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## N-DOPED GRAPHENE QUANTUM DOTS FOR DETECTION OF PALLADIUM(II) IONS AND CARBOFURAN

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### Abstract

We produced Graphene Quantum Dots (GQDs) by electrochemical oxidation of graphite rods and exposed them to gamma irradiation at a dose of 200 kGy, in the presence of ethylenediamine. Before irradiation, oxygen was removed from the GQDs dispersion by purging with Ar. These conditions induced both chemical reduction as well as the incorporation of N atoms in the structure of GQDs. Thus, N-doped GQDs were produced. The morphology of dots was investigated using atomic force microscopy. UV-Vis and photoluminescence spectroscopy were used to investigate the optical properties of modified GQDs. The changes in the intensities of PL emission spectra were studied in the presence of different concentrations of Pd<sup>2+</sup> and pesticide carbofuran. We observed promising results for the application of N-doped GQDs for non-enzymatic PL detection of selected metal ions and molecules of pesticide.

### Introduction

Since they have been discovered in 2008, graphene quantum dots (GQDs) attract great scientific attention [1]. Due to their properties, such as dispersibility in water, biocompatibility, chemical stability, emission of photoluminescence in the visible part of the spectrum, resistivity to photobleaching, GQDs have been studied for different applications [2, 3]. In their structure, a small graphene sheet is a core of a dot, while different O-containing functional groups are located at the edges and on the basal plane [4]. Due to a large number of polar functional groups, these dots are dispersible in water and polar organic solvents. The lateral size of GQDs is below 100 nm, while their height varies depending on the number of the graphene layers in the structure, from 0.5 nm for single-layered to a few nm, in the case of multi-layered dots [3]. Due to size, solubility and optical properties, GQDs are investigated for application in bioimaging [5], sensing [6], photodynamic therapy [7], solar cells [8], etc.

There is a large number of methods for GQDs production and they all can be divided into two main groups: *bottom-up* and *top-down*. When dots are produced from small organic molecules, such as glucose or citric acid, these methods are called bottom-up. If GQDs are obtained by oxidative cutting of bulk material based on graphene, these procedures belong to a top-down group. Electrochemical oxidation of graphite rods is a top-down method, powered by electrical current. Due to the electrolysis of the medium, reactive species such as free radicals are produced and they cause oxidation of graphite [9]. From the graphite surface, GQDs were released into the surrounding medium.

Herein we used electrochemical oxidation to produce GQDs and gamma irradiation to modify GQDs structure. As a medium for irradiation, we used a mixture of water, isopropyl alcohol (IPA) and ethylenediamine (EDA). Water was selected because GQDs are highly dispersible, IPA was added due to its ability to efficiently quench oxygen-based free radicals and to assure reductive conditions, while EDA was added as a source of N atoms [10]. The dose of 200 kGy

was applied. These dots were investigated as a sensor for the detection of carbofuran and palladium(II) ions.

## Experimental

Electrochemical oxidation of graphite rods was used for GQDs synthesis [9]. GQDs were dispersed in water at a concentration of  $1 \text{ mg mL}^{-1}$  and then isopropyl alcohol (3 vol%) and ethylenediamine (4 vol%) were added [10]. Then, the samples were purged with argon for 15 minutes and consequently exposed to gamma irradiation at a dose of 200 kGy at the sterilization facility of the Vinca Institute. This sample is named N-GQDs.

Atomic Force Microscopy (AFM) imaging was conducted using Quesant (Agoura Hills, CA, Unites States) microscope. Tapping mode was chosen, in the air atmosphere. The Q-WM300 rotated, monolithic silicon AFM probe was used. Standard silicon tips (NanoAndMore GmbH, Wetzlar, Germany) were used with a force constant of  $40 \text{ N m}^{-1}$ . Diluted GQDs dispersions in MiliQ water in a concentration of  $0.125 \text{ mg mL}^{-1}$  were deposited with spin-coated on a mica substrate. AFM images were analyzed using Gwyddion 2.53 software.

UV-Vis spectra were recorded at a Shimadzu UV-2600 UV-Visible spectrophotometer (Shimadzu Corporation, Tokyo, Japan). N-GQD dispersion at a concentration of  $0.25 \text{ mg mL}^{-1}$  was measured. Spectra were obtained at room temperature and a normal atmosphere. The selected range was 200-800 nm.

