

FABRICATION OF MERCURY SENSOR USING DITHIZONE–MODIFIED GRAPHENE QUANTUM DOTS

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Abstract

This study presents the fabrication and evaluation of a mercury sensor based on dithizone–modified graphene quantum dots; GQDs. The sensor was fabricated using a filter paper coated with GQDs and functionalized with dithizone, then assembled with gold electrodes for electrochemical measurement. The sensor was tested with various concentrations of mercury (II) chloride to evaluate its sensing performance. The results revealed a noticeable shift in color. The color changed from blue to orange, indicating the formation of a complex between mercury ions (Hg^{2+}) and dithizone–modified GQDs. Electrical measurements revealed a non–ohmic current–voltage response with a consistent threshold voltage of approximately 2.50 V across all conditions. The sensor exhibited a clear correlation between mercury concentration and sensor response, where increased resistance and decreased conductivity corresponded to higher Hg^{2+} levels. Linear regression analysis showed a strong correlation, indicating high sensitivity and potential for quantitative detection. These results suggest that the proposed sensor was a promising low–cost, portable, and reliable tool for monitoring mercury contamination in environmental settings.

Keywords: Graphene quantum dots, Dithizone, Mercury detection, Electrochemical sensor, Heavy metal monitoring

Introduction

Mercury (Hg) is a highly toxic heavy metal that poses significant risks to human health. Exposure to mercury can occur through inhalation, ingestion, or dermal absorption, leading to severe physiological and neurological disorders. Chronic mercury exposure has been linked to kidney damage, cognitive impairment, developmental abnormalities, and cardiovascular diseases (World Health Organization, 2017). Furthermore, mercury contamination in the environment, particularly in water sources, leads to bioaccumulation in aquatic organisms, increasing the risk of mercury poisoning through the food chain. The World Health Organization; WHO recommends a maximum concentration of 0.006 mg/L in drinking water (World Health Organization, 2017). In Thailand, the Pollution Control Department limits mercury in surface water to 0.001 mg/L (Ministry of Natural Resources and Environment, 2023). Mercury contamination in Thailand remains a serious environmental and public health concern. Cosmetics, water bodies, industrial areas, and consumer goods have been identified as key sources of mercury exposure (Ministry of Natural Resources and Environment, 2023). Regulatory measures have been strengthened under the Minamata Convention, but continuous monitoring, enforcement, and public awareness are essential to further reduce mercury pollution and its health impacts. Therefore, analytical techniques are necessary. Current several analytical techniques have been employed for mercury detection in environmental and industrial samples. These methods include atomic absorption spectrometry; AAS, inductively coupled plasma mass spectrometry (ICP–MS), and X-ray fluorescence (XRF) spectroscopy (Gumpu et al., 2015). These conventional methods offer high sensitivity and precision in detecting trace levels of mercury. However, they require sophisticated instrumentation, trained personnel, and substantial operational costs, making them impractical for routine field applications. Despite their accuracy, traditional mercury detection methods have some limitations. The need for complex sample preparation, expensive laboratory infrastructure, and time-consuming analysis restricts their applicability for on-site mercury monitoring. Additionally, these techniques are not suitable for real-time detection, which is important for assessing immediate contamination risks. (Gul, Ullah & Khan, 2022). Consequently, there is a growing demand for low-cost, portable, and user-friendly mercury sensors that provide rapid detection with high selectivity.

