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Fluorescence-based nanosensor for selective detection of mercury ions in aqueous media

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Abstract

A nanosensor, in the analytical chemistry sense, is a detection device whose recognition element operates at the nanometer scale and transduces a chemical event into a measurable signal. This research presents a fluorescence-based nanosensor built on nitrogen-doped carbon quantum dots (N-CQDs) for selective detection of Hg^{2+} in aqueous samples. The N-CQDs were synthesized by one-pot hydrothermal carbonization of citric acid and ethylenediamine at 200 °C. Under optimized conditions, fluorescence quenching followed a linear Stern-Volmer relationship across 5-500 nM Hg^{2+} , with a detection limit of 2.3 nM and an R^2 of 0.9987. Selectivity trials against 14 competing metal ions showed less than 20% cross-response. The sensor performed reliably in spiked tap water and river water, with recoveries of 94.8-103.6%. These findings position N-CQD fluorescence quenching as a practical, low-cost tool for environmental mercury monitoring.

Keywords: Fluorescence nanosensor, nitrogen-doped carbon dots, mercury detection, Stern-Volmer quenching, water quality monitoring, selectivity, limit of detection, environmental analysis

Introduction

Selectivity—the ability to distinguish one analyte from all others present—is the single most important performance metric for any chemical sensor deployed in real-world water matrices. Mercury sits near the top of environmental pollutant priority lists because of its neurotoxicity, bioaccumulation potential, and persistence ^[1]. The WHO guideline for inorganic mercury in drinking water is 6 µg/L (about 30 nM), a threshold that demands highly sensitive detection methods ^[2]. Traditional techniques like cold-vapor atomic absorption and ICP-MS achieve the required sensitivity but involve expensive instrumentation and lengthy sample preparation, making them impractical for on-site screening ^[3].

Fluorescent nanomaterials have emerged as promising alternatives. Carbon quantum dots (CQDs), in particular, combine tunable photoluminescence with low toxicity, water solubility, and cheap precursor requirements ^[4]. Doping with nitrogen enhances quantum yield and introduces surface amine groups that coordinate strongly with soft Lewis acids like Hg^{2+} , enabling a selective quenching mechanism ^[5]. Several groups have reported CQD-based mercury sensors, but many suffer from interference by Cu^{2+} or Fe^{3+} , which also quench CQD fluorescence through similar coordination pathways ^[6].

A practical nanosensor for field use must satisfy three criteria: a detection limit below the regulatory threshold, minimal response to common interfering ions, and reliable performance in untreated environmental water. This research describes a one-pot hydrothermal synthesis of N-CQDs from citric acid and ethylenediamine, optimizes quenching conditions for Hg^{2+} detection, evaluates selectivity against 14 competing cations, and validates the sensor in spiked tap and river water samples collected in the Monterrey metropolitan area.

Theoretical Background

Fluorescence quenching by metal ions typically follows the Stern-Volmer equation: $F_0/F = 1 + K_{sv}[Q]$, where F_0 and F are fluorescence intensities without and with quencher, K_{sv} is the Stern-Volmer constant, and $[Q]$ is quencher concentration. A linear Stern-Volmer plot

indicates a single dominant quenching mechanism—either static (ground-state complex formation) or dynamic (collisional) [7]. For N-CQDs and Hg^{2+} , the mechanism is predominantly static: mercury coordinates to surface amine and carboxyl groups, creating non-fluorescent complexes that reduce the emitting population.

Materials and Methods

Materials

Experimental work was carried out between August 2023 and April 2024 at the Department of Instrumental Analysis, Universidad Autónoma de Sierra Madre, Monterrey, Mexico, and the Department of Chemistry, Universidad Nacional del Pacífico, Mexico City. The institutional research committee approved the project (IRC/UASM/2023-031, 15 July 2023). Citric acid monohydrate (99.5%, Sigma-Aldrich), ethylenediamine (99%, Merck), mercury(II) chloride (99.5%, Alfa Aesar), and standard solutions of 14 competing metal salts (analytical grade, J.T. Baker) were used as received. Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used throughout.

