J Mater Sci (2007) 42:3805–3809
DOI 10.1007/s10853-006-1354-3

Synthesis of encapsulating and hollow onion-like fullerenes from coal

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Received: 31 October 2005 / Accepted: 28 February 2006 / Published online: 11 February 2007

Abstract Onion-like fullerenes (OLFs) with different structures were synthesized from coal by radio frequency plasma. The morphologies and structures of the products were characterized by field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) techniques. The results clearly indicated that two types of uniform OLFs with high purity could be prepared from coal, and Fe in coal favored the growth of OLFs.

Introduction

Since onion-like fullerenes (OLFs) involving concentric shells and hollow-cage structures of giant fullerenes were first reported by Ugrate [1], a large number of efforts have been carried out to research the novel nanomaterial [1–5]. Based on their excellent properties, many potential applications, such as nano-electronic-magnetic devices, gas-storage and biotechnology, have been proposed [6–8].

In recent years, filling the central void of OLFs with nanosized magnetic metal particles or carbidic species has also been actively pursued [9]. Magnetic encapsulating OLFs might have important applications in fields such as high-density magnetic data storage, magnetic toner in xerography and contrast agents in magnetic resonance imaging [10, 11]. It is well known that the role of outer carbon coating or shells can protect the nanosized metal particles from oxidation and degradation. This enlarges the applications of OLFs at the same time.

Up to now, various techniques have been developed to synthesize two types of OLFs [1–5, 9]. High energy conditions and expensive starting materials of these techniques are mainly responsible for the high cost of preparing OLFs and limit their practical application. Coal is one of cheap and readily available carbon sources in nature. Although previously the preparation has been reported of fullerenes such as C_{60} and C_{70} [12], carbon nanotubes [13] and other carbon nanomatericals [14] from coal, there has been few reports for synthesizing various OLFs from coal. In this paper, a novel method for the synthesis of two types of OLFs from coal by radio-frequency plasma (RF plasma) was reported.

Experimental

One typical gas coal from Pingshuo coal mine in Shanxi Province of China was used in this study. The proximate and ultimate analysis of the coal sample is shown in Table 1, and the composition analysis of coal ash is shown in Table 2. The as-received coal sample was crushed and sieved to 200 mesh, and fully dried at 383 K for 12 h before use. Then the coal powder was used directly as reactants and put into reaction chamber. The device used here is SY type 500 W

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Table 1 Analysis data of coal sample

Proximate analysis (wt%)			Ultimate analysis (w_{daf} %)				
M_{ad}	A_d	V_{daf}	C	H	N	O	S
4.17	18.69	39.08	78.76	5.39	1.46	13.71	0.68

Table 2 Composition analysis of coal ash (wt%)

Fe_2O_3	Al_2O_3	SiO_2	TiO_2	CaO	MgO	K_2O	Na_2O
5.47	42.59	41.80	0.80	5.02	0.24	0.42	0.11

radio frequency plasma reactor. The plasma is excited by the high-frequency coil around a quartz chamber in Ar atmosphere. The RF power was maintained at 450–480 W and the substrate was heated directly by plasma without additional heating sources. Ar pressure was kept constant at 30 Pa while the flow rate was 22.0 standard cubic centimeters per minute (sccm). The experiments lasted for 30 min and 60 min, respectively, and then the chamber was cooled down to room temperature in Ar atmosphere. The film-like deposits on the chamber walls were collected and characterized by field emission scanning electron microscopy (FE-SEM, JSM-6700F) and high-resolution transmission electron microscopy (HRTEM, JEM-2010, 200 kV, 0.19 nm) with energy dispersive X-ray spectroscopy(EDS).

FESEM observations were performed by placing the as-synthesized samples on conductive carbon tape. The samples for HRTEM observation were prepared by dispersing the products in ethanol with ultrasonic treatment for 15 min, and then deposited on a carbon-coated copper grid.

Results and discussions

FESEM image of the deposits on the chamber walls (reaction time: 30 min) is shown in Fig. 1. It can be seen that the deposits are mainly spherical particles with clearly identified cores and shells, and the diameter of these particles is around 30–40 nm. No other carbon nanomaterials such as carbon nanotubes are observed.

