Ultratrace Detection of Nickel(II) Ions in Water Samples Using Dimethylglyoxime-Doped GQDs as the Induced Metal Complex Nanoparticles by a Resonance Light Scattering Sensor

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ABSTRACT: This study aimed to synthesize dimethylglyoxime (DMG) (N-source)-doped graphene quantum dots (N-GQDs) via simultaneous pyrolysis of citric acid and 1.0% (w/v) DMG. The maximum excitation wavelength ($\lambda_{\text{max, ex}} = 380$ nm) of the N-GQD solution (49% quantum yield (QY)) was a red shift with respect to that of bare GQDs ($\lambda_{\text{max, ex}} = 365$ nm) (46% QY); at the same maximum emission wavelength ($\lambda_{\text{max, em}} = 460$ nm), their resonance light scattering (RLS) intensity peak was observed at $\lambda_{\text{max, ex/em}} = 530/533$ nm. FTIR, X-ray photoelectron spectroscopy, XRD, energy-dispersive X-ray spectroscopy, and transmission electron microscopy analyses were performed to examine the synthesized materials. The selective and sensitive detection of Ni²⁺ using the RLS intensity was performed at 533 nm under the optimum conditions consisting of both 25 mg L⁻¹ N-GQDs and 2.5 mg L⁻¹ DMG in the ammonium buffer solution of pH 9.0. The linearity of Ni²⁺ was $50.0 - 200.0 \mu$g L⁻¹ with a regression line, $y = 5.031x - 190.4$ ($r^2 = 0.9948$). The limit of detection (LOD) and the limit of quantitation (LOQ) were determined to be 20.0 and 60.0 $\mu$g L⁻¹, respectively. The method precision expressed as % RSDs was 4.90 for intraday ($n = 3 \times 3$) and 7.65 for interday ($n = 5 \times 3$). This developed method afforded good recoveries of Ni²⁺ in a range of 85–108% when spiked with real water samples. Overall, this innovative method illustrated the identification and detection of Ni²⁺ as a DMG complex with N-GQDs, and the detection was highly sensitive and selective.

1. INTRODUCTION

Because of their unique chemical, mechanical, and optical properties, graphene quantum dots (GQDs) have gained a lot of interest in the scientific community.¹⁻⁴ Compared to the standard semiconductor quantum dots (QDs), GQDs have many unique properties such as high biocompatibility, low toxicity, excellent solubility, robust photoluminescence (PL), and tunable band gaps,⁵⁻⁷ which have prompted many possible applications of GQDs that include photodetectors,⁸⁻⁹ bioimaging,¹⁰⁻¹¹ fluorescent agents,¹⁴⁻¹⁷ adsorbent,¹⁸,¹⁹ and sensors.¹⁰⁻¹¹ As a consequence, the identification limit, selectivity, sensitivity, and biocompatibility are very different in GQDs in comparison with that of QDs.¹² Because of their excellent optical, electrical, mechanical, and thermal properties, GQDs have become one of the most common options to incorporate in sensors for detecting toxic metal ions.¹³ The success of GQDs as sensors has been highlighted in several research studies comparing each class of semiconductor QDs.

Heteroatom doping is a powerful way to alter the electronic density of GQDs, and thus, tuning their optical and electrical properties is an important research direction. In GQDs, nitrogen atoms are doped in one of the three states: pyridinic-N, graphitic-N, or pyrrolic-N. The increase in the active sites in the form of pyridinic-N/pyrrolic-N normally happens because of the increased catalytic action of N-doped graphene.²⁴⁻²⁶ Because of its higher electronic conductivity, graphitic-N can boost electrocatalytic activity.²⁷ According to a recent study, nitrogen injected into GQDs could enhance their PL properties,²⁸ although the improved PL characteristics are not yet well known. In a previous research report, N-doped GQDs and C-dots were synthesized by standard synthetic pathways to improve the nitrogen content and quantum yields (QY). Notably, in this case, a...
simple hydrothermal route was followed to use dimethylglyoxime (DMG) as a N source for the doped nitrogen in GQDs. The as-synthesized N-doped GQDs (N-GQDs) had a high pyrrolic-N content that marginally improved PL QY. The improved PL properties were due to the pyrrolic-N formation in GQD areas that replaced the −COOH functional groups at the edges of GQDs. The pyrrolic-N ring-forming process in N-GQDs was also explored in that report.

