Synthesis and Characterization of Polyhedral Graphite Particles

Wen Qian, Qianwang Chen[*], Fangyu Cao and Changle Chen

Hefei National Laboratory for Physical Sciences at Microscale and Department of Materials Science & Engineering, University of Science & Technology of China, Hefei 230026, P.R. China

Abstract: Hollow polyhedral graphite particles with 200~400 nm in diameter have been synthesized by heating oxalic acid, ferrocene and metallic magnesium at 580 °C, typically forming diamond-like octahedral structure. Combined with SEM, TEM, SAED patterns, and Raman spectroscopy, it was shown that the surface of graphite polyhedrons is composed of approximately 30-40 graphene shells; the four- or six- fold symmetric diffraction spots disclosed the nature of octahedral graphite particles; the edge of the graphite polyhedrons exists sp^3-hybridized bonding, which would act as dangling bonds and localized defects in the polyhedron.

Keywords: Nanostructures, chemical synthesis, crystal structure and symmetry.

INTRODUCTION

While the great stability of carbon-carbon bonds has been recognized for more than 100 years, during very long time after this recognition, polyhedral diamond and lamellar graphite were the only allotropic forms of carbon. In diamond, a typical polyhedral carbon elemental crystal, the four bonds to each carbon atom are arranged in an extremely strong three-dimensional (3-D) matrix. Due to the 3-D structure and the symmetrical arrangement of atoms, diamond crystals usually develop into several different polyhedral shapes including octahedron, cubes, dodecahedra, and combinations of them, known as 'crystal habits'. In contrast, the feature is quite different for the 2-D lamellar graphite, which consists of individual graphene layers. Within a single graphene layer, each carbon atom is tightly bonded to three atoms forming a 2-D flat hexagonal network, while between the graphene layers there is weakly van der Waals force, therefore neighboring graphene layers can slide easily. The synthesis of novel allotropic carbon forms has long been of considerable interest. Synthesis of bulk quantities of sp^2-bonded 0-D fullerene molecules [1] and 1-D nanotubes [2] has demonstrated that abundant structures existing in carbon family, and new forms of carbon is possible [3, 4]. Because of the great difference between the force of sp^2 C-C bond in layer and the van der Waals force between layers, it is hard for graphite-like sp^2 carbon atoms to form a stable diamond-like 3-D feature. However, theoretical calculations have suggested the possibility of fairly stable covalent sp^2 carbon crystals such as schwarzites [5] and hollow graphites [6] into a fully 3D architecture, which have given new perspectives on the structure of sp^2 graphitic carbon [7]. Recently, several polyhedral graphite consisting of discrete fragments of curved graphitic sheets have been obtained, such as graphite polyhedral tubular crystals (GPC) with 1~3μm in diameter and 5~15mm in length [8, 9] and polyhedral graphite particles (called '*G* balls') with 300 nm in diameter [10].

Herein, we report a chemically synthesized novelty of graphitic nanoparticles with diamond-like polyhedral structure, typically forming octahedron. The polyhedral graphite particles is as large as 200~400 nm, exhibiting a 3-D symmetrical feature quite different from a 2-D crystal. The unique microstructure characteristics about the polyhedral graphite particles were also discussed.

EXPERIMENTAL SECTION

Ferrocene (98%), oxalic acid (99.95%), ethanol, hydrochloric acid (analytically pure) and metallic magnesium (98%, chemically pure) were all used as purchased. The typical reaction was carried out by heating a mixture of 3.00 g $H_2C_2O_4$, 1.50 g $Fe(C_5H_5)_2$ and 0.80 g metallic Mg in a stainless-steel autoclave with the capacity of 15 ml at 580 °C for 10 h, and then cooling down to room temperature naturally. The as-prepared products were gray in color; then washed with ethanol, distilled water and 4.0 mol/L HCl aqueous solution respectively; afterwards the precipitate was collected by using a microfilter; followed by washed with distilled water for several times, until the pH value was about 6; finally dried at 110 °C.

