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Preliminary Study on Fabrication of Bio-compatible Graphene Quantum Dots by Ion-beam assisted Chemical Vapor Deposition

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1. Introduction

A fantastic two-dimensional (2D) carbon material, graphene, has recently attracted remarkable attention due to its wide range of possible applications in transistors, supercapacitors, gas sensors, solar cells, and flexible displays [1-5]. Because of its promising potential applications, not only graphene but also graphene based nanostructures such as graphene nanoribbons and epitaxial graphene have been also widely studied. Graphene quantum dots (GQDs) which indicate graphene sheets less than tens of nanometer attracted researchers because they exhibit unique optical and electronical properties due to quantum confinement and edge effects. GQDs have many advantages compared with other carbon nanomaterials because they have outstanding biocompatibility, low toxicity, good solubility, and high surface area which lead them to have versatile applications: sensors, bio-imaging, drug delivery, and photo-catalysts [6-14].

Generally, GQDs are formed through top-down approaches by cutting, exfoliation, and cage-opening carbonic precursors such as graphite, graphene, graphene oxide, fullerenes, and carbon fiber, into smaller pieces using chemical methods. The methods have their unique advantages, but they typically require the use of strong oxidants (such as $KMnO_4$ and $KClO_3$) and acids (such as H_2SO_4, HNO_3, and HCl) which limited GQDs (synthesized by conventional chemical methods) to apply to utilization in bio-fields. Furthermore, currently, there is still no universal approach for the preparation of GQDs without byproduct and well-size and property controlled GQDs. [15-19]

Here, we present preliminary study on fabrication of bio-compatible GQDs by ion-beam assisted chemical vapor deposition (CVD) methods at Korea Multi-purpose Accelerator Complex (KOMAC). It is a simple and convenient route to highly pure GQDs by ion-beam assisted CVD. After fabrication of GQDs, only GQDs are remained without any impurities and byproducts. Additionally, the size and properties of GQDs are easily controlled by changing the conditions of ion-beam irradiation and thermal annealing.

2. Methods and Results

In this section, the detailed procedures of preliminary study on fabrication of bio-compatible GQDs by ion-beam assisted CVD are described.

2.1 Fabrication of GQDs by sputtering / ion-beam irradiation assisted CVD

The overall synthesis approach is illustrated in Figure 1. Catalysts for the GQD fabrication are provided on polished Si substrates by sputtering or ion-beam irradiation. An annealing process is carried out at higher than 800 °C for 20 min under vacuum of 1×10^{-2} Torr using argon (atmosphere gas) and methane (carbon source) gases with the flow rate of 100 and 50 (or less than 50) standard cubic centimeters per minute (SCCM), respectively. The produced GQDs are characterized by a Field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDX), a X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo VG Scientific), and a Raman spectrometer (514.5 nm laser, ARAMIS, Horiba Jobin Yvon). Figure 2 shows an annealing system for GQD fabrication by a CVD method.

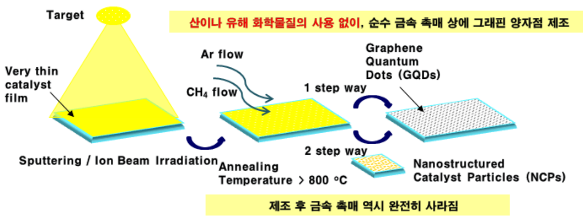

Fig. 1. Preparation of the GQDs by sputtering or ion-beam irradiation-assisted CVD method

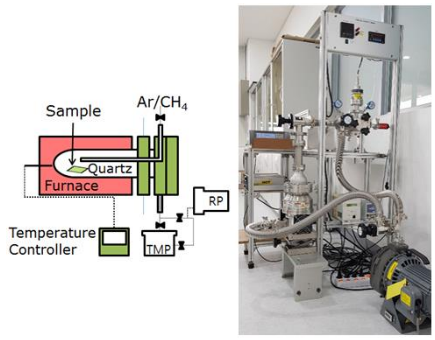

Fig. 2. An annealing system for GQD fabrication by a CVD method

2.2 Structural and Composition Characterization of GQDs

When a Pt thin film was annealed on a Si substrate at 800 ^{o}C during 20min with Ar gas, the Pt thin film was changed to Pt nanoparticles (Figure 3a). Then, when the sample was annealed at higher than 900 ^{o}C with Ar and CH_4 gas, the Pt nanoparticles completely disappeared (Figure 3c), and instead, very small sized (less than 20 nm) GQDs were newly formed as shown in Figure 3b and 3c. Moreover, Raman spectra of the GQDs display three main peaks at 1341 cm^{-1}, 1579 cm^{-1}, and 1445 cm^{-1} (Figure 3d), which correspond to D, G, and CHx peak of GQD.

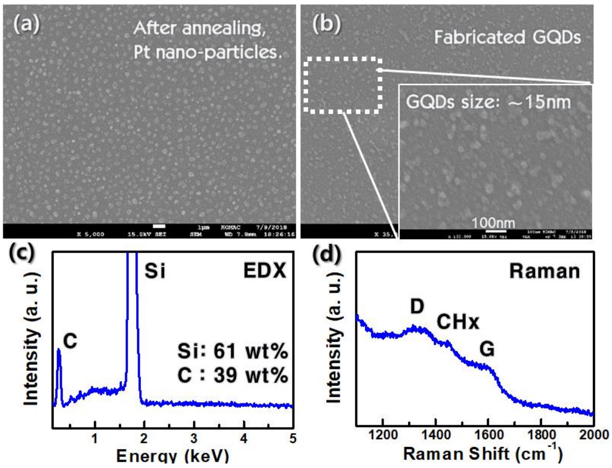

Fig. 3. (a) NCPs and (b) GQDs after annealing processes. (c) EDX and (d) Raman analysis data of the fabricated GQDs.

