Omar S. Shafeq [1]
Omar A. Ibrahim [1]
Ruqia A. Hassan [2]

[1] Department of Physics, College of Science, University of Baghdad, Baghdad, IRAQ
[2] University of Technology, Baghdad, IRAQ

Synthesis and Sensing Properties of Carbon Quantum Dots/Alq_3 Nanocomposite for Hydrogen Sulfide Detection

An electrochemical method was used to fabricate carbon quantum dots (CQDs) based gas sensor by combining the CQDs with Tris(8-hydroxyquinoline) aluminum (III) (Alq_3) polymer. A spin-coating method was utilized to apply the CQDs/Alq_3 composite film onto glass substrates. The CQDs/Alq_3 gas sensor exhibited a sensitivity of around 16% at 300°C, the change in resistance was measured, yielding a response time of 11 s and a recovery time of 25 s. The sensor demonstrated a significant reaction to hydrogen sulfide (H_2S) gas. The CQDs gas sensor subjected to H_2S at 300°C exhibited a sensitivity of 28%, with a response time of 20 s and a recovery time of 29 s. The findings indicate that the CQDs/Alq_3 sensor markedly decreased recovery time, emphasizing the role of the Alq_3 polymer in enhancing the gas sensor's properties.

Keywords: Carbon quantum dots; Gas sensors; Composites; Recovery time
Received: 8 April 2025; **Revised:** 11 June 2025; **Accepted:** 18 June 2025

1. Introduction

The demand for affordable and compact sensor platforms for chemical and biological applications, including those in the biomedical field, has been steadily increasing [1,2]. Organic molecular monolayers with electro-optical properties are essential in various applications, such as dye-sensitized solar cells, metal oxide sensitization, and highly luminescent sensors used for detecting incendiary devices, medications, or biological analytes [3-5]. Molecular monolayers with electro-optical activity are commonly fabricated through solution-based methods [6]. Nanomaterials have proven to be highly effective solutions for numerous applications across various nanotechnology fields [7].

Over the past decade, hybrid composites comprising organic/metal oxides, metal-organic frameworks, and organometallic compounds have garnered significant attention [8]. The sensing properties are primarily influenced by the adsorption and desorption processes of molecules of gas on the active layer. This interaction leads to a reduction in carrier density, which in turn increases the resistance of the films [9]. Multiple studies indicate that the primary determinant of gas sensor performance is the pattern and production of active materials. Thus, the creation of gas sensing materials with great sensitivity, superior discrimination, and low operational temperatures is essential for the progression of sensor technologies and their applications [10].

Colloidal carbon quantum dots (CQDs) possess tunable optical and electronic characteristics, which can be adjusted by altering their composition and crystal structure. Their ability to be processed in solutions at room temperature makes them an appealing choice for developing efficient semiconductor devices on diverse substrates, including solar cells, photodetectors, light-emitting diodes, and chemical sensors. Due to their nanometer-scale size and high surface-to-volume ratio, CQDs offer numerous active adsorption sites, enabling effective interaction with target gas molecules [11]. Carbon quantum dots (CQDs), a unique 0-dimensional (0D) carbon nanomaterial, offer several benefits, including low toxicity, straightforward fabrication, and excellent water solubility. In comparison to other carbon-based nanostructures, CQDs exhibit distinct and desirable properties, making them suitable for various applications [12,13].

Tris(8-hydroxyquinoline) aluminum (III) (Alq_3) serves as a prominent material in the realm of molecular organic light-emitting diodes (OLEDs). This material is frequently utilized as the electron transport layer or the emissive layer in OLED devices. [14-16]. Hydrogen sulfide (H_2S) is a colorless, poisonous, and highly flammable gas. It is frequently encountered in industrial environments, including petroleum refining and wastewater treatment. Given its toxic properties, it is essential to detect H_2S at low concentrations to ensure safety and effective environmental monitoring [17]. Finally, the unique properties of both CQDs and Alq_3 polymer inspired manufacturing sensing devices for high poisonous gases such H_2S.

The aim of this research is to investigate the gas sensing characteristics of CQDs, Alq_3, and their alloy composite (CQDs/Alq_3) to enhance sensitivity, response, and recovery times for H_2S gas detection.

2. Materials and methods:

This study employed an electrochemical method for the fabrication of CQDs, as reported in a prior

investigation by Abd and Ibrahim [12]. The process commenced with the application of an electrical discharge, utilizing a current of 30 mA for a duration of 3 hours, between two submerged carbon electrodes in a solution. The solution was formulated by dissolving 0.3 g of sodium hydroxide (NaOH) in 100 mL of ethanol (C_2H_5OH), followed by diluting the mixture with 0.5 mL of distilled water. The resulting mild, creamy color solution was allowed to sit for several days to yield the CQDs.

