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Highly Sensitive and Selective H_2S Gas Sensor Fabricated with β-Ga_2O_3/rGO

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Hydrogen Sulfide (H_2S) is a common toxic gas released into the environment mainly during the energy production process from coal and crude oil. H_2S causes several neurological damages to the human body which could also be fatal and thus needs to be monitored. Here, we report the incorporation of reduced graphene oxide (rGO) on β-Ga_2O_3 (β-Ga_2O_3/rGO) sensing layers followed by its deposition on alumina substrate by drop casting method for H_2S gas sensing application. The structure and phase purity of the synthesized β-Ga_2O_3, GO and β-Ga_2O_3/rGO samples were characterized using X-ray diffraction (XRD). The gas sensing properties of the coated sensing layers of β-Ga_2O_3 and β-Ga_2O_3/rGO were analyzed by Electrochemical Impedance Spectroscopy (EIS) at 100 °C. The gas sensing results revealed superior sensitivity and selectivity of β-Ga_2O_3/rGO towards H_2S detection when compared with different interfering gases (NH_3, SO_2, CO_2 and CO). Nyquist plots and equivalent circuit fitting values clearly indicate that the grain boundary resistance was highly affected in H_2S gas environment (3 ppm) compared to other interfering gases. Based on the findings the gas sensing mechanism is proposed.
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Hydrogen Sulfide (H_2S) is a toxic gas, released into environment mainly during the processing of coal, crude oil, natural gas and sewage pits. It is also one of the processing gases in a variety of industrial sectors.[1] The sudden inhalation of H_2S damages the nervous systems in humans that could lead to death within a few minutes of exposure. This underlines the need to design sensors that could monitor the level of H_2S continuously in the environment along with other gases.[2,3] Semiconducting metal oxide based materials have been commonly used for gas sensing application due to their significant physical and chemical properties, but their lack of selectivity and poor response makes it difficult to employ them for real time applications.[4]

Gallium oxide (Ga_2O_3) is a wide band gap semiconducting metal oxide. Both pristine and doped Ga_2O_3 are extensively utilized for the development of conducting electrodes for various applications. Ga_2O_3 processes an admirable stable structural strength and is stable at higher temperatures and hence severs as an ideal candidate for development of gas sensors in callous environments. Further, doping with additives and using it as a composite increases the conducting property and gas sensing capability of Ga_2O_3.[5,6]

Reduced graphene oxide (rGO) magnetizes a huge deal of research activity owing to its distinctive physicochemical properties such as high thermal and electrical conductivity, large surface area and high mechanical strength. Combining rGO with the semiconducting metal oxides increases the efficiency of certain functions such as catalytic activity, electrochemical activity and mechanical strength to a certain extent. Graphene based materials can be used to increase the adsorption of gas species on the sensing film to increase the sensing response.[7–9]

Electrochemical impedance spectroscopy (EIS) is unique technique which can be used to measure the gas sensing applications along with prediction of the mechanism.[10] The RC circuits provide information about grain boundary, grain bulk and electrode contact resistance. These properties have more advantages when compared to other gas sensing techniques like Optical, Quartz Crystal Microbalance (QCM), Potentiometric and Resistance based gas sensors. β-Ga_2O_3/rGO based H_2S gas sensor is measured by EIS which is rarely reported in the literature shown in (Table II).[11,12]

In this present study, β-Ga_2O_3/rGO was used as an efficient gas sensing material for the detection of H_2S at a temperature of 100 °C and compared with other gases namely NH_3, SO_2, CO_2, and CO. The β-Ga_2O_3/rGO demonstrates high sensitivity, and selectivity towards the detection of H_2S (3 ppm) and its sensing mechanism for H_2S gas detection has been discussed in this paper.

Materials and Methods

Materials.—Gallium nitrate $Ga(NO_3)_3$, Ammonium hydroxide (NH_4OH), Graphite powder, Sodium nitrate ($NaNO_3$), Potassium permanganate ($KMnO_4$), Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4), and Hydrogen peroxide (H_2O_2), were purchased from Sigma-Aldrich and SRL (AR grade).

