



Quantization of Energy Gap of Nitrogen Doped Graphene Quantum Dots

Open
Access

Wan Ibtisam Wan Omar^{1,2,*}, Okei Yamaoka³, Chin Fhong Soon², Mohd Khairul Ahmad², Masaru Shimomura^{1,3,*}

¹ Graduate School of Science and Technology (GSST), Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka, 432-8011, Japan

² Microelectronic and Nanotechnology-Shamsuddin Research Centre (MINT-SRC), Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia, 86400, Parit Raja, Batu Pahat, Johor, Malaysia

³ Graduate School of Integrated Science and Technology, Department of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka, 432-8011, Japan

ARTICLE INFO

ABSTRACT

Article history:

Received 9 April 2019

Received in revised form 16 September 2019

Accepted 23 October 2019

Available online 30 November 2019

The outstanding photoluminescence (PL) properties of graphene quantum dots (GQDs) had attracted great interest in optical applications such as fluorescent imaging. In this work, a facile one-step hydrothermal method was used to synthesize nitrogen doped GQDs (N-GQDs) with a Teflon-lined autoclave heated at 180 °C for 8 hours. High crystallinity was discovered in the purified N-GQDs with a lattice spacing of 0.21 nm corresponding to in-plane graphene (100 facet). From Tauc plot, the optical band gap of N-GQDs was estimated, derived from their UV-vis absorption spectrum. The as prepared N-GQDs are strongly fluorescent and highly soluble in aqueous solution. Due to the cheap material source, this synthesis provides a feasible route towards the commercial synthesis of N-GQDs. Thus, provides an effective strategy studies of electron transfer and to engineer the optical properties of GQDs.

Keywords:

Graphene quantum dots; hydrothermal; band gap

Copyright © 2019 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

Graphene had attracted numerous attention in many applications due to its strong chemical stability, mechanical, thermal, optical and electronic properties [1–4]. Graphene quantum dots (GQDs) are graphene in less than 20 nm in size. Zero dimensional fluorescent carbon material, graphene has been applied in low-cost optoelectronics devices and biological labelling sensor [5] due to a few properties namely tunable photoluminescence, low cytotoxicity and long term photobleaching resistance [6]. GQDs can be derived either from top down or bottom up approach [7]. As a promising technique to produce GQDs, top down method from exfoliation of bulk graphite through chemical oxidation methods will produce graphene oxide. As a low-cost precursor,

* Corresponding author.

E-mail address: waniibtisamomar@gmail.com (Wan Ibtisam Wan Omar)

* Corresponding author.

E-mail address: shimomura.masaru@shizuoka.ac.jp (Masaru Shimomura)

graphene oxide is a type of carbon based material which has shown as a promising material for different application owing to its excellent aqueous processability, surface functionalization, ease of fabrication and biocompatibility. In this study, hydrothermal method was proposed to synthesize large scale GQDs based on high-temperature and high-pressure exfoliation in a sealed autoclave. The hydrothermal technique is hypothesized to obtain good crystalline morphology for the GQDs.

Moreover, graphene was characterized as a zero band gap material correspond to the conduction band at the minimum Dirac point and convergence of the valence band maximum of a pristine graphene sheet [8]. The band gap of graphene sheet must be opened by means of mechanical cleavage to produce GQDs for photoluminescence that this paper proposed using hydrothermal technique. Band gap or optical energy gap were calculated by using the UV-vis spectrum converted to Tuoc plot by using Eq. (1).

$$Eg = hv - (\alpha hv)^2 \quad (1)$$

where α , h , and ν are the absorption coefficient, Planck constant, and light frequency respectively. Eg is the bulk band gap energy and the value of exponent r denotes the nature of the transition, in which $r = \frac{1}{2}$ is for an indirect band gap material and $r = 2$ for a direct band gap material. By using $r = 2$, good linear fit can be obtained while revealing a direct band gap of N-GQDs [9]. The functionalities of GQDs can be tailored by controlling the size, thus providing quantum confinement effect and provide certain energy levels. However, there are limited reports providing insights on fluorescent and energy properties of GQDs doping with heteroatoms [10]. Hence, this paper presents the quantization of energy gap for nitrogen doping GQDs.

