An effective method of increasing production rate of onion-like fullerenes

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Abstract. Onion-like fullerenes (OLF)s were synthesized by arc discharge in benzene using graphite as electrode and ferrocene as catalyst. The effect of ferrocene on the morphologies and structures of the OLFs was investigated by HRTEM and XRD. Results show that ferrocene directly influenced the morphology and yield of OLFs: The degree of graphitization is better. The diameters of the OLFs can be controlled in the range between 10 and 30 nm. The method described here suggests a novel and promising route to synthesize OLFs in large scales.

1. Introduction
Onion-Like Fullerenes (OLF)s have unique hollow cage and concentric shells structure, They can be promisingly applied as source materials, high-powered and high temperature wearable materials, superconduct materials and bio-medical materials[1-2]. The main methods of synthesis of Onion-like Fullerenes (OLF)s are by arc discharge[3-6], electron irradiation[7], radio frequency plasma[8], chemical vapor deposition[9-10], arc in water or liquid nitrogen.[11-15] etc. ‘Arc in liquid’ method is a cost-effective technique lately proposed to fabricate carbon nanomaterials, which does not require vacuum facilities. However, the production rates of the resulted materials are limited by the evaporation rate of the graphite electrodes. This restriction may cause a limit to apply the ‘arc in liquid’ method to large-scale production[16].

In order to increase the production rate of carbon nanomaterials, Sano[16] first used liquid benzene (C₆H₆) as the quenching media because organic liquid is expected to play a role of carbon source[16]. As a result, CNTs and OLFs are not formed in this condition. In this paper, the author also used liquid
benzene (C₆H₆) as the quenching media, the graphite as the electrode and ferrocene as catalyst. The result indicates that OLFs could be efficiently synthesized in high yield.

2. Experimental
Direct current (dc) arc discharge was generated between a graphite cathode (diameter = 20mm) and an anode (diameter = 6mm) submerged in liquid benzene (1000cm³) of ferrocene (10g) in a glass container. Using the self-sustained arc-discharge mode, the discharge voltage and current were 22–25V and 50A. During arc discharge, an anode was moving with certain speed, the current 50A was sustained for 5 min by adjusting the cathode–anode gap to be approximately 1 mm. Deionized water was continuously supplied into the container to cut the air off from the reaction field to avoid explosion of evaporated C₆H₆. After completion of the arc discharge, the fine powders suspended in the residual liquid C₆H₆ was collected using cyclic filter, the fine powders were put in resistance furnace to heat up to 500°C under the argon atmosphere, maintain 30 min, the elimination condenses organic matter, cooling spare. The products were characterized by high resolution transmission electron microscopy (HRTEM, JEM-2010 at 200 kV) and X-ray diffraction (XRD).

3. Results and discussion
3.1 morphology and structure
Fig.1 shows TEM images of product prepared using benzene as carbon source and ferrocene as catalyst. Fig. 1(a) focused many carbon nanoparticles by HRTEM, mainly is hollow spherical and polyhedron OLFs, The diameters of OLFs are in the range from 10 to 30nm. The degree of graphitization is higher. CNTs clearly could be observed. Fig. 1(b) shows the magnification image of marked part by a white square in (a) and represent hollow spherical OLFs with diameters of about 20 nm, hollow diameter is bigger and about 10nm, Shelled layer constituted by the 12 concentric graphite layer. The degree of graphitization is better. The particle shape was considered to be nearly spherical, though most were not perfect spheres.

![Figure 1. HRTEM images of produces using ferrocene as catalyst](image)

Fig.2 shows TEM images of product prepared by arc discharge in benzene. Obviously, the purity of OLFs in Fig.1 was higher than in Fig.2. Here, it must be reminded that the fine powders suspended in the residual C₆H₆ liquid contains OLFs and MW-CNTs. the cathode deposit did not formed by arc in mixture of benzene and ferrocene. Therefore, the reaction field at the arc zone in C₆H₆ is considered to
be essentially different from that in mixture of benzene and ferrocene environment. Importantly, the production rate of OLFs and CNTs can be increased by use of ferrocene.

