

## Study of the Sensitivity of Carbon Quantum Dots for NO<sub>2</sub> Gas Sensor and improve it Using Graphene

Nuha Salem Sultan<sup>1a</sup> and Omar Abdulsada Ali<sup>1b\*</sup>

<sup>1</sup>*Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq*

<sup>b\*</sup>Corresponding author: [omar.ab@sc.uobaghdad.edu.iq](mailto:omar.ab@sc.uobaghdad.edu.iq)

### Abstract

Gas sensors are essential for detecting noxious gases that have a detrimental effect on people's health and welfare. Carbon quantum dots (CQDs) are the fundamental component of gas detectors. CQDs and graphene (Gr) were prepared using the electrochemical method. The gas sensitivity of these materials was evaluated at different temperatures (150, 200, 250 °C) to assess their effectiveness. Subsequently, experiments were conducted at different temperatures to ascertain that the combination of CQDs and Gr, with various percentages of Gr and CQDs, exhibited superior gas sensitization properties compared to CQDs alone. This was evaluated based on criteria such as sensitivity, recovery time, and reaction time. Interestingly, the combination was highly responsive. The quantum dots on glass substrates could detect NO<sub>2</sub> gas at the temperatures mentioned above. Experimental evidence showed that the gas sensor can only detect graphene at low temperatures. Measurements indicate that the resistance diminishes with various graphene concentrations, accompanied by a decrease in both Response and Recovery times.

### Article Info.

#### Keywords:

*Carbon Quantum Dot, Electrochemical Method, Electrochemical Process, Graphene, Gas sensor.*

#### Article history:

*Received: Jul.10, 2024*

*Revised: Sep 03, 2024*

*Accepted: Nov.03,2024*

*Published: Dec 01,2024*

### 1. Introduction

A sensor is a device that converts an electrical signal into a physical or chemical signal. The primary parts of the device are the active sensing and the transducer components. The ultimate electrical signal is produced through the conversion of the intermediate signal [1]. The output signal of a sensor can be any of the following: voltage, current, or charge. Outcomes of the value might range from a basic, unchanging value to a complex, time-varying signal that undergoes electronic filtering or processing [2]. A sensor is a sophisticated instrument that responds to one or more analyses. The inverse approach converts the initial quantity of a single sample component for aggregate composition analysis into an electrical signal that may be analyzed, regardless of their categorization based on the materials, applications, and techniques used [3, 4]. A sensor can be classified according to its characteristics, such as the range, accuracy, or cost of the sensor [5]. Gas detectors are essential due to the presence of a diverse range of gases in the air, some of which pose a threat to human well-being, along with the pollution due to industry and hospitals. Therefore, the detection of these gases is of utmost importance to ensure the safety of all organisms in the environment [6]. Regarding sensing elements, the three most commonly used materials are: substances composed of metal oxides [6, 7], conductive polymer composites (CPCs) [8], and carbon nanomaterials [9]. Developing gas sensors that are portable, affordable, highly selective, and operate at low temperatures remains a considerable challenge, despite their high desirability. Because of the evident benefits it offers Gas sensor metrics [10].

When the electrical resistance of the chemical sensor is either increased or decreased, it occurs in response to exposure to gas particles. This change is determined



by the kind of gas (reduced or oxidised) and the type of sensor material (n-type or p-type) [11]. In this study, a gas sensor was manufactured using Carbon quantum dots (CQDs) and CQDs/ and Graphene (Gr) composite using an electro-chemical method and a spin-coating technique.

Graphene consists of carbon atoms arranged in a hexagonal configuration. These atoms can either be suspended in space or attached to an external object. The graphene sheet is extremely thin, with a thickness of only one atom. Carbon exhibits a remarkably high level of electrical conductivity. With a complete absence of gaps, it functions as a semiconductor [12, 13]. Researchers have shown great interest in the thermal, mechanical, and electrical properties of graphene. Its numerous beneficial characteristics make it a multipurpose product [14]. P. R. Wallace, the Canadian Research Council commenced research on graphene in 1947. During this period, he formulated predictions regarding the electrical structure of the material. In 1948, Roof et al. conducted experiments and devised a technique for obtaining graphene [15].