The morphology and structure of polyhedral graphitic particles were observed by Field emission scanning electron microscope (FESEM) using a JEOL JSM-6300F SEM, a Hitachi Model H-800 Transmission electron microscope (TEM) with Electron Diffraction, and a JEOL-2010 high-resolution TEM with Energy Dispersive X-ray Detector, using an accelerating voltage of 200 kV. The Raman spectrum was taken on a LABRAM-HR Confocal Laser Micro-Raman spectrometer using an Ar^+ laser with 514.5 nm at room temperature.

RESULTS AND DISCUSSION

Shown in the XRD pattern (Fig. **1**), it is obvious that after the treatment with HCl aqueous solution, the main product of the sample is hexagonal graphite. Fig. (**2a**) shows TEM images of typical polyhedral particles with the average size of 300 nm after HCl treatment (Fig. **2a**) and as-prepared products (Fig. **2a**, insert) respectively. Fig. (**2b**) shows FESEM images of various graphite polyhedron, in which hexahe-

*Address correspondence to this author at the Hefei National Laboratory for Physical Sciences at Microscale and Department of Materials Science & Engineering, University of Science & Technology of China, Hefei 230026, P.R. China; E-mail: cqw@ustc.edu.cn

dron, octahedron, and dodecahedron can be clearly seen. According to TEM and FESEM images observed, the fraction of octahedral particles among the polyhedral particles was approximately 20%. Corresponding EDX spectrum (Fig. **3**) shows C and Cu peaks only, in which Cu signal originated from carbon-coated copper grids. Associated with XRD pattern, the EDX spectrum analysis can confirm that the polyhedral particles are graphite. Fig. (**2c**) displays the TEM images of typical graphite polyhedron, and (Fig. **2d**) is the magnified HRTEM image of boxed area of (Fig. **2c**). The thickness of each face of the octahedron is about 30-40 atomic layers. The inter-sheet between the layers is about 0.35 nm, agrees well with (002) lattice distance in hexagonal graphite (0.34 nm). As to the joint edge between adjacent faces, there exists a discontinuous crystal boundary, which is different from the lattice structure of adjacent faces. Similar results were also found in repeated experiments.
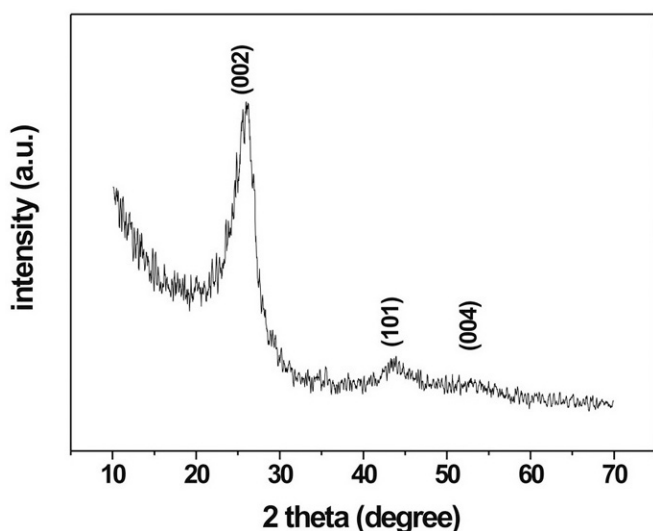

Fig. (1). The XRD pattern of the sample, recorded in the 2θ range of 10-70° by using a Rigaku (Japan) D/max-γA X-ray diffractometer equipped with graphite monochromatized Cu K-alpha radiation (λ=1.542Å).

