

AMINO FUNCTIONALIZED GRAPHENE QUANTUM DOTS - NEW FLUORESCENT SENSOR FOR Co²⁺ IONS

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Abstract

Graphene quantum dots (GQDs) were fabricated by simple electrochemical oxidation of graphite electrodes. Modified GQDs were obtained by gamma irradiation of GQDs, EDA, and IPA mixture at a dose of 25 kGy. In this approach, GQDs with the amino groups were produced (25 γ -GQDs). These GQDs have shown a high uniformity, good dispersibility in water, and strong photoluminescence in the blue part of the electromagnetic spectrum. Modified GQDs were studied in the optical detection of Co²⁺ ions. The PL intensities of GQDs were measured in the presence of Co²⁺ ions in the concentration range 0-7.5 $\mu\text{mol L}^{-1}$. It was demonstrated that PL intensities decreased linearly in the concentration range 0-2.5 $\mu\text{mol L}^{-1}$. The value of the coefficient of determination ($R^2=0.95949$) indicates the potential of 25 γ -GQDs for application in optical sensing of Co²⁺ ions.

Introduction

Due to intensive human activities such as agriculture and industry, a large amount of hazardous substances is present in the environment. Usual pollutants are heavy metals. Cobalt is one of the most widespread trace elements in nature. The only known biological role of cobalt in organisms is that it forms an integral part of vitamin B12 (cyanocobalamin). All other Co compounds are toxic for living beings [1]. Mostly used analytical methods for Co²⁺ detection such as inductively coupled plasma optical emission spectrometry (ICP-OES), colorimetric, and electrochemical methods possess some drawbacks: high-cost instruments, complicated sample preparation, and long duration of the analysis. Therefore, some alternative methods have been developed [2, 3].

Nowadays, photoluminescence (PL) methods attract attention for Co²⁺ ions detection. One of the most investigated materials on the PL detection field are graphene quantum dots (GQDs) [4]. GQDs are 0D carbon nanomaterials built from sp² hybridized C atoms organized in the hexagonal crystal lattice with oxygen contained functional groups (hydroxyl, carboxyl, carbonyl, and epoxy) attached on their surface and edges. The size of GQDs is lower than 10 nm, while the average height is around 2 nm [5]. Thanks to their great features such as absorption of UV and visible light, PL in the visible part of the spectrum, solubility in water and polar solvents, nontoxicity, and biocompatibility, GQDs are widely examined for applications in electronics, bioimaging, drug delivery, and optical sensing [6-8]. The origin of PL in GQDs is still insufficiently explained but is considered that it can be formed by the combination of some different factors: quantum confinement effect, edge effect, functional groups on their surface, etc. [5]. Due to PL, GQDs were investigated as an optical sensor for Co²⁺ ion detection. Boonta et al. produced S, N-doped GQDs for PL detection of bivalent cobalt ions [2]. PL intensities of GQDs were measured in presence of Co²⁺ in the concentration range of 0-60 $\mu\text{mol L}^{-1}$. It was observed that PL of GQDs was quenched by Co²⁺ and that intensities of PL decreased linearly from 0 to 40 $\mu\text{mol L}^{-1}$.

Herein, we produced pristine graphene quantum dots (p-GQDs) from graphite electrodes in a simple *top-down* electrochemical approach. Then, we successfully introduced amino groups in the structure of GQDs by gamma irradiation at a dose of 25kGy using a mixture of water, ethylenediamine (EDA), and isopropyl (IPA) alcohol as a medium for radiation. In this case, EDA was used as a source of amino groups, while IPA served as a quencher of oxygen radicals during irradiation. Before irradiation, a mixture was bubbled with argon to remove dissolved oxygen. In these conditions, we performed a structural modification of GQDs. Obtained GQDs with amino groups were labeled as 25 γ -GQDs. These GQDs were investigated as PL sensors for Co²⁺ ions.

