

Carbon nanotube thin films with ordered structures

Chunsheng Du,^a Jeff Yeh^b and Ning Pan*^a

Received 14th October 2004, Accepted 19th November 2004

First published as an Advance Article on the web 8th December 2004

DOI: 10.1039/b414682d

Carbon nanotube thin films with ordered structures have been developed from a highly concentrated suspension of nanotubes; this is shown to be an attractive approach to fabricating electrodes for high power density supercapacitors.

Owing to their unique electrical and mechanical properties, carbon nanotubes have aroused a great deal of research interest, and a wider range of potential applications have been proposed. For example, carbon nanotubes have been used as electrode materials for rechargeable batteries,^{1–4} supercapacitors,^{5–10} and the reinforcement of nanocomposites.^{11–14} Many of these applications require manipulation of the nanotubes (NTs) in solution or suspension.

Several groups^{15–17} have investigated the dispersion of carbon nanotubes in different solvents and great progress has been made. However, the solubility of carbon nanotubes in the solvents studied is still low and, not surprisingly, the bulk assemblies of nanotubes or fabrication of macro-scale nanostructured materials have been hindered by this lack of solubility in common organic solvents. Alternatively, dispersing nanotubes uniformly in different solvents will facilitate the manipulation of carbon nanotubes and open new doors to many potential applications. Therefore, it is of both theoretical and practical significance to study the dispersion behaviour of carbon nanotubes.

We report here a novel way of preparing a highly concentrated colloidal suspension of carbon nanotubes by combining the oxidation and sonication of nanotubes, and its application to fabricating thin films with ordered structures for use as electrodes of high power density supercapacitors.

The carbon nanotubes used in this study are functionalized multi-walled carbon nanotubes.† Among the solvents studied we found that DMF is the best solvent to prepare high concentration suspensions, followed by distilled water. The functionalized carbon nanotubes can be easily dispersed in either distilled water, a mixture of water and methanol, or DMF at a concentration of 5 mg ml⁻¹. Suspension with an extremely high concentration (25 mg ml⁻¹) can be obtained by prolonging the sonication time in DMF. In comparison, the concentration of the suspension is only 1 mg ml⁻¹ when ethanol was used.

All the suspensions thus prepared remain stable for many months with no aggregation at all precipitated over time. As has been demonstrated previously,¹⁸ the oxidation of carbon nanotubes produces a negatively charged surface, particularly through the ionization of acidic surface groups. The resulting electrostatic repulsion among the nanotubes leads to a dramatic increase in the stability of the colloidal suspension.

Fig. 1 shows the SEM images of the surface of nanotube films prepared by depositing the colloidal suspension of NTs/water and

NTs/ethanol. As can be seen, the nanotubes in Fig. 1(a) show clear local alignment, as opposed to those in Fig. 1(b). In agreement with the concentration of the suspensions, the packing density in the film from the NTs/ethanol suspension is much lower than that of the film from the NTs/water suspension. We speculate that the electrostatic repulsion between the nanotubes and the high concentration of nanotubes in the suspension are the reasons for forming the ordering structure of the thin films. This was also the case in the films fabricated from a highly concentrated NTs/DMF suspension, where considerable alignment of nanotubes was observed [Fig. 2(a)]. We also found that, by heating the NTs film and the substrate in a furnace, the whole NTs film can be peeled off the substrate very easily due to their mismatch in thermal expansion, indicating that the film is very flexible and can be readily handled. In addition to the alignment within the plane, there was also alignment of the nanotubes parallel to the plane of the film. To illustrate this effect, we intentionally scratched the film fabricated from the NTs/DMF suspension. The arrow in Fig. 2(a) shows the scratching direction. It should be noticed that many pleats were formed [Fig. 2(b)] simply because the scratching pushed a fraction of the thin film to the end, again revealing the coherent structure and flexible nature of the nanotube film. A higher resolution image of the pleats [Fig. 2(c)] clearly shows that the nanotubes at the bottom of the film (now on the surface of the pleats) are also well aligned. Shown in Fig. 2(d) is the SEM image of the edge of the film that is perpendicular to the scratching

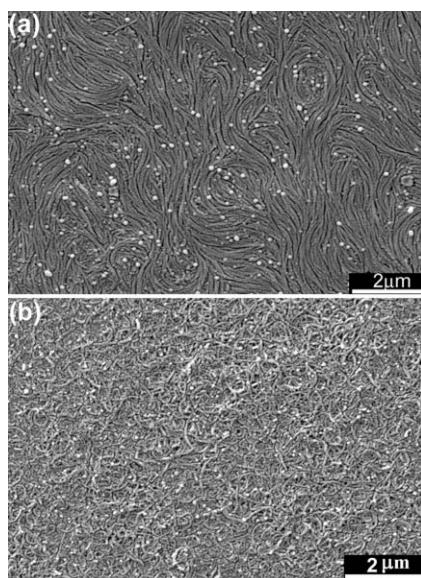


Fig. 1 SEM images showing the surfaces of nanotube films prepared from suspensions using different solvents: (a) distilled water (b) ethanol.

