Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp825-826

In-liquid plasma synthesis of iron-nitrogen-doped carbon nanosheets with highly electro-catalytic activity for fuel cell application

Ryo Hamaji[1], Tomoki Amano[1], Hiroki Kondo[1], Takayoshi Tsutsumi[1], Kenji Ishikawa[1], Makoto Sekine[1], Keigo Takeda[2], Mineo Hiramatsu[2], and Masaru Hori[1]

[1] Univ. of Nagoya
Furo-cho, Chikusa-ku, Nagoya
Aichi 464-8603, Japan
Phone: +81-52-789-3461 E-mail: hamaji.ryo@e.mbox.nagoya-u.ac.jp
[2] Univ. of Meijo
Shiogamaguchi, Yagoto, Nagoya
Aichi 468-8502, Japan

1. Introduction

Carbon nanomaterials including transition-metal and nitrogen are promising candidates as an alternative to platinum catalysts in fuel cell applications. We have reported a high-speed and low-cost synthesis method of high crystalline nanographenes employing the in-liquid plasma [1]. Indeed, micron-sized graphene flakes (CNFL) were also successfully synthesized by adding an iron phthalocyanine (FePc) to ethanol [2]. The CNFL show a highly catalytic activity in an oxygen reduction reaction [3]. However, it has not been solved yet whether the species of alcohols affects to synthesize a certain of active catalytic sites on CNFL or not. Therefore, we placed on a focus of the species of alcohols.

In this study, we have studied the CNFL synthesis using three kinds of alcohols, such as ethanol, propanol, and 1-butanol. The catalytic properties of the CNFL were discussed with Fe-N-C bonding structures and crystallinity of the synthetized materials.

2. General Instructions

15 mg of FePc was dispersed in 40 ml of N,N-dimethylformamide (DMF) using a homogenizer. The 40-ml-FePc-dispersed solution was mixed with 160 ml of ethanol, propanol or 1-butanol. The solution was treated by the in-liquid plasma for 30 min. After the treatments, the synthetic materials were collected by filtration. A standard electrochemical cell was used to evaluate catalytic properties of the CNFL.

3. Result

Fig. 1 shows scanning electron microscope (SEM) images of materials synthesized using (a) ethanol, (b) propanol, and (c) 1-butanol, respectively. The flakes were clearly found in the case using ethanol. Figs. 2(a) and 2(b) are transmission electron microscope (TEM) image and transmission electron diffraction (TED) pattern of the material synthesized using ethanol. Three coaxial rings were clearly observed, and their lattice spacing values were calculated to be 0.34 nm, 0.21 nm and 0.11 nm, respectively. These values are almost similar with the reported values of lattice spacing of 002, 101 and 112 planes of highly oriented pyrolytic graphite (HOPG), respectively. Fig.3 shows Raman spectra of the materials synthesized using ethanol, propanol, and 1-butanol, respectively. Typical peaks of graphene nanosheets, such as G-band (1580 cm^{-1}), D-band (1350 cm^{-1}), and D'-band (1610 cm^{-1}) ones, were clearly found for all samples. Especially, in the case using ethanol, the G-band peak was found to be sharpest, and 2D-band peak largest. In addition, relative intensities of D-band and D'-band peaks were smallest. These results mean that the nanographene materials with the higher crystallinity were synthesized using the lower-molecular weight alcohols. Fig. 4 shows N 1s photoelectron spectrum of the CNFL synthesized using ethanol. As is shown in the figure, the peak component related to Fe-N bonds was clearly found to have the strongest intensity. Chemical shifts and intensity ratios of C 1s and N 1s peaks were different depending on types of alcohols.

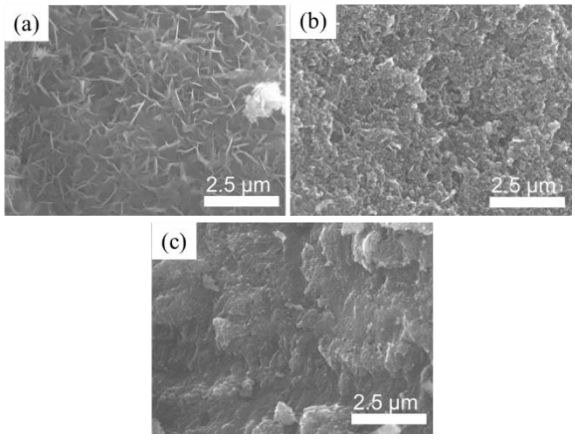

Fig. 1 SEM images of materials synthesized using (a) ethanol (b) propanol, and (c) 1-butanol, respectively.

