

Direct Imaging of Carbon Nanotubes Spontaneously filled with Solvent

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Filling carpet-grown multi-walled carbon nanotubes (MWNTs)

The figures used in the main text of the paper are excerpted from the following cryogenic transmission electron microscopy (cryo-TEM) images of MWNTs dissolved in chlorosulfonic acid. Filled and unfilled regions, internal caps, flattened areas, twisted areas, and buckled areas are all visible in these images. The “bubble” appearance is caused by electron beam irradiation of the vitrified chlorosulfonic acid, as discussed elsewhere.^{1, 2}

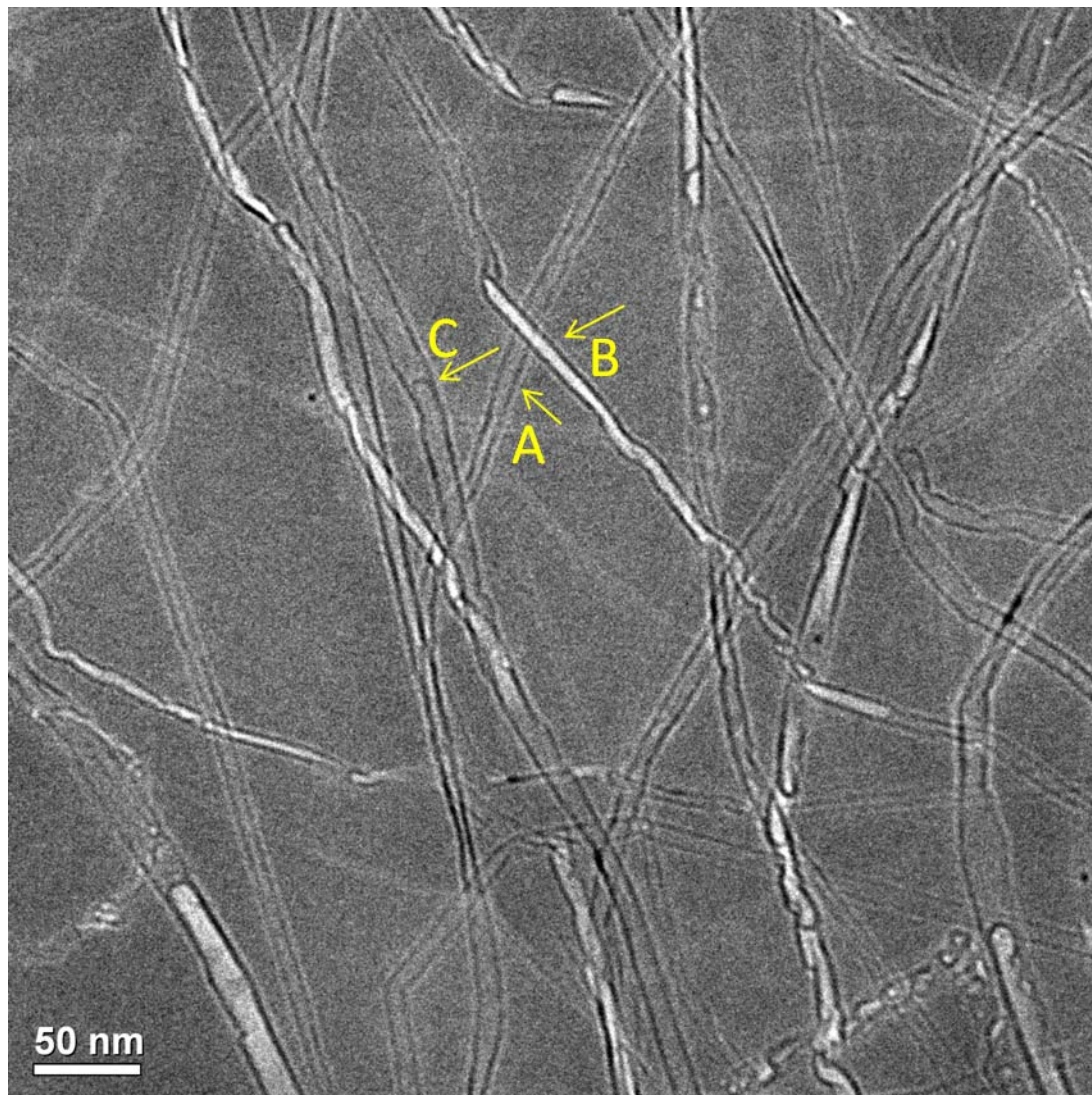


Figure S1: Full image of acid-MWNT system, expanding on the image shown in Figure 1 of the article. (A) Filled MWNT. (B) Unfilled MWNT. (C) Inner cap with acid on both sides.