A film made of Al/CQDs/glass, as shown in Fig. (1), was prepared by applying a CQDs solution onto a glass substrate. Subsequently, the thermal evaporation method was employed to deposit Al electrodes onto the CQDs-coated glass substrate at a pressure of 10^{-2} mbar. The electrodes encompassed a region measuring roughly 0.9×0.9 mm^2. The CQDs film exhibited a thickness of approximately 1 µm, with a cross-sectional area measuring around 2×2 cm^2. The resulting sample was subsequently subjected to thermal treatment in an oven at 60 °C for a duration of 30 minutes to ensure complete drying.

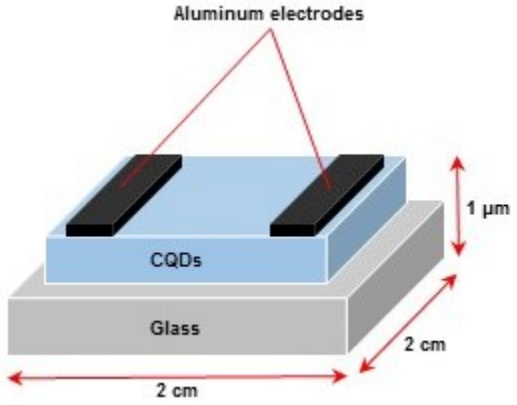

Fig. (1) Schematic diagram of Al/CQDs/glass sample

A solution of Alq_3 polymer was prepared by preparing a high pure chloroform solution containing 30 mg of Alq_3 powder, provided by Tokyo Chemical Industry Company, on a hot plate stirrer at 30 °C for 60 minutes. After that a clear yellow solution was obtained.

Spin coating technique was used to spread the dropped Alq_3 solution on glass substrate for preparing Al/Alq_3/glass film. The spin coating speed and time were 1000 rpm and 30 s, respectively. Thermal treatment was then applied using an oven in order to get our sample drying. Figure (2) depicts the fabricated film.

The composite of CQDs/Alq_3 was synthesized by preparation of Alq_3 polymer of 0.5 mL in 0.5 mL of CQDs solution, achieving a 1:1 ratio of CQDs to Alq_3. The solution was subsequently agitated in an ultrasonic bath for half an hour at 50 °C. The Al/CQDs/Alq_3/glass sample, illustrated in Fig. (3), was fabricated utilizing the spin coating technique, as outlined in the synthesis of CQDs/Alq_3 materials. Following the coating process, the films were subjected to an oven environment at 50 °C for a duration of 30 minutes to ensure thorough drying.

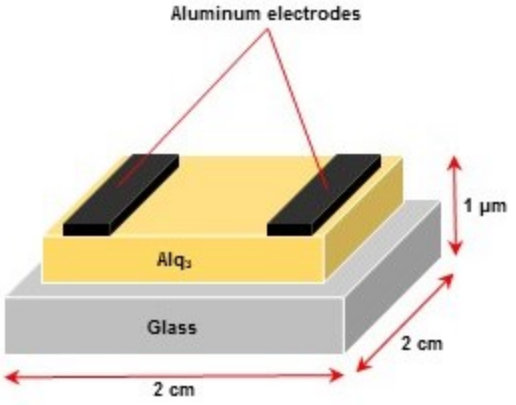

Fig. (2) Schematic diagram of Al/Alq_3/glass sample

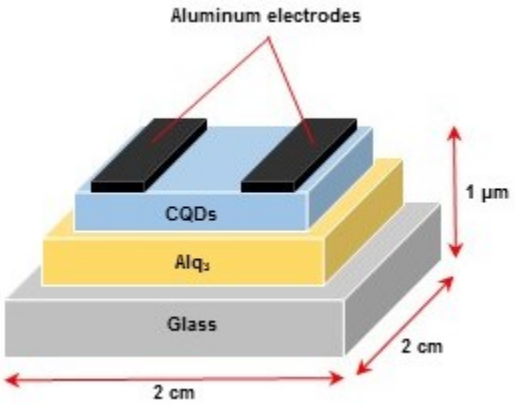

Fig. (3) Schematic diagram of Al/CQDs/Alq_3/glass sample

3. Results and Discussion

The X-ray diffraction (XRD) patterns were conducted to investigate the crystalline structures and phases of the CQDs prepared by spin coating that were displayed in Fig. (4). The peak centered at 2θ=31.7° corresponding to the reflection from the plane of Miller indices (111), the two peaks seen at 45.5° and 66.3° belong to the planes of (311) and (111), respectively. These patterns match with JCPDS card 0558-44 that gives the crystalline phase of the CQDs material. The sharpness and intensity of the peaks indicates CQDs as a promising candidate if combined with a polymer such Alq_3, to improve charge transport and overall device efficiency.

