Original Article

Design and application of nanoporous graphene oxide film for CO$_2$, H$_2$, and C$_2$H$_2$ gases sensing

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**ABSTRACT**

Nanoporous Graphene Oxide (NGO) film sensor is designed by combining the modified Hummer method and the spray pyrolysis technique. The structural, morphological, and optical characterizations of the prepared NGO sensor are carried by FTIR, XRD, SEM, and UV–vis spectrophotometer. Based on the morphological study, a homogenous and uniform NGO film with two-dimensional nanoporous structure is prepared. The structural study reveals the existence of high density of oxygen functional groups on a typical GO surface with d-spacing 0.82 nm. The optical characterization shows intensive and broad absorption band around 335 nm. The NGO film is used as a detector for CO$_2$, H$_2$, C$_2$H$_2$ gases at room temperature (20 °C). The response, response and recovery times, and selectivity of the NGO sensor are investigated. Also, the effect of gases concentrations on the resistance of the film is studied. The response and selectivity of the NGO film are in order CO$_2$ > H$_2$ > C$_2$H$_2$. The sensor response is 37.04, 16.16, and 2.87% at 60 SCCM for CO$_2$, H$_2$, and C$_2$H$_2$, respectively. The response time is 25, 100, and 100 s @ 10 SCCM for CO$_2$, H$_2$, and C$_2$H$_2$, respectively. At concentrations of 30 SCCM, the recovery time is 241.4, 437.2, and 674.7 s for C$_2$H$_2$, H$_2$, and CO$_2$, respectively. Finally, a simple mechanism is explained to show the sensing approach.

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1. **Introduction**

The identification and sensing of greenhouse gases and vaporous substance species received considerable attention concerning the ecological contamination and hazard emission monitoring in the atmosphere [1]. The development of suitable gas detectors ready to sense greenhouse gases continuously with improved sensing properties will fundamentally enhance the air-contamination control and eco-friendly sustainability [2,3]. Semiconductor metal oxides (MOs)-based gas detectors have received progressive research interest owing to their rapid response/recovery, excellent sensitivity, and low-cost [4,5]. A notable decrease in the crystal size of the metal oxides is commonly implemented to upgrade the gas detecting properties. As the particle size is moving towards double the Debye depletion layer depth (typically from 5 to 15 nm), the sensing properties could be greatly improved [6]. Debye depletion layer is realized at the sub-surface of the oxides because of the adsorbed oxygen molecules at the surface of the sensor. Even so, the concomitant drawback is that these nanocrystals are colossally aggregated, particularly at high temperatures, causing deterioration of the sensing properties...
Besides, the traditionally involved MOs often need high temperatures over 200 °C to accomplish their ideal detecting performance. This requests high power consumption and selectivity deficiency stills challenging because of the fundamental undifferentiated catalytic reactions of the MOs with most of the under focused vaporous species [5,6,8,9].

On the other hand, the particular dynamic sites (hot spots) and the high adsorption capacity of carbon-based nanostructured are desirable features [5,6]. Among various carbon nanomaterials; graphene, graphene oxide (GO), and carbon nanotubes (CNTs) hold incredible guarantee for the development of relatively inexpensive gases sensors with high sensitivity and low energy consumption [10–17]. Their high performance relies upon their superior adsorption ability due to the huge surface/volume ratio and incredible electrical properties modulation upon exposure to greenhouse gases and vaporous substance species [3,18–20]. GO is one of the graphite materials that formed from a graphene sheet functionalized by oxygen functional groups [22,23]. GO can be used as a perfect derivative for the development of efficient gas sensors since it contains a varied range of surface hot spots with easily controlled density [24,25]. Many researchers endeavored to utilize the reduced graphene oxide (rGO) in gas detecting applications due to its controllable surface defect density that controls the sensor performance [26–28]. Nevertheless, utilizing rGO rather than graphene in gas sensors required post-chemical or thermal treatment for the reduction process, which raised up the manufacturing cost [29].

In the recent period, some studies are carried out to determine many gases using graphene or GO sensors. Srivastava and Jain conducted a study to detect NO2 gas using SnO2, MWCNT/SnO2, and graphene/SnO2 sensors [30]. SnO2 and MWCNT/SnO2 sensors exhibited a weak and slow response to NO2 at room temperature in comparison to the graphene/SnO2 sensor. Feng et al. fabricated a reduced GO sensor encapsulated Co3O4 nanocrystals utilizing the electropinning method to detect NH3 gas [31]. The sensor has the morphology of nanofibers and exhibits a proper sensitivity with the NH3 gas. Vasi et al. designed a NO2 gas sensor utilizing rGO coated clad etched fiber Bragg grating (EFBG) [32]. The study carried out on different concentrations of NO2 gas. A considerable Bragg wavelength shift is detected in the measured reflection from the sensor after exposure to 0.5 ppm – NO2 gas.

