Preparation of hollow carbon nanospheres at low temperature via new reaction route

Youbao Ni, Mingwang Shao*, Yanhua Tong, Guixiang Qian, Xianwen Wei

Auhui Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui Normal University, Number 1, Beijing East Road, Wuhu City, Anhui province 241000, P.R. China

Abstract

Hollow carbon nanospheres were obtained at 200 °C via a new reaction route, by using magnesium, hexachloroethane and aluminum trichloride as starting materials and benzene as solvent. The products were characterized with X-ray diffraction pattern, transmission electron microscope, high-resolution transmission electron microscope images and Raman spectrum. The reaction conditions are easy to be maintained and controlled. They may provide a new method to produce other carbonaceous materials. A possible mechanism of reaction was proposed.
© 2004 Elsevier Inc. All rights reserved.

Keywords: Nanostructure; Chemical synthesis; Grignard reagent; Hollow carbon nanospheres

1. Introduction

The discovery of carbon nanotubes by Iijima in 1991 [1] has stimulated intense interest in carbon structures. What makes carbon nanotubes and other carbon structures so attractive is their unique structures, special chemical and physical properties, including the capability for the storage of a large amount of hydrogen [2], conductive and high-strength composites [3], nanotweezers [4], gas storage media [5], semiconductor devices [6] and field emission displays [7]. Among the various forms of carbon, hollow carbon nanospheres (HCSs) are of increasing interest due to their low density, large surface area, stability, and surface permeability, and in the medical field, they are expected to act as effective oral sorbents for the removal of uremic waste metabolities from the intestine [8].

Because of carbon's flexible structure, various methods have been demonstrated for the synthesis of HCSs [9–16], such as mixed-valent oxide-catalytic carboniza-

tion process [9], chemical vapor deposition method by using mesoporous silica [10], pyrolysis hydrocarbon via high temperature with certain catalyzers [11,12], shock compression from C_{60} fullerene [13], media-reduction route [14,15], self-assembly approach [16], etc. These methods are very useful and are of widespread importance. However, there are some limitations to their utilities, such as the need of elevated temperature resulting from the high melting temperature of carbon materials ($\approx 4000\,K$), and the use of alkali metals K and Na as reductants for their excellent active property [14,16]; but on account of their violence, it is inconvenient to employ the alkali metals as initial reagents. Therefore, it is a challenge to synthesize the production with other materials at mild conditions.

In this paper, we described how HCSs were prepared via a new reaction route at 200 °C. Alkaline-earth Mg, C_2Cl_6, $AlCl_3$ were employed as starting materials and benzene as solvent. The reactions were under easy control and operated at mild conditions. Based on the experimental results, we proposed a possible mechanism to illustrate the formation of HCSs.

*Corresponding author. Fax: +86 553 386 9303.
E-mail address: zhengcui@mail.ahnu.edu.cn (M. Shao).

2. Experimental procedure

All reagents were commercially available and used without further purification. In a typical experiment, metallic Mg powder (0.206 g, 99%), $AlCl_3$ (0.210 g) and C_2Cl_6 (0.980 g) were added into a vitreous conical flask [17]; 10 mL C_6H_6 was filled in and the mixture was stirred uniformly. Then the flask was put in an autoclave of about 50 mL capacity. The reactor was sealed and maintained at 200 °C for 12 h and then allowed to cool down to room temperature naturally. The dark resultant was collected, washed with absolute ethanol, HCl solution (about 2 mol L^{-1}), and distilled water. Finally, it was dried in a vacuum at 60 °C for 6 h and about 0.08 g samples were obtained.

The phase and crystallography of the products were characterized by X-ray diffraction (XRD) pattern, which was recorded by using a Shimadzu XRD-6000 X-ray diffractometer equipped with $CuK\alpha$ radiation ($\lambda = 0.15406$ nm), and the scanning rate of 0.05 ° s^{-1} was applied to record the pattern in the 2θ range of 10–70°.

The transmission electron microscope (TEM) image was taken with a Hitachi Model H-800 TEM, using an accelerating voltage of 200 kV to determine the morphological features. The high-resolution transmission electron microscope (HRTEM) image was investigated with a JEOL-2010 TEM, using an accelerating voltage of 200 kV.

Raman spectrum was measured on a Spex 1403 Raman spectrometer at ambient temperature, employing an argon ion laser at an excitation wavelength of 514.5 nm.