### 1. 1. Sensitivity (S)

The sensor's response is determined by its exposure to a particular gas. Several factors influence sensitivity, including humidity and gas composition in the background, sensor's temperature, oxide's microstructure, film's thickness, and the duration of gas exposure. The equation that enables its computation is [16]:

$$S = \frac{R_{\text{air}}}{R_{\text{gas}}} = \frac{G_{\text{gas}}}{G_{\text{air}}} \quad (1)$$

Another common approach to report S is shown in the following equations [17]

$$S = \frac{|\Delta R|}{R} \times 100\% = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100\% \quad (2)$$

$$S = \frac{|\Delta G|}{G} \times 100\% = \frac{G_{\text{gas}} - G_{\text{air}}}{G_{\text{air}}} \times 100\% \quad (3)$$

G represents the electrical conductance, whereas R represents the electrical resistance. The term "air" refers to the initial state of dry air as the background, while "gas" indicates the introduction of the analyte gas.

### 1. 2. Selectivity

Specificity or selectivity (SEL) is defined as the ability of a sensor to respond to a certain gas in the presence of other gases [18]. As shown in following equation [19]

$$SEL_{A/B} = \frac{S_{\text{gasA}}}{S_{\text{gasB}}} \quad (4)$$

### 1. 3. Stability

The stability of a gas sensor is influenced by several factors including the operating temperature, gas concentration, and the microstructure of the film. A stable operating temperature is crucial for consistent sensor performance. Additionally, the sensor's response and recovery times are temperature-dependent, which further underscores the importance of stable temperature control for reliable operation [20].

### 1. 4. Response and Recovery Times

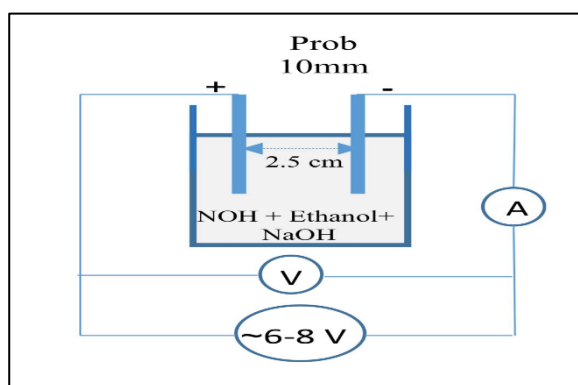
The duration required for the conductance to reach 90% of its maximum value upon the sensor exposure to the target gas is referred to as the reaction time. The recovery time refers to the period it takes for the sensor's conductance to decrease to 10% of its saturation value after the gas is deactivated and the sensor is exposed to clean air. For a sensor to be consistently effective, it must possess a brief response and recovery time [21].

## 2. Materials and Methods

For the purpose of preparing samples for the gas sensor, the following materials must be prepared:

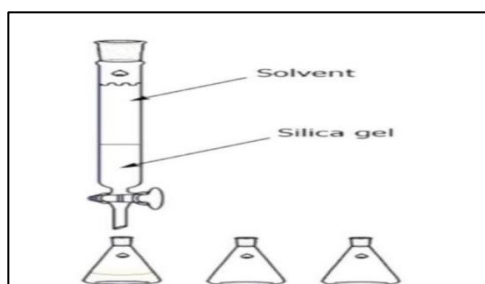
### 2. 1. Carbon Quantum Dots (CQDs)

CQDs can be synthesized using the electrochemical process described in Fig. 1 [22-24].



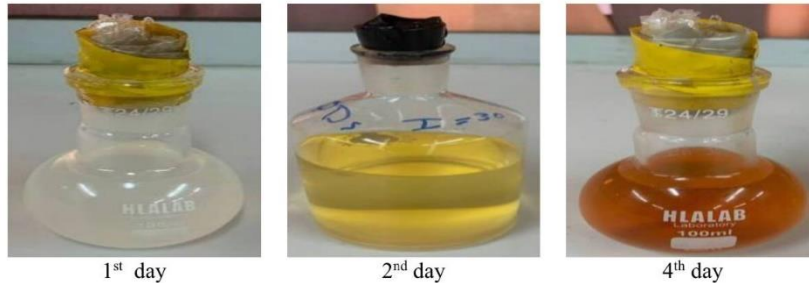
*Figure 1: The electro-chemical method.*

