

# Scalable WS<sub>2</sub>-Graphene Hybrids for Ultralow NO<sub>2</sub> Concentration Detection

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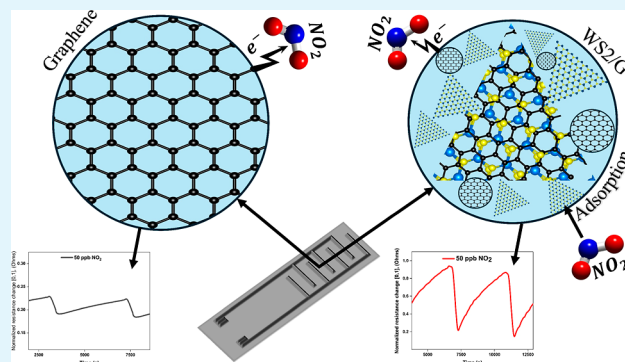
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**ABSTRACT:** This work presents a facile approach for fabricating hybrid heterostructures of tungsten disulfide (WS<sub>2</sub>), synthesized via atmospheric pressure chemical vapor deposition (APCVD) and commercial graphene. A simple airbrushing technique, with nitrogen (N<sub>2</sub>) as the carrier gas, was employed to fabricate the sensors. The morphological and structural characterizations of the hybrid material revealed a sheet-like synthesis of edge-enriched 2D WS<sub>2</sub> decorated with multilayer graphene nanomaterial. The gas-sensing properties of the pristine and hybrid materials were evaluated for nitrogen dioxide (NO<sub>2</sub>) at various operating temperatures. The hybrid sensor with a WS<sub>2</sub> to graphene ratio of 3:1 demonstrated exceptional sensitivity to ultralow NO<sub>2</sub> concentrations (10 ppb) at a remarkably low operating temperature of 100 °C, outperforming both the graphene and WS<sub>2</sub> counterparts. Additionally, the sensor's responses to CO, H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, and NH<sub>3</sub> were examined to assess its selectivity. The sensor was tested under different relative humidity conditions (RH at 25 °C; 25%, 50%, and 75%). The sensor response nearly doubled at RH = 50%, highlighting its potential for practical applications in selective NO<sub>2</sub> detection. The sensor responses eventually reached saturation at 75% RH. In addition, the manuscript provides a detailed discussion of the NO<sub>2</sub> gas sensing mechanism.

**KEYWORDS:** WS<sub>2</sub>, APCVD, sulfurization, gas sensor, NO<sub>2</sub>, TMDs, 2D materials



## INTRODUCTION

Rapid industrial growth and population increase have remarkably elevated the emission of toxic gases and volatile organic compounds (VOCs) into the atmosphere, leading to life-threatening situations.<sup>1</sup> The main contributors to severe respiratory issues, including chronic bronchitis, respiratory irritation, and asthma, are parts per million (ppm) levels of NH<sub>3</sub> and parts per billion (ppb) levels of NO<sub>2</sub>.<sup>2,3</sup> Common sources of these pollutants include power plant exhausts, industrial emissions, vehicular exhausts, and fertilizer production.<sup>4,5</sup> Additionally, NO<sub>2</sub> reacts with ambient compounds, leading to the formation of acid rain and ozone, thus exacerbating air pollution concerns.<sup>4,6</sup>

The United States Environmental Protection Agency (EPA) underscores the adverse effects of prolonged exposure to NO<sub>2</sub>, noting that concentrations as low as several hundred parts per billion (ppb) can induce eye and lung irritation. To address these impacts, the EPA has established a long-term exposure limit of 53 ppb for NO<sub>2</sub>.<sup>7,8</sup> It becomes imperative to identify and quantify the atmospheric concentrations of NH<sub>3</sub> and NO<sub>2</sub> to safeguard chemical processes, monitor human health, and ensure protection against gas leakage and chemical disasters.<sup>2</sup> Therefore, developing gas sensors with high sensitivity, selectivity, accuracy, reliability, and long-term stability is crucial for monitoring low concentrations of these hazardous gases.

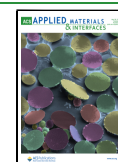
Semiconductor gas sensors, particularly metal oxide-based sensors (MOX), have garnered tremendous attention due to their ease of fabrication, miniaturization, simple operation, and potential for mass production.<sup>6</sup> However, their performance is often constrained by a lack of selectivity and the requirement of high operating temperatures, which compromises stability and increases energy consumption.<sup>6</sup> While polymers offer an alternative due to their flexibility and ability to work at low temperatures, they often lack long-term stability under extreme conditions. In light of this, graphene has emerged as a promising candidate for gas sensing, exhibiting desirable intrinsic properties that surpass those of MOX and polymers. These properties include exceptional thermal conductivity (5000 W mK<sup>-1</sup> at 27 °C),<sup>9</sup> high room-temperature carrier mobility (20,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>),<sup>10</sup> low density (0.77 mg m<sup>-2</sup>),<sup>11</sup> and remarkable chemical stability and mechanical durability (Young's modulus ~1.02 TPa).<sup>12</sup> These attributes make graphene highly suitable for miniaturized, flexible gas sensors with superior sensitivity at low

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operating temperatures.<sup>13</sup> However, despite its advantages, graphene-based gas sensors still face challenges related to sensitivity, selectivity, and recovery speed.<sup>14</sup> Regardless of graphene's many promising qualities as a gas-sensing material, researchers are also exploring other two-dimensional materials for gas-sensing applications.<sup>15</sup>

Two-dimensional transition-metal dichalcogenides (2D TMDs), such as MoS<sub>2</sub> and WS<sub>2</sub>, have attracted attention for their unique electrical, chemical, and optical properties.<sup>16</sup> They represent a promising class of layered van der Waals materials with excellent responses to hazardous gas species, especially NO<sub>x</sub>.<sup>13</sup> Their large surface-area-to-volume ratios provide suitable adsorption sites for gas molecules, and the sensing mechanism is based on direct charge transfer upon gas adsorption.<sup>9,10</sup> However, pristine TMDs face challenges like low sensitivity at enhanced limits of detection (LoD), selectivity issues, and poor recovery.<sup>11</sup> Prolonged exposure of TMDs to atmospheric oxygen can accelerate oxidation, degrading sensing performance.<sup>12</sup> To address these limitations, functionalization strategies have been explored to enhance the performance of TMD-based sensors, with carbon-based materials like graphene being particularly promising. The synergistic effects of combining graphene and TMDs improve sensitivity, selectivity, and stability, making hybrid systems an effective solution for gas sensing applications.<sup>17</sup> The development of hybrids, particularly those combining graphene with other materials like metal oxides, MXenes, or TMDs, has emerged as an effective approach to enhance gas sensor performance at lower operating temperatures.<sup>16</sup> These hybrid systems offer the potential to address the limitations of pristine materials while taking advantage of their individual properties, especially for detecting gases at lower temperatures. Therefore, hybrid nanomaterials, especially the ones based on graphene and TMDs, represent a promising solution to overcome the inherent challenges faced by pristine materials, leading to high-performance gas sensors with lower energy consumption and better overall sensing capabilities. Concurrently, efforts are underway to explore the excellent properties of heterojunctions formed from different 2D materials such as graphene/WSe<sub>2</sub>,<sup>18</sup> graphene/MoS<sub>2</sub>,<sup>19</sup> graphene/MoSe<sub>2</sub>,<sup>20</sup> or graphene/WS<sub>2</sub>.<sup>21</sup> These heterojunctions exhibited excellent prospects for gas-sensing applications due to their enhanced electrochemical properties compared to their pristine counterparts.<sup>22</sup> Besides, diverse 2D layered nanomaterials are stacked to facilitate the regulation and manipulation of charge carrier generation, confinement, and transport.<sup>23</sup> A rational design of hybrids involves understanding the behavior of individual materials and exploiting their combined effects to enhance sensing behavior. Hao et al. investigated the adsorption of ten gas molecules on a graphene/WSe<sub>2</sub> heterostructure using first-principles calculations. The study revealed that NO<sub>2</sub> exhibited the strongest interaction with the heterostructure, acting as an electron acceptor and lowering the Schottky barrier height. Additionally, the application of a positive electric field (+0.5 V/Å) enhanced NO<sub>2</sub> sensitivity, offering insights for designing high-selectivity WSe<sub>2</sub>-graphene based gas sensors.<sup>18</sup> This study also highlights the potential of graphene-TMD heterojunctions as efficient candidates for developing high-performance NO<sub>2</sub> gas sensors. According to the U.S. Environmental Protection Agency (EPA), the threshold limit value (TLV) for short-term exposure to NO<sub>2</sub> is 100 ppb, whereas long-term exposure is set at 53 ppb.<sup>24</sup>

