A Fluorescence Switching Sensor for Sensitive and Selective Detections of Cyanide and Ferricyanide Using Mercuric Cation-Graphene Quantum Dots

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ABSTRACT: This study aims to use graphene quantum dots (GQDs) as a fluorescence switching sensor (turn on−off) for the simultaneous detection of cyanide (CN⁻) and ferricyanide [Fe(CN)₆]³⁻ in wastewater samples. The GQDs were synthesized by pyrolyzing solid citric acid. The intrinsic blue color of the solution was observed under ultraviolet irradiation. The fluorescence spectrum was maximized at both excitation and emission wavelengths of 370 and 460 nm, respectively. The fluorescence intensity of GQDs decorated with Hg²⁺ (turn-off mode as the starting baseline) could be selectively turned on in the presence of CN⁻ and once back to turn-off mode by [Fe(CN)₆]³⁻. The fluorescence switching properties were used to develop a fluorescence turn-on−off sensor that could be used to detect trace amounts of CN⁻ and [Fe(CN)₆]³⁻ in water samples. For highly sensitive detection under optimum conditions (Britton−Robinson buffer solution in the pH range of 8.0−9.0, linearity ranges of 5.0−15.0 μM (R² = 0.9976) and 10.0−50.0 μM (R² = 0.9994), respectively, and detection limits of 3.10 and 9.48 μM, respectively), good recoveries in the ranges of 85.89−112.66% and 84.88−113.92% for CN⁻ and [Fe(CN)₆]³⁻, respectively, were recorded. The developed methods were successfully used for the simultaneous and selective detection of CN⁻ and [Fe(CN)₆]³⁻ in wastewater samples obtained from local municipal water reservoirs.

1. INTRODUCTION

Cations and anions are ubiquitous in nature and play a critical role in daily life. They also find their utility in the industrial, biological, and environmental systems.¹ The absorption of ions through the skin, gastrointestinal tract, and lungs results in health hazards. The side effects include vomiting, convulsions, loss of consciousness, anesthetization of the central nervous system, and inhibition of the aerobic respiration of cells. These can potentially cause dyspnea and eventual death.²⁻⁵ The high toxicity of CN⁻ is caused by its binding with iron present in cytochrome c oxidase. The interaction between CN⁻ and iron in cytochrome c oxidase can prevent the transfer of electrons from cytochrome c oxidase to oxygen, which results in hypoxia.⁶ However, CN⁻ also plays a critical role in multifunctional reactions in many industrial processes such as chemical synthesis, metallurgy, electroplating, plastic production, and extraction of gold and silver. As a result, CN⁻ is released into the environment.⁷ According to the World Health Organization (WHO), the permitted concentration of CN⁻ in drinking water should be lower than 1.9 μM. A concentration of CN⁻ in the range of 0.5−3.5 mg/kg body weight is lethal to human beings.⁸⁻¹⁰

It is known that transition metal cations are very dangerous. In the following sections, the role of ferric ions (Fe³⁺) has been discussed. The Fe³⁺ ion is one of the most abundant elements. This transition metal ion plays an important role in maintaining the proper function of the environmental and biological systems and is an indispensable trace element present in living organisms. It plays an important role in many physiological processes such as DNA synthesis, hemoglobin generation, oxygen transport, and storage. It also helps coordinate brain activity, etc.¹¹,¹² It is important to maintain the proper concentration of Fe³⁺ in the human body. Fe³⁺ is incorporated into the daily diet for the growth and develop-
Fe\textsuperscript{3+} ions mostly accumulate within the liver, spleen, and bone marrow cells. They can also bind to ferritin. However, both its deficiency and overload can potentially cause serious disorders and diseases in humans.\textsuperscript{14} The deficiency of Fe\textsuperscript{3+} can induce iron deficiency anemia (IDA) and reduce the activity of the iron enzyme in the body, resulting in metabolic disorders and diabetes. It also damages the liver and kidney. An excessive amount of Fe\textsuperscript{3+} in the human body can also cause hepatic and renal injury. It can also result in Parkinson’s and Alzheimer’s diseases. Iron deficiency is attributed to coronary heart disease, cancer, immune system dysfunction, and diabetes.\textsuperscript{15–17} Moreover, in the field of environmental quality assessment, the content of Fe\textsuperscript{3+} is an important indicator of water quality as the iron ions are present in their stable forms in solution (present as Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, complex anions, and/or other organo-iron complexes). However, the US Environmental Protection Agency has reported that the limit of detection was lower than the maximum level (0.3 mg/L, equivalent to 5.4 \(\mu\)mol/L) of Fe\textsuperscript{3+} permitted in drinking water.\textsuperscript{18} If Fe\textsuperscript{3+} is intentionally used as ferricyanide ([Fe(CN)\textsubscript{6}]\textsuperscript{3–}), then it can be found in water reservoirs as a highly fluorescent material. In situ and quantitative fluorescent materials. In situ and quantitative detection of the target pollutants helps in rapid and highly sensitive detection.\textsuperscript{19,20} The process is technically simple. Graphene quantum dots (GQDs) are carbon nanoparticles with a diameter of <10 nm and are emerging as fluorescent materials.\textsuperscript{21,22} They can be fabricated as single-, double-, or multi-layered compounds (3 to <10). They also exhibit luminescence properties. These are cost-efficient and exhibit good optical stability, low toxicity, good biocompatibility, and unique electronic properties.\textsuperscript{23} To achieve tunable fluorescence emissions, good photostabilities, favorable biocompatibilities, easy functionalization, and robust chemical inertness, it can also be used as an electron acceptor or donor.\textsuperscript{24–26} Some reports have revealed that the fluorescence intensity of GQDs can be quenched by Hg\textsuperscript{2+} and Fe\textsuperscript{3+} ions.\textsuperscript{27,28} The detection process of turn-off sensors involves the interference of background fluorescence and is inconveniently applied down to the sensing field. The turn-on sensor is superior to the turn-off sensor. It is more valuable and can find its applications in various fields.\textsuperscript{29–31}

