# Large Scale Synthesis of Carbon Hollow Spheres from Metal Zinc Powder and Ethanol

Wu Zhang, Jianwei Liu, Zhen Huang, Dekun Ma, Jianbo Liang, and Yitai Qian*
*Structure research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

(Received July 13, 2004; CL-040829)

A simple method was used to prepare carbon hollow spheres with average size of about 400 nm in diameter from metal zinc powder and ethanol. The FE-SEM and TEM images show that these carbon spheres have a ball-like and vessel-like morphology, all of which have smooth surfaces and a quite uniform diameter.

Carbon materials have attracted much interest across the world since the discovery of fullerenes,[1] carbon nanotubes,[2] and close spherical carbon shells.[3] In recent years, considerable efforts have been made to fabricate different carbon structures and to explore their applications. Carbon materials have a wide range of applications including conductive and high-strength composites,[4] nanotweezers,[5] gas storage media,[6] semiconductor devices,[7] and field emission displays.[8] Among the various forms of carbon, carbon hollow spheres are of increasing interest due to their low density, large surface area, stability, and surface permeability. Previously, carbon spheres have been synthesized by various methods.[9–12]

The use of cheap non-toxic ethanol molecule as the carbon source for the preparation of various carbon materials has long been a goal for synthetic chemists. Recently, our group reported large-scale synthesis of carbon nanotubes by an ethanol thermal reduction process using Mg powder at 600 °C,[13] and hollow carbon cones by the reduction of butyl alcohol with metal Mg powder at 500 °C.[14] Based on the results above, it would be very interesting to study the reaction of other metal and alcohol in solvothermal process.

Herein, we report the preparation and characterization of carbon hollow spheres by reduction of ethanol with zinc powder at 550 °C.

In a typical procedure, the metal Zn powder (1 g; 99%), and ethanol (40 mL) were mixed in a stainless steel autoclave of 60-mL capacity. The autoclave was sealed and maintained at 550 °C for 12 h and then allowed to cool down to room temperature. Obtained dark precipitate was collected and washed with absolute ethanol, dilute HCl aq solution and distilled water in that order. The sample was then dried in vacuum at 65 °C for 6 h.

The phase purity of the as-synthesized products was examined by X-ray diffraction patterns (XRD) using Philips X'Pert PRO SUPER X-ray diffractometer with Cu K$\alpha$ radiation ($\lambda$ = 1.541874 Å). The morphologies of the as-prepared products were examined with field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) using an accelerating voltage of 200 kV. Raman spectra were measured on a LabRAM HR Raman spectrophotometer at an excitation wavelength of 514.5 nm.

Figure 1a shows the XRD pattern of the products that were not washed. Reflections in the figure can be indexed to hexagonal ZnO (JCPDS Card File, no.79-0205) and carbon. Figure 1b is a typical XRD pattern of the as-prepared products washed with dilute HCl aq solution and distilled water. The peak can be indexed to the hexagonal carbon structure (002) plane. At the same time, it is also observed that the position of the (002) peak shifts to lower $2\theta$ angle. The d spacing of (002) plane is 3.4950 Å, which is larger than the reported value of graphite ($d$ = 3.3756 Å, JCPDS card, No.41-1487). This suggests that the spacing between the $sp^2$ carbon layers in the carbon hollow spheres is increased. These investigations imply that the degree of long-range order of these nanostructures is lower than that of graphite. These results confirm that the reaction is similar to that of magnesium and ethanol, in which metal powder reacts with alcohol producing carbon, hydrogen, and metal oxide.

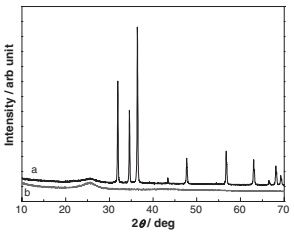


**Figure 1.** XRD patterns of the products: (a) not washed and (b) after HCl treatment.

Further evidence for the hexagonal carbon structure of the sample can be obtained through Raman spectroscopy. Figure 2 shows that there are two strong peaks at 1336 and 1593 $cm^{-1}$. The peak at 1593 $cm^{-1}$ corresponds to G mode of graphite and is related to the vibration of $sp^2$-bonded carbon atoms in a 2-D graphite layer. Compared with the G-band at 1580 $cm^{-1}$ for the graphitic carbons, the G-band of the products shifts towards a higher wavenumber due to the less orderly arrangement of the carbon atoms, which implys that the graphitization degree of carbon spheres is not high, and this agrees well with the XRD result. The peak at 1336 $cm^{-1}$ is attributed to a disorder Raman D mode of graphite.

