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Fabrication of Carbon Quantum Dots/Alq_3 Layer for NO_2 Gas Sensor

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Abstract

The gas sensors were prepared using carbon quantum dots (CQDs) using an electrochemical method after mixing the CQDs with Tris (8-hydroxyquinoline) aluminum (III) (Alq_3) polymer. A spin coating technique was used to deposit CQDs/Alq_3 composite film on glass substrates with a ratio of 1:1. The CQDs/Alq_3 gas sensor showed a sensitivity of about 24 %at a temperature of 300 °C, and this was calculated after measuring the change in the resistance of the samples with a response time of 2 and 8sec recovery time. The sensor showed a good response for nitrogen dioxide (NO_2) gas. However, the sensitivity, response time, and recovery time for the CQDs gas sensor when exposed to NO_2 gas at 300 °C were 78%, 4s, and 129s, respectively. The results showed that the best sensor CQDs/Alq_3 led to a reduction in the recovery time, which shows the importance of the Alq_3 polymer in improving the properties of the gas sensor.

Article Info.

Keywords:
Gas Sensor, Alq_3 Polymer, CQDs, Metal Oxide, Sensitivity.

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1. Introduction

Generally, sensors are devices that detect an input physical quantity and convert it into an electrical or optical signal which can be recognized by a receiver [1]. Gas sensors have become one of the important components in various places, and are of great interest due to a wide range of applications, one of which is in the medical field and the military field [2-4].The working principle of gas sensors is to convert a change in chemical information into a change in electronic signal information, such as resistance [5]. Given the importance of identifying gases that are harmful to the environment and humans, it has become necessary to work on manufacturing environmental sensors with a high response speed to control emissions from factories. Different gas sensors have been manufactured depending on the materials used, such as metal oxides, conductive polymers [6], carbon nanotubes [7-9], acoustic gas sensors [10], optical gas sensors, electrochemical gas sensors, and semiconductor gas. The measurement accuracy of gas sensors depends entirely on temperature and relative humidity. The performance of the sensor depends on many variables, such as sensitivity, recovery time, response time, and efficiency of the sensor, which is measured through these variables. Other factors make the sensor attractive to users, such as its small size, wirelessness, and low power consumption [11]. The basic idea of the metal oxide gas sensor is that the gas acts as either an acceptor or a donor to charge carriers; on this basis, the resistance of these oxides’ changes. The decrease or increase of resistance occurring in the thin films of these oxides depends on the nature of the gas molecules, whether they are reduced or oxidized, and the type of carriers that prevail in these films [12]. Gas sensors made of metal oxides show different behaviors for the gas itself, and this depends on the type of the semiconductor, whether it is p-type or n-type.

If the gas sensor is exposed to an oxidizing gas, this gas acts as an acceptor, leading to an increase in the resistance of the n-type semiconductor and a decrease in the resistance of the p-type semiconductor [13]. The history of gas sensors began in 1962 in Japan when a propane gas explosion motivated Naoyoshi Taguchi to conduct research into gas leak detectors. Consequently, in 1968, the first commercial gas sensor invented by Taguchi appeared in the market [14].

Nitrogen dioxide (NO_2) is a gas that is dangerous to human health and the environment and is produced from vehicle exhausts, industrial emissions and the combustion of fossil fuels [15]. When this gas undergoes a photochemical reaction, it forms ozone and acid rain, which causes various medical conditions in humans, such as nausea, coughing, and eye irritation, even at low concentrations. Therefore, detecting NO_2 gas is important due to its negative impact on humans and environment [16]. Currently, Carbon Quantum Dots (CQDs) have been chosen to improve the efficiency of gas sensors, with particles of the order of 10 nm [17]. CQDs have fast photo-generated electron transfer capabilities and have been successfully used as excellent electron acceptors and donors [18, 19]. The reason for using CQDs as sensors is due to their high stability, their ability not to be affected by natural conditions, and their ease in the reduction and oxidization of oxygen (O_2). Organic materials show significant potential in future display applications from small area handheld telecom devices to large area displays due to their high luminance, low fabrication costs, ease to fabricate large area devices and the ability of adjusting the emission wavelength. Tris(8-hydroxyquinoline) aluminum III (Alq_3) is one of the materials which is the most commonly used in molecular organic light emitting diodes (OLEDs). Alq_3 is typically used as electron transport layer or emissive layer in OLED [20]. In organic light-emitting diodes (OLEDs), Alq_3 is a metal chelate often utilized as an electron transport layer. The first description of the usage of this material in OLEDs was published in 1987 [21], and since then, the interest in Alq_3 has been increasing.