In this study, a simple and low-cost synthetic strategy to prepare Hg\textsuperscript{2+}-quenched graphene quantum dots (Hg\textsuperscript{2+}-GQDs) as a fluorescence turn-on–off sensor has been reported that can be used for the simultaneous selective detection of CN\textsuperscript{−} and [Fe(CN)\textsubscript{6}]\textsuperscript{3–} ions. The complex [Fe(CN)\textsubscript{6}]\textsuperscript{3–} is a complex ligand involved in food anticaking. The uncoordinated nitrogen atoms of the CN\textsuperscript{−} groups can act as efficient hydrogen bond acceptors and are considered as chemically “evergreen”, which is also true for Berlin Blue.\textsuperscript{32,33} Generally, GQDs emit a strong fluorescence in an aqueous solution. Hg\textsuperscript{2+} ions could significantly quench the fluorescence intensity of the GQDs. When CN\textsuperscript{−} ions were added to the Hg\textsuperscript{2+}-GQD solution, they could selectively interact with Hg\textsuperscript{2+}. This can potentially result in the destruction of the Hg\textsuperscript{2+}-GQD complex, and the turn-on fluorescence mode can be recovered. However, the turn-off fluorescence mode could be re-established when [Fe(CN)\textsubscript{6}]\textsuperscript{3–} was selectively added to the test solution. The fluorescence intensity of the Hg\textsuperscript{2+}-GQDs was linearly related to their concentration of the CN\textsuperscript{−} and [Fe(CN)\textsubscript{6}]\textsuperscript{3–} ions. The fluorescence switching sensor can be potentially used for the simultaneous and selective determination of CN\textsuperscript{−} and [Fe(CN)\textsubscript{6}]\textsuperscript{3–} ions with different sensitivity ranges in real water samples.

2. RESULTS AND DISCUSSION

2.1. Characterization of GQDs. The ATR-FTIR spectra of GQDs are shown in Figure 1. The bands corresponding to the stretching vibration of the hydroxyl groups were observed at approximately 3338 cm\textsuperscript{−1}. The C=C stretching bands of
the polycyclic aromatic groups appeared at 1554 cm\(^{-1}\),\(^{34,35}\) and the C–O stretching bands (COH/COC (epoxy) groups) appeared in the range of 1377–1107 cm\(^{-1}\).\(^{36}\) The results revealed that the GQDs could be successfully synthesized by pyrolyzing citric acid that provided the structure identity of graphene.

The obtained sample was characterized using the transmission electron microscopy (TEM) technique to determine the particle size of the GQDs. Figure 2 reveals that the GQDs exhibit a uniform and consistent spherical shape (diameter, 7.12 ± 3.8 nm). The nano GQDs exhibited characteristic fluorescence properties.

The elemental composition of the samples was determined using the energy-dispersive X-ray spectroscopy (EDX) technique (Figure 3). The compositional elements were determined (34.1% O, 31.2% C, and 34.7% Na). Their peaks (GDQ samples) were commonly found in association with C (0.277 keV) and O (0.525 keV). The presence of the Na peak could be attributed to the use of the NaOH solution as the GQD stabilizer.

The XPS technique was used to determine the detailed chemical composition and the chemical bond environment of the GQD samples (Figure 4). In most of the cases, GQDs are composed of C, O, Na, and H (Figure 4a). The high-resolution spectrum of C 1s (Figure 4b) could be deconvoluted into three surface components, corresponding to sp\(^2\) C (C=–C=C–C) at a binding energy of 284.8 eV, sp\(^3\) C (C–OH) at a binding energy of 286.2 eV, and C=O at a binding energy of 288.3 eV. The presence of the sp\(^3\) C peak in the XPS spectral profile suggests a significant reduction in the planarity of the GQDs and the appearance of defects in the prepared GQDs. The high-resolution spectrum of O 1s (Figure 4c) confirmed the
Figure 4. (a) XPS survey spectrum of GQDs, (b) high-resolution C 1s XPS spectra of GQDs, and (c) high-resolution O 1s XPS spectra of GQDs.

