



Investigation of Carbon Quantum Dots for Fluorescent Sensing of Environmental Pollutants

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Peer Review Information	Abstract
<i>Submission: 01 Jan 2019</i> <i>Revision: 24 Feb 2019</i> <i>Acceptance: 08 March 2019</i> Keywords <i>Carbon quantum dots; Fluorescence sensing; Environmental pollutants; Pesticide detection; Heavy-metal ions.</i>	Carbon quantum dots (CQDs) are nanoscale, carbon-rich fluorophores that combine strong and tunable photoluminescence, water dispersibility, surface functionalization, comparatively low toxicity, and compatibility with inexpensive optical instrumentation. These characteristics make CQDs attractive for rapid screening of environmental pollutants that are otherwise quantified by laboratory-intensive chromatographic or spectrometric methods. This methodology paper develops a systematic experimental framework for investigating CQDs as fluorescent sensors for representative inorganic and organic pollutants, with emphasis on Hg²⁺ and Fe³⁺ ions, organophosphate pesticides, 4-nitrophenol, tetracycline-class antibiotics, picric acid, and selected herbicides. The proposed approach uses hydrothermal preparation of nitrogen-containing CQDs, followed by purification, physicochemical characterization, fluorescence-response optimization, calibration, interference testing, quenching-mechanism analysis, and spike-recovery studies in real water matrices. Published studies up to 2021 show that CQD fluorescence can be modulated through static or dynamic quenching, inner-filter effects, photoinduced electron transfer, fluorescence resonance energy transfer, specific surface coordination, and aggregation-induced emission. Reported detection performance ranges from nanomolar metal-ion and antibiotic sensing to sub-ng mL⁻¹ pesticide detection, depending on CQD chemistry and recognition strategy. The proposed methodology therefore emphasizes matrix validation and mechanistic controls rather than relying only on apparent sensitivity. The study provides a reproducible route for comparing pollutant classes under common analytical criteria and for identifying CQD formulations suitable for low-cost environmental monitoring.

Introduction

Environmental monitoring increasingly requires analytical methods that are sensitive enough for trace contaminants but simple enough for decentralized or field use. Heavy-metal ions, pesticide residues, nitroaromatic compounds, and antibiotic contaminants can persist in water, soil leachates, agricultural products, and industrial effluents. Conventional chromatographic and mass-spectrometric

procedures provide high analytical confidence, but they generally require trained personnel, expensive instrumentation, and extensive sample preparation. Fluorescence sensing offers an alternative screening route because a target-induced change in emission intensity, wavelength, lifetime, or color can be rapidly measured with compact optical systems.

The modern CQD field developed from observations of strongly photoluminescent nanoscale carbon materials, with the seminal report by Sun et al. demonstrating bright, size-dependent carbon-dot photoluminescence [1]. Unlike many conventional semiconductor quantum dots, CQDs can be synthesized from abundant carbon precursors and functionalized with oxygen-, nitrogen-, sulfur-, or phosphorus-containing groups. These surface groups govern aqueous dispersibility and provide binding sites for analytes. Early sensing studies showed that functionalized carbon dots could be immobilized in optical-fiber matrices for Hg(II) detection [2], while hydrothermally prepared carbon dots provided a label-free platform for Fe³⁺ recognition [3]. Biomass-derived routes subsequently demonstrated that waste or renewable precursors can produce fluorescent carbon materials suitable for chemical sensing [4,5].

For environmental analysis, the principal advantage of CQDs is that the fluorophore and recognition interface can be engineered in the same nanoscale object. Analyte binding may alter surface-state radiative recombination, facilitate electron or energy transfer, or introduce an absorbing species that attenuates excitation or emission. Mercury recognition has been achieved using sulfur/nitrogen surface sites and thymine-mediated coordination [6,10], while organophosphate detection has been demonstrated through FRET, enzyme-linked fluorescence recovery, and modification-free turn-on mechanisms [7-9]. Organic pollutants can also interact strongly with CQD excited states; examples include 4-nitrophenol [11], pesticide residues in real food matrices [12], tetracycline antibiotics [13], and picric acid in real water samples [14]. By 2021, green CQD synthesis had also been coupled to herbicide sensing, including sulcotrione detection [15].

