Direct imaging of carbon nanotubes spontaneously filled with solvent†

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For the first time, cryo-TEM imaging is used to directly show spontaneous filling of carbon nanotubes immersed in a solvent in the native state at ambient conditions. Multi-walled carbon nanotubes are dissolved in chlorosulfonic acid, and the high contrast between the acid and the carbon shows the difference between filled and unfilled nanotubes.

The exceptional mechanical, thermal, and electrical properties of carbon nanotubes (CNTs) have sparked a wave of research in the liquid phase processing and transport properties of CNTs. One topic of interest is the filling of CNTs with liquids; filling is important for the characterization of CNT wetting and for the use of CNTs in applications such as nanofluidic devices, drug-delivery capsules, and membranes.[1–5]

Prior studies have investigated the filling of CNTs and "carbon nanopipes" with water and other liquids. (For a full account, see the thorough reviews by Holt[6] and Mattia and Gogotsi[7] and also Table S1 in ESI.†) Filling has been confirmed by the presence of liquid menisci in transmission electron microscopy (TEM) images of closed CNTs in vacuum or environmental scanning electron microscopy (ESEM) images of open-ended CNTs in a saturated water gas phase (water vapor enters and condenses inside the CNTs).[1–4] At high temperatures, capillary forces may draw molten metals and salts into open CNTs.[8] Liquid can also enter closed CNTs *via* high-pressure, high-temperature autoclave treatment during synthesis, through open ends or interior-exposing surface defects. These defects are not simple holes in the lattice; they are distinct "wall defects" resembling a broken bone, as in Fig. 4 of Naguib *et al.*[1] This filling of CNT interiors occurs more readily for large inner diameter CNTs but does not depend on the number of walls.[9] Similarly, CNTs with chemically-induced sidewall defects can be filled by hydrated ions from the surrounding solution.[10] CNTs have also been studied as membrane channels, which showed enhanced pressure-driven water flow. In most of these studies, filling is induced by chemical modification, or high temperature, pressure, and voltage.

A few studies report spontaneous filling of CNTs under ambient conditions. Nuclear magnetic resonance (NMR) or Raman spectroscopy has been used to detect indirectly the presence of water inside CNTs after submersion in aqueous solutions.[11–15] The NMR studies rely on the assumption that water is not filling spaces between close-packed CNTs.[15] Mittal *et al.* imaged by TEM chromium oxide (CrO_3) inside CNTs after exposure to a CrO_3/HCl solution and subsequent drying.[16] To date, no study has imaged spontaneously filled CNTs in the native state.

Here, we present new, unique, and direct evidence of CNT filling by imaging through the use of cryogenic transmission electron microscopy (cryo-TEM). The uniqueness of this study lies in the fact that CNT-filling is visualized in the native state, *i.e.*, we directly image a representative sample of the nanotube–solvent system as it is in ambient conditions, with solvent inside and outside; the sample is not altered except by vitrification, which does not modify the location of the liquid.

Notably, the liquid (chlorosulfonic acid) in our system combines two unique traits, acting as both a solvent and a filler for CNTs. Chlorosulfonic acid was recently identified as a true solvent for CNTs because it protonates the side-walls, dissolves the CNTs as individuals (without sonication or functionalization), and promotes the formation of liquid crystals from a wide range of nanotube sources, including multi-walled nanotubes and long carpet-grown CNTs.[17,18] Comparison against theoretical predictions for the onset of liquid crystallinity indicates that chlorosulfonic acid is an athermal solvent for CNTs.[19] The acid's propensity to protonate the outer walls of CNTs suggests that it should wet and fill the CNT interior, as confirmed by the results reported below.

By cryo-TEM, we visualize carpet-grown multiwalled carbon nanotubes (MWNTs, id = 7 nm, od = 12 nm)[20,21] dissolved at 50 ppm in chlorosulfonic acid. Sample preparation was performed in a water-free atmosphere to prevent the evolution of gaseous hydrochloric acid. Cryo-TEM imaging[22] of superacids is a new technique[17,18,23] that avoids the standard issues arising in conventional TEM imaging, *i.e.*, the CNT must be capped or the filler must solidify at room temperature to avoid removal by evaporation in the vacuum of the microscope.[1–4]

Example cryo-TEM images of the observed features are shown in Fig. 1 with illustrations in Fig. 2. (Further images are available in ESI.†) Because the chlorosulfonic acid is rich in relatively heavy atoms (chlorine and sulfur), the acid appears darker than the carbon or the interior of unfilled CNTs.

