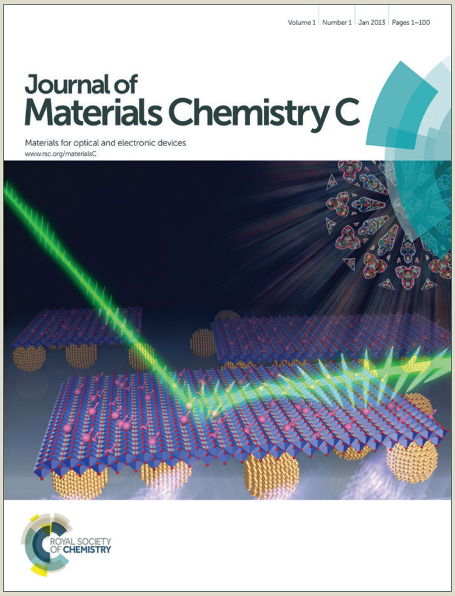
Journal of Materials Chemistry C

Accepted Manuscript



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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 synthesize 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, CH_4:H_2: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 excicitation, 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 microcopy (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 1590cm^{-1} and a D band at 1350 cm^{-1} were observed despite accompanying a very sharp and strong h-BN's charactristic peak arroud 1367cm^{-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 realtive 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 synthesied in this work have not only high qulity 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 consistnet 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 (FMHM) of the emission peak, with significant change in shape. Inreasing 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 obseved 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 monolay-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 thickess 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 excitions 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 semicondtors 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 addation, bio-compatible carbon-based fluorescent quantum dots are more suitable replacement for bio-imaging and bio-labelling.

Conclusionss

In summary, we successfully fabricated GQDs on h-BN substrates without using any metal catalyst by chemical vapor depostion. 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. Realtivley broad and red-shift emission features appeared in the monlolayer 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 optoelctronic devices in solar cells, LED, and flat panel displays, etc.

Acknowledgments

This work was supported by research funding from the Chinese Academy of Science (Grant No. KGCX2-YW-231), the Science and Technology Commission of Shanghai Municipality (Grant No. 10DJ1400600), and the National Science and Technology Major Project (Project No. 2011Zx02707). We also thank the Monentive Company from U.S. for their providing of the h-BN single crystal.

References

[1] Anikeeva, P. O., Halpert, J. E., Bawende, M. G., et al. Quantum dot light-emitting devices with electroluminescence tunable over the entire visible spectrum. Nano Lett. 2009; 9: 2532–6.

[2] Sargent, E. H. Infrared photovoltaics made by solution processing. Nature Photon. 2009; 3: 325–31.

[3] Xingyong Wu, Hongjian Liu, Jianquan Liu, Kari N. Haley1, Joseph A.Treadway1, J. Peter Larson1, et al. Immunofluorescent labeling of cancer marker Her2 and other cellular targets with semiconductor quantum dots. Nature biotechnology. 2003; 21: 41-6.

[4] Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, et al. Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. J. Am. Chem. Soc., 2006; 128: 7756–7.

[5] L. Y. Zheng, Y. W. Chi, Y. Q. Dong, J. P. Lin and B. B. Wang. Electrochemiluminescence of Water-Soluble Carbon Nanocrystals Released Electrochemically from Graphite. J. Am. Chem. Soc. 2009; 131: 4564–5.

[6] R. L. Liu, D. Q. Wu, S. H. Liu, K. Koynov, W. Knoll and Q. Li. An Aqueous Route to Multicolor Photoluminescent Carbon Dots. Angew. Chem., Int. Ed. 2009; 48: 4598–601.

[7] J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, et al. Graphene Quantum Dots Derived from Carbon Fibers. Nano Lett. 2012; 12: 844–9.

[8] Y. Yang, J. Cui, M. Zheng, C. Hu, S. Tan, Y. Xiao, et al. One-step synthesis of

amino-functionalized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan.Chem. Commun. 2012; 48: 380–2.

[9] L. Tang, R. Ji, X. Cao, J. Lin, H. Jiang, et al. Deep Ultraviolet Photoluminescence of Water-Soluble Self-Passivated Graphene Quantum Dots. ACS Nano. 2012; 6: 5102–10.

[10] Xuli Ding, Guqiao Ding, Xiaoming Xie, Fuqiang Huang, Mianheng Jiang. Direct growth of few layer graphene on hexagonal boron nitride by chemical vapor deposition. Carbon. 2011; 49: 2522-5.