Figure 5. UV–visible absorption spectrum and FL excitation and emission spectra of the GQDs.
presence of the C=O (531.1 eV), C−OH (532.3 eV), and O=C−OH (535.7 eV) bonds. These results suggest that the prepared GQDs are rich in oxygen-containing functional groups. The C/O ratio in GQDs, calculated from XPS spectra, was 51.51/48.49.

2.2. Spectral Properties of GQDs. The UV−visible absorption spectral profiles of the GQD samples are shown in Figure 5. A typical absorption band at 365 nm can be observed, which can be ascribed to the π−π* transition in the graphitic sp² domains.37 The fluorescence spectrum of the GQDs shows a strong emission peak at 460 nm when excited at 370 nm. The full width at half maximum (FWHM) was at 100 nm, which resembles that of most of the graphene quantum dots.30 The fluorescence quantum yield of GQDs can also be determined by comparing the data with those obtained using quinine sulfate (quantum yield = 0.54 at 360 nm) as a reference. The quantum yield of the synthetic GQDs was calculated to be approximately 28.7%. It is calculated using the slope of the plot of integrated fluorescence intensity vs absorbance, and n is the refractive index (taken here as 1.33, assuming both solutions exhibit the same refractive index of distilled water). The subscripts S and R refer to the GQD and reference fluorophore (quinine sulfate) solutions, respectively.38

2.3. Linear Quenching Effect Exhibited by GQDs in the Presence of Hg²⁺. The fluorescence intensity of the GQDs was quenched using various concentrations of Hg²⁺ to adjust the signal window of the Hg²⁺-based GQD system. Figure 6a shows the quenching effect of Hg²⁺ concentration on the fluorescence intensity of GQDs. The fluorescence intensity decreases with increasing Hg²⁺ concentration. A linear correlation was obtained in the range of 0−40 μM when the maximum fluorescence intensity at 460 nm was plotted against the Hg²⁺ concentration (Figure 6b). The calibration curve was plotted between F₀ − F and the concentration of Hg²⁺ using 20 μM Hg²⁺. The fluorescence intensity of the GQDs could be quenched with a relative quenching effect of 88.75%. Therefore, this concentration of Hg²⁺ was used for further experiments. The Hg²⁺ quenching effect was also studied using the Stern−Volmer equation36 (Figure 6c). The fluorescence intensities of the GQD samples were almost quenched and could be turned on. The suitable concentration of Hg²⁺ was found to be 30 μM.

Figure 6. (a) FL in the emission spectra of the GQDs at different Hg²⁺ concentrations (0−40 μM), (b) FL in the emission intensity at 460 nm versus the Hg²⁺ concentration in 0.05 M Britton−Robinson buffer (pH 8), and (c) linear relationship of F₀ − F versus the concentration of Hg²⁺ over the range 0−20 μM.
2.4. Optimum Conditions for the Use of Hg$^{2+}$-GQD Fluorescence Sensors for the Selective Detection of CN$^-$ and [Fe(CN)$_6$]$^{3-}$ Detection Using Hg$^{2+}$-GQDs

A water sample was used as a model to simplify the interactions present in the system when Hg$^{2+}$-GQDs were used as the substrate sensors to simultaneously detect CN$^-$ and [Fe(CN)$_6$]$^{3-}$ present in the same sample. A graphical scheme for the fluorescence turn-on–off sensor for the detection of CN$^-$ and [Fe(CN)$_6$]$^{3-}$ using Hg$^{2+}$-GQDs as the background substrate is shown in Scheme 1. Generally, the GQDs exhibit significantly strong blue fluorescence in a basic solution. Following the addition of Hg$^{2+}$, the fluorescence of GQDs gets quenched. The ionic interactions present in Hg$^{2+}$-GQDs might be reversible as labile Hg$^{2+}$ ions are complexed with surface functional groups in GQDs. The fluorescence

Scheme 1. A Graphical Scheme for the Fluorescence Turn-On–Off Sensor of CN$^-$ and [Fe(CN)$_6$]$^{3-}$ Detection Using Hg$^{2+}$-GQDs

Figure 7. Effect of pH on (a) GQDs, (b) Hg$^{2+}$-GQDs, (c) Hg$^{2+}$-GQDs + CN$^-$, and (d) Hg$^{2+}$-GQDs + CN$^-$ + [Fe(CN)$_6$]$^{3-}$.
intensities of GQDs will be self-recovered, which can be used to quantify CN− as Hg2+-GQDs can easily interact with the ligand CN− to form Hg(CN)2 in solution. The fluorescence intensity of the GQDs could be recovered. Similarly, when [Fe(CN)6]3− was added into a solution of Hg2+-GQDs in the presence of CN−, the fluorescence intensity of the GQDs was quenched as the [Fe(CN)6]3− ions could selectively interact with the GQDs (common ion effect of the ferricyanide anion) under the optimal conditions. The experimental conditions, including solution pH, reaction time, sonication time, and concentrations of both ionic strength and masking agents were optimized, to improve the CN− and [Fe(CN)6]3− detection performance.

