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Large-scale synthesis of carbon spheres by reduction of supercritical CO_2 with metallic calcium

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Abstract

Carbon spheres with approximate uniform diameters of about 1–2 μm were synthesized by chemical reduction of supercritical CO_2 with metallic calcium at 550 °C. The products were characterized by techniques including XRD, scanning electron microscope, Raman, and transmission electron microscopy. The formation mechanism was thought to be as follows: the thermal movement of carbon nano-granules on the surface of metallic calcium leads to the formation of carbon spheres, which was confirmed by reference experiments at different temperatures. What is more, the formation mechanism of carbon sphere in supercritical CO_2 system was discussed.

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1. Introduction

The discovery of fullerenes and carbon nano-tubes [1,2] has stimulated intense interest in carbon structures, among which carbon spheres (CPS) attracts more and more attention from both academic and industrial fields. Because of its intrinsic properties such as high strength, high thermal resistance, light weight, carbon spheres could be used as high strength composites, catalyst carriers, lubricants, gas storage media and wear-resistant materials [3]. There have been many attempts in the synthesis of this carbon structure such as the carbon-arc technique [4], the ultrasonic treatment [5], the high-energy electron beam irradiation [6], the thermal treatment of carbonaceous materials [7], the chemical vapor deposition [8], the thermal treatment of pure carbon soot [9], the ultradispersed diamond powders (2–6 nm) [10] and the plasma torch process [11]. Recently, the reduction of carbonate or supercritical carbon dioxide also proves to be practical [12,13].

Our group has successfully prepared diamond [14,15], carbon nano-tubes [16] and carbon spheres [13] by the chemical reduction of CO_2 with alkali metals, which provides new perspectives for the synthesis of large size diamond and other carbon-based materials as well as the comprehensive utilization of CO_2. In order to further explore the reduction mechanism, we substitute alkali metals with metallic calcium, which is an alkali earth metal and formulate a simple way of preparing large-scale carbon spheres. Based on the data obtained, a possible mechanism is suggested to illustrate the formation of carbon spheres in supercritical CO_2 system.

2. Experimental

In a typical experiment, dry ice (freshly made from high purity CO_2 gas (99.99%)) (10.0 g) and metallic Ca (1.2 g) were put into a stainless autoclave of 15-mL capacity. The vessel was then immediately closed tightly and heated to 550 °C, and kept at this temperature for 24 h. If it was not specifically mentioned, most of the reactions were carried out at 550 °C. The reaction took place at an autogenic pressure depending on the amount of carbon dioxide and calcium added. After the cooling of the sample to room temperature, the solid product was collected and rinsed with ethanol three times to get rid of a small quantity of

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unreacted Ca. The main products identified were carbon and $CaCO_3$; $CaCO_3$ was removed by 6.0 mol/L HCl aqueous solutions. The remaining solid precipitate, weighed 0.16 g, was confirmed main containing carbon spheres and amorphous carbon. The volume fraction of the carbon spheres was approximately 80% of carbonaceous materials, which was evaluated from the SEM images.

The X-ray diffraction (XRD) analysis was performed using a Rigaku (Japan) D/max-γA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The scanning electron microscopy (SEM) images and energy dispersive X-ray analysis (EDX) were taken on XT30 ESEM-TMP scanning electron microscope equipped with INCA400 energy dispersive X-ray detector. The Raman spectrum was recorded at ambient temperature on a Spex 1403 Raman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. The transmission electron microscopy (TEM) images were recorded on a Hitachi H-800 transmission electron microscope.

3. Results and discussion

Fig. 1 shows the XRD pattern of the sample after treated by 6.0 mol/L HCl aqueous solutions. The XRD data are typical of so-called ‘non-graphitic’ carbon (also termed ‘turbostratic’ carbon), showing diffuse interference maxima in XRD [17]. Moreover, the broad (1 0) diffraction originates from a two-dimensional lattice. It can also be conformed by the HRTEM image of the sample (not shown).