[11] Xuli Ding, Hong Sun, Xiaoming Xie, Haicang Ren, Fuqiang Huang, and Mianheng Jiang. Anomalous paramagnetism in graphene on hexagonal boron nitride substrates. Phys. Rev. B. 2011; 84: 174417.

[12] Shujie Tang, Guqiao Ding, Xiaoming Xie, Ji Chen, Chen Wang, Xuli Ding, et al., Nucleation and growth of single crystal graphene on hexagonal boron nitride. Carbon. 2012; 50:329-31.

[13] Dengyu Pan, Jingchun Zhang, Zhen Li, and Minghong Wu. Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots. Adv. Mater. 2010; 22: 734–8.

[14] Yan Li , Yue Hu , Yang Zhao , Gaoquan Shi , Lier Deng , Yanbing Hou , et al. An Electrochemical Avenue to Green-Luminescent Graphene Quantum Dots as Potential Electron-Acceptors for Photovoltaics. Adv. Mater. 2011; 23: 776–80.

[15] Dengyu Pan, Lei Guo, Jingchun Zhang, Chen Xi, Qi Xue, He Huang, et al. Cutting sp^2 clusters in graphene sheets into colloidal graphene quantum dots with

strong green fluorescence. J. Mater. Chem. 2012; 22: 3314-8.

[16] Yan Li, Yang Zhao, Huhu Cheng, Yue Hu, Gaoquan Shi, Liming Dai,et al. Nitrogen-Doped Graphene Quantum Dots with Oxygen-Rich Functional Groups. J. Am. Chem.Soc. 2012; 134: 15–8.

[17] Xin Yan, Xiao Cui, Binsong Li, and Liang-shi Li. Large, Solution-Processable Graphene Quantum Dots as Light Absorbers for Photovoltaics. Nano Lett. 2010; 10: 1869–73.

[18] Yiqing Sun, Shiqi Wang, Chun Li, Peihui Luo, Lei Tao, Yen Wei and Gaoquan Shi. Large scale preparation of graphene quantum dots from graphite with tunable fluorescence properties. Phys.Chem. Chem. Phys. 2013; 15: 9907-13.

[19] Ruili Liu, Dongqing Wu, Xinliang Feng, and Klaus Müllen, Bottom-Up Fabrication of Photoluminescent Graphene Quantum Dots with Uniform Morphology. J. Am. Chem. Soc. 2011; 133: 15221–3.

[20] Lei Bao , Zhi-Ling Zhang , Zhi-Quan Tian , Li Zhang , Cui Liu , Yi Lin , et al. Electrochemical Tuning of Luminescent Carbon Nanodots: From Preparation to Luminescence Mechanism. Adv. Mater. 2011; 23: 5801-6.

[21] Li H, He X, Kang Z, Huang H, Liu Y, Liu J, et al. Water-soluble fluorescent carbon quantum dots and photocatalyst design. Angew. Chem. Int. Ed. 2010; 49: 4430-4.

[22] Q. L. Zhao , Z. L. Zhang , B. H. Huang , J. Peng , M. Zhang, D. W. Pang. Facile preparation of low cytotoxicity fluorescent carbon nanocrystals by electrooxidation of graphite. Chem. Commun. 2008; 5116-8.

[23] Goki Eda, Yun-Yue Lin, Cecilia Mattevi, Hisato Yamaguchi, Hsin-An Chen, I-Sheng Chen, et al. Blue Photoluminescence from Chemically Derived Graphene Oxide. Adv. Mater. 2010; 22: 505–9.

[24] Ruiqi Zhao, Jinying Wang, Mingmei Yang, Zhongfan Liu and Zhirong Liu. Graphene quantum dots embedded in a hexagonal BN sheet: identical influences of zigzag/armchair edges. Phys. Chem. Chem. Phys. 2013; 15: 803-06.

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 :

Fig.1 X.L. Ding.

