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Fabrication of flexible La-MoS$_2$ hybrid-heterostructure based sensor for NO$_2$ gas sensing at room temperature

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ABSTRACT

Transition metal dichalcogenides (TMDs) materials are from Two-dimensional (2D) materials family having many benefits, comprising high carrier mobility and conductivity, high optical transparency, outstanding mechanical flexibility, and chemical stability, and also the favorable gas sensing materials because of their high surface-area-to-volume ratio. Nevertheless, their low gas-sensing performance in terms of low response, partial recovery, and poor selectivity obstruct the apprehension as a high-performance 2D TMDs gas sensing materials. At this time, we explain the enhancement in gas-sensing performance of molybdenum disulfide (MoS$_2$) nanoflakes (NF) by decorating with Lanthanum (La) at room temperature (25 ºC). Our experiments show that the dynamic sensing response of the La decorated few-layered MoS$_2$ (La@MoS$_2$) sensor increases by ~6 times than the pristine few-layered MoS$_2$, which positions it first-ever reported values for NO$_2$ gas detection. The sensitivity of the MoS$_2$ and La@MoS$_2$ found 0.627 and 3.346 ppm$^{-1}$, respectively, towards NO$_2$ gas. It is noteworthy that La has introduced to MoS$_2$, and its selectivity towards the volatile organic compounds (VOCs) and other toxic gases improved drastically. Our outcomes show that the suggested method represents a successful approach for improving the gas sensing response of 2D TMDs sensors.

Keywords: Gas sensor; MoS$_2$; La decorated MoS$_2$; Sensitivity, Selectivity; Response -Recovery.

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INTRODUCTION:
The monitoring of human health has become a significant concern because of the rapid increase in environmental pollution nowadays [1]. Toxic gases such as carbon dioxide (CO$_2$), ammonia (NH$_3$), nitrogen dioxide (NO$_2$), nitrogen monoxide (NO), and nitrous oxide (N$_2$O) are derived mainly from factories and vehicles, can impose enormous problems for human health and the environment. Out of all these gases, NO$_2$ is one of the most dangerous, which leads to damage to the upper respiratory tract, lungs, cardiovascular system when inhaled 53 parts per billion (ppb) of NO$_2$ gas [2]. So there is a requirement for developing high-performance gas sensors for detecting the concentration and composition of toxic gases. These gas sensors have applications in many areas, such as industries, medical treatment, resident life, and military [3]. For enhancing the gas sensor's performance, researchers are using nanostructures than bulk materials due to their huge active sites, high surface area per unit volume, excellent adsorption properties, and more reactive locations for redox reactions [4]. A broad range of materials, such as conducting polymers, carbon nanotubes, and semiconducting metal oxides, have been examined for gas sensing [5]. Out of these materials, conducting polymers has benefits of ease of processing, room temperature operation, and ability to include them into sensing devices; however, degradation and humidity effects are the significant limitations. Carbon nanotubes have been tested for high sensitivity and can operate at room temperature, but complex processing and long recovery limit their applications. Graphene has already verified as worthy material for gas sensing applications, but due to its approximately zero bandgap, it is not very useful as a sensing material. Semiconductor metal oxides possess benefits of low cost and high sensitivities; despite serious drawbacks such as low selectivity, large power requirement, and high operating temperatures. Hence, it is required to investigate innovative gas sensing materials with low operating temperatures and high sensitivity [6]. In recent years, many researchers are working extensively on two-dimensional (2D) nanostructures due to their high surface area-to-volume ratio, 2D geometry, and nanoscale thickness. These materials are having distinct applications in electronic devices, chemical gas sensors, energy storage, and biomedical fields [7]. Layered transition metal dichalcogenides (TMDs) including WS$_2$, MoS$_2$, WSe$_2$, MoSe$_2$, ReS$_2$, and, ReSe$_2$ as well as layered group III-VI semiconductors (SnS$_2$, GaSe, and GaS), layered metal oxides (SnO$_2$, and MnO$_3$), h-BN, phosphorene, have drawn attention because of their chemical and physical properties based on their layer’s thickness. Along with other physical properties, these materials possess suitable bandgap, good electrical conductivity, high
adsorption-desorption capability etc. helps these sensing materials for improved gas sensing performance [8]. Molybdenum disulfide (MoS₂) has gained considerable interest as a promising gas-sensing material among TMDs due to its large surface-area-to-volume ratio, air stability, and various active functional sites [9]. From the literature, it is clear that layered MoS₂ is useful for detecting NO₂, NH₃, NO, acetone, and ethanol vapors [10, 11]. However, MoS₂-based gas sensors have some drawbacks at room temperatures like low sensitivity, slow response, and poor recovery, particularly for NO₂ gas [9]. The introduction of other nano reinforced materials (like surfactants, noble metals, and metal oxides etc.) could be an efficient approach to boost up the sensing performance of MoS₂ based sensors at room temperature [12].

