

Flow Field Induced Steady Alignment of Oxidized Multi-walled Carbon Nanotubes

Ai Zhong XU^{1,2,3}, Ming Shu YANG^{2*}, Qiang WU¹, Xiao Ming HU³, Lei JIANG^{3*}

¹School of Resources and Safety Engineering, China University of Mining & Technology, Beijing 100083

²Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Science, Beijing 100080

³Key Laboratory of Organic Solid, Institute of Chemistry, Chinese Academy of Science, Beijing 100080

Abstract: The steady ordered micro-ribbons of oxidized multi-walled carbon nanotubes (MWNTs) were obtained through micro-aperture PTFE membrane by vacuum filtration. After treatment by mixture of concentrated nitric acid and sulfuric acid, the surface functional groups modified MWNTs can be easily dispersed to form a homogeneous suspension. It is found that the steady micro-ribbons existed in the films obtained by vacuum filtration of the suspension. The filtration formed steady flow field and induced steady alignment of oxidized MWNTs. The chemical treatment of MWNTs forming strong interaction between MWNTs is necessary to keep steady of the micro-ribbons microstructure.

Keywords: Carbon nanotubes (CNTs), oxidation, alignment, flow fields.

Carbon nanotubes (CNTs) were discovered by Iijima in 1991, and then have attracted the fancy of many scientists worldwide. Their small size and unusual physical properties make them become a unique material with a whole range of promising applications¹. Many applications require aligned, manipulative or controllable assembled CNTs, and some advances have been obtained. In general, there are two methods to achieve this aim: one is the chemical vapor deposition grown aligned CNTs bundles; another is the field (flow, shear, electric or magnetic *etc.*) induced aligned CNTs. The later method needs two factors: external field and ability of CNTs response to this field²⁻¹³. However, few studies have been done on steady alignment of such structure of CNTs. In this paper, we reported the ordered micro-ribbons of oxidized multi-walled carbon nanotubes (MWNTs), which were prepared by vacuum filtration through micro-aperture PTFE membrane. The reasons of steady alignment and the formation of these ribbons were discussed.

The MWNTs were provided by Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences (China PR), with a purity of more than 95% and an average external diameter of 20-40 nm and length of 0.5-500 μm ¹⁴. The raw MWNTs were

*E-mail: yms@iccas.ac.cn; jianglei@iccas.ac.cn

putted into a mixture of concentrated nitric acid and sulfuric acid (3:1 volume ratio), ultrasonicated at 60°C for 6 h, heated in a boiling water bath for 1 h, and then cooled to room temperature. The cooled mixture was diluted with distilled water first, and then diluted with absolute ethanol. The final diluted mixture was filtered under vacuum in a Buchner filter with a 100 nm micro-aperture PTFE membrane, the filter cake was washed with absolute ethanol until the pH parameter of filtrate was equal to 7, and finally washed with acetone until the solution was colorless. Thus, the paper-shape oxidized MWNTs film was formed on the PTFE membrane. The obtained film was easily peeled from the PTFE membrane and dried for 24 h under vacuum. As a comparison, the raw MWNTs can only form incompact powder on the PTFE membrane.

Figure 1 FT-IR spectroscopy of MWNTs: (a) raw , (b) oxidized.

