

Formation of Nanographite Using GaPO₄-LTA as Template

XI, Chun-Yu(奚春宇) LI, Guo-Dong(李国栋) ZHAO, Xu(赵旭)
TIAN, Ye(田野) ZHANG, Yu(张瑜) CHEN, Jie-Sheng*(陈接胜)

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, Jilin 130023, China

An attempt was made to prepare nanographite with uniform size by pyrolysis of 4-methyl pyridine (MPy), which is the structure-directing agent for the formation of GaPO₄-LTA single crystals, in the GaPO₄-LTA framework at 760 °C. The as-prepared nanographite has been examined by Raman spectroscopy, transmission electron microscopy (TEM), electron spin resonance (ESR) and magnetization characterizations. The TEM image shows that the size of individual nanographite particles is about 7 nm, and it is proved that there are spins of sp²-type (π -type) radical electrons localized on the zigzag edge sites of the nanographite. The magnetic susceptibility of the nanographite shows crossover from a high-temperature diamagnetic to a low-temperature paramagnetic behavior, in good agreement with the theoretical expectation.

Keywords nanographite, GaPO₄-LTA, template, magnetic susceptibility

Introduction

Recently, nanosized graphite with open edges has been targeted for intensive studies due to its interesting electronic properties related to nanosized systems.¹⁻¹³ Nanographite particles represent a new class of mesoscopic intermediate between aromatic molecules and extended graphite sheets. Tanaka¹ and Fujita *et al.*²⁻⁴ theoretically predicted the existence of an edge state of nonbonding π -orbital origin around the Fermi level in the finite-size graphene. The graphene edge of an arbitrary shape comprises two types of edges (Figure 1), zigzag and armchair. The former has a *trans*-polyacetylene structure while the latter has a *cis*-polyacetylene one. According to theoretical studies,^{1,2,5-7} the graphite networks with zigzag edges have a localized edge state at the Fermi level, but those with armchair edges have no such state. The size effect of the edge state is of great significance, since the relative importance of edge state should vanish in bulk graphite. Therefore, graphite networks with a nanometer size are the best candidates to exhibit the special edge state. Meanwhile, the synthesis of nanographite has recently been the subject of much experimental work.^{8,9} These experimental findings suggest that the electronic density of state (DOS) is considerably enhanced due to the presence of the edge-inherited nonbonding π -orbitals at the Fermi level, being consistent with theoretical studies.

In this paper, we describe the preparation of 7 nm sized nanographite particles through pyrolyzing 4-methyl pyridine occluded as a structure-directing template in the cage of GaPO₄-LTA, which is an open-

framework gallophosphate with a chabazite topology. The spins observed in the nanographite system are considered to arise from the nonbonding edge states of π -electron. In the presence of magnetic field, the magnetic susceptibility of these nanographite particles shows a crossover from high-temperature diamagnetic to low temperature paramagnetic behavior, in accordance with the theoretical calculation.¹⁰

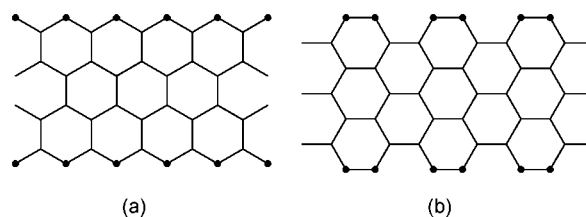


Figure 1 The networks of graphenes with (a) zigzag edges and (b) armchair edges.

Experimental

Preparation

Gallophosphate GaPO₄-LTA single crystals were synthesized by following the procedures described previously.^{11,12} 4-methyl-pyridine (MPy) was used as the structure-directing agent. The as-prepared GaPO₄-LTA sample was placed in the center of a conventional horizontal tubular furnace, followed by the pyrolysis of MPy in the GaPO₄-LTA cages under N₂ flow at 760 °C for 10 h. The heating rate was 5 °C/min from room temperature to 760 °C. A carbon/GaPO₄-LTA compos-

* E-mail: chemcj@mail.jlu.edu.cn; Tel.: 86-431-5168662; Fax: 86-431-5168624

Received April 19, 2004; revised July 5, 2004; accepted August 20, 2004.

Project supported by the National Natural Science Foundation of China (No. 20331010) and the Education Ministry of China.

ite was formed after this treatment. To extract the carbonaceous material from the carbon/GaPO₄-LTA composite, the crystals were soaked in HCl solution (37% in wt) to dissolve the gallophosphate framework of the composite. The carbonaceous material was obtained as an insoluble fraction, which was filtered, washed copiously with deionized water, and dried at room temperature.

Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer by using Cu K α radiation ($\lambda=0.15418$ nm). The Raman spectrum of the carbonaceous material was measured at room temperature with an incident line of 514.4 nm on a Spex 1403 double monochromator Raman spectrometer. The elemental analysis was performed on a Perkin-Elmer 240 element analyzer, whereas the TEM image of the carbonaceous material was taken on a Hitachi-8100IV transmission electron microscope at 200 kV. The infrared spectrum was obtained on a Nicolet 5DX FTIR spectrometer. Prior to measurement, KBr pellet with the sample was mounted in a quartz cell with CaF₂ windows and evacuated at 10⁻² Pa and 150 °C for 1 h, followed by cooling to room temperature. The ESR spectrum was recorded under the protection of pure argon on a Bruker ER 200D ESR spectrometer at X band (9.77 GHz) with a microwave power of 20 mW, and DPPH (1,1-diphenyl-2-picryl-hydrazyl) was used as the standard to determine the *g*-factor value. The magnetic susceptibility was measured with a Quantum Design MPMS-5T SQUID magnetometer in the temperature range of 2–300 K under a magnetic field of 50 kOe.

Results and discussion

As shown in Figure 2, the XRD patterns indicate that the framework of GaPO₄-LTA is not destroyed after thermal treatment at 760 °C. Therefore, the carbonaceous material was formed inside the GaPO₄-LTA crystals. Elemental analysis of the carbonaceous material reveals that the molar ratio of C : H : N is about 4.6 : 1 : 0.3. It is clear that the carbonaceous material extracted from the carbon/GaPO₄-LTA composite mainly consists of carbon, and the minor amount of N and H atoms may exist as hetero atoms on the carbon graphene edges. In the IR spectrum (Figure 3), the bands at 2950 and 2874 cm⁻¹ could be assigned to C—H stretching mode. The bands in the 1400–1600 cm⁻¹ region were assigned to C=C and C=N double bonds, and the band at 1350 cm⁻¹ was assigned to in plane C—H bending. The TEM image of the carbonaceous material is shown in Figure 4, where the regular carbon nano-particles of about 7 nm in diameter can be seen. The MPy, which is the structure-directing agent for the formation of GaPO₄-LTA, is located near the middle of the 8-ring window of the α -cage. During pyrolysis, some parts of the GaPO₄-LTA framework were collapsed to form

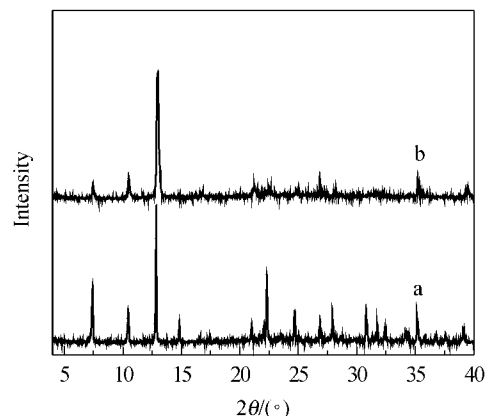


Figure 2 XRD patterns of (a) as-synthesized GaPO₄-LTA and (b) carbon/GaPO₄-LTA composite.

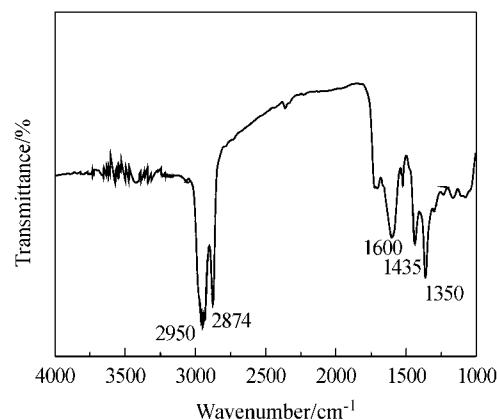


Figure 3 IR spectrum of nanographite extracted from the carbon/GaPO₄-LTA composite.

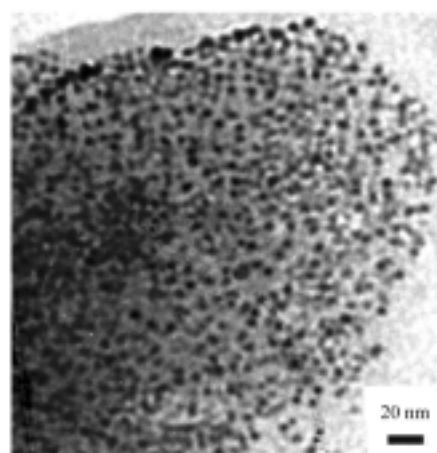


Figure 4 Transmission electron micrograph of the carbon nanographites extracted from the carbon/GaPO₄-LTA composite.

small holes, the diameter of which could be controlled by varying the heating-rate. These holes provided enough space for the formation of nanographite. In this experiment, the particle size of the material is reasonably uniform, in accordance with the fact that the

nanoparticles are formed in the nearly uniform collapsed space of the GaPO₄-LTA host compound.