To protect public health from dietary exposure to toxic metals, it is necessary to control the increasing global environmental emissions by systematic monitoring of toxic heavy metals in water. To evaluate water quality, several criteria and components should be maintained and calculated. Strict regulations for certain elements are required, especially for heavy metals that belong to the first category and capable of resulting in potential harm to human health. Nickel, in particular, is regarded as extremely poisonous and remains in the atmosphere forever and thus can easily bioaccumulate in humans and marine animals. In high concentrations, even though minor quantities of nickel enter the atmosphere, they can be preserved permanently, thereby resulting in adverse environmental effects. The World Health Organization (2000) deemed the absolute maximum permissible limit for nickel in drinking water up to 0.02 mg L$^{-1}$, although the U.S. Environmental Protection Agency permitted a maximum limit of 0.01 mg L$^{-1}$. Therefore, a simple, quick, and convenient detection method is demanding, particularly to detect Ni at the ultratrace level. Several techniques were used for the assessment of heavy metals, including FAAS, ICP–AES, or ICP–OES, and SQT–FAAS. However, these processes have several drawbacks, such as higher cost, requirements of higher sample volume, and complexity of the device. Therefore, we were interested in developing a method for the determination of nickel in water samples via the RLS technique.

The RLS is a special light dispersion that occurs when the dispersed light wavelength is located at or near the molecular absorption band. Conformation, interfacial properties, molecular size, and shape have a strong influence on the spectral characteristics and strength of the dispersions, and these parameters provide more favorable data for the study of biomacromolecular interaction and molecular recognition. In recent years, the RLS technology has been extensively used for the quantitative studies of drugs, surfactants, proteins, and heavy metal ions. In general, it is defined by speed, simplicity, high sensitivity, and ease that can be handled by a common fluorophotometer. In this process, nickel forms a complex with the DMG ligand, which is a chelating substance with a high ability to create stable complexes with heavy metals. Because of certain properties, such as high photostability against photobleaching, linkage, biocompatibility, and low toxicity, nickel–DMG (Ni–DMG) interaction has received much interest, while the use of GQDs as an auxiliary ligand also becomes popular because of their typical characteristics.

Based on the aforementioned background, we have been motivated to develop a new RLS probe for nickel (Ni$^{2+}$) determination based on DMG–GQDs. The RLS amplitude of the N-GQD nanoparticles increased linearly in the presence of nickel ions. The interactions between the analyte and N-GQDs for the aggregation of nanoparticles occurred because of the formation of larger amounts of complexes. The evolved method was further used for calculating the ultratrace nickel levels in actual water samples. Additionally, the details of optimal conditions were analyzed, including the concentration of DMG and GQDs, pH of the solution, ionic strength, masking agent, and interfering ions. To explore the practical utility, the developed method was then implemented for determining the ultratrace nickel in real water samples.

2. RESULTS AND DISCUSSION

2.1. Characterization of GQDs and N-GQDs. Figure 1 and Table 1 depict the FTIR spectra of GQDs and N-GQDs.

![Figure 1. FTIR spectra of GQDs (a), DMG (b), and N-GQDs (c).](https://doi.org/10.1021/acsomega.1c00190)

**Table 1. FTIR Assignment of DMG, GQDs, and N-GQDs**

| functional group | wavenumber (cm$^{-1}$) |
|------------------|-----------------------|
|                  | DMG                   | GQDs                  | N-GQDs                |
| −OH              | 3200                  | 3300                  | 3340 (−OH, −NH)       |
| −NH              | (−OH, −NH)            | (−OH only)            | 1647 (−OH)            |
| −CH              | 2933 (−CH)            | 2940 (−CH)            |                      |
| C≡C              | 1558 (C≡C)            | 1549 (C≡C)            |                      |
| C≡N              | 1435 (C≡N)            | 1449 (C≡N)            |                      |
| C≡O              | 1380 (C≡O)            |                      |                      |
| N−OH             | 1357 (N−OH)           |                      |                      |
| N−O              | 1137−974              |                      | 1279 (N−O)            |

