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Gaseous detonation chemical synthesis of onion-like carbons

Ning Luo,*[a,b] Hongwen Jing,[a,b] Zhanguo Ma[a,b] and Ronghua Chen*[b]

[a] *State Key Laboratory for Geo-mechanics and Deep Underground Engineering, China University of Mining and Technology, 221116 Xuzhou, P. R. China. E-mail: nluo@cumt.edu.cn*
[b] *School of Mechanics and Civil Engineering, China University of Mining and Technology, 221116 Xuzhou, P. R. China*

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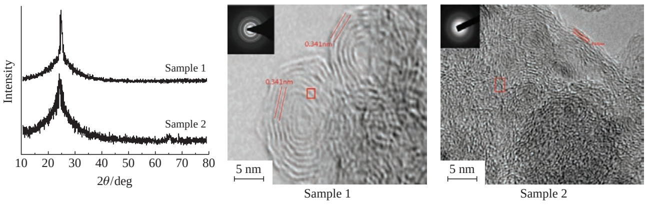
The onion-like carbons (OLCs) were synthesized from the mixtures of gaseous methane, benzene and oxygen by a shock-wave induced rapid chemical chain reaction under extreme conditions (at high temperatures and pressures). The OLCs consisting of spherically concentric graphitic shells with sizes of about 5–30 nm were obtained. The morphology and structure of the products were studied by XRD analysis, TEM, EDX and Raman spectroscopy.



Carbon onions, which are sometimes called carbon nano-onions or onion-like carbons (OLCs), are an intriguing class of carbon nanostructure materials that consist of spherical carbon nanoparticles as sp^2-hybridized multishell fullerenes from nested fullerenes to small (<100 nm) polyhedral nanostructures. Iijima[1] discovered OLCs while looking at a sample of carbon black in a transmission electron microscope; then, Ugarte[2,3] put forth a formation mechanism for spherical graphitic carbon onion structures. Although different methods for the synthesis of OLCs are currently available, the only scalable synthesis route employs the thermal annealing[4,5] of detonation nanodiamond above 1000 °C and high energy annealing methods[6–8] yielding a high level of control over the resulting OLCs. Large-scale syntheses by chemical vapor deposition, combustion, a solvothermal route,[9–11] *etc*. have also been reported. These experimental results show that the active C=C bonds of fullerene nanostructures in various configurations lead to rich structure transformations and the creation of new carbon phases upon compression.[12] Gaseous detonation based on a detonation wave induced gaseous phase precursor has been successfully applied to the synthesis of carbon composites, metal oxides and nitrides.[13–16] However, to our knowledge, the synthesis of carbon nanostructure materials by a gaseous detonation chemical reaction method has been of limited success. Here, we report an efficient synthesis of nanostructure carbon materials in good to excellent yields. The nanoscale structural OLCs were prepared by a rapid and efficient chemistry reaction with gaseous mixtures (the methane–benzene–oxygen system).

In this study a detonation tube was designed for gaseous detonation chemistry reactions using a high-energy igniter, which can provide up to 40 J ignition energy. When a flammable vapor mixture was heated, a rapid detonation reaction was initiated to ignite the vapor mixture. In addition, the ignition end of the detonation tube had a detonation acceleration part 15 mm in diameter and 20 mm in length to extend the detonation tube gaseous ignition area and to effectively promote the rapid and stable growth of a detonation wave for the combustible gas reaction after high-energy ignition of flame front stormed the tube reactor. Astrochemical and combustion models of the formation of polycyclic aromatic hydrocarbons propose molecular weight growth processes through sequential reactions of aromatic and resonance-stabilized free radicals, eventually leading to carbonaceous nanoparticles.[17]

Initially, we attempted to synthesize OLCs from oxygen and benzene. Very large solid amorphous carbon (about 8 wt% of carbon in liquid benzene) was collected at the (C/H):O atomic ratio of about 25–20:13. Meanwhile, the chemical reaction of vapor mixture was performed at 150–180 °C and 0.8–1 atm. Actually, these gaseous reactions are not so easy to control for the preparation of nanoscale materials.[13–15] In order to elevate the detonation temperature, pressure and velocity based on experimental data and numerical calculations,[18,19] CH_4 was introduced into the mixtures.[20] Thus, the mole ratios of gaseous methane and oxygen to benzene vapor were no higher than 5–9, and the initial reaction temperature and pressure were under control in ranges of 150–180 °C and 1.0–1.5 atm, respectively. Table 1 summarizes the experimental process parameters and related synthetic products. Based on the experimental results, the temperature and pressure of detonation chemistry reaction were higher than 1500 K and 3 MPa, which are more conducive to graphitization.[21,22]

