

# Supercritical CO<sub>2</sub>-assisted Heterointerface Engineering of 2D WS<sub>2</sub>/rGO Heterostructures for Enhanced Room-temperature NH<sub>3</sub> Sensing

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The rapid and sensitive detection of trace ammonia (NH<sub>3</sub>) at room temperature is crucial for environmental monitoring, occupational safety, and noninvasive disease diagnosis. However, pristine two-dimensional tungsten disulfide (WS<sub>2</sub>) suffers from oxidative instability in air and sluggish room-temperature gas adsorption/desorption kinetics, limiting its sensing performance. Herein, a supercritical CO<sub>2</sub> (SC CO<sub>2</sub>)-assisted heterointerface engineering strategy was developed to construct interface-purified WS<sub>2</sub>/reduced graphene oxide (rGO) heterostructures via a reductant-assisted one-step process. The results show that SC CO<sub>2</sub> treatment at 180 °C, combined with the reductant, simultaneously promotes WS<sub>2</sub> exfoliation, in situ reduction of GO, and interfacial purification, leading to an “ultrathin nanosheet–clean interface–strong electronic coupling” structure. TEM results confirm that WS<sub>2</sub> nanosheets are uniformly anchored on rGO, while X-ray photoelectron spectroscopy (XPS) reveals markedly reduced W<sup>6+</sup> and sulfate species. Benefiting from the purified heterointerface and enhanced interfacial charge transfer, the SC-WS<sub>2</sub>/rGO sensor exhibits fast response/recovery times of 11.4/11.7 s toward 6 ppm NH<sub>3</sub> at room temperature, stable and reversible responses over the range of 6–900 ppm, a low theoretical detection limit of 13.11 ppb, negligible degradation after 30 days, and a selectivity up to 25 times higher than that toward interfering gases. Mechanistic analysis indicates that the clean heterointerface lowers the carrier transport barrier and exposes active sites, while electron delocalization provides efficient charge transport pathways. An effective interface engineering strategy for high-performance room-temperature NH<sub>3</sub> sensors based on two-dimensional transition metal sulfides is demonstrated in this work.

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## 1. Introduction

Ammonia ( $\text{NH}_3$ ) is a typical toxic and hazardous gas that is widely involved in agricultural production, fertilizer manufacturing, refrigeration systems, chemical industries, and environmental monitoring. Excessive exposure to  $\text{NH}_3$  can cause irritation of the respiratory tract, eyes, and skin, and may even lead to acute pulmonary injury under severe conditions.<sup>(1)</sup> Therefore, the rapid and sensitive detection of low-concentration  $\text{NH}_3$  is of great significance for occupational safety, environmental protection, and health monitoring.<sup>(2)</sup> Occupational exposure standards specify an 8 h time-weighted average exposure limit of 25 ppm and a 15 min short-term exposure limit of 35 ppm for  $\text{NH}_3$ , while 300 ppm is regarded as a concentration immediately dangerous to life and health. Notably, recent studies have revealed that exposure to  $\text{NH}_3$  concentrations even below the recommended threshold limit value may induce acute pulmonary effects and reduce lung function parameters. In addition, breath ammonia has attracted increasing attention as an important biomarker for noninvasive disease diagnosis.<sup>(3)</sup>  $\text{NH}_3$  concentrations in exhaled breath within the range of 2500–5000 ppb have been closely associated with chronic kidney disease, liver dysfunction, diabetes, and other metabolic disorders.<sup>(4)</sup> Accordingly, the development of room-temperature  $\text{NH}_3$  sensors with rapid response, high sensitivity, low detection limits, and long-term operational stability is urgently required.

2D transition-metal dichalcogenides have emerged as promising sensing materials owing to their large specific surface area, abundant surface-active sites, and tunable electronic structures.<sup>(5)</sup> Among them,  $\text{WS}_2$  has received considerable attention because of its typical S–W–S layered structure, in which strong covalent bonding exists within each layer while adjacent layers are connected by weak van der Waals interactions.<sup>(6)</sup> Such a structural feature facilitates the diffusion and adsorption of target gas molecules between layers and provides opportunities for interface modulation and defect engineering. Moreover,  $\text{WS}_2$  exhibits a tunable band gap, good thermal stability, and unique spin-orbit coupling characteristics. Its valence-band splitting is approximately three times larger than that of  $\text{MoS}_2$ , indicating distinctive electronic and charge-transport properties.<sup>(7)</sup> Despite these advantages, pristine  $\text{WS}_2$  still suffers from several limitations for room-temperature  $\text{NH}_3$  sensing. On the one hand, few-layer  $\text{WS}_2$  nanosheets are prone to oxygen adsorption and oxidation in air, particularly in the presence of sulfur vacancies, which can promote the formation of tungsten oxide species and alter the electronic structure and surface-active sites.<sup>(8)</sup> On the other hand, pristine  $\text{WS}_2$  usually exhibits sluggish adsorption/desorption kinetics toward  $\text{NH}_3$  at room temperature, resulting in limited response intensity and unsatisfactory recovery behavior.<sup>(9)</sup> Therefore, improving the room-temperature  $\text{NH}_3$  sensing performance and environmental stability of  $\text{WS}_2$  remains a critical challenge.

