

# Effect of size variation on the cathodoluminescence characteristics of graphene quantum dots



Soo Seok Kang, Soong Sin Joo, Sung Kim, Suk-Ho Choi\*

Department of Applied Physics, College of Applied Science, Kyung Hee University, Yongin 446-701, Republic of Korea

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## ABSTRACT

Cathodoluminescence (CL) has been studied in graphene quantum dots (GQDs) by varying their average size ( $d$ ) from 5 to 35 nm. The size dependence of CL peak wavelength is very analogous to that of photoluminescence (PL) peak wavelength unusually showing non-monotonic behaviors having a maximum at  $d = \sim 17$  nm. The CL behaviors can therefore be attributed to the novel feature of GQDs, *i.e.*, the circular-to-polygonal-shape and corresponding edge-state variations of GQDs at  $d = \sim 17$  nm as  $d$  increases. However, the peak wavelengths of CL are especially much smaller than those of PL at both ends in the size range of GQDs, possibly resulting from the recombination of the electron-beam-excited e-h pairs at higher energy states before thermalization due to fast carrier-carrier scattering dominating over electron-phonon scattering in graphene.

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## 1. Introduction

Graphene, two-dimensional single-atom carbon sheet, has attracted tremendous research interest due to its unique properties such as large surface area, high carrier transport mobility, superior mechanical flexibility, and excellent thermal/chemical stability, which could facilitate numerous device applications [1–3]. However, graphene is a zero band gap semiconductor, thereby limiting its electronic and optoelectronic device applications [4]. Intensive efforts have been made to engineer graphene to open its band gap by employing several techniques such as doping [5] or oxidation [6,7] of graphene and cutting of graphene into nanoscale pieces like graphene nanoribbons [8,9] or graphene quantum dots (GQDs) [10–12]. GQDs have shown several significant properties such as strong carrier-carrier Coulombic interaction [13] and visible luminescence caused by quantum confinement effect [14,15]. We have reported non-monotonic photoluminescence (PL) peak shifts of GQDs in the size range ( $d$ ) from 5 to 35 nm, and shown that the anomalous PL behaviors could be explained by the size-dependent shape and corresponding edge-state variations of GQDs, as confirmed by high-resolution transmission electron microscopy [16,17]. We have also shown that the abrupt changes in the Raman-scattering behaviors of GQDs at  $d = \sim 17$  nm originate from size-

dependent edge-state variation of GQDs at  $d = \sim 17$  nm as  $d$  increases [18]. These results suggest that the edges at the periphery of GQDs may play a major role of determining their optical properties. The strength and tunability of luminescence from GQDs are especially attractive due to their potential applications in light emitting diodes [19], photovoltaic cells [20], biological labeling [21], and medicine [22].

The luminescence of GQDs have been mostly characterized by measuring continuous-wave [10,14,16] and time-resolved [17] PL, whose mapping resolution is not enough to characterize several-nm to several-tens-nm GQDs. In this regard, a technique of cathodoluminescence (CL) has a big advantage due to its high-spatial resolution feature down to several-tens-nm scale. In addition, a scanning electron microscope equipped with a spectroscopic CL facility is available for in-situ concurrent nanostructure analysis together with CL spectroscopy and mapping. In this work, we study CL of GQDs by varying their size, and discuss the CL results based on the size dependence of the GQD structures including shape and edge state.

## 2. Experimental

GQDs were fabricated by following processes. Graphene oxide (GO) sheets were obtained from natural graphite powder by a modified Hummers method [16,23,24]. The GO sheets were subsequently deoxidized in a tube furnace at 250 °C for 2 h under

\* Corresponding author.

E-mail address: [sukho@khu.ac.kr](mailto:sukho@khu.ac.kr) (S.-H. Choi).

Ar ambient to prepare reduced graphene oxide powder, 0.05 g of which were then oxidized in concentrated 10-mL  $\text{H}_2\text{SO}_4$  and 30-mL  $\text{HNO}_3$  for 20 h under mild ultrasonication. The mixture was then diluted with 250-mL deionized (DI) water and filtered through a 200-nm nanoporous membrane to remove the acids. The size-reduced/purified 0.2-g GO powder was re-dispersed in 40-mL DI water and the pH was tuned to 8 with NaOH. The suspension was transferred to a nitrogen-ambient furnace and heated at 250 °C for 10 h. After cooling to room temperature, the resulting powder was re-dispersed in 40-mL DI water for 2 h under ultrasonication. Then, by filtering the resulting suspension through a 200-nm nanoporous membrane, a brown filter solution was separated. Since the colloidal solution still contained some large graphene nanoparticles (<200 nm) emitting weak blue fluorescence, it was further filtered in a dialysis bag of 3500 Da molecular weight overnight, thereby producing strongly fluorescent GQDs. The GQDs were separated as different sizes by using several dialysis bags of 1000–50,000 Da and a 20-nm nanoporous membrane. To make the CL and X-ray photoelectron spectroscopy (XPS) specimens the GQDs were dispersed in DI water, a drop of which was then put on a  $\text{SiO}_2$  substrates and dried.

CL spectra were measured at room temperature using a Zeiss 4300SE field emission scanning electron microscope equipped with a Gatan Mono CL3+. The CL spectra were dispersed by a 1100 lines/mm grating blazed at 500 nm and detected using a Hamamatsu peltier-cooled photomultiplier tube. The CL was excited by electron beam at an acceleration voltage of 10 kV and the CL mapping resolution was 0.5 nm. The atomic bonding states of GQDs were characterized by XPS using Al  $k\alpha$  line of 1486.6 eV.