3. Results and discussion

The XRD pattern of the products (Fig. 1) shows the presence of reflections characteristic of carbon hexagonal phase. Reflections in the figure can be indexed to (002) and (101). The (002) peak is strong while (101) is weak and wide. Compared with the reported data of graphite (JCPDS Card Files, No. 41-1487), the position of the (002) peak shifts a little angle from $2\theta = 26.4°$ to 26.2°, probably owing to the increase in the spacing between sp^2 carbon layers from 0.337 nm for graphite to 0.341 nm for HCSs [18].

The typical morphology of the samples is presented in Fig. 2 via TEM observations. From Figs. 2a and b, it can be seen that most of them are hollow nanospheres with diameter of 30–60 nm. The strong contrast between the dark edge and pale center is the evidence of its hollow nature. The inset in Fig. 2a is the selected area electron diffraction (SAED) pattern of the HCSs, which can be indexed as (002) reflection of the graphite.

Fig. 2c shows the wall structure of typical HCSs observed by HRTRM. The whole sheets thickness is
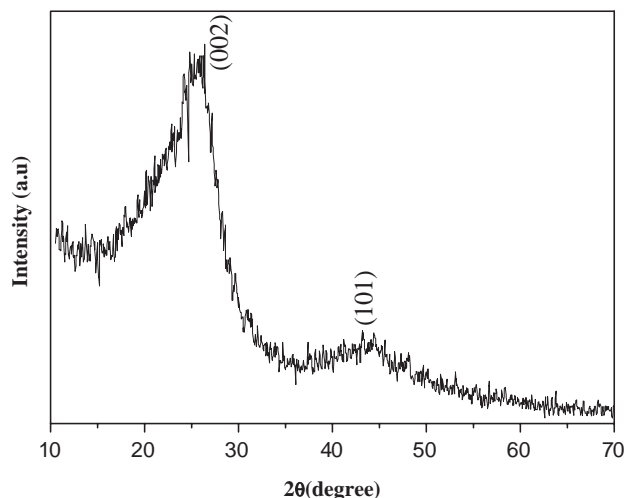

Fig. 1. The XRD pattern of as-prepared products, which indicates a hexagonal phase of carbon.

about 3.8 nm. The exact graphitic sheet number could not be counted for most of them were entangled together.

Further evidence for the purity of products was obtained through the Raman spectrometer. Fig. 3 shows that there exist two strong peaks at 1596 and 1360 cm^{-1}. The peak at 1596 cm^{-1} corresponds to an E_{2g} mode of graphite, related to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer. The peak at 1360 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [19]. This peak is quite broadened, which means that in the basal plane there exists two-dimensional disorder, which is to be expected, as the reaction temperature is low.

A possible mechanism of reaction was proposed. Magnesium, as an active metal, easily forms Grignard reagent with the organic-chloride as $RCl + Mg \rightarrow RMgCl$. Grignard reagent will react with the chlorides of all elements below magnesium in the electromotive series, usually by replacing the chlorine with alkyl group, similar to the reaction $RMgCl + AlCl_3 \rightarrow R_3Al + MgCl_2$. Here, Grignard reagent, functioning as a strong base, is attracted to electron-deficient centers $AlCl_3$, and obtains intermediate products R_3Al [20].