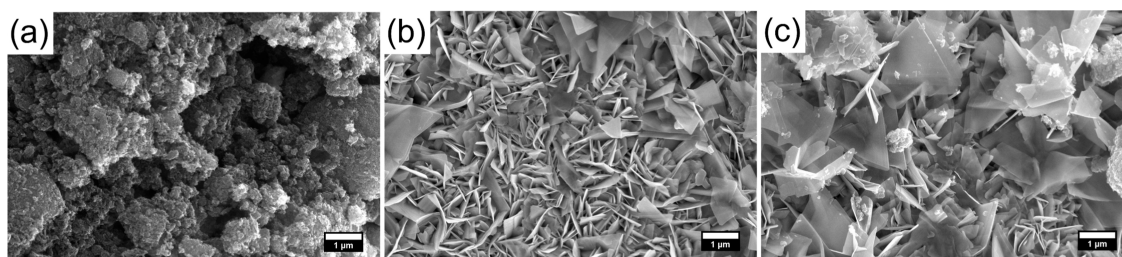
Gas-sensing applications based on graphene and its derivatives often require additional modifications to enhance

adsorption and electronic characteristics. Doping with various heteroatoms has been employed for this purpose.<sup>25</sup> Both graphene and its derivatives, such as reduced graphene oxide (rGO), demonstrate a distinct advantage in NO<sub>2</sub> gas detection due to their high carrier mobility and large surface-to-volume ratio.<sup>25,26</sup> Ma et al.<sup>21</sup> demonstrated self-powered photovoltaic flexible gas sensors through defect engineering controlled by ion irradiation employing a WS<sub>2</sub>/graphene heterostructure. The graphene and WS<sub>2</sub> monolayers were grown via chemical vapor deposition which were then transferred to Si substrate employing wet-chemical processes. The sensors were able to detect as low as 50 ppb of NO<sub>2</sub>. Graphene offers superior electrical conductivity and mechanical strength compared to reduced graphene oxide, making it more suitable for gas sensing applications, electronic devices, and advanced composites.<sup>27,28</sup> Yan et al.<sup>29</sup> investigated the NO<sub>2</sub> sensing characteristics of WS<sub>2</sub>/graphene aerogel (WS<sub>2</sub>/GA) composites under varying humidity (0–60%) and temperature (RT to 180 °C). The WS<sub>2</sub>/GA sensors demonstrated improved NO<sub>2</sub> selectivity compared to standalone graphene or WS<sub>2</sub> aerogels, with detection limits theoretically estimated to be 10–15 ppb. Optimum sensing performance was achieved at 180 °C in a dry atmosphere, while humidity enhanced response and recovery at room temperature, showcasing the composite's potential for adaptable gas sensing applications. Most of the reported works rely on synthesis techniques like hydrothermal synthesis and liquid phase exfoliation (LPE). However, these techniques suffer from challenges such as limited control over the size and quality of the produced materials, leading to variations in material properties. Moreover, the process often involves the use of hazardous solvents, posing environmental and safety concerns. Also, most of the reported methods for heterojunction fabrication involve the drop-casting method, where the thickness of the deposited film is seldom controlled.

Addressing the above-mentioned shortcomings, this work demonstrates an effective hybrid sensing material capable of detecting ultralow concentrations of NO<sub>2</sub>. We present a methodology for fabricating WS<sub>2</sub>/graphene hybrid thin films using a simple airbrush with WS<sub>2</sub> grown using the APCVD technique. The materials were directly deposited on the transducer substrates using an airbrushing technique with precise control over the thickness. The deposited materials were characterized for morphology, microstructure, phase, and chemical composition. The gas sensing properties of the films were studied toward low NO<sub>2</sub> concentrations at various operating temperatures (i.e., RT, 100 °C, and 150 °C) in both dry and humid conditions, as well as toward the interfering species like NH<sub>3</sub>, CO, H<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub>. The hybrid material exhibited exceptional sensitivity to NO<sub>2</sub> with an experimental limit of detection (LoD) as low as 10 ppb, well within the EPA's threshold limits. This study highlights the potential of WS<sub>2</sub>/graphene hybrids for advanced gas sensing applications, offering a reliable and scalable solution for monitoring hazardous gases.

## EXPERIMENTAL SECTION

**APCVD Synthesis of Sheet-Like WS<sub>2</sub>.** Atmospheric pressure chemical vapor deposition (APCVD) technique was used to synthesize sheet-like WS<sub>2</sub> with yield in hundreds of milligrams as reported in our earlier work.<sup>30</sup> The technique has the potential to be scaled to an industrial level. Commercially available tungsten trioxide powder procured from Sigma-Aldrich (CAS: 1314-35-8) was employed and sulfurized to obtain sheet-like WS<sub>2</sub> nanostructures in powder form. The sulfurization was carried out for 60 min at 900 °C using metallic sulfur (Sigma-Aldrich, CAS: 7704-34-9) in a homemade tube in tube furnace



**Figure 1.** FESEM images of (a) graphene, (b) WS<sub>2</sub>, and (c) WS<sub>2</sub>/G1.

with a temperature gradient. The schematic of the furnace is shown in Figure S1. The middle zone of the furnace reaches a set temperature of 900 °C while the zones adjacent to the middle zone reach approximately 400 °C. Three alumina boats were positioned strategically within different temperature zones of the furnace; one boat contained 100 mg of WO<sub>3</sub> precursor powder, while the other two boats contained 1 g of sulfur each. One of the sulfur boats was placed adjacent to the WO<sub>3</sub>-containing boat inside a semisealed secondary quartz tube, both situated in the 900 °C temperature zone. The reaction chamber was flushed with 100 mL/min of argon prior to sulfurization reaction, to remove oxygen present in the reactor. The boat outside the secondary quartz tube was placed upstream of argon flow inside the bigger quartz tube, Figure S1a. The argon flow was kept at 30 mL/min during the reaction. The furnace was programmed to reach the set temperature of 900 °C with a ramp of 40 °C/min. Upon reaching the set temperature (900 °C), the external quartz tube is carefully positioned such that the sulfur boat located outside the furnace is in the 400 °C temperature zone of the furnace, Figure S1b. This configuration ensures a sulfur-rich environment. The furnace was let to cool naturally after the completion of the reaction.

**Pristine and -WS<sub>2</sub>/Graphene Hybrids.** Commercial graphene (CAS 1034343-98-0) was purchased from STREM Chemicals and was used to prepare sensors of pristine graphene and three hybrid combinations, with ratios of 3:1 and 1:1 of WS<sub>2</sub>/graphene, respectively.