In this paper, we are using lanthanum as a favorable material with an assumption that La can interact at the surface of MoS₂. The purpose of selecting La is, it is an active material, its crystal structure is similar to MoS₂ at room temperature, and it can enhance the electrical properties. [13, 14]. Till today, La decoration on MoS₂ for chemiresistive gas sensors for NO₂ gas has not reported in the literature as of our knowledge. In this work, we synthesized La decorated MoS₂ by the ultrasonication method and studied its gas sensing behavior. La decorated MoS₂ sensor was fabricated and monitored its electrical resistance for various gases.

EXPERIMENTAL SECTION:

Materials and chemicals:

Molybdenum disulfide (MoS₂) having 99 % purity and Lanthanum (III) chloride heptahydrate (LaCl₃.7H₂O) were obtained from Sigma-Aldrich Ltd. N-Methyl-2-pyrrolidone (NMP) was brought from HiMedia Laboratories Pvt. Ltd., India, with 99.5 % purity.

Synthesis of La decorated few-layered MoS₂ flakes:

By taking advantage of weak van der Waals force between the layers of bulk MoS₂, we synthesized a few-layered MoS₂ from its bulk powder. We choose the solvent to exfoliate MoS₂ as NMP because of its surface tension (~ 40 mJ/m²) is approximately equal to the surface energies of few-layered MoS₂ (~46.5 mJ/m²) [15]. Initially, we took 0.25 grams of bulk MoS₂ powder in 30 mL of NMP. The solution is bath sonicated for 12 h under 20 °C using an ice bath. After sonication, the complete sample is transferred to a round bottom flask and kept for the reflux method in the oil bath at 150 °C for 12 h for further exfoliation. After that, we centrifuged the solution at 750 rpm for 5 min for discarding the unexfoliated MoS₂, followed by the centrifugation of the supernatant part at 10,000 rpm for 30 min. The settled MoS₂ is a few-layered at this point is cleaned
with DI water several times. Lanthanum (III) chloride heptahydrate (LaCl$_3$.7H$_2$O) was added to a few-layered MoS$_2$ solution at 3, and 5 atomic percentages and bath sonicated in an ice bath under a bubbling Ar atmosphere for 1 hr. The La decorated solution was centrifuged at 10,000 rpm for 15 min, and the settled part is cleaned with ethanol and water to remove chlorine. Final La decorated a few-layered MoS$_2$ sample is transferred into a culture tube and stored for further characterization and testing, as shown in Figure 1.

![Figure 1](image.png)

**Figure 1.** Schematic of material synthesis and flexible sensor fabrication

**Characterizations:**

X-ray photoelectron spectroscopy (XPS) analysis of few-layered MoS$_2$ and La decorated few-layered MoS$_2$ nanoflakes were characterized by PHI 5000 Versaprobe-II. The crystal structure of exfoliated few-layered MoS$_2$ and La @ MoS$_2$ has been analyzed by Rigaku, smart lab XRD with CuK$_\alpha$ X-Ray source of radiation has a wavelength of 1.5405 Å. Surface morphologies of the nanomaterials were studied using field emission scanning electron microscopes (Carl-Zeiss, Zeiss Gemini SEM, and Carl-Zeiss Ultra Plus models). Invia Renishaw Raman spectrophotometer
having an excitation wavelength of 514 nm, was used to study the vibrational analysis of the samples.

**Sensor fabrication and experimental setup:**

In this work, a flexible chemiresistive sensing device was implemented for NO₂ gas sensing. Herein, Polyimide (PI) was used as the flexible substrate. For patterning, the interdigital electrodes (IDE) with finger width of 0.08 mm and a gap width of 0.08 mm, flexible substrate was used for standard photolithography process, and a thin gold was deposited through RF sputtering onto a patterned substrate. The proper dimension of IDE has been given in Figure S1 (see Supporting Information, Figure S1). Two electrical copper wires were attached by a small amount of silver paste for proper electrical connection. A binder (Bondtite, high strength compound) was used to enhance the strength of the connection between flexible IDE and Cu wire. In sensor fabrication, 1-2 µl of few-layered MoS₂ and La@MoS₂ was spin coating process on to the honeycomb structure of the developed flexible IDE and was dried at 60 °C under IR light source (an accessory provided with EZspin-A1 spin coater, Apex Instruments Co. Pvt. Ltd.) for 30 minutes as shown in Figure 1. Then the fabricated sensor device was kept inside a customized box for gas sensing purpose as discussed in our recent work [11] is shown in Figure S2 (see Supporting Information, Figure S2). The box was attached to mass flow controllers (MFCs; 5850E, Brooks Instrument) to control the synthetic air and NO₂ gas concentrations inside the box. On top of the box, two electrodes with copper endpoints were provided for electrical connections.