It is worthy to mention the SAED patterns. Though there is six-fold symmetry in a graphene sheet, the six-fold symmetry is rarely found in the diffraction patterns of graphite because the slide between graphene sheets in graphite destroys the sixfold symmetry in it. Practically, no diffraction spot exists when incident electronic beam is along the (002) orientation of a graphitic single crystal. When incident electronic beam is vertical to the (002) orientation, the diffraction of traditional single crystalline graphite usually shows bisymmetric spots, while polycrystalline graphite shows a diffraction ring. When it comes to carbon nanotubes, the electronic diffraction spots disperse to two small symmetric arcs, whose length depends on the stress of the warped graphene layers. More than two diffraction spots of graphite (002) in one pattern are rarely observed. However, SAED patterns of the octahedral graphitic particles (inset of Fig. **4**), show four- or six- fold symmetric spots corresponding to hexagonal graphite (002) (d = 3.5 Å), quite different from traditional graphite particles. Since there is no axis of tetragonal symmetry in hexagonal graphitic crystal, these diffraction spots should be resulted from the symmetry of the

octahedral particles. Shortly speaking, the emergence of the fourfold or higher symmetric short diffraction arcs is absolutely the unique character of polyhedral graphite particles.
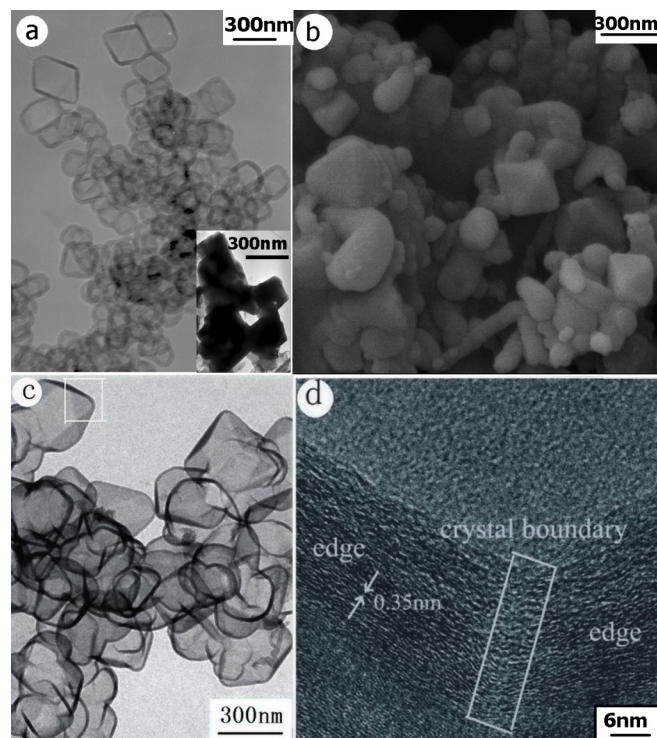

Fig. (2). (**a**,**b**) TEM and FESEM images of large quantities of polyhedral graphite particles with the average size of 300 nm; (**c**) TEM images of typical graphite polyhedron; (**d**) The magnified HRTEM image of boxed area shown in (**c**), shows the discontinuous crystal boundary of polyhedral graphite particle.
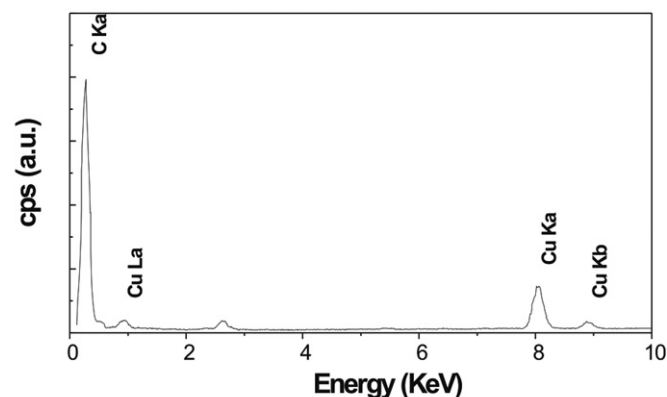

Fig. (3). The typical EDX spectrum of a polyhedral graphite particle, analyzed by a JEOL-2010 HRTEM with Energy Dispersive X-ray Detector.