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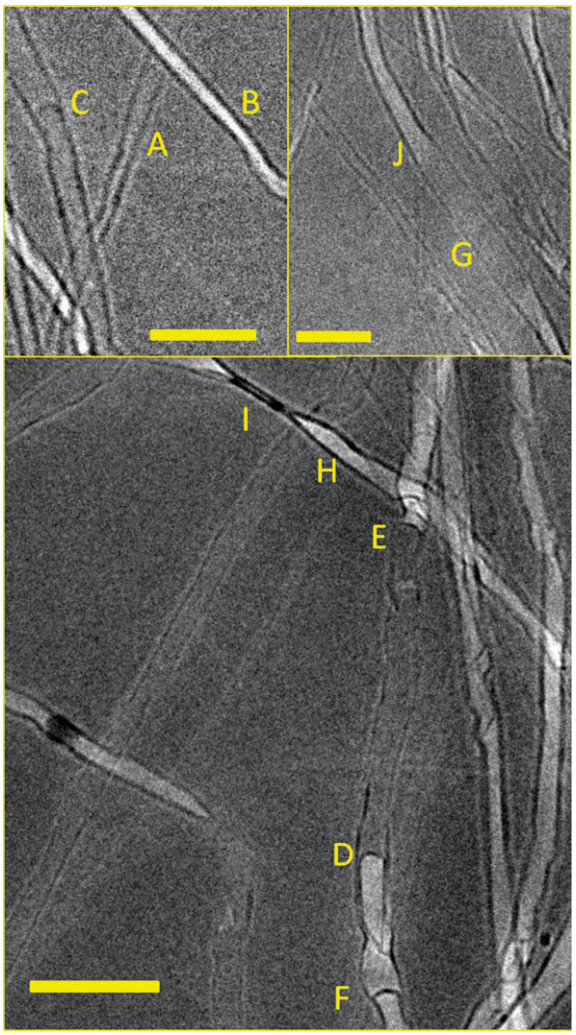

Fig. 1 Cryo-TEM images depicting filling of MWNTs with chlorosulfonic acid. These MWNTs were CVD-grown in vertically-aligned arrays, or "carpets"; they have inner diameters of ~7 nm and outer diameters of ~12 nm. Dark MWNTs indicate filled MWNTs (A) while light MWNTs indicate unfilled MWNTs (B). Scale bars are 50 nm.

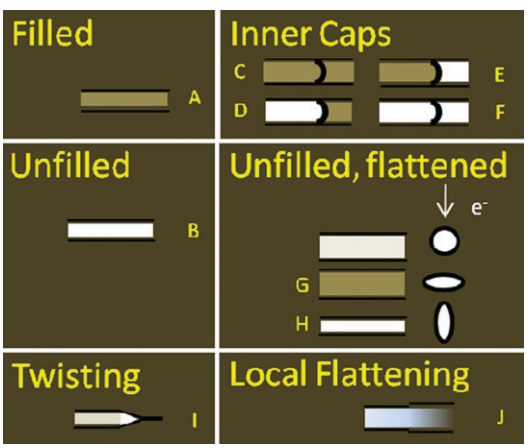

Fig. 2 Illustration of the features observed for filled and unfilled MWNTs. Corresponding cryo-TEM images are shown in Fig. 1.

Locally, the sample consists of a uniform thickness layer of the vitrified acid, in which the CNTs are embedded. Electrons traversing an empty nanotube encounter less acid; thus, that point appears brighter in the image relative to an area of a tube filled with acid. Therefore, unfilled MWNTs appear light against the acid background (B), while filled MWNTs appear to be of the same optical density ("darkness"; A). Such a contrast would be difficult to achieve for other "lighter" liquids. The strong contrast between the electron-rich acid and the nanotube sidewall allows for identification of inner caps, deformation, and partial filling, as described below.

We argue that the dark MWNTs are filled because of the definite contrast associated with the features in (C–F). This sharp transition from light to dark indicates a boundary between a filled and an empty region. At first glance, this appears to be a meniscus. However, because the dark regions are convex in some areas and concave in others (D, E), this contrast cannot be due to menisci. Instead, we interpret these features as caps of an inner layer of the MWNT. Internal caps are also observed that separate two dark sections (C) or two light sections (F); these features are also indicative of internal caps rather than menisci. The observation of these caps forming a sharp separation between light and dark regions (D, E) is strong evidence of acid intercalation into the MWNTs; acid can fill the MWNT sections on either side of a cap (C), or both sides of a cap can be empty (F). If acid is observed in only one side of such a cap, the cap acts as a barrier to the acid, so that the MWNT is only partially filled.

