Synthesis, Characterization and Aspects of Superhydrophobic Functionalized Carbon Nanotubes

Vasilios Georgakilas,*[,†] Athanasios B. Bourlinos,[†]
Radek Zboril,[‡] and Christos Trapalis[†]

Institute of Materials Science, National Center for Scientific Research "Demokritos", Agia Paraskevi, Attikis, Athens 15310, Greece, and Department of Physical Chemistry, Palacky University, Olomouc 77146, Czech Republic

Received November 30, 2007
Revised Manuscript Received January 25, 2008

During the past few years, a great number of nanostructured materials have appeared mainly due to the development of new synthetic methods as well as characterization and manipulation techniques.[1] One of the most interesting and promising issue regarding nanostructures is their use in composite materials. The challenge is to enrich bulk materials such as polymers and organic or inorganic solids with advanced optical, magnetic, electrical, mechanical, and other properties derived from the incorporation of nanomaterials.[2]

A large chapter in nanoscience pertains to carbon nanotubes (CNTs) and their organic derivatives, which show exciting new physicochemical properties, thermal stability, and large surface area.[3] Numerous organic reactions have been applied in order to make CNTs more attractive in various areas of nanotechnology.[4] The 1,3-dipolar cycloaddition of azomethine ylides, which has been broadly utilized in the fullerene field,[5] has been already applied in CNTs with seminal results. The main advantage of this established reaction is the easy attachment of substituted pyrrolidine rings to the sidewalls of the nanotubes. In this way, reconstructed materials with customized properties can be obtained. For this purpose, a specific functionalized aldehyde and an amino acid are combined, leading to 2-substituted pyrrolidine moieties attached on the sidewalls of CNTs. This sort of combination has previously resulted in functionalized CNTs that formed stable solutions in organic solvents,[6] or have been used in polymer composites,[6b] medicinal applications,[6c] drug delivery,[7] and energy conversion.[8]

On the other hand, superhydrophobicity[9] plays an important role in many technological applications including biotechnology, medical devices, waterproof and self-cleaning coatings, lubrication, microfluidics, and stain-resistant finishes.[10] Superhydrophobicity is obtained by a combination of low surface energy and high roughness. The first factor is referred to the chemical composition of the surface and the second to the morphology.[11] Foremost among others, perfluoro compounds are best known to bring dramatic changes in the wetting behavior of a surface, and thus lending excellent superhydrophobic properties.

In this report, the synthesis and characterization of superhydrophobic functionalized CNTs as well their implication in the wetting properties of polymers or textiles are described. In this instance, a perfluoroalkylsilane coating is employed to alter the surface properties of the nanotubes. In recent reports, perfluoroalkylsilanes have been utilized to lend superhydrophobicity to vertically grown CNT thin films.[12] Nevertheless, the fixed nature of the nanotubes in the film strictly confines any further potential use in a wealth of applications. In contrast, the present method can be applied to any kind of CNTs, leading to powder hybrids that can be easily handled in various processes (mixing, blending, dispersion, or impregnation).

In a typical procedure, purchased multiwall CNTs (Aldrich, 95+ %) were first oxidized by piranhas solution to create enough −OH and −COOH groups on the surface.[13] Following, the oxidized nanotubes were used as the substrate

---

* Corresponding author. Tel: 30 210 650 3309. E-mail: georgaki@ims.demokritos.gr.
[†] National Center for Scientific Research "Demokritos".
[‡] Palacky University.

(1) (a) Ozin, G. A.; Arsenault, A. C. In *Nanochemistry: A Chemical Approach to Nanomaterials*; RSC Publishing: Cambridge, U.K., 2005. (b) Rao, C. N. R.; Cheetham, A. K. *J. Mater. Chem.* **2001**, *11*, 2887.

(2) (a) Kuchibhatla, S. V. N. T.; Karakoti, A. S.; Bera, D.; Seal, S. *Prog. Mater. Sci.* **2007**, *52*, 699–913. (b) Heilmann, A. In *Polymer Films with Embedded Metal Nanoparticles*l Springer: New York, 2003. (c) Koerner, H.; Price, G.; Pearce, N. A.; Alexander, M.; Vaia, R. A. *Nat. Mater.* **2004**, *3*, 115–120.

(3) (a) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, P. In *Carbon Nanotubes in Topics in Applied Physics*; Springer: Berlin, 2001. (b) Rao, C. N. R.; Govindaraj, A. In *Nanotubes and Nanowires*; RSC Publishing: Cambridge, U.K., 2005. (c) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.