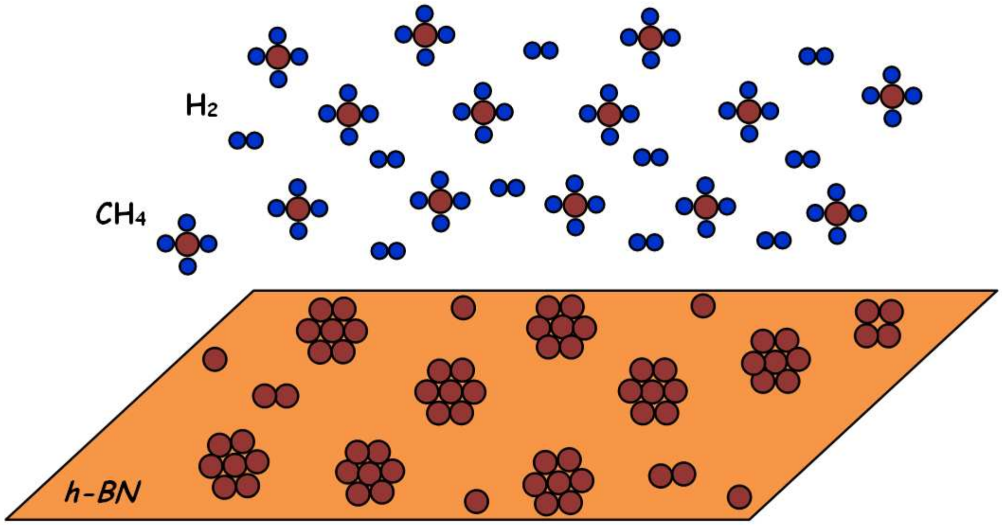

Figure 1. Schematic diagram of CVD growth of GQDs on h-BN substrate.

Figures

Fig.2 X.L. Ding.

