

# Nanographene production and its functionalization using supercritical fluid

Takaaki Tomai\*, Naoki Tamura and Itaru Honma

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku,  
Sendai 980-8577, Japan  
E-mail: tomai@tagen.tohoku.ac.jp

## ABSTRACT

To develop the facile proportion method of zigzag-edge introduced nanographene, we optimized the processing parameters of catalytic etching of graphite simultaneously with the exfoliation of graphene in SCW. As a result, the proportion of zigzag edge in the sample after SCW treatment was enhanced by choosing the appropriate processing time and catalytic nanoparticles concentration.

## INTRODUCTION

Graphene is one of the most promising carbon materials in various engineering fields. Nowadays, graphene application is expanding from the conventional electrical devices, such as transparent conductive film and field effect transistor (FET), to magnetism, photoelectronics, and electrochemical devices. Recent investigations revealed that the electrical, optical and magnetic characteristics of nanometer-sized graphene, nanographene, can be manipulated by controlling its size and edge type such as armchair and zigzag. For example, nonbonding pi-electrons in the zigzag edge region are responsible for the unconventional nanomagnetic properties [1-3]. Moreover, recent our studies indicate that the abundant edge of nanographene shows unique electrochemical characteristics when the nanographene is employed as the electrode materials in fuel cells and electrochemical capacitors[4,5].

In the case of graphene applications as the magnetic materials, and the electrode materials in electrochemical devices, the mass production methods of graphene is mandatory. However, in the case of exfoliation method of graphene from graphite [6], the existing general scalable methods for graphene production, oxygen functional groups and defects introduced during exfoliation via acid oxidation cannot be completely removed and degrade superior graphene properties [7,8].

Recently, facile graphene production using supercritical fluid (SCF) has been developed[9]. In this method, high-quality graphene is exfoliated from graphite immersed in SCF without the introduction of undesired defects and functional groups during chemical oxidation. It is suggested that solvent molecules in supercritical condition diffuse between the graphene layers in graphite and expand the interlayer distance. In this process, exfoliation of graphene from graphite surface is accompanied by fragmentation of graphite, so we can easily obtain high-quality nanographene by using SCF exfoliation method [10].

Moreover, for the development of scalable production method for edge-controlled nanographene, we combined the above-mentioned SCF exfoliation with catalytic etching [11]. We conducted anisotropic oxidative etching/channeling with Ag nanoparticles, which forms zigzag-edge straight trenches on graphite surface, in supercritical water. Because of the exfoliation effect of SCF, graphene was isolated from the graphite simultaneously with the

anisotropic etching. By high-resolution TEM and Raman spectroscopy, the production of multilayer nanographene with zigzag edges was confirmed. Assuming that the pristine pyrolytic graphite has only thermodynamically-stable armchair edge without any defect, the proportion of zigzag edge in the sample after catalytic etching in SCW was estimated as approximately 20%.

In this study, to enhance the proportion of zigzag edge in nanographene, we investigated the dependence on the processing parameters, such as processing time and Ag nanoparticle concentration. As a result, the proportion of zigzag edge in the sample after catalytic etching in SCW was enhanced above 40% by choosing the appropriate processing parameters.

## MATERIALS AND METHODS

In our experiment, 10 mg of graphite powder and Ag nanoparticles ( $\Phi 20\text{--}40$  nm, QSI Nano Silver, QuantumSphere, Inc.) were dispersed in ethanol using a sonication bath, and then we dried it in a vacuum oven at  $70$  °C to attach the Ag nanoparticles to graphite powder surface. Etching in SCW (critical point of water:  $374$  °C,  $22$  MPa) was carried out by placing ultrapure water (Millipore, Q-grade) and the Ag-supported graphite powder into a batch-type Hastelloy reactor with a  $10$  mL capacity. In this reactor,  $8$  mL of gaseous ambient air containing approximately  $7 \times 10^{-5}$  mol of oxygen was also included. SCW is completely miscible with oxygen. Etching reaction in SCW is promoted by catalytic carbon oxidation with oxygen dissolved in SCW.

## RESULTS

Figure 1 shows the examples of SEM images of the sample surface at  $500$  °C and  $0.2$  g/cm<sup>-3</sup> of SCW density. As shown in Figure 1(a), the trench and steps consisted of anisotropic graphene edges can be observed on the surface of multilayer graphene and graphite powder. It is supposed that these structures are formed via the anisotropic etching of graphite surface and exfoliation of graphene fragment from the surface.