2. Experimental Procedure

2.1 Materials

Graphite powder with 45 μm , Potassium Permanganate (KMnO_4), Hydrogen peroxide (H_2O_2), Sulfuric acid (H_2SO_4), Hydrochloric acid (HCl) and N-N-Dimethylformamide (DMF) were purchased from Wako, Japan. Dialysis tubing with molecular weight cut-off (MWCO) 3500 Da was supplied by Fisherbrand, Fisher Scientific (USA).

2.2 Preparation of Graphene Oxide

GO sheets were prepared by modified Hummer's method. Briefly, 2 g of graphite powder was added to 60 ml of H_2SO_4 . The solution was stirred for 30 minutes in an ice water bath. The temperature was kept to below 20 °C due to the exothermic reaction. While stirring at 400 rpm, 7 g KMnO_4 , was slowly added into the graphite and H_2SO_4 solutions. After 30 minutes of stirring, the reaction system was kept at 35 °C and stirred for another 2 hours. 100 ml of distilled water was added and the temperature was increased to 95 °C. The mixture was cooled down to room temperature at 25 °C. Another 400 ml of distilled water was added followed by gradual addition of 15 ml H_2O_2 . The color of graphene oxide changed from dark brown to yellowish solution. Subsequently, the supernatant was removed from both mixtures. After centrifuge, the supernatant was removed, 1:10 ratio of HCl was added in each of the mixtures as the dispersion medium to remove metal ion.

2.3 Preparation of N-GQDs

200 mg of GO was dissolved in 20 mL of DMF to get concentration of 10 mg/ml. The GO/DMF was first sonicated for 30 minutes to exfoliate the GO sheets. The GO/DMF solutions were transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (50 mL) and heated at 180 °C for 8 hours. After this reaction, the reactors were cooled to room temperature. The product contains yellow transparent suspension and black precipitates. The black precipitates were removed by centrifuge the solution at 4000 rpm for 10 minutes. Yellow transparent suspension was purified by dialysis with 3500 Da dialysis membrane for 24 hours.

2.4 Characterization of the Physical and Optical Properties of GQDs

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were performed on JEOL, JEM-2100 (Japan). The surface functional groups of N-GQDs were studied using JASCO FTIR-6300 spectrometer with a resolution of 4 cm⁻¹ and accumulation of 32. UV-VIS absorption spectra were recorded using JASCO, V-670 spectrophotometer and fluorescence spectra were recorded using JASCO, FP-8600 high sensitivity near infrared (NIR) spectrofluorometer. For TEM imaging, sample was prepared by drop-casted the aqueous dispersion onto a copper grid and dried at room temperature. The fluorescence studies were done using purified samples after dialysis.

3. Results and Discussion

In this work, hydrothermal synthesis was used to produce GQDs by taking graphene oxide as the precursor. The samples were then characterized in term of morphology and absorption properties. From TEM and AFM results, isolated island of sp² graphene in nanoscale dimension had been produced using hydrothermal method. HR-TEM showed that the collected N-GQDs was dispersed and had a diameter of 2-5 nm in size as shown in size distribution graph Figure 1(a)-(c). In HRTEM images of N-GQDs with measured lattice spacing, it was shown that N-GQDs has lattice spacing of 0.21 nm correspond to the (1120) as shown in Figure 1 (b) which matches with the previous report [11]. High crystalline lattice fringes of N-GQDs can be observed.

AFM image in Figure 2 shows N-GQDs dispersed on silicon (Si) wafer. The white spots distributed on the Si wafer considered to be N-GQDs based on their sizes as shown in Figure 2(a). Figure 2(b) is the height curve of the N-GQDs along line 1, 2, and 3 on the AFM image. The average heights of this N-GQDs are 3 nm showing that most of the N-GQDs estimated to be single layered or bi-layered, which is similar to the previous literature [12]. Note that the sizes of the quantum dots in Figure 2(b) showing large particles with 20 to 50 nm in diameter when the prepared samples were dropped on the Si substrate. This result shows inconsistency with TEM size distribution result in Figure 1(c). This might be because of large particles were filtered during dropping the sample solution on the TEM copper grid. Moreover, these various sizes of N-GQDs also could have been resulted from non-sufficiently cutting during the hydrothermal process. However, this facile synthesis of N-GQDs still produce illuminates and spectrally different from graphene oxide [13].