The black product was formed by a rapid reaction in the tube reactor for about 3–5 ms. In the products, the yield of solid carbon was significantly enhanced after a detonation reaction process. Finally, the black powders were obtained with a minority of amorphous carbon particles, which were removed with a 10% solution of hydrochloric acid. The OLCs were washed with

Table 1 Synthesis conditions and properties of OLCs (T = 150–180 °C).

P/atm	$CH_4:C_6H_6:O_2$ ratio	Content	Diameter/nm	Characteristics based on HRTEM analysis data
0.8–1	0:6:5	amorphous carbon	–	–
1.0–1.5	18–25:6:3	OLCs-1	22.8	concentric circles (5–30 nm)
1.0–1.5	25–28:6:3	OLCs-2	26.6	concentric circles with amorphous carbon (~30 nm)

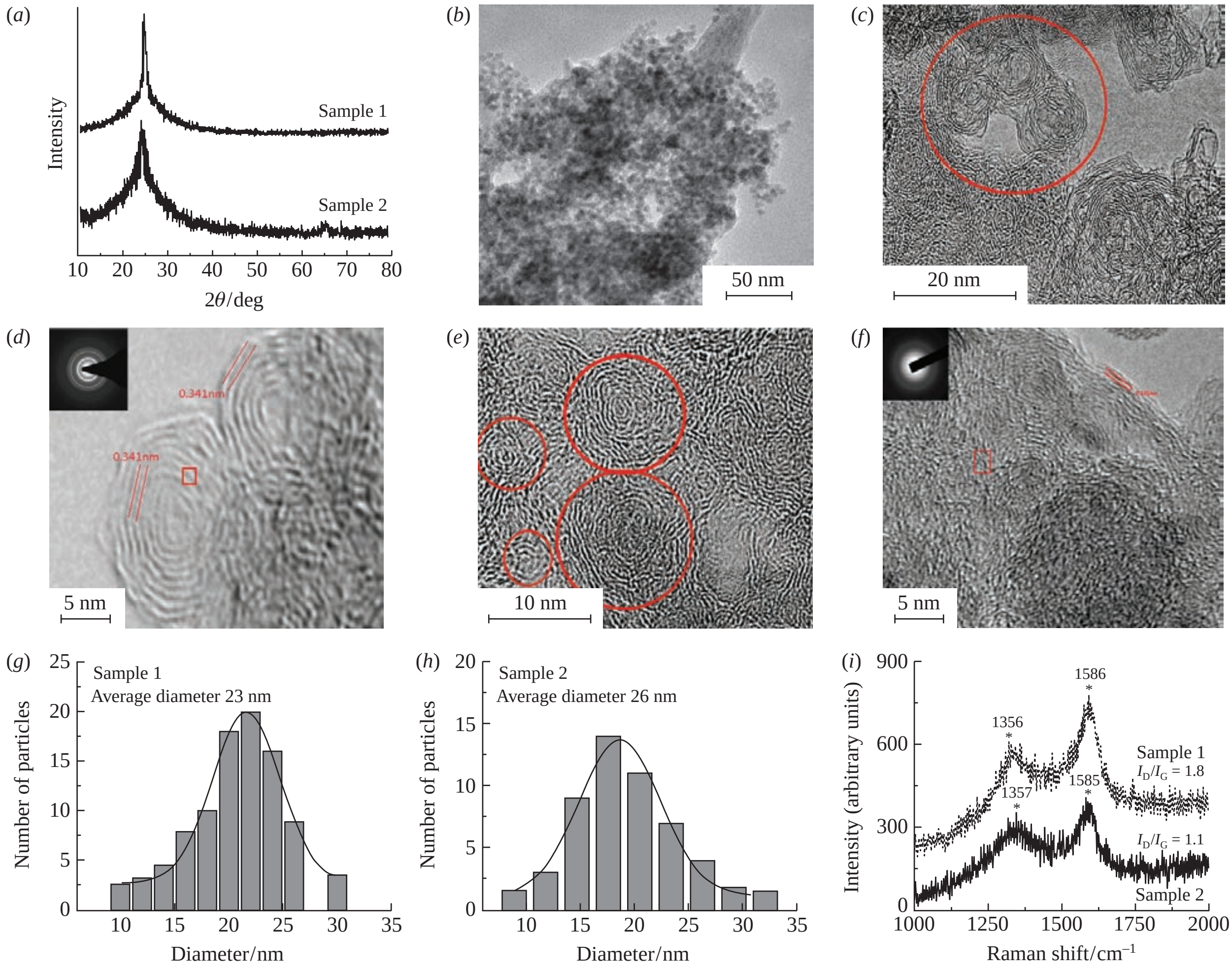


Figure 1 (*a*) XRD spectra of OLC products, (*b*) TEM image of OLCs, (*c*) HRTEM images of well-crystallized OLCs, (*d*) the inserted image is EDX pattern of OLC from sample 1 (the selected square), (*e*) HRTEM images of OLCs with a small quantity of amorphous carbon, (*f*) the inserted image is the EDX pattern of amorphous carbon from sample 2 (the selected rectangle), (*g*) and (*h*) bar diagrams of the OLCs diameters for samples 1 and 2 based on the TEM images, and (*i*) the Raman spectra of OLCs.

absolute ethanol and then dried in air. The OLC content of the obtained black powders was 85–90%. Additionally, the gaseous detonation products mainly contained CO and H_2O, and toxic carbon monoxide was removed by an oxidation–reduction method or recycling utilization.

Figure 1 shows the as-prepared OLC powders.[†] The peaks of OLCs are nearly equal to 25.8°, the 2θ are sharp diffraction peaks close to the graphite (002) plane of 26.4°. The peaks indicate a good degree of crystallization. Furthermore, the layer space is about 0.341 nm, which can be calculated according to the characteristic peak positions. Because of the tensile stress between the graphite layers, the structure of OLCs is slightly different from the presence of graphite. On the other hand, OLC-2 contained large amounts