TẠP CHÍ KHOA HỌC & CÔNG NGHỆ ĐẠI HỌC DUY TÂN
DTU Journal of Science and Technology 02(45) (2021) 29-34

TRƯỜNG ĐẠI HỌC DUY TÂN
DUYTAN UNIVERSITY

Optical properties of Nitrogen and Sulfur doped Graphene quantum dots

Tính chất quang của các chấm lượng tử Graphene pha tạp Nitơ và Lưu huỳnh

Le Xuan Hung[a,b*], Trinh Thi Hue[b,c], Pham Thu Nga[b,c]
Lê Xuân Hùng[a,b*], Trịnh Thị Huế[b,c], Phạm Thu Nga[b,c]

[a]*Institute of Research and Development, Duy Tan University, Da Nang, 550000, Vietnam*
[a]*Viện Nghiên cứu và Phát triển Công nghệ Cao, Trường Đại học Duy Tân, Đà Nẵng, Việt Nam*
[b]*Faculty of Natural Sciences, Duy Tan University, Da Nang, 550000, Vietnam*
[b]*Khoa Khoa học Tự nhiên, Trường Đại học Duy Tân, Đà Nẵng, Việt Nam*
[c]*Institute of Theoretical and Applied Research, Duy Tan University, Hanoi, Vietnam*
[c]*Viện Nghiên cứu Lý thuyết và Ứng dụng, Trường Đại học Duy Tân, Hà Nội, Việt Nam*

(Ngày nhận bài: 03/12/2020, ngày phản biện xong: 07/01/2020, ngày chấp nhận đăng: 12/03/2021)

Abstract

Graphene Quantum Dots (GQDs) are a type of material with a width of several nanometers (nm) and a thickness of a single layer or a few layers of carbon (C) atoms organized in hexagonal shape like a beehive. Since the lattice structure of GQDs only includes carbon atoms, they are a nanomaterial that is friendly to the environment and humans. They have many applications, with one of the main uses being a novel antimicrobial agent. Doping other elements into the GQD lattice is an effective method to alter the defective energy level of GQDs, allowing control and modification of their optical properties and electronic transmission. In this paper, we present new results on the synthesis of nitrogen-doped GQDs (N-GQDs) and sulfur-doped GQDs (S-GQDs) and their respective optical properties such as absorption spectra, fluorescence, and Raman spectra. The fluorescent mechanisms of GQDs, N-GQDs, and S-GQDs will also be clarified and explained. These two types of quantum dots are strong candidates for antimicrobial agents and biomedical imaging.

Keywords: Doped Graphene Quantum Dots; GQDs; N-GQDs; S-GQDs; Optical Properties; Photoluminescence; Raman.

Tóm tắt

Các chấm lượng tử Graphene (GQDs) là loại vật liệu có kích thước nano mét (nm) và chiều dày chỉ là đơn lớp hay vài lớp nguyên tử carbon (C) sắp xếp thành mạng lục giác (hecxagonal) kiểu tổ ong. Do cấu trúc mạng của chấm lượng tử graphene chỉ gồm các nguyên tử carbon, vì vậy GQDs là vật liệu nano thân thiện với môi trường và con người. Chúng có nhiều ứng dụng mà một trong những ứng dụng chính trong y sinh là làm tác nhân kháng khuẩn mới. Việc pha tạp các nguyên tử chất khác vào mạng GQD là một phương pháp hiệu quả để thay đổi mức năng lượng khuyết tật của GQDs, để điều khiển và làm thay đổi các tính chất quang và truyền điện tử của GQDs. Trong bài báo này, chúng tôi trình bày các kết quả mới về việc tổng hợp GQDs pha tạp nitơ (N-GQDs) và GQDs pha tạp lưu huỳnh (S-GQDs) và các tính chất quang học tương ứng của chúng, như phổ hấp thụ, huỳnh quang, phổ Raman. Cơ chế huỳnh quang của các mẫu GQDs, N-GQDs, S-GQDs sẽ được làm rõ và giải thích. Hai loại chấm lượng tử này là những ứng viên sáng giá cho các ứng dụng làm chất kháng khuẩn trong y sinh và hiện ảnh sinh học.

Từ khóa: Chấm lượng tử Graphene pha tạp; GQDs; N-GQDs; S-GQDs; Tính chất quang; Huỳnh quang; Raman.

