Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 177 (2004) 4394–4398

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Functionalized carbon nanotubes containing isocyanate groups

Chungui Zhao, Lijun Ji, Huiju Liu, Guangjun Hu, Shimin Zhang,
Mingshu Yang*, Zhenzhong Yang*

*Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Number 2,
Zhongguancun North 1 St., Beijing 100080, China*

Received 3 August 2004; received in revised form 10 September 2004; accepted 14 September 2004
Available online 10 November 2004

Abstract

Functionalized carbon nanotubes containing isocyanate groups can extend the nanotube chemistry, and may promote their many potential applications such as in polymer composites and coatings. This paper describes a facile method to prepare functionalized carbon nanotubes containing highly reactive isocyanate groups on its surface via the reaction between toluene 2,4-diisocyanate and carboxylated carbon nanotubes. Fourier-transformed infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) confirmed that reactive isocyanate groups were covalently attached to carbon nanotubes. The content of isocyanate groups were determined by chemical titration and thermogravimetric analysis (TGA).

Keywords: Carbon nanotubes; Functionalization; Isocyanate group; Reactivity

1. Introduction

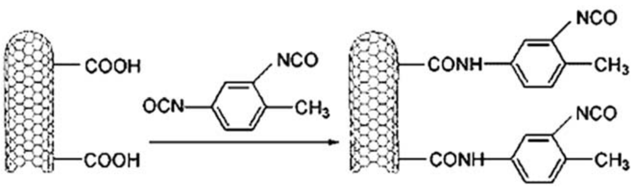
Carbon nanotubes have a wide range of potential applications due to their unique mechanical and electronic properties [1–3]. Many applications require the dispersibility and chemical activity of the carbon nanotubes, thus their surface modification and/or functionalization have attracted increasing attention in recent years [4–6]. Functionalization would enrich their properties [7–10]. Modification of carbon nanotubes by covalent or non-covalent molecules can improve their dispersibility in liquid media [11–18] and the compatibility with polymer matrixes [16–20].

The tested covalent modifications of carbon nanotubes have been well summarized in several review papers [21–24]. In general, major approaches include: (i) amidation or esterification of carboxylated carbon nanotubes, (ii) side-wall covalent attachment of functional groups directly to the pristine carbon nanotubes. In this paper, we are mainly concerned with the functionalization of carbon nanotubes containing isocyanate groups. Isocyanate group has a high reactivity, a wealth of chemistry and can react with many chemicals, such as alcohols, amines and carboxylic acid, etc. [25]. Carboxylated multi-walled carbon nanotubes (MWNT–COOH) are chosen as a starting model nanotube. From the viewpoint of molecular design, toluene 2,4-diisocyanate has been selected as the amidating agent to react with the carboxyl groups on the MWNT–COOH to prepare functionalized multi-walled carbon nanotubes containing isocyanate groups (MWNT–NCO). As shown in Scheme 1, due to steric effect, the *p*-isocyanate group is preferentially covalent with the *o*-isocyanate group reserved. Based on the wealth chemistry of isocyanate groups, the functionalized carbon nanotubes containing isocyanate groups can thus extend nanotube chemistry, and may be promising to prepare for example, polymer/carbon nanotube composites and coatings [26,27].

---

*Corresponding author. Fax: +86 10 6255 9373.
E-mail addresses: yms@iccas.ac.cn (M. Yang), yangzz@iccas.ac.cn (Z. Yang).

0022-4596/$ - see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2004.09.036



Scheme 1. Schematic preparation of the functionalized carbon nanotubes containing isocyanate groups.

2. Experimental

Pristine MWNT, purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China), were first pre-treated using mixed acid according to a conventional method [28] to get MWNT–COOH, and then followed by amidation with toluene 2,4-diisocyanate to obtain functionalized multi-walled carbon nanotubes containing isocyanate groups (MWNT–NCO). In the amidation reaction, 0.2 g of MWNT–COOH was dispersed in 20 mL anhydrous acetone under stirring, and then 0.5 g toluene 2,4-diisocyanate was added. The functionalization was undertaken in a dry nitrogen atmosphere at 50 °C for 24 h. The functionalized MWNT was filtered through a polytetrafluoroethylene (PTFE) membrane and washed with anhydrous acetone to completely remove the residuals. After being dried in vacuum at 50 °C for 4 h, the functionalized multi-walled carbon nanotubes containing isocyanate groups (MWNT–NCO) were obtained.

