Development of Quantum Dots Nanosensors for Heavy Metals Detection

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Resumen

Este estudio demuestra la aplicación potencial de los puntos cuánticos modificados con polietilenimina (PEI) para la detección de metales pesados, específicamente iones de cobre, en matrices acuosas. Los puntos cuánticos fueron sintetizados en fase acuosa, revelando una morfología esférica, un tamaño inferior a 5 nm y una estructura cristalina cubica centrada en las caras. La presencia de PEI en la superficie de los puntos cuánticos mejoró significativamente su fotoluminiscencia en el rango de 400 nm a 650 nm. Para evaluar la capacidad de los puntos cuánticos como sensor, se utilizaron dos precursores de cobre ($CuSO_4$ y $CuNO_3$) a concentraciones de 0 ppm hasta 38 ppm. Se observó una disminución sistemática en la intensidad de fluorescencia con el aumento de la concentración de cobre, estableciendo una relación cuantitativa. Estos hallazgos subrayan el potencial de los puntos cuánticos modificados con PEI como sensores eficientes y selectivos para iones de cobre. La respuesta dependiente de la concentración en la intensidad de fluorescencia refleja la sensibilidad del sistema, sugiriendo aplicaciones prometedoras en el campo de la detección de metales pesados.

Palabras clave: puntos cuánticos, fotoluminiscencia, nanosensor, metales pesados, PEI.

Abstract

This study demonstrates the potential application of polyethyleneimine (PEI)-modified quantum dots for sensing heavy metals, specifically copper ions, in aqueous matrices. Quantum dots were synthesized in aqueous phase, revealing a spherical morphology, a size of less than 5 nm, and a face-centered cubic crystalline structure. The presence of PEI on the quantum dots' surface significantly enhanced their photoluminescence within the range of 400 nm to 650 nm. To assess the sensor capabilities of PEI-capped quantum dots, two copper precursors ($CuSO_4$ and $CuNO_3$) were utilized at concentrations ranging from 0 ppm to 38 ppm. A systematic decrease in fluorescence intensity with increasing copper concentration was observed, establishing a quantitative relationship. These findings underscore the potential of PEI-modified quantum dots as efficient and selective sensors for copper ions. The concentration-dependent response in fluorescence intensity reflects the sensitivity of the system, suggesting promising applications in the field of heavy metal detection.

Keywords: quantum dots, photoluminescence, nanosensor, heavy metals, PEI.

Introduction

Water is the most vital resource for people and ecosystems, serving as a fundamental element for various essential processes. However, the issue of low water quality has emerged as a significant challenge, particularly impacting agriculture and food production. The presence of heavy metals exacerbates this concern, with copper being a notable example. The introduction of heavy metals into the environment is predominantly facilitated through several common pathways. Wastewater discharged by metal finishing industries, paints and dyes, petroleum refining, fertilizers, mining and metallurgy, explosives manufacturing, pesticide application, and steel industries is a primary source of contamination. These industries release effluents containing heavy metals into water bodies, leading to potential environmental degradation. Copper, owing to its widespread use in industrial applications such as electrical wiring, plumbing, and diverse manufacturing processes, emerges as a predominant heavy metal of concern. Consequently, inadequate disposal practices and runoff from these industrial activities significantly contribute to the prevalence of copper in water sources. Addressing the issue of heavy metal contamination in water is crucial for safeguarding both human health and the integrity of ecosystems. Innovative technologies, such as quantum dots-based nanosensors, have shown promise in detecting and monitoring heavy metal levels in water, providing valuable insights for effective environmental management and conservation efforts [1].

On one hand, copper serves as an essential dietary element for animals and plants when present at trace concentrations. Conversely, elevated copper concentrations in water pose a significant threat to algae and crustaceans due to its pronounced toxicity. The aquatic toxicity of copper is often attributed to its ability to disrupt internal ion balance. Human exposure to heightened copper levels may result in adverse effects such as kidney and liver damage, gastrointestinal irritation, hemolytic anemia, respiratory tract issues, cardiovascular toxicity, neurotoxicity, among others [1-2].