Transmission electron microscopy (TEM) analysis reveals the successful formation of spherical CQDs with particles ranging from 20-30 nm, as shown in Fig. (5). The nanoscale dimensions and well dispersion are high demanding in gas sensing performance due to increasing surface reactivity and efficient charge transfer.

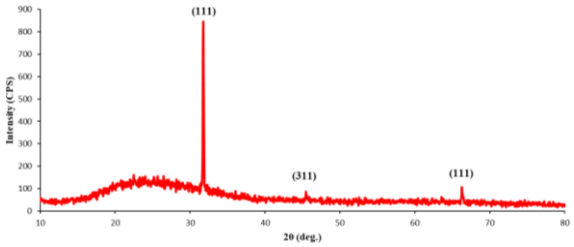

Fig. (4) XRD pattern of the prepared CQDs

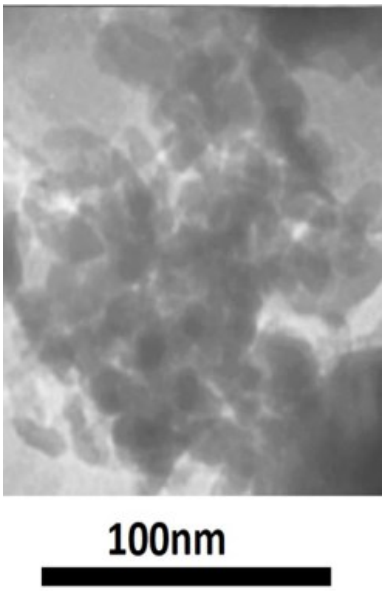

Fig. (5) TEM image of the prepared CQDs

When the Al/CQDs/glass is exposed to H_2S gas at 300°C, it exhibits the highest sensitivity, which can be attributed to gas stability at that temperature. Figure (6) illustrates the variation in the CQDs material resistance with time. Upon exposure to H_2S gas, a significant increasing in resistance is observed (62%), followed by a drop that takes on a Gaussian-like shape. This behavior suggests a dynamic interaction between the CQDs and H_2S gas molecules. The initial increase in resistance could be due to the process of adsorption of H_2S gas molecules on the CQDs outer layer, causing a temporary change in the charge distribution, leading to an increase in resistance. However, as the interaction progresses, the resistance decreases, potentially due to desorption of H_2S molecules or the neutralization of the surface charge, resulting in a shift in resistance toward a more stable state.

When the exposure to H_2S gas is stopped, the resistance undergoes a significant decrease, nearly returning to its original value before exposure (decreasing about 90% from peak value). This behavior suggests that the CQDs undergo a reversible interaction with H_2S gas, where the gas molecules are adsorbed and desorbed over time. The large decrease in resistance after the gas is removed may be attributed to the rapid desorption or dissociation of H_2S from the CQDs surface, restoring the material to its baseline state. This phenomenon highlights the dynamic nature of the sensor's response to H_2S, with the resistance change closely linked to the adsorption and desorption processes occurring on the CQDs surface in the presence of heat and gas.

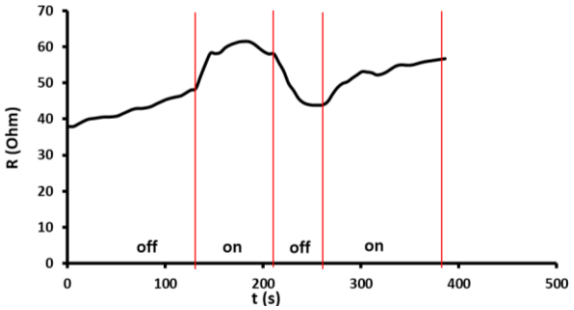

Fig. (6) The variation of resistance of CQDs with time for sensing H_2S gas at 300°C

The extended period for the CQDs resistance to return to the second base level upon the reintroduction of H_2S gas indicates that interactions among the CQDs and gas particles were ongoing. The sensor's resistance failure to return to its original base level after gas removal is associated with the formation of bonds among the atoms of gas and the CQDs sample. The procedure consists of two phases:

(1) The disruption of the attached atoms of gas as they engage with the surface of CQDs, and

(2) The attachment of gas atoms to the material, which causes a prolonged change in the resistance.