In the recent years, a limited number of studies were accomplished to detect CO2, H2, or C2H2 gases. Hafiz et al. studied experimental CO2 gas detector utilizing hydrogen plasma rGO at room temperature [33]. The sensor showed sustainable performance with 4 min recovery time and 4 min response time during the exposure to CO2 gas of 750 and 769 ppm. Moreover, Li et al. synthesized porous ZnO based N-doped rGO (N-rGO-ZnO) via a two-step technique [34]. The pores sizes of N-rGO and N-rGO-ZnO were measured, and the adsorption/desorption analyses of CO2 and N2 were investigated. The sensor selectivity to CO2 was evaluated in the existence of N2 gas. Uddin et al. developed a C2H2 gas sensor of composite (Ag, ZnO, and GO) nanomaterials by a rapid photochemical method [35]. 5 wt.% Ag/ZnO Hrc-rGO hybrid displayed a high performance for C2H2 (12.3 at 100 ppm) at 200 °C with response time 57 s and good selectivity. Zhang et al. synthesized SnO2 of flower-like morphology and a series of SnO2/graphene composites sensors by a simple hydrothermal process for detecting H2 gas at operating temperatures varied from 30 to 180 °C [36]. The SnO2/graphene sensor exhibits high H2 sensing response (87.2%) at 150 °C.

In light of the previous survey, there have been no complete reports about the CO2, H2, and C2H2 gas sensing properties at room temperature (RT) utilizing a nanoporous GO (NGO) film. Also, there is a strong request for ease and straightforward fabrication technique that offers homogeneity of the obtained NGO film, ease of compositional modification, substantial area substrate coating and the ability to scale up to industrial manufacturing. In this work, NGO film is fabricated by a modified Hummer method followed by spray pyrolysis method and characterized by different analysis techniques. The NGO film sensor is used to detect CO2, H2, C2H2 gases at RT. The gas sensor response, selectivity, and response and recovery times are addressed at different concentrations.

2. Materials and experimental details

2.1. Materials

Graphite fine powder was bought from Alpha Chemika, Mumbai. KMnO4 and H2SO4 were obtained from El Nasr chemical company, Egypt. H2O2 and H3PO4 were supplied from Bio-Chem company, Egypt. DMSO (Dimethyl sulfoxide) was purchased from Alpha Aldrich company, USA. All used chemicals were of analytical reagent grade and prepared using deionized (DI) water.

2.2. Preparation of NGO sensor

Firstly, GO nanoparticles are fabricated via the modified Hummer method [37]. This method depends on the graphite powder oxidation using KMnO4 in the presence of a mixture of H3PO4 and H2SO4. One gram of graphite powder is added to a mixture of concentrated H2SO4 and H3PO4 (120 and 14 ml, respectively) in an ice bath. Afterward, KMnO4 (6 g) is dropped over them gradually for 1 h under the magnetic stirring. The obtained mixture is magnetically stirred for 24 h at 50 °C. After that, 0.05 M H2O2 (800 ml) is dropped one by one over them to react with the excess KMnO4. The mixture discharged a considerable measure of bubbles. Also, the color of the mixture is turned into brilliant yellow. For additional purification, the prepared GO nanoparticles are dispersed in DI water. After that, the purified GO dialyzed for seven days to remove any residual acids and salts.

After preparation of the GO nanoparticles, the spray pyrolysis method is used to deposit a nanostructured film from the GO nanoparticles on the surface of a cleaned glass substrate. A glass substrate of thickness 1.3 mm and area 2 × 2 cm2 is cleaned via ultrasonication in C2H5OH (acetone), CH3OH (methanol), and DI water for 10 min each. Formerly, the air gun is used to dry the glass substrates. Then, the substrate is baked for 20 min at 100 °C to eliminate any remaining moisture. After that, the GO solution (1 mg/ml) was sprayed with the rate of 30 μl/min for 20 min over the glass substrate. The spray process was carried out at 300 °C.

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2.3. Characterization of the prepared NGO sensor

The crystal structure of the deposited NGO was investigated by high-resolution X-ray diffractometer (XRD) system (model: PANalytical X’Pert Pro, Holland) with CuKα1 of wavelength 1.5406 Å worked at 40 mA and 45 kV. The charts of XRD were measured at 2θ ranged from 5 to 80°. The XRD charts were matched with the standard JCPDS charts. NGO Morphology was studied by SEM (Model: ZEISS SUPRA 55 VP and ZEISS LEO, Gemini Column). The optical absorbance spectrum of NGO sensor was recorded using UV/Vis/IR spectrophotometer (Lambda 900, Perkin Elmer) at room temperature in the wavelength range 200–900 nm. The functional groups of NGO were characterized by Fourier Transform Infrared (FTIR) spectrophotometer (JASCO, FTIR-6200) within wavenumber range 4000–400 cm⁻¹. Current-voltage (I–V) behaviors were recorded.