**Calibration and sensing measurements of setups:**

The fabricated gas sensor device’s performance was measured on digital pico-ammeter (DPM-111, SES Instruments Pvt. Ltd., Roorkee), which could collect sensor resistance automatically. The experiments were carried out at a potential bias of 1 V through a regulated DC power supply (L-3210, Aplab, India). The fabricated sensors were placed exclusively in the customized testing box and stabilized under dry air conditions for about 20 min to get the baseline resistance before introducing the testing gases (NO₂). The NO₂ gas concentration was varied from 5 to 25 ppm with the help of mass flow controllers (MFCs) at 25 °C (RT) throughout the experiments. Baseline DC electrical resistance in dry air was measured and found to be in the range of 11.82 to 13.25 MΩ and 7.04 to 8.67 MΩ for MoS₂ and La@MoS₂ flakes, respectively. Now we exposed sensor devices to NO₂ gas at different concentrations through MFCs and recorded the simultaneous changes in DC electrical resistance through the data recording system. For the selectivity test of the sensor
with other gases, synthetic air was purged for 20 min into the test chamber to get baseline resistance. The dynamic sensing response is calculated using the following formula [16].

\[
\left( \frac{\Delta R}{R_a} \right) \% = \left( \frac{R_a - R_g}{R_a} \right) \times 100 \tag{1}
\]

where, \( R_a \) and \( R_g \) are the resistance of synthetic air and testing gas (NO\(_2\)), respectively. The time taken to reach 90 \% of the electrical resistance change for adsorption and desorption of gases is known as response and recovery time. The sensitivity is the slope of the fitting curve between percentage sensing response \( \left( \frac{\Delta R}{R_a} \right) \% \) and the concentration of NO\(_2\) gas (ppm).

**RESULTS AND DISCUSSION:**

The chemical nature of synthesized few-layered MoS\(_2\) and La@MoS\(_2\) samples are examined through XPS as shown in Figure 2. From Figure 2(a), it has been found from the survey spectrum that La@MoS\(_2\) nanoflakes contain Mo, S, La, C, and O peaks whereas La peak is not present in case of pure MoS\(_2\) (see Supporting Information, Figure S3). C 1s peak (284.5 eV) is used to calibrate all other binding energy values, and O 1s peak may be due to the presence of air onto the material surface from the environment [17]. In the Mo 3d XPS spectrum, two predominant peaks at the binding energy of 229.1 and 232.2 eV are detected, which confirms the Mo 3d5/2 and Mo 3d3/2 peaks of tetravalent molybdenum from MoS\(_2\), respectively. Another small peak is observed at lower binding energy at 226.2 eV is corresponding to S\(^2-\) 2s, as shown in Figure 2(b). The two major peaks in the S 2p spectrum having binding energy at 161.81 and 163.02 eV could be assigned to S 2p3/2 and S 2p1/2 peaks of S\(^2-\) ions [18]. The binding energies of Mo\(^{4+}\) 3d and S\(^{2-}\) 2p regions disclose the existence of a robust trigonal prismatic structure of MoS\(_2\) nanoflakes. In figure 2(d), the obtained peak at 835.3, 838.5, 851.8, and 854.9 eV due to the binding energies of the La 3d core spectrum validate the presence of La\(^{3+}\) in La@MoS\(_2\) [19]. It has been observed that there is no peak shift in Mo 3d core level (Fig. 2b) after the addition of La demonstrates that Mo atoms do not alter the chemical structure. But, after adding La, S 2p level (Fig. 2c) binding energies shift to the lower side, this may be due to the charge transfer from La side to the far more electronegative S side (Pauling electronegativity of S = 2.58 vs. La = 1.1). Thus, the electron-electron repulsion within the S atoms increases, which in turn moves the S core levels towards the lower side of the binding energy [20] as compared with the XPS study of pure MoS\(_2\) nanoflakes (see Supporting Information, Figure S3). Therefore, it is proved that the presence of La into the depletion layer of MoS\(_2\) in the form of La–S week van der Walls bonds.
The crystal structure of a few-layered MoS$_2$ and La decorated MoS$_2$ are studied using XRD patterns from 5°-70°, as shown in Figure 3. Captured significant peak positions for few-layered MoS$_2$ are observed at 14.4°, 32.8°, 33.6°, 36.0°, 39.6°, 44.2°, 49.9°, 58.4°, and 60.4° having their corresponding miller indices (hkl) values as (002), (110), (101), (102), (103), (104), (105), (110), and (112) respectively. The peak positions are matching with JCPDS card no. 87-2416. In the case of La decorated samples, the peaks corresponding to Lanthanum are observed at 27.8° and 31.6° for 5 at% having (100) and (101) as it’s miller indices, respectively. Lanthanum peak positions are matching with JCPDS card no. 02-0618. The average crystallite size is observed as 30.2 and 26.9 nm in the case of MoS$_2$, 5 at% La decorated MoS$_2$, respectively. The decrease in crystallite size is mainly due to the lattice distortion of the MoS$_2$ because of the strain induced by the bigger atomic size of La compared to the host elements (Mo and S).
The surface morphology of the few-layered MoS$_2$ and La decorated few-layered MoS$_2$ samples is studied using FE-SEM and shown in Figure 4. The samples are spin-coated on glass substrates and dried at 50 °C overnight. The samples are Au coated for 120 sec by sputtering instrument and went for observing the morphologies. Figure 4(a) corresponds to the formation of a few-layered MoS$_2$ but is agglomerated strongly. The nanosheet has rough surface morphology aligned on the substrate. Figure 4(b) corresponds to La decorated a few-layered MoS$_2$. From the image, it has been observed that the La particles are uniformly attached and dispersed on the MoS$_2$ surface.
Figure 4. FE-SEM of (a) few-layered MoS₂, (b) 5 at% La decorated few-layered MoS₂