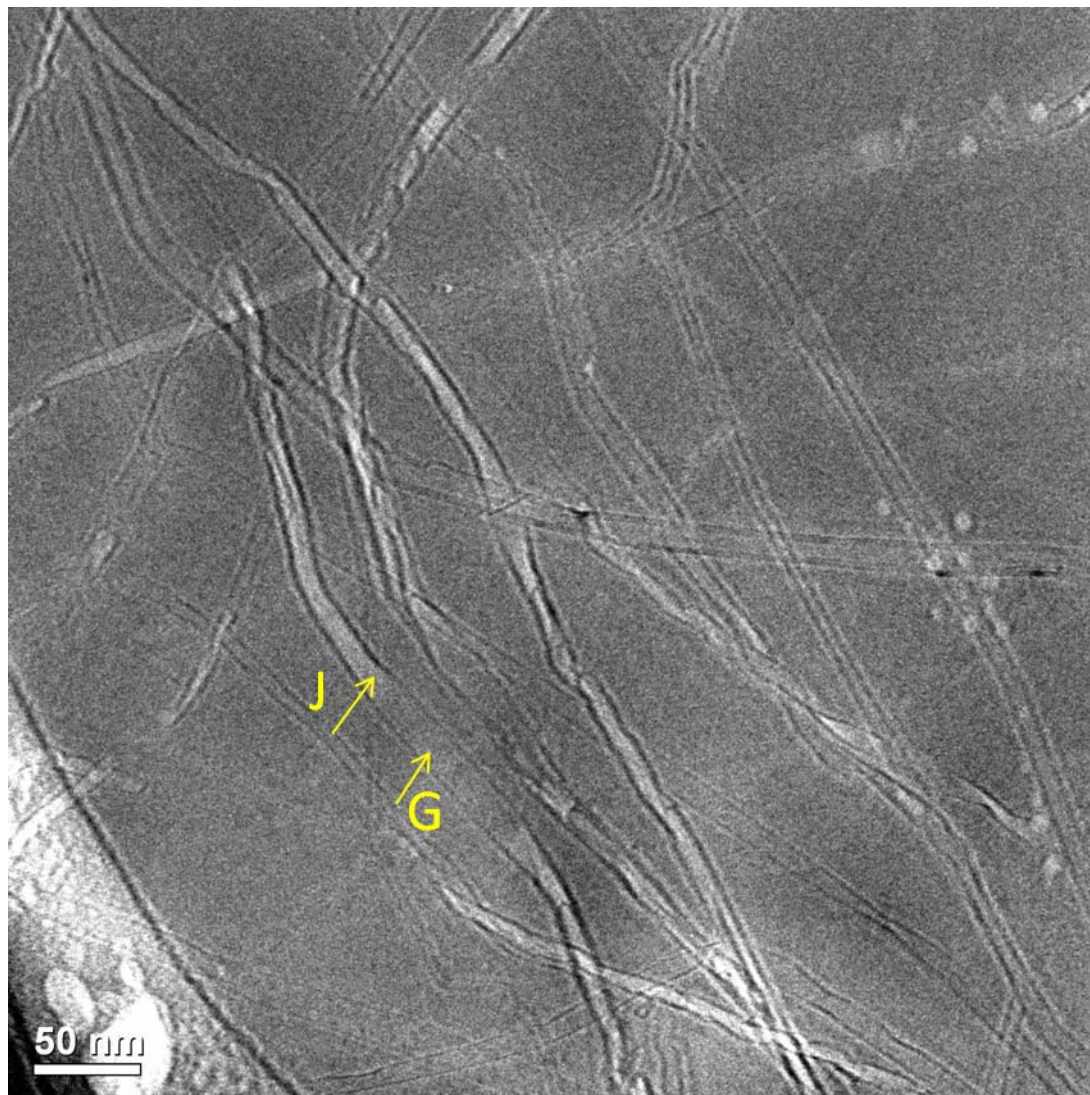


Figure S2: Full image of acid-MWNT system, expanding on the image shown in Figure 1 of the article. (G) Flattened section of a MWNT. (J) gradual transition from light to dark in a given MWNT.