Synthesis of β-Ga_2O_3 and GO.—0.1 M of Gallium (III) nitrate was dissolved in 50 ml of deionized (DI) water and stirred for 40 min at room temperature. Ammonium hydroxide was added drop wise to the resultant solution to increase the pH upto 11. The resulting solution was transferred to RB flask with condenser and stirred for 8 h at 65 °C. The contents were then transferred to an autoclave, sealed and kept in furnace at 180 °C for 12 h in a N_2 atmosphere. After cooling to room temperature, the precipitate were collected and washed several times with DI water and ethanol then dried at 80 °C for overnight. The precipitate (GaOOH) turned into β-Ga_2O_3 after an annealing process at 1000 °C for 5 h in a N_2 atmosphere. Graphene oxide (GO) was synthesized using modified Hummer's method.[21]

Preparation of β-Ga_2O_3/rGO composite.—The β-Ga_2O_3/rGO composite mixture was prepared by mixing aqueous solutions of β-Ga_2O_3 and rGO. Initially, 0.1 g of β-Ga_2O_3 and 0.01 g of GO were dispersed in 20 ml of DI water separately using ultrasonication, then GO was added drop wise to the dispersed β-Ga_2O_3 solution under stirring at room temperature. The resulting mixture was kept under stirring for 4 h and transferred into an autoclave that was kept in furnace at 150 °C for 4 h and then mixture was washed and dried.

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Sensor fabrication.—Alumina substrates were cleaned using ethanol and then 5% (w w^{-1}) of β-Ga_2O_3/rGO were mixed with 5% (v w^{-1}) α-terpineol which was used as a binder to form as paste. This mixture was deposited on the surface of alumina substrate using drop casting method and finally the coated substrates were dried at 150 °C for 2 h. The electrode contacts were made on substrate using silver wire and these electrodes were used for the gas sensing application. A known concentration of the gas was injected into the chamber (volume 500 cm^3) using micro syringe from standard gas canisters. The change of impedance was monitored in the frequency range from 1 MHz to 1 Hz using impedance analyzer with multi-channel electrochemical workstation (PARSTAT MC 2000A).

Results and Discussion

The XRD patterns recorded for (a) β-Ga_2O_3, (b) β-Ga_2O_3/rGO and (c) GO are given in Fig. 1, which provides information about the structure and phase purity of the material. The XRD pattern obtained in Figs. 1a and 1b confirms that β-Ga_2O_3 and β-Ga_2O_3/rGO are present in monoclinic phase and this matches with standard JCPDS No. 43-1012. In Fig. 1b (002) peak for rGO was observed along with the intense peaks of β-Ga_2O_3. This is owing to the reducing of GO through the synthesis of rGO incorporated β-Ga_2O_3. Figure 1c confirms the presence of GO (001) as synthesized by modified Hummer's method.[18] Samples were characterized using X-ay diffraction measurement (Smart Lab X-ray Diffractometer, Rigaku Corporation, Japan).

The Nyquist Impedance plots obtained for Ga_2O_3/rGO sensing layer on exposure to air and different gases (a) NH_3, (b) SO_2, (c) CO_2, (d) CO and (e) H_2S with constant gas concentration (3 ppm) at 100 °C is given in Fig. 2. It plots indicate that the intensity and diameter of the semicircle decreased with different gases. The impedance graphs are fitted with simulated values and the equivalent circuit is shown in Fig. 2f.

Table I summarizes the equivalent circuit fitted values which indicate that R_1 (grain bulk resistance) values decrease for different gases at concentration in 3 ppm range. The R_2 (grain boundary resistance) values decreased significantly than R_1 and this signifies that the grain boundary resistance plays a major role in gas sensing. The R_2 is significantly affected by H_2S gas concentration (3 ppm) compared with other gases at 100 °C. No significant changes in fitted values of the CPE values (Q_2) were observed.