Raman spectrum is used to analyze the effect of La incorporation on the MoS₂ nanoflakes. Molecular vibrations of MoS₂ and La decorated of MoS₂ are studied by this technique, as shown in Figure 5. For few-layered MoS₂, two representative vibration peaks $E_{2g}^1$ phonon mode and $A_{1g}$ phonon mode are observed at 381.3, and 406.2 cm$^{-1}$, respectively. The $E_{2g}^1$ Phonon vibration shows in-plane vibrations of Mo and S atoms, and the $A_{1g}$ corresponds to out-of-plane vibrations of S atoms. The frequency difference between these two vibration peaks is 26.2 cm$^{-1}$, which shows the formation of a few-layered MoS₂ [21, 22]. But, for La decorated few-layered MoS₂, the frequency difference between $E_{2g}^1$ and $A_{1g}$ has been reduced to 24.7 cm$^{-1}$. The vibration peaks got blue-shifted when we decorate a few-layered MoS₂ with La. The shifting in peaks position indicates the hole transport in the MoS₂ upon La decoration, which makes MoS₂ more conductive and becomes p-type in nature.

Figure 5. Raman spectroscopy of few-layered MoS₂ and La decorated few-layered MoS₂

Gas characterization of MoS₂ and La@MoS₂

To study the improved gas-sensing properties of La@MoS₂ sensor than the pristine MoS₂ at room temperature (25 ºC), the sensing response curves (resistance vs. time) of MoS₂ and La@MoS₂ gas
sensors at different NO2 concentration (5, 10, 15, 20 and 25 ppm) are shown in Figure 6(a) and (b). The chemiresistive type gas sensing was performed in synthetic air background (79% N2, 21% O2, and 5 %RH) background using constant bias voltage (+1 V) between IDE and electrical connection. Typically, I-V curve of MoS2 and La@MoS2 gas sensors are measured in synthetic air from -1 to +1 V. From the image, it has been observed that the MoS2 is showing the nonlinear increase in current with increase in voltage, meaning the high Schottky barrier. Due to which, it blocks the electron carrier transport and decreases the sensing response. But, for La@MoS2, Ohmic contact has been formed between sensing material and electrodes; therefore, the sensing response is increased, as shown in Figure S4 (see Supporting Information, Figure S4).

When NO2 gas comes into contact with the surface of the prepared sensors (MoS2 nanoflakes and 5 at% La@MoS2 nanoflakes), the concentration of charge carrier is altered due to which sensors resistance is changed. After exposing NO2 gas (oxidizing gas), the resistance of the MoS2 sensor gets increase, showing n-type response [10]. Whereas, in the case of La@MoS2, the resistance of the sensor got decrease, showing a p-type response. As hole are majority charge carriers in a p-type semiconductor, a decrease in resistance was observed when La@MoS2 is exposed to oxidizing NO2 gas. The improved responsiveness of the La@MoS2 gas sensor can assume that the incorporation of La increases the number of electron transfer channel by creating the rich La/MoS2 heterojunctions, which in turn is highly beneficial for improved La@MoS2 gas-sensing performances [16].

Figure 6(c) shows the sensing response (ΔR/Ra %) of lanthanum decorated MoS2 with different La concentrations (3, 5, and 7 at%). In this figure, it has been observed for 3 at%La@MoS2, the sensing response is ~ 45%, which is more than the pristine MoS2. For selecting the 5 at%La@MoS2, the sensing response is reached the maximum (~ 99%). This increase in sensing response is mainly due to increasing La coverage on the MoS2 surface, where MoS2 serves as the significant electrical conduction pathway. But, furthermore, when the 7 at%La@MoS2 is used as sensing material, the sensing response (~ 80%) is reduced. But, in this case, La film is acting as a major electrical conduction pathway. Thus, from this study, we have chosen the 5 at% of La@MoS2 NF for further gas sensing studies.