To overcome the limitations of conventional detection methods, researchers have focused on developing electrochemical and optical sensor platforms for mercury monitoring (Gumpu et al., 2015). Electrochemical sensors operate by converting the chemical interaction between

mercury ions and the sensor surface into measurable electrical signals—such as changes in current, voltage, or resistance—allowing for precise quantification of mercury concentration. In contrast, optical sensors detect mercury ions by monitoring changes in optical properties like color or fluorescence, which occur when the sensor material reacts with the target analyte. These platforms offer advantages such as rapid response, high sensitivity, low cost, and the ability to perform real-time detection without the need for complex instrumentation. One promising approach involves fabricating sensor with functionalized nanomaterials capable of selectively interacting with mercury ions (Azmi, Ahmad & Low, 2018; Raril & Manjunatha, 2020; Sulthana et al., 2024; Wu, Sun & Zou, 2015). These sensors can facilitate rapid detection through measurable changes in electrical or optical signals, making them suitable for field applications and real-time analysis (Gul, Ullah & Khan, 2022; Ju & Chen, 2015; Sulthana et al., 2024). Dithizone is a well-known chelator widely used in chemical sensors for heavy metal detection. It exhibits a strong affinity for mercury ions, forming stable dithizone- Hg^{2+} complexes that induce observable spectral and electrical changes (Azmi, Ahmad & Low, 2018; Wu, Sun & Zou, 2015). This property makes dithizone an excellent candidate for use in sensor development, enabling highly selective mercury detection even at low concentrations. Graphene quantum dots; GQDs have emerged as a promising nanomaterial for sensor applications due to their unique electronic, optical, and chemical properties (Ju & Chen, 2015). Therefore, the functionalization of GQDs with dithizone is expected to enhance their selectivity toward mercury ions (Hg^{2+}) by utilizing the strong coordination between dithizone and mercury ions. The combination of GQDs and dithizone results in a highly sensitive and portable mercury sensor capable of rapid detection through electrochemical or fluorescence-based mechanisms.

This study aims to fabricate a dithizone-modified GQDs sensor for efficient and accurate mercury detection. By utilizing the strong coordination between dithizone and Hg^{2+} , the sensor was expected to exhibit high sensitivity, selectivity, and portability, making it an alternative to conventional detection methods. The fabrication of the mercury sensor involved the preparation of a sensing pad, where GQDs were coated onto a filter paper substrate and functionalized with dithizone. The gold electrodes were then integrated into the sensor to facilitate electrochemical measurements. Mercury detection was performed using varying concentrations of mercury chloride (HgCl_2) solutions, and the sensor's electrical response was analyzed through current-voltage (I-V) characteristics using a Keithley 6517A electrometer. The high precision of

the electrometer facilitates the characterization of resistive sensors operating in the high-resistance range, which is critical for detecting trace analytes such as heavy metals. Its application in this study ensured accurate sensor evaluation and highlights its versatility in materials research, sensor engineering, and environmental monitoring.

Materials and Methods

1. Preparation of graphene quantum dots

Graphene quantum dots; GQDs were synthesized via the hydrothermal method using citric acid as the carbon source, as previously reported (Li et al., 2015; Raktham, Wongrerkdee & Pimpang, 2024). Specifically, the synthesis involved dissolving 7 g of citric acid in 100 mL of deionized water. The reaction mixture was then heated at 200°C in an autoclave for 10 hours. After synthesis, the GQDs were stored at room temperature, and ethanol was added to maintain the initial volume of 100 mL (Raktham, Wongrerkdee & Pimpang, 2024).

2. Preparation of mercury sensor pads

Figure 1 shows the structure of mercury sensor pad. The sensor pad was prepared using a 6 mm diameter circular filter paper (180 µm thick) as the substrate. To ensure effective mercury detection, the filter paper was first coated with 60 µL of GQDs solution and left to dry at room temperature for 1 hour, allowing uniform distribution of GQDs across the surface. Then, 10 µL of dithizone solution was applied to the GQDS-coated filter paper and dried for an additional 1 hour. The dithizone solution was prepared by dilute 0.10 g of dithizone power (Loba Chemie) in 100 mL of absolute ethanol (RCI Labscan), resulting solution was a 0.10 %w/v. The dithizone modification played a important role in enhancing the selectivity of the sensor toward mercury ions by facilitating complexation reactions with Hg^{2+} (Azmi, Ahmad & Low, 2018; Wu, Sun & Zou, 2015). finally, the sensor pad was integrated with gold electrodes to complete the sensor assembly, making it ready for electrical characterization and mercury detection experiments. Gold was selected because of chemically stable and resistant to oxidation or corrosion, even in harsh environments (Pimpang, Thong-on & Choopun, 2018; Pimpang & Choopun, 2019).

