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Synthesis of Luminescent Graphene Quantum Dots by Ion-beam Assisted Chemical Vapor Deposition

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Abstract

❖ 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. 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. 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 KMnO4 and KClO3) and acids (such as H2SO4, HNO3, 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. Here, we present a study on synthesis 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. Additionally, the size and properties of GQDs are easily controlled by changing the conditions of ion-beam irradiation and thermal annealing.

Introduction

Graphene Quantum Dots (GQDs)

GQDs are graphene nanoparticles with a size less than 100 nm.
Due to their low toxicity, stable photoluminescence, chemical stability and pronounced quantum confinement effect.

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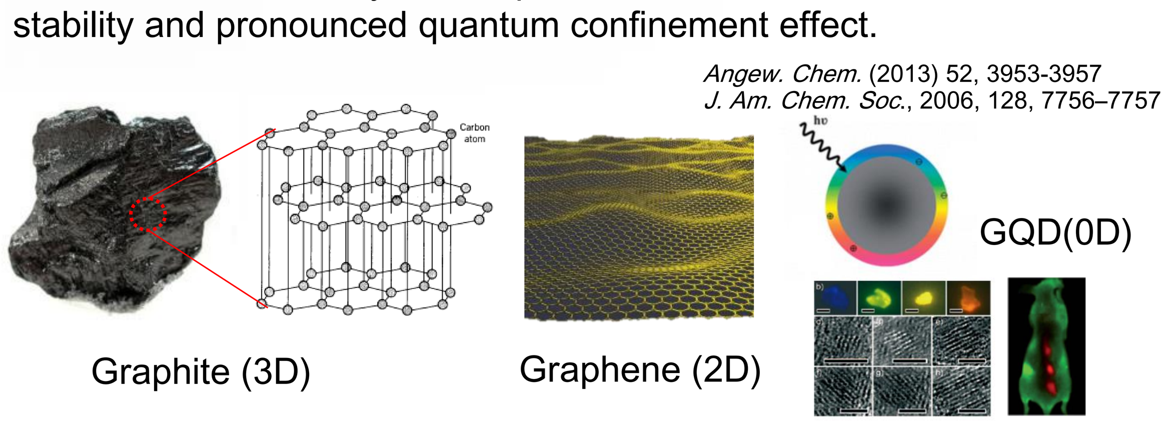
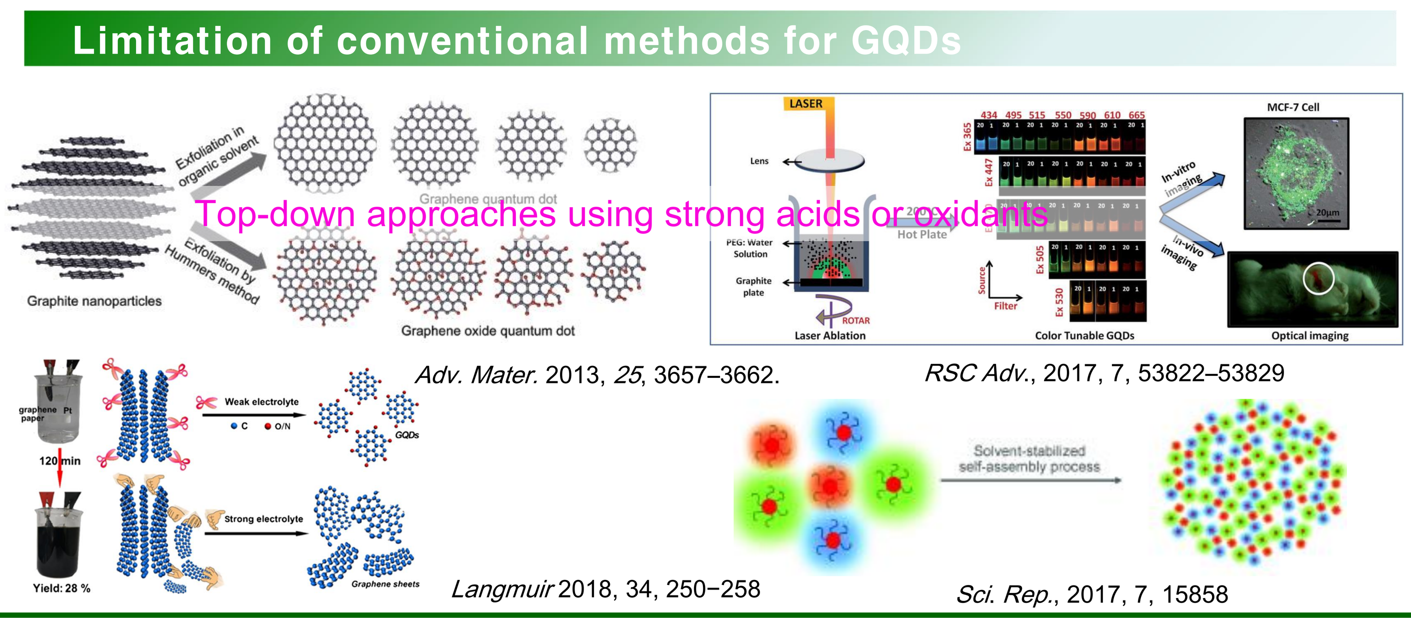
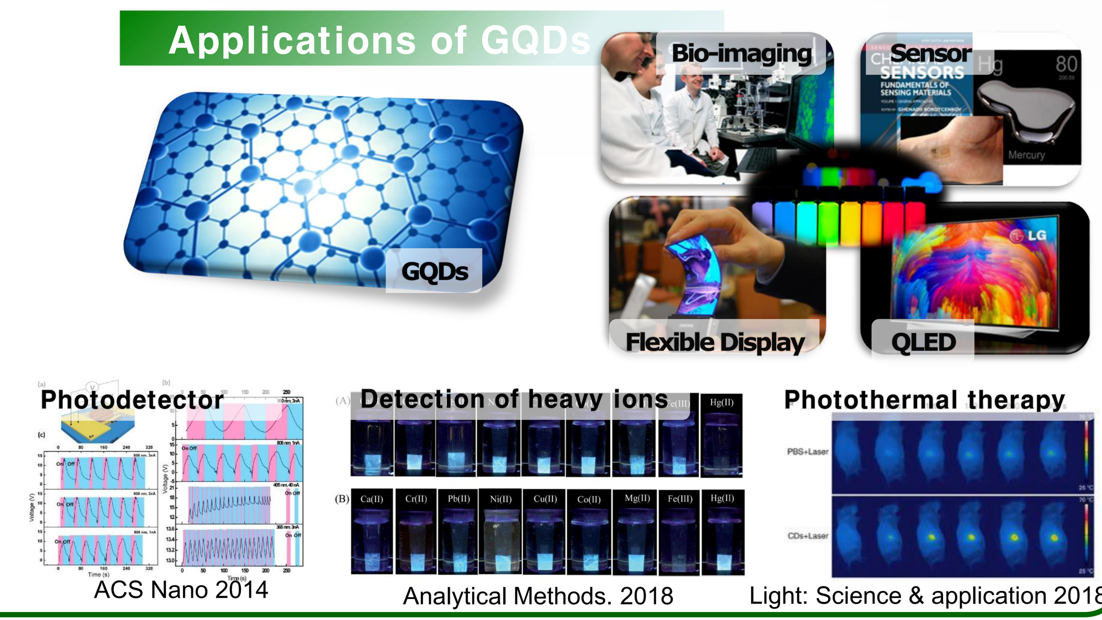