Earlier, some researchers have already tested the bending effect of the thin film based sensors to certain angles [23]. As discussed, the La@MoS2 NF was drop cast on the flexible PI-based IDE. As shown in Figure 6(d), flexible IDE could be manually bent to large angles (up to 120º) and then
recover to an original flat shape. The change in resistance of the La@MoS\textsubscript{2} based flexible sensor was performed under the presence of synthetic air. Such a simultaneous bending and straightening change was carried out repeatedly without harming the sensor structure. During the bending and straightening of the sensor, it shows the negligible change in resistance. We have performed the deformation studies more than 10 times. Both the sensor shows the mechanical toughness during such large-angle deformation and also a stable change in resistance.

![Graphs](image)

**Figure 6.** Sensing response of (a) MoS\textsubscript{2}, (b) La@MoS\textsubscript{2} based sensor under different NO\textsubscript{2} gas concentrations, (c) effect of variation in La content towards dynamic gas sensing at 25 ppm of NO\textsubscript{2}, and (d) resistance change of both the sensors under 0\textdegree{} to 120\textdegree{} in synthetic air.

The definition of response and recovery time is already being published elsewhere [24]. The response and recovery times of La@MoS\textsubscript{2} were way better than pristine MoS\textsubscript{2}, as shown in Figure 7. The slow response and recovery time of the MoS\textsubscript{2} sensor is due to high adsorption energy.
between defective MoS$_2$ sites and NO$_2$ gas molecules [9]. The chemical reactivity of NO$_2$ was more in the case of La@MoS$_2$ as La acts an active material here. The recovery rate of the sensors is an influential parameter of gas sensing performances, has a significant impact on both repeatability and stability. Thus, by calculating the percent recovery ratio, the recovery characteristics of MoS$_2$ and La@MoS$_2$ gas sensors were theoretically calculated by using the below formula [16].

\[
\text{Recovery ratio (\%)} = \left(1 - \frac{R_g - R_r}{R_g - R_a}\right) \times 100 \quad \text{eq.(2)}
\]

where, $R_g$ is the sensor resistance in the presence of testing gas, $R_r$ is the resistance in synthetic air after flushing out the NO$_2$ gas from the test chamber for a given recovery time, and $R_a$ is the resistance in synthetic air background. The calculated recovery ratios (%) of MoS$_2$ and La@MoS$_2$ gas sensors at various NO$_2$ gas concentrations are presented in Table 1.

**Table 1.** The calculated recovery ratios of MoS$_2$ and La@MoS$_2$ gas sensors at different concentrations of NO$_2$ gas

<table>
<thead>
<tr>
<th>NO$_2$ Gas Concentration (ppm)</th>
<th>% Recovery Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MoS$_2$</td>
</tr>
<tr>
<td>5</td>
<td>97.03992954</td>
</tr>
<tr>
<td>10</td>
<td>97.07608836</td>
</tr>
<tr>
<td>15</td>
<td>96.61711903</td>
</tr>
<tr>
<td>20</td>
<td>93.68765655</td>
</tr>
<tr>
<td>25</td>
<td>92.70799641</td>
</tr>
</tbody>
</table>

The prepared MoS$_2$ and La@MoS$_2$ gas sensors show a high percentage of recovery (> 90%) against NO$_2$ gas sensing. But, in the case of pure MoS$_2$ gas sensor, it has been observed that a decrease in percent recovery ratio (97.03 to 92.70%) with an increase in NO$_2$ gas concentration (5 – 25 ppm). This decrease in recovery is mainly due to the presence of strongly adsorbed NO$_2$ gas molecules onto the MoS$_2$ surface. However, the La@MoS$_2$ gas sensor displays a considerably improved percentage recovery ratio (99.63 to 98.41%) for NO$_2$ gas sensing. In this case, La encourages the chemisorption of nitrogen and oxygen species on the MoS$_2$ surface due to its low surface energy at the time of the recovery process.
Figure 7. Response-recovery time of (a) MoS$_2$ and (b) La@MoS$_2$ based sensor under NO$_2$ gas at a different concentration level