2.4.1. Effect of Solution pH. The effect of pH on the fluorescence intensity was investigated as pH-sensitive functional groups were present in GQDs (Figure 7). A series of Britton–Robinson buffer solutions (each 0.05 M) at different pH values were prepared, and the GQD solution together with the Hg2+, CN−, and [Fe(CN)6]3− was added successively to each of the buffer solutions (pH range, 2.0–12.0). The fluorescence intensity of the GQDs at 460 nm was recorded using the buffer solutions. The fluorescence intensity of the GQDs increased sharply within the pH range of 3.0–5.0. Following this, the intensity stabilized under alkaline conditions in the pH range of 6.0–9.0. This implies that the total turn-off–on–off of the Hg2+, CN−, and [Fe(CN)6]3− would be at pH > 6.0. However, it was found that the pH of Hg2+-GQDs + CN− was stabilized in the pH range of 6–9. Thus, the stability of the GQDs was sensitive to solution pH that was set in the range of 8.0–9.0 (Figure 7c).

Figure 8. Effect of sonication time on the fluorescence intensity of the Hg2+-GQDs by CN− and [Fe(CN)6]3− ions in 0.05 M Britton–Robinson buffer (pH 8): (a) GQDs, (b) Hg2+-GQDs, (c) Hg2+-GQDs + CN−, and (d) Hg2+-GQDs + CN− + [Fe(CN)6]3−.

Figure 9. Effect of reaction time on the fluorescence intensity of the Hg2+-GQDs by CN− and [Fe(CN)6]3− ions in 0.05 M Britton–Robinson buffer (pH 8): (a) GQDs, (b) Hg2+-GQDs, (c) Hg2+-GQDs + CN−, and (d) Hg2+-GQDs + CN− + [Fe(CN)6]3−.
2.4.2. Effect of Sonication Time and Reaction Time. Figure 8 reveals the sonication time after adding CN\(^-\) to Hg\(^{2+}\)-GQDs. The fluorescence intensity recorded at 460 nm was plotted against the sonication time, as shown in Figure 8c. After 5 min, the turn-on signal of CN\(^-\) decreased, following which it increased rapidly and remained steady for 30 min. However, in the absence of sonication, the signal remained constant for another 30 min. The effect of reaction time was also studied, as shown in Figure 9. It was observed that when CN\(^-\) or [Fe(CN)]\(_6\)\(^{3-}\) was added to Hg\(^{2+}\)-GQDs (Figure 9c), the turn-on mode of CN\(^-\) increased rapidly and remained constant for 5 min. The turn-off mode of [Fe(CN)]\(_6\)\(^{3-}\) decreased and then remained constant for 5 min (Figure 9d). The results revealed that the reaction time of the turn-on–off sensor was approximately 5 min.

2.4.3. Effects of the Concentration of NaCl in Adjusting the Ionic Strength and EDTA as a Masking Agent. The effect of NaCl (concentrations: 0.05, 0.10, 0.15, 0.20, and 0.25 M) as an ionic strength adjuster was investigated, as shown in Figure 10. The effect of EDTA (concentrations: 0.01, 0.02, 0.03, 0.04, and 0.05 M) as a masking agent was also studied, as shown in Figure 11. It was observed that the ionic strength did not affect the fluorescence intensity of the Hg\(^{2+}\)-GQDs. This is another aim to provide a strong electrolyte to the reactive species of the mixed nanoparticle solution, which could be done in conjunction with the addition of EDTA to mask the interference of some metal ions present in wastewater samples.
However, the EDTA masking agent had an effect on the fluorescence intensity of the Hg\(^{2+}\)-GQDs. When EDTA solution was added, the fluorescence intensity increased rapidly, and then, its slope decreased slowly when the concentration of the EDTA solution reached 0.01 M. Therefore, in the process of decorating the surface of the GQDs with Hg\(^{2+}\), EDTA should be absent in the matrix system. Other interfering metal ions in water samples should be masked with EDTA prior to conducting the tests with the Hg\(^{2+}\)-GQD sensor.

2.4.4. Detection of CN\(^{-}\) Using Hg\(^{2+}\)-GQDs as a Fluorescence Turn-On Sensor. The Hg\(^{2+}\)-GQD solutions were added successively to varying concentrations of CN\(^{-}\) (0–40 \(\mu\)M). At first, the quenching of GQD fluorescence was observed due to the presence of the Hg\(^{2+}\) ions present on the surface of the GQDs. Upon the addition of CN\(^{-}\), it would react with the Hg\(^{2+}\) in the GQD solution, resulting in the increase in the fluorescence intensity of Hg\(^{2+}\)-GQDs with the increase in the CN\(^{-}\) concentration, as shown in Figure 12a. The fluorescence intensities of each solution were recorded, and a linear relationship was obtained in the concentration range of 5–15 \(\mu\)M, when the maximum fluorescence intensity at 460 nm was plotted against the CN\(^{-}\) concentration range of 5–15 \(\mu\)M. The intensity ratios of \(F/F_0\) for the Hg\(^{2+}\)-GQDs in the presence of various anions, including iodide (I\(^-\)), chloride (Cl\(^-\)), bromide (Br\(^-\)), hydroxide (OH\(^-\)), thiocyanate (SCN\(^-\)), acetate (CH\(_3\)COO\(^-\)), nitrate (NO\(_3^-\)), iodate (IO\(_3^-\)), cyanate (CN\(^-\)), carbonate (CO\(_3^{2-}\)), and sulfate (SO\(_4^{2-}\)), were obtained, as shown in Figure 13.