of amorphous carbon from the roughness of XRD patterns. The morphology and microstructure of the samples were investigated by TEM and HRTEM. In the first sample, the diameter of the concentric onion carbon was 5–30 nm [Figures 1(*a*) and (*b*)] with an average diameter of about 23 nm [Figure 1(*g*)]. The HRTEM image [Figure 1(*d*)] indicates well-crystallized onions, which contain four to ten spherical shells with an interlayer spacing of about 0.341 nm. The EDX inset (square box) image verifies the well-crystallized carbon structure.

The second sample is poorly crystallized larger onions [Figure 1(*e*)]; meanwhile, a small quantity of disordered carbon from the holey carbon, that is, amorphous carbon, can also be observed [Figure 1(*f*)]. The EDX inset (rectangle box) image verifies the amorphous carbon structure. The average diameter of the concentric onion carbon was about 26 nm [Figure 1(*h*)]. Our results clearly indicate a spontaneous tendency of the growth of OLCs from carbon-rich mixture precursors and the formation of curved graphitic sheets. Furthermore, the RS results confirm the only presence of carbon in the samples. Figure 1(*i*) shows a high Raman G peak and narrower width, thereby confirming a similar chemical structure of graphite carbon atom layers. Meanwhile, due to the size effect and uneven diameter distribution, the G-peak frequency shift occurs from 1582 to 1586 cm^{-1}. The intensity of the original D peak at 1346 cm^{-1} is weaker, and a shift occurs to 1356 cm^{-1}, which indicates a high degree of graphite to form OLCs. The D band of sample 2 is broader than that of sample 1 and the G band of sample 1 is higher than that of sample 2, which show the higher degree of graphitization [see Figure 1(*g*)]. In other words, the Raman spectra should be normalized with respect to the D band intensity to illustrate changes in the I_G/I_D intensity ratio from 1.8 to 1.1. Obviously, the well-organized sp^2-hybridized OLC was obtained with the introduction of methane. As is well known, carbon onion features