The absorption peaks at 3300, 1558, and 1380 cm$^{-1}$ were observed in the vibration range of GQDs (in Figure 1a, the vibration modes of O−H stretching, C−H stretching, C≡C stretching of polycyclic aromatic hydrocarbons, and C≡O in COH/COC (epoxy) groups are visible). These findings indicated that GQDs were successfully synthesized through citric acid pyrolysis. Figure 1c illustrates the FTIR spectrum of N-GQDs, where the wideband at 2900−3500 cm$^{-1}$ referred to the stretching vibrations of O−H and N−H. The absorption peaks at ∼1647, 1549, and 1218 cm$^{-1}$ indicate the vibration of O−H, C≡C, and N−O, respectively. The IR
spectrum at approximately 1400 cm\(^{-1}\) originated because of the C–NH vibration mode, indicating that the nitrogen atom was successfully doped onto the GQD surface.\(^{44}\) These FTIR spectra could therefore confirm the formation of N-GQDs.

X-ray photoelectron spectroscopy (XPS) was used to determine the structure of elemental compositions including carbon-, oxygen-, and nitrogen-bonding configurations in N-GQDs; the survey spectrum has been shown in Figure 2a. The peaks at ∼284.68, 399.84, and 531.76 eV are assigned to the binding energies of carbon (C 1s), nitrogen (N 1s), and oxygen (O 1s), respectively. The peaks at 531.11, 532.31, and 535.82 eV in the XPS spectrum of O 1s (Figure 2b) indicated the existence of the functional groups C\(\equiv\)O, C\(\equiv\)OH, and C\(\equiv\)O\(\equiv\)C, respectively. This result clearly showed the effective doping of nitrogen into GQDs. In Figure 2c, the high-resolution N 1s of the N-GQDs could be divided into three peaks at 397.98 (pyridinic-N), 399.97 (pyrrolic-N), and 402.04 eV (graphitic-N), and it could be visible that the pyrrolic-N was the main component. As seen in the C 1s high-resolution N-GQD XPS spectrum (Figure 2d), the presence of a variety of functional oxygen groups indicated incomplete carbonization in the process of pyrolysis of citric acid and DMG. In the C 1s spectra of N-GQDs, three additional peaks at 284.78, 285.96, and 288.28 eV were observed. The N-GQDs contained 60.5% carbon, 36.9% oxygen, and 2.53% nitrogen, as calculated by XPS spectra.

Next, the crystallinity and composition of GQDs were evaluated for XRD measurements (Figure 3). Two peaks close to the 2θ value of 31.21° and 35.08° were observed on the XRD QGD pattern, which corresponded to the (100) and (102) hexagonal carbon planes.\(^{45}\) The patterns of N-GQDs revealed that the peaks at the 2θ values of 15.31°, 26.18°, 31.02°, and 35.21° represented the (111), (002), (100), and (102) Miller indices,\(^{46}\) respectively, which confirmed the presence of GQDs. The XRD pattern confirmed the existence of large peaks at 2θ = 26.18°, which was related to the amorphous nature and disordered carbons of N-GQDs.\(^{47}\)

Furthermore, energy-dispersive X-ray spectroscopy (EDX), as seen in Figure 4a,b, confirmed the elementary composition of GQDs and N-GQDs. The compositional components were identified as 34.7% of O, 31.2% of C, and 34.7% of Na in the GQDs and 34.3% of O, 44.4% of C, and 21.3% of Na in the N-GQDs. As the NaOH solution was used in the synthetic process, the peak of Na was observed in both GQDs and N-GQDs.
GQDs. According to the spectra of N-GQDs, the weak N (0.392 keV) signals were overlapped between C and O, and the elemental C content of the N-GQDs was greater than that of GQDs. Hence, according to the data obtained by EDX, both C and O (0.277 keV) were present in N-GQDs. As shown in Figure 5, the transmission electron microscopy (TEM) images of N-GQDs were collected to assess the morphology. The TEM images revealed that the synthesized N-GQDs were relatively uniform and well dispersed. Their sizes were estimated to be around 4.98 ± 1.30 nm.

Figure 4. EDX images of (a) GQDs and (b) N-GQDs.