To study the selectivity of the Hg\(^{2+}\)-GQD sensor for CN\(^{-}\) detection, the intensity ratios of \(F/F_0\) for the Hg\(^{2+}\)-GQDs in the presence of various anions, including iodide (I\(^-\)), chloride (Cl\(^-\)), bromide (Br\(^-\)), hydroxide (OH\(^-\)), thiocyanate (SCN\(^-\)), acetate (CH\(_3\)COO\(^-\)), nitrate (NO\(_3^-\)), iodate (IO\(_3^-\)), cyanate (CN\(^-\)), carbonate (CO\(_3^{2-}\)), and sulfate (SO\(_4^{2-}\)), were obtained, as shown in Figure 13. The concentration of each anion was 100 \(\mu\)M, the same as that of the CN\(^{-}\) in the assay solution. The addition of CN\(^{-}\) to those solutions resulted in an apparent recovery of the fluorescence intensity (turn-on mode), whereas the other remaining anions exerted no effect under the same optimal conditions.

2.4.5. Detection of [Fe(CN)\(_6\)]\(^{3-}\) Using Hg\(^{2+}\)-GQDs-CN\(^{-}\) as the Fluorescence Turn-Off Sensor. It was found that when [Fe(CN)\(_6\)]\(^{3-}\) was added into the mixed solution containing Hg\(^{2+}\)-GQDs and CN\(^{-}\), the fluorescence intensity decreased (turn-off), as shown in Figure 14a,b. The calibration curve was plotted between \(F_0 - F\) and the concentration of [Fe(CN)\(_6\)]\(^{3-}\).

Figure 12. (a) FL in the emission spectra of the Hg\(^{2+}\)-GQDs at different CN\(^{-}\) concentrations (0–40 \(\mu\)M), (b) FL in the emission intensity at 460 nm versus CN\(^{-}\) concentration in 0.05 M Britton–Robinson buffer (pH 8), and (c) linear relationship of \(F - F_0\) versus the concentration of CN\(^{-}\) over the range 5–15 \(\mu\)M.

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(µM), as shown in Figure 14c. The slope in the concentration range of 10−50 µM [Fe(CN)₆]³⁻ significantly decreased with the increase in the concentration of [Fe(CN)₆]³⁻. Following this, the slope gradually decreased and remained constant. [Fe(CN)₆]³⁻ is capable of generating higher oxidation states of iron via the Fenton reaction. Ferricyanide is slowly reduced under a dry air atmosphere, forming cyanogen and ferricyanide in small amounts, according to reactions 2−4⁴⁰

\[
[\text{Fe(CN)}]^{3-} \rightarrow [\text{Fe(CN)}]^{5-} + \text{CN} \quad (2)
\]

\[
\text{CN}^- + [\text{Fe(CN)}]^{3-} \rightarrow [\text{Fe(CN)}]^{5-} + \text{C}_2\text{N}_2 \quad (3)
\]

\[
2\text{CN}^- \rightarrow \text{C}_2\text{N}_2 \quad (4)
\]

The fluorescence intensities of the GQDs in the presence of various metal ions, such as Hg²⁺, Fe³⁺, Mg²⁺, Ni²⁺, Mn²⁺, Co²⁺, Cu²⁺, Zn²⁺, Cr³⁺, Cd²⁺, Pb²⁺, and Fe²⁺, were investigated. The values of \( F/F_0 \) were plotted using 100 µM of each metal. Figure 15 shows that the maximum extent of fluorescence quenching was observed when Hg²⁺ (decorating the surface of GQDs) was added. Similar observations were made when Fe³⁺ (Fe³⁺ from [Fe(CN)₆]³⁻) was added to the reaction mixture containing the Hg²⁺-quenched GQDs. The other cations had no significant effect under the same experimental conditions.

2.5. Method Validation. As shown in Table 1, the analytical characteristics of the developed method were validated under the optimized conditions in terms of linearity, the limit of detection (LOD), the limit of quantification (LOQ), and precision (expressed as the relative standard deviation (RSD)) for Hg²⁺. The results are summarized in Table 1. The fluorescence intensity of the GQDs at different [Fe(CN)₆]³⁻ concentrations (0−400 µM), the fluorescence intensity at 460 nm versus [Fe(CN)₆]³⁻ concentration in 0.05 M Britton−Robinson buffer (pH 8), and the linear relationship of \( F_0 - F \) versus the concentration of [Fe(CN)₆]³⁻ over the range 10−50 µM.
terms of repeatability (intraday precision, respectively. The precision values, which were evaluated in
Table 2, were 3.10 and 9.48% for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively. The values demonstrated an
acceptable reproducibility of the developed method.