**Gas Sensor Fabrication.** Pristine graphene, WS<sub>2</sub>, and WS<sub>2</sub>/graphene hybrid sensing films were deposited on commercial alumina substrates (Ceram Tech GmbH, Germany) using a simple airbrushing technique. The alumina substrates have Pt-interdigitated electrodes with an electrode gap of 300 μm on the front side (2.5 mm × 5.1 mm) and a Pt-resistive heater meander on the back side. The substrates were cleaned with sequential sonication in acetone, ethanol, and deionized water, followed by nitrogen blow drying. The cleaned substrates were placed in a homemade airbrush system consisting of a hot plate, a commercial airbrush, a multimeter, and connectors.<sup>30</sup>

To deposit thin films of pristine graphene and pristine WS<sub>2</sub>, 10 mg of graphene and WS<sub>2</sub> powder were separately sonicated in 10 mL of absolute ethanol (Scharlab, CAS: 64-17-5) for 1 h each, resulting in a black and brownish suspension, respectively. In the case of WS<sub>2</sub>/graphene hybrids (WS<sub>2</sub>/G), a constant total weight of 10 mg was maintained for both WS<sub>2</sub> and graphene. For hybrid WS<sub>2</sub>/G1, 7.5 mg of WS<sub>2</sub> was mixed with 2.5 mg of graphene, while for hybrid WS<sub>2</sub>/G2, 5 mg of WS<sub>2</sub> was mixed with 5 mg of graphene. The sensors are named WS<sub>2</sub>/G1 and WS<sub>2</sub>/G2, respectively. The amount of ethanol was kept constant at 10 mL in all the preparations, which were later transferred to an airbrush system. Preliminary experiments were conducted to evaluate various WS<sub>2</sub>/graphene ratios, including 3:1, 1:1, 1:3, pristine WS<sub>2</sub>, and pristine graphene; however, the 3:1 and 1:1 ratios demonstrated superior gas sensing performance, while the other compositions exhibited significantly lower sensitivity and were excluded from further analysis. The alumina substrates were placed on a hot plate kept at 55–60 °C, and the electrodes were connected to a multimeter in order to monitor, in real time, the resistance of the deposited films. This helps in achieving high reproducibility in the fabricated sensors. The solutions were airbrushed onto the alumina substrates using N<sub>2</sub> as a carrier gas.

**Material Characterization Techniques.** The characterization techniques employed in this study have been detailed in our previous

work.<sup>30</sup> Briefly, the morphology of the materials was examined using Field Emission Scanning Electron Microscopy (FESEM, Thermo Scientific Scios 2). High-Resolution Transmission Electron Microscopy (HRTEM) was performed using a JEOL F200 TEM ColdFEG operating at 200 kV. TEM images were acquired using a Gatan OneView camera, a CMOS-based detector with a resolution of 4096 × 4096 pixels. The crystal structure of WS<sub>2</sub> and the composite materials was analyzed by X-ray diffraction (XRD) using a Bruker-AXS D8-Discover diffractometer, equipped with a parallel beam geometry (Göbel mirror), vertical  $\theta$ - $\theta$  goniometer, XYZ motorized stage, and a VANTEC-500 GADDS detector positioned 15 cm from the sample. The instrument operated at 40 kV and 40 mA to produce CuK $\alpha$  radiation. Raman spectroscopy was conducted using a Renishaw inVia spectrometer with a 514 nm argon-ion laser (Novatech, 25 mW). X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5000 VersaProbe (Physical Electronics) using a monochromatic Al K $\alpha$  source, with spectra recorded at a 45° takeoff angle. A spot size of 200 μm and a pass energy of 20 eV were used for core-level scans (W 4f, S 2p, C 1s). A dual beam charge neutralization system, combining an electron gun (<1 eV) and an argon ion gun (<10 eV), was applied to mitigate surface charging. Data analysis was carried out using CASA-XPS software.

**Gas Sensing Measurements.** The gas sensing measurements were performed using a homemade gas detection system consisting of a Teflon chamber with a net volume of 35 mL. The chamber consists of an inlet and outlet, which are connected to the gas delivery system and exhaust, respectively. A fully automated gas flow measurement system comprising mass flow controllers (MFCs, Bronkhorst High-Tech B.V.) was employed to supply the precise amounts of diluted gas mixtures. Calibrated gas cylinders balanced in dry synthetic air (Air Premier purity: 99.999%) were used for gas sensing measurements. The operating temperatures of the sensors were controlled by connecting the meander heaters of the sensors to an external power supply (Agilent U8002A). Sensor responses were recorded using an Agilent-34972A data acquisition system by monitoring the sensing material resistance changes upon exposure to different concentrations of target gases such as NH<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>, CO, and benzene. The sensor responses were evaluated at three different temperatures: room temperature (RT), 100 °C, and 150 °C. To ensure a stable baseline, a continuous flow of 100 mL/min of dry air was maintained in the chamber for 5 h prior to commencing the gas sensing experiments. The sensors were exposed to a specific gas species for 10 min, followed by a baseline recovery cycle, which was adjusted based on the sensor operating temperature: 60 min for 100 and 150 °C, and 120 min for RT operation. The overall flow of the dry air remained constant at 100 mL/min throughout the gas sensing measurements. The humidity effect on the sensing performance was evaluated by humidifying (at room temperature) the gas stream through a controller evaporator mixer from Bronkhorst. For oxidizing species like NO<sub>2</sub>, the sensor response was calculated using eq 1, while for reducing species like NH<sub>3</sub>, the sensor responses were calculated using eq 2.

$$R = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{air}}} \times 100 \quad (1)$$

$$R = \frac{R_{\text{gas}} - R_{\text{air}}^*}{R_{\text{air}}} 100 \quad (2)$$

$R_{\text{air}}$  and  $R_{\text{gas}}$  are the real time resistances of sensors when exposed to air and to target gas, respectively.

## RESULTS AND DISCUSSION

**Material Characterization.** Field emission electron microscopy (FESEM) was conducted to study the structure and morphology of the materials. Bare graphene, as illustrated in the FESEM image in Figure 1a, reveals a multilayered, highly porous structure, which is desirable for gas sensing applications since it offers more active sites.<sup>31</sup> Figure 1b demonstrates pristine WS<sub>2</sub> with a distinct triangular sheet-like morphology. This peculiar triangular shape of WS<sub>2</sub> has been reported earlier as well.<sup>32–35</sup> The triangular morphology of WS<sub>2</sub> can be attributed to the fact that the crystal growth predominantly relies on the growth rates of two specific types of crystal faces, especially where the zigzag edge of tungsten or sulfur atoms terminate.<sup>36,37</sup> Upon in-depth analysis of the WS<sub>2</sub> using ImageJ software, it was found that the edge-to-edge width of the sheets is  $\sim 700$  nm, with the presence of some large sheets measuring around  $1.5 \mu\text{m}$  with an average thickness of  $\sim 40$  nm. Figure 1c depicts the WS<sub>2</sub>/G1 morphology. As is evident from the figure, the mixture of the two individual materials is uniform and homogeneous. FESEM image of WS<sub>2</sub>/G2 is shown in Figure S2 in the Supporting Information.

X-ray diffraction (XRD) analysis was carried out to study the crystal structure of graphene, WS<sub>2</sub>, and WS<sub>2</sub>/G hybrids. The results are presented in Figure S3 as Supporting Information. All the peaks match well with the standard hexagonal phase of WS<sub>2</sub> (ICDD card number: 84-1398) with lattice constants  $a = 0.3152$  nm and  $c = 1.232$  nm belonging to the P63 space group. The diffractogram reveals the presence of intense peaks at  $14.35^\circ$ ,  $28.95^\circ$ ,  $33.58^\circ$ ,  $44.04^\circ$ ,  $58.49^\circ$ ,  $60.57^\circ$ ,  $68.68^\circ$  and  $76.04^\circ$  corresponding to (002), (004), (101), (006), (110), (112), (200) and (116) crystal planes. As can be seen from the diffractogram, the intense peak at  $26.61^\circ$  can be attributed to the (111) lattice phase of carbon corresponding to graphene (ICDD card number: 75-2078). Furthermore, minor peaks at  $23.14^\circ$ ,  $23.64^\circ$ , and  $24.36^\circ$  corresponding to (002), (020), and (200) crystal planes of triclinic WO<sub>3</sub> traces (ICDD card number 32-1395) were identified with lattice parameters  $a = 7.30$  nm,  $b = 7.522$  and  $c = 7.678$  nm. Transmission electron microscopy (TEM) and high-resolution electron microscopy (HRTEM) were conducted to better understand the morphology and internal structure of the samples, respectively. Figure 2 shows an example of the obtained results for WS<sub>2</sub>/G1. We can observe the presence of large, thin, and transparent WS<sub>2</sub> sheets stacked on top of each other with the presence of graphene as well. The insets in the figure show the interplanar distance of WS<sub>2</sub> and graphene. Upon further examination of the HRTEM images, the interplanar distances were determined to be 0.616 and 0.27 nm, corresponding to the (002) and (101) planes of WS<sub>2</sub> (ICDD card number: 84-1398). The inset, displaying the interplanar distance,  $d = 0.334$  nm (111) plane, is attributed to graphene (ICDD card number: 75-2078). These results confirm the formation of the WS<sub>2</sub>/G hybrid and agree with the XRD results. It is worth noting that similar results were observed from the other hybrid. Figure S4 depicts the HRTEM results of pristine graphene; it shows lattice fringes with interlayer spacing of 0.34 and 0.20 nm, indicative of pure multilayered graphene.