FE-SEM images for the as-prepared products were shown in

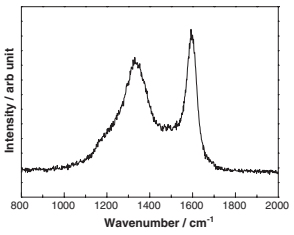


**Figure 2.** Room-temperature Raman spectrum of the as-prepared sample.

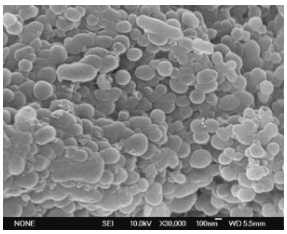

**Figure 3.** FE-SEM image of as-prepared sample.

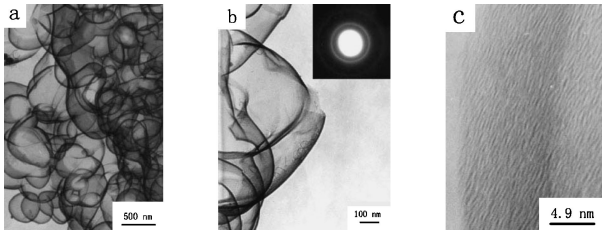


**Figure 4.** (a) TEM images of carbon hollow spheres and vessels; (b) broken carbon hollow spheres and SAED pattern of carbon hollow spheres (insert); (c) HRTEM image of the wall of a carbon hollow sphere.

Figure 3. It is observed that the sample contains a large quantity of hollow carbon spheres and vessels with smooth surface.

Typical TEM images of the sample were shown in Figure 4. From Figure 4a it can be seen that most of the as-prepared products are hollow spheres with diameter of 300–600 nm, which is in agreement with the result of FE-SEM observation. The strong contrast between the dark edge and pale center is evidence of its hollow nature. Broken spheres are revealed in Figure 4b, which provides further proof of the hollow nature. The selected area electron diffraction (SAED) pattern (insert in Figure 4b) of the carbon spheres comprises two diffraction rings corresponding to (101) and (110) reflections of graphite. The absence of the (002) reflection may be due to the fact that the local (001) graphite plane is nearly perpendicular to the electron beam.[15] Figure 4c shows the HRTEM image of the wall structure of a hollow carbon sphere, reveals that the typical spheres are consisted of sheets, and the average sheet thickness is about 10 nm. The inter-space between two adjacent layers was about 0.35 nm, which is in good agreement with the result of XRD.

A possible mechanism for the formation of carbon hollow spheres may be as follows: At a desired temperature (up to 400 °C), ethanol can be reduced continuously by Zn to free carbon atoms, which are dispersed in the molten zinc (melting point: 419.53 °C). The newly formed free carbon atoms are so active that they can directly react with each other to produce hexagonal lattice of $sp^2$-bonded carbon, which exists as graphite sheets. The graphite sheets cover the zinc particles and form carbon spheres, in which some ethanol and $H_2$ may be encapsulated. In the newly formed carbon spheres, ethanol reacts with zinc continuously, and the hollow carbon spheres can be formed after the zinc is consumed. In addition, it is found that the reaction temperatures played a critical role in the formation of these carbon spheres. When the reaction was conducted at 400 °C, the main products were amorphous carbon. When the reaction temperature was at 550 °C, carbon spheres were the main products. However, as the temperature was further increased to 600 °C, some carbon nanotubes could be observed in the as-synthesized sample.

In summary, carbon hollow spheres and vessels have been synthesized from metal zinc powder and ethanol at 550 °C for 12 h. According to the special morphology of hollow spheres, the products have potential applications, such as catalyst carriers and electronic devices.

This work is supported by the National Natural Science Foundation of China and 973 Projects of China.

## References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
2 S. Iijima, *Nature*, **354**, 56 (1991).
3 A. Krishnan, E. Dujardin, M. M. J. Treacy, J. Hugdahl, S. Lynum, and T. W. Ebbesen, *Nature*, **388**, 451 (1997).
4 S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, *Science*, **280**, 1744 (1998).
5 P. Kim and C. M. Lieber, *Science*, **286**, 2148 (1999).
6 A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature*, **386**, 377 (1997).
7 J. Kong, C. Zhou, A. Morpurgo, H. T. Soh, C. F. Quate, and C. Marcus, *Appl. Phys. A: Mater. Sci. Process.*, **69**, 305 (1999).
8 S. Fan, M. G. Chapline, N. R. Frank, T. W. Tommbler, A. M. Cassell, and H. J. Dai, *Science*, **283**, 512 (1999).
9 P. Serp, R. Feurer, P. Kalck, Y. Kihn, J. L. Faria, and J. L. Figueiredo, *Carbon*, **39**, 621 (2001).
10 Y. N. Xia, B. Gates, Y. D. Yin, and Y. Lu, *Adv. Mater.*, **12**, 693 (2000).
11 K. Niwase, T. Homae, K. G. Nakamura, and K. Kondo, *Chem. Phys. Lett.*, **362**, 47 (2002).
12 G. Hu, D. Ma, M. Cheng, L. Liu, and X. Bao, *Chem. Commun.*, **2002**, 1948.
13 J. W. Liu, M. W. Shao, X. Y. Chen, W. C. Yu, X. M. Liu, and Y. T. Qian, *J. Am. Chem. Soc.*, **125**, 8088 (2003).
14 J. W. Liu, W. J. Lin, X. Y. Chen, S. Y. Zhang, F. Q. Li, and Y. T. Qian, *Carbon*, **42**, 667 (2004).
15 Z. L. Wang and J. S. Yin, *Chem. Phys. Lett.*, **289**, 189 (1998).

Published on the web (Advance View) September 18, 2004; DOI 10.1246/cl.2004.1346