Experimental

Pristine graphene quantum dots (p-GQDs) were synthesized using the previously described electrochemical method [8]. A water dispersion of p-GQDs in the concentration of 1 mg mL⁻¹ was mixed with 4% EDA and 3% IPA. In the final stage, Ar was passed through dispersion. Then, the mixture was exposed to gamma irradiation at a dose of 25 kGy. As a source of gamma irradiation, a Co-60 was used.

To investigate a chemical composition of 25 γ -GQDs infrared spectroscopy with Fourier transformation (FTIR) was used. For FTIR analysis, the 25 γ -GQDs powder was used. FTIR spectrum was recorded in attenuated total reflection mode (ATR) on the *Thermo Scientific Nicolet 6700 FTIR* instrument (*Thermo Fisher Scientific*, Waltham, MA, United States). The spectral resolution was 2 cm⁻¹.

Morphology of 25 γ -GQDs was examined by atomic force microscopy (AFM). Water dispersion of 25 γ -GQDs in a concentration of 0.25 mg mL⁻¹ was used for analysis. AFM images were obtained using *Quesant* (Agoura Hills, CA, United States) microscope operating in the tapping mode in air and at room temperature. QWM300 AFM probe, rotated, monolithic, silicon probe for non-contact high-frequency application was used. Standard silicon tips (*Nano and More, GmbH*, Wetzlar, Germany) with a force constant of 40 N m⁻¹ were used. Mica was used as a substrate for imaging. AFM images were analyzed using *Gwyddion 2.58* software.

The optical properties of 25 γ -GQDs were investigated by UV-Vis spectroscopy. Dispersion of 25 γ -GQDs was prepared in a concentration of 0.25 mg mL⁻¹. The absorption spectrum was recorded on Shimadzu UV-2600, UV-Visible Spectrophotometer (Shimadzu, Corporation, Tokyo, Japan) at 20° C in the wavelength range 200-800 nm.

For PL measurement, a dispersion of 25 γ -GQDs in the concentration of 0.125 mg mL⁻¹ in methanol was prepared. PL spectra of 25 γ -GQDs were recorded on *Horiba Jobin Yvon Fluoromax-4* spectrometer (*Horiba*, Kyoto, Japan). PL intensities were measured under the different wavelengths of exciting light in the range 300-400 nm, in air condition, at a temperature of 25°C.

For detection of Co²⁺ ions, water dispersion of 25 γ -GQDs in a concentration of 0.03 mg mL⁻¹ was mixed with selected ions in the concentration range of 0-7.5 μ mol L⁻¹. The PL intensities of 25 γ -GQD in presence of Co²⁺ were measured on *Horiba Jobin Yvon Fluoromax-4* spectrometer (*Horiba*, Kyoto, Japan), under an excitation wavelength of 360 nm. PL spectra were collected at room temperature in air conditions.

Results and discussion

On the UV-Vis spectrum of 25 γ -GQDs (Figure 1a) absorption bands at 206 and one shoulder band around 250 nm can be observed. The band at 206 nm is attributed to the π - π^* transition of C in aromatic bonds. Shoulder band localized around 250 nm steams from n- π^* transitions in C=O bonds. Results obtained by FTIR analysis are presented in Figure 2b. Three lower bands at 2872, 2926, and 2868 cm⁻¹ steam from stretching vibrations of C-H bonds in -CH and -CH₂

functional groups. The band at 1571 cm^{-1} originates from π -conjugated domains in 25γ -GQDs. In the FTIR spectrum of pristine GQDs, the band at 1365 cm^{-1} stems from symmetric stretching of O-C=O groups [8]. In the sample 25γ -GQDs, this band is shifted at 1373 cm^{-1} due to reduction of the carboxyl group, under the gamma irradiation. Two bands at 1068 and 3363 cm^{-1} , which stem from stretching vibrations of C-N and N-H bonds, confirmed the incorporation of amino groups in the GQDs structure.

