Adsorption of Nitrobenzene Using Short Open-Ended Carbon Nanotubes as Adsorbent

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The microstructure changes of carbon nanotubes modified by mechanical ball milling and the effect on the adsorption of nitrobenzene were studied. The experimental results demonstrated different lengths of short open-ended carbon nanotubes could be prepared by mechanical ball milling. The extent of shortening and opening of carbon nanotubes increased with the milling time. The aggregated pores size of carbon nanotubes sharply decreased after milling, while the size of inner cavity enlarged slightly. The saturated adsorptive amount of carbon nanotubes after milling 30 h for nitrobenzene improved obviously from 19.8 to 41.5 mg g⁻¹ compared to unmilled sample. The capillary condensation on both inner cavity and compressed aggregated pores played an important role in liquid phase adsorption.

Keywords: Carbon nanotubes, Capillary condensation, Nitrobenzene, Adsorption.

INTRODUCTION

Nitrobenzene was widely used as raw materials and intermediates in the industry of organic synthesis¹. A large amount of nitrobenzene had been released into the environment annually due to excessive use and improper disposal. Because of high toxicity on human and the environment, nitrobenzene had been listed as the priority control pollutants by Environmental Protection Agencies of many nations². Hence, great effort had been focused on removal of nitrobenzene from polluted water³⁻⁵.

With the emergence of nano science and technology, research had been initiated to exploit the unusual and unique structure and properties of carbon nanotubes (CNTs)⁶⁻⁸. Their hollow and layered nanosized structures made them a good candidate as adsorbents. Many literature⁹⁻¹⁵ reported that carbon nanotubes had excellent adsorption capacity for various inorganic and organic pollutants such as fluoride, chromium, zinc(II), 1,2-dichlorobenzene, methylene blue, phenanthrene. However, the extensive use of carbon nanotubes remained a strict limitation due to the closed ends with length of micron-scale. As adsorbent, it was well known that opening ends of carbon nanotubes was a key issue¹⁶. Commonly, the carbon nanotubes fabricated by chemical vapor deposition (CVD), were long and had closed ends being entangled together. Ultrasound¹⁷, chemical oxidation¹⁸ and ball milling methods¹⁹ had been employed for cutting and opening ends of carbon nanotubes. Ball milling approach had received much attention,

because it was the efficient, compact and clean process for handling production on a large scale without any chemical or thermal treatment²⁰. Here, we performed a ball milling treatment on carbon nanotubes prepared by the chemical vapor deposition method and studied the effect of ball milling on microstructure of carbon nanotubes. The adsorption capability and mechanism of short open-ended carbon nanotubes for nitrobenzene were also investigated.

EXPERIMENTAL

Preparation of short open-ended CNTs: The mixture of some of carbon nanotubes prepared by chemical vapor deposition method and agate balls were put immediately into a planetary ball milling apparatus with a milling container of dimension of $\Phi 53$ mm $\times$ 59 mm. Ball milling process was carried out for 6-30 h with rotation speed of 140 rpm.

Adsorption study: 0.100 g of modified carbon nanotubes was added to 150 mL sealed conical flasks containing 50 mL of nitrobenzene solution with certain concentration. The flask was subsequently shaken at room temperature with 140 rpm in a incubator shaker with thermostat for 24 h to attain equilibrium. Finally, the residual concentration of nitrobenzene in aqueous solution was determined by Agilent 6890 gas chromatography. The equilibrium amount adsorbed by carbon nanotubes was calculated with following equation:

$$Q_e = (C_0 - C_e)V/m$$

where C_0 and C_e were the initial and equilibrium concentration of adsorbate (mg L^{-1}), V was the volume of solution (L) and m was the weight of carbon nanotubes (g).

Characterization of sample: The microstructure of carbon nanotubes was obtained with the JEM-100S transmission electronic microscope. The specific surface area and pore diameter distributions were determined by low-temperature nitrogen adsorption-desorption using a Micromeritics ASAP 2020 automatic surface area analysis instrument.

RESULTS AND DISCUSSION

Influence of ball milling on microstructure of CNTs:

Table-1 depicted the structure of carbon nanotubes milled for different time. It could be seen that abundant carbon nanotubes shorter than $1\ \mu\text{m}$ formed after 12 h milling. Compared with the as prepared carbon nanotubes, the tangled phenomena of carbon nanotubes milled more than 12 h was clearly reduced and tube tips of the carbon nanotubes were open. The even length of carbon nanotubes further shortened along with the prolonged ball milling time. TEM image of the as prepared carbon nanotubes was presented in Fig. 1a. We discovered that the carbon nanotubes before milling were curved and tangled together. The even length was several tens of micron and most tube tips of the carbon nanotubes were close. From Fig. 1b, it was evidently seen that many short open-ended carbon nanotubes were formed after carbon nanotubes milled for 24 h.