Figure 5. TEM images of N-GQDs.

on the GQDs, the emission spectra shifted toward the blue region at 428 nm, attributing to broaden its band gap energy. Because of the increase in stability at the exciting equilibrium state, the spectrum of GQD–DMG shifted toward the shorter wavelength (blue shift) as compared to that of bare GQDs. Thus, the successful doping of DMG in GQDs was verified. The findings revealed a brighter blue emission of the GQD solution than that of the N-GQD solution. The RLS, regardless of the blue solution emission, depends on its measurement, shape, configuration, and interfacial properties.48

The strong fluorescence intensity of N-doped GQDs was also studied by using quinine sulfate solution as a reference. The fluorescence QY of the N-doped GQDs were observed to be 49% higher than that of the GQDs (45%), so this may be concluded that the doped N on the GQD surface significantly increased the fluorescence QY of the GQDs. The QY (Q) of GQDs and N-GQDs were determined using eq 1. Quinine sulfate in 0.1 M H2SO4 was selected as a standard reference compound (Q = 0.54 at 360 nm).

\[
Q = \frac{Q_R \times [m/m_R] \times [n^2/n_R^2]}{\Delta \lambda}
\]  

(1)

Since Q is the QY, m is the slope of the mentioned regression line, n is a refractive index that is assumed to be equal to 1.33 for both solutions, and the subscript R refers to quinine sulfate solution.

2.2. Effect of Excitation Wavelength with N-GQDs. A detailed RLS analysis with different excitation wavelengths was conducted for further characterization of the optical properties of the synthesized N-GQDs, as shown in Figure S1. The wavelength for excitation ranges was between 410 and 590 nm, and the intensities of RLS increased remarkably at the excitation wavelength of 530 nm. This wavelength suited well to resonance light scattering (RLS) measurements of the N-GQDs associated with Ni–DMG complex solution and has been selected for this experiment.

2.3. Effect of the Ni–DMG Complex Associated with N-GQDs. Figure S2 shows the RLS spectra using synchronous excitation and emission maximum wavelengths of \( \lambda_{ex}/\lambda_{em} = 530/533 \) nm (\( \Delta \lambda = 3 \)) of Ni–DMG. For all the examined systems, the RLS spectrum of Ni–DMG exhibited the excitation wavelength at 530 nm, while the emission wavelength was at 533 nm. As shown in Figure S3, the RLS intensity increased after the inclusion of GQDs and N-GQDs in the Ni–DMG complex solution. This could be explained by the graphical mechanism, as suggested in Figure 7. During the analyte interactions, the ligands contributed to the aggregation of the nanoparticles to form large amounts of the metal–ligand complexes; a subsequent increase in the RLS amplitude was observed, which was associated with the size distribution of the complex nanoparticles caused by the solution mixture.

2.4. Effect of DMG Concentration on Ni–DMG Complex Formation. The DMG concentration was optimized for the nickel–DMG complex formation. The effects of DMG solution on Ni2+ RLS was evaluated by using the spectrofluorophotometer at a concentration of 0.5–40 mg L\(^{-1}\) (Figure S4a). The findings revealed that the RLS intensity increased with an increase in the DMG concentration. The increase of the RLS intensity of N-GQD nanoparticles was caused by the interaction of DMG with Ni2+. However, the abundance of the DMG solution (only 2.5 mg L\(^{-1}\)) was chosen to reduce according to the volume of the reagent as required for further experimental conditions.

Figure 6 illustrates the fluorescence spectra of the GQDs, DMGs, and N-GQDs as well as the 365 nm UV illumination photograph of the solutions of the GQDs and N-GQDs. GQDs and GQDs with DMG both produced about 460 nm emission spectrum. When DMG was bound and/or decorated to reduce according to the volume of the reagent as required for further experimental conditions.

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14799
2.5. Effect of Concentration of N-GQDs. In terms of detection sensitivity, N-GQD concentration in the RLS sensor played an important role. The size effects of N-GQDs, which depend on their dimensions, shape, and interface properties, are responsible for their behaviors. Thus, the intensity of the RLS also explicitly contributed to the N-GQDs. By controlling the pH of the solution at 9.0 with 0.5 M ammonium buffer, the N-GQD concentration was ranged from 10 to 500 mg L^{-1} (Figure S4b). As the concentration of N-GQDs increased, the RLS intensities also increased subsequently. The maximal signal was observed to vary across these spectra with the concentration of N-GQD. However, an addition of 25 mg L^{-1} N-GQDs was selected for consistent manipulation.

2.6. Effect of pH. The pH of the solution affected the production of the Ni–DMG–(N-GQDs) complex as an induced component. By controlling the pH of the solution at 9.0 with 0.5 M ammonium buffer, the N-GQD concentration was ranged from 10 to 500 mg L^{-1} (Figure S4b). As the concentration of N-GQDs increased, the RLS intensities also increased subsequently. The maximal signal was observed to vary across these spectra with the concentration of N-GQD. However, an addition of 25 mg L^{-1} N-GQDs was selected for consistent manipulation.