*npan@ucdavis.edu

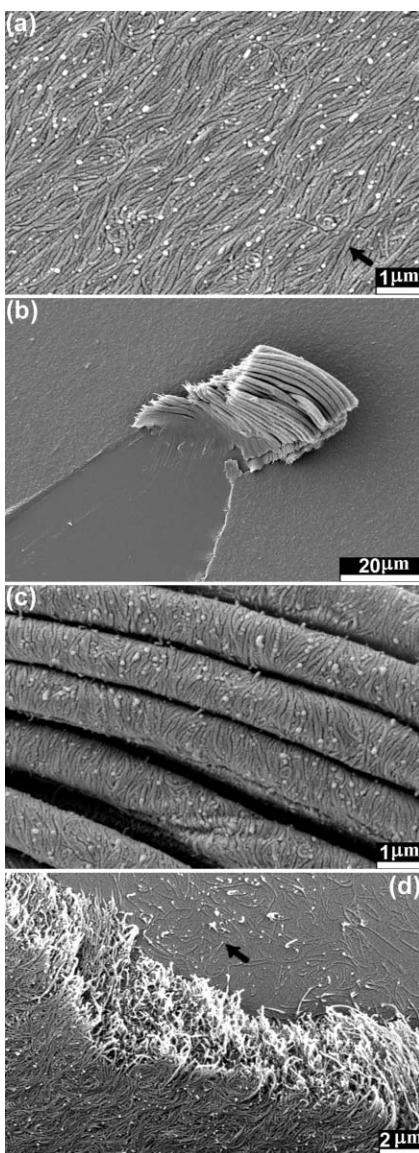


Fig. 2 SEM images of the nanotube film fabricated from the NTs/DMF suspension, showing: (a) the surfaces of the films; (b) and (c) the pleats at the end of a scratch; and (d) the cross-section of the film.

direction (shown by the arrow in the image). It can be seen that almost all of the nanotubes in the films are parallel to the plane of the film, and are aligned in the same way as that of the nanotubes on the surface of the film. The nanotubes randomly lying on the wafer are those tubes that were left behind by the scratching.

Owing to the coherent structure and flexible nature of the thin films thus fabricated, these films have the advantage that no binder is needed to form films on a desired substrate, and thus are promising electrode materials for supercapacitors.

For this electrochemical application study, two electrodes were prepared by depositing 0.1 ml of suspension (concentration: 5 mg of carbon nanotubes in 1 ml of DMF) on two 12×12 mm nickel foils (as current collector) respectively and followed by drying at room temperature. 6N KOH was used as the electrolyte. A glass fiber filter paper immersed in the electrolyte was used as the separator and was placed between the two electrodes. The cyclic

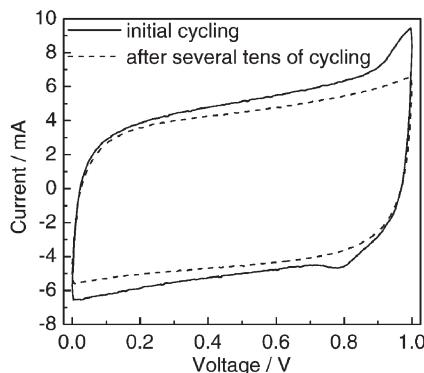
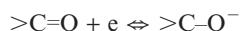
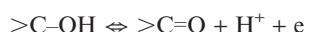


Fig. 3 Cyclic voltammograms with a scan rate of 750 mV s^{-1} of an assembled supercapacitor using the nanotube thin films as electrodes.

voltammetry test was performed with a Potentiostat/Galvanostat (EG&G Princeton Applied Research, Model 263A).

Fig. 3 shows the cyclic voltammogram with a very high scan rate of 750 mV s^{-1} on the assembled capacitor. It was well known that the shape of the loop of the capacitor should be rectangular provided that there are no internal, interfacial and contact resistances.¹⁹ Large resistance distorts the loop, resulting in a narrower loop with an oblique shape, especially at high scan rate. As shown in Fig. 3, during the initial cycling the CV of the capacitor using the ordered films as electrodes is still very close to the ideally rectangular shape even at such a high scan rate of 750 mV s^{-1} , except that there is a strong oxidation peak at 0.9–1.0 V and a reduction peak around 0.8 V. The peaks are attributed to the following redox reactions due to the functional groups on the nanotubes:²



It should also be noted that both peaks gradually diminished after several tens of cycling, probably due to the removal of those functional groups. However, the CV curve still presents a quite rectangular shape that is a clear proof of well developed capacitance properties.

The power density can be estimated from the inner integrated area (current \times voltage).⁵ A very high specific power density of about 17 kW kg^{-1} was obtained from Fig. 3, indicating that this suspension preparation technique can be used to fabricate supercapacitors for surge-power delivery.

In summary, we have demonstrated the ability to prepare highly concentrated suspensions of carbon nanotubes using different solvents. The nanotube thin films fabricated from these suspensions show an ordered structure and high packing density, and are very flexible. Most importantly, no binder is needed to form the film which makes this technique attractive to fabricate supercapacitors for surge-power delivery; we have obtained a very high specific power density of about 17 kW kg^{-1} .