Various methodologies exist for the detection of heavy metal ions, including atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and Fluorescence Spectroscopy (FS). However, these techniques are characterized by their high cost and the need for substantial maintenance [3]. Consequently, there is a critical need to develop a technique characterized by simplicity in operation, a robust response, and the capability for in situ operations.

Smart materials represent a distinctive class of materials capable of responding to external stimuli, such as pH, temperature, magnetic fields, electromagnetic radiation, or bio-stimuli. Among these, quantum dots (QDs) stand out as smart materials due to their small size (ranging from 2 nm to 12 nm) and tunable fluorescence emission. These nanostructures exhibit the ability to modify their optical properties in response to changes in size, showcasing potential in the detection of heavy metal ions by leveraging their fluorescence characteristics. Notably, it has been documented that the presence of heavy metal ions can quench the fluorescence emission of QDs [4].

The proposed quantum dots-based nanosensor for copper ions detection is depicted in Figure 1. Quantum dots, whose surface has been altered with polyethyleneimine (PEI) molecules, establish stable complexes with copper ions. Activation of the quantum dots occurs

through electromagnetic radiation, causing the promotion of electrons from the valence band to the conduction band. Subsequent electron transfer takes place, fi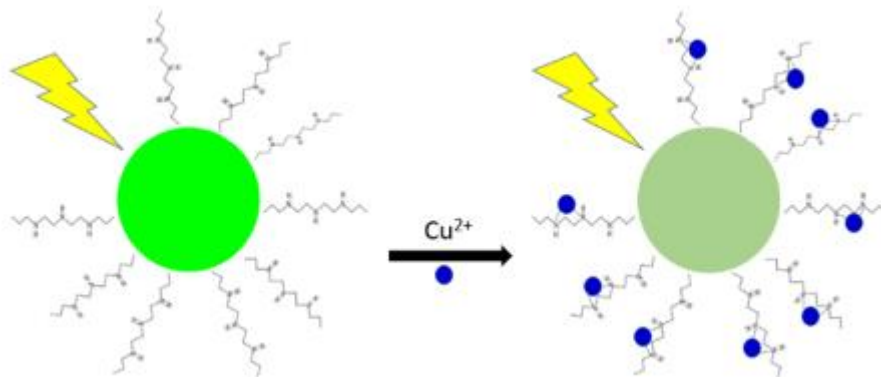rst to PEI molecules and then to copper ions, resulting in the quenching of quantum dots' fluorescence. The reduction in fluorescence is expected to be inversely proportional to the concentration of copper ions associated with PEI molecules [5-7].

Figure 1: Proposed quantum dots-based nanosensor for detection of copper ions from aqueous matrices.

Considering the aforementioned points, this research aimed to explore the utilization of smart nanomaterials, specifically semiconductor QDs, for the detection of heavy metals such as copper. The specific objectives of this study were: i) To synthesize quantum dots with a surface modified using polyethyleneimine molecules, and ii) To assess the sensing capability of quantum dots for copper ions (Cu^{2+}) in aqueous matrices.

Materials and Methods

Synthesis of quantum dots

The production and quality of nanomaterials can be influenced by the presence of contaminants. Consequently, all glassware employed in the synthesis process was immersed in 10% nitric acid overnight, followed by thorough rinsing with deionized water and subsequent drying. Additionally, experimental solutions were prepared using deionized water with a resistivity of 18 MΩ cm.

Cadmium-based QDs were generated using fresh solutions of precursors (i.e., 0.1M cadmium acetate dihydrate, 3% w/w Na_2S, thioglycolic acid, and 1% polyethyleneimine).

In the initial phase, the complexation between cadmium ions and thioglycolic acid was realized under alkaline conditions. Following this, the pH was adjusted to approximate neutrality, and a 1% polyethyleneimine solution was introduced. The resulting mixture underwent a ten-minute heating process within a reflux system, culminating with the addition of 3% w/w sodium sulfide solution.