![Graphs and Images]

Fig. 1 – (A) FT-IR spectrum, (B) XRD pattern, (C, D) SEM images at different magnifications, (E)TEM image, and (F) absorption spectrum of NGO film.
by Keithley measurement- source unit (2400) utilizing a two-point probe method.

2.4. **CO₂, H₂, and C₂H₂ gas sensing measurements**

The sensing performance of NGO sensor towards CO₂, H₂, and C₂H₂ gases was investigated through a specially designed gas sensing system as shown in Figure S1 (Supplementary data). A glass chamber of 1 L volume sealed with rubber O-rings has been used for the gas sensing measurements. The chamber has three holes, two of them for gas inlet and outlet, and the third hole is supported by electrical feedthrough to get the electrical signals. The sources of the target gases (CO₂, H₂ or C₂H₂) are commercially available gas cylinders. The concentrations of the gases are controlled by a mass flow meter ( Alicat Scientific, Inc. Tucson, AZ USA).

For the sensitive detection of gas in our set-up, a load resistance (RL = 491.3 kΩ) is used in series with the NGO sensor and input voltage VC = 1 V was applied from DC power supply (IMPO 11.11, 30 V/3 A). Before measurements, N₂ gas is flow to remove any atmospheric gas in the cell. The recovery occurs using synthetic dry air as a balance gas. The sensor output signal (output voltage, Vout) was recorded across RL using Fluke Digital Multimeters 287/289 interfaced with a computer, whereas the target and carrier gases were switched on/off each cycle. The experimental set-up was operated at RT during the data acquisition. Conducting silver paste was applied to make Ohmic contacts on both ends of the NGO sensor to serve as the electrodes. The NGO sensor was inserted into the glass chamber. Different gas concentrations from the target gas were introduced into the chamber, and the sensor output voltage was measured. The sensor resistance (RL) was calculated with a measured value of Vout by using Eq. (1):

\[ R_L = \frac{V_L - V_{out}}{V_{out}} R_L (1) \]

### Table 1 – The FT-IR analysis of the NGO film.

<table>
<thead>
<tr>
<th>Band position (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>O–H stretching vibrations of hydroxyl groups [38]</td>
</tr>
<tr>
<td>1632</td>
<td>Vibration of C=O carbonyl group [38]</td>
</tr>
<tr>
<td>1630</td>
<td>The coordinated H₂O molecules [39, 40]</td>
</tr>
<tr>
<td>1155 and 1041</td>
<td>The C–O epoxide group stretching [41]</td>
</tr>
<tr>
<td>600</td>
<td>C–H out of plane bending vibration</td>
</tr>
</tbody>
</table>

The XRD chart of the NGO film displays a peak at 2θ = 11.2°, Fig. 1(B). The XRD peak is corresponding to a typical GO film with d-spacing 0.78 nm. The water content has a high effect on the d-spacing of the graphite oxide [42], in which the measured distance equals to one-water molecule-thick layer that is connected through hydrogen-bonded sandwiched between the GO sheets [43]. The average size of the ordered GO sheets that stacked in the NGO film and oriented normal to the plane of growth is estimated utilizing the full width at half mean (β in radians) and Bragg’s angle (θ in degree) of the XRD peak using the Debye–Scherer formula. \( d = \frac{0.94λ}{β \cos θ} \); where λ is the X-ray wavelength (CuKα 1 = 1.5406 Å) [44]. From the equation, the average size of the NGO crystallites is 10.65 nm.

The surface topography of the NGO film is observed by SEM images, Fig. 1 (C, D). The SEM images show the formation of a homogenous and uniform NGO thin film of a two-dimensional nanoporous structure. The pores are randomly distributed on the film surface. This nanoporous nature is ascribed to the self-assembly of GO nanoparticles during the spray pyrolysis deposition. Also, Fig. 1 (E) shows TEM image for the prepared NGO film. From the image, the NGO appears as transparent flat graphene sheets stacked together. The inset of Fig. 1(E) also confirmed the nanoporous nature of the NGO sheet. Fig. 2(A) shows a histogram of pore diameters distributions of NGO film. The pore diameters are ranged from 7.67 to 24.54 nm with a mean value of 14.51 ± 3.72 nm.