The functionalized MWNT were characterized by Fourier-transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Perkin–Elmer System 2000 FTIR spectrometer was employed on the KBr pellets. XPS were conducted on a ESCALab220I-XL using monochromatized Al *K*α radiation ($h\nu = 1486.6\,\text{eV}$). JEOL S-4300F field emission scanning electron microscope was applied to observe the morphology of MWNT–NCO. Perkin–Elmer TGA-7 was used to measure the thermal behavior of the nanotubes in N_2 atmosphere, and the scanning rate is 20 °C/min. Dispersibility behavior was observed by ultrasonically dispersing 0.5 mg nanotubes in 5 ml anhydrous toluene in glass bottles for 2 h following by storage for varied time.

The content of carboxyl groups in MWNT–COOH were determined by acid–base titration according to the literature [29]. The content is evaluated by

$$[-\mathrm{COOH}] = \frac{M_{-\mathrm{COOH}}}{W_1 - 45.02 \times M_{-\mathrm{COOH}}} \times 100\%, \qquad (1)$$

where [–COOH] is the content of –COOH (mol/g), $M_{-\mathrm{COOH}}$ is moles of –COOH, W_1 is the weight (g) of MWNT–COOH, and 45.02 is the molecular weight of –COOH. The content value is calculated basing on the pure carbon nanotubes (organic weight is subtracted).

The content of isocyanate groups in MWNT–NCO was titrated through the following rout: a given weight (W_2, g) of MWNT–NCO, and an excessive amount of 0.1 M di-*n*-butylamine solution in anhydrous acetone was added into an air-tight flask to react at room temperature for 6 h under magnetical stirring. The isocyanate groups have reacted completely with di-*n*-butylamine to form urea. Then the dispersion was filtered through the PTFE membrane and well washed with anhydrous acetone. The filtrate was collected and titrated back using 0.1 M HCl solution to measure the residual amount of di-*n*-butylamine in the filtrate. At the same time, a blank experiment, without MWNT–NCO sample, was done. The content of isocyanate groups attaching to MWNT was calculated by

$$[-\mathrm{NCO}] = \frac{M_{-\mathrm{NCO}}}{W_2 - 175.17 \times M_{-\mathrm{NCO}}} \times 100\%, \qquad (2)$$

where [–NCO] is the content of –NCO (mol/g), $M_{-\mathrm{NCO}}$ is moles of –NCO on the MWNT–NCO, and 175.17 is the molecular weight of organic attachment in MWNT–NCO. The data reported here are the average of three successful tests, and the error is ca. ±3%.

3. Results and discussion

3.1. FTIR

The structure in Scheme 1 is confirmed by FTIR spectra of MWNT–COOH and MWNT–NCO as shown in Fig. 1. The peaks at 1646 and 1580 cm^{-1} are assigned to C=C stretching, which originate from inherent structure of carbon nanotubes. In curve *A*, the peaks at 1714 and 1223 cm^{-1} are in correspondence to C=O, C–O stretching, respectively, indicated the existence of carboxyl groups in MWNT–COOH. For MWNT–NCO (curve *B*), there is a peak at 2264 cm^{-1}, which is characteristic for asymmetric stretching of isocyanate groups. The peaks at 1675 and 1223 cm^{-1} are ascribed to C=O, C–N stretching of amide groups, respectively. Peaks at 2900 and 2825 cm^{-1} are related to C–H stretching of methyl groups.

3.2. XPS

MWNT–COOH and MWNT–NCO have also been characterized by XPS (Fig. 2). There is a large quantity of oxygen in MWNT–COOH, which belongs to carboxyl groups. In the spectrum of MWNT–NCO, the peak of N 1s appears at 400 eV, and its high-resolution spectrum reveals two peaks at 399.4 and 400.2 eV, which are ascribed to –CONH– and –NCO,

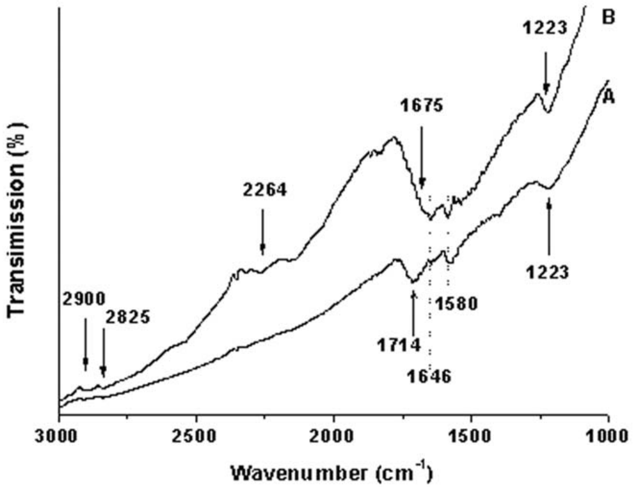


Fig. 1. FTIR spectra of (A) MWNT–COOH and (B) MWNT–NCO.