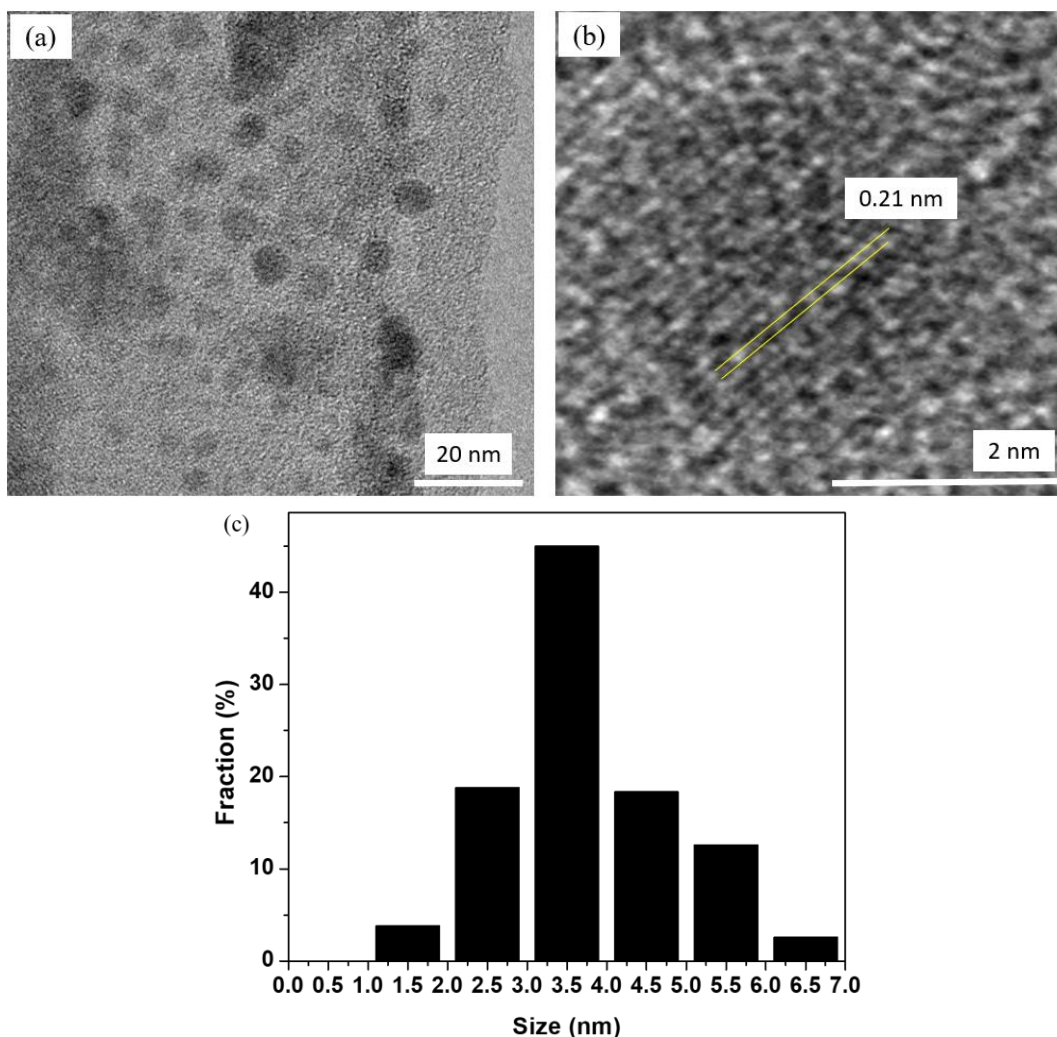


Fig. 1. (a) TEM image of the as-prepared GQDs, (b) high resolution transmission electron microscopy (HRTEM) of the N-GQDs dots with size of lattice constant 0.21 nm, and (c) is the size-distribution of the N-GQDs