[*]*Corresponding Author:* Le Xuan Hung; Institute of Research and Development, Duy Tan University, Da Nang, 550000, Vietnam; Faculty of Naturals Sciences, Duy Tan University, Da Nang, 550000, Vietnam
Email: lexuanhung@duytan.edu.vn

1. Introduction

Graphene materials with 2D forms have attracted research from scientists all over the world, thanks to their interesting physical properties and high applicability, ever since the two scientists Geim and Novoslov received a Nobel Prize in 2010. However, graphene also has some limitations, such as zero bandgap, low absorptivity, etc. [1]. Graphene quantum dots were first fabricated by Ponomarenko and Geim [2]. GQDs have many new properties, and their unique fluorescent properties attribute to their quantum confinement effect. The property modification capability of GQDs is very important for various applications. Besides, GQDs also exhibit good solubility in water due to the large edge effect of GQDs, which can be modified by functional groups. Modification of GQD properties have been initially done by Zhao et al. [3] in 2012 by doping nitrogen (N) into GQDs. Currently, GQD property modification via doping and edge functionalizing is a hot topic for research [1], in which the GQDs are doped with atoms of different elements, such as P, N, B and S. The doping not only changes the emission spectral bands but also increases the quantum yield of doped GQDs. Specifically, doping with sulfur atoms is quite difficult compared to other heteroatoms because of its electronegativity. Until now, there have only been a handful of researches on the fabrication of S-doped GQDs (S-GQDs) reported for sensor applications [4, 5]. Both N-GQDs and S-GQDs have good fluorescence and high potential in biomedical [6] and photoelectronic applications [7]. In this study, we used a simple and cost-effective pyrolysis method to fabricate N-GQDs and S-GQDs using citric acid (CA), urea, and 3-mercaptopropionic acid (MPA) as the sources for carbon, nitrogen (N), and sulfur (S) respectively. These are novel research results to obtain high-quality quantum dots to apply in experiments for antibacterial activity. The aims of this research are: studying the fabrication of GQDs doped with N and S atoms from different carbon sources; studying the morphology of fabricated doped GQDs; studying the identification of the formation of graphene via its characteristic peaks and the effects of doping on these peaks; presenting the emission mechanisms of processes that take place in these samples. The optical properties of these two types of doped GQDs such as Raman spectra, photoluminescence excitation (PLE), and photoluminescence (PL), will be presented in detail and compared to non-doped GQDs.

2. Experiments

2.1. Synthesis of N-GQDs and S-GQDs

For S-GQDs, synthesis from CA and urea was reported in [8] and synthesis from CA and MPA was reported in [4, 5, 9]. For N-GQD synthesis from CA and urea, we liquefy CA from solid form then pyrolyze this CA liquid with urea by microwave at 560 W for 2 min. After the pyrolysis process, this mixture is added to a 50 ml NaOH (10 mg/ml) solution. The obtained liquid is as-synthesized N-GQDs.

In a typical preparation procedure for S-GQDs [5, 9], 300 µl MPA and 2.1 g CA are mixed in a 50 mL beaker. The obtained mixture is put into a microwave at 560 W for 2 min. The resulting mixture, which has a light brown color, is then dripped into a 50 ml NaOH (10 mg/ml) solution under strong stirring. After 30 minutes, we obtain S-GQDs as the product.

2.2. Characterization of N-GQDs and S-GQDs

A JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM) was used to characterize the GQDs and doped-GQDs at an accelerating voltage of 200 kV. Raman spectra were recorded by a HORIBA

XploRA micro-Raman system using a 532 nm excitation laser. The ultraviolet-visible (UV–Vis) absorption spectra of doped-GQDs in water were measured in the wavelength range of 200–1100 nm using a Cary 60 UV–Vis spectrophotometer (Agilent). The PL spectra were recorded on a Fluorolog- 322 system (Horiba Jobin-Yvon) using a Xenon 450 W light with excitation wavelength selected at 460 nm. The excitation-emission mapping (EEM) measurement was carried out on Duetta (Horiba) using a Xenon 75 W light with a CCD detector.

3. Results and discussion

3.1. Morphology of doped-GQDs by HR-TEM images

The shape and size of the synthesized doped-GQDs samples were investigated using HR-TEM images at different magnifications. Fig. 1 are HR-TEM images of N-GQD synthesized samples from CA and urea.