Financial supports from UC Discovery Grant (ele02_10140) and Missile Defense Agency (MDA) are gratefully acknowledged.

Notes and references

† The multi-walled carbon nanotubes (MWNTs) used for this study were produced by chemical vapour deposition (CVD). Synthesis of MWNTs was conducted in a horizontal quartz tube in a furnace. Catalyst power (Fe/Al₂O₃) for producing MWNTs was placed in a ceramic boat which was then loaded into the tube furnace. Hydrogen was introduced into the furnace before it was heated up to 700 °C. The temperature was held for 30 min during which time ethene was introduced into the quartz tube. Ethene supply was then shut off and the system was cooled to room temperature. The so-obtained powder of Fe/Al₂O₃/MWNTs was treated with a HF aqueous solution and hydrochloric acid at room temperature successively to extract the nanotubes by dissolution of Al₂O₃ and iron particles. The nanotubes were then collected by filtration, washed with distilled water and dried. Purified MWNTs were refluxed with concentrated boiling nitric acid for about 10 h, and then washed with distilled water followed by rinsing with ethanol and drying in air at 60 °C. To prepare the colloidal suspension of carbon nanotubes in different solvents, predetermined refluxed carbon nanotubes were placed in a scintillation vial containing 10 ml of solvent, and the vial was then capped and sonicated for 30 min. Distilled water, ethanol, dimethylformamide (DMF), and a mixture of distilled water and methanol were used as solvents in this study.

Colloidal suspensions were deposited directly onto silicon wafers and dried at room temperature. The microstructures of purified nanotubes were investigated by scanning electron microscopy (FEI XL30-SFEG).

1 B. Gao, A. Kleinhammes, X. P. Tang, C. Bower, L. Fleming, Y. Wu and O. Zhou, *Chem. Phys. Lett.*, 1999, **307**, 153.

2 E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy and F. Beguin, *Carbon*, 1999, **37**, 61.

- 3 H. C. Shin, M. L. Liu, B. Sadanandan and A. M. Rao, *J. Power Sources*, 2002, **112**, 216.
- 4 A. S. Claye, J. E. Fischer, C. B. Huffman, A. G. Rinzler and R. E. Smalley, *J. Electrochem. Soc.*, 2000, **147**, 2845.
- 5 K. H. An, W. S. Kim, Y. S. Park, Y. C. Choi, S. M. Lee, D. C. Chung, D. J. Bae, S. C. Lim and Y. H. Lee, *Adv. Mater.*, 2001, **13**, 497.
- 6 C. M. Niu, E. K. Sichel, R. Hoch, D. Moy and H. Tennent, *Appl. Phys. Lett.*, 1997, **70**, 1480.
- 7 B. J. Yoon, S. H. Jeong, K. H. Lee, H. S. Kim, C. G. Park and J. H. Han, *Chem. Phys. Lett.*, 2004, **388**, 170.
- 8 J. N. Barisci, G. G. Wallace and R. H. Baughman, *J. Electroanal. Chem.*, 2000, **488**, 92.
- 9 L. Diederich, E. Barborini, P. Piseri, A. Podesta, P. Milani, A. Schneuwly and R. Gallay, *Appl. Phys. Lett.*, 1999, **75**, 2662.
- 10 C. Y. Liu, A. J. Bard, F. Wudl, I. Weitz and J. R. Heath, *Electrochem. Solid State Lett.*, 1999, **2**, 577.
- 11 J. N. Coleman, S. Curran, A. B. Dalton, A. P. Davey, B. McCarthy, W. Blau and R. C. Barklie, *Phys. Rev. B*, 1998, **58**, R7492.
- 12 C. Park, Z. Ounaies, K. A. Watson, R. E. Crooks, J. Smith, Jr., S. E. Lowther, J. W. Connell, E. J. Siochi, J. S. Harrison and T. L. St. Clair, *Chem. Phys. Lett.*, 2002, **364**, 303.
- 13 J. Sandler, M. S. P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte and A. H. Windle, *Polymer*, 1999, **40**, 5967.
- 14 E. T. Thostenson and T. W. Chou, *J. Phys. D: Appl. Phys.*, 2002, **35**, L77.
- 15 J. L. Bahr, E. T. Mickelson, M. J. Bronikowski, R. E. Smalley and J. M. Tour, *Chem. Commun.*, 2001, 193.
- 16 J. Chen, A. M. Rao, S. Lyuksyutov, M. E. Itkis, M. A. Hamon, H. Hu, R. W. Cohn, P. C. Eklund, D. T. Colbert, R. E. Smalley and R. C. Haddon, *J. Phys. Chem. B*, 2001, **105**, 2525.
- 17 W. Zhao, C. H. Song and P. E. Pehrsson, *J. Am. Chem. Soc.*, 2002, **124**, 12 418.
- 18 K. Esumi, M. Ishigami, A. Nakajima, K. Sawada and H. Honda, *Carbon*, 1996, **34**, 279.
- 19 B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, New York, 1999.