Figures 2 and 3 show a series of TEM and HRTEM images of the carbon particles obtained from the reaction with plasma treatment for 30 min. It can be observed that dark metallic species are encapsulated by spherical, quasi-spherical and a few, if any, irregular carbon shells of OLFs. This kind of encapsulating OLFs are isolated from each other. A limited amount of amorphous carbon particles are also evident (shown by the arrow in Fig. 2). Moreover, some OLFs have a gap between metal Fe crystal (as proven below) and carbon cage, this phenomenon has also been seen by some other researchers [15]. This may be related to the difference in the activities of active sites on the surface of metallic species, resulting from the structural anisotropy of imperfect sphericity. At a higher magnification (Fig. 3), several spherical or quasi-spherical encapsulating OLFs are evident, with the shells being uniform in thickness (about 4 nm). An interface between cores and carbon shells is clearly seen from Fig. 3a and b, which shows that the outer carbon layer is generated as a result of catalysis by inner metal nanoparticles, and a few layers in shells display higher degree of graphitization while others are amorphous carbon (as shown by the elliptic frame in Fig. 3a). The

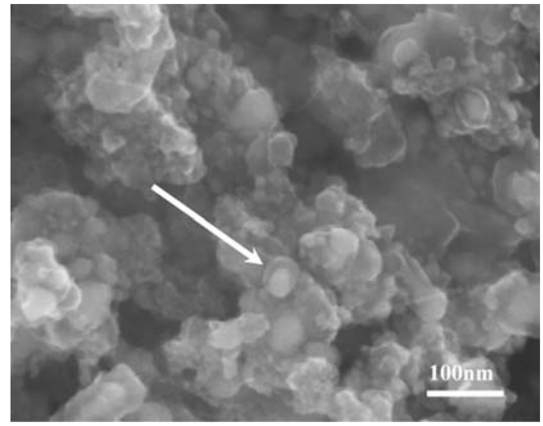

Fig. 1 FESEM image of encapsulating OLFs. The arrow points a typical spherical particle with clearly identified core and shell

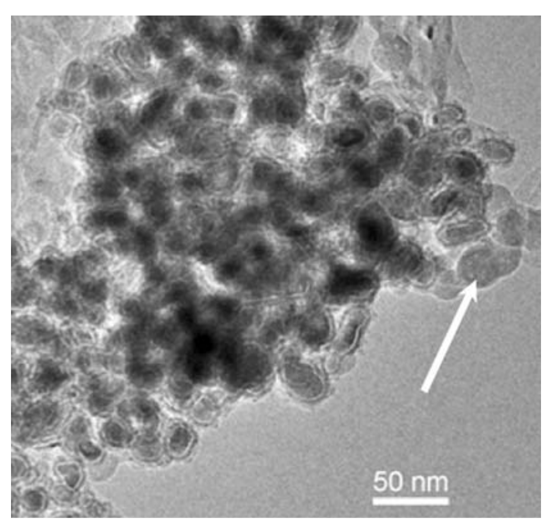

Fig. 2 TEM image of encapsulating OLFs. some amorphous carbon particles are shown by the arrow

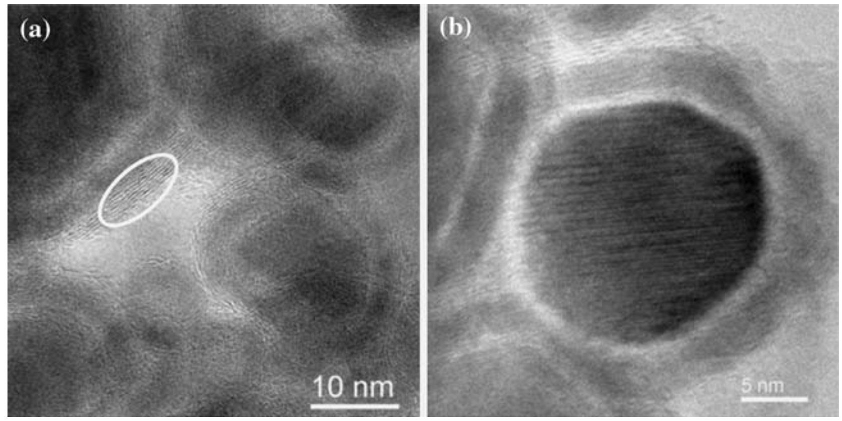

Fig. 3 HRTEM images of encapsulating OLFs (a) several irregular encapsulating OLFs, (b)quasi-spherical encapsulating OLFs. A few graphitic layers are shown by the elliptic frame

carbon of outer layers is a semi-graphitic carbon, which readily develops into well-ordered graphitic carbon via graphitization accelerated by the enclosed iron nanoparticles when further heated at above 1300 K by vacuum heat treatment [16].