The optical characterization of the GO nanoporous film is a major factor for different applications. The UV/Vis absorption behavior of NGO film is represented in Fig. 1(F). This spectrum noticeably displays broad and strong absorption bands about 335 nm. The observed band is originated from various intra- and inter-band transitions. The NGO film absorption is decayed exponentially at wavelengths greater than 450 nm. The NGO absorption is approximated to zero at the IR range. The broad peak that centered at 335 nm is ascribed to the n–σ⁺ and n–π⁺ transitions of C=O bond and the aromatic C–C ring, respectively [45]. In the high absorption region of a film with a band gap Eg, the coefficient of absorption (α) is dependent on the energy of the incident photon (E = hν) according to Tauc equation [45]: \( αE = A(E–E_g)^{2} \). A represents an independent energy constant. The Eg value of NGO film is estimated to be 2.78 eV by extending the linear portion of (αE)^2 versus E curve, Fig. 2 (B). To the best of our knowledge, this value has not been achieved with as- prepared GO (E_g ≈ 3.5 eV), how-

### 3. Results and discussion

3.1. **Structural, morphological, and optical characterization of NGO sensor**

It is well-known that the textural and morphological properties of the film-based sensors influence their sensing performance. Therefore, it was authoritative to explore the surface texture and morphology of the NGO film through FTIR, XRD, and SEM analyses. Figure S2 (supplementary data) shows (a) top-view SEM image of GO and (b) height profile of two GO nanosheets obtained using atomic force microscope (AFM). The obtained dimensions from SEM are width = 3.303 ± 0.65 μm and length = 5.145 ± 1.108 μm. From the AFM height profile, the average value of GO height = 3.92 ± 0.46 nm and 3.19 ± 0.26 nm for the two sheets. Fig. 1(A) and Table 1 show the FTIR spectrum of the NGO film and its analysis, respectively. The characteristic intensive peaks of the NGO film refer to the existence of high content from the oxygen functional groups on NGO surface; hydroxyl group (–O–H), epoxy (–C–O–C–), carbonyl (–C=O), and carboxyl groups (–C–OOH) [38–41]. The XRD
ever much lower values have been reported for reduced GO or post-treated GO [46]. The reduction in the $E_g$ value has been ascribed to the rise in the C/O ratios due to the elimination of a particular functional group or nitrogen doping [47]. Here, we reduced the $E_g$ of the GO itself and achieving control over its morphology to produce a nanoporous film of huge surface area without the elimination of the function groups. These properties are important for gas sensing applications.

Urbach energy, $E_U$, is used to determine the band gap tail width and related to the absorption coefficient and photon energy according to the relation; $E_U = \left[ \frac{\alpha h_\nu}{h_\nu} \right]^{-1}$. $E_U$ is ascribed to the tail in the valence band and conduction band due to the material disorder. From the plot of $\ln(\alpha)$ versus $h\nu$ (Fig. 2(C)) the value of $E_U$ for NGO film is 572 meV. The Urbach energy is commonly used to quantify the structural and thermal disorder [48]. The higher the value of Urbach energy, the higher appearance of localized states associated with the grain boundaries [48].

3.2. Gas sensing properties of NGO sensor

3.2.1. Current-voltage characteristic of the NGO film under different gases exposure

The working rule of the proposed NGO sensor depends on the charge/electron exchange between the adsorbed gas molecules and the NGO film [3]. The current-voltage ($I$-$V$) behaviors of NGO film under exposure to different gases of 50 SCCM at RT ($20^\circ$C) are demonstrated in Fig. 3. The I-V curves of NGO film were measured by differing the voltage ($V$) up to 200 V with an increment of 1.0 V. Fig. 3(a). The behavior of the I-V curves is approximately linear. The plot of $\log (V)$ and $\log (I)$ for NGO film in different environments is presented in Fig. 3(b). This figure can be used to estimate the values of the nonlinear coefficient ($\alpha_n$) based on the relation $I = CV^{\alpha_n}$, where C is a constant. Then, $\alpha_n = d [\log (I)]/d [\log (V)]$. The $\alpha_n$ parameter is used to measure the nonlinearity of an element as a function of the applied voltage. As illustrated in Fig. 3(b), there are two regions (1 and 2) and hence two values of $\alpha$ ($\alpha_1$ and $\alpha_2$). The values of $\alpha_1$ and $\alpha_2$ are listed in Table 2 and indicating to the non-ohmic I-V behaviors of the NGO film.