The most efficient method for synthesizing CQDs is the electrochemical method. For this: 99.5% ethanol ( $C_2H_5OH$ ) was dissolved in 0.5 ml distilled water with thorough mixing for a duration of two hours using a magnetic stirrer. This solution was poured into a 250 ml volumetric beaker, in which two electrodes were placed with a 2.5 cm gap between them. These were connected in an electrical circuit through which a current of 30 mA flowed. The electrodes were periodically rotated every 5 minutes to enhance the migration of ions between them. In this instance, it is possible to synthesize a solution that has a milky-white appearance. After a period of five days, a noticeable transformation in the color of the combination became evident, taking on a yellowish orange. To separate CQDs from the solution, column chromatography was utilized, as depicted in Fig.2. 20 ml of diethyl ether ( $C_2H_5OC_2H_5$ ) is combined with 20 ml of silica gel ( $SiO_2$ ) in a separate small beaker. After thoroughly mixing with 10 ml of petroleum ether ( $C_6H_{14}$ ), the chromatographic column was introduced to the final product, by incorporating CQDs. The final filter is purified, the color of the CQDs varies over time, as depicted in Fig. 3.



*Figure 1 : Column Chromatography filter.*

Subsequently, the films were deposited by drop casting at 50°C. By Tolansky's method, the thickness of the prepared films was around 600 nm. Due to their lack of uniformity, deposited films exhibit some characteristics and unstable conditions. The edges located in the center exhibit a greater thickness. An alternative technique that has arisen to address the expensive and limited solubility of polymer semiconductors is the drop casting approach [25-28].



*Figure 2 : The color change of the CQDs solution with time.*

## 2. 2. Preparation of Graphene

250g of graphene powder was mixed with 5ml of ethanol alcohol  $C_2H_5OH$  using an ultrasonic device for 8 hours, as shown in Fig. 4.



*Figure 3: Mix grapheme with ethanol alcohol  $C_2H_5OH$  by using an ultrasonic bath device.*

## 2. 3. Preparation of CQDs/Gr Composite Gas Sensor Samples

Different volumes (0.01, 0.02, 0.03, and 0.04) mg/ml of the synthesized graphene liquid were mixed with a fixed amount of CQDs (0.1 ml) and subjected to agitation using an ultrasonic bath. The solution was applied to a silicone substrate, which was then subjected to a 30-minute heating process in an oven set at 60°C. This allowed the solvent to evaporate.

## 3. Results and Discussion

### 3.1. Sensing Characteristics of Gr for Gases

As shown in Fig. 6, experimental evidence showed that the gas sensor made of graphene only is incapable of detecting at low temperatures. Increasing the temperature to 200°C and then to 250°C led to a reduction reaction that eliminates the oxygen atoms from  $NO_2$ , resulting in the formation of a more precise molecular structure. Consequently, the emergence of peaks becomes evident. This is noticed at a temperature of 150°C. Fig. 5 illustrates the changes in graphene resistance over time when used as a sensor for  $NO_2$  gas.

Table 1 presents the changes of sensitivity (S%), response time, and recovery time of graphene (Gr) as an  $NO_2$  sensor with temperature.