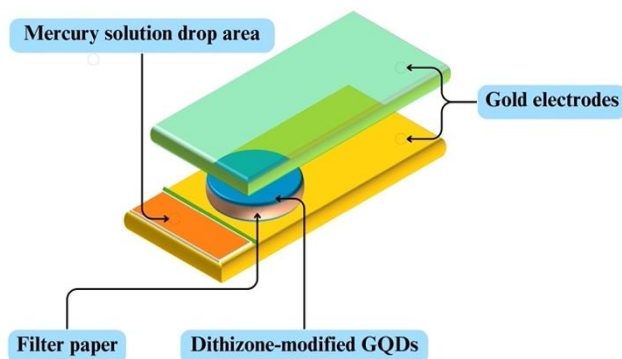


Figure 1 Schematic diagram of the mercury sensor pad.

3. Investigations of mercury sensing properties

Figure 2 illustrates the experimental setup designed to measure the electrical properties of the fabricated mercury sensor. Electrical measurements were carried out using a Keithley 6517A electrometer. The sensor pad was evaluated using mercury(II) chloride (HgCl_2) solutions at concentrations of 0, 50, 75, 100, and 250 ppm, each prepared in 0.10 M KCl, which also served as the supporting electrolyte throughout the experiment. The current–voltage (I–V) characteristics of the sensor were first measured by connecting the pad to the input leads of the electrometer. After applying the HgCl_2 solution to the sensor surface, I–V curves were recorded over a voltage range from 0 to 3 V in 0.10 V increments. In addition, the sensor response at a fixed voltage of 3 V was monitored by recording the change in resistance immediately after each application of HgCl_2 solution. This procedure allowed for the evaluation of the sensor's response behavior toward varying mercury concentrations.

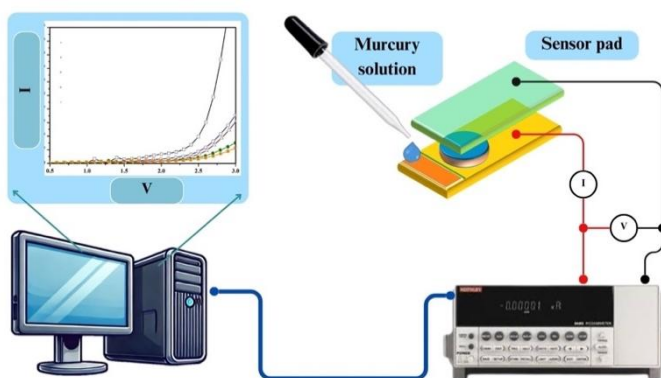


Figure 2 Experimental setup for the sensing properties test.

Results

1. Colorimetric response of the sensor

Figure 3 shows the color of the dithizone solution and the dithizone solution after adding 250 ppm mercury (II) chloride solution. Upon exposure to HgCl_2 , a distinct color change from dark blue to orange was observed in the dithizone solution. This color shift confirms the complexation reaction between dithizone and Hg^{2+} ions, indicating the successful interaction between the sensing material and mercury. The observed color change is consistent with prior studies, further validating the selective chelating ability of dithizone for mercury detection (Azmi, Ahmad & Low, 2018; Danwittayakul et al., 2008; Ntoi, Buitendach & von Eschwege, 2017; Sertova, Petkov & Nunzi, 2000; Wu, Sun & Zou, 2015).