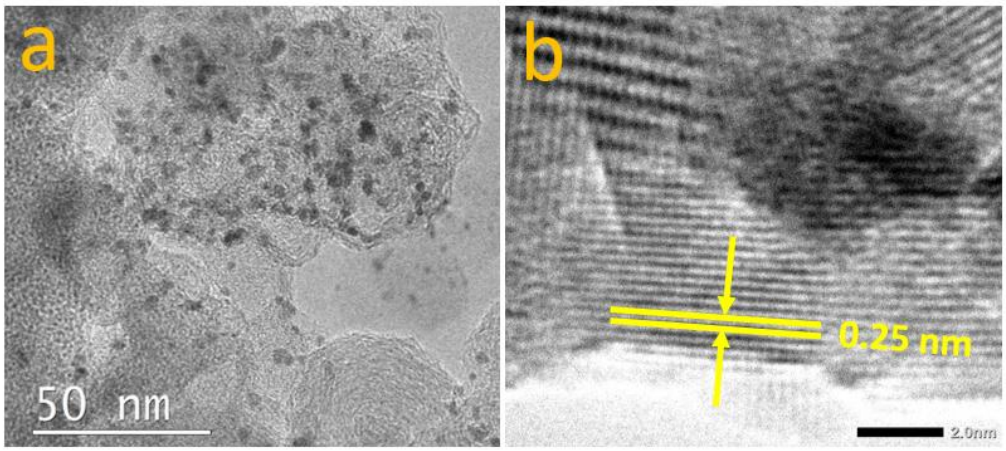

Fig. 1. HR-TEM images of N-GQDs sample synthesized from CA and urea

These HR-TEM images show that fabricating N-GQDs would result in doped-GQD fragments with near-uniform circular shape, narrow size distribution ranging from 10-20 nm when fabricated from CA and urea. The lattice spacing of these N-GQDs has been accurately measured to be 0.248 nm from the HR-TEM image, which is comparable to what other authors have previously published [10].

3.2. Optical properties

Fig. 2 is the PL excitation spectra of GQD, N-GQDs, and S-GQDs samples. For undoped GQD samples, on the PLE spectrum appears only 1 band with a maximum at 310 nm corresponding to $C\pi \rightarrow C\pi^*$ transition. For N-GQDs, the PLE spectrum shows that there are two excitation bands at 310 nm and 370 nm, which correspond to absorption transitions: $C\pi \rightarrow C\pi^*$ and $C\pi \rightarrow N\pi^*$. Similarity interpretation for S-GQDs. Photoluminescence excitation spectra (PLE) show that the best wavelength for excitation of the S-GQD sample is 370 nm, while it is ~ 310 nm for the two GQD and N-GQD samples.

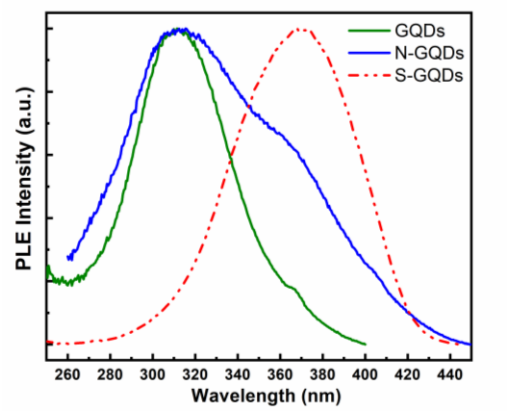

Fig. 2. PLE spectra of GQDs, N-GQDs, and S-GQDs.

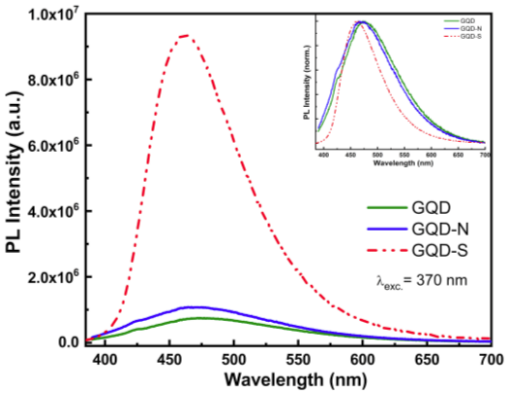

Fig. 3. PL spectra of GQDs, N-GQDs and S-GQDs samples under excitation at 370 nm.

Fig. 3 is the PL spectra of GQD, N-GQDs, and S-GQDs samples. We found that the PL intensity of S-GQD samples was very strong compared to the luminescent intensity of GQD and N-GQD samples. The reason here is that the wavelength of 370 nm is not the appropriate wavelength for excitation of GQD and N-GQD samples. Emission peaks are shifted towards shorter wavelengths compared to N-GQDs. This can be explained as follows: doping S atoms into the GQD lattice causes the energy state to be at a higher-level position than doping N atoms into GQDs.