**Sensitivity of the sensors**

For determining the sensitivity of MoS$_2$ and La@MoS$_2$, a correlation graph between the percentage response ($\frac{\Delta R}{R_\alpha}$, %) vs. NO$_2$ gas concentration (5 to 25 ppm) has been drawn, as presented in Figure 8. From the graph, linear regression based on the least-square method, the straight-line curve formula, i.e., $y = mx + c$ has been followed for the linear fitting curve. where $m =$ sensitivity, $y =$ the response, $x =$ gas (NO$_2$) concentration. Also, the correlation coefficient ($R^2$) has been calculated to check the linear relationship between two variables. From the image, it has been found that the MoS$_2$ gas sensor shows the linear fitting curve denoted as $y = -0.6273x - 1.5948$. The obtained $R^2$ value for the MoS$_2$ gas sensor is 0.9683 (>0.9), indicating the moderate linearity in NO$_2$ gas concentrations. For 5 at% La@MoS$_2$, it is represented as $y = 3.3459x + 14.1463$, $R^2 = 0.9973$. The $R^2$ value is more closely to 1 for 5 at% La@MoS$_2$, which means that 5
at% La@MoS₂ is more sensitive. Good sensitivity is mainly due to the direct gas effect on the sensor sample rather than any environmental effect. The sensitivity of the MoS₂ and La@MoS₂ are found -0.627 ppm⁻¹ and 3.346 ppm⁻¹, respectively. It has also been observed that the negative sign of the sensitivity for MoS₂ sensor indicates the increase in sensor resistance, unlike NO₂ gas concentrations.

![Figure 8](image_url)

**Figure 8.** The correlation of the response of the (a) MoS₂ and (b) La@MoS₂ based sensor with NO₂ gas concentrations

Present research work’s sensing performance was compared with the different available literature on NO₂ gas sensing and presented in Table 2. From Table 2, it is cleared that La@MoS₂ showed significant sensing behavior compared to other materials. So, this sensor can be used for NO₂ gas detection in the environment at room temperature.

**Table 2.** A comparative study of various materials used in chemiresistive type sensor for sensing of NO₂ gas

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sensing materials</th>
<th>Working temperature</th>
<th>Gas concentration range</th>
<th>LOD</th>
<th>Gas concentration/sensing response</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>rGO/ZnO₁₋ₓ</td>
<td>RT</td>
<td>50-400 ppb</td>
<td>50 ppb</td>
<td>400 ppb/18.67%</td>
<td>[25]</td>
</tr>
<tr>
<td>2</td>
<td>ZnO nanowire/ CuO nanoparticles</td>
<td>150 °C</td>
<td>1-100 ppm</td>
<td>1 ppm</td>
<td>100 ppm/ 175%</td>
<td>[26]</td>
</tr>
<tr>
<td>3</td>
<td>MoS₂/Graphene</td>
<td>200 °C</td>
<td>0.2-100 ppm</td>
<td>0.2 ppm</td>
<td>10 ppm/ 69%</td>
<td>[27]</td>
</tr>
<tr>
<td>4</td>
<td>rGO/MoS₂</td>
<td>60 °C</td>
<td>2-8 ppm</td>
<td>5.7 ppb</td>
<td>2 ppm/ 59.8%</td>
<td>[28]</td>
</tr>
</tbody>
</table>
### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Condition</th>
<th>Concentration Range</th>
<th>Response</th>
<th>Concentration</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>MoS$_2$/PbS</td>
<td>RT</td>
<td>5-400 ppm</td>
<td>Not reported</td>
<td>100 ppm/ 25%</td>
<td>[16]</td>
</tr>
<tr>
<td>6</td>
<td>CdTe QDs/ MoS$_2$ NWs</td>
<td>RT</td>
<td>0.1-10 ppm</td>
<td>Not reported</td>
<td>10 ppm/ 40%</td>
<td>[29]</td>
</tr>
<tr>
<td>7</td>
<td>In$_2$O$_3$/ MoS$_2$</td>
<td>RT</td>
<td>0.1-100 ppm</td>
<td>8.8 ppb</td>
<td>100 ppm/ 371.9%</td>
<td>[18]</td>
</tr>
<tr>
<td>8</td>
<td>MoS$_2$</td>
<td>RT</td>
<td>5-25 ppm</td>
<td>4.03 ppm</td>
<td>25 ppm/ 15.09%</td>
<td>This work</td>
</tr>
<tr>
<td>9</td>
<td>La@MoS$_2$</td>
<td>RT</td>
<td>5-25 ppm</td>
<td>0.46 ppm</td>
<td>25 ppm/ 98.07%</td>
<td>This work</td>
</tr>
</tbody>
</table>

### Repeatability of the sensors

Customized excellent repeatability and high selectivity are also notable parameters to be considered for the betterment of gas sensor applications. Repeatability analysis of the La@MoS$_2$ sensor is shown in Figure 9(a) for NO$_2$ gas concentrations ranging from 5 - 25 ppm at room temperature after several repeated tests (continuous 5 times). The tests were also conducted under synthetic air condition. Also, the repeatability of the MoS$_2$ sensor has some irregularity, as shown in Figure S5 (see Supporting Information, Figure S5). From this study, there is no such noticeable signal change is observed after iterating the test consecutive 5 times for 5 at% La@MoS$_2$ sensor, which proves that humidity and environmental pollution does not affect the 5 at% La@MoS$_2$ sample.