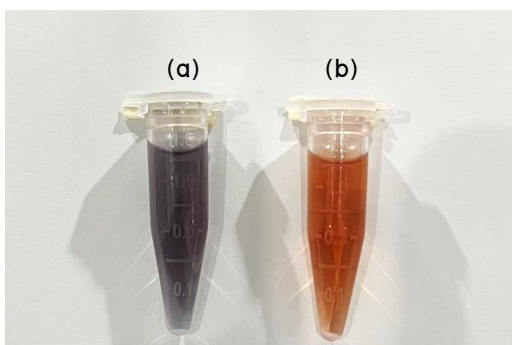


Figure 3 Color of the dithizone solution (a) and the dithizone solution after adding 250 ppm mercury (II) chloride solution (b).

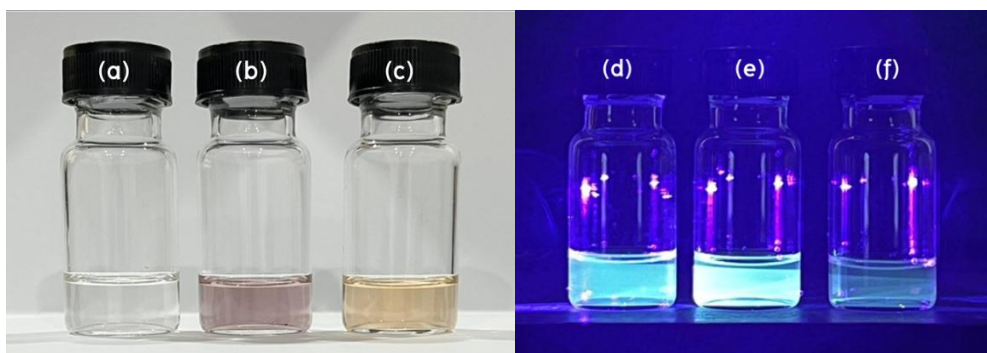


Figure 4 Photograph of the GQDs, the dithizone–modified GQDs, and the dithizone–modified GQDs with 250 ppm mercury (II) chloride, without UV irradiation at 405 nm (a–c) and with UV irradiation at 405 nm (d–f). All solutions were diluted tenfold to facilitate fluorescence observation.

Figure 4 (a–c) displays photographs of pristine GQDs, dithizone–modified GQDs, and dithizone–modified GQDs after the addition of 250 ppm mercury (II) chloride. The observed colors were light yellow for pristine GQDs, blue for dithizone–modified GQDs, and orange for dithizone–modified GQDs in the presence of mercury (II) chloride. The noticeable color transition from blue to orange upon the introduction of Hg^{2+} ions indicated the formation of a complex between the mercury ions and the dithizone–modified GQDs. This distinct color change highlights the potential application of the material as a colorimetric sensor for mercury detection. Figures 4(d) shows the fluorescence of GQDs under UV irradiation at 405 nm. The GQDs exhibit a characteristic blue fluorescence, which is a result of their quantum confinement effect (Pimpang, Sumang & Choopun, 2018). Figures 4(e) and 4(f) compare the fluorescence quenching behavior of the dithizone–modified GQDs before and after interaction with mercury(II) chloride. A clear decrease in fluorescence intensity was observed following the addition of Hg^{2+} ions. This quenching phenomenon is attributed to dynamic quenching, involving non–radiative electron transfer processes that reduce the number of excited electrons, thereby diminishing fluorescence intensity. These findings are consistent with previous reports (Yang et al., 2019; Wongrerkdee & Pimpang, 2022). The reduction in excited electron population was expected to influence the electrical properties of the material, suggesting its potential applicability as a resistive sensor.

2. Characteristics of a resistive sensor based on dithizone–modified GQDs

Figure 5 presents the current–voltage (I–V) characteristics of the mercury detection sensor, analyzed using mercury (II) chloride solutions at concentrations of 0, 50, 75, 100, and 250 ppm. The I–V measurements exhibited non–ohmic behavior, with current flow occurring only after reaching a threshold voltage of approximately 2.50 V under all tested conditions. This threshold voltage corresponded to the activation energy necessary for charge transport through the dithizone–modified GQDs layer, further validating the sensor’s ability to detect mercury ions effectively. Additionally, the results indicated that increasing mercury (II) chloride concentrations result in a progressive decrease in current at a fixed voltage, confirming an inverse relationship between mercury concentration and sensor conductivity.