Raman spectrum is usually used to investigate the vibrational properties of carbon structures, which also allows us to draw further conclusion about the degree of crystallization [11]. Fig. (**5**) represents the experimental Raman spectrum of the sample, as well as the fitting results which were obtained by using the Gaussian method. It is found that the main spectrum can be decomposed into three sets, with the peaks of
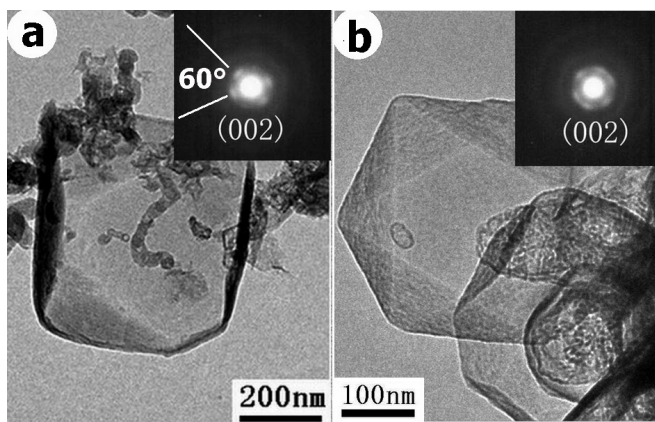
Fig. (4). (**a**,**b**) The typical octahedral-like and polyhedral graphite particles, and the corresponding SAED pattern (insert) consist of four and six diffraction short arcs in the presence of weak diffuse rings respectively.

1332, 1350, and 1598 cm^{-1}. The peak at ~1598 cm^{-1} (G band) corresponding to an E_{2g} mode of graphite is related to the vibration of sp^2-bonded carbon atoms in a 2-D hexagonal lattice, while the peak at ~1350 cm^{-1} (D band) is related to the defects and disorders in the hexagonal graphitic layers [12]. In Fig. (**5**), the value of I_D/I_G is calculated to be 0.63, which means that the sample has the relative disorder and not very highly graphitization degree [13], in agreement with XRD results. Furthermore, it is worthy to be noticed that the peak at ~1332 cm^{-1} corresponds to sp^3-hybridized bonds, indicating the existence of sp^3 bonds environment. Based on theoretical calculations simulating the closed graphitic structures, both De Vita *et al* and V. L. Kuznetsov *et al* had put forward that the sp^3 and sp^2 bonds can coexist, and sp^3 bonds are located at peripheries of graphitic sp^2 sheets [14, 15]. G. Benedek *et al* also predicted the possible *sp^2/sp^3* mixed bonding existing in hollow carbon crystals [6]. All of the above theoretical computations disclosed that the joint edge between adjacent faces of polyhedral graphite particle is likely not composed of sp^2 bond, but connected by sp^3-hybridized bonds, which would act as dangling bonds and localized defects in the polyhedron [16].
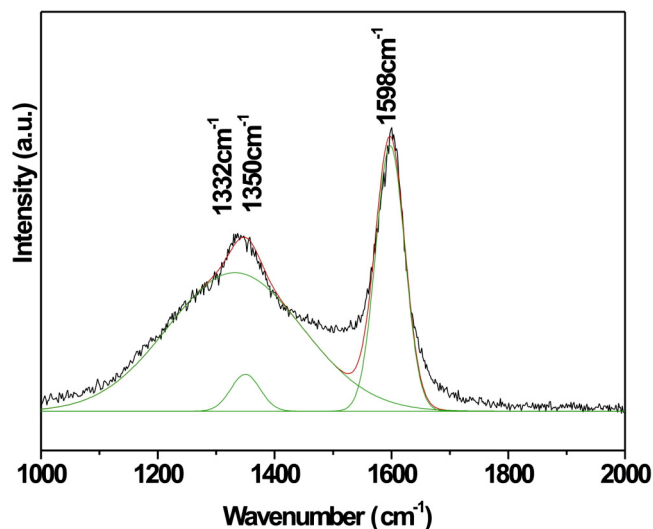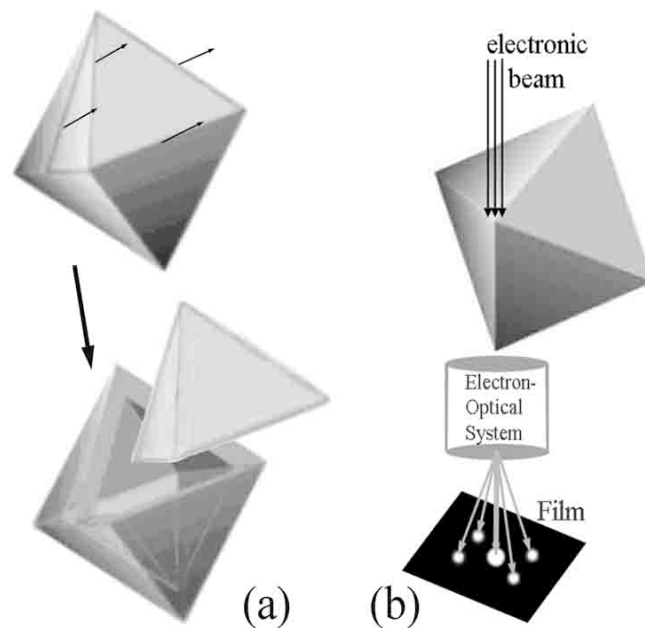