In this study, a gas sensor was manufactured using CQDs and Alq_3 polymer using an electro-chemical method and a spin-coating technique.

2. Method

2.1. Preparation of Alq_3 Polymer Solution

To prepare the Alq_3 polymer solution, 30 mg of Alq_3 polymer (supplied by Ossila company) was dissolved in 3 ml of chloroform (a purity of approximately 99%). A magnetic stirring was used for one hour at room temperature to speed up the dissolving process until a clear yellow solution was obtained, as shown in Fig. 1.

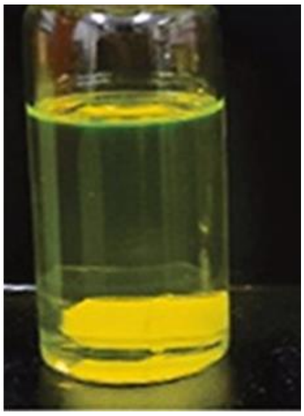

Figure 1: The Alq_3 polymer solution.

2.2. Preparation of CQDs Samples

The CQDs used in this study were prepared using the electro-chemical method, as explained in a previous study by Abd and Ibrahim [22]. The preparation method of the CQDs is by an electrical discharge, using 30 mA current and 3hrs, between two electrodes made of carbon and 99.5 ml of ethanol solution (C_2H_5OH) diluted with

0.5 ml of distilled water and 0.3 g of sodium hydroxide (NaOH) dissolved in ethanol. The resultant mild, milky color solution was left for 5 days to obtain the CQDs.

An Al/CQDs/glass sample, shown in Fig. 2, was prepared as follows: the CQDs solution was dropped onto a glass substrate and the electrodes were deposited onto the CQDs-deposited glass substrate by thermal evaporation method with a pressure of 10^{-5} bar electrodes; the electrodes occupied a region of about (0.8× 0.8) mm. The CQDs film thickness was about 1 µm; the cross-section area of the sample was about (2×2) cm. The samples were placed in an oven at 60 °C for 30 min to complete the drying process.

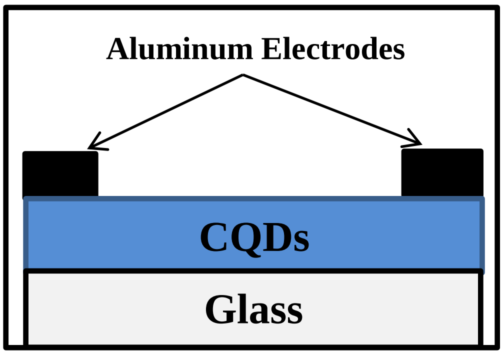

Figure 2: The schematic diagram of Al/CQDs/glass sample.

2.3. Preparation of Alq_3 Samples

Al/Alq_3/glass sample, shown in Fig. 3, was prepared by dropping the Alq_3 polymer onto a glass substrate using the spin coating device where the spin speed of the base was 1000 rpm and the spin time 30s. The samples were placed in an oven at 60 °C for 15 min to complete the drying process.

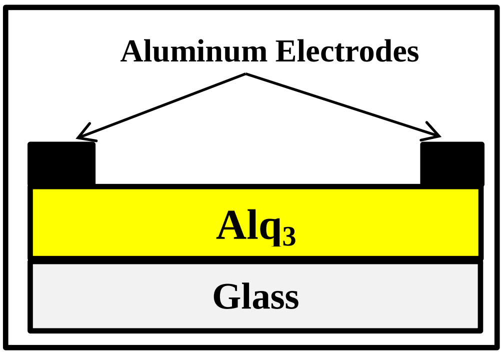

Figure 3: The Schematic diagram of Al/Alq_3/glass sample.