In this method, $AlCl_3$ also plays another role of importance. It can polarize the chlorine atom to aid the attraction on the highly stabilized material C_2Cl_6 according to the route $RCl + AlCl_3 \rightarrow [AlCl_3 \cdot Cl^-] + [R^+]$. Although the intermediated cation R^+ is stabilized to a degree, it is a higher-energy species than the fully conjugated structure of the unsubstitued chloride carbon. So, the R_3Al is easily attacked by an electrophile R^+, to give an intermediate, and obviously, an electrophile eventually must be released from the intermediate to produce a neutral molecule $R–R$ as the
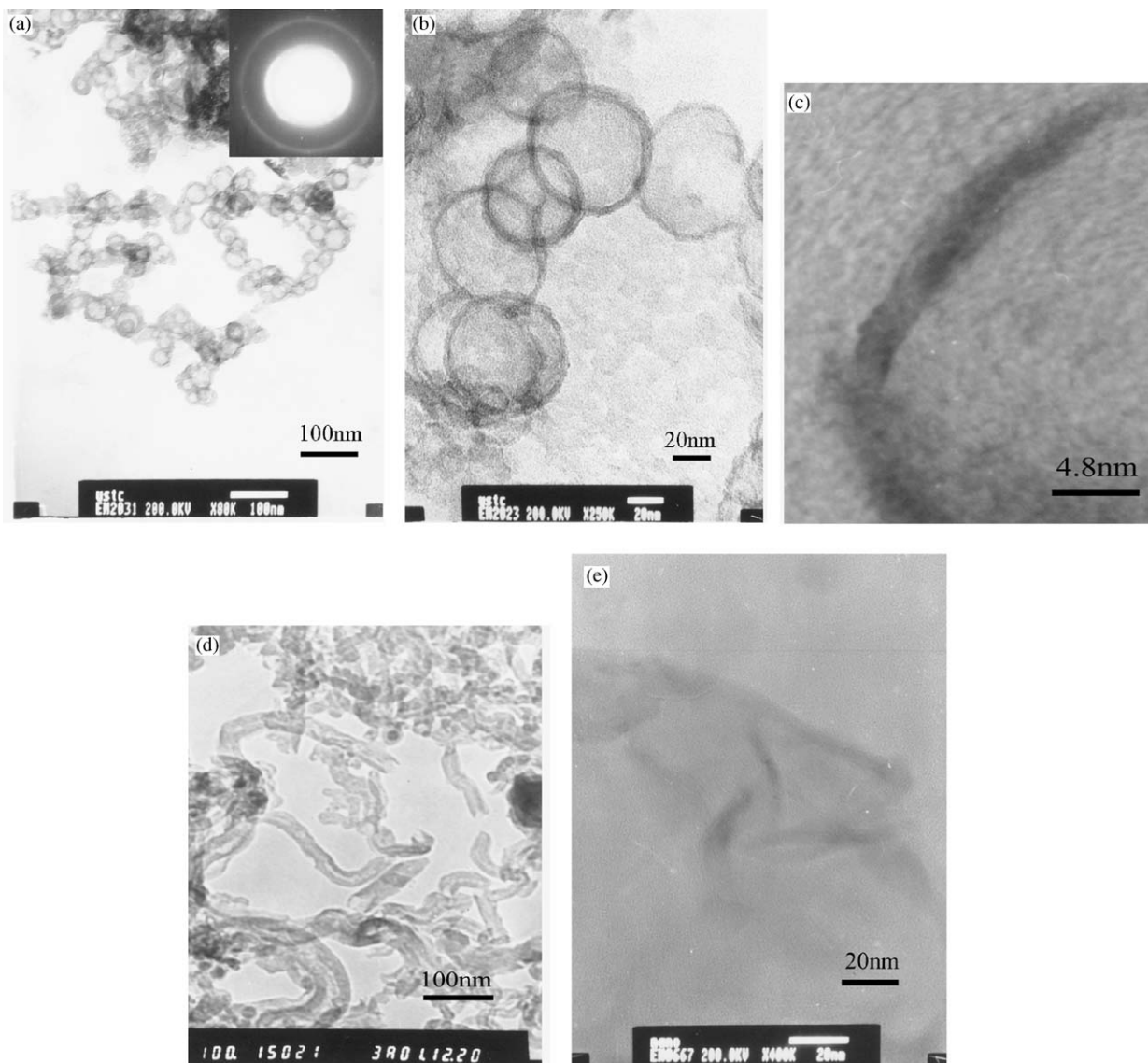
Fig. 2. (a) TEM images of HCSs and SAED pattern (inset); (b) with large magnification of (a); (c) HRTEM images of the wall of HCSs; (d) some short nanotubes could be observed at 300 °C and (e) many sheets of graphite could be seen under 150 °C.
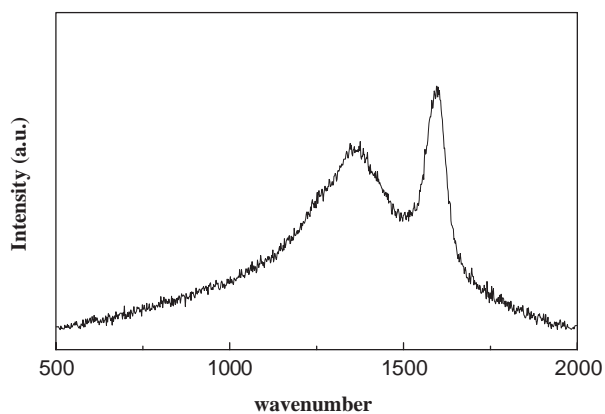

Fig. 3. Raman spectrum of products which shows two graphite peaks at 1350 and 1585 cm^{-1}.