In order to analyze in detail the fluorescent properties of samples to get the big picture of fluorescent spectra and excitation, we carried out Emission-Excitation mapping (EEM) on the Duetta (Horiba) system. The EEM images of N-GQD and S-GQD samples are presented on figure 4. These images show that for N-GQDs, the emission maximum is located at approximately 425 nm with the most effective excitation wavelength at about 310 nm. For S-GQD samples, the emission maximum is shifted towards longer wavelengths compared to N-GQD samples and is located at approximately 460 nm with effective excitation wavelength in the range of 365-370 nm. It can be seen that the synthesized samples have emission bands in the visible region, therefore they can be applied in bioimaging or other applications in medicine.

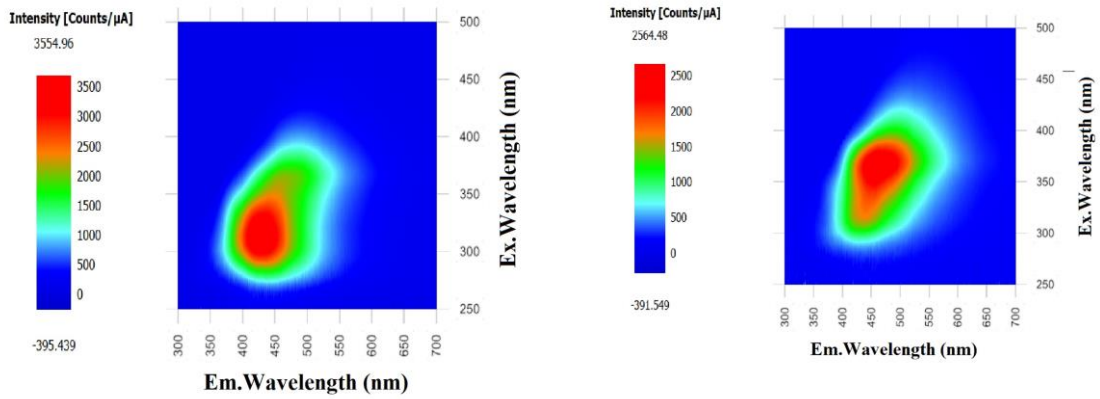

Fig. 4. EEM images of N-GQDs (a) and S-GQDs (b) samples, measure from 300 nm to 700 nm under excitation wavelength from 250 nm to 500 nm.

The possible electron transitions responsible for the photon emission could be as follows: when the doped-GQDs are excited by a light at λ = 310 nm, the photons are absorbed, resulting in the electron transitions of Cπ → Cπ*(1), n (C-N) → Cπ*(2). The excited electrons are deactivated via two mechanisms: one is by direct recombination after vibration relaxation from transition between the same energy levels, leading to PL (3); the other is by vibration relaxation from Cπ* → n-π* and n-π* to surface state transitions, then surface states → Cπ recombination, producing PL (4,5) (see Fig. 5). The resulting emission spectrum of N-GQDs is a wide band, consisting of both mechanisms above.

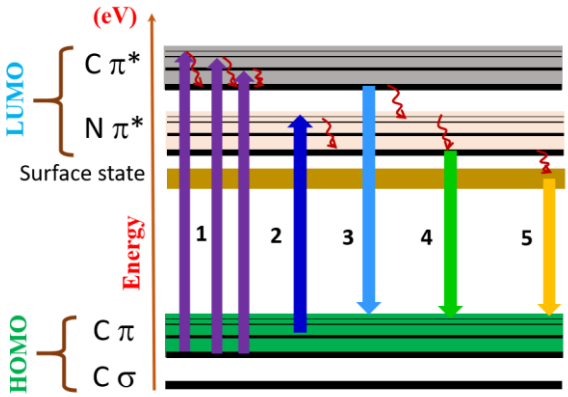

Fig. 5. The possible PL emission mechanism for N-GQDs

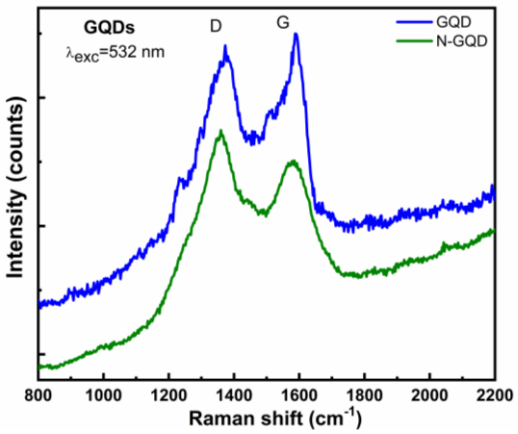

Fig. 6. The Raman spectra of N-GQD samples fabricated from two different carbon sources compared to non-doped GQDs.