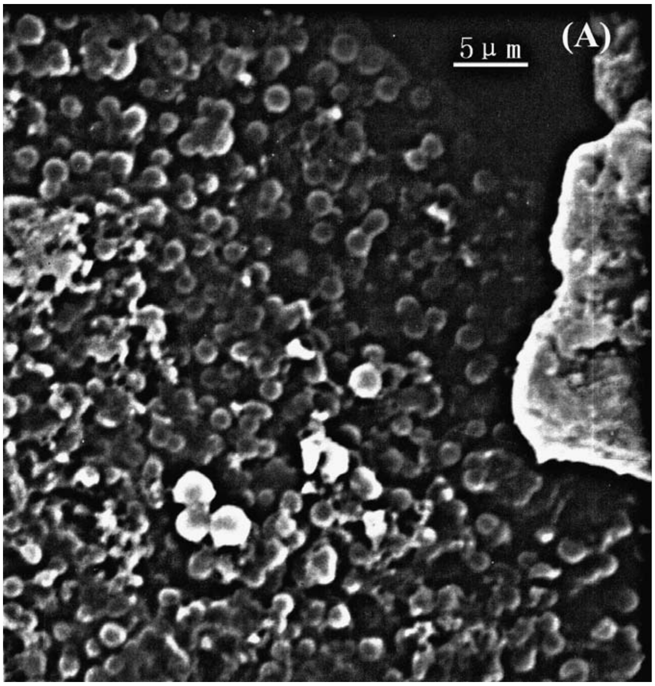


Fig. 2. SEM images of the products grown at 550 °C after treated by HCl aqueous solutions (6 mol/L).

The SEM images of the products (Fig. 2) indicate that the final products consist of a large quantity of carbon spheres and the carbon spheres are in perfect spherical morphology whose surface is very smooth without cracks. It can also be seen that the sample comprises carbon spheres 500–1800 nm in diameter. When the temperature is increased to 600 °C, the diameter of carbon sphere also increases significantly. As shown in Fig. 5A, the carbon spheres with an average diameter about 2500 nm, and the largest ones with sizes around 5 μm found present in the product; moreover, some carbon spheres show the elliptic shape, which is in agreement with the result of TEM observation. The carbon spheres are with a narrow range of diameters, which shows a potential of controlling the size for commercial application.

A typical Raman spectrum (Fig. 3A) of the sample shows that there are two strong peaks at 1600 and 1340 cm^{-1}. The peak at 1600 cm^{-1} (G-band) corresponds

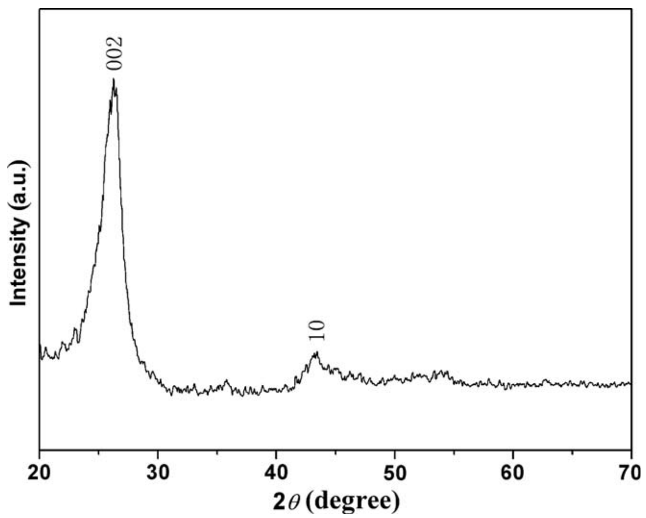


Fig. 1. XRD pattern of the products after treatment by HCl aqueous solutions (6 mol/L).

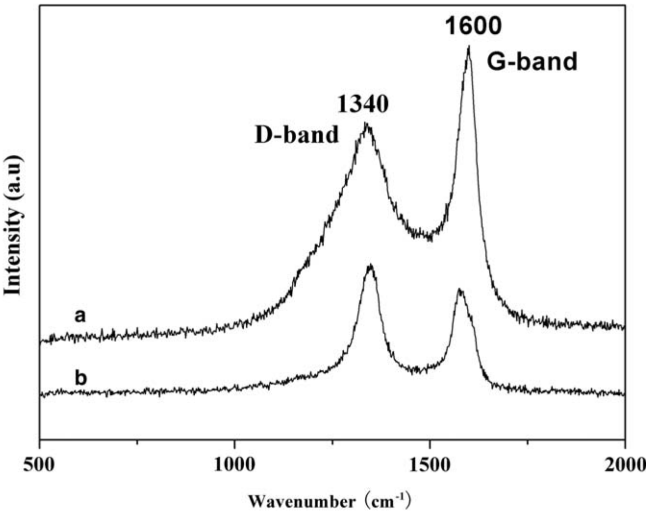


Fig. 3. Raman spectrum of the products after treated by HCl aqueous solutions (6 mol/L): (a) the experiment was carried out at 550 °C and (b) the experiment was carried out at 600 °C.

to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer [18]. The peak at 1340 cm^{-1} (D-band) is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. This peak is quite high indicating that in the basal plane there exist a two-dimensional disorder, which is quite common in mild temperature routes [19]. The value of I_D/I_G is indicative of the graphitization degree of carbon material. I_D/I_G value of the sample in the present study is 0.81, which suggests a decrease in the number of the six fold ring of graphitized plane.

