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## Research Article

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# Fast, eco-friendly synthesis of blue luminescent nitrogen-doped graphene quantum dots in glycerol

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## Abstract

Nitrogen-functionalized graphene quantum dots (N-GQDs) were synthesized by hydrothermal transformation of glycine precursors in glycerol. Functionalization of GQDs with nitrogen was confirmed with FTIR spectroscopy. Atomic force microscopy (AFM) analysis revealed that the thickness of the quantum dots is around  $\sim 10$  Å while the lateral dimensions are in the range from 20 to 80 nm. N-GQDs exhibit strong fluorescence in blue (420 nm) region and they are suitable for bioimaging applications.

**Keywords:** graphene quantum dots, GQD functionalization, glycine, photoluminescence, atomic force microscopy, green synthesis

## Introduction

Graphene quantum dots (GQDs), relatively novel type of carbon-based materials, emerged as a potential new platform for applications in fluorescent biosensing and bioimaging [1-5]. They belong to the class of 0D luminescent nanomaterials with the lattice structure similar to that of graphene. Usually, GQDs are described as small fragments of graphene with a variety of chemical moieties at the edges and basal planes [6]. Due to their specific structure, graphene quantum dots show specific fluorescence and electrocatalytic properties. The mentioned properties coupled with pronounced photostability, water solubility, biocompatibility and non-toxicity make these nanostructured particles suitable for a wide range of novel biomedical applications. Contrary to graphene, which is the zero band-gap material, GQDs have band-gap strongly dependent on their lateral sizes and edge atoms/groups. For this reason, the optical

properties of GQDs can be readily modified by controlling their sizes and the edge-group chemistry [7].

Doping GQDs with heteroatoms (e.g. nitrogen), provides an attractive route for the effective tuning of their intrinsic properties and for improving luminescence efficiency. It was shown that nitrogen doped graphene quantum dots (N-GQDs) exhibit better electrocatalytic activity and tunable luminescence, which extends the area for possible applications. Generally, the methods for fabrication of GQDs can be classified into “bottom-up” and “top-down”. We are focused on bottom-up strategy, which involves the fusion of small precursor molecules (e.g., citric acid, glucose, 1,3,6-trinitrophenylene, etc.) into larger structures to form GQDs. The most important bottom-up methods are hydrothermal, microwave-assisted, soft-template, and stepwise organic synthesis synthetic routes. It is relatively easy to introduce heteroatom doping by hydrothermal method. Considering fabrication N-GQDs, above mentioned methods usually include multi-step synthesis, high temperature and high pressure. Thus, there are continuous research efforts for developing a facile one-pot method for the preparation of N-GQDs [8]. Initial syntheses with citric acid carbonization [9] offered fast, cost-effective procedure for obtaining “regular” GQDs. Recently, Li et al. modified this method by using a glycine precursor for preparation of N-functionalized GQDs in ethylene-glycol [10]. Glycine molecule served as both carbon and nitrogen source, opening a new chapter in facile and green syntheses of N-functionalized GQDs.

In the present paper, we report on green synthesis N-GQD based on glycine precursor, where ethylene-glycol is replaced with even more affordable medium - glycerol. The obtained N-functionalized GQDs have intensive excitation dependent fluorescence in blue region. The particles are further investigated by microscopic and optical methods and the results will provide information necessary for the future studies on their applications in fluorescent bioimaging.

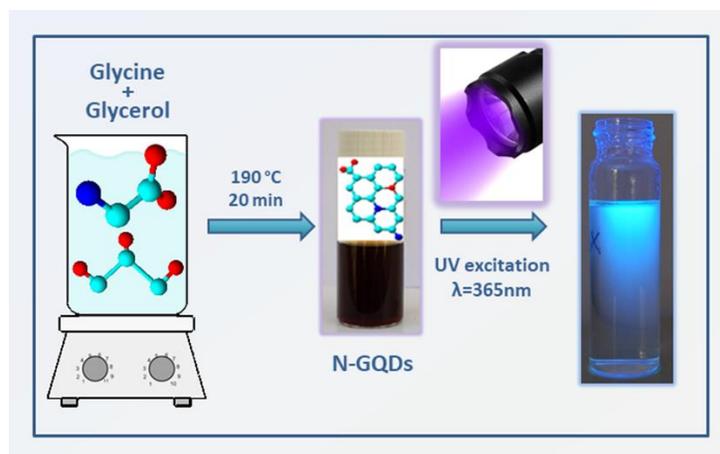
## **Experimental methods**

### *Materials*

Glycine (Merck), glycerol (pharmaceutical), high purity water ( $18.2 \text{ M cm}^{-1}$ )

### *Synthesis of nitrogen-doped NGQDs*

To prepare N-GQDs (Figure 1), the solution of glycine (0.5 g) and glycerol (10 mL) was heated at  $190 \text{ }^\circ\text{C}$  for 20 min under magnetic stirring ( $250 \text{ rmin}^{-1}$ ) and then cooled down to room temperature. The brown-yellow product, diluted 15 times with ultrapure (Milli-Q) water, was put in dialysis membrane (molecular weight: 10,000 Da) for 24 h. After dialysis, remaining N-GQD dispersion was used as a stock solution for further characterizations.