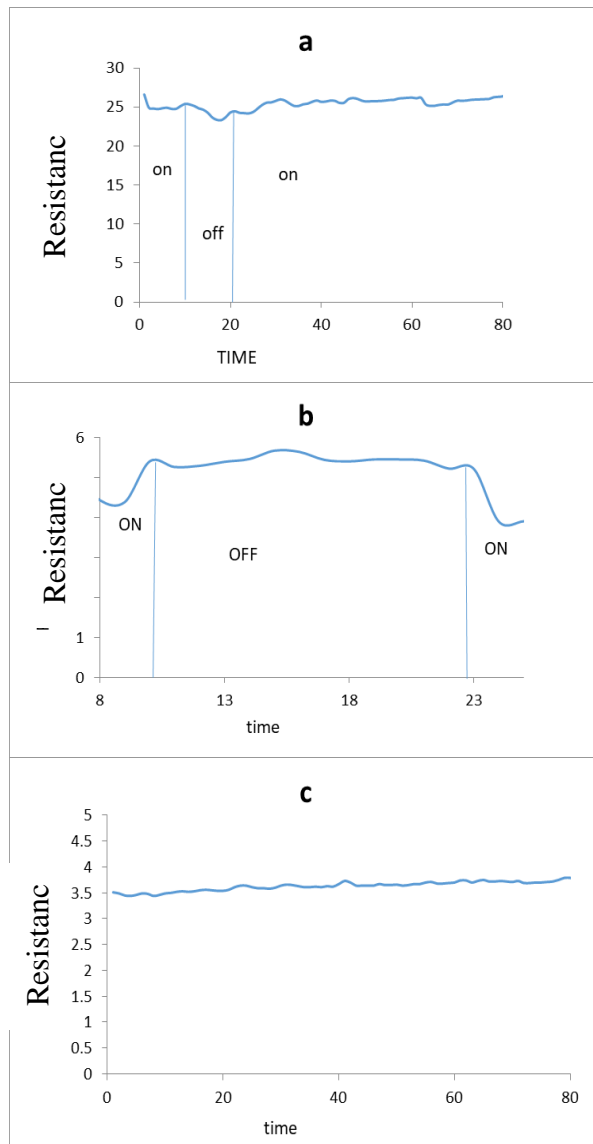


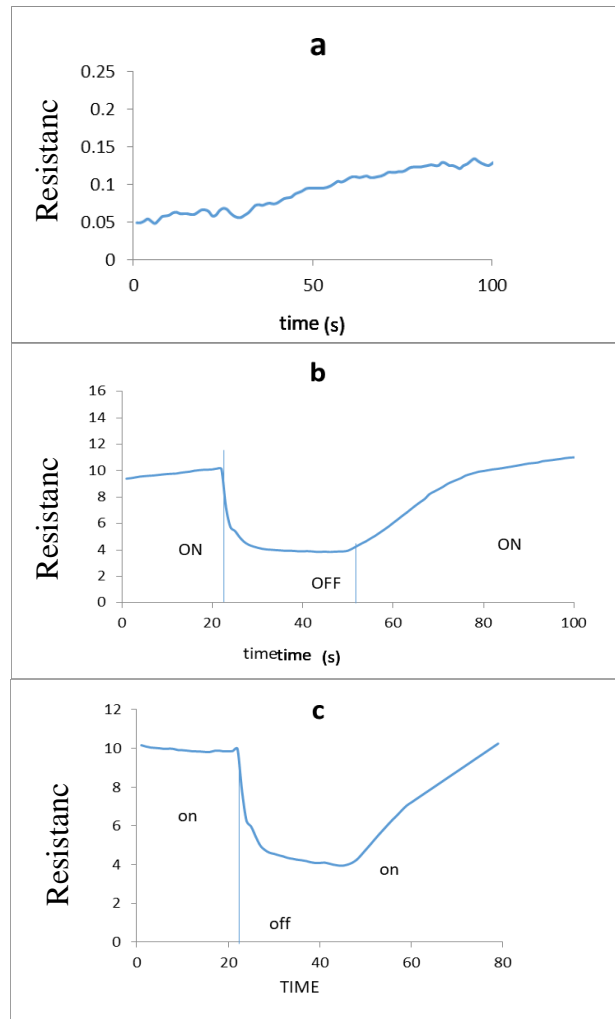
Figure 4 : Variation of the resistance of graphene as a NO<sub>2</sub> sensor with time at different temperatures (a)150 °C (b)200 °C (c)250 °C.

### 3.2. Sensing Characteristics of CQDs for Gases

The quantum dots on glass substrates could detect NO<sub>2</sub> gas at temperatures of 150, 200, and 250°C. The resistance exhibits temporal variability, as indicated by the recorded NO<sub>2</sub> gas temperatures. Experimental results demonstrated that the resistance of CQDs increased when they were subjected to oxidizing gases such as NO<sub>2</sub> at a high concentration and a temperature of 200°C. This provides evidence of the sensitivity of quantum dots to NO<sub>2</sub> gas, indicating their ability to absorb the gas. Due to the molecular interaction between the quantum dots (QDs) and the gas in the passage, the resistance does not return to its original value once the gas is removed. The resistance exhibited an augmentation as the gas resumed its flow, and it endured an excessively protracted duration to revert to its secondary fundamental state after being deactivated. Fig. 6 shown interactions between carbon quantum dots and gas molecules, Table 2 presents sensitivity, response, and recovery time of CQDs at different temperatures.

Table 1: The sensitivity, Response and Recovery time at different temperatures of Gr.

