

## Dry Patterning Process of Luminescent 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  $\text{KMnO}_4$  and  $\text{KClO}_3$ ) and acids (such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HCl}$ ) 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 a study on dry patterning process of luminescent GQDs by ion-beam assisted chemical vapor deposition (CVD) at Korea Multi-purpose Accelerator Complex (KOMAC). Ion-beam assisted CVD is a simple and convenient route to highly pure GQDs. After fabrication of GQDs, only GQDs remained without any impurities and byproducts. Moreover, this approach provides a simple way to pattern GQDs by irradiating Fe ions on the selected region.

### 2. Methods and Results

In this section, the detailed procedures of dry patterning process of luminescent GQDs by ion-beam assisted CVD are described.

#### 2.1 Synthesis of GQDs by ion-beam assisted CVD

The GQDs were prepared by an ion-beam assisted CVD method that combined both the advantages of ion-beam irradiation and CVD techniques, as schematically shown in Figure 1. Catalysts for the GQD fabrication are provided on polished Si substrates by ion-beam irradiation. Ion-beam irradiated Si substrates were annealed at higher than 700 °C for 20 min under Ar atmosphere, and then nano-sized catalysts were produced on the Si substrate. GQDs were synthesized at the nano-sized catalysts using methane gases (carbon source). After GQD fabrication, the nano-sized catalysts were totally removed due to a high temperature, and only pure GQDs remained on the Si substrate.

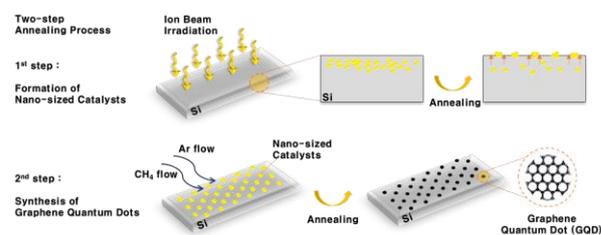


Fig. 1. A schematic of the synthesis process of the GQDs by ion-beam assisted CVD method.

Catalyst ions were implanted into the specific depth of Si substrate by ion-beam irradiation. Then, during an annealing process, the inserted ions are diffused to the surface of Si substrate, and simultaneously the ions are aggregated each other, then nano-sized catalysts are formed on the Si surface (Figure 2a). Under prolonged annealing process, additional ions are combined with aggregated catalysts on the Si surface and larger-sized catalysts are fabricated. The atomic force microscopy (AFM) data show the size distributions of Fe nanoparticles after annealing at 800 °C in Ar (Figure 2b). The heights of nanoparticles range from 2 to 9 nm and the average value is 4.438 nm.

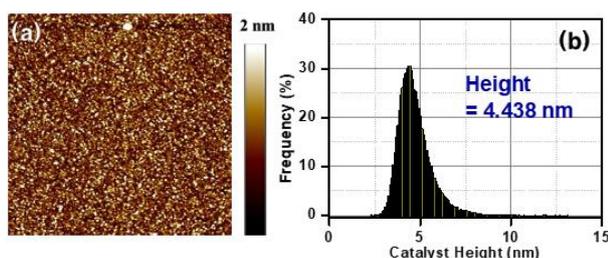


Fig. 2. (a) AFM image and (b) height distribution of the fabricated Fe nanoparticles on Si substrates after annealing, respectively.

Figure 3a shows a high-resolution transmission electron microscope (HRTEM) image of the synthesized GQDs by our ion-beam assisted CVD. The average diameter of the GQDs is  $\sim 3.3$  nm and the lattice fringes with  $\sim 0.25$  nm spacing, which corresponds to the in-plane distance of graphite. Figure 3b is the typical AFM image of the GQDs and the average height is  $\sim 1.5$  nm, suggesting that the GQDs consist of a few layers of graphene. The results of the GQDs reveals that they have a highly-ordered crystalline structure.

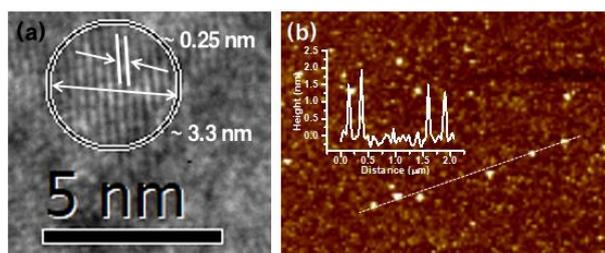


Fig. 3. (a) High-resolution TEM image and (b) AFM data of the synthesized GQDs by our ion-beam assisted CVD.