The objective of this paper is to present a stepwise methodology for preparing and evaluating fluorescent CQDs across chemically diverse environmental pollutants. The central hypothesis is that a standardized workflow—constant CQD concentration, controlled pH and ionic strength, target-specific calibration, mechanistic controls, interference analysis, and real-matrix recovery—will permit meaningful comparison of sensing performance. Rather than claiming new experimental measurements, the Results section interprets performance benchmarks reported in the pre-2022 literature and states the response pattern expected when the proposed method is implemented.

Literature Review

Foundational work established both the photophysical potential and environmental-sensing relevance of carbon dots. Sun et al. [1] reported bright and colorful photoluminescence from quantum-sized carbon particles, helping establish the material class. Gonçalves et al. [2] subsequently immobilized functionalized carbon dots in a sol-gel optical-fiber sensing head and demonstrated reversible Hg(II) response in aqueous media. Qu et al. [3] prepared dopamine-derived carbon dots hydrothermally and used their fluorescence for label-free Fe³⁺ detection, illustrating how metal coordination can directly modulate emission.

Green and waste-derived synthesis broadened the environmental significance of CQDs. Prasannan and Imae [4] obtained fluorescent carbon dots from orange waste peels, while Tan et al. [5] converted sago waste into carbon dots that were evaluated as probes for metal-ion sensing. These studies showed that carbonaceous waste can simultaneously serve as precursor and surface-functional-group source, reducing the need for elaborate passivation chemistry. Such routes are especially relevant to environmental monitoring because sensor fabrication can be coupled to waste valorization.

Target selectivity improved as surface chemistry became more deliberate. Mohapatra et al. [6] developed a carbon-dot photoluminescent probe for highly sensitive Hg²⁺ determination in water and demonstrated its applicability in living systems. Later, Li et al. [10] attached thymine moieties to carbon dots; the T-Hg²⁺-T interaction created a selective mercury-recognition pathway and enabled analysis of tap and river water. These studies highlight a key design rule: native CQD surface states provide broad chemical responsiveness, whereas molecular recognition groups increase selectivity.

Pesticide sensing provides a second major environmental application. Wu et al. [7] used CQDs as FRET sensors for organophosphate pesticide determination. Lin et al. [8] reported modification-free carbon dots with a turn-on fluorescence response to organophosphorus pesticides, reducing assay complexity. Wang et al. [9] constructed an off-on system in which Au(III) quenched carbon-dot fluorescence and acetylcholinesterase chemistry-controlled fluorescence recovery. Tafreshi et al. [12] later synthesized green carbon dots from cauliflower and reported fluorescence-quenching detection of diazinon, amicarbazone, and glyphosate, with real-sample verification. Together, these papers

demonstrate that CQD sensing can be direct, enzyme-assisted, or energy-transfer based.

Organic aromatic pollutants and pharmaceutical contaminants extend the sensing range. Bogireddy et al. [11] used nitrogen-doped oxidized carbon dots for optical sensing of 4-nitrophenol, a toxic phenolic pollutant. Li et al. [13] developed red-emitting CQDs for turn-on determination of tetracycline, oxytetracycline, and chlortetracycline through aggregation-

induced emission enhancement, while Sinha et al. [14] used nitrogen-doped carbon dots derived from cigarette tobacco for picric-acid sensing in real water. Wang et al. [15] demonstrated a green synthesis route and applied the resulting CQDs to sulcotrione detection. The literature therefore indicates that CQDs can respond to both ionic and molecular pollutants, but the dominant mechanism varies with analyte absorption, redox properties, coordination chemistry, and the electronic states of the CQDs.