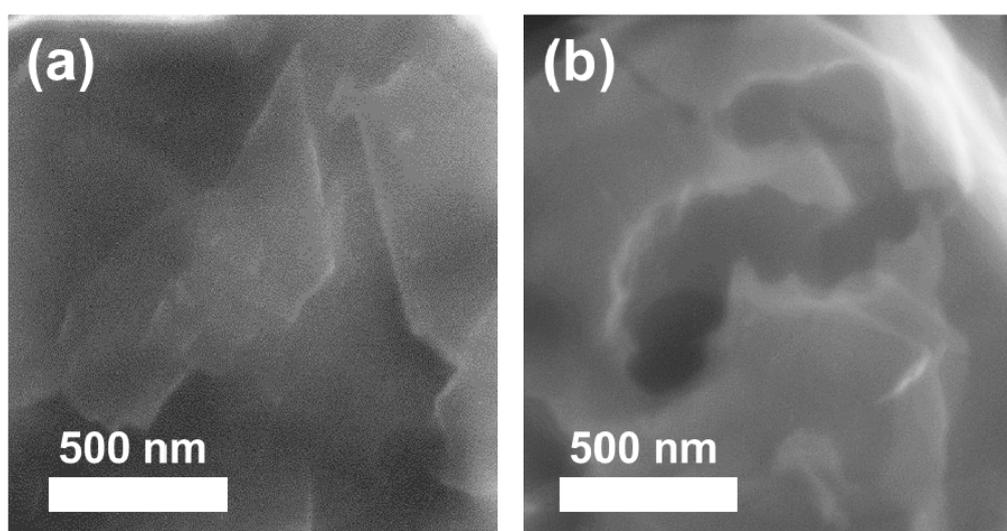
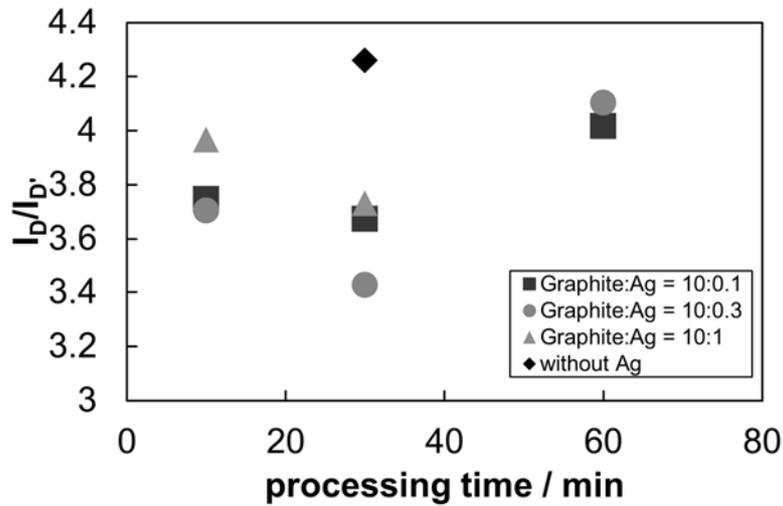


Figure 1 Examples of SEM images of the sample at  $500$  °C and  $0.2$  g/cm<sup>-3</sup> of SCW density



**Figure 2**  $I_D/I_{D'}$  values for the samples treated at 500 °C in supercritical water ( $0.2 \text{ g/cm}^{-3}$ ) on the processing time for various Ag nanoparticle concentrations (weight ratios of graphite to Ag nanoparticles: 10 to 0, 0.1, 0.3, and 1)

It has been reported that the D band at around  $1350 \text{ cm}^{-1}$  and the D' band at around  $1620 \text{ cm}^{-1}$  can be attributed to defect-induced scattering of graphite in addition to the G band at around  $1580 \text{ cm}^{-1}$ . The graphite edge behaves as defects and induces the D and D' band. The D band intensity from a zigzag edge disappears or becomes weaker compared to that from an armchair edge, while the D' band intensity does not show the dependence on the edge type because of the different intrinsic structural properties of the scattering process for different graphite edges [12]. Here, we discuss the introduction of the zigzag edge by using intensity ratio between the D band and the D' band ( $I_D/I_{D'}$ ). In the case of pyrolytic graphite,  $I_D/I_{D'}$  value was 5.0 in our measurement system [11]. To verify the introduction of a zigzag edge to the bulk graphite powder, we conducted a Raman spectroscopic analysis.

Figure 2 shows the dependence of  $I_D/I_{D'}$  for the samples treated at 500 °C and  $0.2 \text{ g/cm}^{-3}$  of SCW density on the processing time for various Ag nanoparticle concentrations. During SCW treatment without Ag nanoparticles, fragmentation of graphite and exfoliation of graphene occur. In this fragmentation process, it is highly supposed that in addition to zigzag edges, thermodynamically-stable armchair edges are preferentially formed at the induced crack of graphene/graphite. Compared to the sample treated in SCW without the attachment of Ag nanoparticle,  $I_D/I_{D'}$  shows smaller value in all cases with Ag nanoparticles. The decrease in  $I_D/I_{D'}$  value by the introduction of Ag nanoparticles indicates the increase in the the proportion of zigzag edge in the sample due to the catalytic etching.