reaction $[R^+] + R_3Al \rightarrow R\text{-}R + Al^{3+}$ [20]. As R–R still contains chlorine atoms, it will act with metal Mg to form Grignard reagent continuously until R–R loses all the chlorine atoms and becomes carbon at last. The fresh carbon atoms assemble into graphite layers, which curl up to produce hollow nanospheres. Al^{3+} can also combine with $[AlCl_3 \cdot Cl^-]$ to provide the initial materials $AlCl_3$. The total reaction can be represented as

$$C_2Cl_6 + Mg \xrightarrow{AlCl_3} C + MgCl_2.$$
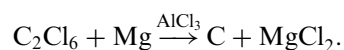
In order to confirm this mechanism, we conducted a control experiment without the use of $AlCl_3$ and kept other experimental invariables; no carbon was obtained. It is supposed that the Lewis acid $AlCl_3$ plays a vital role

in the formation of carbonaceous materials. In addition, we also found that the temperature was important for the formation of hollow nanospheres. When it was increased to 300 °C, a large amount of irregular carbon spheres (not hollow) and some nanotubes could be observed in the as-synthesized products (Fig. 2d). When the temperature conducted to 150 °C, many amorphous sheets of graphite could be found (Fig. 2e). Low temperature resulted in the whole reaction velocity becoming degraded, and the obtained limited fresh carbon atoms could only assemble into graphite sheets.

It is supposed that the reaction took place on the surface of Mg powder. The newly produced carbon atoms connect with each other to form a hexagonal lattice of sp^2-bonded graphite sheets, which cover the magnesium particles. After magnesium is consumed, HCS is formed.

4. Conclusion

In conclusion, HCSs were obtained at 200 °C via a new reaction. The reaction temperature was only 200 °C and time was 12 h. The conditions are easily maintained and controlled. It may provide a new method to produce other carbonaceous materials, such as nanotubes, nanofibres, etc. at mild conditions via other Lewis acid ($FeCl_3$ or $ZnCl_2$) and other halohydrocarbon carbon sources (C_2Cl_4 or CCl_4).

Acknowledgments

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999) 1127.
[3] S. Frank, P. Poncharal, Z.L. Wang, W.A. de Heer, Science 280 (1998) 1744.
[4] P. Kim, C.M. Lieber, Science 286 (1999) 2148.
[5] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, Nature 386 (1997) 377.
[6] J. Kong, C. Zhou, A. Morpurgo, H.T. Soh, C.F. Quate, C. Marcus, H. Dai, Appl. Phys. A 69 (1999) 305.
[7] M. Shim, A. Javey, N. Kam, H.J. Dai, J. Am. Chem. Soc. 123 (2001) 11512.
[8] H. Tamai, T. Sumi, H. Yasuda, J. Coll. Int. Sci. 177 (1996) 325.
[9] Z.L. Wang, J.S. Yin, Chem. Phys. Lett. 289 (1998) 189.
[10] Y.D. Xia, R. Mokaya, Adv. Mater. 16 (2004) 886.
[11] V.V. Kovalevskl, A.N. Safronov, Carbon 36 (1998) 963.
[12] Z.X. Xu, J.D. Lin, Y. Ou, D.W. Liao, Acta Phys. Chim. 19 (2003) 1035.
[13] K. Niwase, T. Homae, K.G. Nakamura, K. Kondo, Chem. Phys. Lett. 362 (2002) 47.
[14] J.W. Liu, M.W. Shao, Q. Tang, X.Y. Chen, Z.P. Liu, Y.T. Qian, Carbon 41 (2002) 1645.
[15] Y.J. Xiong, Y. Xie, Z.Q. Li, C.Z. Wu, R. Zhang, Chem. Commun. (2003) 904.
[16] G. Hu, D. Ma, M.J. Cheng, L. Liu, X.H. Bao, Chem. Commun. 12 (2002) 1948.
[17] (a) The reason why we put starting materials into a vitreous conical flask is mainly because the inner autoclave is made up of polytetrafluorethylene and it might react with the materials;
     (b) Y.B. Ni, M.W. Shao, W. Zhang, Z.C. Wu, Chem. Lett. 33 (2004) 494.
[18] H.B. Zhang, G.D. Lin, Z.H. Zhou, X. Dong, T. Chen, Carbon 40 (2002) 2429.
[19] M.W. Shao, Q. Li, J. Wu, B. Xie, S.Y. Zhang, Y.T. Qian, Carbon 40 (2002) 2961.
[20] G.B. Butler, K.D. Berlin, Fundamentals of Organic Chemistry, The Ronald Press Company, New York, 1972, pp. 487.