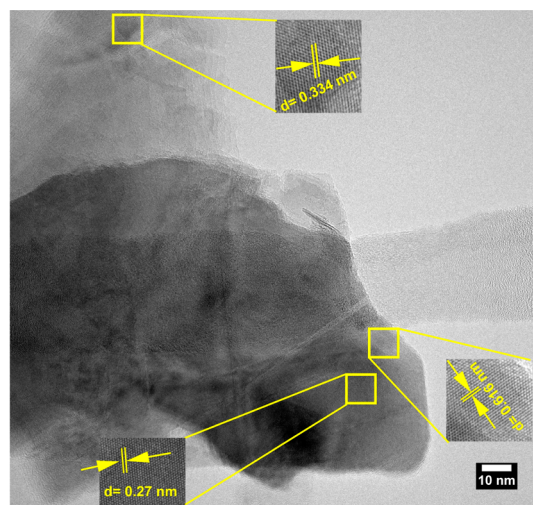


Figure 2. HRTEM image WS<sub>2</sub>/G1.

Regarding pristine WS<sub>2</sub> samples, the obtained results are similar to the ones reported in our previous work.<sup>30</sup>

To study the accurate distribution of elements of WS<sub>2</sub>/G1, EDS elemental mapping was conducted, as shown in Figure S5. The analysis confirms the presence of C, W, and S elements distributed uniformly over the WS<sub>2</sub> sheets. Also, Figure S5f shows the EDX spectra of the hybrid material with respective elements, confirming the high purity of the material.

Figure 3 displays an example of the spectrum obtained from WS<sub>2</sub>/G1. It contains intense and sharp peaks, located at  $352.7$

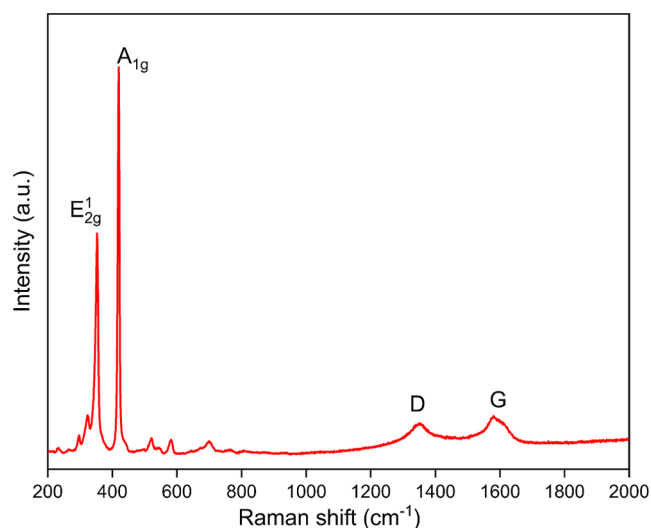
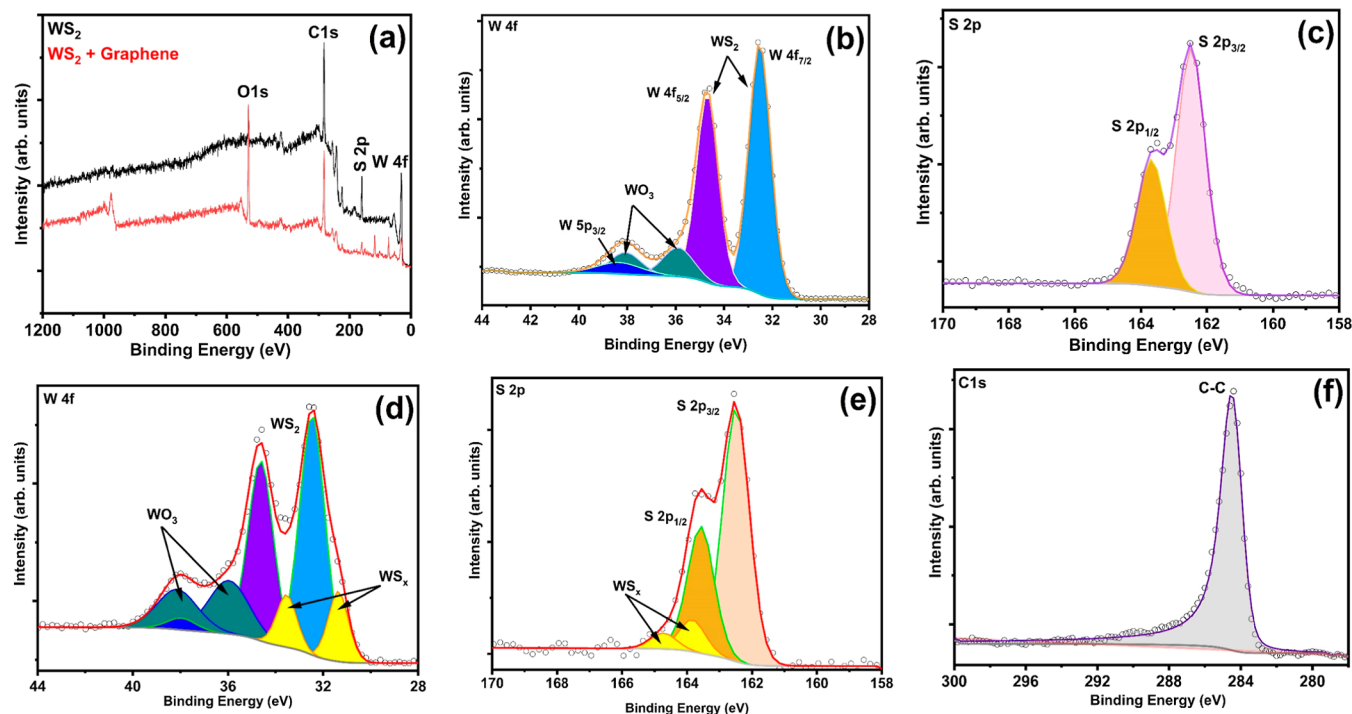


Figure 3. Raman spectra of WS<sub>2</sub>/G1.

and  $419.8 \text{ cm}^{-1}$ , which correspond to  $E_{2g}^1$  and  $A_{1g}$  vibration modes of WS<sub>2</sub>. The  $A_{1g}$  peak denotes the out-of-plane vibrational mode of S atoms and  $E_{2g}^1$  peak indicates vibration modes of W and S atoms. This confirms the formation of 2H phase-WS<sub>2</sub>.<sup>2</sup> Also, the wavenumber difference between the Raman modes depends on the WS<sub>2</sub> film thickness. The difference between Raman shift of ( $A_{1g} - E_{2g}^1$ ) is  $67.1$  indicating the composition of layered WS<sub>2</sub> film.<sup>30,38</sup> Also, the wavenumber difference between these modes ( $\Delta = 67.1 \text{ cm}^{-1}$ ) and the broadening of the peaks are indicative of defect-rich WS<sub>2</sub>, including S vacancies.<sup>38</sup> From the spectrum, the distinctive D



**Figure 4.** XPS spectra of  $\text{WS}_2$  and  $\text{WS}_2$  + graphene ( $\text{WS}_2/\text{G1}$ ): (a) XPS survey scan, (b) W 4f core level of  $\text{WS}_2$ , (c) S 2p core level of  $\text{WS}_2$ , (d) W 4f core level of  $\text{WS}_2$  + graphene, (e) S 2p core level of  $\text{WS}_2$  + graphene, and (f) C 1s core level of  $\text{WS}_2$  + graphene.

and G bands of graphene appear at approximately  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ , respectively. The D band, often associated with structural disorder or defects, arises from a hybridized vibrational mode linked to graphene edges. The G band results from first-order scattering of the  $E_{2g}$  mode within  $\text{sp}^2$  carbon domains. The graphene exhibited an  $I_D/I_G$  value of 0.85, indicating a higher number of defects that facilitate gas adsorption,<sup>39</sup> which is desired for gas sensing applications. The Raman spectra of pristine graphene and pristine  $\text{WS}_2$  are shown in Figure S6a,b, respectively.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical states and composition of both pristine  $\text{WS}_2$  and  $\text{WS}_2/\text{G1}$ . The XPS survey spectra revealed the presence of W, C, S, and O in both samples, Figure 4a. A detailed analysis of the survey spectra of pure  $\text{WS}_2$  indicates that 86% of the tungsten atoms participate in W–S bonding, with the remaining 14% associated with  $\text{WO}_3$  impurities. The spectra recorded in the core-level binding energy regions allowed for the determination of the oxidation states of the elements.