(4) (a) Niyogi, S.; Hamon, M. A.; Hu, H.; Zhao, B. P.; Bhowmik; Sen, R.; Itkis, M. E.; Haddon, R. C. *Acc. Chem. Res.* **2002**, *35* (12), 1105. (b) Tasis, D.; Tagmatarchis, N.; Georgakilas, V.; Prato, M. *Chem.—Eur. J.* **2003**, *9*, 4000. (c) Tagmatarchis, N.; Georgakilas, V.; Prato, M.; Shinohara, H. *Chem. Commun.* **2002**, 2010.

(5) (a) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798. (b) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519. (c) Kordatos, K.; Da Ros, T.; Bosi, S.; Vazquez, E.; Bergamin, M.; Cusan, C.; Pellarini, F.; Tomberli, V.; Baiti, B.; Pantarotto, D.; Georgakilas, V.; Spalluto, G.; Prato, M. *J. Org. Chem.* **2001**, *66*, 4915–4920.

(6) (a) Georgakilas, V.; Tagmatarchis, N.; Pantarotto, D.; Bianco, A.; Briand, J.-P.; Prato, M. *Chem. Commun.* **2002**, *3050*, 3051. (b) Yao, Z.; Braidy, N.; Botton, G. A.; Adronov, A. *J. Am. Chem. Soc.* **2003**, *125* (51), 16015–16024. (c) Pantarotto, D.; Partidos, C. D.; Graff, R.; Hoebeke, J.; Briand, J.-P.; Prato, M.; Bianco, A. *J. Am. Chem. Soc.* **2002**, *124*, 760.

(7) Singh, R.; Pantarotto, D.; Lacerda, L.; Pastorin, G.; Klumpp, C.; Prato, M.; Bianco, A.; Kostarelos, K. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 3357–3362.

(8) Guldi, D. M.; Rahman, G. M. A.; Zerbetto, F.; Prato, M. *Acc. Chem. Res.* **2005**, *38* (11), 871–878.

(9) Cassie, A. B. D.; Baxter, S. *Nature* **1945**, *155*, 21.

(10) (a) Meldrum, D. R.; Holl, M. R. *Science* **2002**, *297*, 1197–1198. (b) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* **2003**, *299*, 1377–1380. (c) Nakajima, A.; Hashimoto, K.; Watanabe, T.; Takai, K.; Yamauchi, G.; Fujishima, A. *Langmuir* **2000**, *16*, 7044–7047.

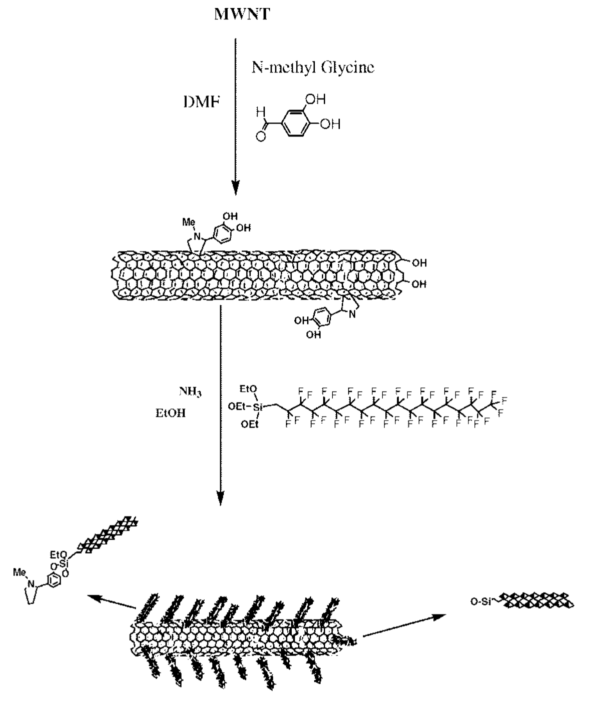
(11) (a) Lafuma, A.; Quere, D. *Nat. Mater.* **2003**, *2*, 457. (b) Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. *Adv. Mater.* **2002**, *14*, 1857.

(12) (a) Lau, K. K. S.; Bico, J.; Teo, K. B. K.; Chhowalla, M.; Amaratunga, G. A. J.; Milne, W. I.; McKinley, G. H.; Gleason, K. K. *Nano Lett.* **2003**, *3*, 1701. (b) Li, H.; Wang, X.; Song, Y.; Liu, Y.; Li, Q.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743. (c) Huang, L.; Lau, S. P.; Yang, H. Y.; Leong, E. S. P.; Yu, S. F.; Prawer, S. *J. Phys. Chem. B* **2005**, *109*, 7746–7748. (d) Li, S.; Li, H.; Wang, X.; Song, Y.; Liu, Y.; Jiang, L.; Zhu, D. *J. Phys. Chem. B* **2002**, *106*, 9274–9276.

