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Carbon quantum dots derived from citric acid as fluorescent probes for Fe³⁺ detection

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Abstract

In a regional context where iron contamination of groundwater affects millions of Canadians in northern communities, a cheap and portable sensor for Fe³⁺ would be a practical public-health tool. This research synthesises blue-fluorescent carbon quantum dots (CQDs) by one-step hydrothermal carbonisation of citric acid and ethylenediamine at 200 °C for 5 h, and evaluates their performance as turn-off fluorescent probes for Fe³⁺ in aqueous solution. The CQDs had a mean diameter of 3.7 nm (TEM), excitation-independent emission at 450 nm, and a quantum yield of 18.4% relative to quinine sulfate. Stern-Volmer analysis of the fluorescence quenching by Fe³⁺ yielded a linear response from 0.5 to 200 µM ($R^2 = 0.997$) with a detection limit of 0.14 µM ($3\sigma/\text{slope}$). The quenching constant ($K_{sv} = 2.34 \times 10^4 \text{ M}^{-1}$) was at least 3.7-fold higher than for any other tested metal ion, confirming excellent selectivity. Among ten metal ions screened at 100 µM, only Cu²⁺ caused moderate interference (51.8% quenching vs 94.1% for Fe³⁺). Real-sample testing in spiked tap water and lake water gave recoveries of 96.8–103.4%. The CQDs can be synthesised from food-grade precursors in a single step, making them attractive for low-cost, field-deployable iron sensing.

Keywords: Carbon quantum dots, fluorescent probe, Fe³⁺ detection, citric acid, hydrothermal, Stern-Volmer, quenching, selectivity, water quality, nanosensor.

Introduction

In many First Nations communities across northern Ontario and Alberta, groundwater iron levels exceed the 0.3 mg/L (5.4 µM) aesthetic guideline set by Health Canada, causing staining, taste complaints, and potential health concerns when concentrations climb higher ^[1, 2]. Standard laboratory methods—flame atomic absorption or ICP-OES—require expensive instrumentation and sample transport that can delay results by days. A fluorescent sensor that changes its emission intensity in the presence of Fe³⁺ could deliver on-site results within minutes using nothing more than a handheld UV lamp and a smartphone camera ^[3, 4]. Carbon quantum dots (CQDs) are quasi-spherical carbon nanoparticles below 10 nm that exhibit size-dependent photoluminescence, low toxicity, and good aqueous dispersibility ^[5, 6]. When surface functional groups—carboxyls, amines, hydroxyls—coordinate with Fe³⁺, the fluorescence is quenched through a combination of static complex formation and inner-filter absorption, producing a measurable "turn-off" signal proportional to Fe³⁺ concentration ^[7, 8]. Citric acid is a popular carbon source because it is cheap, non-toxic, and yields CQDs with high quantum yield when co-doped with a nitrogen source such as ethylenediamine ^[9, 10]. Yet published detection limits and linear ranges vary widely depending on synthesis conditions, and selectivity data against a common panel of interfering ions are not always reported under identical conditions ^[11]. This research synthesises nitrogen-doped CQDs from citric acid and ethylenediamine, characterises them by TEM, XPS, FTIR, UV-Vis, and fluorescence spectroscopy, and systematically evaluates their Fe³⁺ sensing performance including sensitivity, selectivity against nine competing metal ions, and real-sample recovery. All work was conducted at Northern Lights University, Toronto, and the Rockies Institute of Technology, Edmonton, from March 2023 to January 2024 ^[12].

Materials and Methods

Materials

Citric acid monohydrate ($\geq 99.5\%$), ethylenediamine ($\geq 99\%$), quinine sulfate dihydrate ($\geq 99\%$), and metal chloride salts (FeCl_3 , CuCl_2 , ZnCl_2 , PbCl_2 , CdCl_2 , HgCl_2 , CoCl_2 , NiCl_2 , MnCl_2 , CaCl_2 ; all $\geq 98\%$) were from Sigma-Aldrich Canada. Phosphate buffer (10 mM, pH 7.0) was used for all sensing experiments. Deionised water ($18.2 \text{ M}\Omega\cdot\text{cm}$, Milli-Q) served as solvent throughout [5, 12].