Characterization of quantum dots

The as-synthesized quantum dots underwent morphological and optical characterization. A Shimadzu RF-6000 spectrofluorometer equipped with a spectral bandwidth of 5-5 and a 150W xenon arc lamp was employed to acquire the photoluminescence (PL) spectra of the quantum dots in aqueous phase at room temperature and to evaluate the quantum dots sensor capacity. The presence of PEI on

the quantum dots' surface was evaluated by Fourier Transform Infrared Spectroscopy (FT-IR). Nanostructure morphology and elemental composition were analyzed by High-Resolution Transmission Electron Microscopy (HRTEM), using a JEOL JEM-ARM200cF microscope operating at 200 kV.

Conducting sensing tests using quantum dots modified with PEI

The sensing properties of quantum dots (QDs) were assessed at 25°C using a spectrofluorometer. Polyethyleneimine-capped quantum dots, specifically cadmium-based QDs, dispersed in deionized water with concentrations ranging from 1000 ppm to 3000 ppm, were exposed to Cu^{2+} (in the form of either $CuSO_4$ or $CuNO_3$) at the desired concentration. The samples were vigorously stirred, and the fluorescence peaks of PEI-modified cadmium-based QDs were monitored at 520 nm.

Results and Discussion

Optical, morphological, compositional, and structural characterization of Quantum dots modified with PEI

The observed morphology of quantum dots, as illustrated in Figure 2 (A-D), reveals significant insights into the impact of polyethyleneimine modification. The prevalent spherical morphology of the particles underscores the effectiveness of the PEI modification, contributing to the enhancement of their crystalline properties. The high crystallinity is a crucial aspect that influences the quantum dots' performance in various applications. The TEM micrographs showed in Figure 2(A-C) offer a closer look

at the arrangement of quantum dots, demonstrating a noteworthy tendency of these particles to group together in a repetitive pattern. This pattern is indicative of a well-defined and controlled synthesis process, highlighting the precision achieved through PEI modification. The HRTEM image in Figure 2D provides additional valuable information by emphasizing the remarkably small size of the PEI-modified quantum dots. This sub-5.0 nm size range is particularly noteworthy, as it holds promise for applications requiring ultra-small quantum dots.

