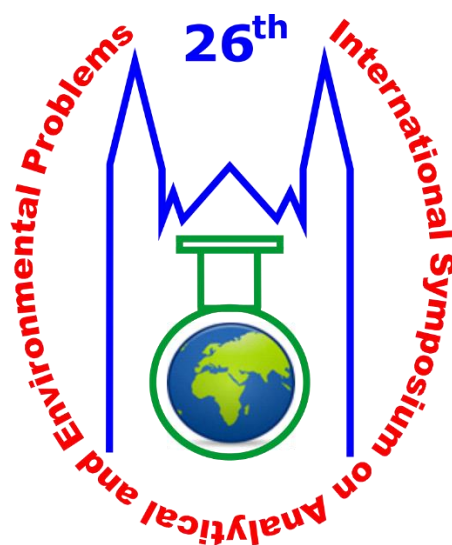




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APPLICATION OF GRAPHENE QUANTUM DOTS IN HEAVY METALS AND PESTICIDES DETECTION

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Abstract

Graphene Quantum Dots (GQDs) were produced using electrochemical oxidation of graphite rods. Obtained GQDs were gamma-irradiated in the presence of the N atoms source, ethylenediamine. Both structural and morphological changes were investigated using UV-Vis, X-ray photoelectron and photoluminescence (PL) spectroscopy as well as atomic force microscopy. The ability of both types of dots to change PL intensity in the presence of pesticides such as malathion and glyphosate, as well as copper (II) ions was detected. These preliminary results indicated a high potential of produced GQDs to be applied as non-enzymatic PL sensors for the detection of selected pesticides and metal ions.

Introduction

Graphene quantum dots (GQDs) are round graphene sheets with a diameter below 100 nm and different O-containing functional groups located on the surface and at the edges of dots [1]. Due to a large amount of these functional groups, GQDs are dispersible in water and polar organic solvents. They showed good biocompatibility and low cytotoxicity [2]. Due to the quantum confinement effect and edge sites/defects, GQDs possess stable photoluminescence (PL) and they are resistive to photobleaching [3]. Considering both biocompatibility and photoluminescence, these dots were often investigated for their possible application in the sensing of different ions and molecules [4].

Due to the overuse of pesticides, they are often found in the ground, water, or agricultural products. Pesticides accumulation in the environment leads to their entering into biosystems [5]. Thus, pesticides such as glyphosate and the products of its degradation were detected in human urine in a concentration of 2.63, 1.26, and 0.89 µg/L in samples from Croatia, Belgium, and Malta [6]. Additionally, the pollution of water, air, and ground lead to a high level of heavy metals which are also toxic for animal, humans, and plants [7]. The analytical techniques that are now in-use for pesticides and heavy metal detection request the usage of expensive instruments, highly educated operators, while the analysis often demands time. Thus, there is a need for a new, simple, and affordable method for the detection of these pollutants.

Herein we prepared GQDs using an eco-friendly approach: electrochemical oxidation of graphite electrodes was achieved without the consumption of aggressive and toxic reagents [8]. Dots were purified by dialysis and structurally modified through gamma irradiation. During gamma irradiation, covalent modification of material can be achieved without the consumption of aggressive, toxic reagents. Thus, this method is considered a green tool for modification. By selecting the medium with N-atoms, the incorporation of N-functional groups was achieved. The effect of the herbicide glyphosate, insecticide malathion, and copper (II) ions on the intensity of photoluminescence of GQDs was investigated.

Experimental

GQDs were produced using a previously described procedure [8]. Gamma-irradiation was conducted in a water solution of isopropanol (3 vol%) and ethylenediamine (EDA, 4 vol%) [9]. Before the irradiation, the sample was purged with argon to remove dissolved oxygen. The sample was irradiated at a dose of 50 kGy.

UV-Vis measurements were performed at a Shimadzu UV-2600 UV-Visible spectrophotometer (Shimadzu Corporation, Tokyo, Japan). Spectra were recorded at 20 °C under a normal atmosphere, in the range of 200-800 nm. The concentration of GQD dispersions was 0.25 mg mL⁻¹.

The PL spectra were recorded on Horiba Jobin Yvon Fluoromax-4 spectrometer (Horiba, Kyoto, Japan). GQDs dispersions in methanol (c=0.25 mg mL⁻¹) were placed in a quartz cuvette with 1 cm path length and 4 mL volume. For the excitation, laser wavelengths were 300, 360 and 400 nm. Spectra were collected under room temperature in the air environment.