Figure 3 shows the proposed gas sensing mechanism based on the experimental values obtained from the interaction between sensing film and gas molecules. β-Ga_2O_3/rGO has major contribution compared to pure β-Ga_2O_3, since the presence of β-Ga_2O_3/rGO ensures the admirable adsorption of H_2S gas molecules. The rGO plays a major role on the excellent electron transfer property which increases the adsorption of H_2S gas molecules and response of sensing materials.

In air, adsorbed oxygen molecules capture free electrons from the conduction band of β-Ga_2O_3/rGO, resulting in the formation of a depletion layer which is responsible for the sensing film resistance. In H_2S gas environment, the adsorbed oxygen ions release the earlier trapped electrons which return to the β-Ga_2O_3/rGO conduction band, resulting in an increase in electron concentration. This results in a decrease in the potential barrier height and also an increase in conductance. These changes further confirm that H_2S gas significantly affects the grain boundary resistance.[21,22] The following chemical reactions given in Eq. 1 shows the H_2S gas sensing reaction mechanism.

$$H_2S + 3O^{2-} \rightarrow H_2O + SO_2 + 6e^- \quad [1]$$

The selectivity of β-Ga_2O_3 and β-Ga_2O_3/rGO coated substrate upon exposure to different gases (NH_3, SO_2, CO_2, CO, and H_2S) with a concentration of 3 ppm at 100 °C, as shown in Fig. 4. β-Ga_2O_3/rGO sensor has superior response (R_S 84.1013) towards H_2S when compared to other gases which confirms the superior selectivity of β-Ga_2O_3/rGO sensor towards H_2S detection compared with β-Ga_2O_3. This gas sensing response (Rs) is calculated from impedance data using the following Eq. 2. The comparison of gas sensing performance on β-Ga_2O_3 based gas sensors is shown in Table II.

$$Rs = \frac{|Z|\ a - |Z|\ g}{|Z|\ a} \times 100 \quad [2]$$

$|Z|\ a-$ Total impedance of Air
$|Z|\ g-$ Total impedance of Gas

Conclusion

GO, β-Ga_2O_3, and β-Ga_2O_3/rGO were successfully synthesized using modified Hummer's method and hydrothermal method respectively. The XRD patterns of β-Ga_2O_3 and β-Ga_2O_3/rGO were indexed on the basis of monoclinic phase and presence of rGO and GO were confirmed. The gas sensor was fabricated after coating β-Ga_2O_3/rGO on alumina substrates and it was exposed to different gases (3 ppm). Based on the response, it was found that the sensing electrode was highly selective towards H_2S when compared with other gases (NH_3, SO_2, CO_2, and CO). Nyquist impedance and equivalent circuit values further confirms the sensitivity. The grain boundary resistance was drastically affected in H_2S environment and potential barrier height was decreased when conductivity of the sensor increased. Based on these results it can conclude that β-Ga_2O_3/rGO can act as a stable H_2S gas sensor at 100 °C.

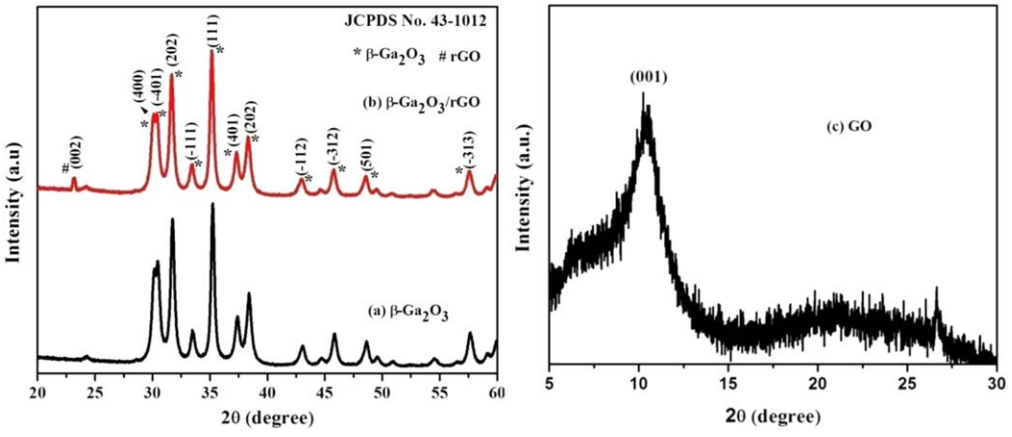

Figure 1. XRD patterns of (a) β-Ga_2O_3, (b) β-Ga_2O_3/rGO and (c) GO.