Limitation of conventional methods for GQDs

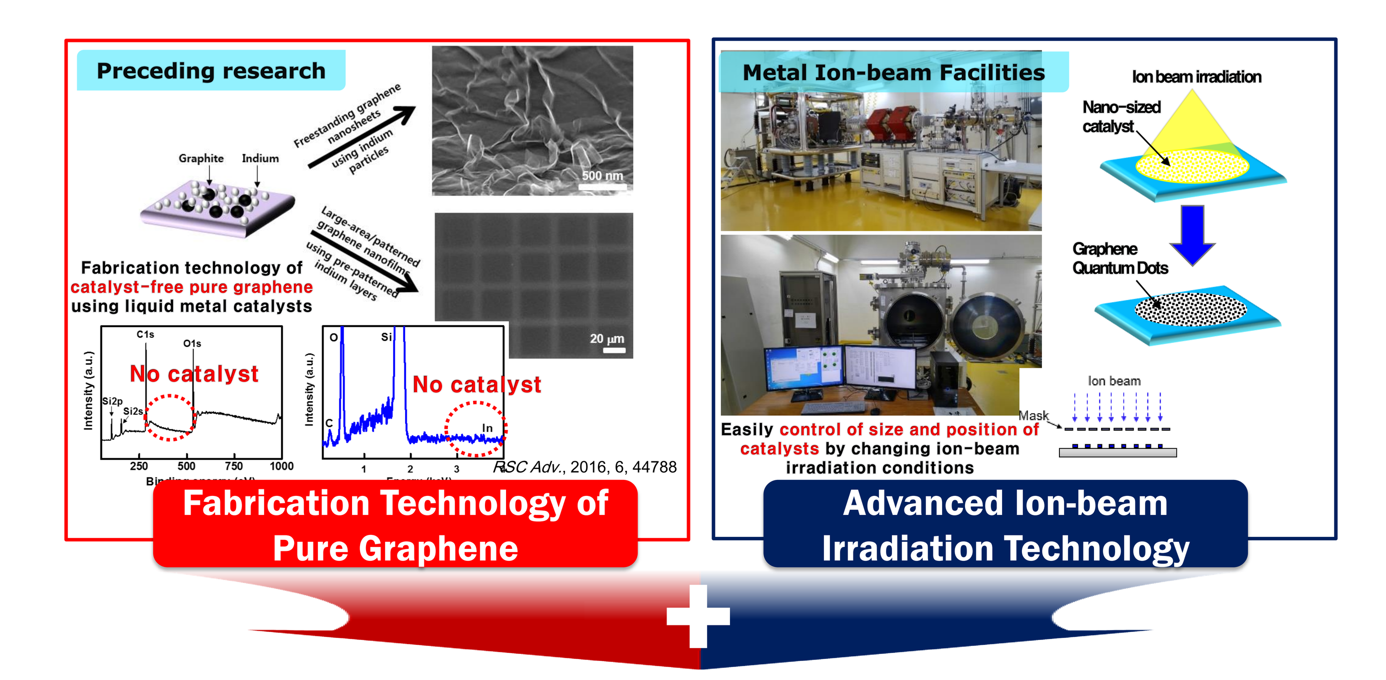


Applications of GQDs



Result & Discussion

Concept for Synthesis of Bio-compatible GQDs by Ion-beam Irradiation



Synthesis of Bio-compatible GQDs by Ion-beam Irradiation

Fabrication of nano-sized catalysts through an ion-beam irradiation approach

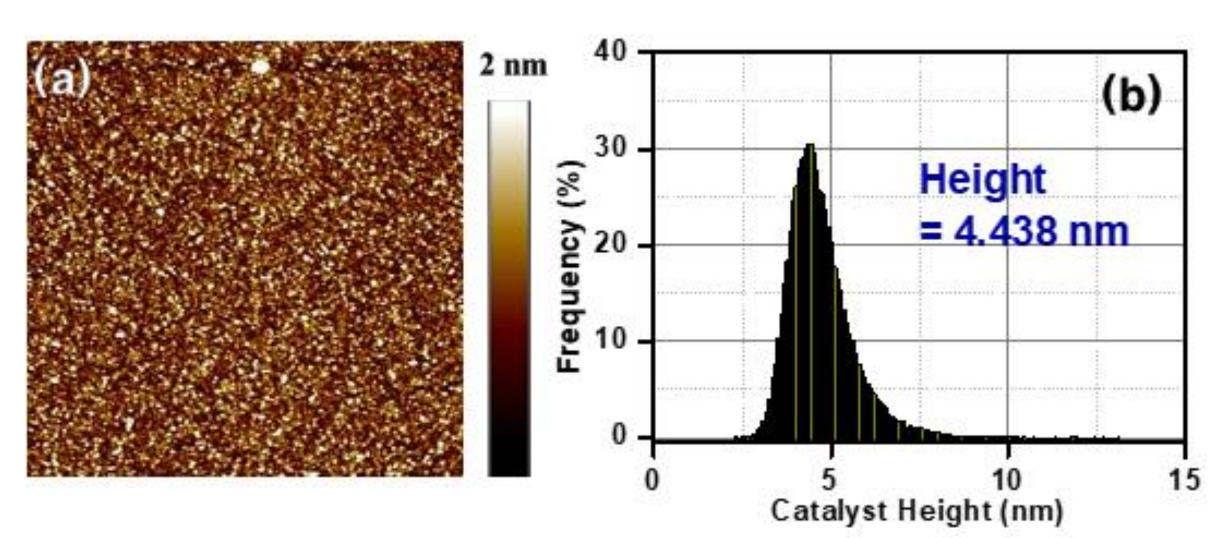
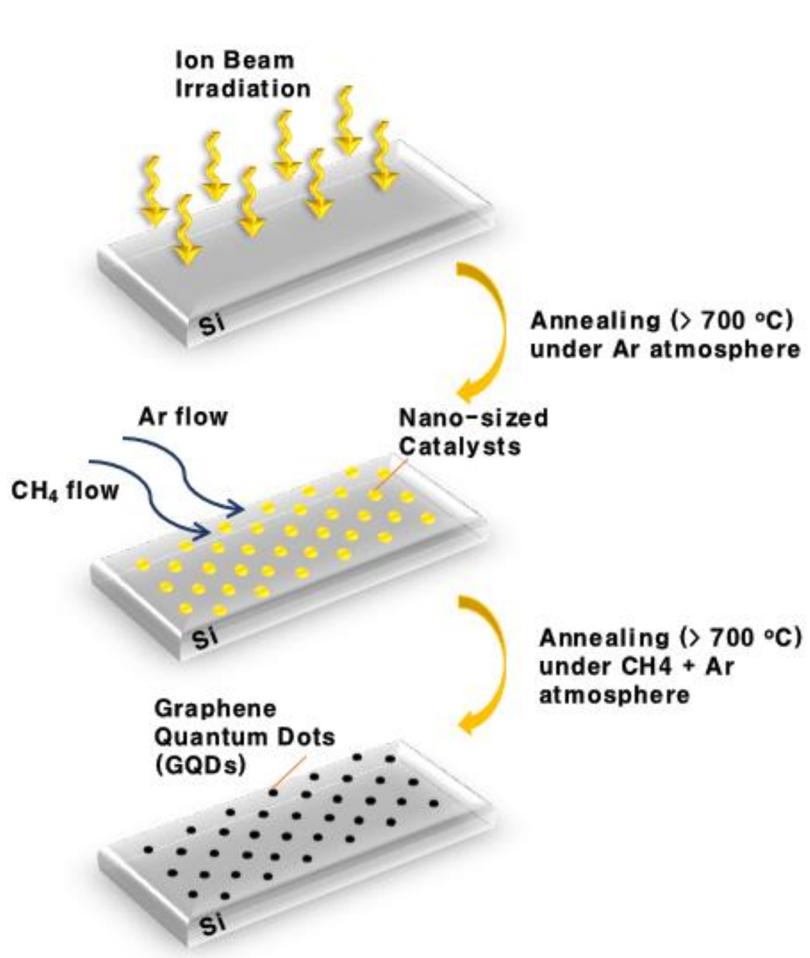


Figure 2. (a) AFM image and (b) height distribution of the fabricated Fe nanoparticles on Si substrates after annealing, respectively.

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 of Figure S3 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.

Synthesis of luminescent GQDs by Ion-beam assisted CVD methods



Fabrication procedures 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 ℃ 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.