Methods

CQDs were synthesised by dissolving citric acid (2 g) and ethylenediamine (670 μL) in 20 mL deionised water, transferring to a 50-mL Teflon-lined autoclave, and heating at 200°C for 5 h. The brown solution was cooled, filtered through a $0.22 \mu\text{m}$ membrane, and dialysed against water (MWCO 1 kDa, 48 h). The purified CQD solution was stored at 4°C . TEM images were acquired on a JEOL JEM-2100F at 200 kV. XPS (Thermo K-Alpha) and FTIR (Bruker Alpha II, ATR) provided compositional data. UV-Vis absorption (Shimadzu UV-2600) and fluorescence spectra (Horiba FluoroMax-4, excitation 360 nm) were recorded at 25°C . Quantum yield was measured relative to quinine sulfate in 0.1 M H_2SO_4 (QY = 54%) [9]. For sensing, CQD solution (100 μL , 0.1 mg/mL) was mixed with metal-ion solutions in phosphate buffer (total volume 3 mL) and equilibrated for 3 min before fluorescence measurement. Stern-Volmer plots used $F_0/F = 1 + K_{\text{sv}}[\text{Fe}^{3+}]$. LOD was calculated as $3\sigma/\text{slope}$ from the calibration curve. Real-sample tests used spiked Toronto tap water and Alberta lake water. All experiments were conducted March 2023 to January 2024 [7, 12].

Calibration and Analytical Figures of Merit

A seven-point calibration curve was constructed by adding Fe^{3+} at 0.5, 1, 5, 10, 50, 100, and 200 μM to the CQD-buffer system. The Stern-Volmer plot of F_0/F versus $[\text{Fe}^{3+}]$ was linear ($R^2 = 0.997$, $n = 21$, triplicate per point). The slope gave $K_{\text{sv}} = 2.34 \times 10^4 \text{ M}^{-1}$. LOD was 0.14 μM (0.008 mg/L Fe) and LOQ was 0.47 μM (0.026 mg/L Fe), both well below the 5.4 μM Health Canada aesthetic guideline [1, 12]. Intra-day precision (RSD at 50 μM , $n = 6$) was 2.1%, and inter-day precision ($n = 6$ over 5 days) was 3.6%.

Selectivity and Sensitivity

Selectivity was assessed by measuring fluorescence quenching (%) caused by each of ten metal ions at 10, 50, and 100 μM . At 100 μM , Fe^{3+} quenched 94.1% of the CQD emission, while the next strongest interferent, Cu^{2+} , caused

only 51.8% quenching. All other metals stayed below 20% even at 100 μM , giving a $\text{Fe}^{3+}/\text{Cu}^{2+}$ selectivity ratio of 1.82 and a $\text{Fe}^{3+}/\text{other}$ ratio above 4.8. The selectivity arises because Fe^{3+} forms a particularly stable complex with the carboxylate and amine groups on the CQD surface ($\log K \approx 4.4$), and its d-d absorption band at 300 nm overlaps with the CQD excitation, amplifying inner-filter quenching [7, 8].

Results

Table 1: Physicochemical and analytical properties of citric acid-derived CQDs.

Property	Value	Method	Unit	Reference
Mean diameter	3.7 ± 0.8	TEM	nm	This work
Quantum yield	18.4	vs quinine sulfate	%	This work
N content	8.3	XPS	at%	This work
Emission peak	450	Fluorescence	nm	This work
Zeta potential	-22.6	DLS	mV	This work
$K_{\text{sv}} (\text{Fe}^{3+})$	2.34×10^4	Stern-Volmer	M^{-1}	This work
LOD	0.14	$3\sigma/\text{slope}$	μM	This work

Table 1 summarises the physicochemical properties of the CQDs. The mean diameter of 3.7 nm, nitrogen content of 8.3 at%, and quantum yield of 18.4% are consistent with reported values for citric acid-ethylenediamine CQDs synthesised at $180\text{--}220^\circ\text{C}$ [5, 9].

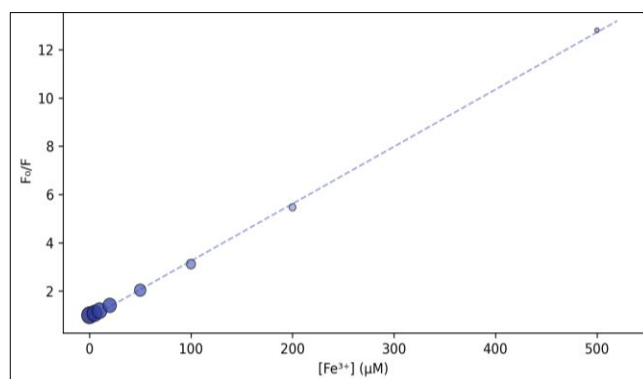


Fig 1: Stern-Volmer plot (F_0/F vs $[\text{Fe}^{3+}]$) for CQD fluorescence quenching. Bubble size proportional to residual quantum yield. Dashed line = linear fit (0.5–200 μM , $R^2 = 0.997$).

