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Fabrication of Two-Dimensional 10 nm Graphene Dot Array and Optical Characterization

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Abstract

Graphene quantum dots have attracted much attention due to their potential for many applications, for example, fluorescence markers in biological and optical devices. However, current understanding of Graphene quantum dots and their industrial applications are not sufficient because of their inhomogeneous size and difficulty of orientation. We propose a unique Graphene quantum dot fabrication method to overcome these problems by using bio-template and the neutral beam etching techniques. With this method, we succeeded in fabricating graphene quantum dots with a two-dimensional array structure on a substrate. Photoluminescence and Raman spectra suggest that our fabricated Graphene quantum dots are highly oriented and exhibit a narrow size distribution, which will enable them to be applied in technologies such as optoelectronics.

1. Introduction

Graphene is one of the most interesting materials due to its unique properties; hence, it has attracted much attention since the discovery of a simple method of obtaining a single layer of graphene [1]. Recently, significant progress has been reported on the synthesis and characterization of zero-dimensional Graphene quantum dots (GQDs), which emit visible light with quantum confinement and edge effect. Photoluminescence (PL) from GQDs is an especially interesting issue. In fact, strong emission from GQDs in the visible light region may lead to new possibilities of GQD applications, e.g., fluorescence bio-markers and light emitting material [2]. Chemical synthesis is well known for synthesis of GQDs because of its simplicity. The chemical methods reported so far involve using acid or heat to oxidize and cut Graphene. Thus, size controllability is not high, leading to wide range emission, which makes industrial use difficult in terms of light source and handling, especially for optoelectronics applications. Additionally, the wide distribution of GQD size inhibits basic property investigation; thus, a homogeneous GQD fabrication method is required. In this paper, we propose a unique top-down nano-fabrication method for GQD fabrication. Our top-down method is based on the combination of the bio-template and neutral beam (NB) techniques [2]. Protein is used as the sub-10nm etching mask and damage-less etching is possible with the NB technique, which involves no UV photons and high energy charged particles that cause defect formation during etching. We report on our fabrication method and the optical properties of 10nm-in-diameter-GQDs on a substrate with high size uniformity.

2. Experiment

Graphene was grown on copper film by using the chemical vapor deposition method [4]. The Graphene was coated with poly-methyl-methacrylate (PMMA) as a supporting material, and the copper film was etched using $FeCl_3$ solution for more than 4 hours. The sample was cleaned using HNO_3 to completely remove the $FeCl_3$. The sample was then transferred to a sapphire substrate. After removal of PMMA with acetone and annealing in H2/Ar mixture atmosphere at 350 °C for 4 hours, we obtained Graphene on the substrate. For GQD fabrication, we used the combined bio-template and NBE technique. Ferritin is aligned closest to the packing structure on the substrate, resulting in a two-dimensional dot array. To use it for GQD fabrication, a 3-nm Si layer was deposited by electron beam evaporation and oxidized using the NB technique. After protein removal by annealing, the oxide layer between the Fe cores was etched by NF_3 radical treatment. Finally, NBE was carried out using Cl_2 gas. The structure was observed using a scanning electron microscope (SEM), and micro Raman spectroscopy, and PL measurement was done using a custom made system using a 532 nm CW laser.

3. Result and Discussion

Figure 1 shows SEM images of ferritin and an Fe core. Under optimum conditions, ferritin is aligned closest to the packing structure, as shown in Fig. 1 (a), and its orientation is maintained even after the protein removal process. A two-dimensional array of Fe cores was used as the etching mask. After the Si cap layer was removed from the Graphene, a dot structure was observed, as shown in Fig. 2. The dots were isolated and in high density. The average

diameter, center to center between dots, and density were 11±4 nm, 19.27±7.21, and 3.2 x 10^{11} cm^{-2}, respectively. This is close to the ideal closest packing value. After NBE, GQDs were obtained, as shown in Fig. 2. Homogeneousness was slightly lost in this process.