2.4. Preparation of CQDs/Alq_3 Composite Gas Sensor Samples

The CQDs/Alq_3 composite films were prepared by dissolving 0.5 ml of the Alq_3 polymer in 0.5 ml of the CQDs solution i.e., the ratio between CQDs and Alq_3 is (1:1). The solution was then stirred using an ultrasonic bath for 15 min at 60 °C. The Al/CQDs/Alq_3/glass sample, shown in Fig. 4, was prepared using spin-coating as explained in preparation of CQDs/Alq_3 samples. The samples were placed in an oven at 60°C for 30 min to complete the drying process.

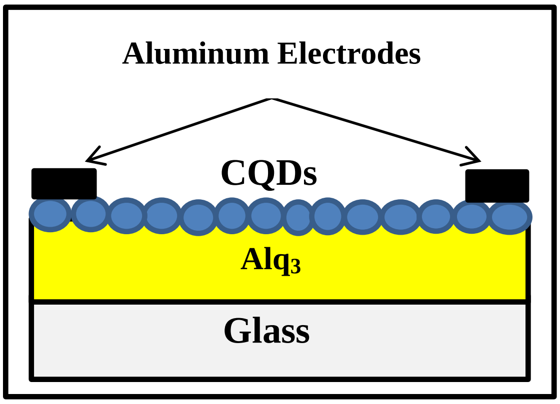

Figure 4: The schematic diagram of the Al/CQDs/Alq$_3$/glass sample.

3. Results and Discussion

3.1. X-Ray Diffraction of CQDs, Alq$_3$ and CQDs /Alq$_3$

The XRD pattern of the CQDs was obtained with an XRD diffractometer (XRD-6000- Shimadzu) with CU Kα radiation of wavelength 1.5406Å and a scanning range of 5–80°. Fig. 5 displays the XRD pattern showing peaks at 2θ equal to 31.7319° and 66.250°, corresponding to (100) and (200) planes, confirming the material to be CQDs.

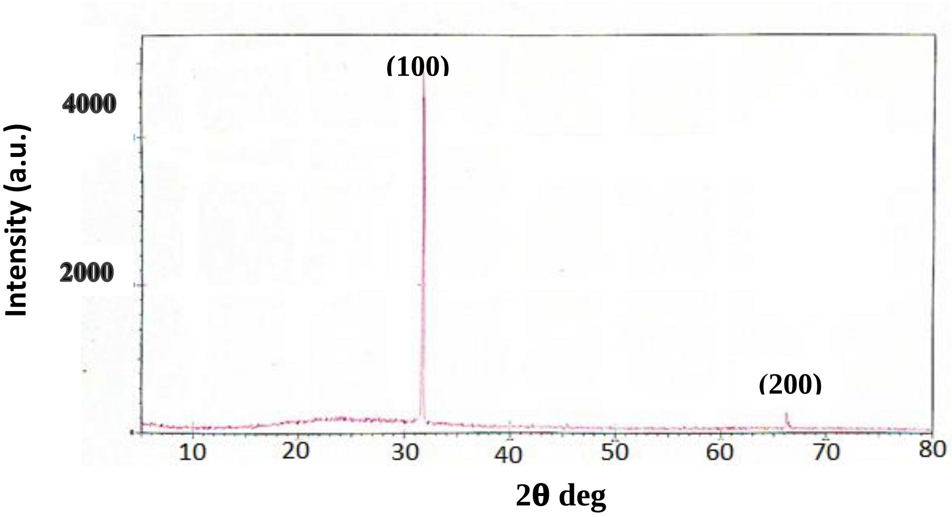

Figure 5: The XRD pattern of the CQDs sample.

The XRD pattern of the as-prepared Alq$_3$ is shown in Fig. 6. All the clear diffraction peaks can be assigned to the cubic Alq$_3$, in agreement with the standard reported values (JCPDS 26-1550). The figure shows a peak at 2θ of 4°, and the angles less than 5° belong to organic materials, indicating that the peak belongs to Alg$_3$.

