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Nanofluids in carbon nanotubes using supercritical CO_2: a first step towards a nanochemical reaction

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ABSTRACT Nanofluids were obtained by filling carbon nanotubes (CNTs) with toluene using supercritical fluid technology. The method reported here should open a novel route to developing nanoscale chemical reactions using CNTs as nanoreactors.

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1 Introduction

Nanoscale chemical reactions using carbon nanotubes (CNTs) as nanoreactors [1] are of great importance for testing and understanding fundamental concepts concerning the role of dimensionality and size in determining chemical properties [2]. Particularly intriguing are the results of molecular dynamics simulations [3] that suggest the matter within the narrow confines of a CNT may exhibit an unusual feature, which cannot occur in the bulk material, that would allow for the direct and continuous transformation of liquid matter into a solid. Another interesting work, which extends our understanding of how liquids behave on the nanoscale, is a computer simulation [4] that shows the spontaneous and continuous filling of a non-polar CNT with a one-dimensionally ordered chain of water molecules. Experimentally, the prerequisite for studying nanoscale behaviour and reactions of liquids in CNTs is the capacity to fill nanotubes with organic solvents in an efficient and systematic way. Earlier attempts to fill nanotubes have employed capillarity forces, which drive some metallic [5–7] and inorganic [8–10] materials into CNTs in a molten or liquid state. Although solidification with decreasing temperature prevented the materials in the tubes from being removed, this method suffers from a low filling efficiency (1% [5], 3% [10]) and is difficult to control.

Broughton and Pederson predicted, on the basis of computer simulations, that open nanotubes can be filled with liquid by capillary suction [11]. The reported cutoff value of the surface tension of 100–200 mN/m is sufficiently high to allow water (72 mN/m) and organic solvents (< 72 mN/m) to wet and fill the interior of CNTs [10]. Rivera et al. [12] have

studied by computer simulation the phase equilibrium and layering behavior of the liquid phase in water and water+CO_2 systems inside single-walled CNTs. However, few experiments of filling nanotubes with organic solvents have been reported, because of the fact that during the filling process, capillarity forces compete with factors such as material viscosity, contact angle, nanotubular diameter, and so on [6, 13], in addition to surface tension. Recently, the mobility of an aqueous solution in nanotube channels has been studied [14]. Nanotubes containing an encapsulated aqueous solution have also been synthesized in situ by the hydrothermal method [15, 16]. More recently, Ye et al. [17] demonstrated supercritical fluid fabrication of metal nanowires and nanorods templated by multi-walled CNTs. The adsorption of CF_4, an odourless and colourless compressed gas, on the internal and external surfaces of single-walled CNTs has been studied with a vibrational spectroscopy [18].

In this communication, we report an efficient method for filling CNTs with organic solvents by using supercritical carbon dioxide (sc CO_2). Supercritical CO_2 is nonflammable, essentially nontoxic, and environmentally benign [19]. Its low critical temperature and pressure of 31.1 °C and 73.8 bar, respectively, are easily accessible, and thus researchers have promoted CO_2 as a sustainable and "green" solvent [20]. Supercritical fluids tend to have much lower viscosities than liquid solvents. Moreover, sc CO_2 has an extremely low surface tension and surface energy – lower even than many perfluorocarbons – which gives this solvent remarkable wetting properties [21, 22]. Coupled with the possibility of easy separations and the reduction of organic solvent usage, these factors have led to our considerable interest in filling CNTs using dense CO_2.

2 Experimental

Multi-wall CNTs were synthesized by pyrolysis of iron phthalocyanines using the methods reported in the literature [23, 24]. The CNTs were purified and shortened via the procedures reported by Hiura et al. [25] and Liu et al. [26], respectively. The resulting nanotubes were characterized by inner diameters of 10–40 nm and lengths of 0.5–5 μm. In a typical filling experiment, 20 mg of the shortened nanotubes and 1.5 ml of toluene were loaded into a high-pressure vessel in a constant temperature bath of 40 °C. After thermal equilib-

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rium had been obtained, CO_2 was charged into the vessel until the pressure reached 11.0 MPa, and the system was maintained under these conditions for 1 h. The vessel was allowed to cool to room temperature and depressurized. CO_2 was then vented as a vapor, leaving the nanotubes filled with toluene. The filled nanotubes were characterized by transmission electron microscopy (TEM: Hitachi H-600 and H-800; HRTEM: JEOL JSM-2010F).