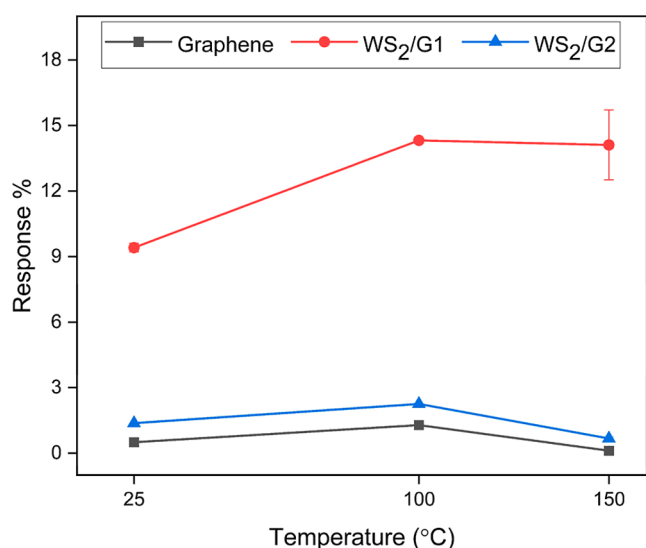
For the pristine  $\text{WS}_2$  sample, the W 4f binding energy region is well reproduced by one singlet and two doublets, as can be seen in Figure 4b. The singlet is centered at 38.4 eV, corresponding to the W  $5p_{3/2}$  core level. The W  $4f_{7/2}$  peaks associated with the two doublets are centered one at 32.5 eV, which corresponds to tungsten atoms in the  $\text{W}^{4+}$  valence state, and the other at 35.9 eV which corresponds to tungsten atoms in the  $\text{W}^{6+}$  valence state within  $\text{WO}_3$ .<sup>35</sup> The S 2p spectrum is characterized by the S  $2p_{1/2}$  and S  $2p_{3/2}$  peaks at 163.7 and 162.5 eV, respectively, with a spin–orbit energy separation of 1.2 eV, consistent with the  $\text{S}^{2-}$  oxidation state in  $\text{WS}_2$ , Figure 4c. Notably, the spectrum does not exhibit any discernible S–O bond component at 168.8 eV,<sup>30,35</sup> confirming the formation of  $\text{WS}_2$  with minimal  $\text{WO}_3$  impurities. Although the S 2s lines were initially referenced, this analysis highlights that the bonding environment of oxygen is exclusively associated with tungsten. The lower intensity of the S

2p peak and the absence of S–O bonds (which would appear at  $\sim 168.8\text{ eV}$ ) suggest the presence of S vacancies.<sup>40</sup>

For the graphene-loaded  $\text{WS}_2$  sample ( $\text{WS}_2/\text{G1}$ ), the XPS analysis revealed a higher relative concentration of carbon due to the addition of carbon nanostructures. The C 1s peak shows an asymmetric line characteristic of C–C  $\text{sp}^2$  bonding, corresponding to the carbon nanomaterial (graphene), as is depicted in Figure 4f. In the W 4f binding energy region, an additional doublet with the W  $4f_{7/2}$  component centered at 32.5 eV appeared compared to the pristine  $\text{WS}_2$  sample, representing W–S bonding in  $\text{WS}_x$ , as can be seen in Figure 4d. This component accounts for 15% of the tungsten atoms, while 22% corresponds to  $\text{WO}_3$  and 63% to  $\text{WS}_2$ . The S 2p spectrum of the graphene-loaded  $\text{WS}_2$  sample does not exhibit any discernible S–O bond component at 168.8 eV,<sup>41</sup> Figure 4e. However, a low-intensity doublet attributed to  $\text{WS}_x$  was observed, indicating the presence of a minor phase of  $\text{WS}_x$  alongside the dominant  $\text{WS}_2$  phase.<sup>40</sup>

Based on the XPS analysis, the graphene-loaded  $\text{WS}_2$  sample ( $\text{WS}_2/\text{G1}$ ) exhibits a complex chemical composition comprising of  $\text{WS}_2$  (primary phase),  $\text{WS}_x$  with  $x < 2$  (minor phase), and  $\text{WO}_3$  (trace impurities), along with a  $\text{sp}^2$  bonded carbon (graphene). The analysis for the other hybrid sensor exhibits a similar composition, suggesting consistent formation of hybrid  $\text{WS}_2$ -based structures with graphene.

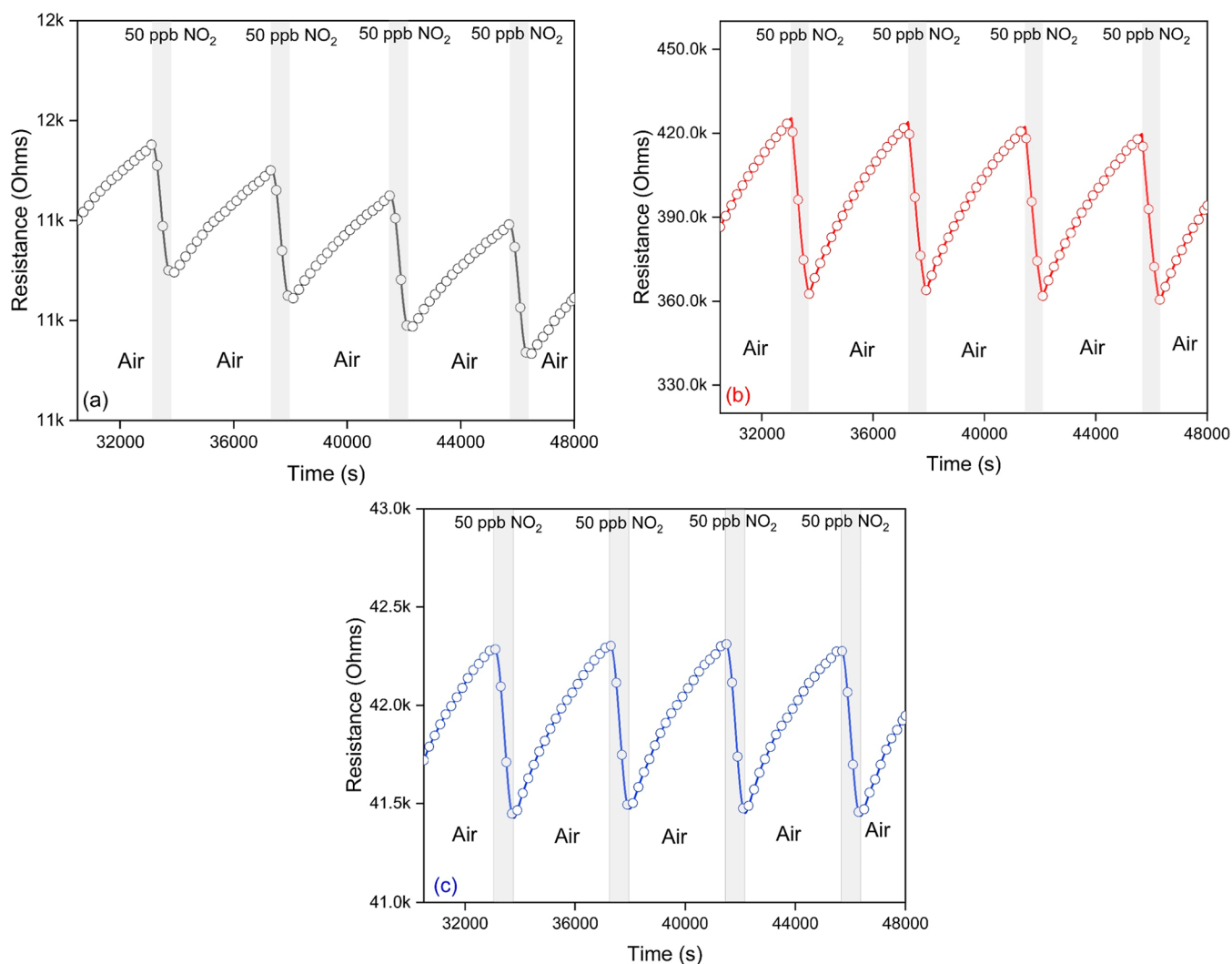
**Gas Sensing Results.** The gas sensing properties of graphene,  $\text{WS}_2$ , and  $\text{WS}_2/\text{G}$  hybrid sensors were tested for 50 ppb of  $\text{NO}_2$  at various operating temperatures ranging from room temperature to  $150\text{ }^\circ\text{C}$ . It is worth noting that the operating temperature did not exceed  $150\text{ }^\circ\text{C}$  to avoid the evaporation of sulfur, which could deteriorate the sensing layer by forming a  $\text{WO}_3/\text{WS}_2$  complex.<sup>35</sup> The optimal working temperature is an important parameter for evaluating overall sensor performance, impacting sensitivity, selectivity, response, and recovery speeds. Figure 5 shows the sensor responses of