It is well-known that Raman spectroscopy provides important information on graphite structure.^{14,15} Figure 5 shows the Raman spectrum for the extracted carbonaceous material. There are two broad peaks at around 1610 and 1380 cm⁻¹. The one at 1610 cm⁻¹ was attributed to stretching mode of the individual sheets in graphite (*E*_{2g} mode),¹⁶ and the other around 1380 cm⁻¹ was assigned to an *A*_{1g}-type mode called the disorder band.¹⁷ The appearance of these two peaks is in agreement with the finite size of the nanographite particles. Using the empirical formula $L_a = 4.4 \times I_{1610}/I_{1380}$,¹⁸ where *I*₁₆₁₀ and *I*₁₃₈₀ are the intensities of peaks corresponding to the *E*_{2g} and *A*_{1g} modes respectively, *L*_a (the in-plane carbon particle diameter) can be estimated to be *L*_a = 6.9 nm. This particle coincides with the size observed from the TEM image as indicated earlier in this paper.

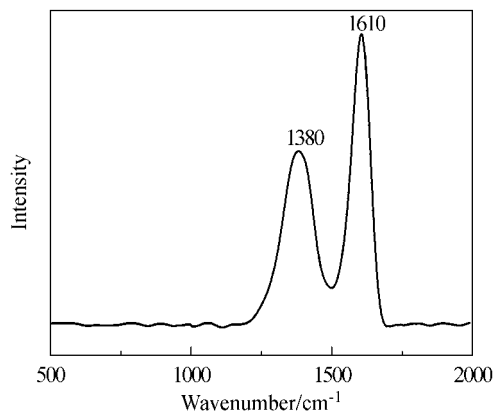


Figure 5 Raman spectrum of the nanographite extracted from the carbon/GaPO₄-LTA composite.

Both TEM and Raman spectroscopy suggest that the carbonaceous material consists of graphite fragments of nanometer scale, that is, nanographite. Nanographites represent a new class of mesoscopic system intermediates between aromatic molecules and extended graphite sheets. In these systems the boundary regions play an important role so that edge effects may strongly influence the π -electron states near the Fermi energy. There are two basic shapes for graphite edges, namely, armchair and zigzag ones. Theoretical study^{1,2,5-7} has shown that graphite networks with zigzag edges have a localized edge state at the Fermi level, but those with armchair edges have no such state. The edge structure in a real micrographite is naturally rather irregular and complicated. The general edge shapes of the real carbon material can be represented as a mixture of zigzag and armchair sites. The studies by Dresselhaus and coworkers³ suggest that three or four zigzag sites in a sequence are enough to show a non-negligible edge state, when the size of graphite particle is in a few nanometer scale.

Figure 6 illustrates the ESR spectrum of the carbo-

naceous sample where a strong ESR signal appears. For comparison, the ESR spectrum was also recorded for the as-synthesized GaPO₄-LTA. No ESR signal was observed for the crystals, indicating that the ESR signal of the nanographite is not due to the presence of magnetic impurities in the GaPO₄-LTA framework. In the nanographite system, two possibilities arise to account for the strong signal. One is sp³-type carbon with σ dangling bonds in the peripheries of the graphene sheets, and the other is π -type edge-carbon atoms. Before carrying out the ESR experiment, the nanographite particles were exposed to air for a few days, so that the foreign chemical species such as hydrogen or oxygen tended to react with the σ dangling bonds to form completed bonds in the atmosphere. Therefore, the paramagnetic behavior of the nanographite can not be due to the σ dangling bonds, and the only possibility for the observed paramagnetism is π -type spins.

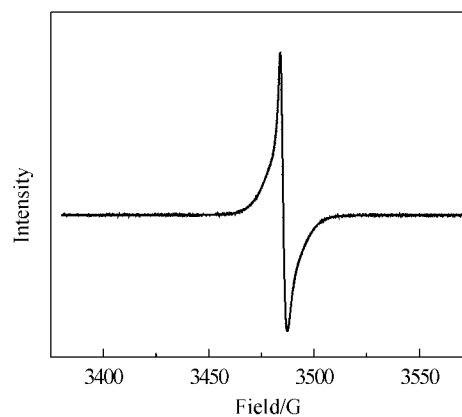


Figure 6 ESR spectrum of the nanographite extracted at room temperature.