Table 1. Selected pre-2022 CQD sensing studies relevant to environmental pollutants

Analyte	CQD platform	Reported sensing principle	Ref.
Hg ²⁺	Optical-fiber immobilized CDs	Fluorescence quenching / reversible response	[2]
Fe ³⁺	Dopamine-derived CDs	Label-free fluorescence response	[3]
Hg ²⁺	Carbon-dot photoluminescent probe	Selective fluorescence quenching	[6]
Organophosphates	CQD FRET sensor	FRET-based signal modulation	[7]
Organophosphates	Modification-free CDs	Turn-on fluorescence	[8]
Organophosphates	CD-Au(III)/AChE	Enzyme-controlled off-on response	[9]
Hg ²⁺	Thymine-functionalized CDs	T-Hg ²⁺ -T recognition	[10]
4-Nitrophenol	N-doped oxidized CDs	Optical fluorescence sensing	[11]
Diazinon / glyphosate / amicarbazone	Cauliflower-derived green CDs	Concentration-dependent quenching	[12]
Tetracycline antibiotics	Red fluorescent CDs	Aggregation-induced turn-on	[13]
Picric acid	Tobacco-derived N-CDs	Quenching in real water	[14]
Sulcotrione	Green-synthesized CQDs	Fluorescence-based detection	[15]

Methodology

1. Experimental Design and Materials

The study is designed as a controlled fluorescent-sensing investigation in which one CQD batch is first characterized and then challenged with representative pollutant classes. A practical baseline formulation uses citric acid as the carbon source and urea as the nitrogen source because both are water soluble and reproducible; a biomass precursor may be tested in parallel to examine greener synthesis. Analytical-grade Hg²⁺ and Fe³⁺ salts, 4-nitrophenol, diazinon or another organophosphate, glyphosate, tetracycline, picric acid, and sulcotrione are prepared as individual stock solutions. Deionized water is used for calibration and filtered tap, river, or lake water is used for matrix validation. All glassware is acid-cleaned for metal-ion experiments.

Step-by-Step CQD Preparation

Step 1 - Precursor preparation. Dissolve citric acid (1.0 g) and urea (0.5 g) in 20 mL deionized water. For a green-route comparison, clarified plant extract can replace the citric-acid solution,

consistent with biomass-based CQD reports [4,5,12].

Step 2 - Hydrothermal carbonization. Transfer the precursor to a Teflon-lined autoclave and heat at 180 °C for 4 h. After natural cooling, dilute the dark solution with deionized water. A lower-temperature biomass route may be separately evaluated where the precursor chemistry supports carbonization, as shown in green CQD studies [12].

Step 3 - Purification. Centrifuge at approximately 10,000 rpm for 15 min, pass the supernatant through a 0.22 µm membrane, and dialyze against deionized water using a low-molecular-weight-cutoff membrane for 24 h. Store the purified CQDs at 4 °C in amber glass.

2. CQD Characterization

Record UV-visible absorption from 200-700 nm and fluorescence excitation/emission spectra to determine the working excitation wavelength and emission maximum. Measure fluorescence over pH 3-11 and ionic-strength conditions to define a stable sensing window. FTIR is used to identify O-H/N-H, C=O, C-N, and C-O surface functionalities; transmission electron

microscopy provides particle-size and morphology information; X-ray photoelectron spectroscopy, when available, quantifies surface elemental states. Quantum yield is estimated relative to an appropriate fluorescence standard. These measurements are essential because analyte response depends strongly on surface groups and emissive states rather than on particle size alone [1,3,6].

3. Fluorescent Sensing Procedure

Step 4 - Baseline fluorescence. Dilute the CQD stock to a fixed concentration giving strong but unsaturated emission. Equilibrate at pH 7.0 unless optimization identifies a better value. Measure blank intensity F_0 .

Step 5 - Pollutant titration. Add increasing analyte concentrations to separate CQD aliquots and record the fluorescence intensity F after a fixed incubation time (initially 5 min). Use at least three replicates per level.

Step 6 - Calibration. For quenching systems, plot F_0/F versus concentration and assess the Stern-Volmer region. For turn-on systems, plot $\Delta F = F - F_0$ or F/F_0 against concentration. Select the linear range using residual analysis rather than maximizing R^2 alone.