The same dispersion was used for the measurement of PL spectra. They were recorded using Horiba Jobin Yvon Fluoromax-4 spectrometer (Horiba, Kyoto, Japan). The excitation wavelengths were from 300 to 400 nm. The concentration of N-GQD dispersion in water was  $0.0065 \text{ mg mL}^{-1}$ . Spectra were collected at room temperature in the air environment.

PL spectroscopy was used to investigate the possibility of detection of Pd(II) ions and pesticide carbofuran. First, GQDs were dispersed in the concentration of  $0.3 \text{ mg mL}^{-1}$ . To this dispersion, the analytes were added. The concentrations of CF were varied from 10 to  $100 \text{ } \mu\text{mol L}^{-1}$  while Pd(II) ions were added  $5\text{-}200 \text{ } \mu\text{mol L}^{-1}$ . For CF testing, the medium was N-methyl pyrrolidone, while Pd(II) ions water was used as a solvent. After a short incubation time (5 minutes), mixtures of GQDs with analytes were recorded on PL.

## Results and discussion

The morphology of GQDs was investigated using AFM (figure 1a and b). As-synthesized GQDs showed an average height of around 1.3 nm and a lateral size between 10 and 30 nm. For the N-GQDs sample, large aggregates can be observed. The average diameter was around 18 nm for p-GQDs, and 15 nm for  $50\gamma$ -GQDs.

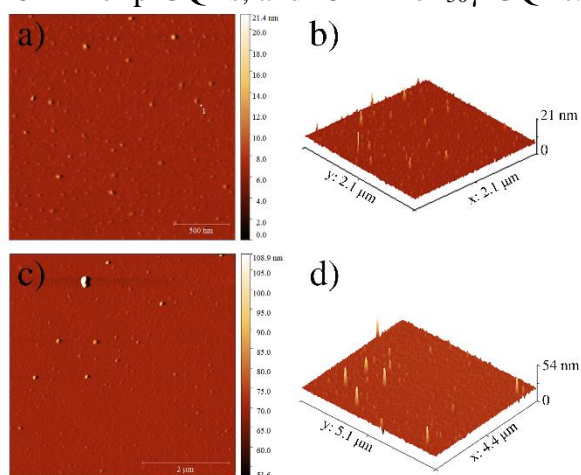


Figure 1. AFM images of p-GQDs (a, b) and N-GQDs (c, d).

UV-Vis spectrum of N-GQDs showed the main absorption peak at around 204 nm and second, shoulder band at 274 nm (Figure 2a). The band at 204 nm has been assigned to  $\pi$ - $\pi^*$  transitions in  $\pi$ -domains of GQDs. The second, shoulder band is attributed to  $\pi \rightarrow n$  transitions of C=O groups. Based on this spectrum it is concluded that N-GQDs have both aromatic  $\pi$ -domains in their structure, but also polar C=O groups were detected too. The previous study showed that these dots also have amino groups in the structure [10]. Other optical properties, such as photoluminescence was studied as well. In figure 2b, PL emission spectra of N-GQDs excited with light of wavelengths from 300 to 400 nm are presented. At different excitation wavelengths, the center of the emission band was changed from 430, 432, 433, 441, 452, 465 nm for excitation at 300, 320, 340, 360, 380 and 400 nm, respectively. This phenomenon is called excitation-dependent photoluminescence and it is associated with a diversity of dots size and chemical composition [11]. The highest intensity of the emission band was detected when the excitation wavelength was 360 nm (figure 2b). Modified dots emit blue light, which is explained by the aromatic domains and  $sp^2$  core of the dots [12].