TABLE-1
STRUCTURAL DESCRIPTIONS OF THE CARBON NANOTUBES MILLED FOR DIFFERENT TIME

Carbon nanotubes	Even length	Tube tips	Tangled phenomena
0	Tens of micron	Close	Serious
6	Tens of micron	Close	Serious
12	600-800 nm	Open	Clearly reduced
18	400-600 nm	Open	Clearly reduced
24	300-400 nm	Open	Clearly reduced
30	100-200 nm	Open	Clearly reduced

Fig. 1. TEM images of carbon nanotubes not milled (a) and milled for 24 h (b)

Calculation of the elastic modulus of carbon nanotubes demonstrated that they were extremely rigid in the axial direction but most likely to be distorted in the perpendicular direction. Therefore, carbon nanotubes would be prone to break in perpendicular direction during ball milling process due to the high velocity impact of the agate balls²¹, consequently short open-ended nanotubes could be formed. The rupture of milled nanotubes tended to occur at the sites of structural defects, such as bends, thus also causing the part of carbon nanotubes to be straight. Moreover, ball milling could cause tremendous structural change and make of more defects which would be in favor of further rupture of carbon nanotubes. The specific surface area of carbon nanotubes increased from 192 to 221 $\text{m}^2\ \text{g}^{-1}$ after ball milling for 24 h, which indicated the treatment with ball milling was helpful for opening the tube tips.

Adsorption of nitrobenzene on modified carbon nanotubes: The adsorption capacity of nitrobenzene on carbon nanotubes milled for different time was shown in Table-2. The saturated adsorption amount enhanced remarkably after milling for 12 h, then gradually rose along with increasing milling time. It showed that the adsorption capacity of nitrobenzene on carbon nanotubes improved obviously with the increase of ball milling time. The highest adsorption capacity of the carbon nanotubes milled for 30 h dramatically increased to $41.5\ \text{mg g}^{-1}$ after the sample milled for 30 h, in comparison to that of $19.8\ \text{mg g}^{-1}$ on the unmilled sample.

TABLE-2
EFFECT OF MILLING TIME ON THE ADSORPTIVE CAPACITY OF CARBON NANOTUBES FOR NITROBENZENE

Milling time (h)	0	6	12	24	30
Initial concentration (mg L^{-1})	150.0	150.0	150.0	150.0	150.0
Final concentration (mg L^{-1})	110.5	101.2	74.4	71.8	67.0
Saturated adsorptive amount (mg g^{-1})	19.8	24.4	37.8	39.1	41.5

In general, the adsorptive ability of adsorbent depended on specific surface area of adsorption material. It was worth pointing out that the specific surface area of carbon nanotubes milled for 24 h increased about 15 % but the saturated adsorption amounts increased about 97 % compared with untreated samples. So it was different from the monolayer adsorption. We deduced the enhancement of adsorption capacity of carbon nanotubes for nitrobenzene was mainly attributed to the formation of short open-ended carbon nanotubes but not only the increase of specific surface area. Similar to many straight capillary, short open-ended carbon nanotubes provided more tube interior space and promoted kinetic adsorption rate, which finally resulted in a higher adsorption capacity of carbon nanotubes for nitrobenzene.

Adsorption mechanism: In order to investigate the adsorption mechanism, N_2 adsorption-desorption isotherms and pore size distribution of carbon nanotubes before and after ball milling were measured. Fig. 2 indicated the pore diameters of carbon nanotubes milled for 24 h changed from 30 to 12 nm, which was assigned as aggregated pores in carbon nanotubes. It was thought that the space between the carbon nanotubes had been compressed by collision between agate balls and materials. The diameter of inner pore around 3-4 nm enlarged slightly. Fig. 3 showed the N_2 adsorption-desorption

Fig. 2. Pore diameter distribution of carbon nanotubes before and after milling

Fig. 3. Nitrogen adsorption-desorption isotherms of carbon nanotubes before and after milling

isotherms of carbon nanotubes before and after ball milling. A clearly visible hysteresis loop appeared at the lower relative pressure of $p/p_0 = 0.4$, whereas it did not generate in the isotherm of unmilled carbon nanotubes. Yang *et al.*²² considered that the appearance of hysteresis loop at medium relative pressure was associated with capillary condensation in small mesopores, which was the inner hollow cavity of the short open-ended carbon nanotubes as shown in Fig. 2. From Fig. 3, we also discovered a hysteresis loop occurred at the higher relative pressure of $p/p_0 = 0.85$, which was likely to be due to aggregated pores. Therefore, it is concluded that the increase-ment of adsorption capability was due to the capillary adsorption on both inner cavity and compressed aggregated pores.

