2D graphitic nanodots shed bright light

Seokwoo Jeon and Sung Ho Song

The first graphene-quantum-dot LEDs made with high-quantum-yield nanodots obtained via graphite intercalation compound synthesis exhibit luminance in excess of 1000 cd/m².

As a result of the successful synthesis of core and core/shell quantum dots (QDs), state-of-the-art QDs show superiority to conventional dyes and polymeric fluorescents in a number of areas. They offer bright fluorescence, high photostability, and resistance to metabolic degradation in bio-applications. Most high-performance QDs are, however, based on cadmium, the toxicity of which presents an obstacle for broad applications.

Extensive efforts have been made to develop low-toxicity or nontoxic fluorescent nanomaterials that can act as alternatives to toxic QDs. Recently discovered carbon-based QDs (CQDs) with tunable emissions could prove to represent the next generation of inexpensive and safe QDs. However, CQDs developed using efficient synthetic methods still fall short for practical use, in terms of both desired brightness and optical property control. The development of novel strategies to synthesize high-quality CQDs on a large scale, in addition to a better understanding of the fluorescence mechanism, are crucial. Due to graphene’s simpler chemical structure, graphene-based QDs (GQDs) could provide a good model system for understanding the underlying mechanisms of fluorescence. GQDs may even one day replace CQDs in compact or flexible light-emitting systems.

Due to the absence of an energy gap in graphene (which consists of a pure sp² layer of carbon), fluorescence should only be possible by exploiting phonons (collective vibrational excitations of atoms). However, researchers have found that graphene oxide—graphene oxidized by a severe acidic treatment, GO—has very dim fluorescence near UV wavelengths. When GO is broken into nanoparticles of about 10 nm size to form GQDs, their fluorescence becomes much stronger, covering a wide range of visible wavelengths. This luminescence may arise due to the quantum confinement effect, in which particles probabilistically tunnel through the walls of a potential well, or edge effects, in which the geometry of the material edge influences its optical properties. However, the complexity of the disrupted sp² network in GQDs fabricated from GO makes it extremely difficult to be sure about the cause of this luminescence.

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To gain an understanding of the fluorescence mechanism, we carried out controlled oxidation of GQDs synthesized by etching from single-layer, chemical vapor deposition (CVD)-grown graphene using a self-assembled block copolymer. When GQDs are prepared with minimum oxidation, their fluorescence center is located near 400nm, regardless of their physical size. Further oxidation and reduction completely suppresses their fluorescence. The introduction of electron-donating and electron-withdrawing functional groups on GO-based GQDs leads to peak shifts of fluorescence. These results support the potential existence of a subdomain in GQDs, which was first proposed by Manish Chhowalla’s group.

We have discovered that a novel route for synthesizing GQDs could increase the number of subdomains, thereby enabling the development of GQDs with low oxidation, higher photoluminescence (PL) efficiency, and even PL tunability. By employing our expertise in the formation of non-oxidized graphene flakes from graphite intercalation compounds (GICs), we have invented numerous synthetic strategies for the development of transparent electrodes, polymer composites, and gas barrier films for potential applications in energy storage.

Figure 1 illustrates our general synthetic procedure for the fabrication of high-quality GQDs from GICs. A simple GIC dissolution process in water, using graphite and sodium potassium tartrate, enables the generation of a large number of GQDs (>50% yield) in the stable form of a 5nm GQD powder, which can be dispersed in aqueous solution without any surfactants. This method is cost-effective, eco-friendly, and can be easily scaled up. Moreover, in contrast with the visible emission of most GQDs synthesized from GO, ours emit at ~400nm. This is the same emission wavelength that we achieved in GQDs fabricated from the CVD-grown graphene.

The high quantum yield (4.5%) achieved for GQDs in aqueous solution without any further surface functionalization enables the luminescence of organic LEDs (OLEDs) to be increased. We added these GQDs to the active poly(N-vinylcarbazole) (PVK) matrix layer of an OLED: see Figure 2. Careful design of the layer configuration allows electron and hole injection to be balanced, resulting in GQD-LEDs with luminance of 1000cd/m². This value, obtained in a device with 3.0wt% GQDs at 16V, is well above the typical brightness level achieved in current smartphone displays. The GQDs dispersed in PVK appear to provide additional carrier transport and injection pathways, resulting in an enhancement to the overall current density. Although the overall efficiency (~0.65cd/A) is much lower than that found in conventional LEDs, we expect to improve this in the near future by employing optimized material processes and device structures. GQD-LEDs such as these could enable the development of foldable, paper-like displays.

In summary, the emergence of fluorescent GQDs promises a new class of optical material with a variety of useful properties, including tunable luminescence, superior photostability, low toxicity, and chemical resistance. For the first time, we have demonstrated GQD-LEDs with an electroluminescence exceeding 1000cd/m². Our novel and simple synthesis method, based on GICs, enables the creation of high-quality GQDs with high quantum yields (~4.6%) and is suitable for mass production. These GQDs are highly promising for use in diverse applications, ranging from bio-imaging to optoelectronics. We are currently working to extend the emission of our GQD-LEDs to all visible wavelengths, near-IR, and even IR.

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Author Information

Seokwoo Jeon and Sung Ho Song
Materials Science and Engineering
Korea Advanced Institute of Science and Technology (KAIST)
Daejeon, Korea

Seokwoo Jeon received his PhD in materials science and engineering in 2006 from the University of Illinois at Urbana-Champaign. In 2008, he joined the faculty of materials science and engineering at KAIST.

Sung Ho Song received his PhD in materials science and engineering in 2015 from KAIST.

References