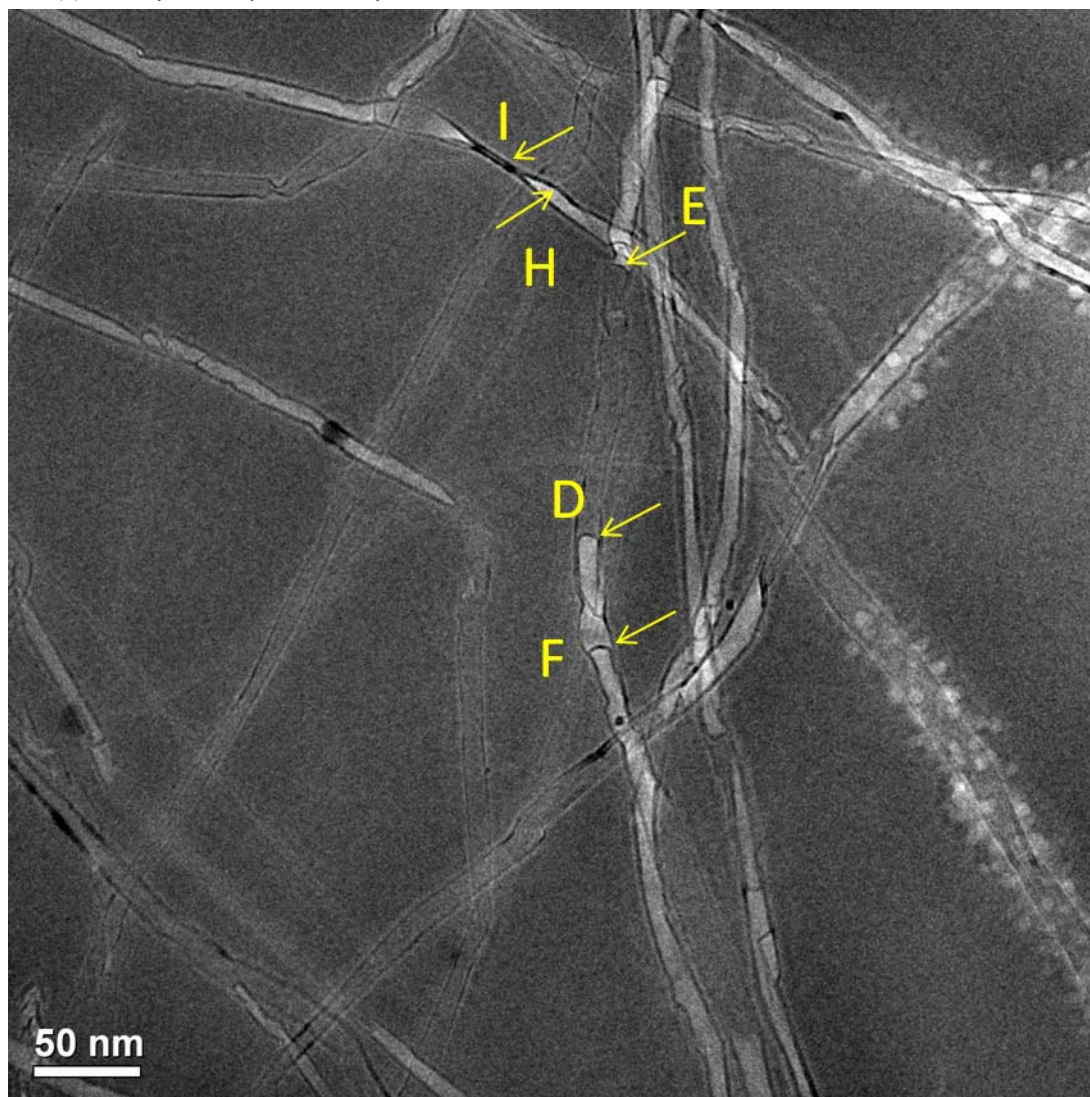


Figure S3: Full image of acid-MWNT system, expanding on the image shown in Figure 1 of the article. (D, E) Sharp transitions from light to dark, indicating a boundary between a filled and empty region. Convex in one case and concave in the other. (F) Inner cap with no acid on either side. (H, I) a section of MWNT is flattened to be edge-on to the detector.

Filling carpet-grown single-walled carbon nanotubes (SWNTs)

