

Continuous Production of Carbon Nanotubes by Using Moving Bed Reactor

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Abstract: High-quality carbon nanotubes were continuously produced by using moving bed reactor. The studies of scanning electron microscopy and transmission electron microscopy reveal their homogeneity both in inner (~ 10 nm) and outer diameter (20-40 nm) of the tubes. The studies of Xray photoelectron spectroscopy and the oxidation of carbon nanotubes in air demonstrate that the tubes have good graphitic degree.

Keywords: Carbon nanotubes, moving bed reactor, production.

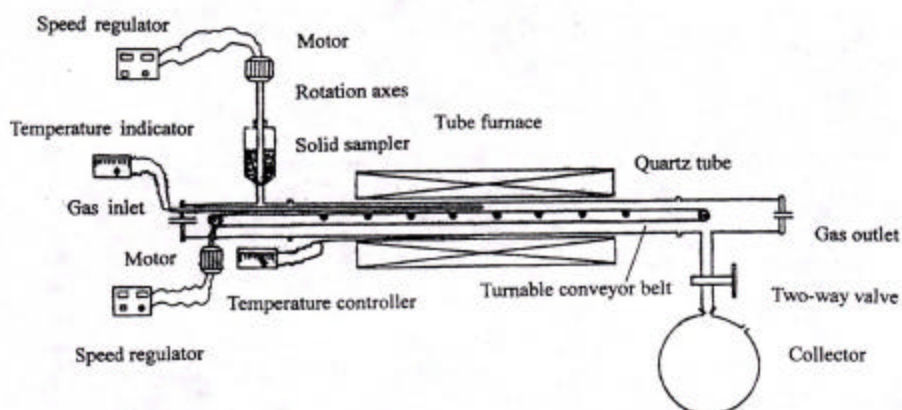
Since the discovery in 1991¹, carbon nanotubes have been the subject of intensive research due to their extraordinary mechanical and electronic properties²⁻⁷. However, lack of sufficient amount of materials limited the study of the fundamental properties and development of more practical applications. It is highly desirable to have large quantities of pure nanotubes. To date, few methods have been developed for the production of high-quality tubes which can adapted to industrial production levels.

Here, we describe a novel synthesis method by which the reaction can run in a continuous fashion and can be scaled up for industry. The produced carbon nanotubes are in high quality and at high production rates.

The moving bed reactor is illustrated schematically in **Figure 1**.

The precursor catalyst of (LaCoO₃) was prepared and reduced using the method reported previously^{6,7}. The prereduced catalyst was packed into the solid sampler in an inert environment, followed by heating the reactor in a flow of purified N₂ from room temperature to the desired reaction temperature. Then speed regulator was operated, the prereduced catalyst dropped down automatically and covered the conveyor belt evenly, and the belt moved forward automatically. Subsequently, CH₄ was introduced at a flow rate of 50 sccm, and carbon nanotubes were formed on the belt by deposition of carbon atoms obtained from decomposition of CH₄. Finally, the sample of a black powder dropped into the collector. Thus, we have synthesized carbon nanotubes without purification. The carbon nanotubes were then purified by washing with nitric acid. In this way, we can synthesize about 1 kg of multi-walled carbon nanotubes with a purity of 98% per day.

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Figure 1 Schematic diagram of moving bed reactor used for carbon nanotubes

The morphologies and microscopic structure of carbon nanotubes were characterized by the scanning electron microscopy (SEM) (KYKY-AMRAY-1000B), transmission electron microscopy (TEM) (JEOL JEM-100CX), X-ray photoelectron spectroscopy (XPS) (VG ESCA MARK II). The oxidation of carbon nanotubes in air were performed over thermogravimetry (TG) (Perkin-Elmer TGA7) (scanning rate= $10^{\circ}\text{C}/\text{min}$, 3.194 mg of sample).

Figure 2 is the TEM images of as-produced CNTs samples. It shows that the tubes are thin, having an inner diameter of ~ 10 nm, outer diameter of 20-40 nm.