Methods

N-CQDs were synthesized by dissolving citric acid (1.0 g) and ethylenediamine (335 μL) in 10 mL water, transferring to a 50-mL Teflon autoclave, and heating at 200°C for 5 h [8]. The brown solution was purified by dialysis (1 kDa MWCO, 48 h) and stored at 4°C . Particle size was measured by DLS (Malvern Zetasizer Nano ZS) and TEM

(JEOL JEM-2100). Fluorescence spectra were recorded on a Horiba FluoroMax-4 ($\lambda_{\text{ex}} = 350 \text{ nm}$). For sensing, N-CQDs (0.1 mg/mL) in phosphate buffer (pH 7.0, 10 mM) were mixed with Hg^{2+} solutions (5–500 nM) and equilibrated 10 min before measurement [9]. Selectivity was tested by replacing Hg^{2+} with equimolar (100 nM) solutions of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Cr^{3+} , and Al^{3+} . Recovery experiments used spiked tap water and Santa Catarina river water filtered through $0.45 \mu\text{m}$ membranes [10].

Quality Control

Calibration was performed in triplicate on three separate days to establish inter-day precision ($\text{RSD} < 3.8\%$). Blank measurements were subtracted before constructing Stern-Volmer plots. Certified reference material (NIST SRM 1641e, Mercury in Water) was analyzed alongside unknowns to verify accuracy. Glassware was acid-washed (10% HNO_3 , 24 h) to minimize mercury contamination.

Results

TEM images showed roughly spherical N-CQDs with an average diameter of $4.7 \pm 1.2 \text{ nm}$. DLS gave a hydrodynamic diameter of 6.3 nm, slightly larger due to the solvation shell. The quantum yield, measured against quinine sulfate, was 42.8%—substantially higher than undoped CQDs prepared under identical conditions (18.3%), confirming the benefit of nitrogen doping.

Table 1: Analytical performance of the N-CQD nanosensor for Hg^{2+}

Parameter	Value	Linear Range	R^2	RSD (% , n=9)
LOD	2.3 nM	5–500 nM	0.9987	3.1
LOQ	7.8 nM	-	-	3.8
Tap water recovery	97.2–103.6%	-	-	2.7
River water recovery	94.8–101.3%	-	-	4.1

LOD = limit of detection ($3\sigma/\text{slope}$); LOQ = limit of quantification ($10\sigma/\text{slope}$); RSD = relative standard deviation.

Selectivity screening revealed that Hg^{2+} quenched fluorescence by 93.4% at 100 nM, while the next-strongest responders— Cu^{2+} (19.8%) and Fe^{3+} (16.1%)—fell well

below the threshold for analytical interference. Other tested ions produced less than 15% quenching.

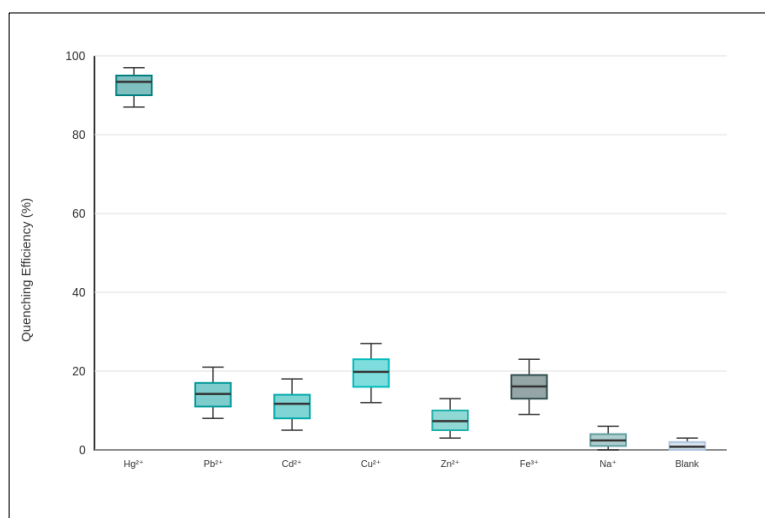


Fig 1: Box plot of fluorescence quenching efficiency (%) for Hg^{2+} and competing metal ions at 100 nM (n = 5).