Temp. (°C)	S%	T <sub>C</sub> (s)	T <sub>S</sub> (s)
150	18.18	53.1	18.9
200	61.6	50.4	21.6
250	58.53	54.9	17.1



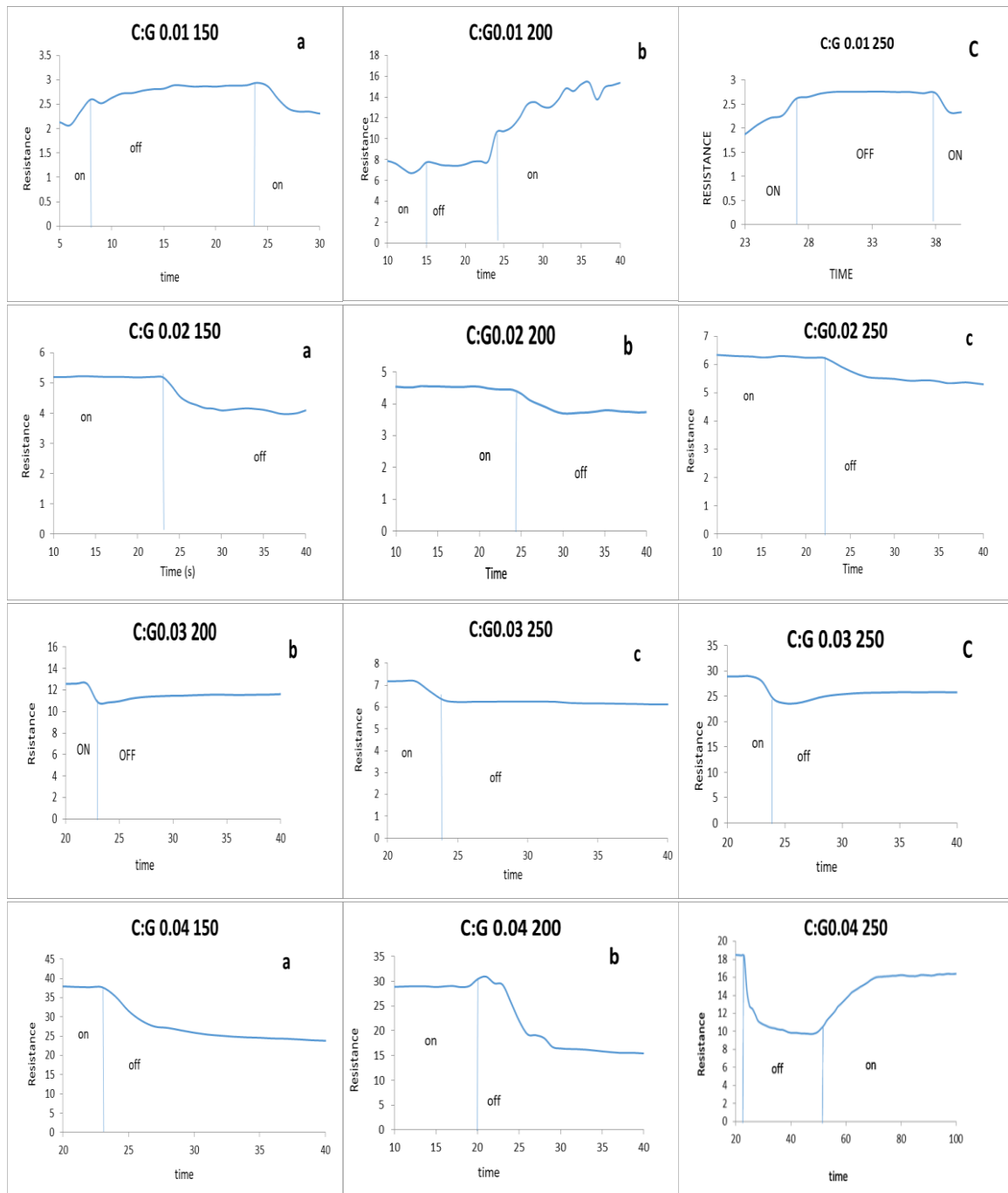
**Figure 5: Variation of the resistance of CQDs as a  $\text{NO}_2$  sensor with time at different temperatures (a) 150 °C (b) 200 °C (c) 250 °C.**