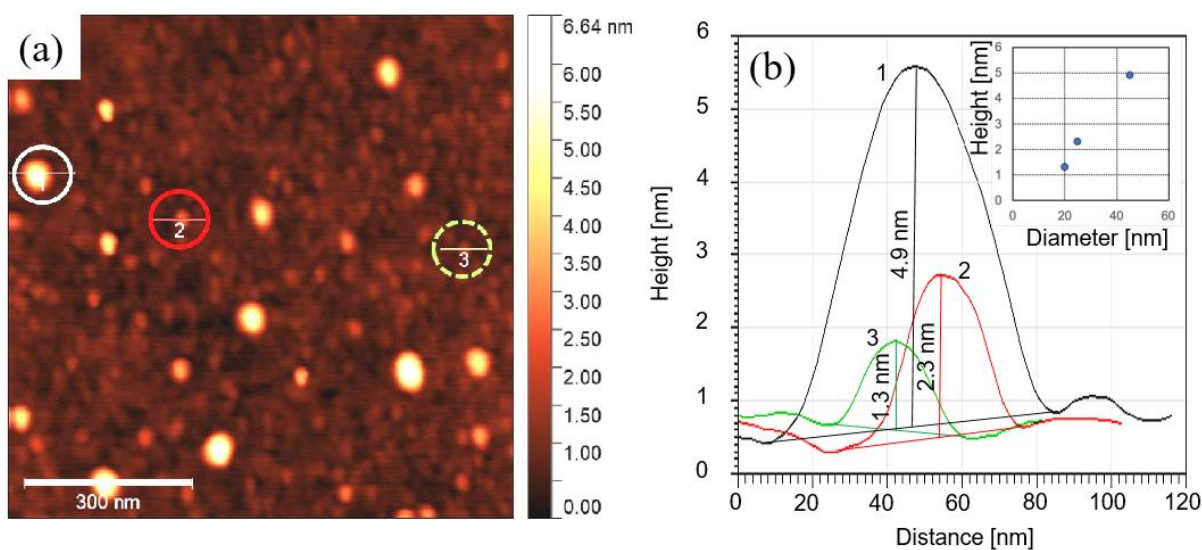


Fig. 2. AFM images of (a) N-GQDs dispersed on silicon wafer and (b) line profile showing the thickness of N-GQDs along the line labelled 1, 2 and 3

The FTIR spectra of the samples presented in Figure 3 shows the obtained N-GQDs. The presence of multiple functional groups was revealed from the infra-red spectra. From this spectra, absorption of broad peak at 3420 cm^{-1} can be assigned to N-H stretching of amine, originated from decomposition of DMF. This result show there are presence of nitrogen functional group attached on the GQDs surface and is in good agreement with the previous study of nitrogen doping GQDs [10]. At 2780 cm^{-1} , a small absorption peak was observed which represent the stretching vibration of CH_3/CH_2 [14]. Additionally, the N-GQDs showed absorption of C=O (carboxyl) and C-O-C (epoxy) groups at 1466 cm^{-1} and 1120 cm^{-1} attached to the N-GQDs surface, respectively. An aromatic absorption peak at band 1580 cm^{-1} was assigned to $-\text{C}=\text{C}-$. The spectral results have many oxygenated functional groups on their surfaces enabling the solubility in water.