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[†] The morphology and structure of the synthesized OLCs samples were studied using a TECNAIF-30 transmission electron microscope (TEM and HRTEM) operated at 300 kV, a point resolution of 0.205 nm and a line resolution of 0.102 nm with an energy dispersive X-ray (EDX) detector. The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX2400 instrument operated at a step size of 0.02 in a range of 10–80° with CuKα radiation (k = 0.15406 nm; voltage, 40 kV; and current, 30 mA). Raman spectroscopy (RS, Renishaw micro-Raman 2000, 632.80 nm He–Ne laser excitation) was used to determine the basic components of OLCs.

are mainly multiple shells of sp^2-hybridized carbon, varying degree of carbon ordering within the shell, shape varying from spherical to polyhedral and possible presence of non-sp^2-hybridized carbon, typical sizes varying in the range of 10–40 nm in our experimental results. Apparently, the other features of OLCs are different from those of the graphite carbon, especially, in microstructure characteristics. These features can be characterized and confirmed by XRD, TEM, RS, EDX and other methods.

Thus, we reported an effective, fast and low cost technique to synthesize various mesoscale carbon and carbon composite materials by employing detonation shock wave induced extreme chemical reaction conditions. This technique results in a substantial drop in the cost of OLCs and a widening of applications.

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References

1 S. Iijima, *J. Cryst. Growth*, 1980, **50**, 675.
2 D. Ugarte, *Nature*, 1992, **359**, 707.
3 D. Ugarte, *Carbon*, 1995, **33**, 989.
4 K. Bogdanov, A. Fedorov, V. Osipov, T. Enoki, K. Takai, T. Hayashi, V. Ermakov, S. Moshkalev and A. Baranov, *Carbon*, 2014, **73**, 78.
5 J. K. McDonough, A. I. Frolov, V. Presser, J. Niu, C. H. Miller, T. Ubieto, M. V. Fedorov and Y. Gogotsi, *Carbon*, 2012, **50**, 3298.
6 R. Borgohain, J. Yang, J. P. Selegue and D. Y. Kim, *Carbon*, 2014, **66**, 272.
7 A. V. Gubarevich, J. Kitamura, S. Usuba, H. Yokoi, Y. Kakudate and O. Odawara, *Carbon*, 2003, **41**, 2601.
8 Z. Zhu, *Mod. Phys. Lett. B*, 2003, **17**, 1477.
9 C. He, N. Zhao, C. Shi, X. Du, J. Li and L. Cui, *J. Alloys Compd.*, 2006, **425**, 329.
10 M. Choucair and J. A. Stride, *Carbon*, 2012, **50**, 1109.
11 J. P. Xiao, M. G. Yao, K. Zhu, D. Zhang, S. J. Zhao, S. C. Lu, B. Liu, W. Cui and B. B. Liu, *Nanoscale*, 2013, **5**, 11306.
12 A. R. Kamali and D. J. Fray, *Chem. Commun.*, 2015, **51**, 5594.
13 E. G. Gillan, *Chem. Mater.*, 2000, **12**, 3906.
14 X. J. Li, X. Ouyang, H. H. Yan, N. Luo and F. Mo, *Rare Metal Mater. Eng.*, 2011, **40**, 11.
15 N. Luo, H. Jing and Z. Ma, *Mater. Lett.*, 2014, **137**, 164.
16 N. Luo, T. Chen, K. Liu and Y. Shen, *Mendelev Commun.*, 2013, **23**, 153.
17 B. B. Dangi, D. S. N. Parker, T. Yang, R. I. Kaiser and A. M. Mebel, *Angew. Chem. Int. Ed.*, 2014, **53**, 4608.
18 Z. Fu, K.-X. Liu and N. Luo, *Chin. Phys. B*, 2014, **23**, 020202.
19 N. Luo, H. Jing, Z. Ma, Y. Wang, G. Sun and W. Liu, *Particulogy*, 2016, **26**, 102.
20 G. Ferrara, A. Di Benedetto, E. Salzano and G. Russo, *J. Hazard. Mater.*, 2006, **137**, 654.
21 E. A. Skryleva and N. Yu. Shulga, *Fullerenes Nanotubes Carbon Nanostruct.*, 2012, **20**, 459.
22 W. Zhang, M. Yao, X. Fan, S. Zhao, S. Chen, C. Gong, Y. Yuan, R. Liu and B. Liu, *J. Chem. Phys.*, 2015, **142**, 34702.

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