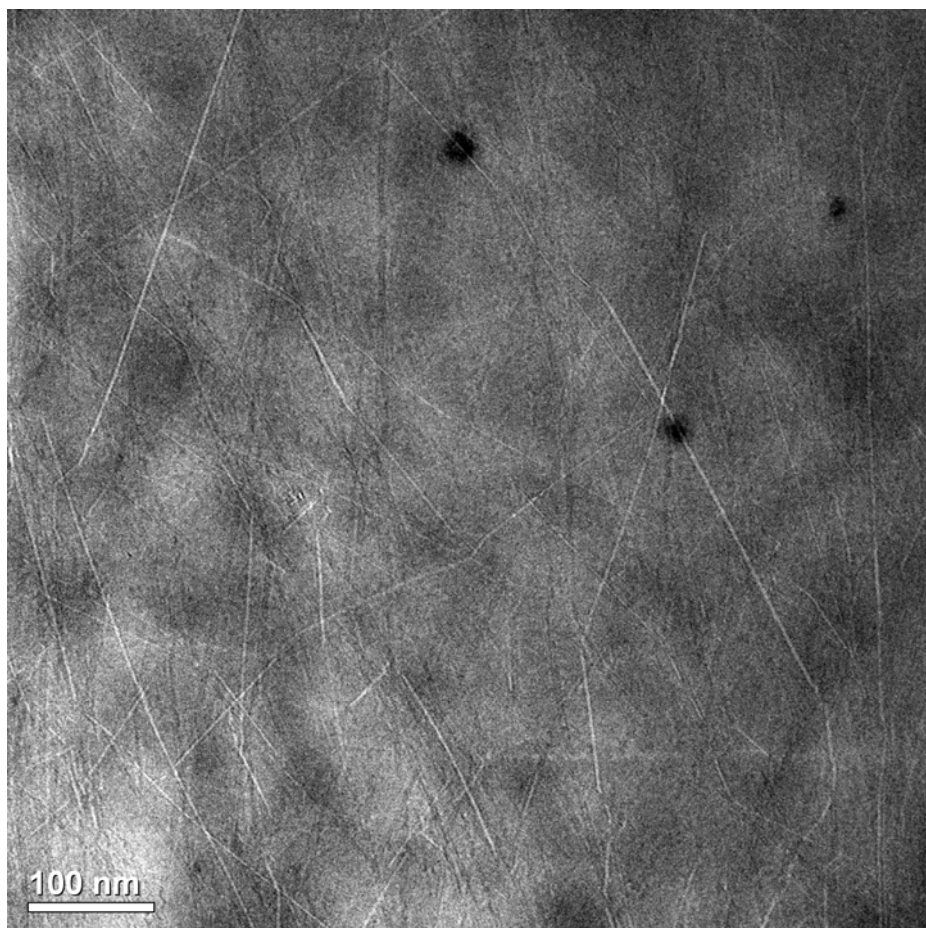


Figure S4: Both light and dark carpet-grown SWNTs (grown at Rice, further details in Parra-Vasquez *et al.*,²) can be seen, indicating the presence of both