X-ray Photoelectron Spectroscopy (XPS) was acquired by using a ULVAC-PHI PHI500 VersaProbe II scanning microprobe (ULVAC-PHI, Inc., Chigasaki, Japan), with an Al K α source (1486.6 eV), 100 μ m spot, 25 W power, 15 kV acceleration, and 45° take-off angle. All spectra were collected using a dual neutralization system (both e⁻ and Ar⁺).

Atomic Force Microscopy (AFM) measurements were performed using Quesant (Agoura Hills, CA, United States) microscope operating in tapping mode, in the air, at room temperature. We used the Q-WM300 AFM probe, rotated, monolithic silicon probe for non-contact high-frequency applications. Standard silicon tips (NanoAndMore GmbH, Wetzlar, Germany) were used, with a force constant of 40 N/m. GQDs were dispersed in MiliQ water in a concentration of 0.25 mg mL⁻¹ and deposited with spin-coated on a mica substrate. Gwyddion 2.53 software was used for image analysis.

Results and discussion

UV-Vis spectroscopy showed that p-GQDs had a peak of absorption centered around 230 nm while after gamma irradiation, this band was narrow, shifted to 205 nm with a shoulder band at 260 nm. The first band was due to π - π^* transitions of sp² C in aromatic bonds, while the second was assigned to π →n transitions of C=O groups. These results indicated the changes in the amount of O functional groups occurred during gamma irradiation. PL spectra showed that after gamma irradiation the highest intensity of emission band was observed with an excitation wavelength of 400 nm (figure 2c) while for p-GQDs, the highest emission was detected at excitation of 300 nm. The excitation-dependent photoluminescent behavior was observed for both samples. AFM analysis (figure 1d and e) showed that irradiation caused the lowering in the average GQDs height, from 1.73 nm as measured for p-GQDs to 1.25 nm. The average diameter was around 18 nm for p-GQDs, and 15 nm for ⁵⁰ γ -GQDs. XPS analysis showed that GQDs had C and O atoms, while ⁵⁰ γ -GQDs had C, O and N atoms in the structure (figure 1f).

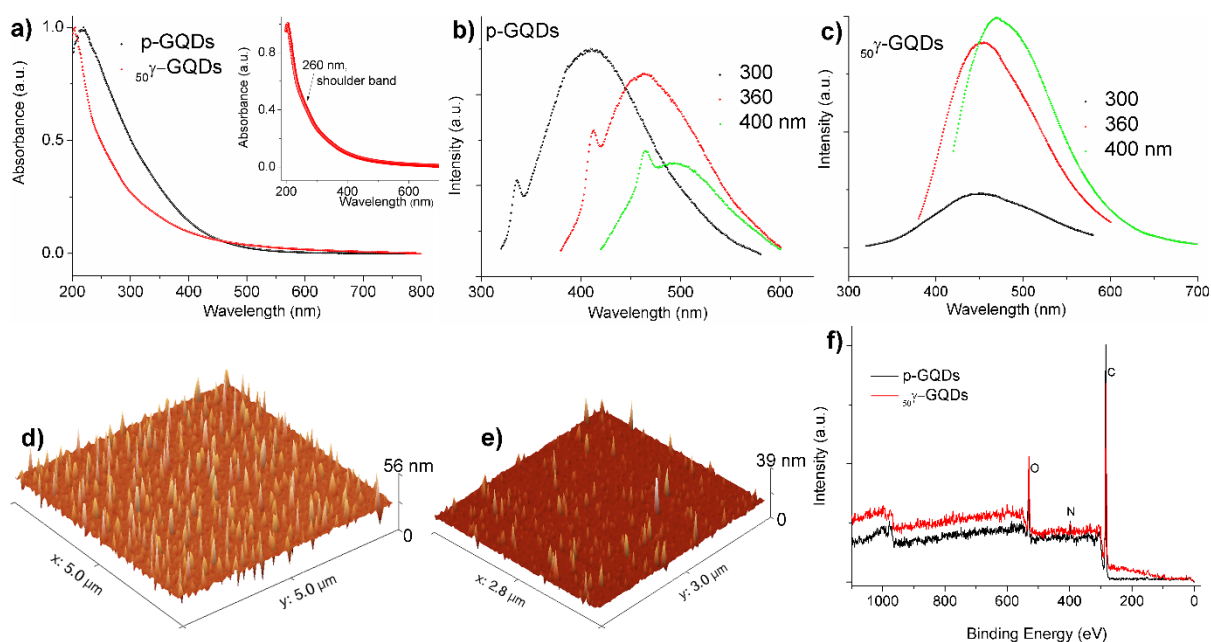


Figure 1. UV-Vis spectra of p-GQDs and 50γ-GQDs (a), PL spectra, and AFM images of p-GQDs (b, d) and 50γ-GQDs (c, e), as well as XPS survey of samples (f).