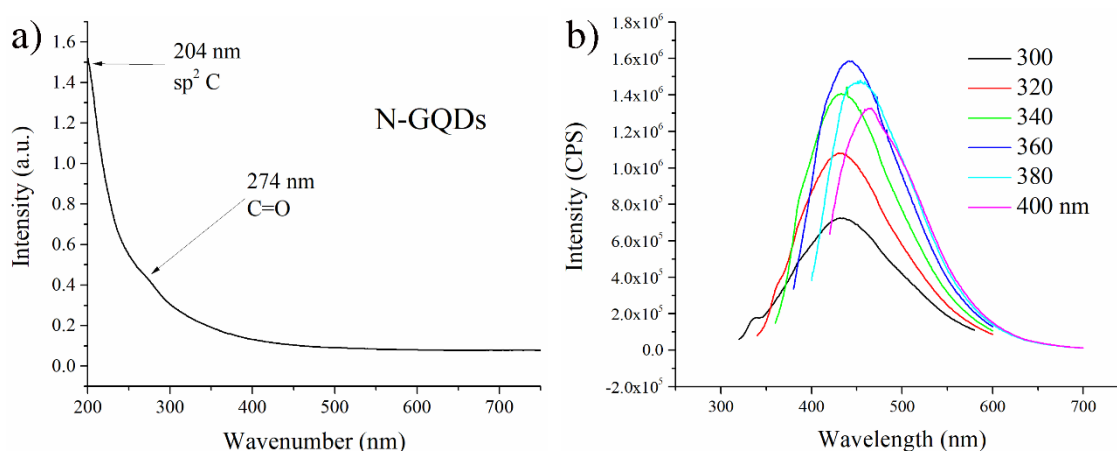


Figure 2. UV-Vis (a) and PL spectra (b) of N-GQDs.

The possibility of N-GQDs usage in non-enzymatic PL detection of pesticide carbofuran (CF) and Pd(II), was investigated using PL spectroscopy and these results are presented in figure 3. First, CF was mixed with N-GQDs in concentrations of 10, 50 and 100  $\mu\text{mol L}^{-1}$ , while the concentration of GQDs was the same (0.3  $\text{mg mL}^{-1}$ ). As a solvent, N-methyl pyrrolidone was used, due to the insolubility of CF in water. With the increase of CF concentration, the PL intensity was increased as well. These preliminary results indicated that N-GQDs are possible sensor for CF detection, while the mechanism of detection is „turn-on“.

In the case of Pd(II) ions, the PL intensity was decreased with the increase of the ion concentrations (figure 3b). These results suggest that PL spectra of N-GQDs are sensitive to the presence of Pd(II) ions, and these changes are particularly emphasized at low ion concentration (5  $\mu\text{mol L}^{-1}$ ).

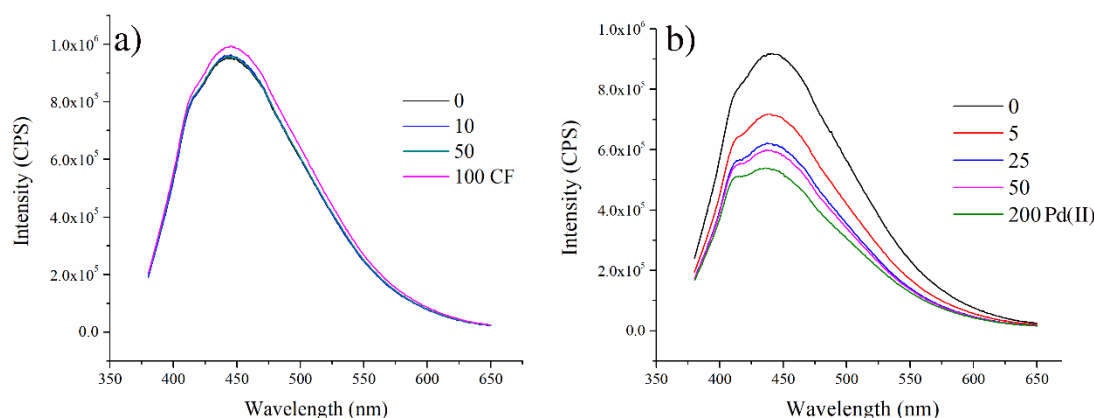


Figure 3. PL spectra of N-GQDs with different concentrations (in  $\mu\text{mol L}^{-1}$ ) of carbofuran (a) and Pd(II) ions (b).

Presented results showed that PL spectra of N-doped GQDs were changed in the presence of CF and Pd(II) ions. It was detected that PL intensity was increased in the presence of CF while ions induced the lowering in the PL intensity. Thus, the future investigation will be deduced to find the concentration range where the linear response between the PL intensity and analyte concentrations is occurring.

### Conclusion

In this study, the possibility of the application of GQDs for sensing pesticide carbofuran and Pd(II) ions was explored. GQDs were produced using the ecologically acceptable, electrochemical approach, while gamma irradiation modified their structure. Modified GQDs showed the ability to change their PL intensity in the presence of selected analytes. Namely, the intensity of PL spectra was lowered in the presence of Pd(II) ions and increased when carbofuran was added. These results indicate the ability of N-GQDs to serve as a sensor for selected analytes.

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