unfilled and filled or flattened SWNTs.

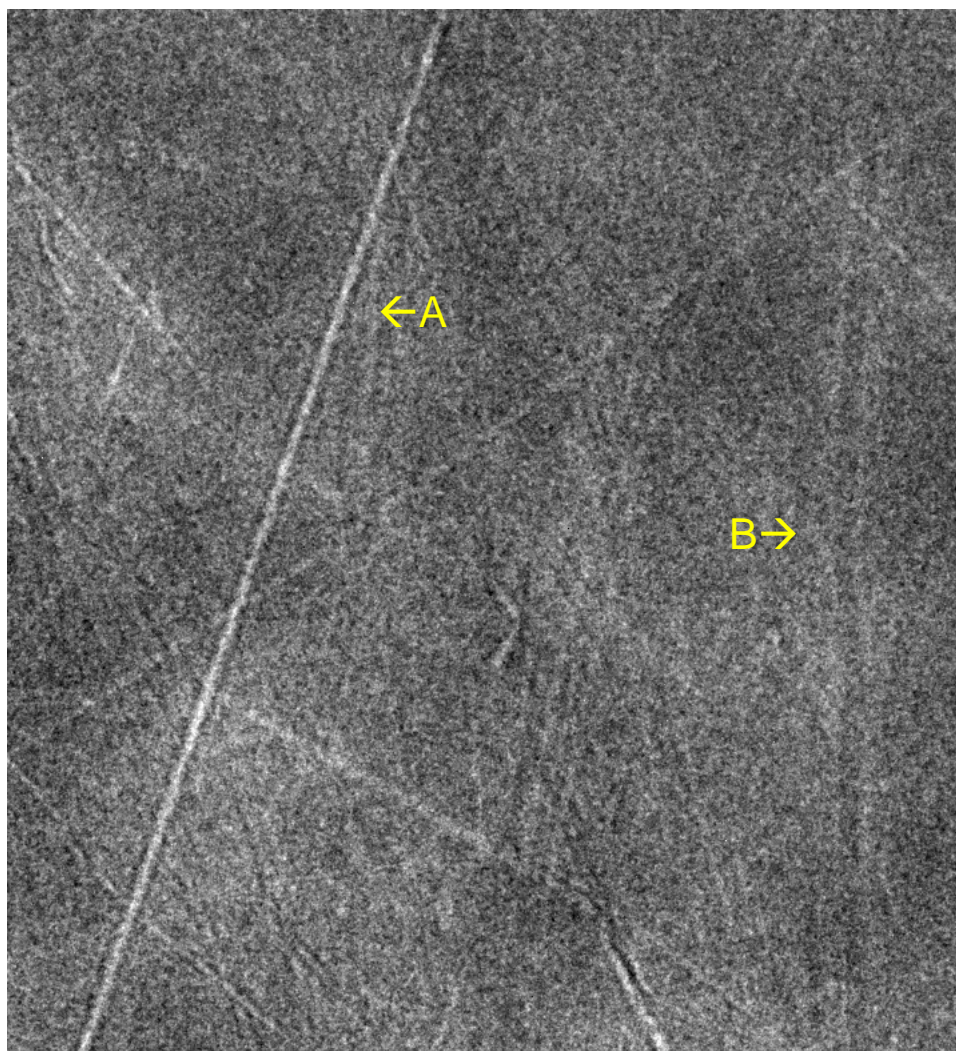


Figure S5: An enhanced view of Figure S4 is shown of the upper left corner with unfilled (A) and filled (B) areas labeled.