### Long-term stability

Long-term stability is experimented at every alternative 5 days by exposing MoS$_2$ and La@MoS$_2$ sensors towards 5 and 25 ppm of NO$_2$ gas at 25 °C (RT) for 45 days continuously. From Figure S6 (see Supporting Information, Figure S6), it has been observed that in the case of MoS$_2$, there is no significant change in the response up to 30 days; after that, it starts noticeable degradation. It is mainly due to the effect of the environment and dust particle inclusion. But, as shown in Figure 9(b), the response for the La@MoS$_2$ sample is highly prominent for 5 ppm of NO$_2$, abrupt, and continuously decreased with time after 25 days. The first and foremost reason is the environmental effect on La, which degrades the sample over time. Because La is a very active element. Also, the presence of dust particles in the air due to external pollution is responsible for this type of detrimental response. Again, there may be another reason why the absorption sites became more inactive following multiple exposures to the target gas [28].
**Limit of detection (LOD) and limit of quantification (LOQ)**

The formula for measuring the detection limit (LOD) and quantification limit (LOQ) of the gas sensor has already been published elsewhere [11]. Thus, the theoretical NO₂ detection limit (LOD) is found for MoS₂ and 5 at% La@MoS₂ to be 4.03 and 0.46 ppm. Also, the LOQ is observed for MoS₂ and 5 at% La@MoS₂ to be 13.44 and 1.54 ppm in our work. It has been found that the theoretical values of LOD and LOQ of 5 at% La@MoS₂ is better than the MoS₂. It may be due to the less hindrance effect offered by humidity and other pollutants present in the air. Thus the calculated standard deviation (S.D.) value for the 5 at% La@MoS₂ is found lesser than the MoS₂ because there is no such variation in the blank sample (resistance of the sensor in synthetic air).

The sensing responses of La@MoS₂ in between the LOD and LOQ range for NO₂ gas are observed and shown in Figure 9(c).

![Graph](Image)

**Figure 9.** (a) Repeatability study of 5 at% La@MoS₂ at 25 and 5 ppm of NO₂ gas, (b) long-term stability of 5 at% La@MoS₂ at 25 and 5 ppm of NO₂ gas, and (c) limit of detection of 5 at% La@MoS₂ based sensor to NO₂ gas
Selectivity of the sensors

An excellent sensor should possess high selectivity, i.e., the sensor should distinguish the target gas without any interference [30]. In order to check the selectivity of the fabricated sensor, various volatile organic compounds (VOCs) such as acetone, chloroform, ethanol, isopropanol, and methanol at 500 ppm each and toxic gases such as CO₂ and NH₃ with 500 ppm and 25 ppm, respectively were tested in synthetic air background. As per the world health organization (WHO) standard, ~ 35 ppm of NO₂, ~ 45 ppm of NH₃, and ~ 5% CO₂ gas are a risk to human health.

Figure 10(a) shows the sensing responses of 5 at% La@MoS₂ against the above mentioned VOCs and toxic gases. It is clear from the image that the sensing response of acetone is 20.01% at 500 ppm concentration, which shows a good response, even though acetone act as an electron acceptor. For other VOC’s like chloroform, ethanol, isopropanol, and methanol, the response is minimal. On the other hand, CO₂ gas again shows a decrease in response, while this acts as an electron donor when adsorbed on the sensor surface. For ammonia gas, the sensor response is very minimum. But in the case of MoS₂, the selectivity is weak as compared with 5 at% La@MoS₂ as shown in Figure S7 (see Supporting Information, Figure S7). From Figure S7, it has been found that MoS₂ sensor response for acetone and ethanol is almost the same as NO₂ gas. Thus, the 5 at% La@MoS₂ based sensor shows good selective towards NO₂ gas compared to other interferents at room temperature and could be used as an exceptional gas sensing material for detecting NO₂ gas even when other gasses exist.

Figure 10. The selectivity study of 5 at% La@MoS₂ based sensor (a) dynamic sensing response, and (b) response-recovery time to different analytes