**Figure 5.** Sensor responses as a function of temperature toward 50 ppb of NO<sub>2</sub>, graphene, WS<sub>2</sub>/G1 and WS<sub>2</sub>/G2.

graphene and WS<sub>2</sub>/G1 and WS<sub>2</sub>/G2 toward 50 ppb of NO<sub>2</sub> at different operating temperatures, ranging from RT (25 °C) to 150 °C. As illustrated, the sensor response increases from room temperature, peaks at 100 °C, and then decreases at higher temperatures. Thus, 100 °C was established as the optimal operating temperature for all subsequent studies. Notably, this working temperature is relatively low compared to that of metal oxide-based gas sensors.<sup>6,42,43</sup> It is worth mentioning that the pristine WS<sub>2</sub> sensor did not show any response to NO<sub>2</sub> at concentrations lower than 100 ppb. Therefore, it is not discussed.

In this study, the WS<sub>2</sub>/G hybrid sensor demonstrated a significant enhancement in sensitivity, with the detection range decreasing from 100 to 10 ppb. This improvement can be attributed to the addition of graphene, which not only lowered the optimal operating temperature of the sensor but also facilitated enhanced electron mobility between the WS<sub>2</sub>/graphene interface and the adsorbed analyte species.<sup>44</sup> Graphene offers high carrier mobility, a large specific surface area, and strong chemical stability.<sup>44,45</sup> The addition of graphene lowers the baseline resistance of the WS<sub>2</sub>. These properties are advantageous for the WS<sub>2</sub>/G hybrid sensor, as they increase the contact area, promote efficient charge transfer across the hybrid



**Figure 6.** Dynamic resistance changes of (a) graphene, (b) WS<sub>2</sub>/G1, and (c) WS<sub>2</sub>/G2 toward 50 ppb of NO<sub>2</sub> at 100 °C.

interface, and reduce charge transport time. The  $sp^2$  carbon orbitals of graphene enable quick and efficient charge transfer,<sup>35,46</sup> offering substantial benefits for  $WS_2/G$  hybrid-based sensors by increasing the contact area and supporting effective charge transfer across the hybrid interfaces.

Figure 6 depicts the dynamic resistance changes of the pristine graphene,  $WS_2/G1$ , and  $WS_2/G2$  sensors when exposed to 50 ppb of  $NO_2$  while being operated at 100 °C. Upon being exposed to  $NO_2$ , an oxidizing gas species, the sensors respond as p-type semiconductors, showing a decrease in the resistance. This is in accordance with earlier research.<sup>3,35</sup> The decrease in resistance upon  $NO_2$  exposure can be attributed to the spontaneous adsorption of  $NO_2$  gas molecules on the sensing material surface. In this process, electrons are withdrawn via the valence band, leading to an increase in hole concentration and resulting in an overall decrease in the electrical resistance of the sensing film.<sup>35,47,48</sup> Moreover, when the target gas is removed during the recovery cycle, the sensors return completely to the original baseline resistance in a dry air environment.<sup>42,43</sup> The significant resistance change observed in  $WS_2/G1$  can be attributed to the optimized 3:1 ratio of  $WS_2$  to graphene, which enhances  $NO_2$  adsorption and charge transfer efficiency. In contrast, pristine graphene exhibits a smaller resistance change due to the lack of active sites for  $NO_2$  interaction, while  $WS_2/G2$  (1:1 ratio) shows insignificant performance due to reduced active site density and less efficient charge transfer dynamics. The edge-enriched  $WS_2$  nanosheets in  $WS_2/G1$  further contribute to its superior sensing performance by providing abundant adsorption sites and facilitating strong interactions with  $NO_2$  molecules. Additionally, we noticed a slight drift in the baseline resistance of pure graphene, suggesting the synergistic effect of  $WS_2$  and graphene on the gas sensing properties and stability toward  $NO_2$ .

Pure graphene and  $WS_2/G2$  exhibited responses of  $1.28 \pm 0.01\%$  and  $2.24 \pm 0.03\%$ , respectively, while  $WS_2/G1$  displayed the highest response of  $14.32 \pm 0.04\%$ , which is 11-times higher than the one of pristine graphene.

Moreover, the sensors were tested toward a wide range of  $NO_2$  gas concentrations ranging from 10, 20, 30, 40, and 50 ppb at the optimal working temperature. Figure 7 shows the

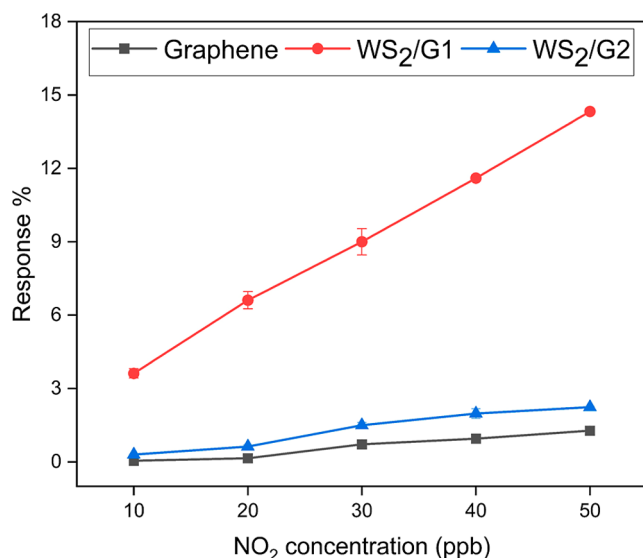


Figure 7. Sensor responses as a function of  $NO_2$  concentration at 100 °C.

responses of the sensors as a function of the  $NO_2$  concentrations. As it is evident from the figure, there is a linear increase in the response with the increase in the  $NO_2$  concentration. As expected, the resistance changes recorded increase when the  $NO_2$  concentration is also increased. The dynamics of the gas sensor film changes toward different  $NO_2$  concentrations are presented in Figure S7.  $WS_2/G1$  can efficiently detect as low as 10 ppb of  $NO_2$ . These detected concentrations are much lower than the permissible  $NO_2$  concentrations.<sup>49</sup> Indeed, The American Conference of Governmental Industrial Hygienists (ACGIH) has established occupational guidelines for  $NO_2$ , suggesting a time-weighted average (TWA) of 3 ppm and short-term exposure limits (STEL) of 5 ppm. Meanwhile, the National Institute for Occupational Safety and Health (NIOSH) recommends a short-term exposure limit of 1 ppm over 15 min<sup>49,50</sup> Moreover, it can be seen from Figure S7a and c that there is no response from Pristine graphene and  $WS_2/G_2$  sensors toward 10 ppb of  $NO_2$ . The relatively poor performance of the  $WS_2/G2$  sensor is primarily due to the  $WS_2$  to graphene ratio, which affects the charge transfer dynamics, the density of active sites, and the overall morphology of the hybrid material. We compared our sensor responses against the top-performing sensors reported in the literature, focusing on those utilizing TMDs and/or TMD-graphene composites. Remarkably, our sensors demonstrated superior performance across all evaluated parameters. Table S1 in the Supporting Information provides a detailed comparison, showcasing the exceptional  $NO_2$  sensing characteristics of our sensors relative to other highly responsive TMD and TMD-graphene composite-based sensors.

