

High-speed synthesis and crystallinity control of nanographene using in-liquid plasma in alcohol

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High-speed synthesis and crystallinity control of nanographene using an in-liquid plasma in alcohol, which was generated from a nonequilibrium micro-hollow atmospheric pressure plasma with an ultrahigh electron density, were investigated. The synthesis rate of carbon materials was 0.61 and 1.72 mg/min using ethanol and butanol, respectively. Multilayer nanographene structures obtained using ethanol had an interlayer spacing of 0.33 nm, corresponding to that of (002) planes in graphite. The G-, D-, D'-, and 2D-band peaks in the Raman spectrum also confirmed the formation of nanographene. The mechanism of gradual growth of six-membered ring structures was clarified by gas chromatography of the filtrate.

Applications of nano-carbon materials, such as nanographene, have been attracted much attention due to their excellent and unique electrical, physical and morphological properties in recent years. In graphene sheets, electron mobilities of $15000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature have been reported[1-2]. Therefore, nanographene is attractive as a channel material for the next generation of ultrahigh-speed transistors[3]. In addition, since graphene is a transparent material, nanographene is also expected to be applied as transparent electrodes in solar cells[4]. Nano-composite materials that include nanographene are also promising as nanostructural materials. However, high equipment and process costs in conventional chemical vapor deposition (CVD) and arc discharge methods are generally tough issues for practical applications. Recently, graphene synthesis by reduction of chemically prepared graphite oxide (GO) has been investigated as a low-cost method. However, the crystallinity of the synthesized graphene is not high, because insufficient reduction takes place. In this study, the synthesis of nanographene using an in-liquid plasma was investigated. The system employed a nonequilibrium micro-hollow atmospheric pressure plasma source, with ethanol or butanol as carbon precursors. The rate of synthesis of nanographene was compared for these two different alcohols. In addition, the crystal structure of the material synthesized using ethanol was investigated in detail. The chemical composition of the filtrate was analyzed using gas chromatography-mass spectrometry (GC-MS) in order to clarify its synthesis mechanisms.

Figure 1(a) shows a schematic of an experimental setup used in this experiment. A high-voltage (~10 kV) 60 Hz ac-voltage was applied to the electrodes, which are located above and below the alcohol. The upper electrode has a micro-hollow cathode structure at its edge. A non-equilibrium atmospheric pressure plasma with an ultrahigh electron density of more than 10^{16} cm^{-3} was generated in the micro-hollow region[5]. After the plasma discharge for 15 minutes, micrometer-sized and black-colored materials dispersed in the alcohol were collected by a filtration method. The collected substances were measured by Raman spectroscopy. Figure 1(b) shows the time dependence of the weight of black material synthesized from ethanol, propanol, and butanol. The synthesis rate of nanographene materials were found to be 0.34, 0.67, and 1.00 mg/min using ethanol, propanol, and butanol, respectively. These values are about 5 to 15 times larger than those for conventional CVD methods. Figure 2 shows TEM images of the purified material produced using ethanol. The fringe contrast is a clear indication of a multilayer structure; this is shown in more detail in the magnified

image in the insert. From these fringes, an interlayer spacing of 0.33 nm was determined, which is the same as the reported interlayer spacing for graphite (002) planes. Figure 3 shows the Raman spectrum obtained from the samples synthesized using ethanol, propanol, and butanol, respectively. The G-band peak at 1582 cm^{-1} indicates the six-membered ring structure of graphene. On the other hand, in general, the D-band and D'-band peaks at 1343 and 1621 cm^{-1} , respectively, originate from structural imperfections in graphene. It is found that the shape of G-band peak for the ethanol case is sharper than those for the propanol and butanol cases. These results indicate that nanometer-sized graphene crystallites with a high degree of crystallinity are synthesized using the ethanol. It is expected that this new in-liquid plasma method will lead to a breakthrough in the high-speed synthesis and precise control of nanographene materials.

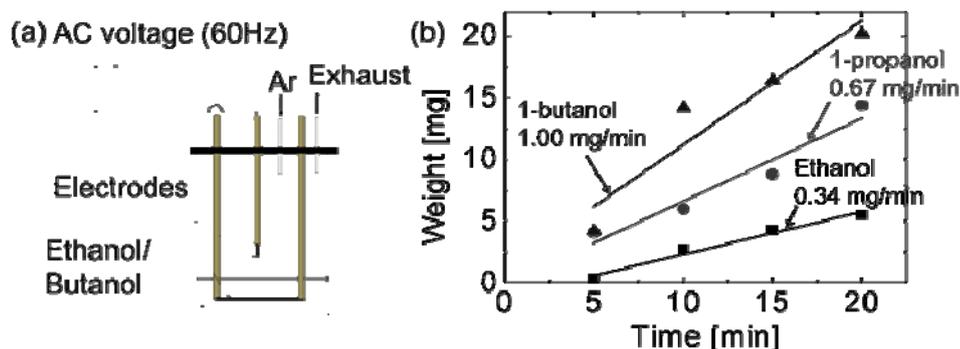


Fig. 1: (a) Schematic illustration of experimental apparatus and (b) synthesis rate of carbon materials using an in-liquid plasma with butanol or ethanol.

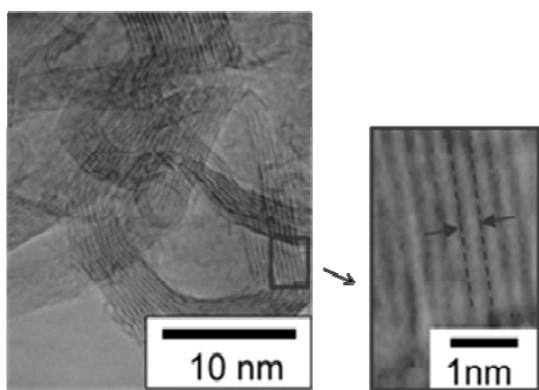


Fig. 2: TEM images of nanographene synthesized using ethanol.

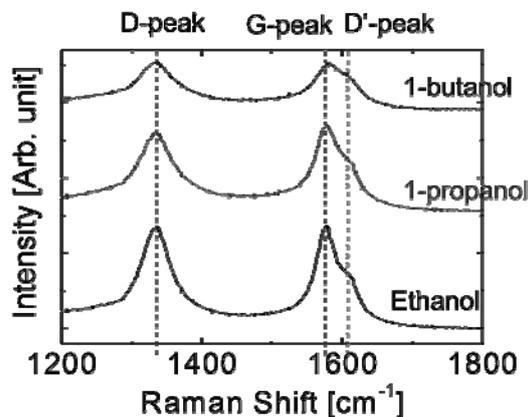


Fig. 3: Raman spectra of nanographene materials synthesized using ethanol, propanol, and butanol, respectively.

References

- [1] M. Orlita, C. Faugeras, P. Plochocka, P. Neugebauer, G. Martinez, D. K. Maude, A. -L. Barra, M. Sprinkle, C. Berger, W. A. de Heer, and M. Potemski: *Phys. Rev. Lett.* 101 (2008) 267601.
- [2] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer: *Solid State Commun.* 146 (2008) 351.
- [3] L. Liao, J. Bai, R. Cheng, Y. C. Lin, S. Jiang, Y. Qu, Y. Huang, and X. Duan: *Nano Lett.* 10 (2010) 3952.
- [4] X. Wang, L. Zhi, and K. Müllen: *Nano Lett.* 8 (2008) 323.
- [5] M. Iwasaki, H. Inui, Y. Matsudaira, H. Kano, N. Yoshida, M. Ito, and M. Hori: *Appl. Phys. Lett.* 92 (2008) 081503.