Gas sensing mechanism
The logic for the n-type effect of few-layered MoS$_2$ and p-type La decorated few-layered MoS$_2$ can be resolved by analyzing the ultraviolet photoelectron spectroscopy (UPS) in the presence of helium resonance lamp (photon energy of He(I) = 21.2 eV). The energy band alignment of few-layered MoS$_2$ and La@MoS$_2$ are measured by using UPS analysis, as shown in Figure 11(a). The UPS spectrum exhibits a two cut-off energy (Low BE cutoff and High BE cutoff) and the low binding energy (BE) cutoff from the tangent line is called as HOMO energy ($E_{\text{HOMO}}$). $E_{\text{HOMO}}$ for the few-layered MoS$_2$ and La@MoS$_2$ is found to be 1.43 and 0.62 eV, respectively. From the graph, the high binding energy cutoff values are 16.95 and 16.14 eV in the case of MoS$_2$ and La@MoS$_2$, respectively. We evaluate the work function of MoS$_2$ and La@MoS$_2$ as 3.44 and 5.06 eV, respectively, because of the difference between the He(I) value 21.2 eV and the high BE cutoff value is recognized as work function. From Figure 11(b), it has been found that the Fermi level of La@MoS$_2$ decreased by 0.81 eV from the Fermi level of MoS$_2$ (p-type doping effect), whereas the work function of La@MoS$_2$ is increased. The decrease in energy between the Fermi level and valence band maximum implies the n-type MoS$_2$ nanoflakes has been changed to p-type MoS$_2$ after incorporation of La [31]. Because of the p-type effect, electrical conduction value is increased while exposed to oxidizing gas (NO$_2$), depending on the increased hole concentration of La@MoS$_2$. Again it has been noted from Figure 11(b) that the difference of work function between the metal contact (Au ~ 5.10 to 5.47 eV) and MoS$_2$ (3.44 eV) is high as compared to the La@MoS$_2$ (5.06 eV). Due to the large difference of work function between the MoS$_2$ and Au electrode is favourable for creating a high Schottky barrier (acting as a diode) in which interns decreased the sensor sensitivity. But for La@MoS$_2$, the Schottky barrier is comparatively shallow in the presence of La. It has been observed that La helps to conduct the current in both directions without any alteration because of its ohmic effect. Thus, a transfer channel is formed over the sensor material rather than the only contacts [32]. This occurrence has already been proved by the I-V characteristics of MoS$_2$ and La@MoS$_2$ sensors (Figure S4).

Now, we briefly introduce the sensing mechanism of La@MoS$_2$ sensing material against NO$_2$ gas, as shown in Figure 11(c). From the literature, it has been observed that the sensing mechanism is highly dependent upon the operating temperature, which is oxygen adsorption reaction phenomena during the synthetic air purging. At room temperature, the O$_2$ gas molecule is physisorbed onto the sensor surface and ionized to O$_2^-$ by tapping the free electrons of the particles. The mechanism of gas sensor is purely depending on the charge transfer mechanism between the sensor materials.
and gas (NO₂). When the purged NO₂ gas as an oxidizing agent is coming to the contact of the La@MoS₂ sensor surface, the physisorption of NO₂ molecules started by capturing the electrons from La@MoS₂ surface due to its upper electron affinity (220 kJ mol⁻¹) as compared to an oxygen molecule (42 kJ mol⁻¹) [33]. Thus, a decrease in resistance is observed for La@MoS₂ for 5-25 ppm of NO₂ gas due to its enough electrons capturing [Figure 11(c)]. This is resulting in an increase in higher hole concentration than the electron concentration on the La@MoS₂ surface. Therefore, the conduction in full hole dependent. This behaviour is opposite for MoS₂ NF because the MoS₂ is showing the n-type characteristics.

**Figure 11.** Schematic showing (a) UPS results of pure MoS₂ and 5 at% La@MoS₂, (b) Band alignment of pure MoS₂ and 5 at% La@MoS₂ determined by UPS data, (c) gas sensor mechanism for NO₂ gas

CONCLUSIONS
In brief, a substantial improvement of the La decorated MoS\textsubscript{2} sample in the NO\textsubscript{2} gas-sensing performance is validated, which allows MoS\textsubscript{2} to be exceeded in respect of low response & recovery time, sensitivity, and selectivity at room temperature. Herein, the La@MoS\textsubscript{2} sensor material shows a ~ 6 times better sensing response and ~ 5 times better sensitivity towards NO\textsubscript{2} gas as compared to a few-layered MoS\textsubscript{2} through the creation of electron transfer channel by La with MoS\textsubscript{2}. Because of the good sensitivity of La@MoS\textsubscript{2}, LOD and LOQ is around 0.46 and 1.54 ppm as compared to pristine MoS\textsubscript{2} (4.03 and 13.44 ppm), respectively. Remarkably, good selectivity to other interferents (like acetone, chloroform, ethanol, isopropanol, methanol, CO\textsubscript{2}, and NH\textsubscript{3}) by La@MoS\textsubscript{2} is also achieved. Thus, La decorated MoS\textsubscript{2} can be considered as an adaptable solution in regards of good response & recovery time, and sensitivity to resolve the detection of low concentration NO\textsubscript{2} gas sensing irrespective of the environmental pollution.

**Author Contributions**

K.R. has done all the material synthesis, characterization, gas sensing measurement, and analysis of the data. A.N.K. has done some part of the characterization and writing of the draft paper. K.P has contributed to check the data, validation of the results. The final manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**