Figure 7 shows the temperature dependence of magnetic susceptibility for the nanographite in the temperature range of 2–300 K. From 50 to 300 K, the total magnetic susceptibility is *ca.* -0.25 emu/mol, indicative of diamagnetism. At temperatures below *ca.* 50 K, the susceptibility shows a Curie-type increase. On the basis of the theoretical prediction by Wakabayashi,¹⁰ the total susceptibility mainly consists of orbital diamagnetism χ_{orb} and Pauli paramagnetism χ_{p} . The χ_{p} is related to the DOS at the Fermi level, which represents an important component in zigzag nanographite where an enhanced DOS appears at the Fermi level. Note that χ_{p} is negligible in armchair nanographite, aromatic molecules and graphite sheets, because their DOS is suppressed at the Fermi level. As a result of competing χ_{p} and χ_{orb} , a crossover occurs from a high-temperature diamagnetism to a low-temperature paramagnetism as observed for the nanographite prepared.

Conclusions

Using GaPO₄-LTA framework as template, nano-sized graphite particles with uniform size of about 7 nm can be prepared through pyrolyzing MPy. ESR and

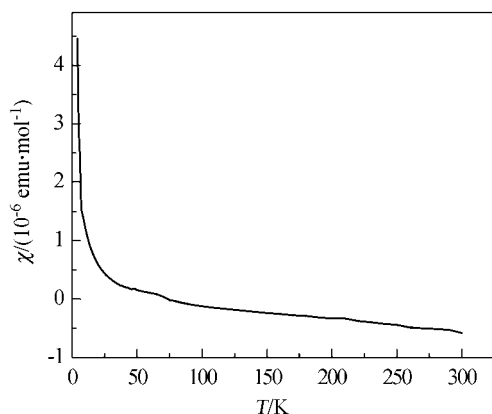


Figure 7 Temperature dependence of mass magnetic susceptibility of the nanographite extracted.

magnetic susceptibility measurements show the presence of open π -bond edges in the nanographite material. This interesting electronic feature was considered to be associated with the specific size of the graphite particles.

References

- 1 Tanaka, K.; Yamashita, S.; Yamabe, H.; Yamabe, T. *Synth. Met.* **1987**, *17*, 143.
- 2 Fujita, M.; Wakabayashi, K.; Nakada, K.; Kusakabe, K. *J. Phys. Soc. Jpn.* **1996**, *65*, 1920.
- 3 Nakada, K.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B* **1996**, *54*, 17954.
- 4 Fujita, M.; Igami, M.; Nakada, K. *J. Phys. Soc. Jpn.* **1987**, *66*, 1864.
- 5 Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 3721.
- 6 Hosoya, H.; Gao, Y.-D.; Nakada, K.; Ohuchi, M. In *New Functionality Materials*, Eds.: Tsuruta, C. T.; Doyama, M.; Seno, M., New York, **1993**, 27.
- 7 Fujita, M.; Yoshida, M.; Nakada, K. *Fullerene Sci. Technol.* **1996**, *4*, 565.
- 8 Andersson, O. E.; Prasad, B. L. V.; Sato, H. *Phys. Rev. B* **1998**, *58*, 16387.
- 9 Shibayama, Y.; Sato, H.; Enoki, T. *Phys. Rev. Lett.* **2000**, *84*, 1744.
- 10 Wakabayashi, K.; Fujita, M.; Ajiki, H.; Sigrist, M. *Phys. Rev. B* **1999**, *59*, 8271.
- 11 Yu, J.-H.; Chen, J.-S.; Xu, R.-R. *Microporous Mater.* **1996**, *5*, 333.
- 12 Yao, Y.-W.; Pang, W.-Q.; Xu, Y.-H.; Xu, R.-R. *Proceeding of the 12th International Zeolite Conference MRS*, **1999**, p. 1751.
- 13 Xu, J.-Z.; Zhu, J.-J.; Chen, H.-Y. *Chin. J. Chem.* **2003**, *21*, 1088.
- 14 Tuinstra, F.; Koenig, J. L. *J. Compos. Mater.* **1970**, *4*, 492.
- 15 Inagaki, M.; Shiraiishi, M.; Nakamizo, M.; Hishiyama, Y. *Tanso* **1984**, *118*, 165.
- 16 Nemanich, R. J.; Solin, S. A. *Phys. Rev. B* **1979**, *20*, 392.
- 17 Tuinstra, F.; Konig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126.
- 18 Knight, D. S.; White, W. B. *J. Mater. Res.* **1989**, *4*, 385.

(E0404195 ZHAO, X. J.)