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Direct synthesis of graphene quantum dots on hexagonal boron nitride substrate

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ABSTRACT

We report the fabrication and characterization of a large-scale graphene quantum dots (GQDs) grown on hexagonal boron nitride (h-BN) substrate with different layers and similar size of island diameters. The GQDs on h-BN synthesized by chemical vapor deposition (CVD) exhibit excellent morphology, unambiguous interfaces and well-ordered arrangement. These characteristics were achieved through adjusting the control parameters in the growth process, including gas flow rate, temperature and pressure. The synthesized GQDs were shown to possess the thickness-dependent photoluminescence (PL) feature. Broad and red-shift emission features in monolayer GQDs suggest that the inhomogeneity of the surfaces, shapes and edges in the quantum dots of nearby one-layer thickness affect sensitively the PL spectra. However, the GQDs with thickness over ten layers emit very sharp PL spectra with nearly identical shape and position independent of the excitation wavelength. The results suggest routes towards creating large-scale optoelectronic devices in solid-state

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white-light emission, photovoltaic solar cells, and flat panel displays.

**KEYWORDS**

Graphene quantum dots, Hexagonal boron nitride, Chemical vapor deposition, Photoluminescence.

**Introduction**

Quantum Dot (QD) is one of the most active research topics currently in the material science, photovoltaics and cell biology because of their unique characteristics with tunable bandgap, large optical absorptivity, sensitive bioimaging and biosensing [1-3]. However, the bottle-neck to the development of QDs is the known toxicity (e.g. CdSe, CdTe), high prices and strict synthesis conditions. Correspondingly, carbon QDs are an alternative to traditional semiconductor QDs due to their non-toxicity, biocompatibility, and luminescence. Graphene quantum dots (GQDs) has stirred great interest due to their superior physical properties with wider and more potential applications. Obtaining luminescence from GQDs is very attractive owing to their promising applications in flat-panel display and LEDs especially in the visible range. However, the fabrication of GQDs is usually limited by required special equipment, low yield, uncontrollable sizing and time-consuming processes [4-9]. It is desirable to prepare GQDs with cheap and commercially available methods to obtain size controllable batch of products. Chemical vapor deposition (CVD), a relatively cost-economical and versatile technique for producing massive graphene, is regarded as the most promising avenue. Graphene has been grown on a large number of metal substrates by CVD methods, but it is still a great challenge to be directly synthesized
on insulators. As described in the reports [10-12], we have developed a graphene CVD growth process on hexagonal boron nitride (h-BN) insulating substrates. In this paper, we first report a facile one-step direct synthesis of GQDs from decomposition of methane on h-BN substrate without using any metal catalyst, and then we present their PL emissions that are directly associated with the thickness of the GQDs. Although the PL properties of size-dependent carbon dots have been reported [13-15], studies concerning the thickness-dependent PL properties of GQDs obtained by CVD methods remain scarce.

1. Experimental

The synthesis of GQDs was carried out by chemical vapor deposition (CVD) on h-BN substrates through controlling methane flow rate and reaction pressure at different temperature. The fundamental mechanism for GQDs prepared on h-BN substrate by CVD procedure is illustrated in Figure 1. In a typical procedure, the GQDs were directly synthesized on h-BN substrates by atmospheric pressure chemical vapor deposition without any metal catalyzer. The insulator h-BN substrates were put into a furnace and heated to 1000°C under the protection of atmospheric argon gas. Methane and hydrogen mixture gases are then flowed through the furnace while the argon gas was kept on flowing during the whole experimental process as the carrier gas. To obtain different graphene quantum dots thickness, CH₄:H₂:Ar =30:60:180, 40:80:200, and 50:100:200 were adopted to adjust the thickness of the quantum dots while fixing the growth time at 40min. The average thickness and diameter of the GQDs were determined by the repeated AFM (Digital Instrument Dimension 3100, Vecco)
measurements with touching model to obtain the final quantitative values between the AFM tip and the substrates. The Ranman (Thermfisher, 532 nm laser excitation, 10 mW power) spectra were adopted to further characterize the quality and the layers number of the obtained samples. The X-ray photoelectron spectrometer (XPS) were measured in a PHI 5000C ESCA system with C1s = 284.6eV as the benchmark for binding energy correction. The PL spectra were recorded on a Hitachi 7000 fluorescence spectrophotometer. The detection of PL spectrum was carried out at room temperature and the samples were excited using a tunable excitaion wavelength (200nm to 2200 nm). The luminescence was resolved with a monochromator equiped with a 1200 grooves/mm grating blazed at 1.5um.