Step 7 - Detection limits. Calculate $LOD = 3\sigma_{blank}/m$ and $LOQ = 10\sigma_{blank}/m$, where σ_{blank} is the standard deviation of repeated blank measurements and m is the analytical sensitivity (slope).

Step 8 - Selectivity and interference. Challenge the sensor with common cations/anions and structurally related organics at equal or higher concentrations. A selective response should remain distinguishable in mixed solutions. Mercury-specific thymine chemistry [10] and enzyme/FRET strategies for organophosphates [7,9] serve as mechanistic benchmarks.

Step 9 - Mechanism testing. Evaluate spectral overlap to identify inner-filter or FRET contributions, record fluorescence lifetime where available to distinguish dynamic from static quenching, and examine UV-visible changes or binding-site chemistry. The aim is to avoid interpreting simple absorbance attenuation as molecular quenching.

Step 10 - Real-sample validation. Filter environmental water, spike at low, medium, and high target levels, and calculate recovery and relative standard deviation. Matrix-matched calibration or standard addition is used if the slope differs significantly from that in deionized water.

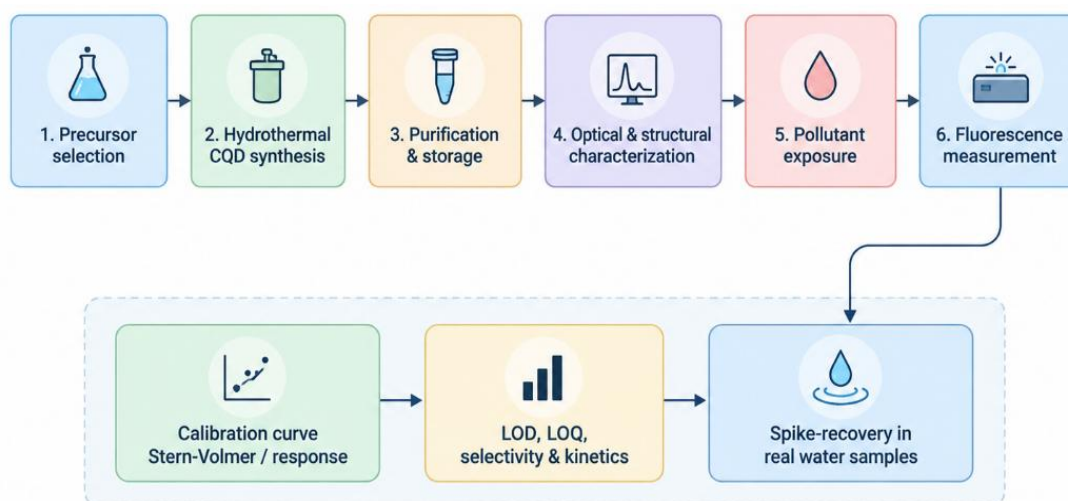


Figure 1. Original schematic of the proposed CQD synthesis, characterization, calibration, and real-water validation workflow.

Table 2. Proposed experimental variables and acceptance criteria

Parameter	Test	Decision criterion
CQD batch quality	Emission maximum, quantum yield, particle size, FTIR/XPS	Stable emission and reproducible batch response
pH optimization	pH 3-11	Select pH giving maximum signal-to-blank ratio

Parameter	Test	Decision criterion
Response time	0-30 min	Time to reach $\geq 95\%$ of stable response
Calibration	At least 6 concentration levels + blank	R ² reported with residual check
Precision	n = 3-5 per level	RSD preferably <5%
Selectivity	Common ions and co-contaminants	Target response remains distinguishable
Real-water accuracy	Spike recovery	80-120% exploratory; 90-110% preferred
Stability	Storage at 4 °C	Signal retention monitored over 2-4 weeks

Results

Because this is a methodology paper, the values below are treated as literature benchmarks and expected analytical behavior rather than newly generated laboratory data. The literature indicates that CQD fluorescence can support environmental sensing over a wide concentration range. Mercury sensing was demonstrated early using CQD-based optical-fiber platforms [2] and was later improved through selective photoluminescent probes [6] and thymine-functionalized recognition chemistry [10]. For iron, dopamine-derived CQDs provided direct label-free detection through fluorescence modulation [3]. These examples support the use of metal-ion tests as positive controls when validating a newly synthesized CQD batch.