## 2.2 Patterning of GQDs by ion-beam assisted CVD

Moreover, this approach provides a simple way to pattern GQDs by irradiating Fe ions on the selected region. To demonstrate this,  $\text{Fe}^+$  ions were irradiated to Si substrates by using a metallic mask (Figure 4a). A 400-mesh copper grid was used for the mask. Only Fe ions that passed through the mask irradiate to the substrate, which were clearly confirmed from the FESEM image, as shown in Figure 4b, led to a patterned array. The size of a square pattern is  $42 \mu\text{m} \times 42 \mu\text{m}$ , and the pitch between the patterns is  $62 \mu\text{m}$ , which corresponds to the shape of the shadow mask. A patterned GQD array was prepared by the two-step annealing process that used the pre-patterned substrate (Figure 4a). The fluorescent microscope images of the GQD pattern are displayed in Figure 4c and d, which were excited by 340-380 nm and 450-490 nm, respectively. As seen in the fluorescence images, the luminescent color of the GQD array changed from blue to green by altering the excitation wavelength. Another

thing to note here is that, compared with the FESEM image shown in Figure 4b, the luminescent region in the fluorescence images coincides exactly with the irradiated area (indicated by orange arrows in Figure 4b, c, and d). Consequently, the GQDs were only generated at the irradiated part of the substrate with an ion beam.

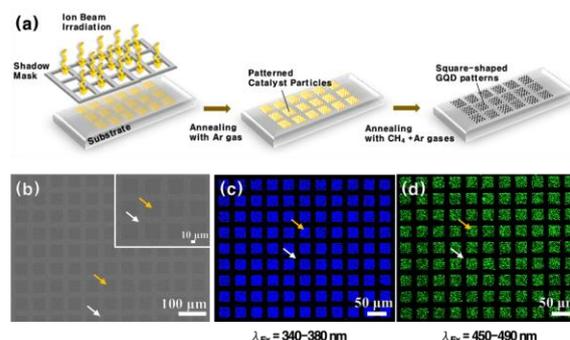


Fig. 4. (a) A schematic illustration of the dry patterning process of GQDs through our ion-beam assisted CVD method. (b) FESEM and magnified FESEM images of the pre-patterned Si substrate by ion-beam irradiation with a shadow mask (inset). Fluorescence microscopy images of the patterned GQD array excited by (c) 340-380 nm and (d) 450-490 nm, respectively. The irradiated and un-irradiated regions are indicated by orange and white arrows, respectively.

This result is further supported by the energy-dispersive X-ray spectroscopy (EDX) data of the GQD pattern exhibited in Figure 5. The EDX mapping image of carbon, which is the basic element of GQDs, matches the shape of the GQD array, as shown earlier.

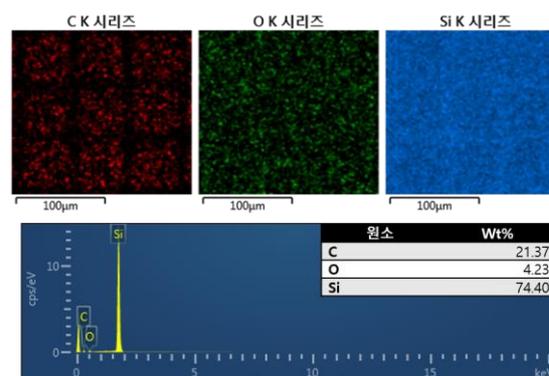


Fig. 5. EDX mapping data of the patterned GQD array using a 400-mesh copper grid as a shadow mask.

## 3. Conclusions

The GQDs were successfully synthesized and patterned by ion-beam assisted CVD and analyzed using various devices such as AFM, HRTEM, fluorescent microscope, EDX and so on. Ion-beam irradiation provides catalyst sources for the GQD

creation. Ion-beam irradiation can provide a catalyst source for the GQD creation at the selective region, leading to a luminescent pattern array composed of only GQDs. We believe that the present approach is very useful for diverse applications such as optoelectronics, nanophotonics, and sensing.

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