The elemental composition of the cores and the shells were analyzed by EDS (Fig. 4). It was found that Fe and trace of Cu existed besides C which was resulted from carbon shells. The presence of Cu may result from copper grid used to support the products. Clearly Fe was one of the ash subcomponents of the parent coal, as shown in Table 2. Previous studies showed that a few mineral matters in coal were in favor of the formation of carbon nanotubes [13, 17]. So it was thought that Fe in coal sample may act as the catalyst for encapsulating OLFs growth. By accurate measurement of several HRTEM images of the cores, the inter-planar spacing was determined to be 0.207 nm, probably corresponding to the (210) plane of Fe_3C crystal. Because the atomic number of Fe is higher than that of carbon, the contrast of Fe_3C is darker than that of the carbon shell observed from TEM.

The degree of graphitization would usually become higher if carbon layers are further treated by plasma for longer time, so the reaction time was prolonged to 60 min. It is interesting to find that a large amount of hollow OLFs were formed in the deposits although the yield of the deposits was not increased obviously. Figure 5 shows the FESEM image of the carbon particles obtained from coal with a reaction time of 60 min. It is found that this deposit contains spherical particles with diameter in the range of 15–30 nm, which is smaller than encapsulating OLFs. CNTs are not observed. HRTEM (Fig. 6a, b) observation reveals that the as-synthesized OLFs display clear elliptic (as shown by the arrow in Fig. 6a) or perfect spherical morphology with hollow center, and about 0.342 nm in shell spacing. The degree of graphitization is quite higher than the encapsulating OLFs as shown above. These OLFs are different from those synthesized by electron beam radiation (usually quasi-spherical shape, and the innermost graphite shell diameter is close to that of C_{60}) [2], but are similar to those synthesized by arc discharge [4]. They may potentially act as medicine supports applied in medicine field in future because of their uniform hollow-cage structure as same as C_{60} and hollow Si nanoparticles.