### 3. 3. Sensing Characteristics of (CQDs/Gr) for Gases

A thin layer of carbon quantum dots/graphene solution with different concentrations of graphene was deposited on a glass substrate. These were used as a  $\text{NO}_2$  sensor, tested at various temperatures (150, 200, 250) °C. Regardless of its composition, carbon is essentially a reducing substance. As the temperature increases, it attracts oxygen molecules with a valence of 2 from the  $\text{NO}_2$  gas, or it removes 2 electrons from the surface of the material. This phenomenon results in a decrease in the number of available electrons within the material, leading to an increase in resistance due to a decrease in conductivity and a reduction in surface area. Due to the material's activation upon heating, a decrease in the rise and recovery times was noted. The findings indicated that the resistance decreased as the concentration of graphene was increased, leading to a decrease recovery time. This phenomenon occurs due to the direct relationship between temperature and resistance of graphene. As the temperature increases, the resistance of graphene also increases, resulting in reduced stability and a hindered ability to rapidly establish bonds with  $\text{O}_2$  in  $\text{NO}_2$ . This results in an augmentation of the material's electrons due to the material's failure to adsorb onto the surface. Graphene assumes a specific configuration as shown in Fig. 7 and Table 3 show the sensitivity, response, and recovery time at different temperatures and concentrations of CQDs/Gr.

**Table 2: The sensitivity, Response and Recovery time at different temperatures of CQDs.**

Temp. (°C)	S%	T <sub>C</sub> (s)	T <sub>S</sub> (s)
150	18.18	53.1	18.9
200	61.66	50.4	21.6
250	58.53	54.9	17.1



**Figure7: Variation of the resistance of CQDs/Gr as a NO<sub>2</sub> sensor with time at different temperatures and different concentrations.**

**Table 3: The sensitivity, Response and Recovery time at different temperatures and different concentrations of CQDs/Gr.**

Con. CDQs: Gr (mg/ml)	Temp (°C)	S%	T <sub>C</sub> (s)	T <sub>S</sub> (s)
0.01	150	30.2	46.8	23.4
	200	92.5	51.3	20.7
	250	47.2	59.4	11.7
0.02	150	30.2	46.8	23.4
	200	92.5	51.3	20.7
	250	47.2	59.4	11.7
0.03	150	30.2	46.8	23.4
	200	92.5	51.3	20.7
	250	47.2	59.4	11.7
0.04	150	30.2	46.8	23.4
	200	92.5	51.3	20.7
	250	47.2	59.4	11.7

#### 4. Conclusions

Quantum dots (QDs) were synthesized through the electrochemical method. Due to the significant alteration in their electrical properties caused by their nanostructure, this technology has achieved exceptional outcomes in developing very sensitive sensors. Based on the results, environmental sensors exhibit increased sensitivity over time when graphene and carbon quantum dots are present.

#### Acknowledgements

The authors would like to thank University of Baghdad, College of Science, Department of Physics for their assistance in carrying out this work.

#### Conflict of interest

Authors declare that they have no conflict of interest.

#### References

1. R. K. Goyal, *Nanomaterials and Nanocomposites: Synthesis, Properties, Characterization Techniques, and Applications* (Boca Raton, CRC Press, 2017).
2. J. Hodgkinson, J. Saffell, J. Luff, J. Shaw, J. Ramsden, C. Huggins, R. Bogue, and R. Carline, *Nanotech. Percep.* **5**, 71 (2009). DOI: 10.56801/nano-ntp.v5i1.33.
3. W. Wang, *Progresses in Chemical Sensor*. 2016, IntechOpen: Rijeka.
4. L. A. Abdullah, O. A. Ibrahim, and O. A. Ali, *Mat. Lett.* **377**, 137534 (2024). DOI: 10.1016/j.matlet.2024.137534.
5. G. Sinha, *Advances in Modern Sensors: Physics, Design, Simulation and Applications* (London, UK, IOP Publishing, 2020).
6. U. Resch-Genger, *Standardization and Quality Assurance in Fluorescence Measurements I: Techniques*. 2009, Springer Berlin, Heidelberg: Berlin, Germany.
7. D. Degler, *Sensors* **18**, 3544 (2018). DOI: 10.3390/s18103544.
8. H. Bai and G. Shi, *Sensors* **7**, 267 (2007). DOI: 10.3390/s7030267.
9. E. Llobet, *Sens. Actuat. B Chem.* **179**, 32 (2013). DOI: 10.1016/j.snb.2012.11.014.
10. M. M. Faris and A. K. Ayal, *Iraqi J. Phys.* **21**, 1 (2023). DOI: 10.30723/ijp.v21i4.1150.
11. T. A. Hassan, Ph.D Thesis, University of Baghdad, 2013.
12. D. R. Patil, L. A. Patil, and D. P. Amalnerkar, *Bull. Mat. Sci.* **30**, 553 (2007). DOI: 10.1007/s12034-007-0086-6.
13. Q. G. Hial, Ph.D Thesis, University of Baghdad, 2011.
14. E. R. Beach, Ph. D Thesis, The Ohio State University, 2009.
15. E. X. Perez, Ph. D Thesis, Tarragona, 2007.
16. A. S. Zamil and A. N. Naje, *J. Opt.* **53**, 3486 (2024). DOI: 10.1007/s12596-023-01481-7.
17. O. A. Ali and S. S. M. Al-Awadi, *Iraqi J. Sci.* **62**, 1873 (2021). DOI: 10.24996/ij.s.2021.62.6.13.