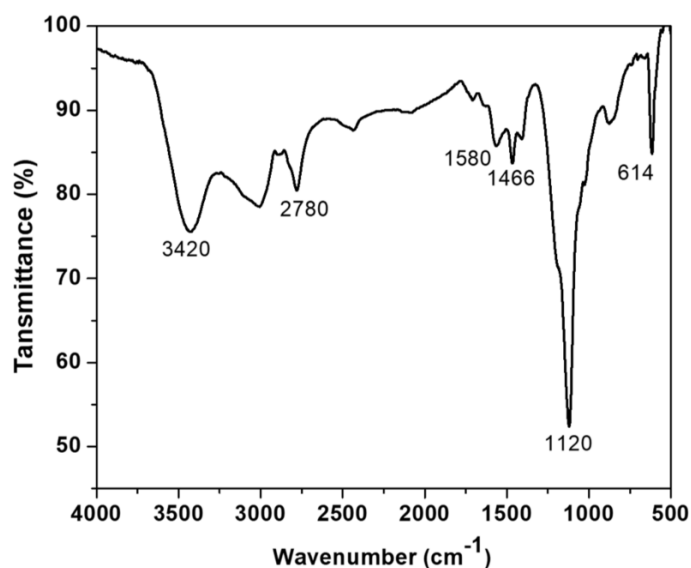


Fig. 3. FTIR spectra of N-GQDs

Two absorption peaks was shown in UV-vis spectrum around 272, $\sim 332\text{ nm}$ and a long tail extending into the visible range (Figure 4(a)). The peak at 272 nm can be ascribed to the $\pi - \pi^*$ transition absorption peak of benzene or aromatic sp^2 domains. The significant absorption peak approximately at 332 nm reveals an $n - \pi^*$ transition in the conjugated structure. From Figure 4(b), the calculated E_g value of the quantum dots from the x-axis intercept of an extrapolated line from the linear curve is approximately at 3.12 eV. Therefore, discrete quantities of energy levels can be achieved. Through those discrete energy level, photo-excited electron hole pairs will undergo radiative providing band gap and creating emission for the graphene quantum dots.

For modulating of PL emission wavelength, band gap engineering is important. From Figure 4(c), the PL spectrum shows the maximum emission wavelength is located at 523 nm. The inset image in Figure 4(c) shows the N-GQDs suspension showing under bright light and UV light, respectively. Photograph of N-GQDs giving bright green PL taken under UV light could be derived from surface defect of N-GQDs from hydrothermal cutting process. Furthermore, when the excitation wavelength increased from 400 to 500 nm, a maximum emission wavelength of N-GQDs was red shifted from 527 to 577 nm (Figure 4(d)). The PL intensity behaviour decrease which can be attributed to the active groups such as carboxylic and methylamine attached to the GQDs [15]. The PL efficiency of N-GQDs will increase effectively since the $n - \pi^*$ transition often appears in fluorescent dyes [16]. The changes in PL emission characterized by different excitation wavelength as shown in Figure 4(d) suggesting that they may be used as fluorescence probe for biomedical imaging.