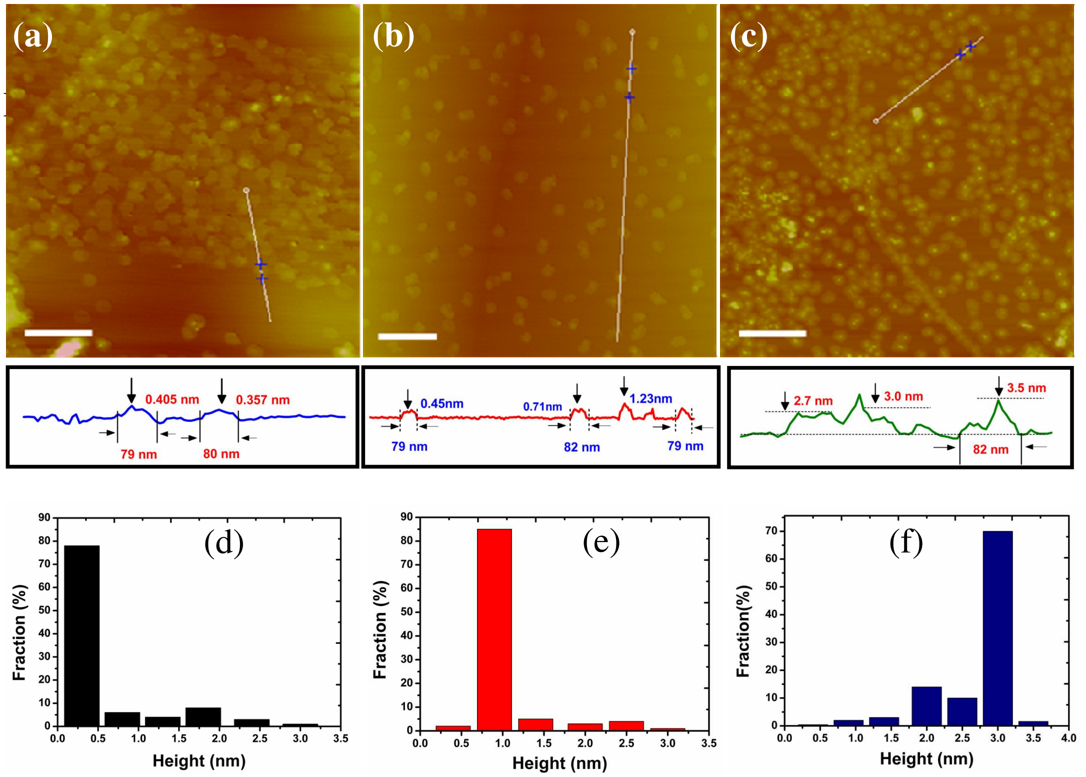

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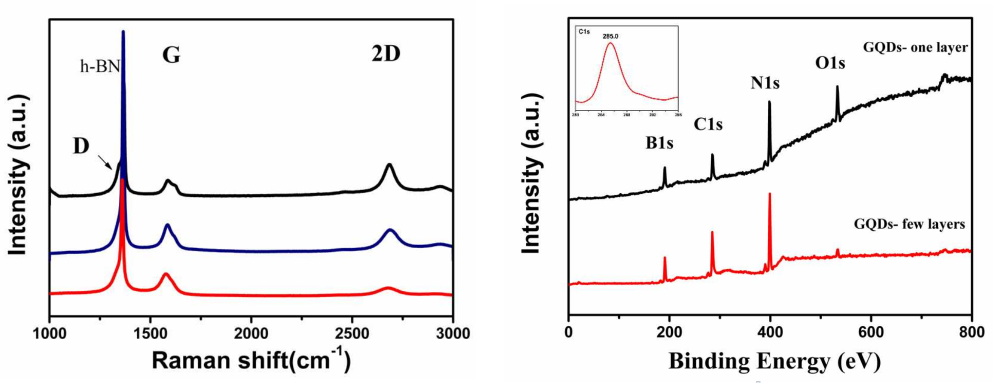
Fig.3 X.L. Ding.



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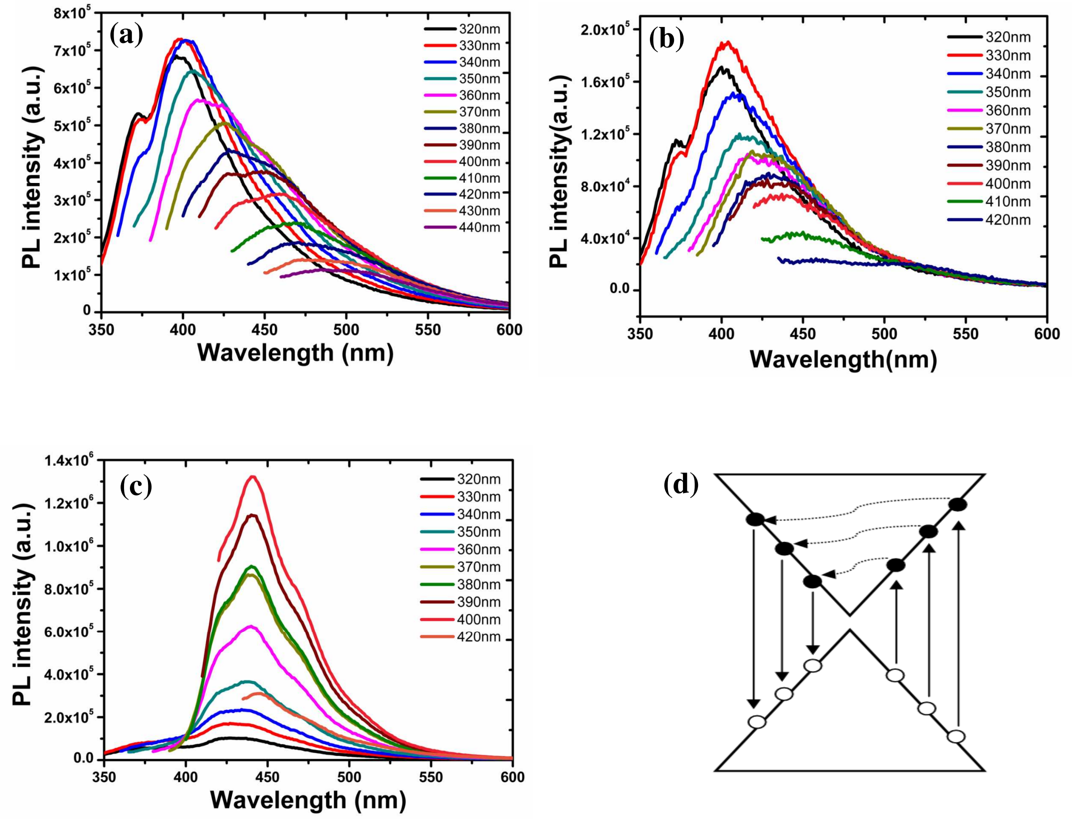

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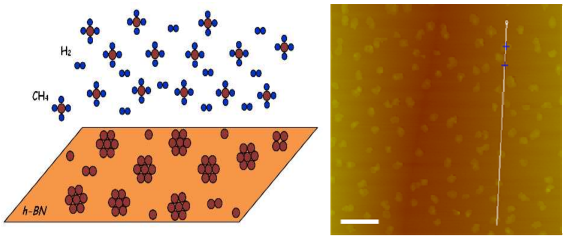

The novel PL properties of GQDs synthesized on h-BN by CVD without any metal catalyst were revealed.