3   Results and discussion

Figure 1 shows three different magnification images, observed under a Hitachi H-600 operated at 75 kV, indicating the filling of CNTs with toluene by sc CO_2. Figure 1a is TEM image of empty CNTs for comparison with the images of filled tubes. It is clearly shown from the filled images that more than 80% of the nanotubes were filled by this supercritical fluid technology. Such a high filling efficiency, in stark contrast with previous reports [5, 10], results from the unusual physical properties of sc CO_2.

Marti et al. [27–29], based on the results of simulations, reported that water can enter a hydrophobic channel of a CNT. The key lies in the energetics of hydrogen bonding. The average number of hydrogen bonds between water molecules inside CNTs is far smaller than that in bulk water, which provides enough of a difference in the chemical potential to drive water into tube [30]. However, in our case, there are no hydrogen bonds. The driving force must come from the reduction of the surface tension due to the addition of CO_2, because no toluene was observed in the CNTs without CO_2. The gas-like viscosity of sc CO_2 results in higher diffusion rates of toluene, and the near-zero surface tension makes it essentially infinitely wetting. Therefore, toluene molecules easily enter nanoscale channels of CNTs with the assistance of sc CO_2.

It should be pointed out that the filling rates observed depended strongly on the models and operating conditions of the TEM. The filling rates under the Hitachi H-600 (75 kV, 2×10^{-4} Torr), H-800 (100 kV, 2×10^{-5} Torr), and JSM-2010F (200 kV, 1×10^{-7} Torr) were ca. 80, 40, and 5%, respectively. These results can conceivably be interpreted from the viewpoint that the filled toluene is evaporated more rapidly under higher vacuum and electron beam irradiation with higher strength. From H-600, H-800, to JSM-2010F, the energy of the electron beam irradiation used in imaging the nanotubes increases gradually, and so does the vacuum of the cavity in which the nanotubes are observed. Under both high vacuum and electron beam irradiation, toluene can be evaporated partially out of the channel of a CNT, causing lower filling rates to be observed.

The demonstrated results shown in Fig. 2 confirm the above argument. Figure 2a is a TEM image of a toluene-filled nanotube with a diameter of 52 nm. After heating via electron irradiation for 10 min under a Hitachi H-800 TEM, toluene was evaporated out from the tube, leaving hollow compartments clearly visible (Fig. 2b). Figure 2c shows another toluene-filled nanotube, in which the middle was intercalated by a metal catalyst elongated iron nanoparticles [31], after electron irradiation. Toluene to the right (near the open end of the tube) of the iron catalyst was evaporated, leaving

a hollow compartment. However, toluene to the left could not overflow because the outlet was blocked up by the iron catalyst, and existed as several bubbles, the formation of which is the result of liquid evaporation at the gas/liquid interface near the closed end [14]. The filling process may be as follows: due to the high pressure (11.0 MPa) and the low surface tension and surface energy of sc CO_2, toluene carried by sc CO_2 fills with the open CNTs; as the pressure is reduced, the more volatile CO_2 evaporates from the tube cavities and the less volatile toluene is left behind.
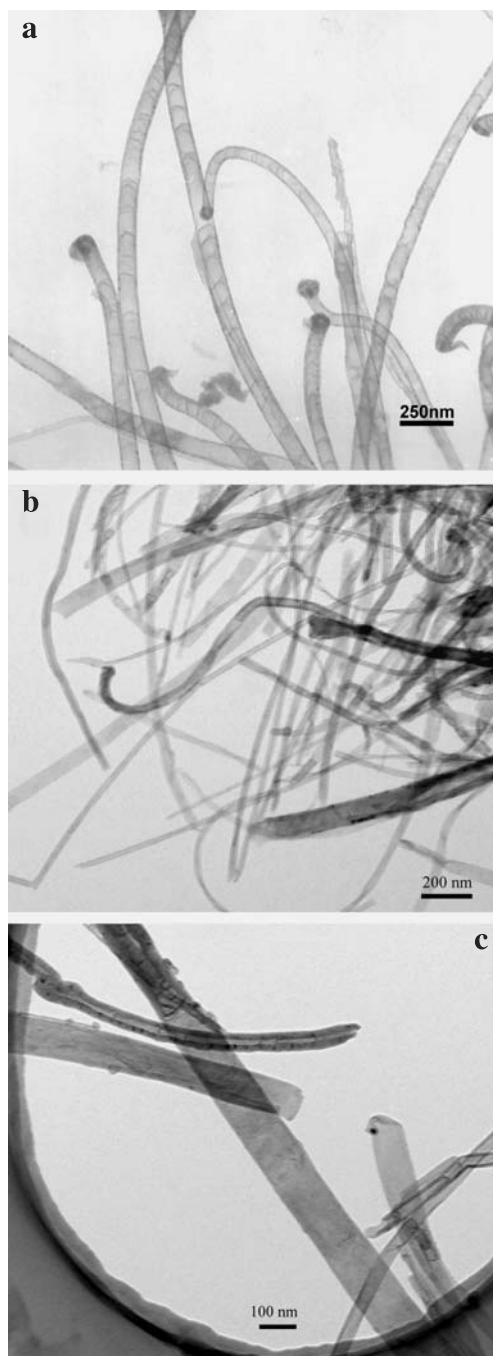

