

Formation of macroscopically ordered carbon nanotube membranes by self-assembly

H. Shimoda^{a,*}, L. Fleming^a, K. Horton^b, O. Zhou^{a,b}

^aDepartment of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

^bCurriculum in Applied and Material Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

Abstract

In this paper, we report the formation membranes of the aligned single-wall carbon nanotube (SWNT) bundles on a substrate by self-assembly. SWNTs produced by the laser ablation method and purified by reflux and filtration were chemically etched to short bundles by ultrasonic-assisted oxidation. After removing the acid by filtration, the processed SWNTs were dispersed in de-ionized water. Thin film appears on the surface of a soaked glass substrate in the SWNTs/water dispersion with natural vaporization of water. Transmission electron microscopy measurements show that the SWNT bundles are uniaxially aligned. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nanotubes; Align; Self-assembly

Production of macroscopically aligned nanotube film is one of the most effective ways to study the intrinsic 1-D properties and anisotropic behaviors of the nanotubes. Various methods were already demonstrated to align the nanotubes, such as a mechanical enforcement [1,2], applying huge magnetic [3] or electric field [4]. However, formation of ordered carbon nanotubes by self-assembly has not been observed. Here, we report that short SWNT bundles can form membranes uniaxially aligned SWNTs by self-assembly.

SWNTs used in this study were synthesized by the laser ablation method [5]. As-grown materials were purified by a two-step process involving first refluxing SWNTs in H₂O₂ then filtration [6]. Typical purified materials contained over 90%

SWNT bundles. The bundle and individual nanotube diameters were in the range of 10–50 and 1.3–1.5 nm, respectively. The purified SWNTs were chemically etched to short bundles using a previously reported procedure [7]. The nanotubes were dispersed in a 3:1 mixture of concentrated sulfuric and nitric acids and sonicated for 24 h. After 10 times diluted, the acids mixture filtered through a membrane with 0.2 μm pore then rinsed with water. Retrieved, etched SWNTs were dried at 200°C under the vacuum condition for 8 h. Electron microscopy studies showed that samples etched for 24 h are still in the form of small bundles with the average bundle length of 0.5 μm and bundle diameter of 10 nm.

When a clean glass slide was immersed into the stable SWNT/water suspension, nanotubes were found to assemble on the glass at the air/liquid/substrate triple line. The coverage area increased to continue a SWNT film as the triple line

*Corresponding author. Tel.: +1-919-843-8973; fax: +1-919-962-0480.

E-mail address: hshimoda@physics.unc.edu (H. Shimoda).

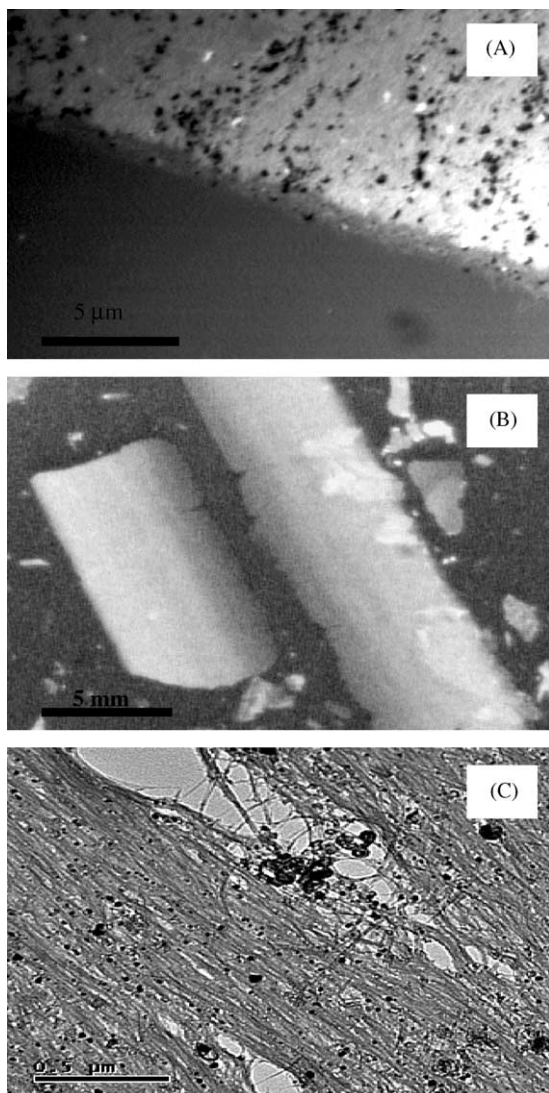


Fig. 1. (A) A self-assembled SWNT film on a glass substrate. The dark spots are micro-pores on the film surface. (B) Free-standing SWNT membranes floating on water surface. (C) TEM image of a thin SWNT film comprising $0.5\ \mu\text{m}$ length bundles. The film is only a few bundles thick and was partially torn when picked up by the TEM grid. The dark particles are the residual metal catalysts.

progressed downward with natural evaporation of water. The film thus formed has a smooth surface and is uniform in thickness (Fig. 1A). By increasing the concentration of the SWNT/water suspension, thick SWNT films can be formed, which can

be subsequently peeled off by stirring the glass in water. The peeled-off films were usually torn into smaller pieces ($\sim 3 \times 5\ \text{mm}$) of free-standing and rectangular-shaped membranes that can float on the water surface (Fig. 1B). Transmission electron microscopy (TEM) examinations showed, surprisingly, that the SWNT bundles were uniaxially aligned in the direction of the air/water/substrate triple line (Fig. 1C) over a large area. The degree of alignment depended on the aspect ratio of the SWNTs and the concentration of the suspension. The best result was obtained from short SWNT bundles ($\sim 0.5\ \mu\text{m}$ average length) and a $0.2\ \text{mg/ml}$ SWNT/water suspension (Fig. 1C).

The ability of carbon nanotubes to self-assemble into ordered higher-level architectures as demonstrated in this communication opens new opportunities for materials fabrication and for investigation of their macroscopic properties.

Acknowledgements

This work was partially supported by the Office of Naval Research through a MURI program at UNC and the National Science Foundation.

References

- [1] L. Jin, C. Bower, O. Zhou, *Appl. Phys. Lett.* 73 (1998) 1197.
- [2] Y. Zhang, S. Iijima, *Phys. Rev. Lett.* 82 (1999) 3472.
- [3] B.W. Smith, Z. Benes, D.E. Luzzi, J.E. Fischer, D.A. Walters, M.J. Casavant, J. Schmidt, R.E. Smalley, *Appl. Phys. Lett.* 77 (2000) 663.
- [4] X.Q. Chen, T. Saito, H. Yamada, K. Matsushige, *Appl. Phys. Lett.* 78 (2001) 3714.
- [5] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fischer, R.E. Smalley, *Science* 273 (1996) 483.
- [6] X.P. Tang, A. Kleinhammes, H. Shimoda, L. Fleming, C. Bower, S. Sinha, O. Zhou, Y. Wu, *Science* 288 (2000) 492.
- [7] J. Liu, A. Rinzler, H. Dai, J. Hafner, A.R. Bradley, P. Boul, A. Lu, T. Iverson, A.K. Shelimov, C. Huffman, F. Rodriguez-Macias, Y. Shon, R. Lee, D. Colbert, R.E. Smalley, *Science* 280 (1998) 1253.