To complement the morphological analysis, Energy-Dispersive X-ray (EDX) analysis was performed on the PEI-capped quantum dots. The confirmation of cadmium and sulfur in the synthesized nanostructures through EDX provides essential elemental validation of the quantum dot composition. The quantification of cadmium and sulfur, as depicted in Figure 3, reveals a composition ratio of 71.3% cadmium to 28.7% sulfur. This precise composition information is vital for tailoring quantum dots to specific applications, ensuring optimal performance and stability. Furthermore, the crystallographic analysis indicated that the crystal structure of the quantum dots aligns with a zinc-blende crystal structure or face-centered cubic array. This alignment sheds light on the internal organization of the quantum dots, further supporting the understanding of their unique properties. The cubic arrangement is known for its stability and is consistent with the observed high crystallinity, reinforcing the reliability of the PEI modification in maintaining the structural integrity of the quantum dots.
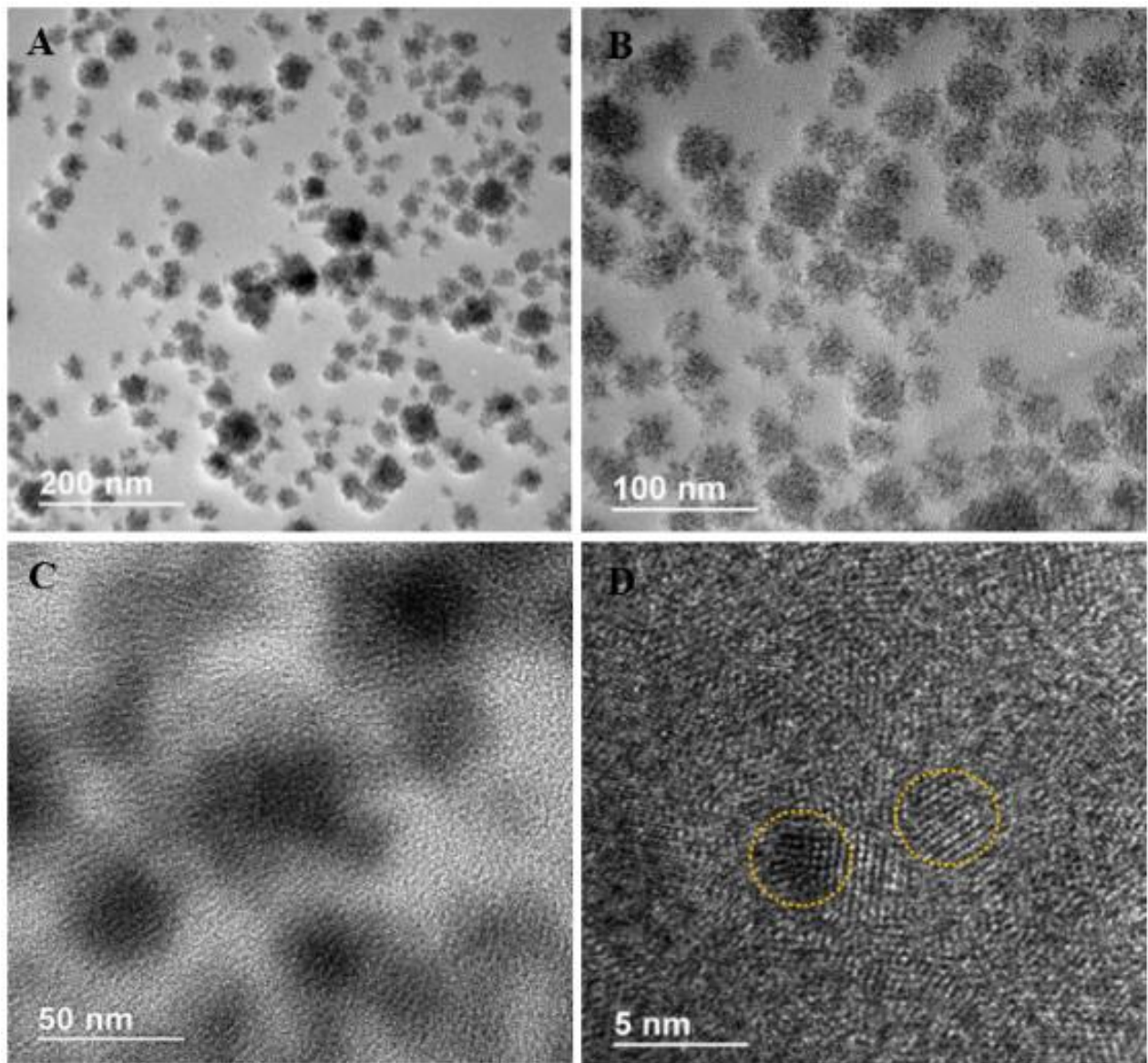
Figure 2: Transmission electron micrographs at low magnification (A, B, C) and high magnification (D) of PEI-capped quantum dots.
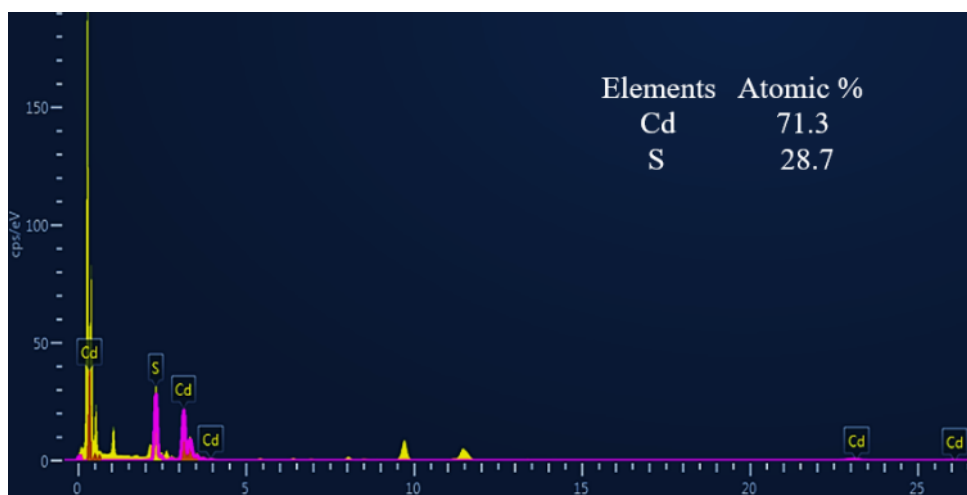
Figure 3: Energy Dispersive X-ray spectrum of PEI-capped quantum dots.