To investigate the possibility of GQDs application in non-enzymatic PL detection, GQDs were mixed with Cu(II) ions, pesticide malathion and the herbicide glyphosate. After a short incubation time (5 minutes), mixtures of GQDs with analytes were recorded on PL spectroscopy and obtained spectra are presented in figure 2. By adding Cu(II) ions, the maximum of the intensity of PL emission spectra was lowered for both p-GQDs and 50γ-GQDs. In the case of malathion which was added in a concentration of 18.1 mM, the PL intensity was increased, while in the case of glyphosate the increase in PL intensity was observed for two concentrations: 10 and 5000 ng mL⁻¹. A higher increase in PL intensity was observed in the case of p-GQDs/malathion while in the case of glyphosate the higher changes were detected for gamma-irradiated GQDs.

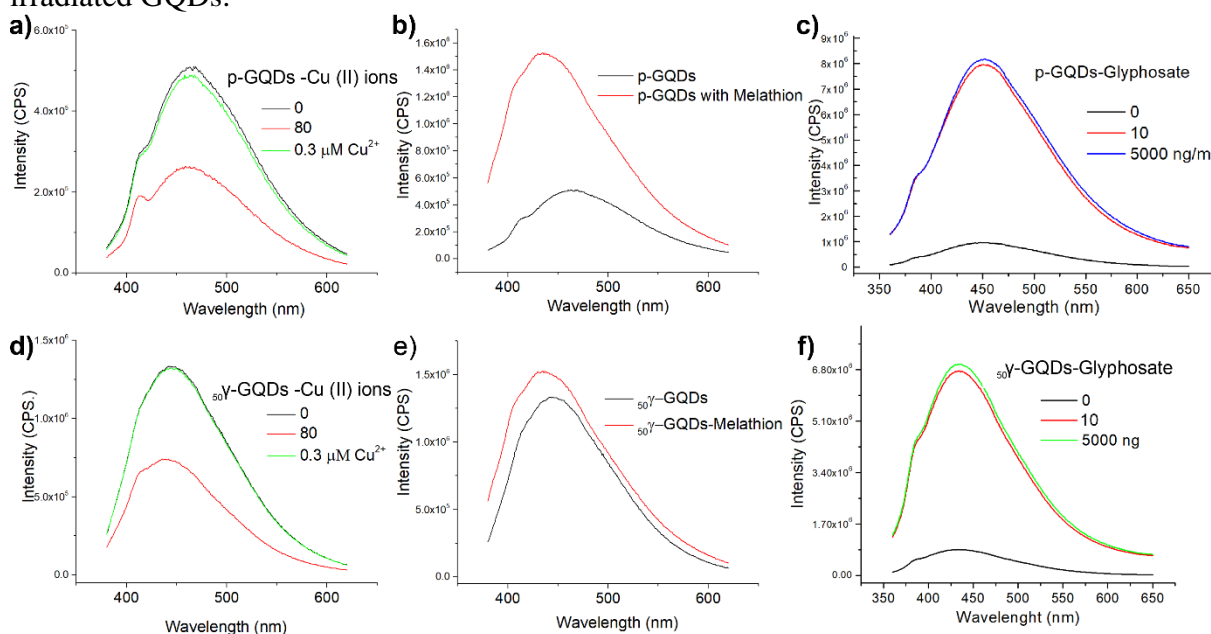


Figure 2. PL p-GQDs with Cu (II) ions (a), malathion (b), glyphosate (c) and 50γ-GQDs with the same analytes at (d), (e) and (f), respectively.

These preliminary results showed that both non-modified and modified GQDs possess the potential for their application in Cu(II) ions, malathion and glyphosate detection. In the case of Cu(II) ions, it was suggested that the lowering in PL intensity was due to the electrostatic destabilization and coagulation of negatively charged GQDs. On the opposite, pesticide malathion and glyphosate induced an increase in PL intensity of GQDs. In future research we will analyze if the increase in pesticide concentration leads to a linear increase of the PL intensity for a wide range of pesticide concentrations.

Conclusion

The potential of GQDs application in the detection of metal ions and pesticides was investigated. GQDs were synthesized in an electrochemical approach and modified by gamma irradiation. This treatment induced the lowering in GQDs height and diameter, and resulted in the incorporation of N atoms in the GQD structure. Both modified and non-modified GQDs were investigated as sensors in PL detection of Cu ions, malathion and glyphosate. A preliminary investigation showed the changes in the PL intensity when these analytes were added: Cu (II) lowered while malathion and glyphosate increased PL intensity.

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