These sharp boundaries between light and dark regions indicate that the acid, in which the nanotubes are submerged, does indeed fill some MWNTs. These images also feature far more dramatic contrast between filled and unfilled regions than those noted in previous studies. A number of other unusual features are visible in the images; Fig. 1J shows a gradual transition from light to dark in a given MWNT, and Fig. 1I shows a MWNT narrowing to form a thin line. These various features can be explained by local flattening and twisting of unfilled MWNTs at various angles relative to the electron beam, as explained in Fig. 2G and H. If a section of MWNT is flattened as in (G), the area appears darker because a larger portion of the total film thickness is taken up by the acid; likewise, if a section of MWNT is flattened to be edge-on to the detector as in (H), the area appears lighter because a large portion of the total film thickness is taken up by the unfilled MWNT. It is unlikely that such flattening could happen in a filled MWNT. (If filled MWNTs were flattened, there would be little contrast because the acid would be both inside and outside the sidewall.) Nanotubes of sufficiently large diameter are known to flatten because of van der Waals forces; such a flattening effect has been observed previously in HR-TEM images of MWNTs.[24,25] In scenarios where the gradual light–dark transition is observed, the darker region (G) typically appears broader, while the lighter region (H) appears narrower. This observation lends strong support to the hypothesis that these effects are caused by local flattening. Fig. 1 shows a region of local flattening (G) flanked by a transition (J) to a lighter, less flat region.

Light and dark distinctions were also seen in filled and unfilled carpet-grown single-walled carbon nanotubes (depicted in ESI†)

with diameters of 2–3 nm.[20,21] Because the diameter of the CNT approaches the resolution attainable for the system, the visibility of the effect is diminished. Nevertheless the difference between filled and empty CNTs is still striking. Although it is possible that the acid enters the interior of the CNT through open ends, the number of twists, buckles, and breaks in the CNTs also make it likely that the acid enters the interior through "wall defects," as described by Naguib *et al.*[1] In fact, the region between (D) and (E) in Fig. 1 is evidence of this. Thus, these images directly confirm that imbibition can occur through sidewall defects; they also confirm that the inner caps in MWNTs can prevent the liquid from completely filling the tube interior.

These filling effects are relevant for applications that rely on CNT solubility in acids, such as the processing of CNT-based fibers and films.[26] The acid dopes the CNTs, increasing the electrical conductivity of fibers and films[27,28]; acid filling explains the (desirable) high stability of such doping.[29,30] Spontaneous filling by acids may also lead to new routes for the chemical modification of CNT sidewall interiors, which could be useful in various applications (*e.g.*, membranes and nano-capsules). The filling of CNTs also has immediate relevance for CNT separation by type, diameter, and chirality through ultracentrifugation.

In conclusion, we show by cryo-TEM that chlorosulfonic acid spontaneously fills the interior of CNTs. Primary evidence is the sharp separation between light and dark regions separated by inner caps. The acid enters either through CNT ends or through wall defects. We systematically analyze the observed features and categorize them in terms of filling and flattening of the CNTs. These results are the first to directly image CNTs in the native state spontaneously filled with the surrounding solvent. This study is also the first to use cryo-TEM to show liquid filling of CNTs. This direct imaging is a novel and critical advance in the rich field of CNTs imbibition, providing important evidence of new features of filled nanotubes such as deformation in solution, interior liquid boundaries, and filling impeded by inner caps.