Materials and methods

Our cryo-TEM techniques follow those by Davis *et al.*¹. The standard cryo-TEM procedure³ was modified to account for the unique hurdles associated with working with superacids. CNTs (carpet grown SWNTs and carpet grown MWNTs) were dispersed in 97 % reagent grade chlorosulfonic acid at 50 ppm. Dispersions were prepared and allowed to mix for a day in a dry glove box (dew point of -50 °C) in a nitrogen gas atmosphere to prevent contact with water and consequent evolution of gaseous hydrochloric acid. 2 mL of either dispersion was transferred to a small vial and placed in the vitrification apparatus along with a glass filter paper and glass pipette. The entire set-up was placed in a glove bag and purged with ultra-pure nitrogen (99.9995%) for 30 min. A drop of the SWNT dispersion was then placed on a lacey carbon covered grid (Ted Pella, 200 copper mesh). The glass filter paper (unreactive with chlorosulfonic acid) was then used to blot the sample, leaving a thin film of liquid. The grid was then quickly vitrified in liquid nitrogen and placed in a cryo-holder for transfer to the TEM. The samples were imaged by an FEI T12 transmission electron microscope operated at 120 kV, using a Gatan 626 cooling holder operated at about -180 °C.

Materials used in this study were carpet-grown SWNTs (produced at Rice University by the authors) with diameter ranges from 0.8 - 4 nm and carpet-grown MWNTs (produced at Rice University by the Ajayan group). Carpet-grown SWNTs were prepared with Co-Mo catalyst particles on alumina substrates, with acetylene as the carbon source, with three different growth procedures: grown at 750 °C for 15 min (60 μm), grown at 750 °C for 30 min (100 μm), and grown at 550 °C for 15 min (16 mm)⁴. Carpet-grown MWNTs were prepared on thermally oxidized silicon wafers by the chemical vapor deposition of xylene (C₈H₁₀) and ferrocene (Fe(C₅H₅)₂) at 850 °C until nanotube heights were 500 μm on average⁶.

Cryo-TEM Resolution

Cryo-TEM images are collected under very different conditions than those encountered in room-temperature microscopy. The samples are almost always very sensitive to the electron beam, thus low-dose imaging is mandatory. Typically one uses 10,000 to 100,000 times fewer electrons per unit area than what is customary in high-resolution (room temperature) TEM of materials such as metals or ceramics. This leads to worse signal-to-noise ratio in the recorded images. In addition, cryo-TEM specimens have quite often very low inherent contrast, thus one normally resorts to enhancing contrast by defocusing the objective lens. This could limit the resolution of the images, but typically not below 0.5 nm, which is quite acceptable in cryo-TEM.

Because the chlorosulfonic acid is rich in the relatively heavy atoms, chlorine and sulfur, the acid appears darker than the carbonaceous material in the sample, namely the CNTs. At least locally the sample is made of a uniform thickness layer of vitrified acid, in which the CNTs are embedded. Electrons traversing an empty tube will see less acid, thus that point will appear brighter in the image relative to an area of a tube filled with acid. Good examples are points J, or E in Figure 1 of the paper. The change in contrast at those points is very abrupt.

The fact that the sidewalls of “dark” nanotubes are fainter than that of “light” nanotubes is connected to the defocusing of the objective lens to enhance phase-contrast, explained above. This defocus leads to the formation of light and dark Fresnel fringes at points of abrupt change of mass-thickness. This is responsible for the darker appearance of the walls of empty tubes. It is a result of the higher abrupt change of mass-density across the wall of an empty tube relative to that of a filled tube.