For pesticides, different signal architectures produced markedly different behavior. Wu et al. [7] exploited FRET for organophosphate determination, whereas Lin et al. [8] reported a modification-free turn-on response and Wang et al. [9] used an Au(III)/acetylcholinesterase off-on system. Tafreshi et al. [12] reported cauliflower-derived CQDs that detected diazinon, amicarbazone, and glyphosate by concentration-

dependent fluorescence quenching; reported detection limits were 0.25, 0.5, and 2 ng mL⁻¹, respectively, and the method was tested in cherry-tomato samples. These results indicate that green CQDs can be analytically useful, but analyte discrimination in mixtures can remain challenging when several compounds produce the same direction of fluorescence change.

Organic aromatic pollutants show similarly strong but mechanism-dependent responses. Bogireddy et al. [11] reported N-doped oxidized carbon dots for 4-nitrophenol optical sensing. Li et al. [13] demonstrated red CQDs with aggregation-induced emission enhancement for tetracycline antibiotics, reporting nanomolar detection limits for individual tetracycline-class compounds. Sinha et al. [14] demonstrated picric-acid sensing with tobacco-derived N-doped carbon dots in real water samples, and Wang et al. [15] extended green CQDs to sulcotrione detection. The expected outcome of the proposed workflow is therefore not one universal quenching relationship; rather, each pollutant class should be assigned the calibration model that best matches its physicochemical interaction with the CQD surface.

Table 3. Representative literature benchmarks used to interpret the proposed study

Pollutant	CQD system	Signal	Reported LOD	Ref.
Diazinon	Cauliflower-derived CDs	Turn-off / quenching	0.25 ng mL ⁻¹	[12]
Amicarbazone	Cauliflower-derived CDs	Turn-off / quenching	0.5 ng mL ⁻¹	[12]
Glyphosate	Cauliflower-derived CDs	Turn-off / quenching	2 ng mL ⁻¹	[12]
Tetracycline	Red fluorescent CDs	Turn-on / AIE enhancement	12 nM	[13]
Oxytetracycline	Red fluorescent CDs	Turn-on / AIE enhancement	23 nM	[13]
Chlortetracycline	Red fluorescent CDs	Turn-on / AIE enhancement	25 nM	[13]
Hg ²⁺	Thymine-functionalized CDs	Selective quenching	3.5 × 10 ⁻⁸ mol L ⁻¹	[10]

Conclusion and Discussion

The evidence available through 2021 supports CQDs as a versatile fluorescent platform for environmental sensing, but it also shows that sensitivity alone is not sufficient to establish analytical usefulness. Surface composition,

excitation wavelength, pH, ionic strength, analyte absorbance, and matrix components can all change the observed signal. Metal-ion sensing commonly relies on coordination-driven quenching or specific recognition motifs [2,3,6,10], whereas pesticides may require direct

FRET, enzyme-linked recovery, or nonspecific quenching pathways [7-9,12]. Organic pollutants such as 4-nitrophenol, tetracyclines, picric acid, and sulcotrione illustrate that electron transfer, inner-filter effects, and aggregation-related emission can also dominate [11,13-15]. Accordingly, the proposed methodology places mechanism verification, interference testing, and real-water recovery at the same level of importance as LOD. A successful CQD sensor should demonstrate a reproducible synthesis, a stable optical window, a statistically defensible calibration range, acceptable precision, resistance to relevant interferents, and recovery in realistic matrices. Future work can improve field applicability through ratiometric or multi-emission CQDs, paper or fiber immobilization, smartphone-based fluorescence readout, and recognition layers that distinguish pollutants producing similar quenching signatures. Overall, CQDs offer a low-cost and chemically adaptable route toward rapid environmental screening, particularly when green synthesis is combined with rigorous analytical validation.

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