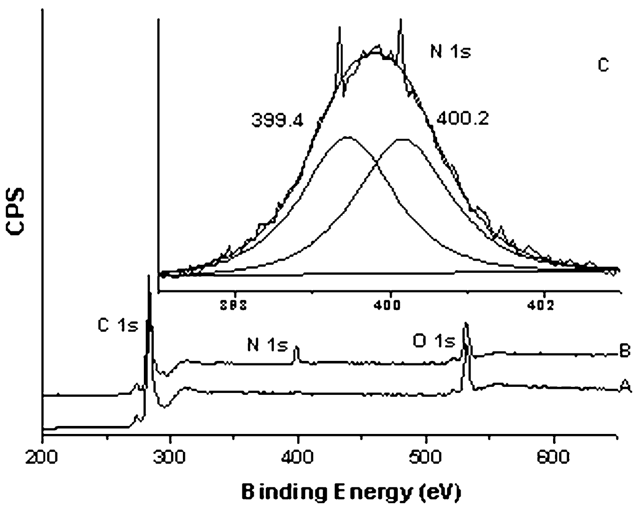


Fig. 2. XPS spectra of (A) MWNT–COOH, (B) MWNT–NCO and (C) N 1 s high-resolution for MWNT–NCO.

respectively. The [–NCO]/[–CONH–] is 1:1 measured through their area ratio.

3.3. Dispersibility

The dispersibility of MWNT–COOH is remarkably changed after the modification. MWNT–COOH are hydrophilic and well dispersed in water. However, some bubbles are released when MWNT–NCO contact water, indicating MWNT–NCO are highly reactive and have reacted with water. In anhydrous toluene, MWNT–COOH agglomerate and sediment at the bottom (Fig. 3, left), but MWNT–NCO are well dispersed (Fig. 3, right).

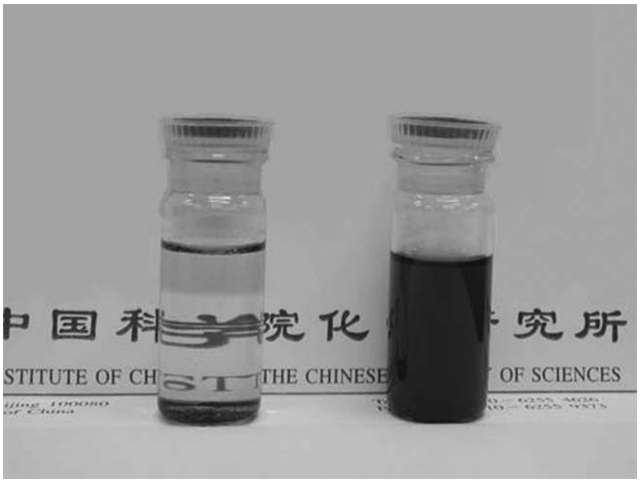


Fig. 3. Dispersibility behavior of MWNT–COOH (left) and MWNT–NCO (right) in anhydrous toluene after stored for 24 h.

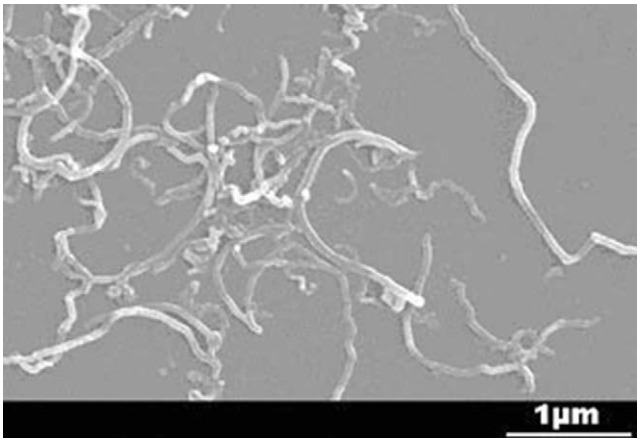


Fig. 4. Field emission scanning electron micrograph of MWNT–NCO.