From the I-V characteristics, the calculated slope in the CO$_2$ environment is more significant than its value in the other environments. In the CO$_2$ atmosphere, the value of current increases with high rate by increasing the applied voltage, this refers to the high sensitivity of the NGO film towards CO$_2$ gas. For H$_2$ and C$_2$H$_2$ gases, there is a slow increase in current by increasing the voltage value. The air current value represents the standard value in the relationship between current and voltage. The values of conductance ($G_{dc}$) and resistance (R) were calculated from Fig. 3(a) and presented in Table 2. As shown, the values of the dc conductance ($G_{dc}$) of NGO sensor is increased in the CO$_2$ environment because less number of carriers are trapped in the boundaries of the grains and more electrons are liberated. In the other hand, the $G_{dc}$ value is decreased in the H$_2$ or C$_2$H$_2$ environment. This decrease arises because of the incomplete bonds between the atomic layers working as heat sinks for catching the charge carriers and reducing the conductivity of the film [37]. Also, adsorption of H$_2$ or C$_2$H$_2$ leads to oxygen vacancies due to out diffused oxygen [7,49]. This increases the density of the surface defects and decreases the surface conductivity [38]. In general, the existent gas concentration could be detected by measuring the resistance/conductance change of the NGO film in different gases [50]. From Table 2, the conductance of NGO film is changed according to the type of the gas, in which it takes the order $G_{CO_2} > G_{air} > G_{H_2}$ or $G_{C_2H_2}$. In contrast, the values of resistance of the NGO film decrease by the same order for these different gases. From these conductance or resistance values, the concentration of any gas can be determined.

3.2.2. Effect of CO$_2$, H$_2$, and C$_2$H$_2$ gases concentrations

Fig. 4 illustrates the variation in the resistance of NGO film versus the exposure time to different gas concentrations of CO$_2$, H$_2$, and C$_2$H$_2$ gases ranging from 10 to 60 SCCM at RT.
Fig. 3 – (a) I-V and (b) Log (I) - Log (V) plots for NGO film under different gases of 50 SCCM.

Table 2 – The resistance, conductance, and nonlinear coefficient parameters ($\alpha_1$ and $\alpha_2$) of NGO film under different gases of 50 SCCM.

<table>
<thead>
<tr>
<th>Type of gas</th>
<th>CO₂</th>
<th>Air</th>
<th>C₂H₂</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance (Ω)</td>
<td>$4.4182 \times 10^6$</td>
<td>$14.141 \times 10^6$</td>
<td>$17.618 \times 10^6$</td>
<td>$37.471 \times 10^6$</td>
</tr>
<tr>
<td>Conductance (S)</td>
<td>$22.634 \times 10^{-8}$</td>
<td>$7.072 \times 10^{-8}$</td>
<td>$5.676 \times 10^{-8}$</td>
<td>$2.669 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>3.57</td>
<td>4.83</td>
<td>5.59</td>
<td>5.15</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>1.075</td>
<td>1.078</td>
<td>1.076</td>
<td>1.042</td>
</tr>
</tbody>
</table>

Fig. 4 – Resistance variation and steady state of NGO thin film versus operation time at RT (20 °C) for different concentrations of gases (A, A⁻) CO₂; (B, B⁻) H₂; and (C, C⁻) C₂H₂, respectively.
(20°C). For all gases, the flow time was adjusted to 5 min and the recovery gas was the air environment. CO₂ appears to act as an oxidizing agent gas, while H₂ and C₂H₂ are reducing agent gases to the NGO film. As shown in Fig. 4 (A), there are decreases in the resistance values of NGO film with time under the flow of CO₂ gas of different concentrations. Also, the rate of decline in the resistance value increases by increasing the CO₂ concentrations from 10 to 60 SCCM. This behavior is due to the pole of the oxidizing CO₂ agent, which takes electrons from the NGO film surface and increases the numbers of holes. Then, the mobility of the electrons increases and the resistance decreases [50,51]. As a result, the nanoporous NGO film sensor shows a high response to deficient concentrations of CO₂. After 5 min, the flow of the CO₂ is stopped, and the recovery occurs using the air environment. But, the recovery is not so fast and takes about 9 min to reach the reference resistance. This refers to a very strong adsorption of CO₂ on the NGO film and hard desorption [52,53]. Also, the steady state of the GO sensor for 60 SCCM CO₂ gas is about 5 s, Fig. 4(A−), which represents a -1.66% delay in response time to CO₂ gas at room temperature. This small value refers to the high response of the NGO sensor towards CO₂ gas.