Prior work in the area of imbibition in CNTs

The following table was compiled as a summary of prior work in the area of filling CNTs with liquids to complement the discussion in the text. The interested reader is referred to the thorough reviews by Holt⁷ and Mattia and Gogotsi⁸.

Table S1: Prior work on filling CNTs with liquid; methods include optical microscopy, use of fluorescent dyes, observation of flow, TEM, environmental scanning electron microscope (ESEM), Nuclear magnetic resonance (NMR), and X-ray diffraction (XRD).

| Description | Reference (representative methods) |
|---|--|
| Filling during synthesis | ⁹⁻¹³ (TEM) |
| Filling by vapor in autoclave | ¹⁴⁻²⁰ (ESEM, XRD, TEM, NMR) |
| Filling of very large nanotubes (100+ nm) | ^{19, 21-25} (optical microscopy, fluorescent dye) |
| Filling with molten substances | ^{26, 27} (both TEM) |
| Spontaneous filling at ambient conditions | ²⁸ (Raman), ²⁹⁻³¹ (NMR), ³² (TEM of chromium oxide) |
| Pressure driven flow through membrane | ³³⁻³⁶ (flow) |
| Voltage driven flow/wetting | ^{36, 37} (TEM) |
| Filling of carbon pipes | ^{38, 39} (TEM) |

References

1. 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, *Nature Nanotechnology*, 2009, **4**, 830-834.
2. 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.
3. Y. Talmon, *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, 1996, **100**, 364-372.
4. C. L. Pint, S. T. Pheasant, A. N. G. Parra-Vasquez, C. Horton, Y. Q. Xu and R. H. Hauge, *Journal of Physical Chemistry C*, 2009, **113**, 4125-4133.
5. C. L. Pint, S. T. Pheasant, M. Pasquali, K. E. Coulter, H. K. Schmidt and R. H. Hauge, *Nano Letters*, 2008, **8**, 1879-1883.
6. H. W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtai and P. M. Ajayan, *Science*, 2002, **296**, 884-886.
7. J. Holt, *Microfluidics and Nanofluidics*, 2008, **5**, 425-442.
8. D. Mattia and Y. Gogotsi, *Microfluidics and Nanofluidics*, 2008, **5**, 289-305.
9. J. Libera and Y. Gogotsi, *Carbon*, 2001, **39**, 1307-1318.
10. Y. Gogotsi, J. A. Libera and M. Yoshimura, *J. Mater. Res.*, 2000, **15**, 2591-2594.
11. Y. Gogotsi, J. A. Libera, A. Guvenc-Yazicioglu and C. M. Megaridis, *Appl. Phys. Lett.*, 2001, **79**, 1021-1023.
12. Y. Gogotsi, N. Naguib and J. A. Libera, *Chem. Phys. Lett.*, 2002, **365**, 354-360.
13. C. M. Megaridis, A. G. Yazicioglu, J. A. Libera and Y. Gogotsi, *Phys. Fluids*, 2002, **14**, L5-L8.
14. A. I. Kolesnikov, J. M. Zanotti, C. K. Loong, P. Thiyagarajan, A. P. Moravsky, R. O. Loutfy and C. J. Burnham, *Phys. Rev. Lett.*, 2004, **93**, 4.
15. N. Naguib, Y. Haihui, Y. Gogotsi, A. G. Yazicioglu, C. M. Megaridis and M. Yoshimura, *Nano Letters*, 2004, **4**, 2237-2243.
16. S. H. Mao, A. Kleinhammes and Y. Wu, *Chem. Phys. Lett.*, 2006, **421**, 513-517.
17. Y. Maniwa, H. Kataura, M. Abe, A. Udaka, S. Suzuki, Y. Achiba, H. Kira, K. Matsuda, H. Kadowaki and Y. Okabe, *Chem. Phys. Lett.*, 2005, **401**, 534-538.
18. Y. Maniwa, K. Matsuda, H. Kyakuno, S. Ogasawara, T. Hibi, H. Kadowaki, S. Suzuki, Y. Achiba and H. Kataura, *Nat. Mater.*, 2007, **6**, 135-141.
19. M. P. Rossi, Y. Haihui, Y. Gogotsi, S. Babu, P. Ndungu and J.-C. Bradley, *Nano Letters*, 2004, **4**, 989-993.
20. Y. Maniwa, H. Kataura, M. Abe, S. Suzuki, Y. Achiba, H. Kira and K. Matsuda, *J. Phys. Soc. Jpn.*, 2002, **71**, 2863-2866.
21. G. Korneva, H. H. Ye, Y. Gogotsi, D. Halverson, G. Friedman, J. C. Bradley and K. G. Kornev, *Nano Letters*, 2005, **5**, 879-884.
22. B. M. Kim, S. Qian and H. H. Bau, *Nano Letters*, 2005, **5**, 873-878.
23. B. M. Kim, S. Sinha and H. H. Bau, *Nano Letters*, 2004, **4**, 2203-2208.
24. D. Mattia, H. H. Ban and Y. Gogotsi, *Langmuir*, 2006, **22**, 1789-1794.
25. J. R. Freedman, D. Mattia, G. Korneva, Y. Gogotsi, G. Friedman and A. K. Fontecchio, *Appl. Phys. Lett.*, 2007, **90**, 3.