3.4. SEM

The tubular structure of carbon nanotubes is well retained after functionalization. This is confirmed by the morphology observation of MWNT–NCO under SEM (Fig. 4).

3.5. Chemical titration

The functional groups attached to MWNT are quantitatively determined by titration. [–COOH] in MWNT–COOH is 2.5×10^{-3} mol/g (values calculated by the weight of pure MWNT). In MWNT–NCO, [–NCO] is 2.6×10^{-3} mol/g, which almost equals to the value of carboxyl groups in MWNT–COOH. This shows that carboxyl groups in MWNT–COOH have 1:1 stoichiometrically reacted with toluene 2,4-diisocyanate as shown in Scheme 1. The carboxylation of carbon

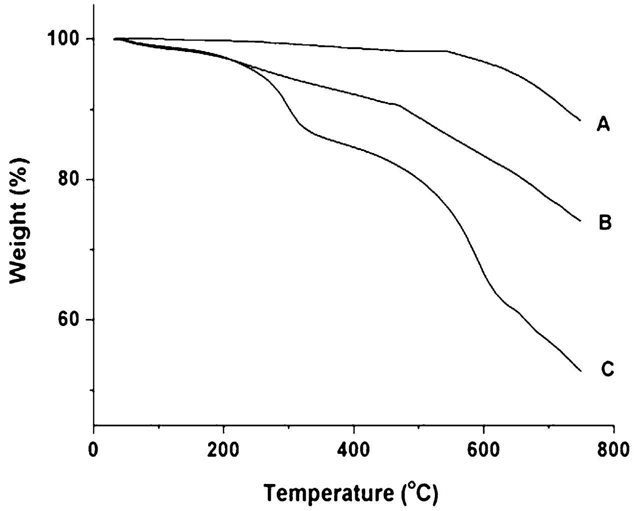


Fig. 5. TGA curves of (A) the pristine MWNT, (B) MWNT–COOH and (C) MWNT–NCO in N_2 atmosphere.

nanotubes is facile and the content of carboxyl groups attached can be easily controlled by the kind of acids, acid concentration, and the duration of acid treatment. This is to say, the present approach for preparing functionalized carbon nanotubes containing isocyanate groups is facile and controllable. From the content of isocyanate groups, the organic attachment content in MWNT–NCO has been calculated, which is 31.5 wt% (based on the total weight of MWNT–NCO).

One of the isocyanate group in toluene 2,4-diisocyanate have 1:1 stoichiometrically reacted with the carboxyl group of MWNT–COOH, and another reserved, indicating MWNT–NCO were successfully prepared. Due to the steric effect of methyl group, the reactivity of the *p*-isocyanate group in toluene 2,4-diisocyanate is higher than that of the *o*-isocyanate group. So for the most of MWNT–NCO, it should be the *p*-isocyanate group reacted with carboxyl group to form chemical bonding and the *o*-isocyanate group reserved (just as Scheme 1). However, there is also a small part of MWNT–NCO in which the *o*-isocyanate group reacted but the *p*-isocyanate group reserved.

3.6. TGA

Thermal behavior of the nanotubes is measured by TGA (Fig. 5). Onset temperatures of MWNT–COOH (460 °C) and MWNT–NCO (239 °C) become dramatically lower due to the organic attachment compared with that of the pristine MWNT (615 °C). The attached organic content is estimated according to the residual weight of the functionalized MWNT at 600 °C. The estimated organic attachment content of MWNT–NCO is 31 wt%, consistent with the titration result.

4. Conclusions

In conclusion, functionalized carbon nanotubes containing isocyanate groups were prepared by reaction between toluene 2,4-diisocyanate and carboxylated carbon naotubes. This method is facile, and organic attachment content is controllable. Functionalized carbon nanotubes containing isocyanate groups can extend nanotube chemistry, and may be promising in applications such as polymer/carbon nanotube composites, coatings, as well as many others.