Nevertheless, as the  $NO_2$  concentration increases beyond 100 ppb, pristine  $WS_2$  sensors start to exhibit an elevated response, surpassing that of all other sensors. These results are summarized in Figure 8, with an inset showing sensor responses

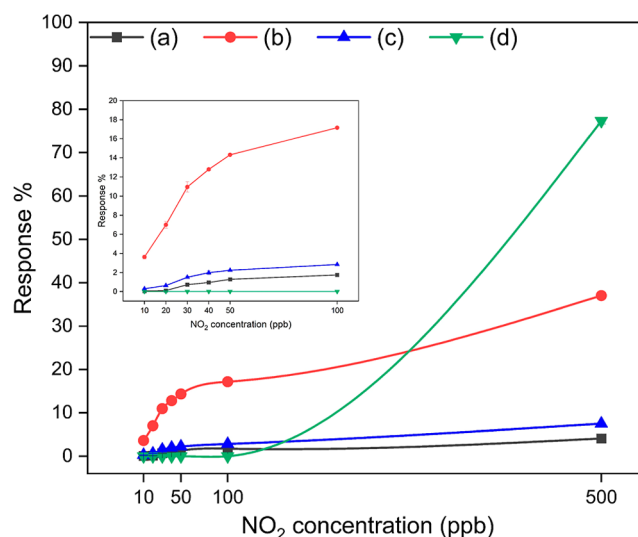


Figure 8. Sensor responses as a function of  $NO_2$  concentration at 100 °C, (a) graphene, (b)  $WS_2/G1$ , (c)  $WS_2/G2$  and (d)  $WS_2$ .

across a range from 10 to 100 ppb  $NO_2$ . The sensing characteristics of pristine  $WS_2$  emphasize its strong sensitivity to higher  $NO_2$  concentrations (above 100 ppb). However, while pristine  $WS_2$  shows a remarkable response at elevated concentrations, its sensitivity decreases at sub-100 ppb levels. In contrast,  $WS_2/G1$  sensors address this limitation by detecting  $NO_2$  at concentrations below 50 ppb, effectively minimizing

cross-sensitivity issues. This improved limit of detection (LoD) in WS<sub>2</sub>/G1 sensors improves the NO<sub>2</sub> LoD.

Selectivity is one of the important criteria for determining sensor performance. The selectivity of the sensors was evaluated toward fixed concentrations of various interfering species, viz. Carbon monoxide (CO), benzene (C<sub>6</sub>H<sub>6</sub>), ammonia (NH<sub>3</sub>), and hydrogen (H<sub>2</sub>) at the optimum working temperature of 100 °C. The fixed concentrations of the different gases were selected, keeping in view the permissible exposure limits of the respective analytes. Figure S8 shows the responses of the sensors toward the tested gases at 100. The results show that WS<sub>2</sub>/G1 responds to an extremely low concentration of NO<sub>2</sub> (50 ppb) with the highest response of approximately 14%. The results suggest a high selectivity of the WS<sub>2</sub>/G1 toward a meager NO<sub>2</sub> concentration of 50 ppb. All the gas concentrations tested are way below the permissible limits.<sup>50</sup> The combination of porous graphene and edge-enriched WS<sub>2</sub> particularly enhances sensitivity toward NO<sub>2</sub>.<sup>4</sup>

The gas sensing properties of WS<sub>2</sub>/G are significantly enhanced by the presence of defects in graphene. The defects in graphene are well demonstrated in Raman spectra (Figures 3 and S6). The graphene layer plays a crucial role in improving charge transfer between WS<sub>2</sub> and the target gas.<sup>25</sup> Furthermore, the presence of graphene (a layer in which charge carriers can move efficiently) enhances the collection of the generated charge carriers by the sensor device electrodes. Specifically, in the case of NO<sub>2</sub>, the oxygen functional groups on WS<sub>2</sub> facilitate the adsorption of nitrogen dioxide molecules,<sup>51</sup> leading to the creation of more holes in the material and a subsequent decrease in sensor resistance. Pristine monolayer graphene, characterized by high electron mobility ( $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and a large specific surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ),<sup>52,53</sup> exhibits distinct gas sensing properties.

The sensing characteristics of pristine WS<sub>2</sub> highlight its strong response to higher concentrations of NO<sub>2</sub> (above 100 ppb), where it demonstrates high sensitivity. When exposed to 5 ppm of NH<sub>3</sub> at 100 °C, pristine WS<sub>2</sub> sensors also show a significant response. Interestingly, even though the ammonia concentration is 100 times greater than that of NO<sub>2</sub>, WS<sub>2</sub> sensors retain a preferential and selective sensitivity toward NO<sub>2</sub>. This underscores the inherent specificity of WS<sub>2</sub> toward NO<sub>2</sub>, even when exposed to a lower NO<sub>2</sub> concentration compared to NH<sub>3</sub>. However, while pristine WS<sub>2</sub> shows a remarkable response for NO<sub>2</sub> at high concentrations, its responsiveness diminishes at sub-100 ppb levels. In contrast, the WS<sub>2</sub>/G1 sensors address this limitation by detecting NO<sub>2</sub> concentrations below 50 ppb and thus effectively minimizing cross-sensitivity issues. This enhanced sensitivity observed in WS<sub>2</sub>/G1 sensors improves the LoD for NO<sub>2</sub>.

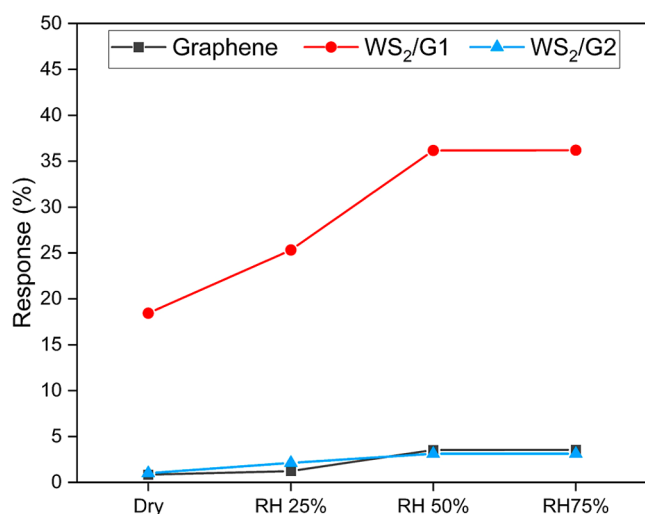
**Sensing Mechanism.** The sensing mechanism of graphene, WS<sub>2</sub>, and WS<sub>2</sub>/G is driven by charge transfer interactions between the sensing materials and the target gases.<sup>54,55</sup> NO<sub>2</sub> being an oxidizing gas, acts as an electron acceptor. When graphene is exposed to NO<sub>2</sub>, the NO<sub>2</sub> molecules adsorb onto its surface and withdraw electrons. As a result, the hole concentration in p-type graphene rises, leading to a reduction in its resistance. In the case of pure WS<sub>2</sub>, the multilayer structure provides abundant active sites accessible to the surroundings, facilitating efficient gas adsorption on exposed surfaces. Our earlier study demonstrated that the dominant interaction between gas molecules and WS<sub>2</sub> occurs through physisorption, accompanied by a moderate degree of electronic charge transfer.<sup>30</sup> Compared to pure WS<sub>2</sub>, the hybrid structure has an

even greater number of exposed active sites, leading to enhanced gas adsorption on the surface. This increased availability of active sites in the hybrid structure results in a higher response.