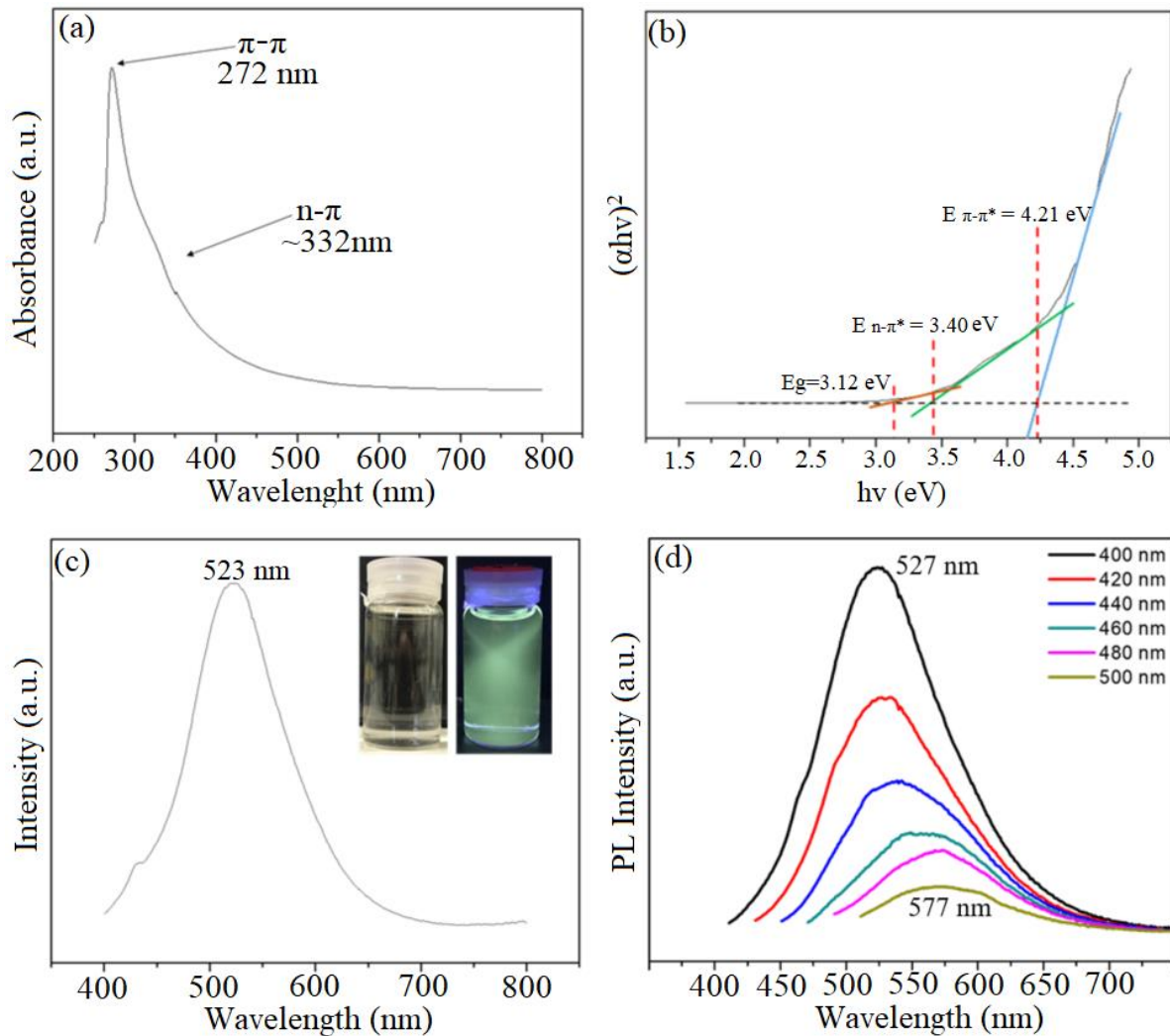


Fig. 4. (a) UV-vis absorption spectrum, (b) $(\alpha hv)^2$ vs $h\nu$ curve of N-GQDs (black curve), (c) photoluminescence excitation ($\lambda_{em} = 375$ nm), and (d) PL emission spectra at multiple excitation wavelength from 400 nm to 500 nm. The inset in (c) showing the N-GQDs suspension under bright light and UV light ($\lambda = 365$ nm), respectively

4. Conclusion

In summary, physical and chemically derived N-GQDs had been produced using hydrothermal method. Green luminescence of N-GQDs with an average size of 3.5 nm and 3 nm in height were obtained. Tauc plot indicated the quantum dots have a direct band gap material with 3.12 eV optical energy gap. Photoluminescence (PL) was found in the visible, and near infrared (NIR) and red wavelengths shifted under excitation might be applicable for labelling different types of biomolecules.

Acknowledgement

The authors are grateful to Shizuoka University and University Tun Hussein Onn Malaysia for giving opportunity to pursue Double Degree Program (DDP) for this research. This project was supported by Postgraduate Research Grant (GPPS), Vot No. U707 awarded by Universiti Tun Hussein Onn Malaysia.