![Image](image.png)

**Figure 2.** Images of products not using ferrocene as catalyst

### 3.2 XRD analysis

The XRD spectra of the samples are shown in Fig. 3. There was a strong peak at $2\theta$ 26.1°, close to $2\theta$ 26.41 for graphite, with the dvalues being about 0.351nm and 0.348 nm, a little larger than 0.336nm for graphite. The peak in the curve is for plane (002) of OLFs. Meanwhile appeared a strong peak in this peak behind, It may be due to the presence of structure curvature or some structure.

![Graph](graph.png)

**Figure 3.** XRD pattern of OLFs prepared from mixture of benzene and ferrocene

### 3.3 Influence on yield and quality of the onion-like fullerenes by ferrocene.

The catalyst is an essential condition of preparing OLFs. Many kinds of catalyst are used to synthesizing Onion-like Fullerenes (OLF) by arc discharge, like Fe,Co,Ni,Yi and so on. Used the benzene as the discharge medium to play a role of carbon source, the catalyst activity is considered when choosing catalyst, meantime, it is considered that whether catalyst can dissolve in the liquid benzene, metal organic compounds eg ferrocene is quite appropriate for catalyst. Using ferrocene as catalyst, the reaction field at the arc zone in C₆H₁₀ is as follows:

$$
C_6H_{10} + Fe(C_2H_3)_2 \quad 3727^\circC \quad 5min \pm 0.08min \quad C_n + C_6H_6 + H_2 + Fe
$$
(in the formula: C₆H₆- benzene Fe(C₂H₅)₂- ferrocene C₇₆₇₆- fullerence C₆H₆- the organic matter H₂- hydrogen).

Direct current arc discharge was generated between a graphite cathode and an anode, temperature can reach 3727 °C, C₆H₆ will decompose to play a role of carbon source. Ferrocene will decompose into Fe and C₂H₅, Fe maybe act as the catalyst of OLFs growth. There are numerous studies on the catalytic growth of fullerenes using metallic nanoparticles[17,18]. Among these studies, a plausible mechanism for the formation of nanotubes and onion-like fullerenes on metallic catalysts could be summarized as carbon-solvation and diffusion in the catalyst particle or surface diffusion, and precipitation growth of graphitic structures. Here, it should be noted that if carbonaceous precursors were not continuously supplied to the Fe nanoparticles, fullerenes could not grow along length. Thus spherical onion-like fullerenes were preferably formed. Therefore, adding ferrocene increased the production rate of OLFs in the same experimental parameters. The result was shown in Table 1.

**Table 1.** Products synthesized by arc discharge in benzene and in mixture of benzene and ferrocene under the condition of same current.

| Current (I/A) | formation rate of product collected in benzene (mg/s) | Anode consumption rate (mg/s) | A formation rate of cathode deposit (mg/s) |
|--------------|-----------------------------------------------------|-------------------------------|------------------------------------------|
| 50           | 20.5                                                | 1.5                           | No                                       |
| 50           | 9.2                                                 | 1.5                           | 9.5                                      |

Arc discharge was generated between a graphite cathode and an anode, which can provide enough energy to decompose C₆H₆ into some aromatic fragments, some aromatic fragments will be further broken up into C₁ or C₂ carbon units, surfaces of the Fe play a role of active sites, the aromatic fragments were nucleated at the surfaces of Fe. Before the chemical bonds are broken up, the aromatic fragments have obtained enough energy to reorganize on the surface of the catalysts and curve with the help of the pentagonal rings. If the smaller aromatic fragments or C₁ and C₂ carbon units act as building blocks in the innermost shell, the central hollow will be smaller, or the central hollow will be larger. After the nucleation is formed and excited to vapor, the aromatic fragments in the vapor continue to bond with the nucleation. Concerning the possible arrangement of concentric defect-free graphite cages, polyhedral OLFs have all the shells in the same orientation, so that all the corners (pentagons) are perfectly superimposed. If the pentagons of the concentric shells are not aligned, the final shapes of OLFs should be much closer to quasi-spherical morphology[19].

4. Conclusions

In summary, The OLFs with high yields have been first synthesized by arc discharge in benzene using graphite as electrode and ferrocene as catalyst. The OLFs display polyhedral or spherical morphology with hollow center. The diameters of the OLFs can be controlled in the range between 10 and 30 nm. The method described here suggests a novel and promising route to synthesize OLFs in large scales.
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