, 1473–1476.
15 Y. Wang, Z. Iqbal and S. Mitra, *Carbon*, 2005, **43**, 1015–1020.
16 J. L. Delgado, P. de la Cruz, F. Langa, A. Urbina, J. Casado and J. T. Lopez Navarrete, *Chem. Commun.*, 2004, 1734–1735.
17 J. Li and H. Grennberg, *Chem.–Eur. J.*, 2006, **12**, 3869–3875.
18 E. Widenkvist, J. Li, U. Jansson and H. Grennberg, *Carbon*, 2007, **45**, 2732–2736.
19 C. J. Ko, C. Y. Lee, F. H. Ko, H. L. Chen and T. C. Chu, *Microelectron. Eng.*, 2004, **73–74**, 570–577.
20 E. Vázquez, V. Georgakilas and M. Prato, *Chem. Commun.*, 2002, 2308–2309.
21 M. T. Martínez, M. A. Callejas, A. M. Benito, W. K. Maser, M. Cochet and J. M. Andres, *et al.*, *Chem. Commun.*, 2002, 1000–1001.
22 C. M. Chen, M. Chen, Y. W. Peng, C. H. Lin, L. W. Chang and C. F. Chen, *Diamond Relat. Mater.*, 2005, **14**, 798–803.
23 F. H. Ko, C. Y. Lee, C. J. Ko and T. C. Chu, *Carbon*, 2005, **43**, 727–733.
24 H. Li, L. Feng, L. Guan, Z. Shi and Z. Gu, *Solid State Commun.*, 2004, **132**, 219–224.
25 C. M. Chen, M. Chen, F. C. Leu, S. Y. Hsu, S. C. Wang and S. C. Shi, *et al.*, *Diamond Relat. Mater.*, 2004, **13**, 1182–1186.
26 A. R. Harutyunyan, B. K. Pradhan, J. Chang, G. Chen and P. C. Eklund, *J. Phys. Chem. B*, 2002, **106**, 8671–8675.
27 A. R. Harutyunyan, B. K. Pradhan, G. U. Sumansekera, J. Chang, G. Chen and G. Gugang, *et al.*, *Mater. Res. Soc. Symp. Proc.*, 2001, **706**, 35–39.
28 A. Haruryunan and T. Tokune, *US Pat.* 0191157 A1, 2004.
29 M. R. Austwick, G. A. D. Briggs and A. N. Khlobystov, *WO Pat.* WO2004/052781 A1, 2004.
30 P. C. Eklund, A. Hartyunyan and B. K. Pradhan, *US Pat.* 7014737, 2006.
31 A. Harutyunyan and T. Tokune, *US Pat.* 7150865, 2003.
32 U. J. Kim, C. A. Furtado, X. Liu, G. Chen and P. C. Eklund, *J. Am. Chem. Soc.*, 2005, **127**, 15437–15445.

33 D. Tasis, N. Tagmatarchis, A. Blanco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105–1136.

34 *CRC Handbook of Chemistry and Physics*, ed. R. E. Weast, CRC Press, Boca Raton, FL, 65th edn, 1985.

35 A. Wadhawan, D. Garrett and J. M. Perez, *Appl. Phys. Lett.*, 2003, **83**, 2683–2685.

36 J. Li, K. Chajara, J. Lindgren and H. Grennberg, *J. Nanosci. Nanotechnol.*, 2007, **7**, 1525–1529.

37 K. R. Moonoosawmy and P. Kruse, *J. Am. Chem. Soc.*, 2008, **130**, 13417–13424.

38 M. Park, S. M. Camphausen, A. F. Myers, P. T. Barletta, V. Sakhrani and L. Bergman, *et al.*, *Mater. Lett.*, 1999, **41**, 229–233.

39 R. E. Morjan, *Licentiate of Philosophy thesis*, Department of Experimental Physics at Göteborg University and Chalmers University of Technology, 2003.