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Notes and references

1 N. Naguib, Y. Haihui, Y. Gogotsi, A. G. Yazicioglu, C. M. Megaridis and M. Yoshimura, *Nano Lett.*, 2004, **4**, 2237–2243.
2 M. P. Rossi, Y. Gogotsi and K. G. Kornev, *Langmuir*, 2009, **25**, 2804–2810.
3 M. P. Rossi, Y. Haihui, Y. Gogotsi, S. Babu, P. Ndungu and J.-C. Bradley, *Nano Lett.*, 2004, **4**, 989–993.
4 A. L. Yarin, A. G. Yazicioglu, C. M. Megaridis, M. P. Rossi and Y. Gogotsi, *J. Appl. Phys.*, 2005, **97**, 124309.
5 B. J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas and L. G. Bachas, *Science*, 2004, **303**, 62–65.
6 J. Holt, *Microfluid. Nanofluid.*, 2008, **5**, 425–442.
7 D. Mattia and Y. Gogotsi, *Microfluid. Nanofluid.*, 2008, **5**, 289–305.
8 P. M. Ajayan and S. Iijima, *Nature*, 1993, **361**, 333–334.
9 M. Rana, *Proc. – Indian Acad. Sci., Chem. Sci.*, 2007, **119**, 367.
10 B. Sitharaman, K. R. Kissell, K. B. Hartman, L. A. Tran, A. Baikalov, I. Rusakova, Y. Sun, H. A. Khant, S. J. Ludtke, W. Chiu, S. Laus, E. Toth, L. Helm, A. E. Merbach and L. J. Wilson, *Chem. Commun.*, 2005, 3915–3917.
11 W. Wenseleers, S. Cambre, J. Culin, A. Bouwen and E. Goovaerts, *Adv. Mater.*, 2007, **19**, 2274–2278..
12 S. Ghosh, K. V. Ramanathan and A. K. Sood, *Europhys. Lett.*, 2004, **65**, 678–684.
13 W. Sekhaneh, M. Kotecha, U. Dettlaff-Weglikowska and W. S. Veeman, *Chem. Phys. Lett.*, 2006, **428**, 143–147.
14 Q. Chen, J. L. Herberg, G. Mogilevsky, H. J. Wang, M. Stadermann, J. K. Holt and Y. Wu, *Nano Lett.*, 2008, **8**, 1902–1905.
15 H. J. Wang, X. K. Xi, A. Kleinhammes and Y. Wu, *Science*, 2008, **322**, 80–83.
16 J. Mittal, M. Monthioux, H. Allouche and O. Stephan, *Chem. Phys. Lett.*, 2001, **339**, 311–318.
17 V. A. Davis, A. N. G. Parra-Vasquez, M. J. Green, P. K. Rai, N. Behabtu, V. Prieto, R. D. Booker, J. Schmidt, E. Kesselman, W. Zhou, H. Fan, W. W. Adams, R. H. Hauge, J. E. Fischer, Y. Cohen, Y. Talmon, R. E. Smalley and M. Pasquali, *Nat. Nanotechnol.*, 2009, **4**, 830–834.
18 A. N. G. Parra-Vasquez, N. Behabtu, M. J. Green, C. L. Pint, C. C. Young, J. Schmidt, E. Kesselman, A. Goyal, P. M. Ajayan, Y. Cohen, Y. Talmon, R. H. Hauge and M. Pasquali, *ACS Nano*, 2010, **4**, 3969–3978.
19 M. J. Green, A. N. G. Parra-Vasquez, N. Behabtu and M. Pasquali, *J. Chem. Phys.*, 2009, **131**, 084901.
20 C. L. Pint, S. T. Pheasant, A. N. G. Parra-Vasquez, C. Horton, Y. Q. Xu and R. H. Hauge, *J. Phys. Chem. C*, 2009, **113**, 4125–4133.
21 H. W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtai and P. M. Ajayan, *Science*, 2002, **296**, 884–886.
22 Y. Talmon, *Ber. Bunsen-Ges. Phys. Chem.*, 1996, **100**, 364–372.
23 N. Behabtu, J. R. Lomeda, M. J. Green, A. L. Higginbotham, A. Sinitskii, D. V. Kosynkin, D. Tsentalovich, A. N. G. Parra-Vasquez, J. Schmidt, E. Kesselman, Y. Cohen, Y. Talmon, J. M. Tour and M. Pasquali, *Nat. Nanotechnol.*, 2010, **5**, 406–411.
24 M. Motta, A. Moisala, I. A. Kinloch and A. H. Windle, *Adv. Mater.*, 2007, **19**, 3721–3726.
25 S. B. Sinnott and R. Andrews, *Crit. Rev. Solid State Mat. Sci.*, 2001, **26**, 145–249.
26 N. Behabtu, M. J. Green and M. Pasquali, *Nano Today*, 2008, **3**, 24–34.
27 H. Z. Geng, K. K. Kim, K. P. So, Y. S. Lee, Y. Chang and Y. H. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 7758–7759.
28 J. Vavro, M. C. Llaguno, J. E. Fischer, S. Ramesh, R. K. Saini, L. M. Ericson, V. A. Davis, R. H. Hauge, M. Pasquali and R. E. Smalley, *Phys. Rev. Lett.*, 2003, **90**, 065503.
29 W. Zhou, J. Vavro, C. Guthy, K. I. Winey, J. E. Fischer, L. M. Ericson, S. Ramesh, R. Saini, V. A. Davis, C. Kittrell, M. Pasquali, R. H. Hauge and R. E. Smalley, *J. Appl. Phys.*, 2004, **95**, 649–655.
30 B. Dan, G. C. Irvin and M. Pasquali, *ACS Nano*, 2009, **3**, 835–843.