2.6. Real Sample Analysis. Both CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\) were determined in wastewater samples collected from
municipal water reservoirs in Khon Kaen City. To demonstrate the applicability and reliability of the developed method, it was
successfully used to analyze the natural water samples under optimum conditions. The contents of CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\) in
these samples were determined (Table 2). The results showed that trace amounts of CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\) were not
detectable in the water samples under study. The accuracy of the developed method was verified by calculating the recovery in
the real samples to evaluate the matrix effect. Each sample was spiked with three concentrations (5.0, 50.0, and 100.0
μM) of the standard solution of CN\(^{-}\) and with three concentrations (5.0, 50.0, and 250.0 μM) of the standard
solution of [Fe(CN)\(_6\)]\(^{3-}\). The relative percentage recoveries were calculated as follows\(^{41}\)

\[
\%\text{recovery} = \left(\frac{C_{\text{found}} - C_{\text{real}}}{C_{\text{added}}}\right) \times 100 \quad (5)
\]

where \(C_{\text{found}}\), \(C_{\text{real}}\), and \(C_{\text{added}}\) are the concentration of an analyte after addition of a known amount of a standard in the
real sample, the concentration of an analyte in the real sample, and the concentration of a known amount of a standard that
was spiked in the real sample, respectively. The recoveries were expressed as the mean values of three independent
determinations. The recovery ranged from 85.89 to 112.66% and 84.88 to 113.92% for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively,
indicating that they were free of matrix interferences. The methods provide acceptable recovery, demonstrating that they
can be efficiently used for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\) determination in the real samples. The results using the developed
method were also compared with previously reported results, as shown in Table 3.\(^{42-48}\)

3. CONCLUSIONS

In summary, we reported a new method for the fabrication of a
fluorescence turn-on--off sensor using the Hg\(^{2+}\)-quenched GQDs for the simultaneous determination of CN\(^{-}\) and
[Fe(CN)\(_6\)]\(^{3-}\) present in wastewater samples obtained from municipal water reservoirs. The advantage of the proposed
method is its simplicity. The proposed method can be used for the rapid detection of both anions present in an aqueous
solution. Interestingly, the Hg\(^{2+}\)-GQD sensor could selectively detect [Fe(CN)\(_6\)]\(^{3-}\) in the presence of the acceptable levels of
CN\(^{-}\) under the optimum conditions. This detection procedure was not affected by other interfering ions. The Hg\(^{2+}\)-GQD
fluorescence sensor was highly sensitive with limits of detection of 3.10 and 9.48 μM for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively. The fluorescence switching sensor can be effectively used for the simultaneous detection of trace amounts of CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\) in real water samples.

4. MATERIALS AND METHODS

4.1. Chemicals. All of the chemicals used were of analytical
grade. Citric acid, mercury chloride, potassium cyanide, and
boric acid were obtained from Qrec (New Zealand). Potassium ferricyanide was purchased from BOH Chemicals Ltd.
(England). Sodium hydroxide was obtained from Carlo Erba

Figure 15. Quenching of the fluorescence intensity of the GQDs by
different metal ions. All the ions were at 100 μM concentration. F and
\(F_o\) are the emission intensities of the GQDs at 460 nm either in the
presence or in the absence of some metal ions in 0.05 M Britton–
Robinson buffer (pH 8).

### Table 1. Analytical Characteristics of the Hg\(^{2+}\)-GQD System for the Simultaneous Determination of CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\)

| analytical parameter | analytical range (μM) | [Fe(CN)\(_6\)]\(^{3-}\) | CN\(^{-}\) |
|----------------------|------------------------|------------------------|---------|
| linear range (μM)    | 5–15                   | 10–50                  |
| linear equation      | \(y = 28.047x - 68.911\) | \(y = 3.4616x + 53.658\) |
| correlation coefficient (\(R^2\)) | 0.9976                 | 0.9994                |
| limit of detection (μM, n = 11) | 3.10                   | 9.48                  |
| limit of quantification (μM, n = 11) | 5.17                   | 15.81                 |
| relative standard deviation (%) for intraday analysis (n = 9) | 0.47                   | 1.94                  |
| relative standard deviation (%) for interday analysis (n = 11) | 4.47                   | 9.72                  |