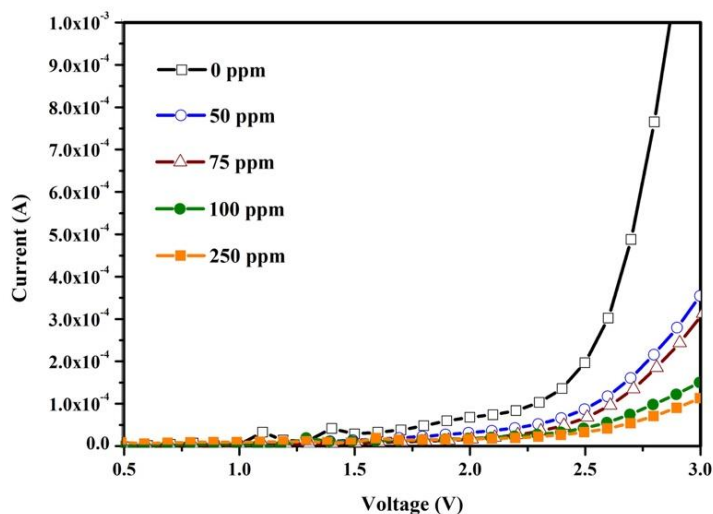


Figure 5 Current–voltage (I–V) characteristics of the mercury detection sensor using mercury (II) chloride solution at concentrations of 0, 50, 75, 100, and 250 ppm.

3. Effect of mercury concentration on sensing properties

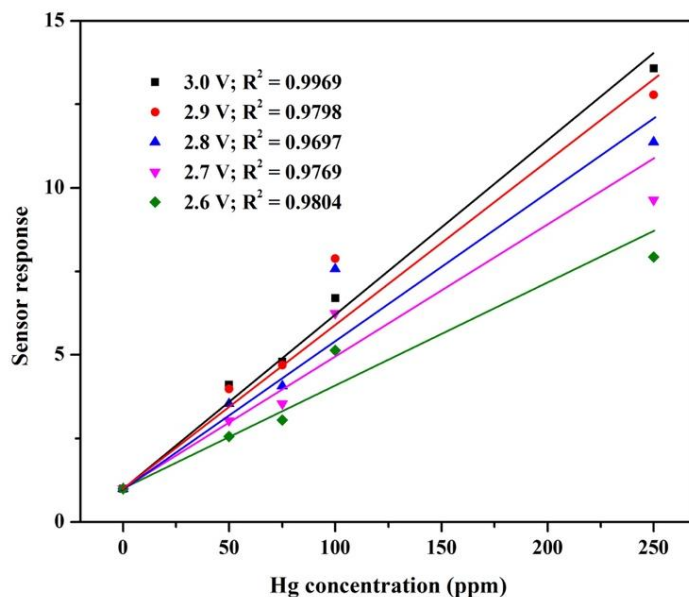


Figure 6 The relationship between the sensor response and mercury (II) chloride concentration at various applied voltages (2.60–3 V).

The sensor's performance was further evaluated under varying applied voltages ranging from 2.60 V to 3 V to investigate its linear response toward mercury (II) chloride concentration. As shown in Figure 6, a strong linear relationship between sensor response and Hg^{2+} concentration was observed at all voltage levels, with coefficients of determination (R^2) exceeding 0.96. The highest linearity was achieved at 3 V ($R^2=0.9969$), indicating optimal performance for quantitative mercury detection at this voltage. The sensor exhibited increasing sensor response with increasing mercury concentration, and the steepest slope was observed at 3 V, reflecting enhanced sensitivity at higher voltages. Although the sensor response was lower at 2.60 V, the high R^2 value suggests that it still provides reliable detection, potentially with reduced power consumption. These results confirm that the sensor was capable of accurate and quantitative mercury detection within the linear range of 50–250 ppm, regardless of the applied voltage, making it adaptable to various operational settings.