Fig. 4 shows the TEM images and electron diffraction pattern of the as-prepared carbon spheres. TEM image (Fig. 4A, D) of the samples grown at 550 °C investigations indicate the carbon spheres in the sample appear to be of nearly perfect spheres with diameters range from 500 to 1500 nm. Smaller carbon spheres with sizes around 500–900 nm and carbon nano-rods are also found present in the product (Fig. 4D). Fig. 4B, C shows the samples obtained at 600 °C consist of carbon spheres 2.5–5 μm in diameter, and the elliptic carbon spheres are observed. In Fig. 4E, the produces grown at 500 °C contain carbon nano-rods, but no carbon spheres are seen. The selected area electron diffraction pattern (Fig. 4F) of the carbon spheres grown at 550 °C comprises two diffraction rings corresponding to (002) and (10) reflections of graphite, confirming the XRD result.

To investigate the effect of reaction condition on the formation of carbon spheres a series of experiments were carried out by altering experimental parameters of the process. It was found that the reaction temperature played a critical role in the formation of these carbon spheres. The process proceeded at the temperatures lower than 450 °C could not initiate the reaction. When the reaction was conducted at 500 °C, the main products were nano-rods and graphite. Carbon spheres became the major products at 550 °C, as shown in Fig. 2A. As the temperature was further increased to 600 °C, a large number of the larger carbon spheres formed in the as-synthesized sample, as shown in Fig. 5. In the above reactant conditions, it was also found that no CNTs were formed.

Compared with my previous work that carbon spheres consisting of amorphous carbon cores and graphene shells were once synthesized by reduction of CO_2 using Li as the reducing agent and proposed a possible growth mechanism that nano-scale rough surface of lithium formed at the interface between supercritical carbon dioxide and liquid lithium took the roles of both the reductant for reduction of carbon dioxide to carbon and the template for growth of carbon spheres [13], there are many differences in them. Firstly, the melting point of metallic Ca is 847 °C, which means that its phase in the reaction system is solid. In order to make sure whether the metallic Ca is solid in the reaction system, we conducted experiments exactly the same as that described above except