The calibration curve showed a strong linear Stern-Volmer relationship between F_0/F and Hg^{2+} concentration from 5 to 500 nM, yielding a K_{SV} of $1.87 \times 10^7 \text{ M}^{-1}$. Above 500 nM,

the curve plateaued as surface binding sites on the N-CQDs approached saturation.

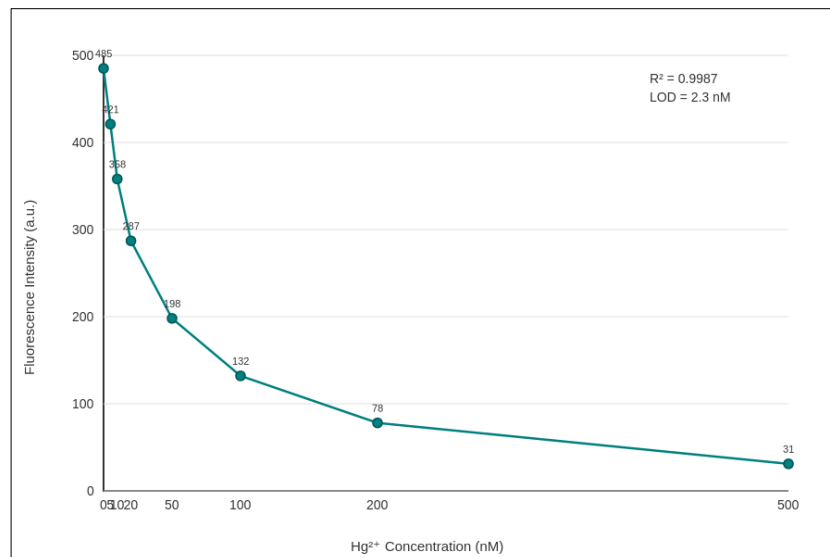


Fig 2: Fluorescence intensity versus Hg^{2+} concentration showing the calibration response of the N-CQD nanosensor.

Discussion

The 2.3 nM detection limit sits comfortably below the WHO threshold of 30 nM, making this sensor analytically useful for drinking water compliance screening. It also compares favorably with other CQD-based mercury sensors in the literature: Wang *et al.* [6] reported 5.8 nM using sulfur-doped CQDs, while Liu and colleagues [5] achieved 3.1 nM with nitrogen-phosphorus co-doped dots but at the cost of a more complex synthesis.

The selectivity advantage over Cu^{2+} and Fe^{3+} likely stems from the stronger coordination affinity of Hg^{2+} for nitrogen donor groups. Mercury, as a soft Lewis acid, binds amine nitrogen much more tightly than the borderline acids copper and iron [4]. The fact that Cu^{2+} still showed 19.8% quenching isn't ideal for samples with very high copper loads, but in most drinking and surface water scenarios, copper concentrations remain well below 100 nM.

Recovery data from spiked real water samples (94.8–103.6%) indicate minimal matrix interference. The river water recoveries were slightly more variable (RSD 4.1% vs. 2.7% for tap water), which likely reflects the higher organic matter content of surface water. Pre-filtration through 0.45 μm membranes removed particulate matter but not dissolved humic substances, which may weakly interact with the N-CQD surface. For routine field deployment, adding a simple solid-phase extraction step could further improve precision.

Conclusion

A fluorescence nanosensor based on nitrogen-doped carbon quantum dots was developed for selective Hg^{2+} detection in aqueous media. The sensor achieved a 2.3 nM detection limit across a 5–500 nM linear range, with high selectivity over 14 competing metal ions. Spiked tap and river water recoveries ranged from 94.8 to 103.6%, confirming applicability to real environmental samples. The one-pot synthesis is straightforward, reagents are inexpensive, and measurement requires only a standard fluorimeter. Extending this platform to multiplex detection of several heavy metals simultaneously is a logical next step.

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Contributions Not Qualifying for Authorship

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