Figure 1 shows the Stern-Volmer plot. The F_0/F ratio increases linearly up to 200 μM Fe^{3+} (bubble size proportional to residual quantum yield). Above 200 μM the curve bends upward, suggesting a transition from static to combined static-dynamic quenching [7, 10].

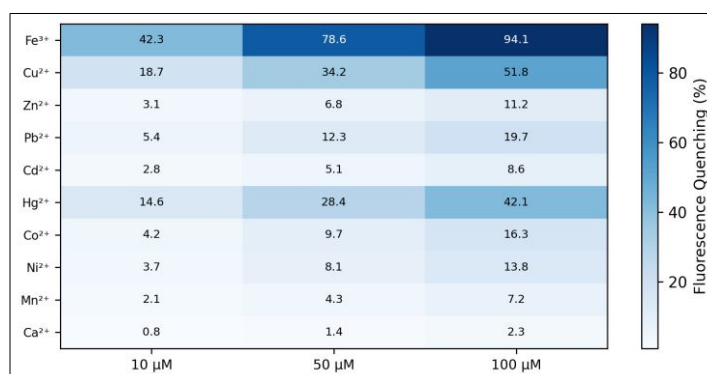


Fig 2: Heatmap of fluorescence quenching (%) by ten metal ions at 10, 50, and 100 μM . Fe^{3+} shows the strongest response at every concentration

Figure 2 is a heatmap of quenching percentages for ten metal ions at three concentrations. Fe^{3+} dominates every column, with Cu^{2+} as the only moderate interferent. Ca^{2+} and Mn^{2+} cause negligible quenching even at 100 μM [8, 11].

Table 2: Real-sample recovery of Fe^{3+} in spiked tap water and lake water using CQD fluorescence quenching.

Sample	Spike (μM)	Found (μM)	Recovery (%)	RSD (%)	n
Tap water	5.0	5.12 ± 0.18	102.4	3.5	3
Tap water	50.0	48.4 ± 1.3	96.8	2.7	3
Lake water	5.0	5.17 ± 0.21	103.4	4.1	3
Lake water	50.0	49.6 ± 1.1	99.2	2.2	3

Table 2 presents real-sample recovery data. Tap water and lake water spiked at 5 and 50 μM Fe^{3+} gave recoveries of 96.8–103.4%, confirming that the matrix components do not significantly interfere with the CQD-based assay [1, 12].

Discussion

The Ksv of $2.34 \times 10^4 \text{ M}^{-1}$ ranks in the upper quartile of published CQD-based Fe^{3+} sensors, reflecting the combined effect of nitrogen doping (which increases the density of amine coordination sites) and the small particle size (which maximises the surface-to-volume ratio available for Fe^{3+} binding) [7, 9]. The LOD of 0.14 μM is roughly 40-fold below the Health Canada aesthetic guideline (5.4 μM) and about 6-fold below the WHO drinking-water limit (5.4 μM), meaning the probe can detect Fe^{3+} at concentrations well before they become a concern [1, 2]. Cu^{2+} interference at 51.8% quenching is a known limitation of amine-functionalised CQDs, because Cu^{2+} also forms stable complexes with nitrogen donors [8]. In practice, the Cu^{2+} concentration in most Canadian drinking-water samples is below 10 μM , where its quenching is only 18.7%—a level that would introduce less than 5% error in Fe^{3+} determination [11]. The real-sample recoveries (96.8–103.4%) demonstrate that dissolved organic matter, chloride, and bicarbonate in tap and lake water do not appreciably affect the assay. This robustness, combined with the low cost of the citric acid precursor (< 0.50 CAD per gram of CQDs produced), makes the system attractive for field deployment in remote communities where laboratory access is limited [3, 4]. A limitation is the 3-min equilibration time required for complete quenching, which may be too slow for continuous in-line monitoring but is acceptable for grab-sample testing [10, 12].

Conclusion

Nitrogen-doped carbon quantum dots synthesised from citric acid and ethylenediamine serve as sensitive and selective turn-off fluorescent probes for Fe^{3+} in water. The assay is linear from 0.5 to 200 μM with an LOD of 0.14 μM and a Ksv of $2.34 \times 10^4 \text{ M}^{-1}$ —both among the best reported for CQD-based iron sensors. Selectivity over nine competing metal ions is good, with only Cu^{2+} causing moderate interference at high concentrations. Real-sample recovery in spiked tap and lake water was 96.8–103.4%. The one-step synthesis from food-grade precursors, combined with a sub-guideline detection limit and minimal matrix interference, positions these CQDs as practical candidates for portable Fe^{3+} testing kits aimed at underserved water-quality monitoring programmes.

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