To identify the formation of graphene, Raman spectra were used to observe the changes and effects produced by GQD heteroatom doping. Fig. 6 is the Raman spectra of N-GQD samples fabricated from two different carbon sources compared to non-doped GQDs. The D and G peaks of the non-doped bare GQD sample are observed at 1369.6 cm^{-1} and 1588 cm^{-1} on the Raman spectra, close to those values observed by other authors for N-GQDs [9, 10]. However, for N-doped samples, we see that the D peak is shifted towards shorter frequencies, while the G peak is shifted towards longer frequencies (for N-GQDs fabricated from pyrene) or shorter, depending on each case. The position of the G peak is also an indicator for the size, number of layers, and amount of doped N in GQD fragments. Therefore, more detailed experiments on the shift of G peak according to the nature of N-GQD samples is necessary. Besides, we also observed a D' peak on the Raman spectra of the two N-GQD samples due to the doping of N atoms into the GQD lattice.

4. Conclusion

In summary, we have successfully fabricated N-GQD and S-GQD samples. However, the fabrication method optimization is still a work in progress to find the optimal doping concentration of N or S atoms for the best luminescence. Raman spectra were used to briefly evaluate the quality of synthesized N-GQD samples. More detailed studies are still being carried out.

Acknowledgments

This research is funded by NAFOSTED under grants: number 103.03-2020.22. The

authors thank Duy Tan University and the National Key Laboratory for Electronic Materials and Devices of IMS for the use of facilities.

References

[1] P. Tian, L. Tang, K.S. Teng, et al., *Graphene quantum dots from chemistry to applications*, Materials Today Chemistry, 2018, 10, 221-258.

[2] L.A. Ponomarenko, F. Schedin, M.I. Katsnelson, et al., *Chaotic Dirac Billiard in Graphene Quantum Dots*, Sci, 2008, 320 (5874), 356-358.

[3] Y. Zhao, C. Hu, Y. Hu, et al., *AVersatile, Ultralight, Nitrogen-Doped Graphene Framework*, Angew. Chem. Int. Ed., 2012, 51, 11371 –11375.

[4] N.T. Ngoc Anh, P.-Y. Chang, R.-A. Doong, *Sulfur-doped graphene quantum dot-based paper sensor for highly sensitive and selective detection of 4-nitrophenol in contaminated water and wastewater*, RSC Advances, 2019, 9 (46), 26588-26597.

[5] S. Kadian, G. Manik, *A highly sensitive and selective detection of picric acid using fluorescent sulfur-doped graphene quantum dots*, Luminescence, 2020, 35 (5), 763-772.

[6] F. Valentini, A. Calcaterra, V. Ruggiero, et al., *Functionalized Graphene Derivatives: Antibacterial Properties and Cytotoxicity*, Journal of Nanomaterials, 2019, 1-14.

[7] H. Bian, Q. Wang, S. Yang, et al., *Nitrogen-doped graphene quantum dots for 80% photoluminescence quantum yield for inorganic γ-CsPbI3 perovskite solar cells with efficiency beyond 16%*, Journal of Materials Chemistry A, 2019, 7 (10), 5740-5747.

[8] H.Y. Nguyen, X.H. Le, N.T. Dao, et al., *Microwave-assisted synthesis of graphene quantum dots and nitrogen-doped graphene quantum dots: Raman characterization and their optical properties*, Advances in Natural Sciences: Nanoscience and Nanotechnology, 2019, 10 (2), 025005.

[9] S. Kadian, G. Manik, K. Ashish, et al., *Effect of sulfur doping on fluorescence and quantum yield of graphene quantum dots: an experimental and theoretical investigation*, Nanotechnology, 2019, 30 (43), 435704.

[10] R. Das, S. Parveen, A. Bora, et al., *Origin of high photoluminescence yield and high SERS sensitivity of nitrogen-doped graphene quantum dots*, Carbon, 2020, 160, 273-286.