References

- [1] Lee, Changgu, Xiaoding Wei, Jeffrey W. Kysar, and James Hone. "Measurement of the elastic properties and intrinsic strength of monolayer graphene." *science* 321, no. 5887 (2008): 385-388.
- [2] Balandin, Alexander A. "Thermal properties of graphene and nanostructured carbon materials." *Nature materials* 10, no. 8 (2011): 569.
- [3] Zhou, Yong, Qiaoliang Bao, Lena Ai Ling Tang, Yulin Zhong, and Kian Ping Loh. "Hydrothermal dehydration for the "green" reduction of exfoliated graphene oxide to graphene and demonstration of tunable optical limiting properties." *Chemistry of Materials* 21, no. 13 (2009): 2950-2956.
- [4] Neto, AH Castro, Francisco Guinea, Nuno MR Peres, Kostya S. Novoselov, and Andre K. Geim. "The electronic properties of graphene." *Reviews of modern physics* 81, no. 1 (2009): 109.
- [5] Lim, Shi Ying, Wei Shen, and Zhiqiang Gao. "Carbon quantum dots and their applications." *Chemical Society Reviews* 44, no. 1 (2015): 362-381.
- [6] Cao, Li, Xin Wang, Mohammed J. Meziani, Fushen Lu, Haifang Wang, Pengju G. Luo, Yi Lin et al. "Carbon dots for multiphoton bioimaging." *Journal of the American Chemical Society* 129, no. 37 (2007): 11318-11319.
- [7] Rashid, Suraya Abdul, Syazwan Afif Mohd Zobir, Shutesh Krishnan, Mohd Murshid Hassan, and Hong Ngee Lim. "One-pot synthesis of graphene oxide sheets and graphene oxide quantum dots from graphite nanofibers." *Journal of Nanoparticle Research* 17, no. 5 (2015): 225.
- [8] Zhang, Yuanbo, Tsung-Ta Tang, Caglar Girit, Zhao Hao, Michael C. Martin, Alex Zettl, Michael F. Crommie, Y. Ron Shen, and Feng Wang. "Direct observation of a widely tunable bandgap in bilayer graphene." *Nature* 459, no. 7248 (2009): 820-823.
- [9] Zhu, Chong, Siwei Yang, Gang Wang, Runwei Mo, Peng He, Jing Sun, Zengfeng Di et al. "Negative induction effect of graphite N on graphene quantum dots: tunable band gap photoluminescence." *Journal of Materials Chemistry C* 3, no. 34 (2015): 8810-8816.
- [10] Li, Yunhai, Huabing Shu, Xianghong Niu, and Jinlan Wang. "Electronic and optical properties of edge-functionalized graphene quantum dots and the underlying mechanism." *The Journal of Physical Chemistry C* 119, no. 44 (2015): 24950-24957.
- [11] Yan, Shuai, Siwei Yang, Lin He, Caichao Ye, Xun Song, and Fang Liao. "Quantum size effect of poly (o-phenylenediamine) quantum dots: From controllable fabrication to tunable photoluminescence properties." *Synthetic Metals* 198 (2014): 142-149.
- [12] Zhu, Shoujun, Junhu Zhang, Chunyan Qiao, Shijia Tang, Yunfeng Li, Wenjing Yuan, Bo Li et al. "Strongly green-photoluminescent graphene quantum dots for bioimaging applications." *Chemical communications* 47, no. 24 (2011): 6858-6860.
- [13] Alfaggy, Ghada I., Mashael M. Albayyalli, M. Alsalhi, and V. Masilamani. "Photoluminescence of Graphene Oxide and Graphene Quantum Dots." *Sensors & Transducers* 225, no. 9 (2018): 36-40.
- [14] Joseph, Julin, and Aji A. Anappara. "White light emission of carbon dots by creating different emissive traps." *Journal of Luminescence* 178 (2016): 128-133.
- [15] Sun, Jing, Siwei Yang, Zhongyang Wang, Hao Shen, Tao Xu, Litao Sun, Hao Li et al. "Ultra-High Quantum Yield of Graphene Quantum Dots: Aromatic-Nitrogen Doping and Photoluminescence Mechanism." *Particle & Particle Systems Characterization* 32, no. 4 (2015): 434-440.
- [16] Kumar, Vinod, Vimal Singh, Sima Umrao, Vyom Parashar, Shiju Abraham, Anand K. Singh, Gopal Nath, Preeti S. Saxena, and Anchal Srivastava. "Facile, rapid and upscaled synthesis of green luminescent functional graphene quantum dots for bioimaging." *Rsc Advances* 4, no. 40 (2014): 21101-21107.