The delayed rise in resistance suggests that the CQDs undergo a more complex interaction with the H_2S molecules compared to simpler adsorption events. Specifically, the surface of the CQDs may undergo a transformation due to the chemical bonding with the H_2S gas, leading to a slower recovery process. Additionally, the increase in resistance could be a result of the oxidation of the CQDs surface, which occurs as a consequence of the reaction with the oxidizing gas, further contributing to the delayed return to baseline resistance. This extended recovery time highlights the significant and lasting interaction between the CQDs and H_2S gas.

The response of the CQDs to H_2S gas at 300 °C was assessed. The performance of a sensor is determined by its degree of sensitivity, time of response, and time to recovery. The response time denotes the duration necessary for the detector to reach 90% of the total resistance alter (t_{90}) from its starting resistance when exposed to gas. The recovery time denotes the period required for the sensor to return to 10% of its total resistance change following the removal of the gas. The sensitivity of the CQDs, applied to a glass substrate and subjected to H_2S gas at 300 °C, was calculated to be 28%, indicating that the

CQDs serve as an effective sensor, and the recovery time was relatively short.

Experimental results for Alq_3 polymer, filmed on a glass substrate at 300 °C and exposed to H_2S gas, indicated that Alq_3 does not exhibit sensitivity to the gas. This is due to the fact that organic materials exhibit minimal susceptibility to oxygen, resulting in negligible oxidation or reduction processes. Figure (7) demonstrates the variation in resistance of Alq_3 with time.

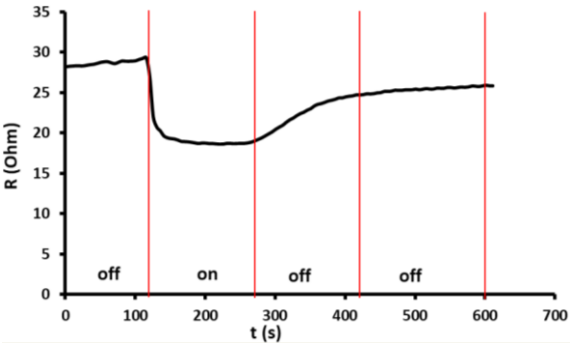

Fig. (7) The variation of resistance of Alq_3 with time for sensing H_2S gas at 300°C

The sensing properties of CQDs/Alq_3 film structure deposited on a glass substrate at 300 °C were investigated in the presence of H_2S gas. The experimental findings revealed a significant resistance enhancement of the CQDs/Alq_3 film structure - approximately 88% - when exposed to the reducing H_2S gas. This increase in resistance corresponds to a reduction in conductance of the material when exposed to gas. However, once the gas exposure was terminated, the resistance returned to its original value, indicating the reversible nature of the sensing process.

The observed behavior can be attributed to H_2S that interacts with the CQDs/Alq_3 material, it will potentially donate electrons, leading to a decrease in the number of holes and, consequently, a decrease in conductivity. The incorporation of Alq_3 polymer as a host for the CQDs enhances the process of charge transfer between the CQDs and the H_2S molecules, facilitating better gas sensing performance. This increase in conductivity, as a result of the charge transfer, improves the overall conductance, as demonstrated in Fig. (8). Table (1) summarizes the obtained data for all fabricated sensors.

Table (1) Response, recovery time and sensitivity of CQDs, Alq_3 and CQDs/Alq_3 sensors when exposed to H_2S gas at 300°C

Sensor	Response Time (s)	Recovery Time (s)	Sensitivity (%)
CQDs	20	29	28
Alq_3	20	105	36
CQDs/Alq_3	11	25	16

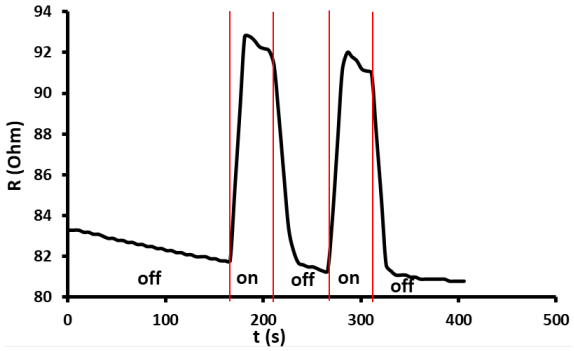

Fig. (8) The variation of resistance of CQDs/Alq_3 structure with time for sensing H_2S gas at 300°C