Fig. 5 is Kouteck-Levich (K-L) plots of the oxygen reduction reaction (ORR) characteristics of the materials synthesized using different types of alcohols in (a) acid and (b) alkaline solutions, respectively. higher catalytic activity corresponded with the Fe-N bond contents of the CNFL in the case of ethanol in both alkaline and acid. Depending on the kind of alcohols, the in-liquid plasma enables to synthesize Fe-N-C bonding features, thereby enhancing the catalytic activity in ORR.

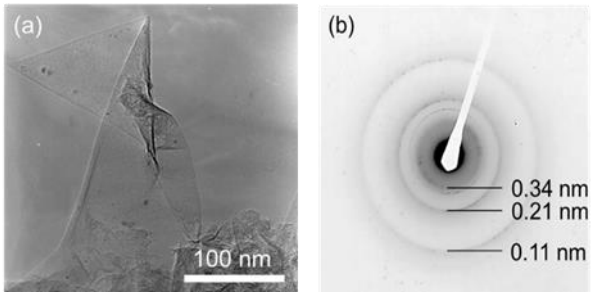

Fig. 2 (a)TEM image and (b)TED pattern of materials synthesized using ethanol.

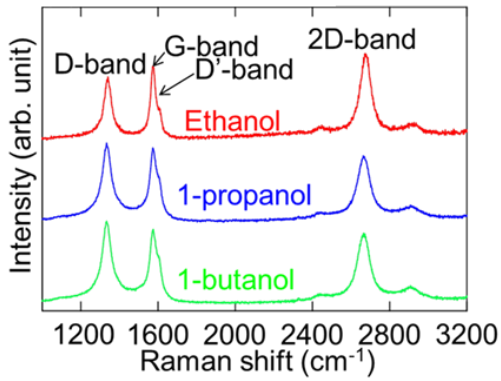

Fig. 3 Raman spectra of the materials synthesized using ethanol, propanol, and 1-butanol, respectively.

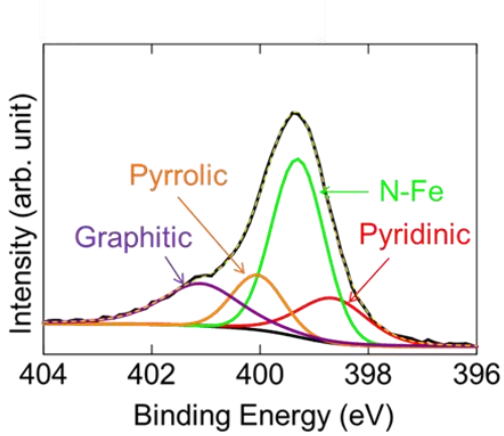

Fig. 4 N 1s photoelectron spectrum of the CNFL synthesized using ethanol.

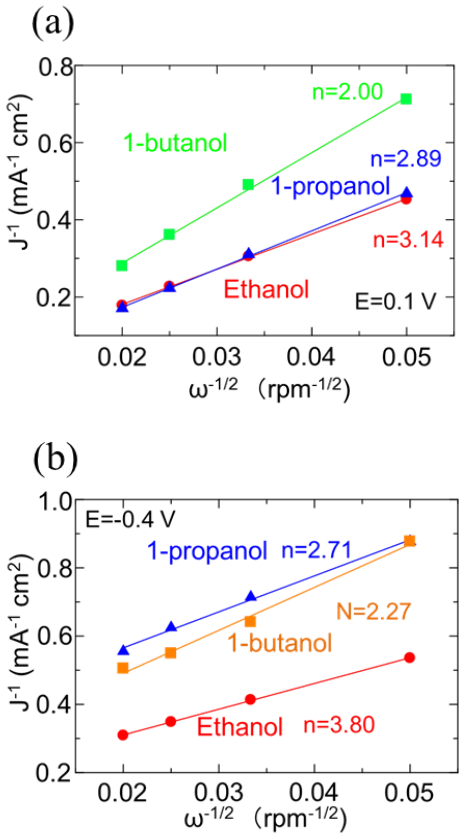

Fig. 4 Kouteck-Levich (K-L) plots of the oxygen reduction reaction (ORR) characteristics of the materials synthesized using dif-ferent types of alcohols in (a) acid and (b) alkaline solutions, respectively

3. Conclusions

The CNFL syntheses using three kinds of alcohols, such as ethanol, propanol, and 1-butanol were investigated, and their catalytic properties were evaluated with Fe-N-C bonding structures and crystallinity. The CNFL synthesized using the lower-molecular weight alcohol showed the higher content of Fe-N bonds and resulting higher catalytic activity. Theses results and obtained knowledge will open the way to realized controlled synthesis of carbon nanomaterials with high catalytic activity.

References

[1] T. Hagino, et al.: Appl. Phys. Express, 5 (2012) 035101.
[2] T. Amano et al., Japan. J. Appl. Phys. 57 (2018) 040303.
[3] T. Amano et al., Appl. Phys. Express 11 (2018) 015102.