Fig. (5). Typical Raman spectrum and corresponding fitting results of the sample.

In addition, TEM images and SAED patterns have revealed that the polyhedral graphite particles are hollow inside, as shown in Scheme **1**. Each face of the hollow polyhedron consists of graphene multilayers (approximately 30-40 shells). When the incident electron beam is along the edge of one polyhedron, paralleling to the two faces sharing the edge, SAED pattern shows four graphite (002) diffraction spots, which are two series of bisymmetric spots with the center spot as the symmetric center. The separation angle of two corresponding spots from the center spot, which is 60° (Fig. **4a**), is equal to the dihedral angle formed by two adjacent faces of a polyhedron, showing that the polyhedron is octahedron. When a facet of another octahedron is near and parallel to the electronic beam, two more bisymmetric spots may present in the diffraction pattern, as shown in Fig. (**4b**).

Scheme 1. (**a**) Structural model of hollow octahedral graphite particle, consisting of eight plate-like graphite single crystals; and (**b**) Model of the appearance of the four-fold electronic diffraction spots.

These polyhedral graphite particles cannot be obtained without the present of $H_2C_2O_4$ or ferrocene, indicating that carbon in $H_2C_2O_4$ and ferrocene plays different role in the growth of the polyhedrons. As to the possible growth model of polyhedral graphite particles, we would suggest as following: first, $H_2C_2O_4$ is easily decomposed to CO_2, CO, and H_2O when heated over 100 °C, and CO and CO_2 were deoxidized to carbon by metallic Mg slowly, forming initial closed nucleus due to pentagons and heptagons giving rise to a curved geometry at the edges [17]; then catalyzed by iron atoms or iron carbide originating from ferrocene [18], more and more carbon atoms were deposited simultaneously at high temperature, leading to possible concentric growth; eventually terminating with the formation of Fe or Fe_3C nano-crystals encapsulated in polyhedral carbon cages [19, 20], as shown in Fig. (**2a**) insert. Finally, the as prepared products were treated with HCl aqueous solution, so Fe or Fe_3C nano-crystals were removed, forming hollow graphite polyhedron. Further work is still needed to figure out the growth mechanism and illustrate the structure of polyhedral graphite particle clearly.

CONCLUSIONS

In conclusion, we have successfully synthesized the novel hollow graphite particles with polyhedral feature by introducing oxalic acid, ferrocene and metallic magnesium at 580 °C, especially some of them were octahedron-like in shape. The surface of the hollow graphite octahedron is composed of concentric sp^2 graphitic shells, but at the crystal boundary, there exists sp^3-hybridized bonds, which would act as dangling bonds and localized defects. The easily synthesized octahedral graphite particles reported in this letter would give us a new understanding of the 'crystal habits' that a two dimensional crystal like graphite may also crystallize in form of diamond-like three dimensional feature. Moreover, the octahedral graphite would be added in to the family of elemental carbon as a new member, like fullerenes and carbon nanotubes.

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