2. Results and discussion

To investigate their morphology, the synthesized samples were characterized by atomic force microscopy (AFM). In Fig.2 we present the typical AFM images of GQDs synthesized on h-BN substrates where the smooth and planar surfaces of the h-BN are clearly visible. As indicated in the height profiles in Fig. 2, the average diameter of the prepared GQDs was of 80±2 nm for all the samples (Fig.2 (a-c)) used in this work. It was found that the obtained GQDs consisted mainly of homogenous nanosheets. Owing to the special plane essence of the h-BN substrates, the GQDs prepared in this work exhibit very good distribution and arrangement on the surface of h-BN. Moreover, the number of layers and size for different samples were verified by the AFM height profile curves, as depicted in the plots at the bottom of each figure in Fig.2, where the profiles along the white lines clearly show the steps with a thickness
of about one layer (Fig.2 (a)), 2~3 layers (Fig.2 (b)), and few layers (~10 layers, Fig.2(c)). Fig. 2(d-f) show the topographic height distribution of the GQDs, for each sample, more than 80% the GQDs consist of similar thickness. The growth mechanism for graphene quantum dots synthesized on h-BN as described in our previous work [10, 12] is mainly epitaxy growth.

Raman spectra as shown in Fig.3 (a) were used to further confirm the layers number and high degree crystallinity of the synthesized samples. As indicated in the Fig.3 (a), a G band at 1590 cm\(^{-1}\) and a D band at 1350 cm\(^{-1}\) were observed despite accompanying a very sharp and strong h-BN’s characteristic peak around 1367 cm\(^{-1}\). Unlike the GQDs synthesized with previously reported methods [7,13-18], the 2D-band for the samples in this work is relatively high, similar to that of high quality larger-area graphene, the relative intensity of the 2D-band to G-band is near 2 for monolayer GQDs, 0.9 for 2~3 layers and 0.5 for few layer samples. These features indicate that the GQDs synthesized in this work have not only high quality but also high surface density of the dots, which shows the uniqueness for the h-BN substrate-based CVD method developed here for GQD preparation.

The X-ray photoelectron spectroscopy (XPS) was carried out to investigate the microstructure and composition of as synthesized GQDs samples. As shown in Fig.3 (b), the XPS spectra exhibit obvious C1s peak at 285.0 eV from the as-prepared GQDs and B1s peak at 189.2 eV and N1s peak at 398.4 eV from the h-BN substrate, as well as O1s peak at 533 eV. In the XPS results, the C1s spectrum at 285.0 eV as shown in the inset of Fig.3 (b) indicated the graphitic sp\(^2\) carbon signal for the
as-synthesized GQDs on the h-BN surfaces, which is consistent with the C-C bonding value as indicated in the work [18]. The higher C1s peak relative to the corresponding O1s peak seen for the GQDs (few-layer) compared to the monolayer GQDs suggested that oxygen absorption on the surface of GQDs occurred during the CVD preparation of GQDs.

The carbon quantum dots could be made luminescence by inducing a bandgap through reduction of the connectivity of the π-electron network. The luminescence properties of the obtained GQDs were further explored. Remarkably, the quantum dots exhibit excellent PL properties along with strong luminescence in the visible range as shown in Fig.4 (a-c). The PL spectra exhibit excitation dependent feature that similar to previous reports [13-14, 18-20]. Increasing excitation wavelength also lead to the longer emission wavelength, both emission peak positions and peak intensities of GQDs varied when they were excited at different excitation wavelength. Even though different luminescence mechanisms have been proposed by several groups [4, 13, 21-24], further work are necessary to reveal the intrinsic origins of luminescence for GQDs. Different from the previous reports, it is important to note that the CVD process we developed does not involve complex chemicals. GQDs made by CVD method consist of more clean and pure chemical composition compared to the previously reported results. Therefore the GQDs synthesized by the CVD can reflect further the nature of luminescence of the carbon quantum dots. The most interesting finding in this work is the observation of the novel PL behavior that the PL emission spectra of the GQDs exhibit thickness dependent features. As the thickness of GQDs
was increased from one-layer to 2~3 layers and towards more than ten layers, we observed a distinct decrease in the full width at half maximum (FWHM) of the emission peak, with significant change in shape. Increasing thickness in the basic range above ten layers led to the disappearance of 370 nm shoulder peak and the appearance of two sharp peaks near 420 and 470 nm. Analysis of the data in Fig.4 (a-c) for GQDs with different thickness revealed more complex PL emission mechanism than that reported previously [13, 21-23]. For GQDs with monolayer, we observed that 420 nm emission was efficiently induced by 340 nm excitation, but when the sample was adjusted to nearly ten layers, the strongest emission with excitation wavelength 400 nm is emitted at 450 nm. Due to the large surface-to-volume ratio of the graphene nanomaterial, not only different size in the two-dimensional plane but also different thickness of quantum dots will sensitively affect the PL properties. The monolayer-GQDs are very sensitive to the excitation wavelength, where the FWHM and emission peak is broadened and red-shifted, respectively, as the excitation wavelength increases. Broad-band room temperature photoluminescence may arise from the radiation of excitations from the non-equilibrium states. The photoexcited carriers with transition from valence to conduction band were scattered by phonons from lattice vibration before recombination took place accompanied by photons emission. The emission spectra throughout the visible spectrum range appeared to have energy lower than the exciting one due to the electron energy loss in inelastic scattering.