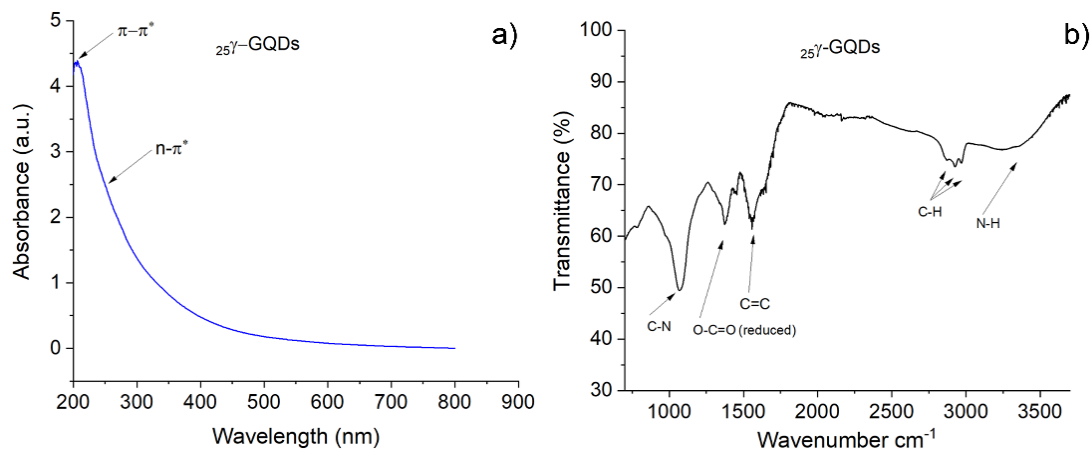


Figure 1. UV-Vis absorption (a) and FTIR (b) spectra of 25γ -GQDs.

AFM images of 25γ -GQDs (Figure 2 a, b, and c) show that these GQDs are spherical, well-dispersed nanoparticles. According to their height profiles (Figure 2 d and e), the measured height was between 0.5 and 2 nm which indicates that these dots are structured from one graphene layer.

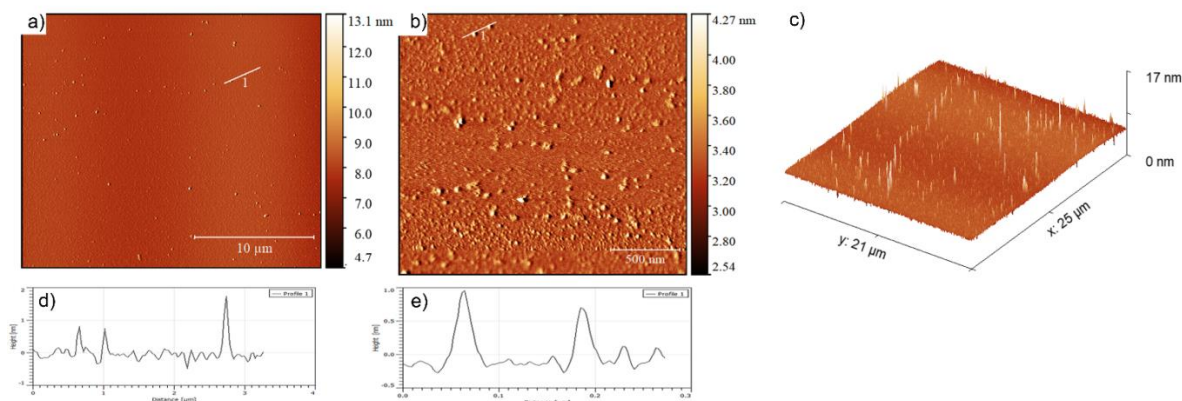


Figure 2. AFM images (a, b) with height profiles (d, e) and 3D AFM picture (c) of 25γ -GQDs.

Emission spectra of 25γ -GQDs under excitation wavelength 300 , 340 , 380 , and 400 nm are presented in Figure 3. Obtained results show that the maximum emission peak was shifted under the different wavelengths of exciting light. This behavior in literature was described as excitation-depended PL, and it is a consequence of various factors (quantum size effect, etc.) [5]. Maximum of emission peak of 25γ -GQDs was found at 455 nm under an excitation wavelength of 380 nm which means that 25γ -GQDs emit light in the blue part of the spectrum.