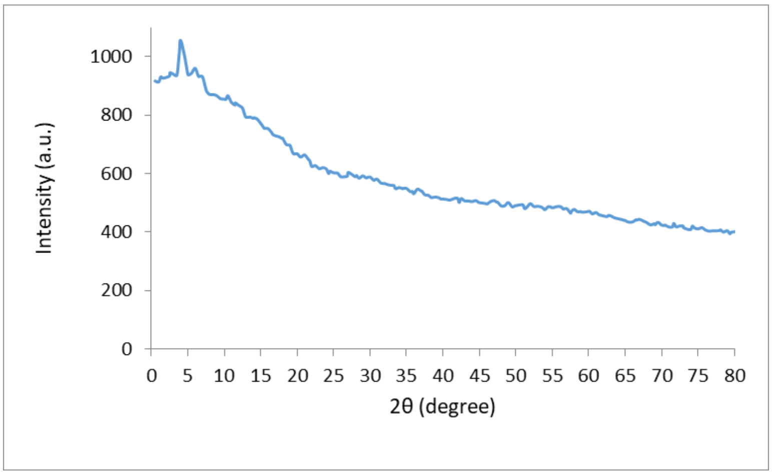

Figure 6: The XRD pattern of Alq_3 polymer.

The Scanning electron microscopic (SEM) examination showed that the sizes of the CQDs were 245, 27, 78, and 188 nm, and this represents the grain size, whereas the UV-Vis absorption spectrum showed that E_g is 3.4 eV and E_g from photoluminescent (PL) is 3.5 eV.

Fig. 7 shows the XRD pattern of the CQDs/Alq_3 composite film prepared using the spin coating technique. The pattern shows a clear peak at $2\theta = 10.67°$ associated with the Miller indices (001). A shift in the CQDs diffraction angle was noticed, indicating the occurrence of interphase between the CQDs and Alq_3.

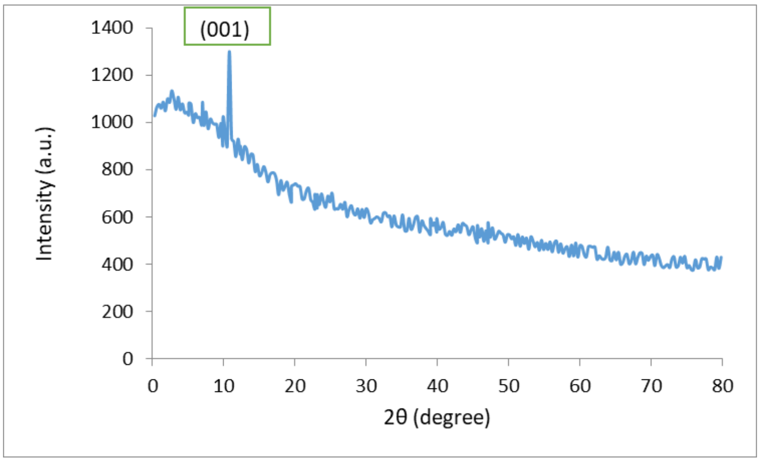

Figure 7: The XRD pattern of the CQDs/Alq_3 composite film.

3.2. Sensing Characteristics of CQDs for Gases

The surface of the prepared CQDs samples get oxidize when exposed to air, the percentage of the existing oxygen is changed with the increase or reduction of the oxidizing gas. These CQDs oxides have a specific resistance; when an oxidizing gas passes through, the sample resistance increases; as the gas is cut off, the resistance does not return to its previous value since some of the O_2 molecules are liberated from the surface.

The CQDs sample is sensitive at 300 ^{o}C and this is due to the stability of the gas at this temperature. Fig 8 shows the relationship between variations of resistance of the CQDs sample as a function of time at 300^{o}C as it is exposed to NO_2 gas. The experimental results showed an increase in the resistance of the CQDs when exposed to the oxidizing gases NO_2 by about 57 % and this is evidence of the sensitivity of the CQDs to NO_2 gas (i.e., occurrence adsorption). However, when the gas was stopped, the resistance did not return to its original value before the exposure to the NO_2 gas, and this is due to the synergy between the CQDs and the particles of NO_2 gas. So, the resistance is stabilized and become a base resistance, because of the presence of heat and the gas which led to interaction between the CQDs and NO_2 forming another base resistance.