When we focus on the dependence of  $I_D/I_{D'}$  on the processing time, it was found that until 30 min,  $I_D/I_{D'}$  value decreases as the processing time elapses. This indicates that etching reaction and the introduction of zigzag edge progresses with time. However, in the case of 60 min of processing time,  $I_D/I_{D'}$  shows larger value than that in the case of 10 and 30 min. This catalytic etching progresses with the movement to catalytic nanoparticles. When Ag nanoparticles meet together during the process, coalescence of them occurs and make larger Ag particle. It is known that large catalytic particle shows rotational (random) movement in addition to the straight movement as shown in Figure 1(b) [13], and armchair edges are also introduced. It is supposed that this coalescence of Ag nanoparticles results in the decrease in the proportion of zigzag edge in the sample in the case of 60 min of processing time.

This tendency can be seen in the dependence on the Ag nanoparticle concentration. As the weight ratio of graphite to Ag nanoparticle increases until 10 to 0.3,  $I_D/I_{D'}$  value decreases. However, at the weight ratio of graphite to Ag nanoparticle of 10 to 1,  $I_D/I_{D'}$  shows large value. Although the increase in the Ag nanoparticle concentration should enhance the introduction of zigzag edges due to the increase in the number of etching point, high concentration of Ag nanoparticles induce high coalescence frequency. Therefore, we supposed that too high concentration of Ag nanoparticle resulted in the decrease in the proportion of zigzag edge.

Finally, from the  $I_D/I_{D'}$  values for pyrolytic graphite and the sample treated in SCW for 60 min with the weight ratio of graphite to Ag nanoparticle of 10 to 0.3, it is indicated that the estimated proportion of zigzag edge in the sample can be approximately 40% by this SCF process.

## CONCLUSION

In this study, by investigating the processing parameter in the one-step production method of anisotropically etched graphene using SCW, we improved the introduction rate of zigzag edge in the graphene sample. This scalable and facile production method for the graphene with controlled edge will contribute to the enhancements of electrochemical device performances and future application of graphene as magnetic materials.

## REFERENCES

- [1] Enoki, T., Kobayashi, Y. J., *Mater. Chem.* 15, **2005**, 3999.
- [2] Joly, V. L. J., Kiguchi, M., Hao, S.-J., Takai, K., Enoki, T., Sumii, R., Amemiya, K., Muramatsu, H., Hayashi, T., Kim, Y. A., Endo, M., Delgado, J. C., Urías, F. L., Méndez, A. B., Terrones, H., Terrones, M., Dresselhaus, M. S., *Phys. Rev. B* 81, **2010**, 245428.
- [3] Tada, K., Haruyama, J., Yang, H. X., Chshiev, M., Matsui, T., Fukuyama, H., *Appl. Phys. Lett.* 99, **2011**, 183111.
- [4] Mitani, S., Sathish, M., Rangappa, D., Unemoto, A., Tomai, T., Honma, I., *Electrochim. Acta* 68, **2012**, 146.
- [5] Tomai, T., Kawaguchi, Y., Sathish, M., Honma, I., *Electrochim. Acta* 92, **2013**, 421.
- [6] Hummers, W., Offeman, R., *J. Am. Chem. Soc.* 80, **1958**, 1339.
- [7] Park, S., An, J., Piner, R. D., Jung, I., Yang, D., Velamakanni, A., Nguyen, S. B. T., Ruoff, R. S., *Chem. Mater.* 20, **2008**, 6592.
- [8] Mattevi, C., Eda, G., Agnoli, S., Miller, S., Mkhoyan, K. A., Celik, O., Mastrogiovanni, D., Granozzi, G., Garfunkel, E., Chhowalla, M., *Adv. Funct. Mater.* 19, **2009**, 2577.
- [9] Rangappa, D., Sone, K., Wang, M., Gautam, U. K., Golberg, D., Itoh, H., Ichihara, M., Honma, I., *Chem. –Eur. J.* 16, **2010**, 6488.
- [10] Tomai, T., Kawaguchi, Y., Honma, I., *Appl. Phys. Lett.* 100, **2012**, 233110.
- [11] Tomai, T., Tamura, N., Honma, I., *ACS Macro Lett.* 2, **2013**, 794.
- [12] Cancado, L. G., Pimenta, M. A., Neves, B. R. A., Dantas, M. S. S., Jorio, A., *Phys. Rev. Lett.* 93, **2004**, 247401.
- [13] Schäffel, F., Warner, J. H., Bachmatiuk, A., Rellinghaus, B., Büchner, B., Schultz, L., Rummeli, M. H., *Nano Res.* 2, **2009**, 695.