After measuring the CO₂ gas, the sensor is applied to detect other gases (H₂ and C₂H₂). After each gas measurements, the NGO sensor is annealed for 2 h at 60°C in the air. So, several hours of annealing at high-temperatures in a vacuum is not necessary to get rid of the adsorbed gases molecules [54]. As shown in Fig. 4 (B, C), there is an increase in the resistance values with the exposure time at the applied concentrations. The rate of change of the resistances for C₂H₂ < H₂ < CO₂ gas is shown in Fig.4. Also, the steady states of the GO sensor for (60 SCCM) H₂ and C₂H₂ gases are 19 and 32 s, Fig. 4(B−, C−), which represents a -6.33 and -10.66% delay in response time to H₂ and C₂H₂ gases respectively, at room temperature. From the steady-state values, the sensor response to gases is in order CO₂ > H₂ > C₂H₂.

From the behavior of the resistance with exposure time, the sensing process could be explained. H₂ and C₂H₂ are electron donors. So, they can donate the electrons when the adsorption process occurs at the NGO surface. This reduces the holes’ concentration in the graphene oxide and then increase the resistance as observed [55]. Also, H₂ or C₂H₂ would diffuse through the nanostructure of the graphene oxide and occupy active sites on the nanoporous film. The adsorption of more H₂ or C₂H₂ on the NGO (p-type) would, therefore, donate more and more electrons to the bulk [51]. As a result, a further increase in the resistance is detected in Fig. 4(B, C)

### 3.2.3. NGO response

The response of the film is calculated from the electrical resistance upon exposure to gas (Rg) and air (Ra) by Eq. (2) [56]:

$$\text{Response} = \frac{R_g - R_a}{R_a} \times 100(2)$$

Fig. 5 illustrates the change of the calculated NGO response versus the concentration of CO₂, H₂, and C₂H₂ gases. For all gases, the sensor response nature of the NGO sensor is increased by increasing the gas concentration from 20 to 60 SCCM. This is owing to the increase in the rate of adsorbed gas molecules as the concentration increased. Hence, more active sites are occupied on the NGO surface. The response of the NGO film is in order S<sub>CO₂</sub> > S<sub>H₂</sub> > S<sub>C₂H₂</sub>. For example, at 60 SCCM, the sensor response is 37.04, 16.16 and 2.87% for CO₂, H₂ and C₂H₂, respectively. GO sensor shows a higher response towards CO₂ because of the existence of several polar functional groups on NGO film that attracts the polar CO₂ gas [57]. In addition, the response of the sensor resistance to methanol, ethanol, and acetone gases is studied and shown in Fig.S3 (Supplementary data). From Fig.S3 and Eq.2, the values of GO sensor response to methanol, ethanol, and acetone are 0.03, 0.03, and 0.08% @ 60 SCCM. These values are so small compared to the sensor response towards CO₂ gas. This indicates the higher selectivity of the sensor towards the CO₂ gas.

### 3.2.4. NGO selectivity

Gas sensor selectivity towards a specific gas molecule is the ratio between its response to this gas molecule and its...
response to another interfering gas molecule in the atmosphere [58], which can be calculated from Fig. 4. Fig. 6 illustrates the relation between GO sensor selectivity and gas concentration at 20°C. From this figure, the NGO film has the best selectivity to CO2 in the existence of both C2H2 and H2 gases. Also, the selectivity of the GO sensor for H2 gas is more than the selectivity for C2H2. This relation confirms the higher adsorptivity of CO2 gas molecules on the NGO surface than the adsorptivity of H2 or C2H2 gas molecules. This behavior is a result of the polar oxygen-containing groups of GO, which leads to higher polar surface energy and higher binding energy (hundred meV/molecule) [12,59,60]. This binding energy is more significant to the polar CO2 gas than the other nonpolar gases. From Fig. S3, the sensor selectivity for methanol, ethanol, and acetone is very poor (≤3 × 10⁻³). This indicates the higher selectivity of the studied sensor towards the CO2 gas.

### 3.2.5. Response time and recovery time

The required time for a relative resistance variation to reach 90% of the steady-state resistance after the injection of the targeted gas is known as the response time [3]. The values of the response time for different gases at different concentrations are estimated from Fig. 4. Fig. 7(A) represents the variation of the estimated response time with the concentration of the gas molecules. The response time of the NGO sensor is increased with increasing the concentration of the studied gases from 10 to 60 SCCM, indicating that a higher number of active sites required more time to saturate [61]. The response time of the NGO sensor for H2 or C2H2 is higher than that for CO2 gas. The obtained results are agreed well with previously testified data for graphene-based sensors [62,63]. At 10 SCCM, the response time is 24.58, 100.12, and 114.99 s for CO2, C2H2, and H2, respectively.