**Figure 1** Scheme of the experimental set-up. The obtained NGQD colloid shows pronounced fluorescence upon excitation with UV flashlight ( $\lambda = 365 \text{ nm}$ ).

### *Characterization of nitrogen-doped NGQDs*

Fourier transformed infra-red (FTIR) spectra were recorded in the region from  $400$  to  $4000 \text{ cm}^{-1}$  (with resolution of  $0.5 \text{ cm}^{-1}$ ) using a Nicolet iS50 FT-IR, Thermo Fisher Scientific spectrophotometer equipped by Smart iTR attenuated total reflectance (ATR) sampling accessory by placing powder samples on diamond plate and fixing them with pressure tower.

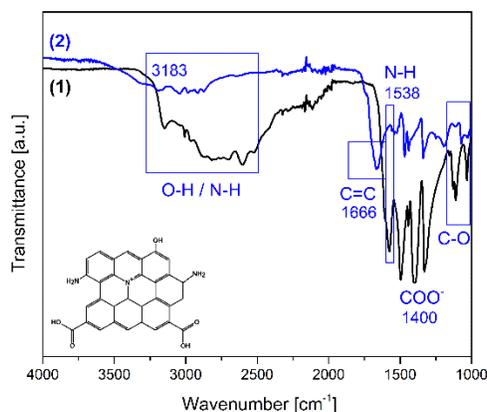
Atomic force microscopy (AFM) measurements were carried out on a Quesant atomic force microscope.  $20 \mu\text{l}$  of NGQD dispersion was deposited on freshly cleaved mica surface using a spin coating method ( $3500 \text{ rpm}$ ,  $1 \text{ min}$ ). Images were recorded in a tapping mode at room temperature, using premounted standard silicon probes Q-WM300 with force constant  $40 \text{ N/m}$  (Nano and More, Germany).

The photoluminescence (PL) measurements of the samples were conducted on Horiba Jobin Yvon Fluoromax-4 spectrometer (Horiba, Kyoto, Japan), equipped with Peltier element and magnetic stirrer for cuvette, using quartz cell with  $1 \text{ cm}$  path length and  $4 \text{ mL}$  volume. Excitation wavelengths were in the  $300\text{-}400 \text{ nm}$  range. The spectra were collected in the air environment at a temperature of  $25 \text{ }^\circ\text{C}$ .

## **Results and Discussion**

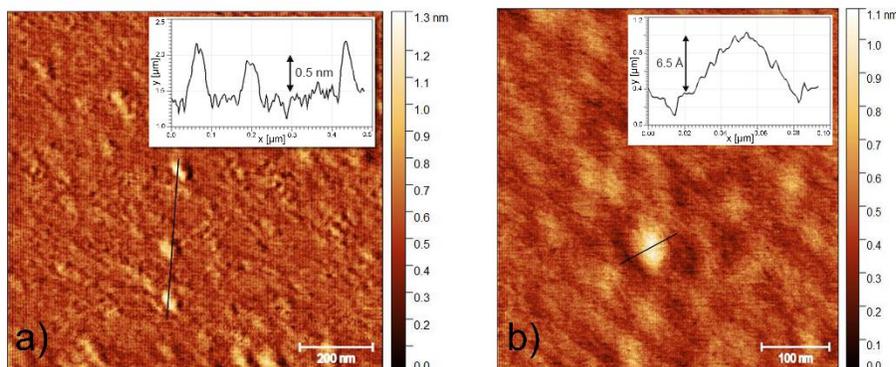
Figure 2 shows the FTIR spectra of glycine and the obtained N-GQDs. The quantum dots show typical bands of glycine, but slightly red-shifted, which possibly originates from hydroxyl bending vibrations [9]. A pronounced peak at  $1666 \text{ cm}^{-1}$  and multiple weaker bands at  $1466 \text{ cm}^{-1}$  in N-GQD spectrum correspond to C=C stretching vibrations, confirming formation skeletal polycyclic aromatic hydrocarbons [11,12]. Peaks at  $3183 \text{ cm}^{-1}$  (N-GQDs) and  $3147 \text{ cm}^{-1}$  (glycine) originate from N-H stretching vibrations, while peaks at  $1538 \text{ cm}^{-1}$  (N-GQDs) and  $1574 \text{ cm}^{-1}$  (glycine) correspond to  $\text{NH}_3^+$  symmetric bending. The broad absorption area at  $2800\text{-}3200 \text{ cm}^{-1}$