The investigation into the fluorescence properties of Cd-based nanoparticles, synthesized in the presence of polyethyleneimine, as depicted in Figure 4, sheds light on the critical influence of surface modification on the optical characteristics of quantum dots. Notably, the incorporation of PEI onto the quantum dots' surface resulted in a substantial enhancement of fluorescence when compared to particles synthesized in the absence of PEI. This enhancement can be attributed to the unique interaction between PEI and the quantum dots, leading to improved quantum yield and stability.

Furthermore, a distinctive feature observed in the fluorescence spectra is the conspicuous blue-shift (520 nm) in the excitonic peak of quantum dots modified with PEI. This phenomenon is of particular interest and merits careful consideration. The blue-shift can be rationalized by the effective reduction of surface defects in the quantum dots due to the presence of PEI. The interaction between PEI and the quantum dot surface likely plays a crucial role in passivating defects, thereby enhancing the overall optical properties of the nanoparticles. The shift to smaller wavelengths suggests a fine-tuning of the emission characteristics, potentially opening avenues for tailored emission profiles that are valuable in various optoelectronic devices such as sensors [8-9].

The emission spectra, presented in a sequential arrangement from left to right, further corroborate the distinct optical features of the synthesized samples. CdS modified with PEI exhibits a pronounced emission in the blue range, while unmodified CdS nanoparticles display emission in the yellow-orange range. This stark difference in emission coloration emphasizes the role of PEI in influencing the optical properties and emission characteristics of the quantum dots.
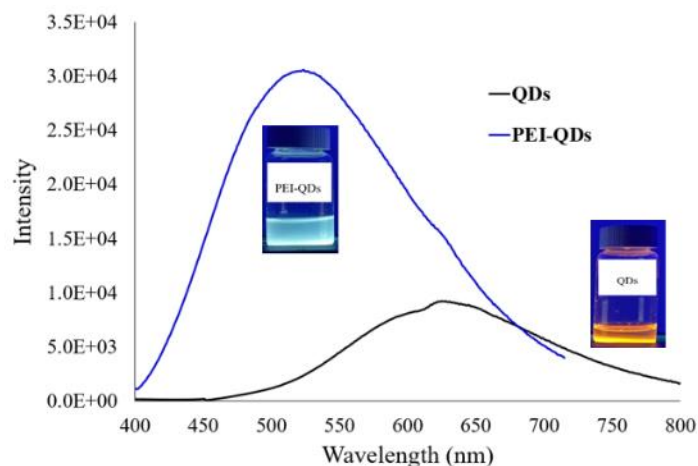
Figure 4: Photoluminescence spectra of PEI-capped QDs (*blue line*) and QDs (*black line*).

