Evaluation of metal ion catalyst characteristic for fabrication of graphene quantum dots using ion beam irradiation

Seung Ho Lee [a,b], Hyeok-Jung Kwon [a,b], Jun Mok Ha[a*]
[a]*Korea Multi-purpose Accelerator Center(KOMAC), Korea Atomic Energy Institute(KAERI)*
[b]*Department of Accelerator and Nuclear Fusion physical Engineering, University of Science & Technology(UST)*
[*]*Corresponding author*

1. Introduction

Graphene quantum dots (GQDs) is zero dimension carbon-based materials that several nanometer. It has unique characteristic such as luminescence, biocompatibility, excellent mechanical / electrical properties and inexpensive characteristics[1]. Therefore, carbon based GQDs has recently attracted attention as a substitute for existing inorganic material-based quantum dots[2]. Typical two method for fabrication of GQDs are 'Top-down' and 'Bottom-up' process. These can efficient and large fabrication GQDs, but acid or harmful chemicals and inorganic materials are necessarily used during the fabrication process and this results in harmful side effects to the human body[3, 4]. Many researcher are studying to completely eliminate toxicity and fabricate biocompatible GQDs[5]. However, it is hard to apply it directly because small amount of residue may have some effect on the human body. We have studied pure and biocompatible GQDs fabrication technique using metal ion beam irradiation. In this study, we have studied the characteristics of metal ion catalyst in high temperature condition as pre-study for fabrication of pure and biocompatible GQDs.

2. Experimental

In this section, we introduce metal ion catalyst and high-temperature annealing process for fabrication catalyst of GQDs.

2.1 Metal ion catalyst

Metal ion catalyst can be fabricated by metal ion beam irradiation and high temperature annealing process. This is similar to the conventional bottom up method. One of the important characteristics in catalyst selection is carbon solubility. The catalyst has selective absorption only carbon and produces carbon nanomaterials with sp^2 structure through carbon precipitation and rearrangement. In case of catalysts with low carbon solubility, it is difficult to fabrication carbon nanomaterials with sp^2 structure. But very high quality carbon nanomaterials can be fabricated. On the other hand, in the case of a catalyst with high carbon solubility, a large amount of carbon nanomaterials is fabricated. However, it fabricates amorphous carbon as well as carbon nanomaterials with sp^2 structure. Thus, carbon nanomaterials with poor quality are fabricated. For this reason, we have selected catalyst that is usually used by reference[5]. Therefore, we irradiated two species metal ion (Cu, Fe) in the samples.

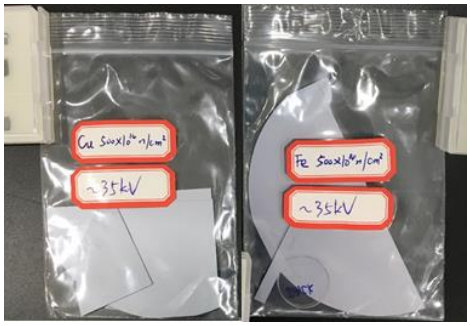

Fig 1. Metal ion beam irradiated samples (Cu, Fe)

2.2 High Temperature annealing process

Irradiated metal ion species are distributed near the surface of the sample. We conducted annealing process at the high temperature condition using the high temperature vacuum furnace to fabricate the metal ion species into nano-size catalyst. Fig 2. shows real picture and schematic diagram for fabrication of catalyst. The furnace can be moved in one-axis and heat up to 1100ºC at the furnace center. The sample can be loaded inside the quartz tube and vacuum inside quartz can be maintained under $5x10^{-3}$ Torr using scroll pump. We also designed an independent gas supply line and MFC, it can be supplied gas into the quartz. We kept vacuum condition during high temperature annealing and inert condition are through make supply of argon gas[6].

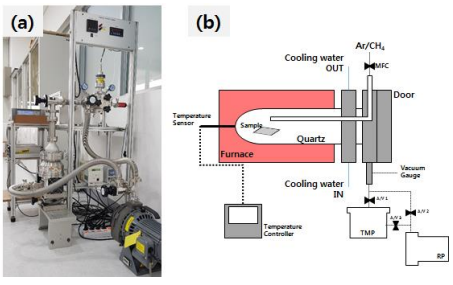

Fig 2. High temperature furnace
(a) Real image (b) Schematic diagram

3. Results and Discussion

When metal ion beam is irradiated onto sample using accelerator, the metal catalyst is distributed not only on the sample surface but also in the depth direction. The irradiated metal catalyst is difficult to catalyze because it exists in the size of several Å scale. Therefore, the irradiated samples were analyzed by SEM image after high temperature annealing. When the irradiated sample is annealing, distributed the metal ions are moved to the surface in the sample. And it is possible to fabricate catalysts of few nano-size due to the agglomeration. Fig 3. shows the sample annealed at 800 ºC and 1050 ºC for 20 minutes after irradiating by $5x10^{14}$ ions/cm^2 with Cu ion beam. As a result of SEM analysis, the Cu catalyst cannot obtain on the sample surface. On the other hand, it can be obtained that the Cu catalyst is fabricated on the surface of the sample annealed to 1050 ºC. The Cu catalyst was uniformly fabricated about 200nm on the sample surface. As a results, it is necessary to fabricate a high temperature condition of 800ºC or more in order to fabricated a Cu catalyst.