Constructing heterostructures is an effective strategy for enhancing the gas-sensing properties of  $\text{WS}_2$ . By coupling  $\text{WS}_2$  with conductive carbon materials, metal oxides, or other 2D materials, interfacial charge-transfer pathways can be established, carrier concentration and band alignment can be modulated, and additional gas adsorption sites can be introduced, thereby

improving the response, selectivity, and stability of the sensor.<sup>(10)</sup> Reduced graphene oxide (rGO), with its high specific surface area, excellent electrical conductivity, and interconnected flexible network, is particularly attractive for constructing WS<sub>2</sub>-based sensing composites. The incorporation of rGO can facilitate electron transport, suppress the aggregation of WS<sub>2</sub> nanosheets, and provide more efficient gas diffusion channels. However, conventional liquid-phase assembly and post-treatment methods often suffer from insufficient interfacial contact, residual impurities, and inefficient charge transfer across the heterointerface, which restrict further improvement in the sensing performance of WS<sub>2</sub>/rGO composites.

Supercritical CO<sub>2</sub> (SC CO<sub>2</sub>) technology has recently shown unique advantages in the exfoliation, intercalation, surface modification, and heterostructure construction of 2D materials because of its low viscosity, high diffusivity, near-zero surface tension, and excellent mass-transfer capability.<sup>(11–13)</sup> SC CO<sub>2</sub> can effectively penetrate the interlayer space of layered materials, promote nanosheet exfoliation and interfacial reconstruction, and reduce solvent residues and interfacial contamination, thus providing a promising route for constructing high-quality two-dimensional heterostructures.<sup>(14–16)</sup> In this work, a supercritical CO<sub>2</sub>-assisted heterointerface engineering strategy is proposed to fabricate WS<sub>2</sub>/rGO heterostructures through a reductant-assisted one-step process. This strategy enables interfacial purification and electronic structure optimization of the WS<sub>2</sub>/rGO composite, which helps suppress the oxidative instability of WS<sub>2</sub> in air and enhances interfacial coupling and charge transport between WS<sub>2</sub> and rGO. The resulting SC-WS<sub>2</sub>/rGO composite exhibits excellent room-temperature NH<sub>3</sub> sensing performance, including rapid response/recovery times of 11.4/11.7 s toward 6 ppm NH<sub>3</sub>, superior selectivity, and long-term stability. The findings of study provide a feasible strategy for designing high-performance room-temperature NH<sub>3</sub> sensing materials and highlights the potential of supercritical CO<sub>2</sub> technology for interface regulation in 2D heterostructures.

## 2. Materials and Methods

### 2.1 Preparation of 2D SC-WS<sub>2</sub>/rGO

Graphene oxide (GO) dispersion with a concentration of 10.0 mg/mL was first prepared using a modified Hummers' method.<sup>(17)</sup> Subsequently, 20 mg of WS<sub>2</sub> was dispersed in 20 mL of an ethanol/water mixed solution containing 45 vol% ethanol, with GO used as the dispersant. The mass ratio of WS<sub>2</sub> to GO was maintained at 2:1. The mixture was ultrasonicated for 30 min to obtain a uniform dispersion. Then, 10 µL of hydrazine hydrate was added as the reducing agent. After vigorous stirring, the obtained suspension was transferred into a stainless-steel high-pressure autoclave equipped with a supercritical CO<sub>2</sub> reactor. The reactor was heated to 180 °C and pressurized to 20 MPa with CO<sub>2</sub>. The reaction was maintained for 3 h under magnetic stirring to promote effective coupling between WS<sub>2</sub> and rGO. After the reaction, heating was stopped, and the autoclave was naturally cooled to room temperature. The resulting suspension was collected and dried in a forced-air oven at 60 °C for 24 h. The obtained powder was denoted as the 2D WS<sub>2</sub>/reduced graphene oxide heterostructure, namely, SC-WS<sub>2</sub>/rGO.