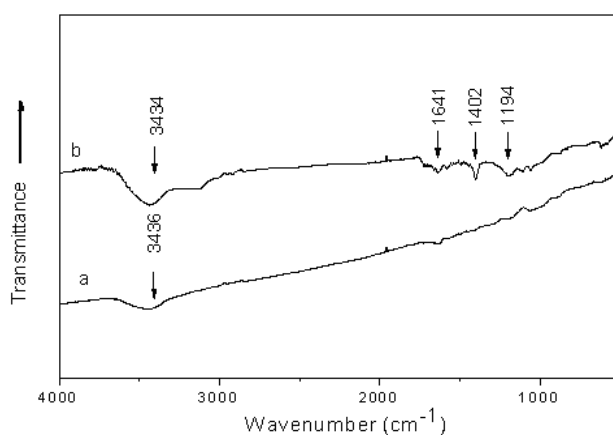
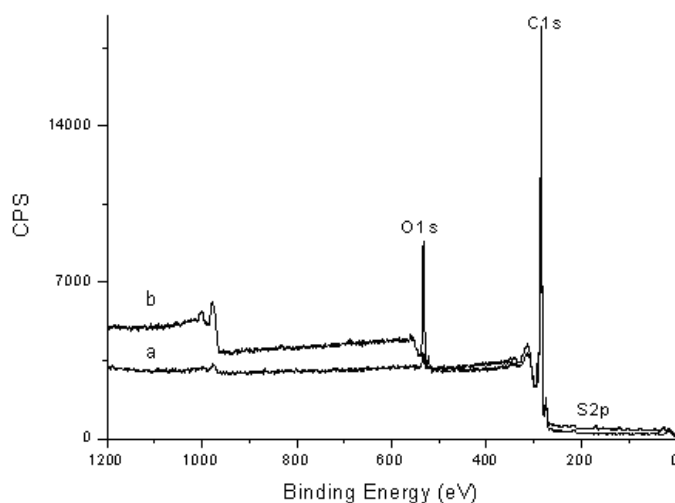


Figure 2 XPS spectra of MWNTs: (a) raw, (b) oxidized.



The oxidation results of MWNTs were determined by the Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectrum (XPS). After the oxidation the peaks at 3434 cm^{-1} , 1641 cm^{-1} , 1194 cm^{-1} are appeared in FT-IR of MWNTs (see **Figure 1**). This indicates that carboxylic, hydroxyl and sulfuric functional groups are chemically bonded to the surface of the MWNTs. The XPS results show that the atom ratio O1s/C1s of MWNTs increased from 0.018 to 0.142, and 0.6 % atom content of sulfur appeared after the mixed acid treatment (see **Figure 2**).

The oxidized MWNTs films were ultrasonic treated in ethanol, dropped on the vitreous flake, and observed with an optical microscope (OM). The microstructure of MWNTs has also been observed by a field emission scanning electron microscope (FE-SEM). As shown in **Figure 3** and **Figure 4**: the raw MWNTs have floccules structure, they are made up of randomly oriented bundles; while the mixed acid treated MWNTs have micro-ribbon structure, and the oxidized MWNTs have well-ordered structure.

Figure 3 OM images of MWNTs: (a) raw, (b) and (c) oxidized

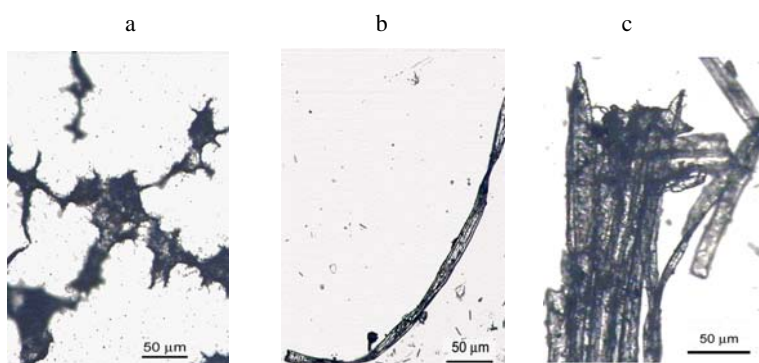
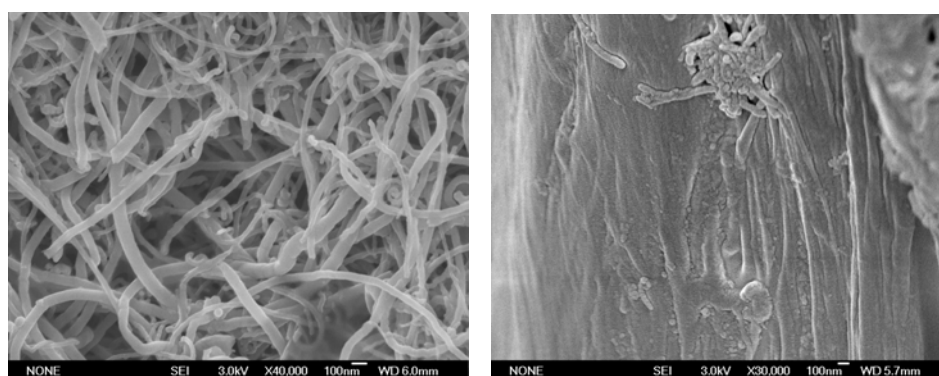