Acknowledgment

Z. Yang thanks for the partial support by NSF of China (50325313).

References

[1] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Science 297 (2002) 787–792.
[2] C.N.R. Rao, B.C. Satishkumar, A. Govindaraj, M. Nath, Chem. Phys. Chem. 2 (2001) 78–105.
[3] O. Zhou, H. Shimoda, B. Gao, S. Oh, L. Fleming, G. Yue, Acc. Chem. Res. 35 (2002) 1045–1053.
[4] A. Hirsch, Angew. Chem. Int. Ed. 41 (2002) 1853–1859.
[5] Y.P. Sun, K. Fu, Y. Lin, W. Huang, Acc. Chem. Res. 35 (2002) 1096–1104.
[6] K.S. Coleman, S.R. Bailey, S. Fogden, M.L.H. Green, J. Am. Chem. Soc. 125 (2003) 8722–8723.
[7] S.S. Wong, E. Jolselevich, A.T. Wooley, C.L. Cheung, C.M. Lieber, Nature 394 (1998) 52–55.
[8] J.E. Riggs, Z. Guo, D.L. Carroll, Y.P. Sun, J. Am. Chem. Soc. 122 (2000) 5879–5880.
[9] J.L. Bahr, J. Yang, D.V. Kosynkin, M.J. Bronikowski, R.E. Smalley, J.M. Tour, J. Am. Chem. Soc. 123 (2001) 6536–6542.
[10] A. Star, Y. Liu, K. Grant, L. Ridvan, J.F. Stoddart, D.W. Steuerman, M.R. Diehl, A. Boukai, J.R. Heath, Macromolecules 36 (2003) 553–560.
[11] J. Chen, M.A. Hamon, H. Hu, Y. Chen, A.M. Rao, P.C. Eklund, R.C. Haddon, Science 282 (1998) 95–98.
[12] W. Huang, S. Fernando, Y. Lin, B. Zhou, L.F. Allard, Y.P. Sun, Langmuir 19 (2003) 7084–7088.
[13] M. Holzinger, J. Abraham, P. Whelan, R. Graupner, L. Ley, F. Hennrich, M. Kappes, A. Hirsch, J. Am. Chem. Soc. 125 (2003) 8566–8580.
[14] H. Pan, L. Liu, Z.X. Guo, L. Dai, F. Zhang, D. Zhu, R. Czerw, D.L. Carroll, Nano Lett. 3 (2003) 29–32.
[15] H. Peng, L.B. Alemany, J.L. Margrave, V.N. Khabashesku, J. Am. Chem. Soc. 125 (2003) 15174–15182.
[16] Y. Qin, L. Liu, J. Shi, W. Wu, J. Zhang, Z.X. Guo, Y. Li, D. Zhu, Chem. Mater. 15 (2003) 3256–3260.
[17] A. Eitan, K. Jiang, D. Dukes, R. Andrews, L.S. Schadler, Chem. Mater. 15 (2003) 3198–3201.
[18] D.E. Hill, Y. Lin, A.M. Rao, L.F. Allard, Y.P. Sun, Macromolecules 35 (2002) 9466–9471.
[19] C.A. Dyke, J.M. Tour, J. Am. Chem. Soc. 125 (2003) 1156–1157.
[20] X. Gong, J. Liu, S. Baskaran, R.D. Voise, J.S. Young, Chem. Mater. 12 (2000) 1049–1052.
[21] S. Banerjee, M.G.C. Kahn, S.S. Wong, Chem. Eur. J. 9 (2003) 1898–1908.

[22] S. Niyogi, M.A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M.E. Itkis, R.C. Haddon, Acc. Chem. Res. 35 (2002) 1105–1113.

[23] D. Tasis, N. Tagmatarchis, V. Georgakilas, M. Prato, Chem. Eur. J. 9 (2003) 4000–4008.

[24] J.L. Bahr, J.M. Tour, J. Mater. Chem. 12 (2002) 1952–1958.

[25] R.T. Morrison, R.N. Boyd, Organic Chemistry, fourth ed, Allyn and Bacon Inc., Boston, 1983 (p. 844).

[26] K. Fujili, N. Tsubokawa, Y. Sone, Polym. J. 22 (1990) 661–670.

[27] D. Neumann, M. Fisher, L. Tran, J.G. Matisons, J. Am. Chem. Soc. 124 (2002) 13998–13999.

[28] J. Liu, A.G. Rinzler, H. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, Y.S. Shon, T. Randall Lee, D.T. Colbert, R.E. Smalley, Science 280 (1998) 1253–1256.

[29] H. Hu, P. Bhowmik, B. Zhao, M.A. Hamon, Phys. Lett. B 345 (2001) 25–28.