Raman spectrum measurement was carried out after Si cap removal (Fig. 3). The G- and 2D-bands were clearly observed even after etching, indicating that the feature structure of the Graphene was maintained in the 10-nm-in-diamter grapheme GQD array. The decrease in intensity is believed to be the reduced graphene area when subjected to the etching process. By comparing before and after etching, the D-band intensity appeared to increase. Part of reason is attributed to the large exposed Graphene edge; thus, the intensity change in the D-band can be explained by the increase in the edge ratio in the measured area. In addition, the width of the G-band did not increase during the etching process. Although it is not part of quantitative analysis, defect formation was considered to be suppressed. Figure 4 shows the PL spectra of the GQD array with different measurement temperatures. PL was observed at 693 nm, which corresponds to 1.7 eV. Peak intensity decreased with an increase in temperature, indicating thermal quenching occurs. The peak position slightly shifted to a lower energy level; however, the shift was less than 2 meV. Therefore, our GQDs emitted light independent of temperature. The PL signal was quite sharp and exhibited an HMFW of 1.1 nm at 10 K. This sharpness of the peak is due to extremely uniform size distribution of the GQDs. The SEM and PL spectrum imply that the size distribution of our fabricated GQDs is in the range of 7 to 15 nm, which is a narrower distribution that what was previously reported [2,5]. Our fabricated size-controlled GQDs on substrate will be very promising for advanced nanodevices..

4. Conclusion

By using the combined bio-template and NB technique, we succeeded in fabricating 10-nm-in-daimeter GQDs of a two-dimensional array on a substrate. The GQDs exhibited narrow width of PL and temperature independence. This GQD array has the possibility of not only application for optoelectronics, but also for fundamentally understanding the physics of GQDs.

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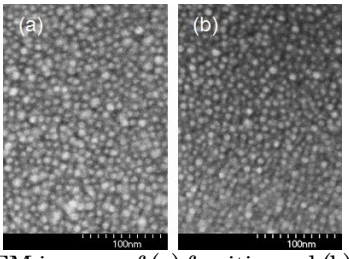

Fig. 1 SEM images of (a) ferritin and (b) Fe core

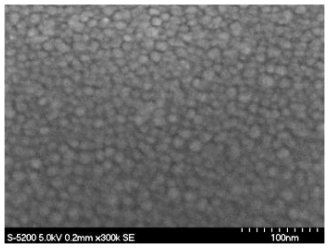

Fig. 2 SEM image of GQDs with Si cap

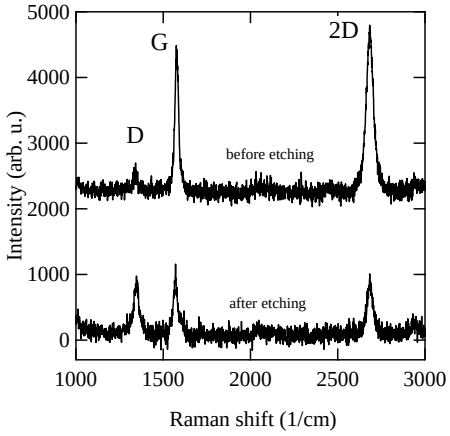

Fig. 3 Raman spectra of Graphene and GQDs

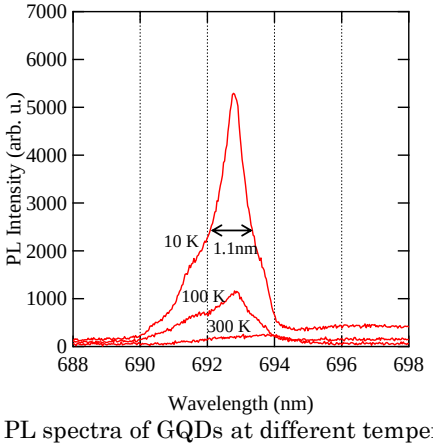

Fig. 4 PL spectra of GQDs at different temperatures