The verification of particle functionalization with polyethyleneimine through infrared analysis stands as a crucial step in understanding the surface modifications of the synthesized nanoparticles. As illustrated in Figure 5, the infrared spectra for both PEI and the particles synthesized in the presence of PEI offer valuable insights into the chemical interactions and bonding that have occurred during the functionalization process. The distinctive features observed in the infrared spectrum of the quantum dots synthesized with PEI provide compelling evidence of successful functionalization. Notably, the presence of prominent vibration peaks corresponding to N-H, C-H, and C-N bonds is indicative of the incorporation of PEI onto the surface of the particles [10]. The appearance of these specific peaks aligns with the expected functional groups of PEI, affirming the effective grafting of the polymer onto the quantum dots.
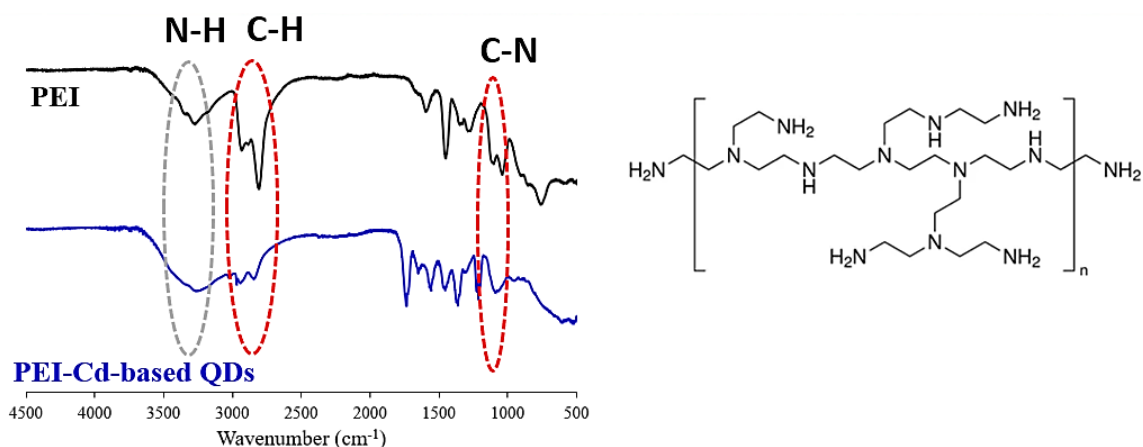

Figure 5: FT-IR spectra of PEI-capped QDs and PEI (*left*) and chemical structure of PEI (*right*).

The phenomenon of fluorescence quenching observed in Figure 6 provides a compelling insight into the potential utility of PEI-modified quantum dots as sensitive sensors for heavy metal detection, particularly focusing on copper ions. A copper ions solution at 1000 ppm was used. The quenching effect, indicative of a dynamic interaction between the quantum dots and copper species, serves as a fundamental basis for exploring the nanoparticle's responsiveness to varying concentrations of copper solutions.

In Figure 7, the plotted fluorescence intensity of PEI-modified quantum dots against the concentration of Cu^{2+} (ppm) reveals a systematic and concentration-dependent decrease in fluorescence. This clear trend signifies a robust and discernible response of the quantum dots to the presence of copper ions. The concentration range considered, from 0 ppm to 38 ppm of copper (in the form of $CuSO_4$ or $CuNO_3$), covers a spectrum relevant to environmental and analytical contexts, making the functionalized quantum dots a promising candidate for practical applications in heavy metal sensing. The observed quenching behavior can be attributed to the specific interactions between the copper ions and the quantum dot surface. It is plausible that the introduction of copper ions induces changes in the electronic structure of the quantum dots, leading to alterations in their fluorescence properties [11-12]. The systematic decrease in fluorescence intensity as a function of increasing copper concentration establishes a quantitative relationship, laying the foundation for the development of a reliable sensor. The sensitivity demonstrated in this study positions these functionalized nanoparticles as promising candidates for environmental monitoring, industrial quality control, and other applications where precise detection of heavy metal contaminants is paramount.
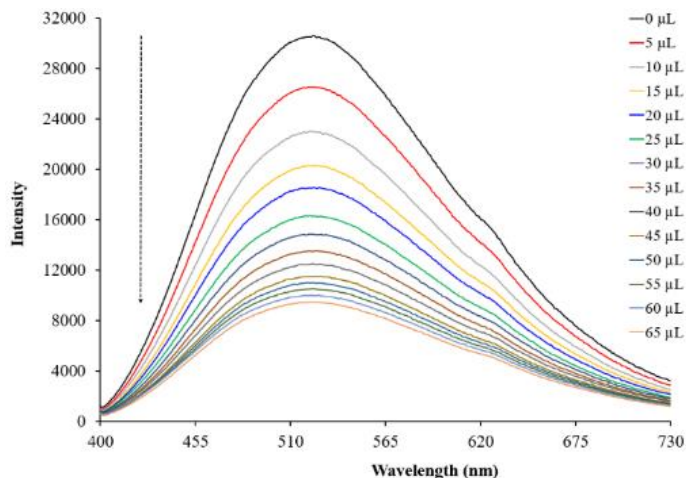