The layer-dependent PL properties may also be explained by the linear dispersion
relation of valence and conduction band touched with each other at Dirac point. The linear dispersion of the electron energy bands implied that for any excitation there will always be electron-hole pair in resonance, the photoexcited electron kinetics in the linear energy levels dispersion for the one-layer GQDs is shown in Fig.4 (d). Not only one-layer but also ten-layer GQDs, a small energy gap can be opened between valence and conduction band due to the quantum confinement effects. However, when the quantum dots thickness is more than ten atom layers, the GQDs become common graphite C-dots and the energy levels dispersion near the Dirac points recover to parabolic type band structure. The excitatoin and radiative recombination in the quasi-continuous energy states in the thicker C-dots are likely to be responsible for the progressively narrowing PL emission as we observed in Fig.4(c). At the same time, the monolayer GQDs likely have more variable emission sites or surface states on the quantum islands which lead to the broadening and red-shift radiative recombination of excitations from not only of different sizes in the samples but also a distribution of different emissive trap sites. The thicker quantum dots are more like the graphite dots, the narrowing PL bands can be attribute to the carrier redistribution within the ensemble of samples. All these factors mentioned above may be the causes that lead to diverse layers behavior of the PL bands as shown in the Fig. 4 (a-c). In addition, the surface dots density is also a key issue to control the whole PL intensity. The less intense PL indicated in Fig.4 (b) was assigned to the lower surface quantum dots density which can be confirmed further through Fig.2 (b) as compared with the dots density shown in Fig.2 (a) and (c). The higher quantum dots density, the stronger
luminescence intensity. Therefore the layer-controllable GQDs can be particularly valuable for emission with multiple colors, especially in solid white light emission. Although some suppositions about the luminescence mechanism of the GQDs have been proposed including quantum-confinement effects. Whatever the origin, the fluorescent inorganic and innoxious carbon-based semiconductors are of particular importance for low-cost optoelectronics, ranging from light-emitting devices and solar cell to photodetectors, touch screens and flexible smart windows. In addition, bio-compatible carbon-based fluorescent quantum dots are more suitable replacement for bio-imaging and bio-labelling.

**Conclusions**

In summary, we successfully fabricated GQDs on h-BN substrates without using any metal catalyst by chemical vapor deposition. The PL properties of the GQDs with different layers were investigated. We have found strongly thickness-dependent visible PL characteristic from the CVD synthesized GQDs. Realtime broad and red-shift emission features appeared in the monolayer GQDs while sharp and nearly identical emission with different excitation wavelength appear in the thick GQDs. It is demonstrated that these GQDs have tunable luminescence properties controlled by the thickness of the graphene layers. The results presented here offer a new route of preparing batches of commercially available graphene nanomaterials by a simple and easy method which are promising for new active materials in optoelectronic fields. Moreover, our results will promote further studies towards the application of GQDs
due to the advantage of the CVD method that provides high density integration of high-quality GQDs. The large-area orderly arranged GQDs enable the large-scale fabrication of flexible and transparent optoelectronic devices in solar cells, LED, and flat panel displays, etc.

Acknowledgments

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Figure captions:

Figure 1. Schematic diagram of CVD growth of GQDs on h-BN substrate.

Figure 2. AFM images of GQDs on h-BN substrates with width and height profiles along the white lines in the images at the corresponding lower parts for (a-c): (a) Monolayer GQDs, (b) Bilayer GQDs, (c) Few-layer GQDs. (d-f) Height distribution of the GQDs corresponding to (a)-(c). Height ≤ 0.5 nm, monolayer; ≤ 1.2nm, bilayer; ≤ 3.5 ten-layer. The scale bars in a, b, c are 200 nm.

Figure 3. (a) Raman spectra for different thickness GQDs on h-BN substrates: Monolayer GQDs (black); Bilayer GQDs (red); Few-layer GQDs (blue). (b) XPS spectrum of GQDs on h-BN substrate. Inset is the C1s peak.

Figure 4. (a) PL spectra of monolayer GQDs. (b) PL spectra of bilayer GQDs. (c) PL spectra of few-layer GQDs. (d) Schematic diagram of photoexcited electron kinetics in linear band dispersion for one-layer GQDs.
Figures:

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