When a thin Pt layer on a Si substrate was annealed with Ar and CH_4 gas, GQDs were formed on the Si substrate. But using thick Pt film, carbon nanotubes (CNTs) were fabricated, instead of GQDs (Figure 4). Also all Pt was removed after annealing processes at high temperature due to the evaporation.

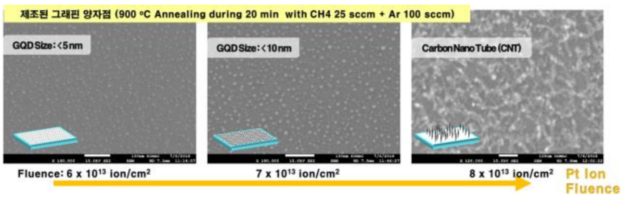

Fig. 4. FESEM images of the synthesized GQDs and carbon nanotube on Si substrates using sputtered Pt of 6 x 10^{13} #/cm^2, 7 x 10^{13} #/cm^2, and 8 x 10^{13} #/cm^2.

The size of GQDs can be controlled by changing the annealing temperature and amounts of carbon source (CH4 gas). Figure 5 exhibits that smaller GQDs were formed at higher temperature (1050 ^{o}C) and larger GQDs were fabricated with high gas pressures of the carbon source. It means that the size and properties of GQDs can be easily controlled by changing synthesis conditions.

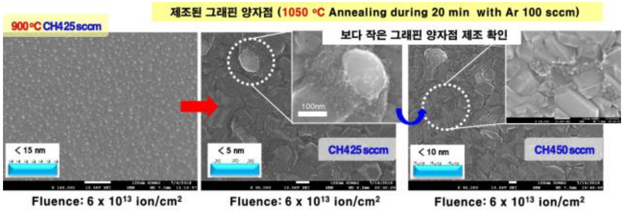

Fig. 5. FESEM images of the GQDs fabricated at different conditions (temperature and amounts of carbon source).

3. Conclusions

We have presented a novel route to GQDs by sputtering or ion-beam assisted CVD. The structure and size of GQDs could be easily controlled by changing the annealing temperature and inserted gas amounts. Furthermore, using FESEM, Raman, and EDX, the fabricated GQDs were well analyzed. At a next step, we will analyze photo-luminescence properties GQDs and also carry out a cellar toxicity test on GQDs for further applications such as bio-imaging, light-emitting device, and photo detector.

4. Acknowledgement

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REFERENCES

[1] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, ACS Nano 2008, 2, 463-470.
[2] H. I. Joh, S. Lee, T. W. Kim, S. Y. Hwang, J. R. Hahn, Carbon 2013, 55, 299-304.
[3] S. V. Samsonau, S. D. Shvarkov, F. Meinerzhagen, A. D. Wieck, A. M. Zaitsev, Sens. Actuators B 2013, 182, 66-70.
[4] Z. J. Li, B. C. Yang, S. R. Zhang, C. M. Zhao, Appl. Surf. Sci. 2012, 258, 3726-3731.
[5] K. Y. Sheem, E. H. Song, Y. H. Lee, Eletrochim. Acta 2012, 78, 223-228.
[6] M. J. Ma, X. Y. Hu and C. B. Zhang, J. Mater. Sci.: Mater.
Electron., 2017, 28, 6493–6497.
[7] L. Tang, R. Ji and X. Cao, ACS Nano, 2012, 6, 5102–5110.
[8] C. Pedro, G. Ignacio and Y. Luis, Carbon, 2016, 109, 658–665.
[9] M. Zhang, L. Bai and W. Shang, J. Mater. Chem., 2012, 22, 7461–7467.
[10] W. F. Chen, G. Lv, W. M. Hu, D. J. Li, S. N. Chen and

Z. X. Dai, Nanotechnol. Rev., 2018, 7, 157–185.
[11] W. S. Kuo, H. H. Chen and S. Y. Chen, Biomaterials, 2017, 120, 185–194.
[12] X. Z. Xu, J. Zhou, J. Jestin, V. Colombo and G. Lubineau, Carbon, 2017, 124, 133–141.
[13] L. L. Du, X. Luo and F. Zhao, Carbon, 2016, 96, 685–694.
[14] A. Witek, Carbon, 2016, 100, 484–491.
[15] W. L. Chen, S. Fu, C. X. Wu and T. L. Guo, Appl. Phys. Lett., 2014, 104, 063109.
[16] J. Peng, W. Gao and B. K. Gupta, Nano Lett., 2012, 12, 844–849.
[17] C. K. Chua, Z. Sofer, P. Šimek, O. Jankovský, K. Klímová and S. Bakardjieva, ACS Nano, 2015, 9, 2548–2555.
[18] C. F. Zhou, W. Jiang and B. K. Via, Colloids Surf., B, 2014, 118, 72–76.
[19] Y. Posudievsky, O. A. Khazieieva, V. G. Koshechko and V. D. Pokhodenko, J. Mater. Chem. A, 2012, 22, 12465–12467.