2.7. Effect of Incubation Time. Incubation times were evaluated, as seen in Figure S4d, after combining Ni^{2+} with DMG and DMG–(N-GQDs). The incubation time effect was analyzed within 5–60 min of the reaction time. According to the results, the RLS of the reaction system increased at 30 min, indicating that the testing solution should be done within 30 min. After mixing Ni^{2+} with Ni–DMGs, the DMG–(N-GQDs) exhibited a stable signal during the incubation period, indicating the contribution of N-GQDs to the complex stability.
2.8. Effect of Temperature. After mixing Ni\(^{2+}\) with DMG and DMG–(N–GQDs), the influence of temperature was also assessed and has been shown in Figure S5a. In the temperature range from 10 to 50 °C, the temperature effect was studied. The results indicated that a higher sensitivity of the RLS could be achieved at 10 °C.

2.9. Effect of Ionic Strength. As shown in Figure S5b, the influence of ionic strength on RLS was examined. The NaCl solutions with varying concentrations (0.001–1.0 M) were selected as the ionic model. The findings indicated that the RLS increased with a concentration of 0.05 M NaCl. Thus, the strength of the ion was found to dominate the electrostatic reaction.\(^5\) The increase in the NaCl concentration resulted in the aggregation of nanoparticles because of the influence of the electrostatic interaction.\(^5\) Notably, there was no light scattering action to prefer the presence of 0.05 M NaCl concentration as an ionic strength.

2.10. Effect of a Masking Agent. Also, the impact of the masking agent on the RLS intensity was studied with the 0.005–0.5 M EDTA (Figure S5c). The signal of the RLS was observed at a range from 0.05 to 0.1 M, while the levels of EDTA increased gradually. Consequently, the concentration of 0.1 M EDTA was selected as the optimal condition for the proposed system to mask other intervening metal ions.

2.11. Effect of Foreign Ion Interference. Further, the effects of interferences on the determination of Ni\(^{2+}\) by the RLS method were explored for the environmental samples. In addition to the target analysis, the interfering ions for the

| Table 2. Comparison of Different Methods for the Detection of Ni\(^{2+}\) |
|---------------------------------|-----------------|-----------------|-----------------|
| material                        | technique       | LOD             | linear          | reference |
| CD–imidazole                     | fluorescence    | 0.93 mM         | 6–100 mM        | 52        |
| sodium dodecyl sulfate-coated alumina | FAAS          | 9.31 × 10\(^{-3}\) mM | 0.17–17.24 mM | 53        |
| monohydrazide of quinoxaline aldehyde | UV–vis        | 1.2 × 10\(^{-4}\) mM | 0.17–2.59 mM | 55        |
| AgNPs                            | colorimetric method | 1.8 µM         |                 | 56        |
| hydrazide-based sensor           | colorimetric method | 0.4 µM         |                 | 57        |
| NBD-based sensor                 | colorimetric method | 67 µg L\(^{-1}\) |                 | 58        |
| ACDA                             | UV–vis spectroscopy | 1000 µg L\(^{-1}\) |           | 59        |
| 1-(2-pyridylazo)-2-naphthol     | fluorescence    | 0.17 µmol L\(^{-1}\) | 1.70–85.20 µmol L\(^{-1}\) | 60        |
| DMG–(N–GQDs)                     | RLS             | 19.0 µg L\(^{-1}\)a | 50.0–200.0 µg L\(^{-1}\)b | this work |

\(^{a}\)LOD, 19.0 µg L\(^{-1}\) = 6.53 × 10\(^{-8}\) M. \(^{b}\)Linear range, 50.0–200.0 µg L\(^{-1}\) = 1.72 × 10\(^{-7}\)–6.88 × 10\(^{-7}\).
assessment of Ni\textsuperscript{2+} that were known to be present in drinking water were also investigated. The results are summarized in Table S1.