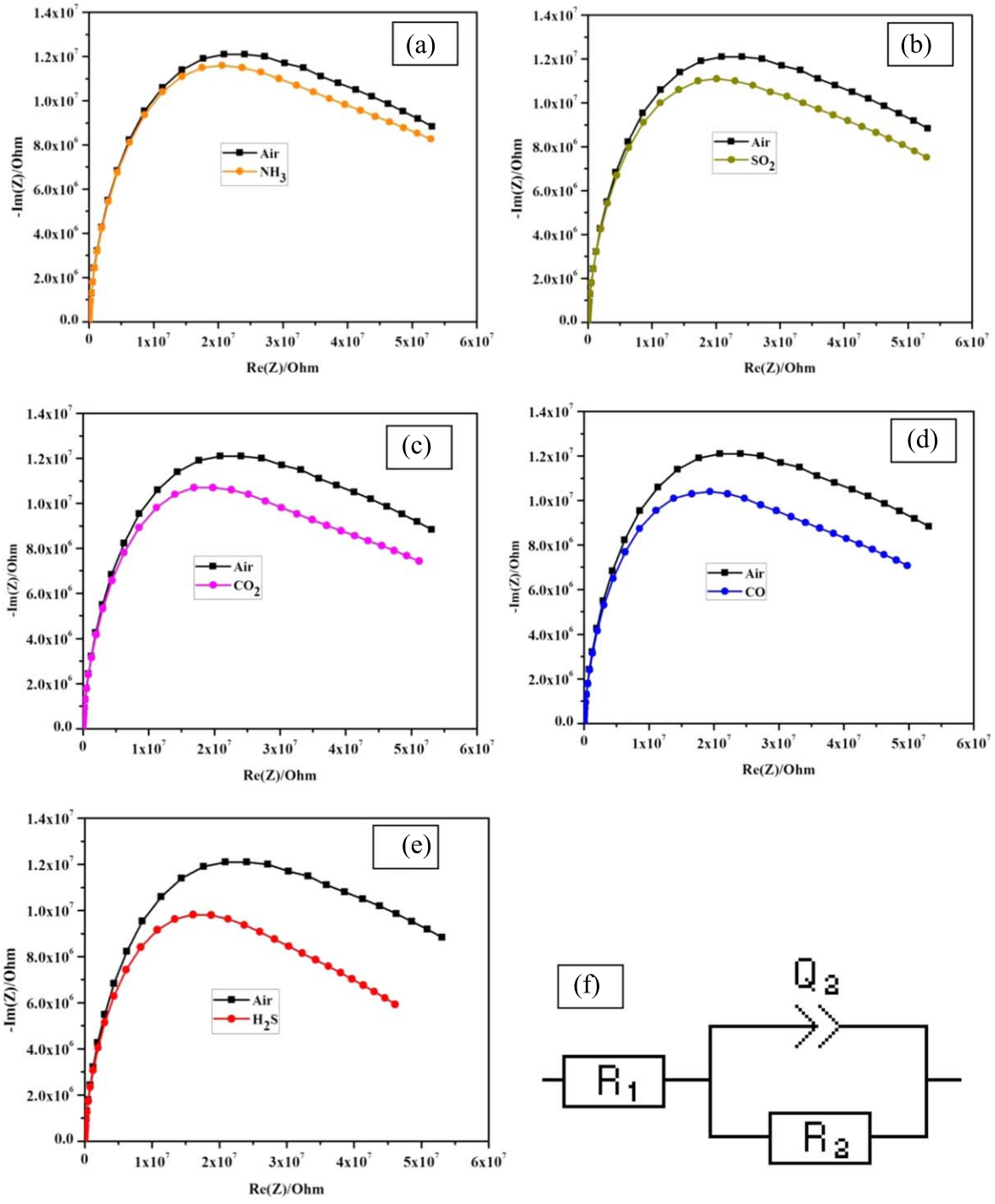

Figure 2. Nyquist Impedance shows β-Ga_2O_3/rGO exposed to air and different gases (a) NH_3, (b) SO_2, (c) CO_2, (d) CO, (e) H_2S with constant gas concentration (3 ppm) at 100 °C and (f) equivalent circuit.

Table I. β-Ga_2O_3/rGO gas sensor equivalent circuit fitted values for various gases (3 ppm) at 100 °C.