26. D. Ugarte, T. Stockli, J. M. Bonard, A. Chatelain and W. A. de Heer, *Appl. Phys. A-Mater. Sci. Process.*, 1998, **67**, 101-105.
27. E. Dujardin, T. W. Ebbesen, H. Hiura and K. Tanigaki, *Science*, 1994, **265**, 1850-1852.
28. W. Wenseleers, S. Cambre, J. Culin, A. Bouwen and E. Goovaerts, *Advanced Materials*, 2007, **19**, 2274-+.
29. S. Ghosh, K. V. Ramanathan and A. K. Sood, *Europhys. Lett.*, 2004, **65**, 678-684.
30. W. Sekhaneh, M. Kotecha, U. Dettlaff-Weglikowska and W. S. Veeman, *Chem. Phys. Lett.*, 2006, **428**, 143-147.
31. Q. Chen, J. L. Herberg, G. Mogilevsky, H. J. Wang, M. Stadermann, J. K. Holt and Y. Wu, *Nano Letters*, 2008, **8**, 1902-1905.
32. J. Mittal, M. Monthieux, H. Allouche and O. Stephan, *Chem. Phys. Lett.*, 2001, **339**, 311-318.
33. J. K. Holt, H. G. Park, Y. M. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy and O. Bakajin, *Science*, 2006, **312**, 1034-1037.
34. M. Majumder, N. Chopra, R. Andrews and B. J. Hinds, *Nature*, 2005, **438**, 44-44.
35. M. Whitby, L. Cagnon, M. Thanou and N. Quirke, *Nano Letters*, 2008, **8**, 2632-2637.
36. M. Majumder, X. Zhan, R. Andrews and B. J. Hinds, *Langmuir*, 2007, **23**, 8624-8631.
37. J. Y. Chen, A. Kutana, C. P. Collier and K. P. Giapis, *Science*, 2005, **310**, 1480-1483.
38. X. B. Fan, J. E. Barclay, W. C. Peng, Y. Li, X. Y. Li, G. L. Zhang, D. J. Evans and F. B. Zhang, *Nanotechnology*, 2008, **19**, 5.
39. M. G. Schrlau, E. Brailoiu, S. Patel, Y. Gogotsi, N. J. Dun and H. H. Bau, *Nanotechnology*, 2008, **19**, 5.