The recovery time is the needed time for a sensor to reach a resistance of 10% above the steady-state value [35]. The values of the recovery time are estimated from Fig. 4 and illustrated in Fig. 7 (B). For all gases, the recovery time of the NGO sensor is increased with increasing the concentration of the gas molecules from 10 to 60 SCCM. The recovery time increases from 175.75 to 284.8 s for C2H2, 185.75 to 963.60 s for H2, and 146.17 to 1003.19 s for CO2 as the concentration increased. The short recovery time in case of C2H2 gas molecules could be ascribed to the feeble interaction between the gas molecules and the NGO film [63]. The behavior of response time and recovery time clearly indicates the higher sensitivity and selectivity of the NGO sensor to CO2 than H2 or C2H2 gas.

### 4. Sensor stability and humidity effect

The NGO sensor stability is investigated by evaluating its response and recovery to CO2, H2, and C2H2 gases daily for 6 days in air environment as displayed in Fig. 8 (A–Q). The recovery occurs using an air environment with a relative humidity of 39.7%. The measurements take place at room temperature for gases of concentration 60 SCCM. From the figure, the sensor has almost the same values for the response and recovery behaviors to all gases for six days. The high stability of the NGO sensor is ascribed to its high efficiency and its ability to adsorb and desorb the gases on its surface that has a lot of active sites. Therefore, the acceptable responses, recoveries, repeatability, and stability reveal the excellent practical viability of the fabricated NGO sensor for the detection of these gases, especially CO2 gas.

It is well known that humidity plays an important role in the testing of sensitivity. To study the effect of humidity in the response of NGO sensor, we measured the NGO response in dry and humid air with relative humidity changed from 20.2 to 69.9% at room temperature. As the humidity increased, the sensor response decreased from 37.04 to 33.60% as illustrated in Fig. S4(a) (supplementary data). This validates the real application of NGO to gas sensors.

In addition, in an ideal test environment, the interference from NO2 can be avoided. But in a real application, maybe NO2 is mixed with the target gas. NO2 is an oxidizing gas. Therefore, it will capture electrons and increase the hole density in P-type NGO, decreasing the sensor’s resistance. Therefore, the cross-sensitivity test is used to determine the NGO ability to differentiate a target gas (i.e. CO2) in the presence of interfering NO2 gas. The cross-sensitivity test was carried out to detect CO2 in dry air, followed by a second one to detect CO2 in the existence of NO2 (10 SCCM). As a result, the NGO film sensor shows an increasing response in the existence of the interfering NO2 gas, the increase reached 8% at 60 SCCM CO2, Fig.S4(b) (supplementary data).

### 4.1. Role of NGO and sensing mechanism

The NGO is distinct from Pristine GO and characterized by a large surface area and nanoporous topography, small energy gap (2.78 eV), high content from the oxygen functional groups (hydroxyl, epoxy, carbonyl, and carboxyl groups) and respectable electric conductivity. Figs.1–3. Then, NGO is a type of graphene-oxide sheet with abundant hydroxyl groups and nanoporous surface to enhance the electrostatic interaction with the analytes, facilitate the electron transfer between gas molecules and the sensor, and improve the adsorption/desorption capabilities due to the presence of high density of the charged sites. All of these making NGO ideal key material for the design of selective, sensitive, and stable room temperature gas sensors, Figs. 4–8. These results agree well with previously reported data for atomically thin porous graphene, electron beam-irradiated GO, rGO/ZnO nanofibers and microwave irradiated ZnO/graphene nanocomposites [64–67].

The gas detecting mechanisms using 2D nanomaterials-based sensors are not entirely described until now and only attributed to the gas molecules adsorption/desorption on the surface [48,68,69]. The adsorbed gas molecules are working as electron acceptors or donors on the GO surface, which prompts changes in the GO conductance [59,69,70]. Additionally, the small band gap is another key to enable the NGO sensor to operate at RT depending on Van der Waals forces (physisorption), which enable the quick response and recovery properties of the NGO film at RT. Moreover, the huge surface/volume ratio, nanoporous nature, high crystallinity, and the high density of oxygen functional groups in the NGO surface lead to fast and stable adsorption of gas molecules.
molecules are adsorption decrease of gas shown ever, the NGO film, as shown in Fig. 4, i.e., the resistance of NGO decreases with CO2 gas at room temperature. The charge transfers between CO2 and graphene (due to the reduction of GO) allow the detection of CO2 in the air under standard conditions. The interaction of CO2 with hydroxyl ions of NGO leads to the formation of carbonate (CO$_2^{2-}$) ions [CO$_2^{+}$ (gas) + OH$^-$ + HCO$_3^{-}$ (pores) and then HCO$_3^{-}$ + OH$^-$ + CO$_2^{2-}$ (bulk) + H$_2$O (gas)]. Besides, at low temperature (25 °C), the dissociated OH$^-$ and H$^+$ ions from H$_2$O molecules at the surface of NGO can react with CO2 to form CO$_2^{2-}$ ions [CO$_2^{+}$ (gas) + H$^+$ + 2e$^-$ ↔ HCO$_3^{-}$ (surface) and HCO$_3^{-}$ → CO + OH$^-$ (surface)] [71]. Then, the presence of CO2 causes a decrease in the resistivity of P-type NGO due to the increase in the number of positive holes and then the increase in the adsorption rate. As a result, the desorption process occurs at a low rate due to the high contact with the polar NGO surface. Therefore, the CO2 gas can be easily detected at RT without oxygen environment.