The layered architecture of WS<sub>2</sub>/G enhances NO<sub>2</sub> adsorption and facilitates its diffusion through the interlayer spaces of the WS<sub>2</sub> nanosheets. Additionally, the ample WS<sub>2</sub> edge sites contribute significantly to NO<sub>2</sub> uptake and accelerate the reaction kinetics.<sup>56</sup> The porous architecture of WS<sub>2</sub>/G provides a greater number of active sites on the graphene surface for NO<sub>2</sub> interactions. Moreover, the electron-deficient nature of WS<sub>2</sub> is effectively balanced by electron donation from graphene, facilitating charge transfer between the two components in the hybrid. This interaction induces notable change in the resistance in the WS<sub>2</sub>/G composite, thereby enhancing its sensing performance as compared to individual WS<sub>2</sub> or graphene. Also, the work function of pristine graphene is 4.2 eV,<sup>57,58</sup> and that of WS<sub>2</sub> is 4.5 eV.<sup>59</sup> Due to the difference in work function between graphene and WS<sub>2</sub>, electrons in graphene are preferentially transferred to the WS<sub>2</sub> nanosheets, leaving holes in graphene, thus, higher resistance changes and higher gas sensing responses.<sup>60</sup> As shown in Figure 6, the gas sensing response curves reveal that both graphene and WS<sub>2</sub>/G exhibit p-type semiconductor behavior, characterized by a reduction in resistance upon exposure to NO<sub>2</sub>. This resistance drop is attributed to electron withdrawal by NO<sub>2</sub> molecules. When the sensor is re-exposed to air, NO<sub>2</sub> molecules desorb from the surface, returning electrons to the sensing material and restoring its resistance to the initial baseline. The outstanding sensitivity and the ultralow detection limit observed can be attributed to the material's porous surface structure and the abundance of sulfur edge sites in WS<sub>2</sub>, which result from the random three-dimensional stacking of WS<sub>2</sub> nanosheets.<sup>35</sup> Density functional theory (DFT) calculations demonstrate that edges on WS<sub>2</sub> enhance gas sensing performance.<sup>30</sup> Additionally, DFT calculations show that adsorption is weakest at the basal planes of WS<sub>2</sub> and highest at the edges. This stronger adsorption can induce a larger charge transfer compared to adsorption on the basal planes, thereby leading to remarkable sensitivity of WS<sub>2</sub>/G. The proposed gas sensing mechanism is based on the adsorption/desorption of the gas molecules at the active sites of WS<sub>2</sub>/G and is illustrated by the schematic sketch in Figure S9.

The capability of the WS<sub>2</sub>/G material to detect ultralow concentrations of NO<sub>2</sub> can thus be mainly attributed to the following three factors. (i) Both the materials used in the hybrid are of high specific surface area ultimately leading to an increase in the average specific surface area. This, in turn, leads to a significant increase in the adsorption sites available, which increases the adsorption rate and, hence, gas response.<sup>61</sup> (ii) The hybrid formed consists of two materials with different Fermi levels. The formation of p-p heterojunction leads to an increase in the charge carrier mobility. (iii) The presence of defects, especially sulfur (S) vacancies in WS<sub>2</sub>, leads to enhanced response toward NO<sub>2</sub>.<sup>41,62,63</sup> These factors also help the sensing material to sense the ultralow concentrations of NO<sub>2</sub> in humid conditions.

**Humidity Studies.** To verify the practicability of the sensors, the impact of relative humidity on the sensor responses toward NO<sub>2</sub> was investigated. The sensors were tested toward 50 ppb of NO<sub>2</sub> at 100 °C in 25%, 50%, and 75% humidified air background. The results are summarized in Figure 9. The results indicate a clear trend in the sensing response corresponding to the varying humidity levels. At 25% RH, there was a noticeable increase in the sensing responses. When the relative humidity



**Figure 9.** Dry and relative humidity cross-sensitivity to 50 ppb NO<sub>2</sub> at 100 °C.

was increased to 50%, the sensing response of WS<sub>2</sub>/G1 was significantly enhanced, showing almost a 2-fold increase compared to the response at dry conditions, Figure S10. Interestingly, when the relative humidity was further elevated to 75%, the responses of the sensors were comparable to the responses observed at 50% RH. Figure S11a–c shows the dynamic resistance change of the sensors in a 50% humid and dry environment. It is observed that the sensor baselines increased under a humid environment. These results are in agreement with previously published results.<sup>64,65</sup> The increase in the baseline resistance under a humid environment could be explained on the basis of charge transfer between water molecules and the sensitive film. The adsorbed water molecules are known to behave like electron donors.<sup>66,67</sup> WS<sub>2</sub>/G behaves as a p-type semiconducting material, and the increase in ambient humidity results in electronic charge (i.e., minority charge carriers) injected into the film, followed by recombination, which results in the reduction of hole density, leading to an increase in baseline resistance. In general, when testing sensors in a humid environment, there is competition between the target gas molecules and water vapor (hydroxyl groups) at the active sites. If the relative surface distribution of the hydroxyl group surpasses that of oxygen species, the sensor performance declines and the impact of humidity becomes more pronounced. Conversely, a sensor with strong resistance to moisture shows consistent performance, as adsorbed oxygen species occupy the majority of active sites. The influence of humidity on the sensor response highlights the need for humidity compensation to ensure reliable operation in real-world applications. Humidity affects the work function of the sensor by introducing water molecules that compete with NO<sub>2</sub> for adsorption sites and alter the baseline resistance. To address this, we propose several strategies for humidity compensation, including baseline correction, humidity-dependent calibration, and the integration of humidity sensors for real-time compensation.

Moreover, Figure S11d–f shows insets of the 10 ppb responses of the respective sensors, which are not observable under dry conditions. The increased responses in humid conditions and the stability of the response in a wide range of environmental humidity levels suggest that the WS<sub>2</sub>/G sensors are excellent candidates for real-life applications.

## CONCLUSION

This study highlights the potential of two-dimensional (2D) transition metal dichalcogenides (TMDs) for advanced low-temperature NO<sub>2</sub> gas sensing applications. APCVD was used as a high-yield synthesis method to synthesize edge-enriched WS<sub>2</sub>. As synthesized, WS<sub>2</sub> was mixed with commercial graphene to form a WS<sub>2</sub>/G hybrid to be used as a gas sensing material—a facile airbrushing technique with N<sub>2</sub> as the carrier gas was used to fabricate the sensors. The WS<sub>2</sub>/G sensors demonstrate exceptional sensitivity to ultralow concentrations of NO<sub>2</sub> (10 ppb) at a notably low operating temperature of 100 °C, significantly outperforming their pristine WS<sub>2</sub> and graphene counterparts. Cross-sensitivity tests confirmed the negligible influence of interfering gases, including CO, H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, and NH<sub>3</sub>, at the optimal working temperature of 100 °C, further emphasizing the sensor's excellent selectivity. Additionally, the sensor response was evaluated at 25%, 50%, and 75% RH, with results showing that the response nearly doubled at 50% RH, highlighting its strong potential for practical applications in selective NO<sub>2</sub> detection. The response reached saturation at 75% RH. This comprehensive approach lays the foundation for the development of highly efficient, selective, and scalable gas sensors capable of operating under real-world applications. The combination of TMDs and graphene, coupled with facile fabrication techniques, paves the way for next-generation gas sensing technologies, offering solutions to pressing environmental and industrial monitoring challenges.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.5c03302>.

Schematics of APCVD, FESEM image of graphene, XRD diffractograms; HRTEM images of graphene; Color mapping and EDS of WS<sub>2</sub>/G1.; Raman spectra of pristine graphene and pristine WS<sub>2</sub>; resistance dynamics toward different NO<sub>2</sub> concentrations; selectivity graph, proposed sketch of sensing mechanism, humidity data, comparison table with literature (PDF)

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## Notes

The authors declare no competing financial interest.

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