Ultrafast Synthesis of Nanographene Employing an Ultrahigh-density In-liquid Alcohol Plasma

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1. Introduction

Applications of nano-carbon materials, such as nanographene, have attracted much attention due to their excellent and unique electrical, physical and morphological properties in recent years [1]. However, high equipment and process costs in conventional chemical vapor deposition (CVD) or arc discharge methods are generally tough issues for practical applications. Therefore, a new method, which makes a much higher-growth rate and lower-cost synthesis possible, is strongly required. A reduction treatment of graphite oxide (GO), which is synthesized by a chemical method, is one of well-known methods for this purpose [2]. An atmospheric pressure plasma treatment is used as a reduction treatment. However, the crystallinity of synthesized graphene is not sufficient for electrical uses so that the further improvement of the reduction method is strongly necessary.

In this study, we focused on an in-liquid plasma process. Since a liquid-phase has a higher density compared with a gas-phase, a higher-rate chemical reaction can be realized compared with a gas-phase reaction. Very recently, we have realized the high-speed synthesis of the nanographene materials using in-liquid plasma [3]. And synthesis speed of nanographene employing an ethanol is 0.36 g/min. However, details of their growth mechanisms and crystallographic features have not been sufficiently clear yet. Therefore, dependences of nanographene growth processes and their crystalline structures on types of alcohols used in the synthesis processes were investigated in this study. Crystalline structures of synthesized graphene materials were analyzed in details by the transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and Raman spectroscopy. Synthesis processes were discussed based on results obtained employing the gas chromatography.

2. Experimental procedure and results

In this experiment, a nonequibrium micro hollow atmospheric pressure plasma source was employed. This newly developed plasma source can generate plasmas with ultrahigh electron density of over 10^{16} cm⁻³ and that is powered by a compact and inexpensive 60 Hz alternating current (AC) power supply.[4] The size and cost of this power supply are approximately 50 and 20 times smaller than those of a conventional dielectric barrier

discharge (DBD) system, respectively. Thus, this plasma source has high advantage in terms of cost, size, and process performance at the atmospheric pressure. A high-voltageac-voltage (ca. 10kV) was applied to the two electrodes to generate the plasma in the liquid. Ethanol and butanol were used as alcohol solutions. After the plasma discharge for 10 minutes, black-colored and dispersed materials with a size up to micron-meter were generated in the ethanol or butanol, and collected by a filtration method. After the filtration, yellow-colored liquids were obtained in the beakers.



Figure 1. TEM image of nanographene materials synthesized employing in-liquid ethanol plasma in this study.



Figure 2. X-ray diffraction profile of nanographene materials synthesized employing in-liquid ethanol plasma in this study.

Figure 1 shows the TEM image of the nanographene materials synthesized in this experiment using ethanol. Multi-layered structures with lattice fringes are clearly found in the figure. An interlayer spacing value of these fringes is obtained to be 3.35 Å, which is equal to the reported value of graphite (3.35 Å). This result means that any structural change such as an intercalation by any atoms or molecules didn't occur during this synthesis process. Figure 2 shows the powder X-ray diffraction profiles of the synthesized nanographene materials synthesized using ethanol. Cu-K $_{\alpha}$ radiation was used as an incident X-ray source. Clear rings were observed at 25.8° (d=3.45 Å) and 44.1° (d=2.06 Å), respectively. These detected angles were slightly smaller than the reported values of 26.5° (d=3.35 Å) and 44.6° (d=2.03 Å) for the graphite (002) and (101) planes, respectively. This is attributed to the background owing to small angle scattering from the many voids in the powder sample. Figure 3 shows Raman spectra of the nanographene materials synthesized using ethanol and butanol. A peak at 1582 cm⁻¹ (G-peak) can be assigned to a graphene structure. Peaks at 1343cm⁻¹ (D-peak) and 1621 cm⁻¹ (D'-peak) are originated from a structural imperfection of graphene, respectively. On the other hand, The peak at 2686 cm⁻¹ which is called as 2D-peak, is related to layer numbers of stacked graphene sheets. In the case using ethanol, the G-peak is shaper and D'-peak is smaller compared to the case using butanol. Furthermore, the 2D-peak for the ethanol case is larger than that for the butanol case, although relative the intensity of D-peak is smaller. These results indicate that the nanographenes synthesized using ethanol have higher crystallinity and smaller amount of stacked layers compared with those for the butanol case. On the other hand, the full width at half maxima (FWHM) value of the G-peak of nanographenes synthesized using ethanol was estimated to be about 30 cm⁻¹. This value is much smaller than that for the nanographene synthesized by reduction of GO (75 cm⁻¹) [2]. The obtained FWMH value is even closer to that for the highly oriented pyrolytic graphite, HOPG (15 cm⁻¹). These results mean the high crystallin-



Figure 3. Raman spectra of nanographene materials synthesized using ethanol and butanol, respectively.

ity of the nanographene materials synthesized by this method. Figure 4 shows the possible pathways of graphene formation suggested based on the results of gas chromatography of the yellow liquid. From synthesis results, the synthesize rate of nanographene from the butanol was larger than that from the ethanol. The suggested pathway from butanol to six-membered ring structures is shorter than that from ethanol as shown in Fig. 4. Therefore, according to these experimental results, it was found that the high-speed synthesis of the high-crystallinity nanographene could be realized by control of in-liquid plasma processes.



Figure 4. Models of nanographene synthesis processes by in-liquid plasma using ethanol and butanol, respectively.

3. Conclusions

The nanographene materials were synthesized by the high-density in-liquid plasma using the ethanol and butanol in this study. According to the TEM image, powder XRD profile and Raman spectroscopy, it is found that the synthesized nanographene materials have the high crystallinity comparable to the bulk graphite. Crystallinity of nanographene synthesized using ethanol was higher than that from butanol. On the other hand, higher synthesis rate using butanol is attributed to the shorter synthesis pathway to reach nanographene, according to the gas chromatography. These acknowledges obtained in this study will open the way to realize high-speed synthesis and precise control of nanographene materials by in-liquid plasma.

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