In contrast, H$_2$ and C$_2$H$_2$ are reducing agent gases to the NGO film, Fig. 4. Then, the presence of reducing gas (H$_2$ or C$_2$H$_2$) causes an increase in the resistivity due to the effect of the negative charge on reducing the positive charge carrier (hole) concentration [51]. In the case of the nonpolar H$_2$ gas, the remaining carboxylic and epoxide groups in the NGO film are electron-withdrawing and holes promoting in the valence band (VB) [11]. Then, the interaction with H$_2$ or C$_2$H$_2$ electron-donating or reducing gases, could cause depletion of holes from the VB [72]. As a result, the resistance of the NGO film will increase. But the adsorption/desorption processes occur with a low rate in the case of C$_2$H$_2$ due to its large size and low diffusivity compared to H$_2$.

**Fig. 7** – (A) Response time and (B) recovery time of the NGO sensor at RT as a function of the gas concentration.

**Fig. 8** – Stability of the NGO sensor for (A) CO$_2$, (B) H$_2$, and (C) C$_2$H$_2$ gases at a concentration of 60 SCCM.

Furthermore, the amplification effects of the combination of the grain boundary, intra-grain regions, and percolation effect also contribute to the improvement of the sensor performance.

It is well known that CO2 is not a typical oxidizing gas, however, CO$_2$ behaves as an oxidizing agent gas to the NGO film as shown in Fig. 4. The presence of CO$_2$ decreases with CO$_2$ gas at room temperature. The charge transfers between CO$_2$ and graphene (due to the reduction of GO) allow the detection of CO$_2$ in the air under standard conditions. The interaction of CO$_2$ with hydroxyl ions of NGO leads to the formation of carbonate (CO$_2^{2-}$) ions [CO$_2^{+}$ (gas) + OH$^-$ + HCO$_3^{-}$ (pores) and then HCO$_3^{-}$ + OH$^-$ + CO$_2^{2-}$ (bulk) + H$_2$O (gas)]. Besides, at low temperature (25 °C), the dissociated OH$^-$ and H$^+$ ions from H$_2$O molecules at the surface of NGO can react with CO2 to form CO$_2^{2-}$ ions [CO$_2^{+}$ (gas) + H$^+$ + 2e$^-$ ↔ HCO$_3^{-}$ (surface) and HCO$_3^{-}$ → CO + OH$^-$ (surface)] [71]. Then, the presence of CO2 causes a decrease in the resistivity of P-type NGO due to the increase in the number of positive holes and then the increase in the adsorption rate. As a result, the desorption process occurs at a low rate due to the high contact with the polar NGO surface. Therefore, the CO2 gas can be easily detected at RT without oxygen environment.

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**5. Summary and conclusions**

The highly sensitive sensor of 2D nanoporous GO thin film was prepared for the efficient detection of CO$_2$, H$_2$, and C$_2$H$_2$ gases at 20 °C. The preparation of the sensor was occurred using the spray pyrolysis method for GO nanopowder synthesized via a modified Hummer method. The structural, morphological, electrical, and optical properties were characterized by different analytical techniques. The NGO gas sensing performance was evaluated by studying the sensitivity, selectivity, response time, and recovery time of the designed sensor towards CO$_2$, C$_2$H$_2$, and H$_2$ gases at varying concentrations.

The sensitivity of the NGO sensor was in the order S$_{CO2}$ > S$_{H2}$ > S$_{C2H2}$ at all concentrations. The sensitivity was 37.04, 16.16, and 2.87% at 60 SCCM of CO$_2$, H$_2$, and C$_2$H$_2$, respectively. For all gases, the NGO response time and recovery time were increased with increasing the gas concentration. The response time and recovery time for CO$_2$ gas 10 SCCM were 25 and 150 s, respectively. At the same concentration, the NGO sensor shows higher recovery time for H$_2$ than C$_2$H$_2$ gas. Finally, a simple gas sensing mechanism at room temperature was explained. Our straightforward and low-cost approach allows us to introduce 2D nanoporous GO film as an active
gas detector working at RT, which opens the possibility for a broad range of applications.

Conflicts of interest

The authors declare no conflicts of interest.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.07.064.

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