(13) Ziegler, K. J.; Gu, Z.; Peng, H.; Flor, E. L.; Hauge, R. H.; Smalley, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 1541–7.

10.1021/cm7034079 CCC: $40.75

Scheme 1. Synthesis Steps for the Perfluorinated CNTs[a]



[a] Note that the starting nanotubes have been oxidized with piranha solution before the cycloaddition step.

for the 1,3-cycloaddition reaction with the 3,4-dihydroxybenzaldehyde/N-methyl glycine couple for the additional incorporation of pending dihydroxyphenyl groups (Scheme 1). This two-step treatment ensures a high concentration of pending oxygen-containing groups on the surface prior fixation of the perfluoroalkylsilane in a compelling manner. On the basis of thermogravimetric analysis, the precursor contains one dihydroxy phenyl group per 80–100 carbon atoms. In the last step, perfluoro-octadecyl-triethoxy silane reacted with these surface exposed centers to eventually form a dense coating around the nanotubes through Si−O−C covalent bridges (Scheme 1). Experimental details are given in the Supporting Information.

The as-perfluorinated CNTs showed an apparent dispersability in DMF or hexafluoroisopropanol (about 2 mg mL^{-1}) and a distinct superhydrophobic character (Figure 1). In particular, a colored water droplet (methylene blue-dyed) was placed on a film of neat superhydrophobic CNTs and formed a contact angle of 170°. This angle is much higher than 150°, i.e., the superhydrophobicity onset.[14] For comparison, superhydrophobic silica nanoparticles exhibit contact angles between 150 and 165°.[15] The droplet was removed completely with a roll off angle lower than 5°. We suggest that the following two factors determine the superhydrophobic character of the hybrid: (i) the high surface roughness due to void spaces between the randomly orientated, interwoven nanotubes; (ii) the dense surface coverage of the nanotubes by the perfluoroalkyl groups that in turn induces a low surface enegy. Note that surface oxidation of the pristine MWNT by piranhas solution and subsequent bonding of the prefluoroalkyl silane also gave a hybrid material; however, the contact angle was found less than 150°, i.e the corresponding film was simply hydrophobic. This discrepancy is ascribed to the smaller oxygen content of the nanotubes and in turn to the less efficient surface coverage by the silane. These properties could be valuable in applications dealing with water repellent surfaces.

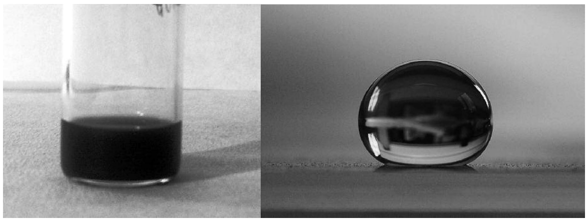


Figure 1. Left: stable colloidal solution of superhydrophobic functionalized CNTs in hexafluoroisopropanol. Right: a colored water droplet on a film of neat perfluorinated carbon nanotubes (diameter ~2 mm). The film was obtained by casting and evaporating the left solution over a glass surface.

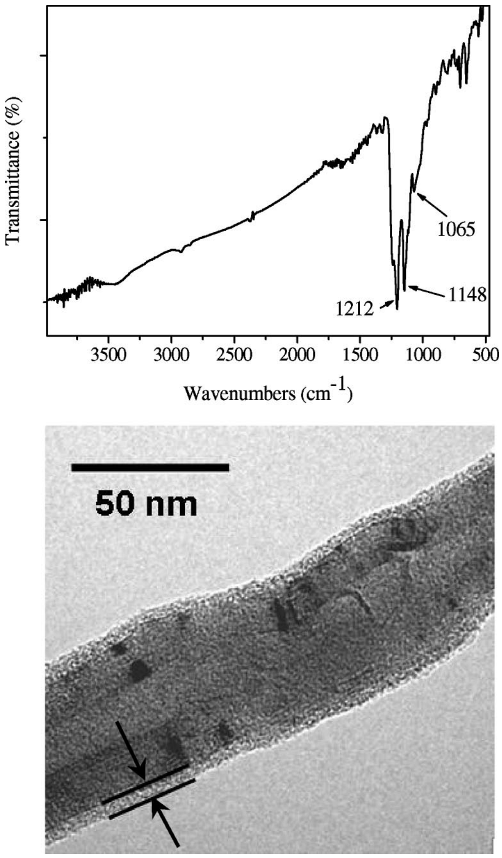


Figure 2. FT-IR spectrum of the perfluorinated CNTs (top). The TEM image depicts a surface coated carbon nanotube (bottom).