can be attributed to O-H bonds. The N-H and O-H stretching vibrations in this area indicate presence of hydroxyl and amino groups, which confirms hydrophilic nature of N-GDQs. The FTIR spectrum of N-GQDs in the area around  $2146\text{ cm}^{-1}$  is very similar to the corresponding area in glycine spectra, which indicates incomplete carbonization of glycine after synthesis [10]. Absorption peaks at  $1000\text{ cm}^{-1} - 1300\text{ cm}^{-1}$  (C-O stretching),  $1400\text{ cm}^{-1}$  ( $\text{COO}^-$  stretching) and  $1337\text{ cm}^{-1}$  (C-C stretching) in N-GDQs spectrum are matching glycine peaks in the same spectral range [11,13].



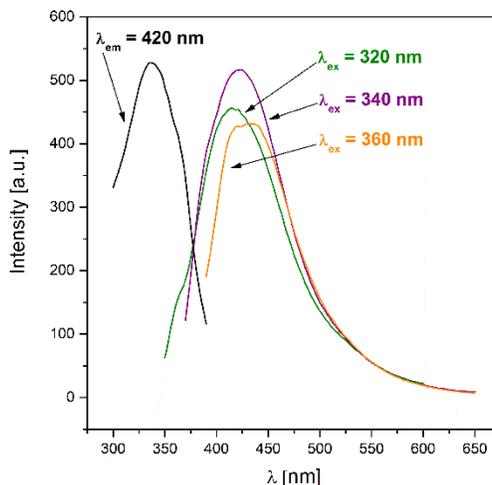
**Figure 2** FTIR spectra of glycine (1) and N-GQDs (2); the inset shows chemical structure of N-GQDs with characteristic functional groups

Surface morphology of N-GQDs was investigated by atomic force microscopy (AFM). Figure 3a shows typical graphene quantum dots. Height profiles of multiple N-GQDs reveal average heights of  $7.2\text{ \AA}$  and average diameters of  $68\text{ nm}$  [14]. Figure 3b shows the AFM image of a single N-GQD particle with corresponding height profile. Based on AFM measurements, it can be concluded that the size distribution of N-GQDs is relatively uniform and that the particles consist of one or few layers of graphene.



**Figure 3** AFM images and average height profiles of a) N-GQDs, b) of a single N-GQD particle

Figure 4 shows photoluminescence (PL) emission spectra of dialyzed NGQD sample recorded at various excitation wavelengths in the range from 300-400 nm and photoluminescence excitation (PLE) spectrum that corresponds to emission  $\lambda_{em} = 420$  nm.



**Figure 4** Photoluminescence (PL) emission spectra of N-GQDs recorded at different excitation wavelengths. Photoluminescence excitation (PLE) spectrum was recorded at  $\lambda_{em} = 420$  nm

It can be seen that the position of the emission band initially at 415 nm red-shifts with increasing in excitation wavelength. Typically, blue emission of GQD at  $\sim 420$  nm is related to both the size and the surface state of  $sp^2$  domains [15]. In N-GQD, it is suggested that two type of transitions contribute to PL spectrum:  $\pi \rightarrow \pi^*$  transitions of carbon  $sp^2$  and  $n \rightarrow \pi^*$  transition of N state [16]. The excitation-dependent photoluminescence in Figure 4 suggests that the distribution of  $sp^2$  domains is not uniform probably due to variation in size distribution and chemical composition of the dots [16]. This also opens a possibility for tuning PL emission by controlling the nature of  $sp^2$  sites via changing size, shape, and fraction of  $sp^2$  domains.

## Conclusion

We suggested fast, green, and cost-effective synthesis of luminescent nitrogen functionalized GQD in glycerol. This study successfully continues a new trend in GQD synthesis, employing cheap and non-toxic materials (glycine and glycerol). FTIR spectral analysis showed successful transformation of glycine molecules into N-functionalized GQDs. The obtained N-GQDs in glycerol are suitable for biomedical applications and it is our aim to use their intensive blue, excitation dependent, fluorescence in future bioimaging studies.

## Acknowledgments

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## Statements and Declarations

The authors have no competing interests to declare that are relevant to the content of this article.

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