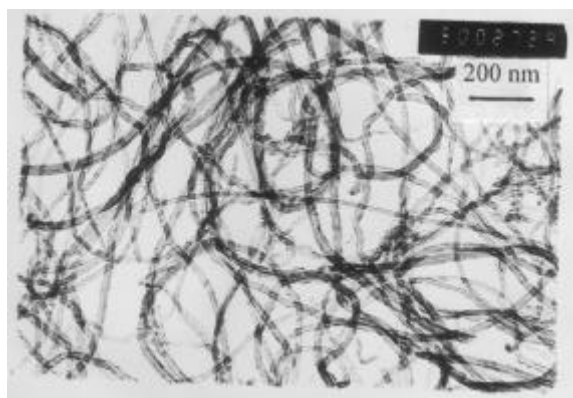
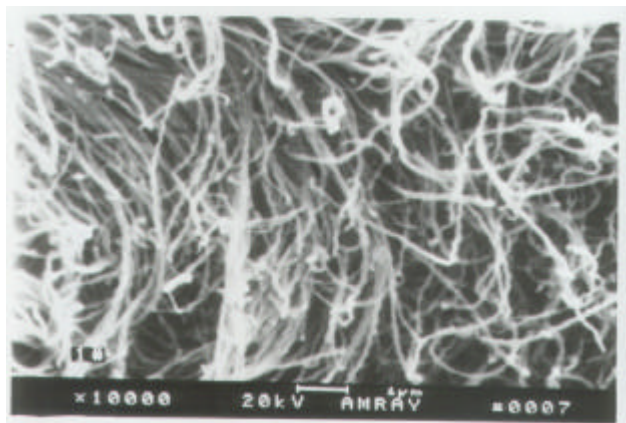
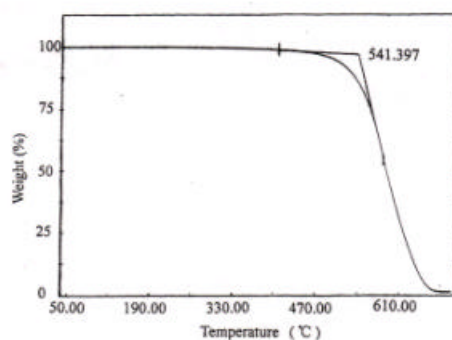
Figure 2 TEM image of carbon nanotubes

Figure 3 is the SEM images of as-produced CNTs samples. It clearly illustrates the purity and homogeneity of the tubes.

Figure 3 SEM image of carbon nanotubes

The oxidation of obtained carbon nanotubes in air has been studied over thermogravimetry. The results are shown in **Figure 4**. It clearly shows that the oxidation of carbon nanotubes occurred at *ca* 541 °C, which was higher than that reported by Kukovitsku (*ca* 420 °C)⁸. It has been reported that graphite could be oxidized at *ca* 520 °C⁸. XPS shows that the binding energy of C1S_{1/2} was 284.14 eV. These implied that the carbon nanotubes had good graphitic degree.

Figure 4 The TG plot during oxidation of carbon nanotubes

In conclusion, the continuous production of carbon nanotubes possessing high quality was carried out using moving-bed reactor.

Acknowledgments

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References

1. S. Iijima, *Nature*, **1991**, 354, 56.
2. W. A. de Heer, A. Chatelain, D. Ugarte, *Science*, **1995**, 270, 1179.
3. M. M. J. Treacy, T. W. Ebbesen, J. M. Gibson, *Nature*, **1996**, 381, 678.
4. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, P. N. Provencio, *Science*, **1998**, 282, 1105.
5. A. A. Setlur, S. P. Doherty, J. Y. Dai, R. P. H. Chang, *Appl. Phys. Lett.*, **2000**, 76, 3008.
6. B. C. Liu, L. Z. Gao, Q. Liang, S. H. Tang, M. Z. Qu, Z. L. Yu, *Catal. Lett.*, (in the press).
7. B. C. Liu, Q. Liang, S. H. Tang, L. Z. Gao, B. L. Zhang, M. Z. Qu, Z. L. Yu, *Chin. Chem. Lett.*, **2000**, 11, 1031.
8. E. F. Kukovitskii, L. A. Chernozatonskii, S. G. Lvov, N. N. Melnik, *Chem. Phys. Lett.*, **1997**, 266, 323.

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