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

Characteristics of synthesized GQDs through our ion-beam strategy

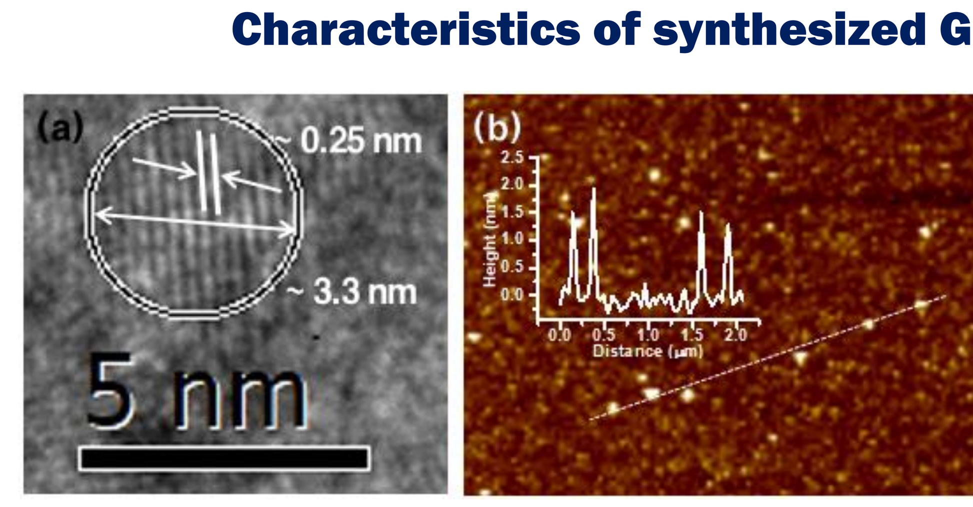


Figure 3. (a) High-resolution TEM image and (b) AFM data of the synthesized GQDs by our ion-beam assisted CVD.

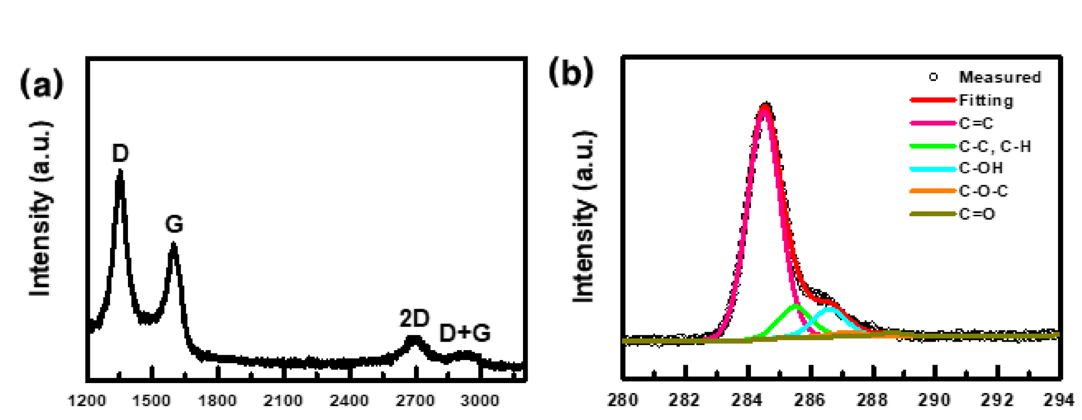


Figure 4. (a) Raman spectrum and (b) C1s XPS spectra of the GQDs.

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 ~3.3 nm and the lattice fringes with ~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 ~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. Figure 4 shows the structural characterization of GQDs prepared by our ion-beam assisted CVD method. Raman spectrum of the GQDs display three main peaks at 1352 cm-1, 1598 cm-1, and 2700 cm-1 (Figure 4a), which correspond to D, G, and 2D peaks of graphene. The presence of D+G peak at 2918 cm-1 in the Raman spectrum is attributed to the defects in graphene layers and the surrounding edges of the GQDs. Raman intensity ratio of I2D/IG is ~0.4, which corresponds to a characteristic of multi-layer graphene. X-ray photoelectron spectroscopy (XPS) was measured to further confirm the chemical structure of the GQDs. C1s peak in the XPS spectra of the GQDs (Figure 4b) indicates that a small amount of C-C, C-H, C-OH, C-O-C, and C=O bonds exist within the main sp2 carbon (C=C) structure, which is the elementary unit of graphene.

CONCLUSION

❖ The GQDs were successfully synthesized by ion-beam assisted CVD and analyzed using various devices such as AFM, HRTEM, Raman, XPS and so on.
❖ Ion-beam irradiation provides catalyst sources for the GQD creation, and the luminescent GQDs are generated using a Fe-implanted Si wafer by a two-step annealing process.
❖ We believe that the present approach is very useful for diverse applications such as optoelectronics, nanophotonics, and sensing.

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