Conclusion

Abundant different lengths of short open-ended carbon nanotubes could be prepared by mechanical ball milling. The

extent of shortening and opening was proportional to the milling time. The adsorptive capacity of nitrobenzene improved obviously on carbon nanotubes modified by ball milling. The size of inner pore of carbon nanotubes remained unaltered basically after ball milling, while the size of aggregated pores obviously decreased owing to the collision and friction with the agate ball. It was inner cavity and compressed aggregated pores, which was adsorption positions of capillary adsorption, made carbon nanotubes show higher adsorption capability for nitrobenzene.

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REFERENCES

1. P. Tang, J.T. Zhou and J. Wang, *Ind. Water Treat.*, **23**, 16 (2003).
2. P.S. Majumder and S.K. Gupta, *Water Res.*, **37**, 4331 (2003).
3. Y. Mu, H.Q. Yu, J.C. Zheng, S. Zhang and G.P. Sheng, *Chemosphere*, **54**, 789 (2004).
4. Q.D. Qin, J. Ma and K. Liu, *J. Colloid Interf. Sci.*, **315**, 80 (2007).
5. Z. Chen, Z. Wang, D.L. Wu and L.M. Ma, *J. Hazard. Mater.*, **197**, 424 (2011).
6. S.H. Ng, J. Wang, Z.P. Guo, J. Chen, G.X. Wang and H.K. Liu, *Electrochim. Acta*, **51**, 23 (2005).
7. W.D. Zhang and W.H. Zhang, *J. Sensors*, **2009**, 16 (2009).
8. Z.Q. Liu, J. Ma, Y.H. Cui, L. Zhao and B.P. Zhang, *Appl. Catal.*, **101**, 74 (2010).
9. Y.H. Li, S.G. Wang, X.F. Zhang, J.Q. Wei, C.L. Xu, Z.K. Luan and D.H. Wu, *Mater. Res. Bull.*, **38**, 469 (2003).
10. J. Hu, C. Chen, X. Zhu and X. Wang, *J. Hazard. Mater.*, **162**, 1542 (2009).
11. C. Lu and H. Chiu, *Chem. Eng. J.*, **139**, 462 (2008).
12. X. Peng, Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian and Z. Jia, *Chem. Phys. Lett.*, **376**, 154 (2003).
13. Y. Yao, F. Xu, M. Chen, Z. Xu and Z. Zhu, *Bioresour. Technol.*, **101**, 3040 (2010).
14. O.G. Apul, T. Shao, S. Zhang and T. Karanfil, *Environ. Toxicol. Chem.*, **31**, 73 (2012).
15. X. Ren, C. Chen, M. Nagatsu and X. Wang, *Chem. Eng. J.*, **170**, 395 (2011).
16. A.M. Zhang, J.L. Dong, Q.H. Xu, X.L. Rhee and X.L. Li, *Catal. Today*, **93**, 347 (2004).
17. K.L. Lu, R.M. Lago, Y.K. Chen, M.L.H. Green, P.J.F. Harris and S.C. Tsang, *Carbon*, **34**, 814 (1996).
18. V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis and C. Galiotis, *Carbon*, **46**, 833 (2008).
19. N. Pierard, A. Fonseca, Z. Konya, I. Willems, G. Van Tendeloo and J. B.Nagy, *Chem. Phys. Lett.*, **335**, 1 (2001).
20. Y.A. Kim, T. Hayashi, Y. Fukai, M. Endo, T. Yanagisawa and M.S. Dresselhaus, *Chem. Phys. Lett.*, **355**, 279 (2002).
21. J. Tersoff and R.S. Ruoff, *Phys. Rev. Lett.*, **73**, 676 (1994).
22. Q.H. Yang, P.X. Hou, S. Bai, M.Z. Wang and H.M. Cheng, *Chem. Phys. Lett.*, **345**, 18 (2001).