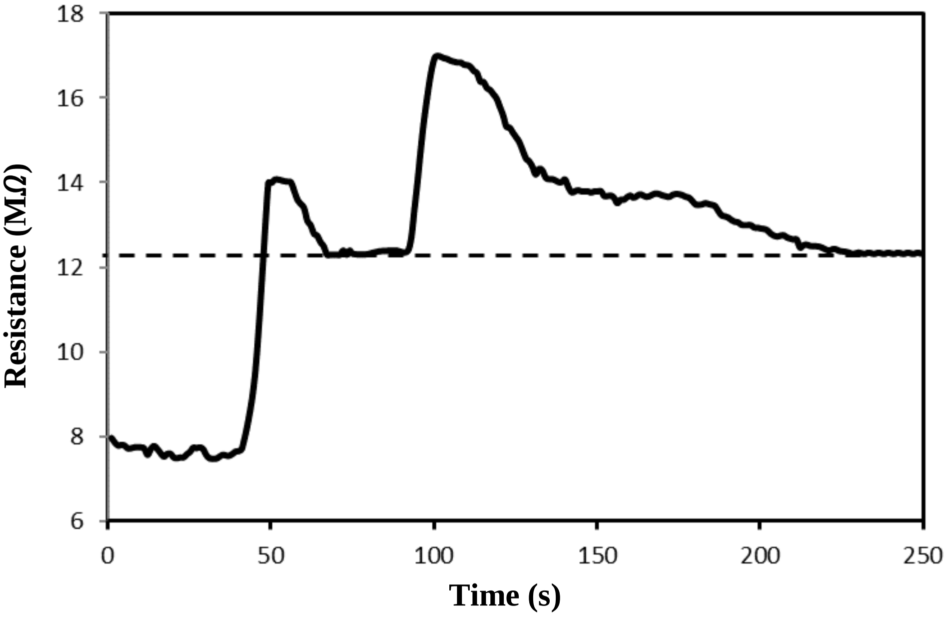

Figure 8: The resistance-time variation of Alq_3 for sensing NO_2 gas at 200^oC.

As the gas was passed again, the CQDs resistance increased by a ratio of 70 %. When turning the gas off, the CQDs took a very long time to return to the second base resistance, indicating interactions between the CQDs and the gas particles.

In general, the failure of the resistance of the sensor to return to its base resistance after cutting off the gas is due to the formation of bonds between one of the gas atoms and the sample. This process occurred in two stages:

1- Breaking the bonds between gas atoms.
2- Adsorption of the gas atoms on the material.

the resistance of the sample was increased due to the oxidation of its surface as a result of the oxidizing gas.

Sensitivity (S) of a sensor is defined as the ratio of the change in the resistance value upon exposure to the target analyte to the resistance value (R_a) of the sensor in air. The sensitivity is calculated as follows [23]:

$$S\% = \frac{R_g - R_a}{R_a} \times 100 \quad (1)$$

where R_a and R_g are the resistances of the sensor in air and in the presence of NO_2 gas, respectively.

The sensitivity of CQDs at 300 °C for NO_2 gas was calculated by Eq. 1. The effectiveness of a sensor is determined by its sensitivity, response time and recovery time. The response time is the time the sensor takes to reach 90% of the total resistance change (t_{90}) from its initial resistance in the presence of a gas. While the recovery time is the time the sensor takes to reach 10% of its total resistance change when the gas is cut off. The sensitivity of the CQDs deposited on a glass substrate upon exposure to NO_2 gas at 300°C calculated using Eq. 1, was 78%; its response time was very short of

4 secs, indicating that the CQDs is a good sensor, but the recovery time was relatively long 129sec, as shown in Fig. 8 and Table 1.