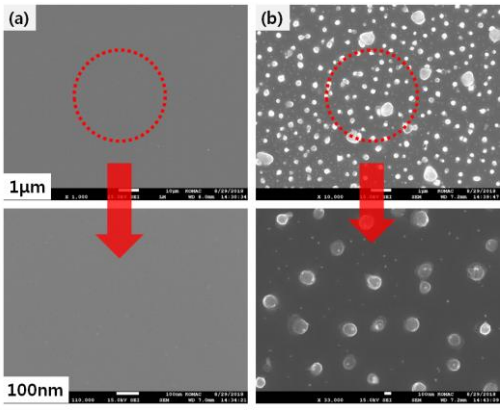

Fig 3. SEM image of Cu catalyst
(a) 800ºC Annealing (b) 1050ºC Annealing

Fig 4. shows the sample in which Fe ions irradiated by $5x10^{14}$ ions/cm^2, and experiment was performed under the same conditions as the above experiment. We have obtained that the Fe catalyst fabricated on the sample surface different that Cu catalyst at the 800 ºC. As a result, we have confirmed that the Fe catalyst has a different tendency from the Cu catalyst. Also we have obtained that the Fe catalyst is fabricated on the sample surface at annealed 1050 ºC. The fabricated Fe catalyst size was about 300nm, it is larger than of the Cu catalyst under the sample conditions. As a result, we confirmed that Metal catalyst for fabrication of GQDs can be fabricated with metal ion beam irradiation at high temperature.

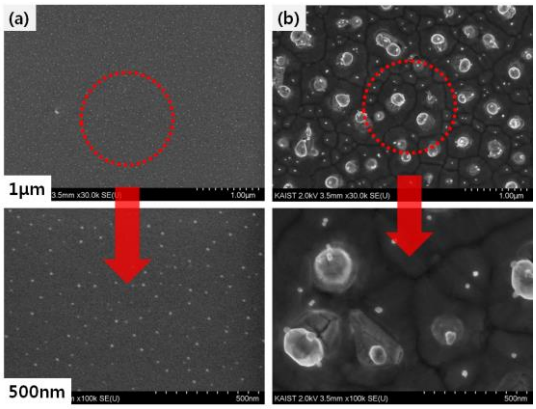

Fig 4. SEM image of Fe catalyst
(a) 800ºC Annealing (b) 1050ºC Annealing

4. Conclusions

We have studied on the fabrication of metal catalyst for GQDs using metal ion beam irradiation. First, we selected a catalyst for the fabrication of GQDs and obtained, and then the metal catalyst change with several of annealing condition. As a result, we have confirmed that it is possible to fabricate metal catalysts of uniform size. We will study that GQDs are fabricated by metal catalyst and analyze characteristics such as PL, Raman, XPS in future studies.

REFERENCES

[1] M. Andreucci et al., Side Effects of Radiographic Contrast Media: Pathogenesis, Risk Factors, and Prevention, BioMed Research International, Vol. 2014, p. 1-20, 2014.
[2] M. Andreucci et al. Reversal of radiocontrast medium toxicity in human renal proximal tubular cells by white grape juice extract, Chemico-Biological Interactive, Vol. 229, p. 17-25, 2015.
[3] H. J. Sun et al., Synthesis of Fluorinated and Nonfluorinated Graphene Quantum Dots through a New Top-Down Strategy for Long-Time Cellular Imaging, Chem. Eur. J. Vol. 21, p. 3791-3797, 2015
[4] R. Liu et al., Bottom-Up, Fabrication of Photoluminescent Graphene Quantum Dots with Uniform Morphology", J. Am. Chem. Soc., Vol. 133, p. 15221-15223, 2011
[5] J. K. Sim, S. Kang, R. Nandi, J. Y. Jo, K. U. Jeong and C. R. Lee, Implementation of graphene as hole transport electrode in flexible CIGS solar cells fabricated on CU foil, Solar Energy, Vol. 162, p. 357-363, 2018
[6] J. M. Ha et al., Freestanding graphene nanosheets and large-area/patterned graphene nanofilms from indium-catalyzed graphite, RSC Adv., Vol. 6, p. 44788-44793, 2016