deviation (%RSD) of the calibration slope obtained from both
intraday and interday analysis) to estimate the efficiency and
feasibility of the method for use with water samples. The
linearity ranges were found to be 5–15 μM (\(R^2 = 0.9976\)) and
10–50 μM (\(R^2 = 0.9994\)) for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively. The limit of detection (LOD) was defined as
3SD/m (where SD is the standard deviation of a very low
concentration of CN\(^{-}\) or [Fe(CN)\(_6\)]\(^{3-}\) and m is the slope of the
calibration graph), and the values were 3.10 and 9.48 μM for
CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively. The limit of quantification (LOQ) is defined as 3SD/m, and the values were
5.17 and 15.81 μM for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively. The precision values, which were evaluated in
terms of repeatability (intraday precision, \(n = 3 \times 3\)), were 0.47
and 1.94% for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively, and the reproducibilities (work performed during 5 × 3 consecutive
days, interday RSD) were 4.47 and 9.72% for CN\(^{-}\) and [Fe(CN)\(_6\)]\(^{3-}\), respectively. The values demonstrated an
acceptable reproducibility of the developed method.
both the UV experiments. A quartz cuvette (1 cm path length) was used in emission slit width of 5 nm was primarily used to conduct the experiments. A fresh solution of Hg²⁺-quenched GQDs was also prepared. One milliliter of approximately 1.0 mg mL⁻¹ GQD solution and Britton–Robinson buffer (0.05 mol L⁻¹, pH 8) were mixed in a 10 mL volumetric flask. Subsequently, various concentrations of either CN⁻ or [Fe(CN)₆]³⁻ ions were added to an aliquot of the buffered GQD solution (10 mL final volume) at room temperature. The Hg²⁺-quenched fluorescence spectrum of each solution was recorded immediately at \( \lambda_{ex} / \lambda_{em} = 370/460 \) nm. The spectral data were used to plot the quenching linear curve to determine the optimum condition for setting the turn-off baseline of the Hg²⁺-GQD sensor.

### 4.3. Preparation of GQDs and Hg²⁺-Quenched GQDs.

Graphene quantum dots (GQDs) were prepared following the citric acid pyrolysis method. Citric acid (1.0 g) was transferred to a 100 mL round-bottom flask, which was heated at 220 °C for approximately 5 min using a paraffin oil bath. The solid citric acid was liquefied, and its color changed to yellow. Following this, 50 mL of NaOH (0.25 M) was added to the round-bottom flask, and the mixture was continuously stirred for 30 min at room temperature. The obtained solution of GQDs was refrigerated (4 °C) for further experiments. A fresh solution of Hg²⁺-quenched GQDs was also prepared. One milliliter of approximately 1.0 mg mL⁻¹ GQD solution and Britton–Robinson buffer (0.05 mol L⁻¹, pH 8) were mixed in a 10 mL volumetric flask. Subsequently, various concentrations of either CN⁻ or [Fe(CN)₆]³⁻ ions were added to an aliquot of the buffered GQD solution (10 mL final volume) at room temperature. The Hg²⁺-quenched fluorescence spectrum of each solution was recorded immediately at \( \lambda_{ex} / \lambda_{em} = 370/460 \) nm. The spectral data were used to plot the quenching linear curve to determine the optimum condition for setting the turn-off baseline of the Hg²⁺-GQD sensor.

### 4.4. Simultaneous Detection and Method Validation of CN⁻ and [Fe(CN)₆]³⁻.

Various concentrations of either CN⁻ and/or [Fe(CN)₆]³⁻ ions and 30 \( \mu \)L of the Hg²⁺-quenched GQD solution were mixed with Britton–Robinson buffer solution (0.05 mol L⁻¹) adjusted to various pH values (10 mL final volume) at room temperature. For the selective determination of CN⁻ and [Fe(CN)₆]³⁻ ions, a suitable and known concentration of CN⁻ solution (turn-on mode) was used to generate the linear curve of the [Fe(CN)₆]³⁻ solution before recording the fluorescence spectrum (turn-off mode) of each solution (at \( \lambda_{ex} / \lambda_{em} = 370/460 \) nm). Such spectral

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### Table 2. The Contents and Their Recoveries of CN⁻ and [Fe(CN)₆]³⁻ in Water Samples Using the Hg²⁺-GQD System (n = 3)