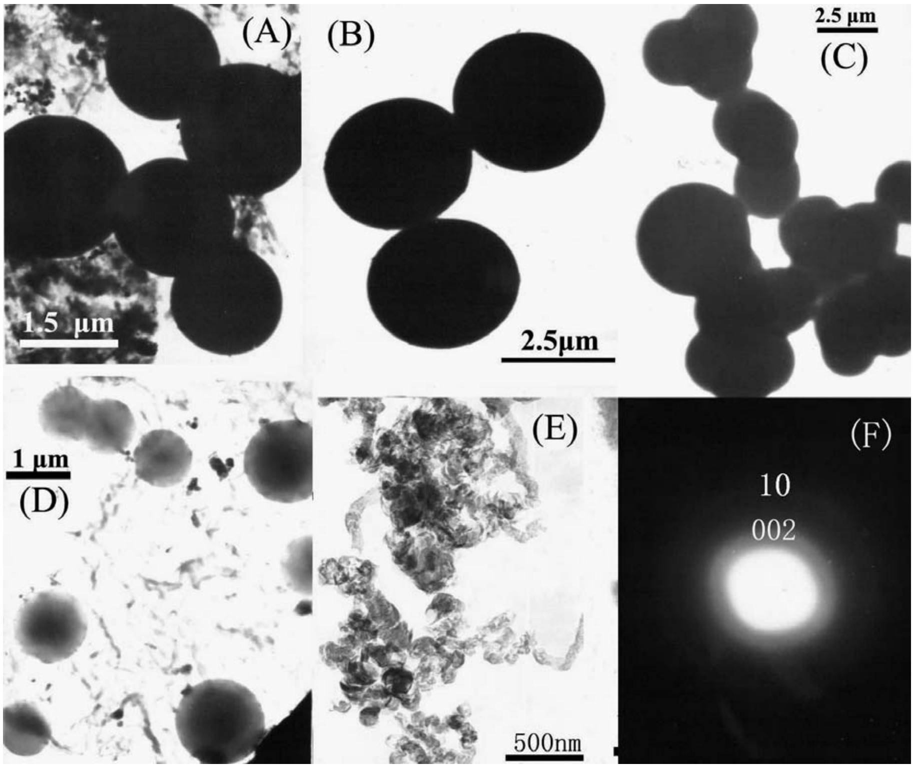
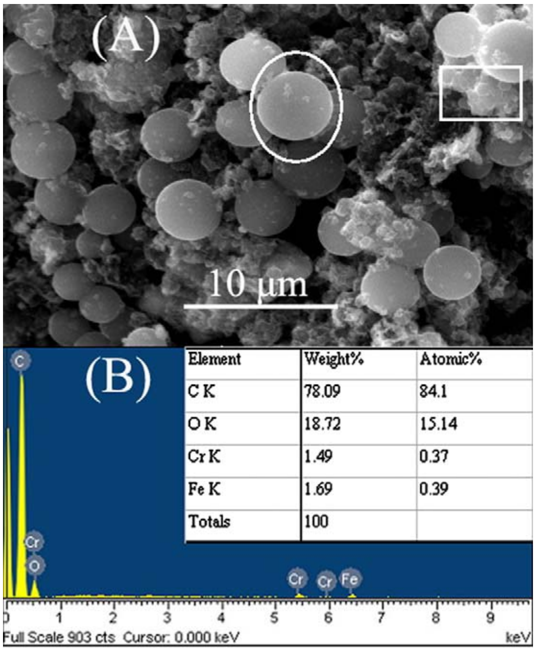


Fig. 4. The TEM images and electron diffraction pattern of the as-prepared carbon spheres: (A, D) TEM images of the samples obtained at 550 °C; (B, C) TEM image of the samples grown at 600 °C; (E) the TEM image of the products grown at 500 °C and (F) the electron diffraction pattern of a carbon sphere grown at 550 °C.



Element	Weight%	Atomic%
C K	78.09	84.1
O K	18.72	15.14
Cr K	1.49	0.37
Fe K	1.69	0.39
Totals	100	

Fig. 5. (A) SEM image of the products grown at 600 °C without any treatment, the quadrangled-boxed area shows carbon spheres in the initial stage of the growth (B). EDX of carbon spheres shown in the elliptic-boxed area in (A).

that 3.0 g Ca was used. The shape of the Ca we used was spherical shapes with diameters of 1–2 mm. After the experiment, the shape remained but the diameters diminished, indicating that the Ca did not melt during the experiment. Therefore, the droplet models cannot be adopted in the Ca–CO_2 system to describe the formation of carbon spheres. Secondly, the crystallinity of carbon spheres and the reaction temperature decreased. Finally, the yield and the content of carbon spheres increased significantly, and no CNTs were grown.

We propose a possible mechanism for the formation of carbon spheres. In our experiment, metallic Ca atom bonds with O atom in CO_2 molecule, forming CaO and CO, then Ca atom reacts with CO and lead to the emergence of carbon nano-granules. At the same time, at certain reaction temperature CO could decompose as follows:

$$CO \rightarrow CO_2 + C$$

While this reaction could not form a large quantity of carbon products, because of the excess amount of CO_2. So the resulted C from the above reaction might account for amorphous carbon other than carbon spheres in the products. Then if the temperature is high ($\geqslant 550$ °C), the thermal movement of the carbon nano-granules will be fierce, and the nano-granules could roll on the surface of the metallic calcium and incorporate new carbon atoms, which leads to the formation of carbon spheres. Because of the statistic rule of thermal movement, most of the carbon spheres are perfect spherical. In the framework of our hypothesis, the synthesized carbon spheres should follow a process of ‘growing’ from small to large, and the SEM image of the quadrangled-boxed area in Fig. 5A clearly shows such small carbon spheres in the initial stage of the growth, although most of the spheres show relative uniform diameters. At the same time, higher temperature means larger size and more defects and disorders in carbon spheres, which are confirmed by TEM images (Fig. 4C) and Raman spectrum (Fig. 3B). At 600 °C carbon spheres are 2–5 μm larger than those of 550 °C in general. At 600 °C the thermal movement becomes much fiercer and leads to the formation of more defects and disorders in carbon spheres. This could be conformed by Raman analysis shown in Fig. 3B, in which I_D/I_G value is 1.16, much higher than that of the products at 550 °C; moreover, a very small proportion of the carbon spheres show the elliptic shape (Fig. 4B). While the temperature is at 500 °C, the carbon nano-granules tend to stay at certain place, causing the formation of carbon nano-rods (Fig. 4E). This could explain the fact that the nano-rods are short and do not have uniform diameters. The TEM image (Fig. 4D) of the products synthesized at the critical temperature: 550 °C shows the co-presence of carbon spheres and carbon nano-rods, with carbon spheres as dominant products, providing further evidences to our proposed mechanism. Then considering the fact that the main products are carbon nano-rods at 500 °C and carbon spheres at 550 °C, the conclusion could be drawn that the temperature play an important role on the final shape of the products, which means that we could control the shape of the products as well as the size of spheres by carefully designing the reaction conditions. According to our mechanism, between the calcium atom and carbon atom lays oxygen atom, which means that there should be no calcium in the as-synthesized carbon spheres. We carry out SEM–EDX analysis of the carbon sphere (the product without any treatment) shown in the elliptic-boxed area in Fig. 5B, and no calcium was detected in it. As to the other elements than carbon, oxygen atom may be due to the influence of O_2 in the air, while Cr and Fe elements may come from the steel reactor.

4. Conclusions

In summary, approximate uniform diameter carbon spheres have been successfully synthesized in high yield by chemical reduction of dense CO_2 with metallic calcium at 550 °C. It is found that the reaction temperature has crucial effects on the morphology of the final product. At the same time, the growth mechanism of carbon spheres in supercritical CO_2 system is suggested. This experiment may provide a new method for the large-scale preparation of carbon spheres as well as the comprehensive treatment of CO_2.

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References

[1] H.W. Kroto, J.R. Heath, S.C. Obrien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[2] S. Iijima, Nature 354 (1991) 56.

[3] M. Inagaki, Synthetic Met. 125 (2002) 139.

[4] A.M. Mikiyoshid, R. Castillo, S. Ramos, L. Rendon, S. Tehuacanero, Carbon 32 (1994) 231.

[5] Z.X. Wang, L.P. Yu, W. Zhang, Z.Y. Zhu, G.W. He, Y. Chen, G. Hu, Phys. Lett. A 307 (2003) 249.

[6] D. Ugarte, Nature 359 (1992) 707.

[7] X.M. Sun, Y.D. Li, Angew Chem., Int. Ed. 43 (2004) 597.

[8] X.B. Yan, T. Xu, S. Xu, G. Chen, H.W. Liu, S.R. Yang, Carbon 42 (2004) 2769;
X.B. Yan, T. Xu, S. Xu, G. Chen, H.W. Liu, S.R. Yang, Carbon 42 (12–13) (2004) 2769.

[9] W.A. Deheer, D. Ugarte, Chem. Phys. Lett. 207 (1993) 480.

[10] V.L. Kuznetsov, A.L. Chuvilin, Y.V. Butenko, I.Y. Mal'kov, V.M. Titov, Chem. Phys. Lett. 222 (1994) 343.

[11] N. Hatta, K. Murata, Chem. Phys. Lett. 217 (1994) 398.

[12] J.W. Liu, M.W. Shao, Q. Tan, X.Y. Chen, Y.T. Qian, Carbon 41 (2002) 1682.

[13] Z.S. Lou, Q.W. Chen, J. Gao, Y.F. Zhang, Carbon 42 (2004) 229.

[14] Z.S. Lou, Q.W. Chen, Y.F. Zhang, W. Wang, Y.T. Qian, J. Am. Chem. Soc. 125 (2003) 9302.

[15] Z.S. Lou, Q.W. Chen, Y.F. Zhang, Y.T. Qian, W. Wang, J. Phys. Chem. B 108 (2004) 4239.

[16] Z.S. Lou, Q.W. Chen, W. Wang, Y.F. Zhang, Carbon 41 (2003) 3063.

[17] W. Ruland, B. Smarsly, J. Appl. Cryst. 35 (2002) 624.

[18] F. Tuinstra, J.L. Koenig, J. Chem. Phys. 53 (1970) 1126.

[19] M.W. Shao, Q. Li, J. Wu, B. Xie, S.Y. Zhang, Y.T. Qian, Carbon 40 (2002) 2961.