Elements	Air	NH_3	SO_2	CO_2	CO	H_2S
R_1 Ohm	1441	1387	1363	1348	1320	1293
Q_2e^{-12} F.s^(a-1)	13.79	13.37	13.12	13.06	12.85	12.17
R_2 Ohm*e^6	3.938	2.991	2.695	2.316	1.908	1.128

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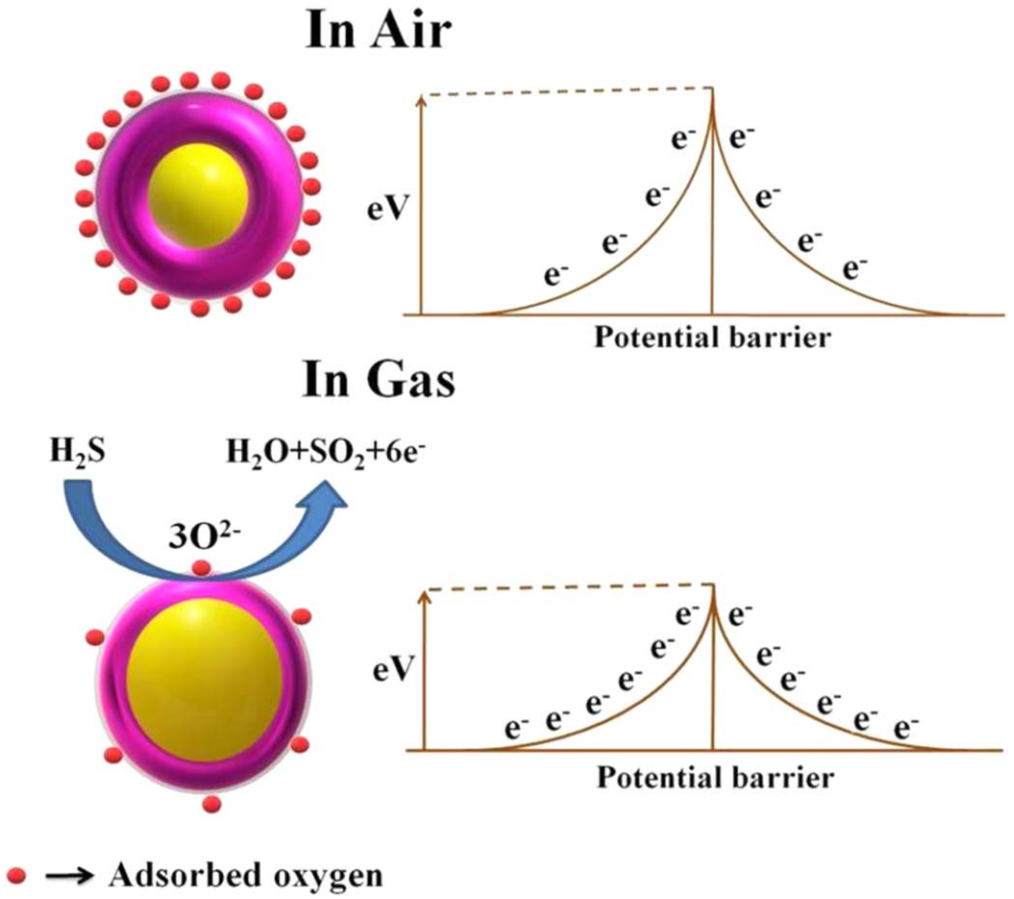

Figure 3. Schematic representation for gas sensing mechanism.