The attachment of the perfluoroalkyl groups on the surface of the nanotubes was unveiled by FT-IR spectroscopy (Figure 2).

The intense band at 1212 cm^{-1} is attributed to the stretching vibration of C−F bonds whereas the bands at 1148

---

(14) Nakajima, A.; Hashimoto, K.; Watanabe, T. *Langmuir* **2000**, *16*, 7044–7047.

(15) (a) Ming, W.; Wu, D.; van Benthem, R.; de With, G. *Nano Lett.* **2005**, *5*, 2298–2301. (b) Bravo, J.; Zhai, L.; Wu, Z.; Cohen, R. E.; Rubner, M. F. *Langmuir* **2007**, *23*, 7293–8. (c) Hikita, M.; Tanaka, K.; Nakamura, T.; Kajiyama, T.; Takahara, A. *Langmuir* **2005**, *21*, 7299–7302.

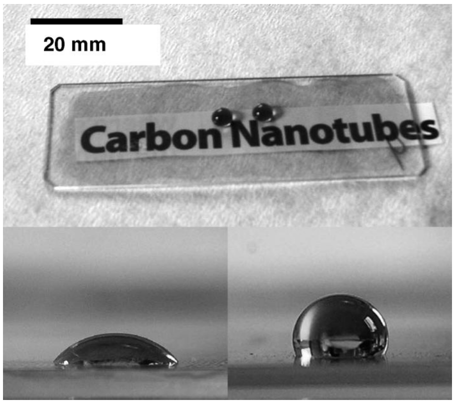


Figure 3. Top: an optically transparent, superhydrophobic PMMA composite film. Bottom, left: side-view of a colored droplet on neat PMMA film. Bottom, right: side-view of the same droplet over the superhydrophobic composite film (diameter ~2 mm).

and 1065 cm^{-1} are characteristic for the formation of Si−O−C bonds. According to TGA, the perfluorinated derivative contains 30% w/w CNTs and 70% w/w organics. Taking into consideration that the organic content is by a large margin attributed to the attached perfluoroalkyl chains, then the particular composition corresponds to a dense surface coverage of silane molecules per carbon atoms. Indeed, TEM study revealed a dense surface coating around the nanotubes thereby signaling the formation of a core–shell type hybrid (Figure 2).

A notable change in the wetting behavior of polymers or textiles was observed upon incorporation of the superhydrophobic CNT adduct. More specifically, an amount of the CNT derivative was dispersed in hexafluoro-isopropanol forming a stable black colloid. A small portion of this colloid was then added in a solution of polymethylmethacrylate (PMMA) in acetic acid. The clear mixture was spread on a glass slide and air-dried forming an optically transparent, slightly gray superhydrophobic film with no signs of phase separation (Figure 3). The contact angle of a dyed water droplet was 152°. In contrast, the contact angle of the same droplet on a neat PMMA film was 30°, showing the hydrophilic nature of the polymer. In this case, the perfluorinated MWNT residing near the surface contribute to the roughness and low energy of the film's surface.

Figure 4. Collared water droplet (diameter ~2 mm) over a superhydrophobic cotton textile after its coating with perfluorinated MWNTs.

In another example, the same solution of superhydrophobic CNTs in hexafluoroisopropanol was used to impregnate a piece of a cotton textile (Figure 4). As a result, the cotton textile became strongly superhydrophobic, with the contact angle of a dyed water droplet being 170°. The droplet was totally removed with a roll off angle less than 5° leaving the textile completely dry. The cotton textile is hydrophilic in nature albeit its intrinsic surface roughness. However, when the perfluorinated MWNT are absorbed at the external surface of the textile, further roughness and low surface energy are achieved.

In summary, superhydrophobic multiwall CNTs were derived in a three-step procedure that comprises oxidation, 1,3-cycloaddition and silylation with a perfluoroalkylsilane. Incorporation of these nanotubes in polymers or textiles in small proportions significantly altered their wetting behavior and rendered them superhydrophobic.

Acknowledgment. R.Z. greatly acknowledges the support by the Projects of the Ministry of Education of the Czech Republic (1M619895201 and MSM6198959218).

Supporting Information Available: Details of experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM7034079