FIGURE 1   **a** TEM image of an empty CNT, and **b** low and **c** high magnification TEM images (Hitachi H-600, 75 kV) of CNTs filled with toluene by sc CO_2
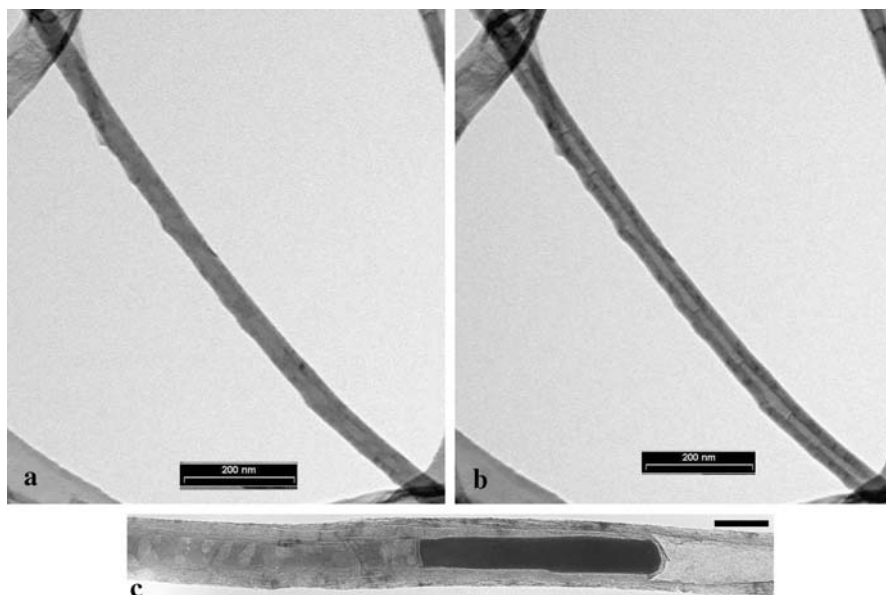
FIGURE 2 TEM image of a toluene-filled nanotube with an inner diameter of 16 nm **a** before and **b** after heating via electron irradiation for 10 min under a Hitachi H-800 TEM. **c** Another toluene-filled nanotube intercalated with elongated iron nanoparticles after electron irradiation. Toluene at the *right side* (near an open end of the tube) of the iron catalyst has been evaporated, leaving a hollow compartment. However, toluene at the *left side* could not overflow, because the outlet was blocked by the iron catalyst, and existed as several bubbles. The *bar* in **c** is 50 nm long

The electrochemical behavior of toluene-filled nanotubes on a gold electrode is described elsewhere. The investigation showed that the toluene-filled nanotube films on the electrode exhibit a catalytic response to biomolecules such as dopamine and epinephrine, while as-synthesized nanotubes have no or less catalytic response to these biomolecules. This suggests that toluene-filled nanotubes may have some particular properties compared with as-prepared nanotubes.

4   Conclusions

In summary, we obtained a large quantity of nanofluids by filling CNTs with toluene using supercritical fluid technology. It is the first communication reporting the filling of nanotubes with an organic solvent by a novel and efficient method. Such a strategy would allow for interesting nanoscale experiments if the nanotubes could be filled with other organic solvents in a systematic way. Moreover, toluene is a good organic solvent for fullerenes and endofullerenes. The method reported here might open a novel route to filling nanotubes with fullerenes and endofullerenes, and thus fabricating an intriguing "peapod" [32–34] that may be used as a building block for nanoelectronic devices.