2.12. Analytical Features of the Proposed Method. A linearity, LOD, LOQ, accuracy (% RSD), and precision (% recovery) were validated to determine the RLS of the present system for quantitative applications. Figure S6 illustrates the RLS value of the DMG–(N-GQDs) at various levels of Ni\textsuperscript{2+}. After increasing the concentration of Ni\textsuperscript{2+} from 50.0 to 200.0 μg L\textsuperscript{-1}, the sensitivity of RLS increased linearly as a result of the increase in the amounts of Ni\textsuperscript{2+}. The results demonstrated a strong linear connection between the RLS and concentration of Ni\textsuperscript{2+}. The regression equation was found to be $y = 5.031 \times [\text{Ni}^{2+}] (\mu g \text{ L}^{-1}) - 31.0$, with $r^2 = 0.9948$.

Table 2 displays the effects of Ni\textsuperscript{2+} in several methods, such as FAAS, UV–visible spectrophotometry, fluorescence sensor, and colorimetry. The major inductive effects of ionic interactions between Ni\textsuperscript{2+} and DMG were nanoparticle aggregation and their tendency to form rigid structures for generating stable complexes of heavy metals. Furthermore, the complex Ni\textsuperscript{2+}–DMG could be calculated using the light scattering approach based on the complex structure, form, and composition, which has high efficiency and sensitivity (in ppb level). This paper revealed that the lowest LOD of 19.0 μg L\textsuperscript{-1} ($6.53 \times 10^{-8}$ M) was located in the N-GQD used for Ni\textsuperscript{2+} detection.

The RLS signal limitation was assessed by the LOD and LOQ. In the context of the optimum conditions, including the concentration of N-GQDs (25 mg L\textsuperscript{-1}) and ammonium buffer of pH 9.0, the linear range of Ni\textsuperscript{2+} was 50.0–200.0 μg L\textsuperscript{-1} along the regression line, $y = 5.031x - 190.4$ ($r^2 = 0.9948$). The LOD and LOQ of the present method were derived from the nickel level, which generated the test signal for a highly sensitive Ni\textsuperscript{2+} detection using the intensity of RLS at 533 nm. Then, LOD and LOQ were detected at concentrations of 20.0 and 60.0 μg L\textsuperscript{-1}, respectively. The relative standard deviation (RSD) in repeatability and reproducibility was examined. The reproducibility of the linearity slopes (intraday, $n = 3 \times 3$) and the reproducibility (interday, $n = 5 \times 3$) were also obtained. Table S2 displays intraday and interday precisions at 4.90% and 7.65%, respectively. Table S3 summarizes the optimal conditions for the identification of nickel in drinking water and tap water and provides optimal chemical values and response times.

2.13. Real Sample Analysis. In different water sample matrices, including drinking water and tap water, a method was suggested for the identification of Ni\textsuperscript{3+}. The accuracy of the process was checked by measuring the recovery study for the samples. The standard Ni\textsuperscript{3+} solution was spiked with three concentrations (125, 200, and 500 μg L\textsuperscript{-1}). The relative recoveries of the percentage were then determined accordingly.$^{52}$

$$\% \text{ recovery} = \frac{C_{\text{spiked}} - C_{\text{unspiked}}}{C_{\text{added}}} \times 100 \hspace{1cm} (2)$$

where $C_{\text{found}}$, $C_{\text{real}}$, and $C_{\text{added}}$ are the concentration of the analyte after the addition of a known amount of standard in the real sample, the concentration of the analyte in the real sample, and the concentration of the known amount of standard that was spiked in the real sample, respectively; the results are shown in Table 3. The Ni\textsuperscript{2+} recovery efficiencies were achieved with 85–108%, which, under ideal conditions, are well acceptable. The validation method was also contrasted with the ICP–OES method, allowing statistical comparison between the measurements made with the standard method by the proposed method, which indicated that this method was acceptable for evaluating Ni\textsuperscript{2+}.

3. CONCLUSIONS

A new analytical approach for the induction of the DMG-doped N-GQD nanoparticles linked to the Ni–DMG complex has been presented in this report. The produced DMG–(N-GQDs) nanoparticles offered greater sensitivity and specificities to the RLS intensity. Other metal ions in the sample water scarcely bothered them. DMG–(N-GQDs) represented an excellent linear relationship with Ni\textsuperscript{2+} in the range of 50–200.0 μg L\textsuperscript{-1} ($r^2 = 0.9948$), and LOD was reduced at the ultratrace level of 19.0 μg L\textsuperscript{-1}. The findings showed that the Ni\textsuperscript{2+} identification could be done in the environment using DMG–(N-GQDs). The developed analytical method was very basic, quick, efficient, and environmentally friendly.