18. N. A. Abd and O. A. Ibrahim, Iraqi J. Phys. **22**, 1 (2024). DOI: 10.30723/ijp.v22i1.1214.
19. D. R. Cooper, B. D'anjou, N. Ghattamaneni, B. Harack, M. Hilke, A. Horth, N. Majlis, M. Massicotte, L. Vandsburger, E. Whiteway, and V. Yu, Int. Schol. Res. Not. **2012**, 501686 (2012). DOI: 10.5402/2012/501686.
20. A. F. Sultan, Iraqi J. Phys. **14**, 150 (2016).
21. C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, Sensors **10**, 2088 (2010). DOI: 10.3390/s100302088.
22. L. Xuekun, Y. Minfeng, H. Hui, and S. R. Rodney, Nanotechnology **10**, 269 (1999). DOI: 10.1088/0957-4484/10/3/308.
23. L. A. Essa and R. K. Jamal, J. Opt. **53**, 1574 (2024). DOI: 10.1007/s12596-023-01328-1.
24. N. A. Abd and O. A. Ibrahim, J. Opt. **53**, 2757 (2024). DOI: 10.1007/s12596-023-01462-w.
25. N. S. Sultan and O. A. Ali, J. Opt., (2024). DOI: 10.1007/s12596-024-02000-y.
26. D. Jung, M. Han, and G. S. Lee, ACS Appl. Mat. Inter. **7**, 3050 (2015). DOI: 10.1021/am506578j.
27. S. Abdullahi, A. Aydarous, and N. Salah, J. Lum. **242**, 118588 (2022). DOI: 10.1016/j.jlumin.2021.118588.
28. C. Subramaniam, Y. Yasuda, S. Takeya, S. Ata, A. Nishizawa, D. Futaba, T. Yamada, and K. Hata, Nanoscale **6**, 2669 (2014). DOI: 10.1039/C3NR05290G.

## دراسة حساسية نقاط الكربون الكمومية لمستشعر غاز $\text{NO}_2$ وتحسينها باستخدام الجرافين

نهى سالم سلطان<sup>1</sup> وعمر عبد السادة علي<sup>1</sup>  
 أقسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

### الخلاصة

تعد أجهزة استشعار الغاز ضرورية للكشف عن الغازات الضارة التي لها تأثير ضار على صحة الناس ورفاهيتهم. تعمل النقاط الكمومية الكربونية (CQDs) كعنصر أساسي في أجهزة الكشف عن الغاز. تم تحضير نقاط الكم الكربونية (CQDs) والجرافين باستخدام الطريقة الكهروكيميائية. تم تقييم حساسية الغاز لهذه المواد عند درجات حرارة مختلفة (150، 200، 250) لتقييم فعاليتها. بعد ذلك، أجرينا تجارب عند درجات حرارة مختلفة (150، 200، 250 درجة مئوية) للتأكد من أن الجمع بين CQDs و Gr أظهر خصائص فائقة لحساسية الغاز مقارنةً بـ CQDs وحدها. قمنا بتقييم ذلك بناءً على معايير مثل الحساسية ووقت التعافي ووقت رد الفعل. تم تغيير النسب المئوية للجرافين و CQD. ومن المثير للاهتمام أن هذا المزيج سريع الاستجابة. تشير القياسات إلى أن المقاومة تقل مع تركيزات الجرافين المختلفة، مصحوبة بانخفاض في كل من أوقات الاستجابة والاسترداد.

الكلمات المفتاحية: نقاط الكربون الكمومية، التحضير الكهروكيميائي، الطريقة الكهروكيميائية، الكرافين، المتحسس الغازي.