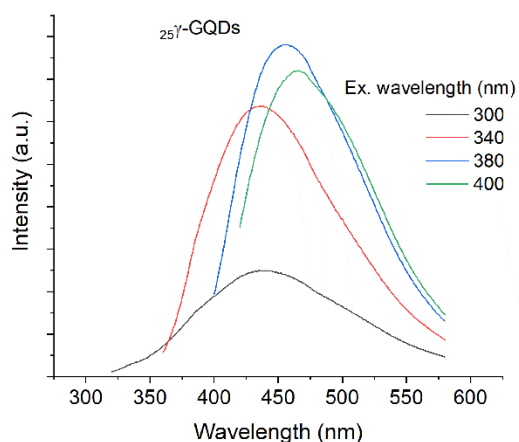


Figure 3. PL spectra of 25γ-GQDs under different excitation wavelengths (300, 340, 360 and 400 nm).

Emission spectra of 25γ-GQDs in presence of Co^{2+} in the concentration range $0\text{--}7.5 \mu\text{mol L}^{-1}$ show that PL intensities decreased with the increase in the concentration of Co^{2+} ions (Figure 4a). It can be assumed that Co^{2+} leads to quenching of PL intensity which can be described by the Stern-Volmer equation:

$$A_0/A = 1 + K_{sv} [Q]$$

where A_0 presents an integrated area under emission peak in absence of quencher, A is the integrated area under the emission peak in presence of quencher, K_{sv} is Stern-Volmer constant which presents a slope of the curve obtained by linear fitting of dependence A_0/A of quencher concentration data.

By the results obtained from linear fitting of A_0/A dependence of quencher concentration data (Figure 4b, c), it can be observed that PL intensity of 25γ-GQDs decreases linearly in the concentration range $0\text{--}2.5 \mu\text{mol L}^{-1}$. The value of the coefficient of determination $R^2 = 0.95949$ makes 25γ-GQDs a good potential sensor for Co^{2+} ions.

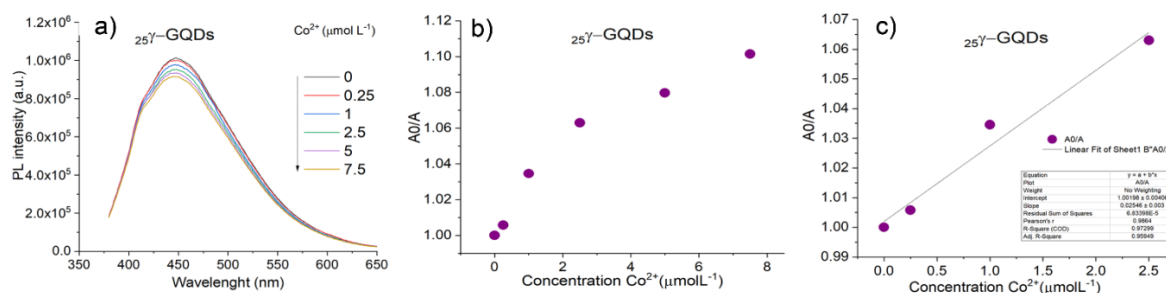


Figure 4. PL spectra of 25γ-GQDs a), A_0/A in the dependence of Co^{2+} concentration b), results obtained by linear fitting of experimental data c).

Conclusion

In this work, we successfully introduced amino groups in GQDs structure by gamma irradiation in an easy, low-cost, eco-friendly procedure without using toxic chemicals. The presence of amino groups in GQDs structure was proved by FTIR spectroscopy. 25γ-GQDs emit blue light and were investigated as a PL sensor for Co^{2+} ions. Obtained results show great potential for the use 25γ-GQDs for optical sensing of Co^{2+} ions, and maybe other similar heavy metals.

Acknowledgments

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