REFERENCES

1 W. Han, P. Kohler-Redlich, C. Scheu, F. Ernst, M. Rühle, N. Grobert, M. Terrones, H.W. Kroto, D.R.M. Walton: Adv. Mater. **12**, 1356 (2000)
2 H. Dai, E.W. Wang, Y.Z. Lu, S. Fan, C.M. Lieber: Nature (London) **375**, 769 (1995); W. Han, S. Fan, Q. Li, Y. Hu: Science **277**, 1287 (1997)
3 K. Koga, G.T. Gao, H. Tanaka, X.C. Zeng: Nature (London) **412**, 802 (2001)
4 G. Hummer, J.C. Rasalah, J.P. Noworyta: Nature (London) **414**, 188 (2001)
5 P.M. Ajayan, S. Iijima: Nature (London) **361**, 333 (1993)
6 P.M. Ajayan, T.W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki, H. Hiura: Nature (London) **362**, 522 (1993)
7 R.M. Lago, S.C. Tsang, K.L. Lu, Y.K. Chen, M.L.H. Green: J. Chem. Soc. Chem. Commun. 1355 (1995)
8 S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green: Nature (London) **372**, 159 (1994)
9 P.M. Ajayan, O. Stephen, P. Redlich, C. Colliex: Nature (London) **375**, 564 (1995)
10 D. Ugarte, A. Châlelain, W.A. de Heer: Science **274**, 1897 (1996)
11 M.R. Pederson, J.Q. Broughton: Phys. Rev. Lett. **69**, 2689 (1992)
12 J.L. Rivera, C. McCabe, P.T. Cummings: Nano Lett. **12**, 1427 (2002)
13 Y. Dujartsi, T.W. Ebbsen, H. Hiura, K. Tanigaki: Science **265**, 1850 (1994)
14 Y. Gogotsi, J.A. Libera, A. Güvenc-Yazicioglu, C.M. Megaridis: Appl. Phys. Lett. **79**, 1021 (2001)
15 J.M. Calderon-Moreno, M. Yoshimura: J. Am. Chem. Soc. **123**, 8624 (2001)
16 Y. Gogotsi, J.A. Libera, M. Yoshimura: J. Mater. Res. **15**, 2591 (2000)
17 X.R. Ye, Y.H. Lin, C.M. Wang, C.M. Wai: Adv. Mater. **15**, 316 (2003)
18 O. Byl, P. Kondratyuk, S.T. Forth, S.A. FitzGerald, L. Chen, J.K. Johnson, J.T. Yates, Jr.: J. Am. Chem. Soc. **125**, 5889 (2003)
19 A. Furstner, L. Ackermann, K. Beck, H. Hori, D. Koch, K. Langemann, M. Liebl, C. Six, W. Leitner: J. Am. Chem. Soc. **123**, 9000 (2001); P.S. Shah, S. Husain, K.P. Johnston, B.A. Korgel: J. Phys. Chem. B **105**, 9433 (2001)
20 A.I. Cooper: Adv. Mater. **13**, 1111 (2001)
21 D. Li, Z. Liu, B. Han, D. Zhao: Polymer **42**, 2333 (2001)
22 D. Li, B. Han: Macromolecules **33**, 4555 (2000)
23 X.B. Wang, Y.Q. Liu, D.B. Zhu: Chem. Phys Lett. **340**, 419 (2001)
24 X.B. Wang, Y.Q. Liu, D.B. Zhu: Chem. Commun. 751 (2001)
25 H. Hiura, T.W. Ebbsen, K. Tanigaki: Adv. Mater. **7**, 275 (1995)
26 J. Liu, A.G. Rinzler, H. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Lverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T.R. Lee, D.T. Colbert, R.E. Smalley: Science **280**, 1253 (1998)
27 J. Martí, M.C. Gordillo: Phys. Rev. B **63**, 165 430 (2001)
28 M.C. Gordillo, J. Martí: Chem. Phys. Lett. **329**, 341 (2000)
29 M.C. Gordillo, J. Martí: Chem. Phys. Lett. **341**, 250 (2001)
30 M.S.P. Sansom, P.C. Biggin: Nature (London) **414**, 156 (2001)
31 X.B. Wang, W.P. Hu, C.F. Long, Y. Xu, Y.Q. Liu, S.Q. Zhou, D.B. Zhu: Carbon **39**, 1533 (2001)
32 B.W. Smith, M. Monthioux, B.E. Luzzi: Nature (London) **396**, 323 (1998)
33 J. Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z.W. Wang, T. Okazaki, H. Shinohara, Y. Kuk: Nature (London) **415**, 1005 (2002)
34 D.J. Hornbaker, S.-J. Kahng, S. Misra, B.W. Smith, A.T. Johnson, E.J. Mele, D.E. Luzzi, A. Yazdani: Science **295**, 828 (2002)