3.3. Sensing Characteristics of Alq_3 for Gases

The experimental results of Alq_3 polymer deposited on a glass substrate at 200 °C for NO_2 gas showed that Alq_3 is not sensitive to the gas. This is because organic materials are weakly affected by oxygen, and do not suffer from oxidation or reduction. Fig. 9 shows the change of resistance of Alq_3 with time.

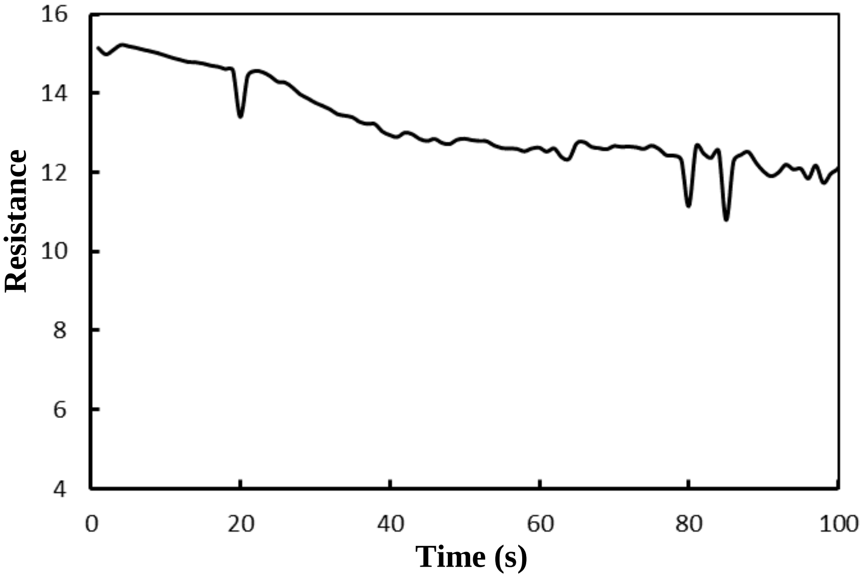

Figure 9: The resistance-time variation of Alq_3 for sensing NO_2 gas at 200^oC.

3.4. Sensing Characteristics of $CQDs/Alq_3$ for Gases

The sensitivity of $CQDs/Alq_3$ thin film deposited on a glass substrate at 300 °C for NO_2 gas was studied. The experimental results indicated an increase in the $CQDs/Alq_3$ resistance of about 75% when exposed to NO_2 oxidizing gas, i.e., an increase in conductance of $CQDs/Alq_3$ when exposed to oxidizing gas. However, the resistance decreased and returned to its original value when the gas was cut off. Due to the highly oxidizing nature of NO_2 gas, a transfer in the charges from $CQDs/Alq_3$ to NO_2 occurred. Adding Alq_3 polymer done as a matrix for implant CQDs accelerates the charge transfer process between the CQDs and molecular NO_2 gas [24]. When the surface of the $CQDs/Alq_3$ is exposed to the oxidizing NO_2 gas, the surface of this film absorbs the gas. The Fermi level moves towards the valence band, and hence the number of holes increases and conductivity increases also (thus enhancing conductance), as shown in Fig. 10.