4. Conclusion

With a remarkably quick response and recovery time, this study showed that carbon quantum dots (CQDs) are efficient sensors for detecting H_2S gas. A CQDs/Alq_3 composite film structure was studied as an H_2S gas sensor. The CQDs' sensitivity to H_2S was greatly increased by the addition of Alq_3. Both response and recovery times were found to decrease, suggesting that the gas sensor's performance had improved. The Alq_3 polymer improved the charge transfer between the H_2S molecules and CQDs and could improve the sensor's electrical characteristics. It can enhance the sensor's sensitivity by promoting improved conductivity and charge transfer when paired with CQDs. Faster reaction times may result from this enhancement in electrical characteristics since the sensor will be able to identify changes in the gas environment more quickly.

References

[1] F.J. Hameed et al., "Enhancing Optical and Electrical Gas Sensing Properties of Polypyrrole Nanoplate by Dispersing Nano-Sized Tungsten Oxide", *ECS J. Solid State Sci. Technol.*, 10(10) (2021) 107001.

[2] R. Shinar et al., "Structurally integrated organic light emitting device-based sensors for gas phase and dissolved oxygen", *Anal. Chim. Acta*, 568(1-2) (2006) 190-199.

[3] A.A. Mahmood et al., "Preparation and Photoluminescence Spectra of Organometallic Complexes Containing Nanoparticles as Random Gain Media", *Indonesian J. Chem.*, 22(1) (2022) 205-211.

[4] S.K. Allawi and M.A. Akraa, "Synthesis and Structural Characteristics of Natural Antibacterial Metal-Organic Complexes", *Iraqi J. Appl. Phys.*, 21(1) (2025) 33-38.

[5] A. Mahmood et al., "Preparation and Physical Properties of Hydroxyquinoline Complexes in Different Solvents", *Iraqi J. Mater.,* 1(4) (2022) 157-166.

[6] A. Räupke et al., "Conformal and highly

luminescent monolayers of Alq_3 prepared by gas-phase molecular layer deposition", *ACS Appl. Mater. Interfaces*, 6(2) (2014) 1193-1199.
[7] F.S. Abed and L.K. Abbas, "Structural, electrical, and thermal properties of Ba-substituted B(Pb)SCCO superconductors prepared by sol-gel method", *J. Sol-Gel Sci. Technol.*, 112(3) (2024) 837-845.
[8] A.J. Noori and I.M. Ali, "Optimization photodetection performance: investigation of doping effect on PVA/Y_2O_3 composite material", *J. Opt.*, (2024), doi: 10.1007/S12596-024-02210-4.
[9] M.H. Suhail et al., "Chemical surface treatment with toluene to enhance sensitivity of NO_2 gas sensors based on CuPcTs/Alq_3 thin films", *J. Sci. Adv. Mater. Devices*, 2(3) (2017) 301-308.
[10] Z. Yu et al., "Fabrication of ZnO/Carbon Quantum Dots Composite Sensor for Detecting NO Gas", *Sensors,* 20(17) (2020) 4961.
[11] M. Li et al., "Grain Size-Engineering of PbS Colloidal Quantum Dots-Based NO_2 Gas Sensor", *IEEE Sens. J.*, 22(4) (2022) 3017-3023.
[12] A.H. Abd and O.A. Ibrahim, "Synthesis of Carbon Quantum Dot by Electro-Chemical Method and Studying Optical, Electrical, and Structural Properties", *Chem. Methodol.*, 6(11) (2022) 823-830.
[13] Y. Qin, X. Liu and J. Xie, "Humidity-enhanced NH3 sensor based on carbon quantum dots-modified SnS", *Appl. Surf. Sci.*, 634 (2023) 157612.
[14] M. Stössel et al., "Impact of the cathode metal work function on the performance of vacuum-deposited organic light emitting-devices", *Appl. Phys. A Mater. Sci. Process.*, 68(4) (1999) 387-390.
[15] A.A. Mahmood et al., "Spectral and Physiochemical Studying for Some 8-HQ Complexes", *Adv. Mech.*, 9(3) (2021) 1199-1214.
[16] A. Mahmood et al., "Some Physical Properties of Metal-Hydroxyquinoline Complexes in Different Solvents", *Iraqi J. Appl. Phys.*, 17(1) (2021) 9-16.
[17] C. Duc et al., "Hydrogen Sulfide Detection by Sensors Based on Conductive Polymers: A Review", *Front. Mater.*, 7 (2020) 556223.