### 3. Results and discussion

It has been reported that after the hydrothermal treatment in the fabrication processes of GQDs, several oxygen-functional groups (OFGs) could remain at the edges of GQDs, thereby possibly affecting the luminescence behaviors of GQDs [10,22]. We studied the effect of the OFGs on the structure of GQDs by XPS for various-size GQDs. Fig. 1(a) shows size-dependent XPS spectra, which are resolved into four main peaks at 284.5, 286.4, 287.8, and 288.5 eV, corresponding to C-C/C=C in aromatic rings, C=O (epoxy and alkoxy), C=O (carbonyl), and COOH (carboxylic)

groups, respectively [25]. As summarized in Fig. 1(b) and (c), the size-dependent variations of the XPS peak intensities and the FWHMs do not give any evidence that the population of the OFGs depends on the size of GQDs. This suggests that despite the presence of the OFGs in GQDs, they do not give any size-dependent effect on the structures of GQDs, resulting in a negligible effect on the size-dependent luminescence behaviors of GQDs.

Fig. 2 compares the scanning electron microscopy (SEM) and CL images of  $\text{SiO}_2$ , graphene/ $\text{SiO}_2$ , and 5-nm GQDs/ $\text{SiO}_2$ . In Fig. 2(c) and (d), the bare surface of  $\text{SiO}_2$  is well distinguished from the region of  $\text{SiO}_2$  with graphene on its surface. It is clear that CL is almost invisible from  $\text{SiO}_2$  as well as from graphene. As shown in Fig. 2(e), the GQDs exist on the full  $\text{SiO}_2$  surface, but most of them are almost uniformly distributed especially within the circular regions on  $\text{SiO}_2$ , as indicated by the dashed line. Fig. 2(f) shows corresponding uniform CL emitted from the same circular regions.

Fig. 3 compares CL spectra of  $\text{SiO}_2$ , graphene/ $\text{SiO}_2$ , and 5-nm GQDs/ $\text{SiO}_2$ . The CL spectra of  $\text{SiO}_2$  and graphene/ $\text{SiO}_2$  are almost identical with a few low-intensity peaks, possibly resulting from oxygen-deficient or oxygen-excess defect centers [26,27]. In contrast, the 5-nm GQDs/ $\text{SiO}_2$  shows a strong CL peak at  $\sim 395$  nm. These results suggest that the strong CL at  $\sim 395$  nm really originates from GQDs. Fig. 4 shows CL spectra of GQDs for various sizes. Fig. 5 summarizes the CL peak shift as a function of GQD size, very analogous to the size-dependent behaviors of PL peak wavelengths, showing maximum PL wavelength at an average GQD size of  $\sim 17$  nm, as published before by us [16]. However, the peak wavelengths of CL are especially much smaller than those of PL at both ends in the size range of GQDs.

By a detailed analysis of the high-resolution transmission electron microscopy images for GQDs, we have previously found that GQDs appear as the circular shape with mixed edges of zigzag and armchair for  $d < \sim 17$ , but as the polygonal shape mostly with armchair edges for  $d \geq \sim 17$  nm [16]. The CL peak wavelength increases as  $d$  increases as long as GQDs keep their shape circular for  $d \leq \sim 17$  nm, consistent with the quantum confinement effect (QCE). When the shape of GQDs varies into polygons for  $d > \sim 17$  nm, the CL peak wavelength decreases with increasing  $d$ , in other words, the QCE no longer holds. These anomalous behaviors are very similar to those of the PL, as

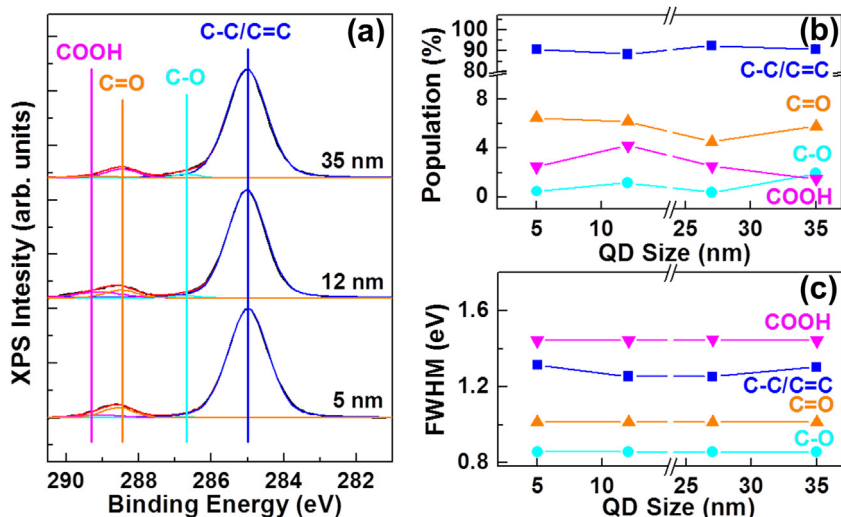


Fig. 1. (a) XPS spectra of GQDs for various average sizes. (b) XPS peak intensities and (c) FWHMs of C-C/C=C, C=O, C=O, and COOH groups as functions of GQD size.

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