The sensing behavior of the dithizone–modified GQDs–based mercury sensor was evaluated by analyzing its electrical response to varying concentrations of HgCl_2 and measured at a constant voltage of 3 V, as shown in Table 1. As the concentration of HgCl_2 increased from 0 to 250 ppm, a significant rise in electrical resistance was observed from 338 Ω at 0 ppm to 4590 Ω at 250 ppm. Correspondingly, the conductivity of the sensor decreased from 18.838 mS/m to 1.387 mS/m, indicating that the formation of the dithizone–mercury complex impedes electron transport across the sensor surface. This effect is consistent with the binding of Hg^{2+} ions to the dithizone–modified surface, which creates an insulating layer that reduces conductivity (Gul, Ullah & Khan, 2022). Moreover, the sensor response, expressed as the ratio of initial current to current after mercury exposure (I_0/I_{Hg}), increased progressively with higher Hg^{2+} concentrations, reaching a maximum of 13.58 at 250 ppm. These results clearly demonstrate the sensor's high sensitivity and its capability for quantifying mercury concentrations based on measurable changes in electrical properties.

Table 1 Sensing properties of mercury sensor based on dithizone–modified GQDs, measured at a constant voltage of 3 V.

[HgCl ₂] (ppm)	Resistance (Ω)	Conductivity (mS/m)	Sensor Response
0	338	18.838	1.00
50	1410	4.516	4.18
75	1590	4.005	4.70
100	3270	1.947	9.67
250	4590	1.387	13.58

4. Sensor Sensitivity and Quantification

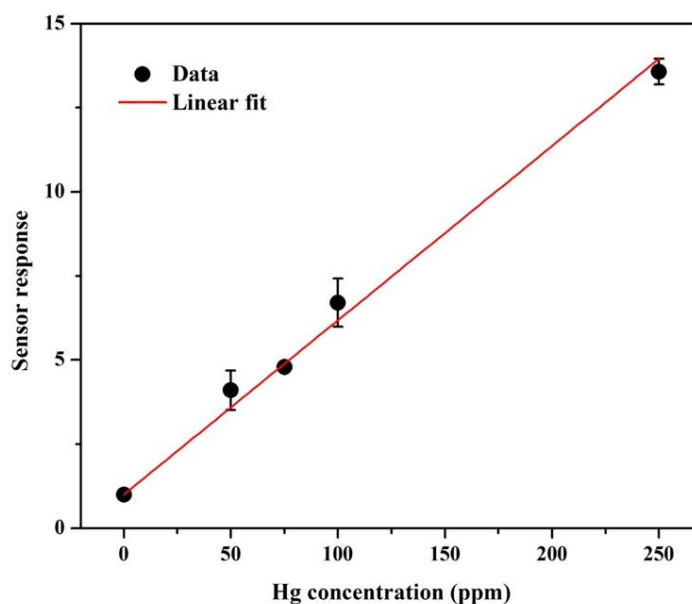
**Figure 7** The relationship between the sensor response and mercury (II) chloride concentration, measured at a constant voltage of 3 V.

Figure 7 illustrates the relationship between the sensor response and mercury (II) chloride concentration, measured at a constant voltage of 3 V and modeled using linear regression. The analysis yields the following equation 1

$$\text{Sensor Response} = 0.0518 \times [\text{HgCl}_2] + 1.0000; R^2 = 0.9969 \quad (1)$$

This equation indicates a strong positive linear correlation between the concentration of HgCl_2 and the sensor response. The slope of 0.0518 suggests that for every 1 ppm increase in mercury concentration, the sensor response increases by 0.05 units. The coefficient of determination ($R^2=0.9969$) confirms the robustness of this model, indicating that approximately 99.69% of the variance in sensor response can be attributed to changes in mercury concentration. This strong correlation demonstrates that the sensor provides a reliable, consistent, and quantifiable electrical response, making it highly suitable for the detection and monitoring of mercury in various environments.