Figure 4 FE-SEM images of MWNTs: (a) raw, (b) oxidized



The functional groups of the oxidized MWNTs provide additional interactions, which produce a compact alignment of MWNTs under the flow field during the vacuum filtration. The ordered micro-ribbon structure of oxidized MWNTs is steady even after ultrasonic treatment in the ethanol. After the heat treatment at 500°C for 2 h, the oxidized MWNTs form only flocculated structure, but not the ordered micro-ribbon structure. It is clear that this behavior is due to remove the functional groups from the surface of oxidized MWNTs after the heating treatment¹⁵.

In summary, the steady alignment micro-ribbons of oxidized MWNTs could be easily obtained through flow field by vacuum filtration with no necessity of surfactant or high temperature, due to the suspended oxidized MWNTs response to flow fields during the vacuum filtration. The chemical modification of MWNTs and introduction of a flow field are two determinative factors in the formation of such ordered bundles structure of MWNTs. In addition, the shortening of length of MWNTs during the oxidation may also favorite the orientation of MWNTs^{16,17}. Further studies on exploring the effect of the chemical treatment, microstructure by external field and properties of the ordered CNTs will be interested.

References

1. M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris., *Carbon Nanotubes: Synthesis, Structure, Properties, and Application*, Springer, Berlin Heidelberg, **2001**.
2. P. Poulin, B. Vigolo, P. Launois, *Carbon*, **2002**, *40*, 1741.
3. B. Vigolo, A. Pénicaud, Coulon, *et al.*, *Science*, **2000**, *290*, 1331.
4. Y. H. Li, C.L. Xu, B.Q. Wei, *et al.*, *Chem. Mater.*, **2002**, *14*, 483.
5. H. H. Gommans, J. W. Alldredge, H. Tashiro, *et al.*, *J. Appl. Phys.*, **2000**, *88*, 2509.
6. B. W. Smith, Z. Benes, D. E. Luzzi, *et al.*, *Appl. Phys. Lett.*, **2000**, *77*, 663.
7. J. E. Fischer, W. Zhou, J. Vavro, *et al.*, *J. Appl. Phys.*, **2003**, *93*, 2157.
8. J. Hone, M. C. Llaguno, N. M. Names, *et al.*, *Appl. Phys. Lett.*, **2000**, *77*, 666.
9. X. H. Li, J. Zhang, Q. W. Li, *et al.*, *Carbon*, **2003**, *41*, 598.
10. X. Gao, T. J. Hu, L. Q. Liu, *et al.*, *Chem. Phys. Lett.*, **2003**, *370*, 661.
11. Y. Ando, X. L. Zhao, K. Hirahara, *et al.*, *Chem. Phys. Lett.*, **2000**, *323*, 580.
12. Z. L. Li, P. Dharap, S. Nagarajaiah, *et al.*, *Adv. Mater.*, **2004**, *16*, 640.
13. M. J. Casavant, D. A. Walters, J. J. Schmidt, *et al.*, *J. Appl. Phys.*, **2003**, *93*, 2153.
14. Shenzhen Nanotech Port Co. Ltd, <http://www.seasunnano.com/ntp/specification.htm>, accessed on October 30, **2004**.
15. A. Kuznetsova, D. B. Mawhinney, V. Naumenko, *et al.*, *Chem. Phys. Lett.*, **2000**, *321*, 292.
16. Z. J. Shi, Y. F. Lian, X. H. Zhou, *et al.*, *Chem. Commun.*, **2000**, *6*, 461.
17. T. Saito, K. Matsushige, K. Tanaka, *Phys. B*, **2002**, *323*, 280.

Received 29 June, 2004