| water sample          | CN⁻ added (μM) | found (μM) | recovery (%) ± SD | [Fe(CN)₆]³⁻ added (μM) | found (μM) | recovery (%) ± SD |
|-----------------------|----------------|------------|-------------------|------------------------|------------|-------------------|
| drinking water brand 1| 5.0            | 4.29       | 85.89 ± 0.32      | 5.0                    | 5.10       | 102.09 ± 2.52     |
|                       | 50.0           | 47.32      | 94.64 ± 0.47      | 50.0                   | 50.33      | 100.65 ± 1.64     |
|                       | 100.0          | 95.52      | 95.52 ± 0.64      | 250.0                  | 248.35     | 99.34 ± 2.18      |
| drinking water brand 2| 5.0            | 4.83       | 96.64 ± 0.96      | 5.0                    | 5.20       | 104.08 ± 3.11     |
|                       | 50.0           | 53.18      | 106.36 ± 1.09     | 50.0                   | 50.89      | 101.78 ± 2.32     |
|                       | 100.0          | 112.66     | 112.66 ± 2.0      | 250.0                  | 245.18     | 98.07 ± 0.84      |
| drinking water brand 3| 5.0            | 4.62       | 92.42 ± 2.38      | 5.0                    | 4.32       | 86.33 ± 2.47      |
|                       | 50.0           | 52.34      | 104.68 ± 1.22     | 50.0                   | 44.52      | 89.04 ± 2.32      |
|                       | 100.0          | 106.36     | 106.36 ± 0.95     | 250.0                  | 232.07     | 92.83 ± 1.46      |
| drinking water brand 4| 5.0            | 4.73       | 94.89 ± 1.19      | 5.0                    | 4.44       | 108.72 ± 2.34     |
|                       | 50.0           | 51.12      | 102.23 ± 2.48     | 50.0                   | 55.23      | 110.46 ± 1.43     |
|                       | 100.0          | 104.42     | 104.42 ± 2.14     | 250.0                  | 258.15     | 103.26 ± 1.66     |
| drinking water brand 5| 5.0            | 4.78       | 95.67 ± 1.21      | 5.0                    | 4.31       | 86.27 ± 2.42      |
|                       | 50.0           | 52.21      | 104.42 ± 2.11     | 50.0                   | 42.44      | 84.88 ± 1.37      |
|                       | 100.0          | 101.43     | 101.43 ± 1.22     | 250.0                  | 225.92     | 90.37 ± 2.06      |
| tap water 1            | 5.0            | 4.42       | 88.49 ± 2.37      | 5.0                    | 4.71       | 94.21 ± 6.72      |
|                       | 50.0           | 52.45      | 104.90 ± 1.76     | 50.0                   | 50.36      | 100.71 ± 1.74     |
|                       | 100.0          | 109.86     | 109.86 ± 2.55     | 250.0                  | 242.20     | 96.88 ± 1.35      |
| tap water 2            | 5.0            | 4.98       | 99.64 ± 2.54      | 5.0                    | 5.37       | 107.34 ± 2.56     |
|                       | 50.0           | 52.12      | 104.32 ± 2.51     | 50.0                   | 55.36      | 110.72 ± 2.34     |
|                       | 100.0          | 110.02     | 110.02 ± 2.49     | 250.0                  | 264.95     | 105.98 ± 2.11     |
| tap water 3            | 5.0            | 4.75       | 94.97 ± 2.14      | 5.0                    | 5.70       | 113.92 ± 6.38     |
|                       | 50.0           | 51.82      | 103.63 ± 1.27     | 50.0                   | 55.17      | 110.34 ± 2.49     |
|                       | 100.0          | 107.48     | 107.48 ± 1.30     | 250.0                  | 269.20     | 107.68 ± 2.85     |

| carbon-based material | analytes | LOD (μM) | reference |
|-----------------------|----------|----------|-----------|
| azoic dye with benzenoamide | cyanide | 20 | 42 |
| C-dots | ferric | 9.97 | 43 |
| PVA-containing azoic dye with trifluoroacetyl | cyanide | 39 | 45 |
| SBA-15-DNPH | ferric | 0.91 | 46 |
| Rhodamine-based arylpropenone azo dyes | cyanide | 1.29 | 47 |
| N-acetylalmito aldehyde hydradione azo dye | cyanide | 1.37 | 48 |
| CD₁ | ferric | 3.10 | 49 |
| Hg²⁺-GQDs | cyanide | 9.48 | 50 |

### Table 3. Comparison of Different Methods for the Detection of CN⁻ and [Fe(CN)₆]³⁻ Ions

| carbon-based material | analytes | LOD (μM) | reference |
|-----------------------|----------|----------|-----------|
| citric acid | cyanide | 20 | 42 |
| C-dots | ferric | 9.97 | 43 |
| PVA-containing azoic dye with trifluoroacetyl | cyanide | 39 | 45 |
| SBA-15-DNPH | ferric | 0.91 | 46 |
| Rhodamine-based arylpropenone azo dyes | cyanide | 1.29 | 47 |
| N-acetylalmito aldehyde hydradione azo dye | cyanide | 1.37 | 48 |
| CD₁ | ferric | 3.10 | 49 |
| Hg²⁺-GQDs | cyanide | 9.48 | 50 |
measurements were used to plot the increasing calibration curve for CN\(^-\) and the quenching calibration curve for [Fe(CN)\(_6\)]\(^{3-}\).

The optimum conditions for the dual detection of CN\(^-\) and [Fe(CN)\(_6\)]\(^{3-}\) were also investigated in detail. Moreover, to evaluate the performance of the developed method, the optimized conditions were validated in terms of linearity, limits of detection, limits of quantification, and precision (expressed as the relative standard deviation (%RSD) of the calibration slope obtained from intraday and interday analysis). Finally, the Hg\(^{2+}\)-GQD-based switching sensor was used to detect trace amounts of CN\(^-\) and [Fe(CN)\(_6\)]\(^{3-}\) in wastewater samples obtained from municipal water reservoirs in Khon Kaen, Thailand.

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