Discussion

The experimental results revealed that the dithizone–modified GQDs sensor exhibited both colorimetric and electrochemical responses to mercury (II) chloride. The color change from blue to orange upon the addition of Hg^{2+} ions confirms the formation of a dithizone–mercury complex, validating the selective interaction between dithizone and mercury ions (Azmi, Ahmad & Low, 2018; Wu, Sun & Zou, 2015). Figure 8 shows sensing mechanism of the electrochemical response through Hg^{2+} ion binding with dithizone molecules on the graphene quantum dot; GQDs surface. The sensor demonstrated non–ohmic behavior, with current flow occurring only after a threshold voltage of approximately 2.50 V. This threshold voltage corresponds to the energy required to initiate charge transport across the sensing layer. As the mercury (II) chloride concentration increased, the electrical resistance of the sensor increased while the conductivity decreased, indicating a stronger interaction and more extensive complex formation (Azmi, Ahmad & Low, 2018; Gul, Ullah & Khan, 2022; Wu, Sun & Zou, 2015). The sensor response, expressed as the I_o/I_{Hg} ratio, increased with mercury concentration, highlighting the sensor's sensitivity and its capability for quantitative detection. The proposed sensing mechanism suggested that as mercury ions bind with dithizone molecules on the GQDs surface, a stable dithizone–mercury complex forms, resulting in the creation of an insulating layer. This layer significantly hinders the transport of charge carriers such as K^+ and Cl^- ions, thereby increasing the electrical resistance and reducing the overall current flow, as illustrated in Figure 8. On the left side of the diagram, in the absence of mercury, charge carriers moved freely across the GQDs surface, enabling efficient electron transport and low resistance. In contrast, the right side depicts the condition in the presence of mercury ions, where the formation of the dithizone– Hg^{2+} complex disrupted the conductive pathways, making charge transport more difficult and

increasing resistive behavior. Furthermore, the electrical properties of the sensor changed immediately upon the application of mercury solution to the sensing pad, without requiring sample pretreatment. This immediate response demonstrates the sensor's potential for real-time detection.

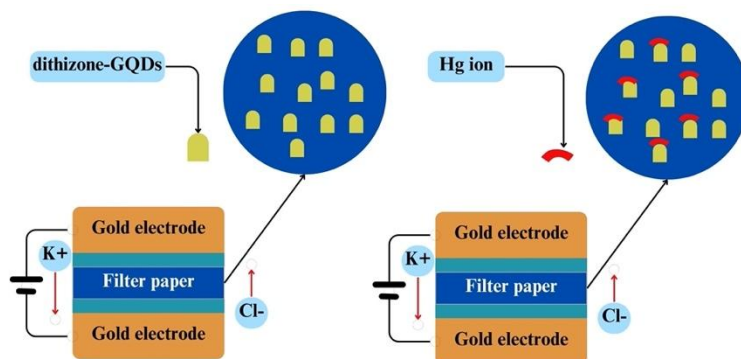


Figure 8 Sensing mechanism of the electrochemical response of dithizone modified GQDs, based on the formation of a dithizone–mercury complex.

Conclusion

In conclusion, this study successfully fabricated a dithizone–modified graphene quantum dot (GQDs) sensor capable of detecting mercury ions through electrochemical mechanisms. The sensor demonstrated a significant variation in electrical response corresponding to different concentrations of mercury (II) chloride. A strong linear correlation between mercury concentration and sensor response confirmed the sensor's high sensitivity and quantifiability, with increased resistance and decreased conductivity resulting from the formation of dithizone– Hg^{2+} complexes. These findings validate the proposed sensing mechanism and highlight the sensor's effectiveness for mercury detection. Overall, the sensor offers a promising alternative to conventional techniques, providing a portable, cost–effective, and reliable solution for environmental mercury monitoring.

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