4. EXPERIMENTAL SECTION

4.1. Chemicals. All chemical products used in this work belonged to analytical grade. Citric acid and sodium hydroxide were purchased from Carlo Erba (Italy). Ammonium chloride (Ajax Finechem, Australia), ammonium hydroxide (QRec, New Zealand), nickel(II) nitrate hydrate (BDH, England), and DMG (Sigma-Aldrich, Germany) were the other chemicals used in this research work. Paraffin oil was purchased from Ajax Finechem (Australia). During the tests, deionized water (Simplicity Water Purification System, Model Simplicity 185, Millipore, USA) was used.

4.2. Apparatus. A spectrofluorophotometer (Shimadzu RF-5301PC, Japan) with excitation and emission slit widths of 3–5 nm was used. The pH meter (Model Proline B21, Beckthai Equipment & Chemical, Thailand), analytical balance (Model LX 220A, Precisa, Thailand), quartz cell with 1 cm path length (Fisher Scientific, USA), and ultrasonic cleaner (Model VGT-2300, GT SONIC, Hong Kong) were also used. A round-bottomed flask (Pyrex, England) and hot plate with a magnetic stirrer in association with a paraffin oil bath were utilized for the pyrolysis of citric acid.

4.3. Synthesis and Characterization of GQDs and N-GQDs. Citric acid pyrolysis was performed to prepare GQDs. In short, 1 g of citric acid was taken into a 100 mL round-bottomed flask and heated to 230 °C for 5 min in a paraffin bath. It liquidated the citric acid and changed the color quickly to yellow. A dropwise addition of 25 mL of 0.25 M NaOH was then dissolved, with continuous stirring for 30 min. The solution obtained was deposited at 4 °C before operation.

The citric acid was concurrently treated with DMG for the synthesis of N-doped GQDs to find out the optimum condition for N-doping. Citric acid (0.9 g) and 1% (w/v) DMG were transferred into a 100 mL round-bottomed flask, which was heated to 230 °C in an oil bath for 5 min and then dissolved into 25 mL of 0.25 M NaOH solution, as mentioned above. Finally, the N-GQD solution was stored at 4 °C before use.

4.4. RLS Measurements. In a 10 mL volumetric flask, 25 mg L\textsuperscript{-1} N-GQD was combined with 2.5 mg L\textsuperscript{-1} and 0.5 M ammonium buffer of pH 9. Ni\textsuperscript{2+} ions of different concentrations were then added to the portion of the reaction complex (10 mL final volume). Each induced metal complex
nanoparticles were registered with Ni\(^{2+}\) RLS intensity immediately at \(\lambda_{\text{ex}}/\lambda_{\text{em}} = 530/533\) nm. Then, the RLS measurements were performed to plot the RLS external calibration curve for Ni\(^{2+}\).

4.5. Real Sample Analysis. To ensure the practical applicability of the proposed approach for actual water samples, including drinking and tap water, further experiments were carried out to assess the N-GQD RLS sensor for Ni\(^{2+}\) detection simultaneously on an artificial device. Drinking water of five different brands was taken from a store in Khon Kaen, Thailand. Tap water samples were obtained from the laboratories using a polyethylene bottle. They were pretreated with 1% v/v nitric acid. During this process, 1 mL of the water sample was transferred to a 10.0 mL volumetric flask with 0.25 mL of N-GQD (25 mg L\(^{-1}\)) solution. The standard Ni\(^{2+}\) solution was then spiked into three stages of sample mixtures (125.0, 200.0, and 500.0 \(\mu g\) L\(^{-1}\)).

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00190.

RLS emission spectra of Ni–DMG–(N-GQDs), absorption and RLS emission spectra of Ni–DMG \(\lambda_{\text{em}}^\text{ex} = 533/530\) nm, RLS spectra of Ni–GQDs, Ni–(N-GQDs), and Ni–DMG–(N-GQDs), effect of DMG concentration, effect of N-GQD concentration, effect of pH, effect of incubation time, effect of temperature, effect of ionic strength, effect of concentration of EDTA, linearity of Ni\(^{2+}\) in \(\mu g\) L\(^{-1}\) of Ni–DMG–(GQD–DMG), tolerance limits and recoveries of Ni ions, intraday and interday precision of the proposed method, and optimum conditions of nickel analysis in real water samples (PDF).

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