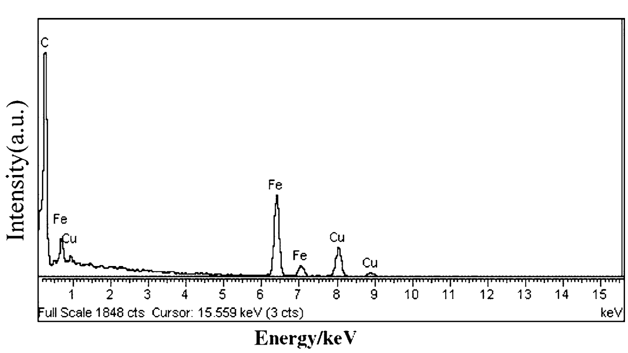

Fig. 4 EDS spectrum of individual encapsulating OLFs as shown in Fig. 3b

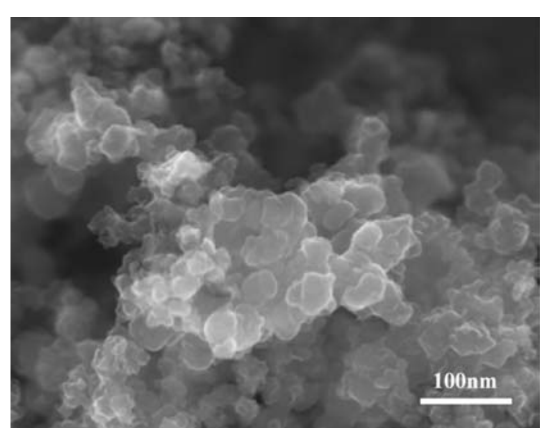

Fig. 5 FESEM image of hollow OLFs

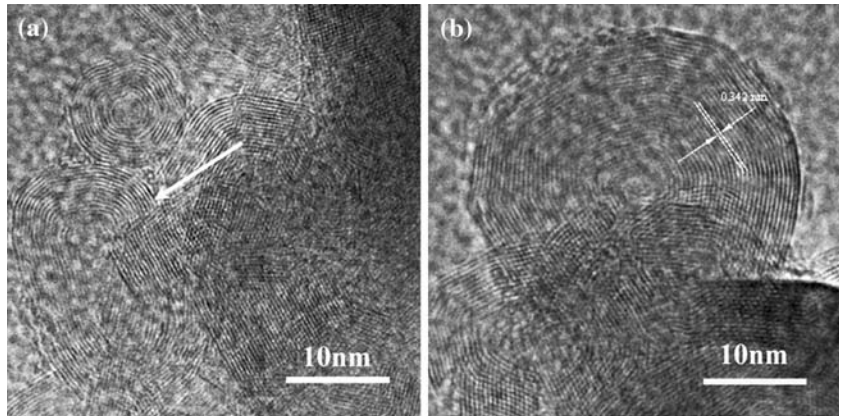

Fig. 6 HRTEM images of various shapes of hollow OLFs: (a) elliptic OLFs, (b) spherical OLFs

The formation mechanisms of encapsulating OLFs and hollow OLFs are not well understood because of limited available information at present. Nevertheless, it must be related to the chemical structure of coal and RF plasma method. Fixed carbon (Fc_{daf}) is an important index of coal. Active carbon concentration taking part in the formation of carbon nanomaterials is higher when carbon content in coal increases, so Pingshuo coal with higher carbon content should be a good starting material for preparing fullerenes. As is well known, RF plasma is one of non-equilibrium plasma, the temperature of heavy particles such as ions and atoms can be only 300–500 K, but electron temperature can reach as high as 10^4K. Once reaction begins, the relatively weak cross-links between adjacent aromatic units in the organic macromolecular structure of coal would be broken easily by the high energy Ar^+, and a large amount of aromatic fragments would be released [18]. Though some aromatic fragments will be further broken up into C_1 or C_2 species under the violent bombardment of high energy electrons, aromatic fragments are dominant. In addition, some components in coal such as Fe, Si, Al oxides (Table 2) are in favor of carbon nanomaterials formation. The mineral matter in coal will be gasified along with the evaporation of fixed carbon under RF plasma condition, and quickly decomposed into small species such as Fe after colliding with Ar^+, which mix with carbon species and suspend in plasma center zone. If the surfaces of metal nanoparticles have enough active sites, the aromatic fragments or C_1 and C_2 species will reorganize and epitaxially form encapsulating OLFs. Fe plays the role of catalyst for the growth of the OLFs, as proved by EDS analysis. A small amount of amorphous carbon particles and graphite debris are also produced in the absence of catalyst. Volatile matters are mainly composed of C_2H_2 and H_2 molecules under Ar plasma condition, carbon layers can be etched in the presence of hydrogen in the plasma [19]. With the reaction time extended, the system temperature will be gradually enhanced because energy consuming heteroatom atoms vanish. Plasma zone resembles a vacuum heat treatment chamber here, so Fe would escape from carbon layers in final annealing process, and some amorphous carbon species etched by H atom would deposit on the surface of previously formed OLFs and grow there. According to the lowest energy rules [20], single-shell graphitic molecules containing thousands of atoms are unstable and will collapse to form multi-layer OLFs. Apparently, much work is needed, such as further improving OLFs yield, optimizing the reactor and the operation parameters, before this technique can be put into practical application.

Conclusions

Two types of OLFs were synthesized selectively from coal by radio frequency plasma. The OLFs display spherical or quasi-spherical morphology with Fe-including core structure and small hollow center separately. Both of the OLFs have relatively narrow size distribution. The growth mechanisms of these OLFs were discussed briefly in terms of the chemical structure of coal and RF plasma method. The experimental results confirmed that Fe from the mineral matter in coal plays an important role for the growth of OLFs in this process. The method described here suggests a novel and promising route to synthesize OLFs on a large scale at low cost.

Acknowledgements The authors acknowledge financial support from National Basic Research Program of China (Grant No. 2004CB217808), Key Project of National Natural Science Foundation of China (Grant No. 90306014), National Natural Science Foundation of China (Grant No. 20471041), National Science Foundation of Shanxi Province (Grant No. 20051018) and Shanxi Scientific Research Foundation for Returned Scholars (Grant No. 200428).

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