Figure 6: Quenching of PI-capped Quantum dots in the presence of 1000 ppm of copper ions.
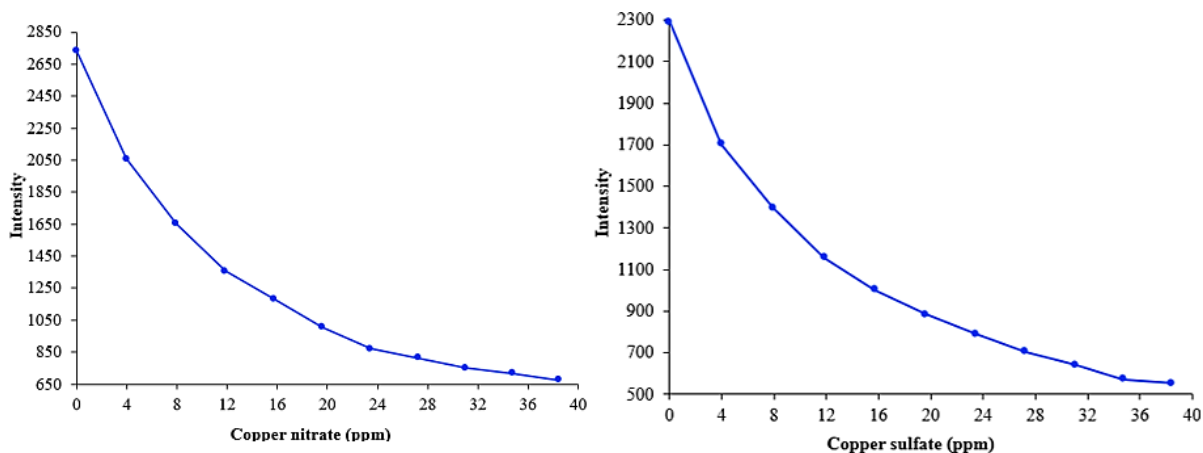
Figure 7: Sensing experiments with different copper solutions (*copper nitrate at the left and copper sulfate at the right*), in the presence of PEI-capped QDs.

Conclusions

PEI-capped quantum dots, synthesized directly in aqueous medium, exhibit a predominantly spherical morphology, a size of less than 5.0 nm, high crystallinity, and a face-centered cubic arrangement. These nanostructures manifest a prominent photoluminescent peak centered at 520 nm, attributed to the presence of PEI on the quantum dots' surface. This presence of PEI not only mitigates non-radiative processes but also enhances fluorescence. Moreover, the introduction of PEI increases the affinity of quantum dots to copper ions, resulting in the formation of stable complexes. When light activates the quantum dots, electrons promoted from the valence band to the conduction band are transferred to the PEI structure and eventually to copper ions (as the electron-deficient centers). This process leads to the quenching of quantum dots' fluorescence.

The observed fluorescence quenching of PEI-modified quantum dots in the presence of copper ions represents a significant advancement in the field of nanoscale sensing. This underscores their potential as key components in the development of advanced sensing platforms for heavy metal detection.

Acknowledgements

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