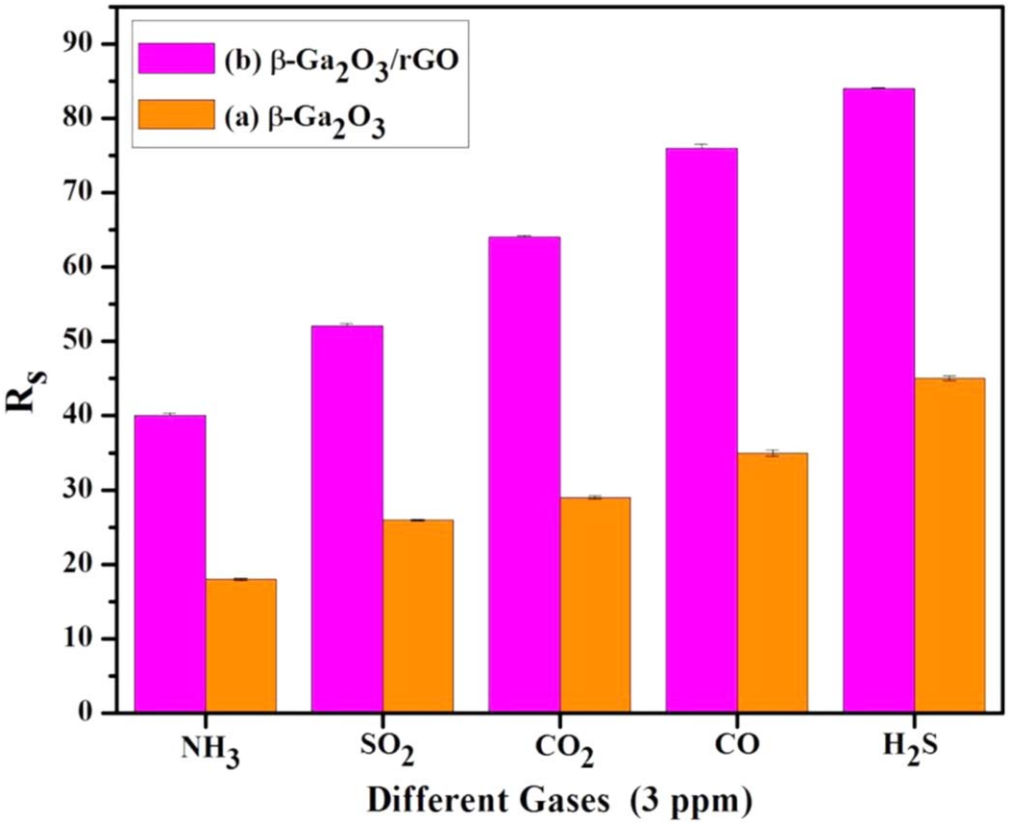

Figure 4. Selectivity of β-Ga_2O_3 and β-Ga_2O_3/rGO coated substrate upon exposure among different gases at 100 °C.

Table II. The comparison of gas sensing performance of β-Ga_2O_3 based gas sensors.

Sensing Material	Analyte Gases	Temperature (°C)	Concentration (ppm)	References
Ga_2O_3/WO_3	C_2H_5OH	200	200	13
Ga_2O_3/ZnO	NO_2	300	10–200	14
Ga_2O_3-WO_3	C_2H_5OH	275	14–100	15
Ga_2O_3	H_2	400	100	16
GaOOH and β-Ga_2O_3	CO_2	Room Temperature	2000–10000	17
Ga_2O_3	O_2 and CO_2	100–500	200	18
Ga_2O_3	CO	150	10–200	19
β-Ga_2O_3	CO	100	1–5	20
β-Ga_2O_3/rGO	H_2S	100	3	Present Work

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