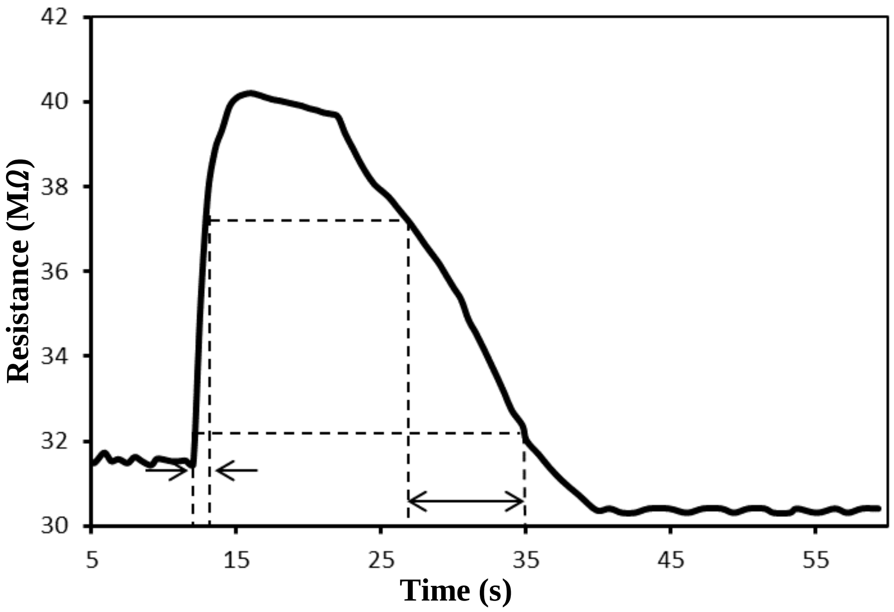

Figure 10: The resistance-time variation of CQDs/Alq$_3$ as a sensor to NO$_2$ gas at 300^{o}C.

The recovery time, response time and sensitivity of the CQDs/Alq$_3$ deposited on a glass substrate upon exposure to NO$_2$ gas at 300 °C were 2 secs, 8 secs and 24%, respectively, as listed in Table 1. Adding Alq$_3$ polymer to CQDs decreased the recovery time, which is an improvement in the properties of the gas sensor. When CQDs and Alq$_3$ were used alone or mixed with silicon, no response occurred, and this is because a mismatch occurred between the materials and the silicon [25].

Table 1: Response, recovery time and sensitivity of CQDs and CQDs/Alq$_3$ samples when exposed to NO$_2$ gas at 300 °C.

Samples	t_s (sec)	t_c(sec)	S%
CQDs	4	129	78
CQDs/Alq$_3$	2	8	24

4. Conclusions

The present study illustrated that CQDs are good sensors because the response time is very short, whereas the recovery time is relatively long. Therefore, when using oxidants or reducing gases, the percentage of oxygen changes, and one of the disadvantages of these samples is that the oxides formed with the substance are strongly bonded, so it is not possible to dispose the substance from oxygen O$_2$. In this study, the manufactured mixture or hybrid thin film of CQDs/Alq$_3$ was studied as a gas sensor for NO$_2$ gas. The addition of the Alq$_3$ contributed to the sensitivity increase of CQDs. It was noticed that the response time decreased with a decrease in the recovery time; this decrease is considered an improvement in the properties of the gas sensor. The addition of Alq$_3$ polymer accelerated the charge transfer process between CQDs and molecular NO$_2$ gas because it works as a matrix for implant CQDs.

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Conflict of interest

Authors declare that they have no conflict of interest.

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تصنيع نقاط الكربون الكمومية / طبقة Alq_3 لمستشعر غاز NO_2

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الخلاصة

تم تصنيع متحسس الغازي باستخدام نقاط الكم النقطية المحضربالطريقة الكهروكيميائية بعد أن تم خلطه مع بوليمر Alq_3 بواسطة جهاز طلاء الدوراني لترسيب الفيلم المركب نقاط الكم النقطية/ Alq_3 على ركائز زجاجية وكانت النسبة بين نقاط الكم النقطية وAlq_3 (1:1) وتم اخذ عدة نسب وهذه افضل نتيجة. اظهر حساس الغاز نقاط الكم النقطية/ Alq_3 حساسية حوالي 24٪ عند درجة حرارة 300 درجة مئوية تم حسابها بعد قياس التغير في مقاومة العينات مع زمن استجابة 2 ثانية وزمن استرداد 8 ثانية يُظهر المستشعر استجابة جيدة لغاز NO_2. في حين أن أوقات الحساسية والاستجابة والاسترداد لنقاط الكاربون الكمية عند التعرض لغاز NO_2 عند 300 درجة مئوية كانت 78 % و 4s و 129s على التوالي، حيث اظهرت النتائج ان افضل حساس نقاط الكم النقطية/ Alq_3 كان يؤدي الى تقليل زمن الاسترداد وهذا يدل على اهمية بوليميرAlq_3 في تحسين خواص متحسس الغاز.

الكلمات المفتاحية: المتحسس الغازي، بوليمر Alq_3، نقاط الكم النقطية، أكسيد المعدن، الحساسية.