## 2.2 Preparation of control samples

To systematically investigate the effects of reaction temperature, GO incorporation, and WS<sub>2</sub> pre-exfoliation on the structure and gas-sensing performance of the composites, three control samples were prepared by varying the key processing parameters while maintaining the same basic synthetic procedure.

### 2.2.1 Preparation of SC-WS<sub>2</sub>/rGO-80

The SC-WS<sub>2</sub>/rGO-80 sample was prepared following the same procedure as that used for SC-WS<sub>2</sub>/rGO, except that the SC treatment temperature was adjusted to 80 °C. Briefly, WS<sub>2</sub> and GO were dispersed in an ethanol/water mixed solution containing 45 vol% ethanol at a WS<sub>2</sub> mass ratio of 2:1. After ultrasonication and the addition of the reducing agent, the suspension was transferred into an SC CO<sub>2</sub> reactor and treated at 80 °C under 20 MPa CO<sub>2</sub> for 3 h. After the reaction, the autoclave was naturally cooled to room temperature, and the product was dried at 60 °C for 24 h. The obtained sample was denoted as SC-WS<sub>2</sub>/rGO-80. This sample was used to evaluate the influence of a relatively low reaction temperature on WS<sub>2</sub> exfoliation and the interfacial structure of the composite.

### 2.2.2 Preparation of SC-WS<sub>2</sub>

To clarify the role of GO in the composite, a control sample was prepared without adding GO. Typically, 20 mg of WS<sub>2</sub> powder was directly dispersed in 20 mL of an ethanol/water mixed solution containing 45 vol% ethanol, followed by ultrasonication for 30 min to obtain a homogeneous dispersion. The resulting suspension was transferred into the SC CO<sub>2</sub> reactor and treated under the same conditions as those used for SC-WS<sub>2</sub>/rGO, namely, 180 °C and 20 MPa CO<sub>2</sub> for 3 h, but without adding the reducing agent. After the reaction, the autoclave was naturally cooled to room temperature, and the product was dried at 60 °C for 24 h. The obtained pure WS<sub>2</sub> control sample was denoted as SC-WS<sub>2</sub>. This sample was used to compare the effect of GO incorporation on the structural evolution and sensing performance of WS<sub>2</sub>.

### 2.2.3 Preparation of SC-WS<sub>2</sub>/rGO-L

To investigate the influence of liquid-phase pre-exfoliation on the microstructure of WS<sub>2</sub> and its subsequent hybridization with rGO, bulk WS<sub>2</sub> was first pre-exfoliated. Specifically, 50 mg of bulk WS<sub>2</sub> powder was placed in a 100 mL round-bottom flask, followed by the addition of 10 mL of an ethanol/water mixed solution containing 45 vol% ethanol as the dispersion medium. The flask was sealed and immersed in an ice-water bath, and the suspension was ultrasonicated for 6 h to achieve preliminary liquid-phase exfoliation of WS<sub>2</sub>. The resulting dispersion was then centrifuged at 5000 rpm for 30 min to remove unexfoliated bulk aggregates. The supernatant was collected and dried at 60 °C for 24 h to obtain pre-exfoliated WS<sub>2</sub> powder.

The pre-exfoliated WS<sub>2</sub> powder was then used for subsequent composite preparation in accordance with the synthesis procedure of SC-WS<sub>2</sub>/rGO. Briefly, the pre-exfoliated WS<sub>2</sub> was dispersed in 20 mL of an ethanol/water mixed solution containing 45 vol% ethanol, and GO dispersion was added at a WS<sub>2</sub> mass ratio of 2:1. After ultrasonication for 30 min, 10 µL of hydrazine hydrate was introduced as the reducing agent. The mixture was vigorously stirred and then transferred into the supercritical CO<sub>2</sub> reactor, where it was treated at 180 °C under 20 MPa CO<sub>2</sub> for 3 h. After natural cooling to room temperature, the product was dried at 60 °C for 24 h. The obtained sample was denoted as SC-WS<sub>2</sub>/rGO-L, where “L” represents the liquid-phase pre-exfoliation treatment. This sample was used to assess the effects of pre-exfoliation on the thinning degree of WS<sub>2</sub>, interfacial impurity content, and final gas-sensing performance.

### 2.3 Material characterization

The crystal structures of the samples were characterized using X-ray diffraction (XRD, Malvern Panalytical Empyrean). The crystal phase, lattice parameters, and crystallinity of the samples were analyzed from the corresponding diffraction patterns to identify their phase compositions. The microstructure and morphology of the samples were observed by TEM (FEI Talos F200x G2). High-resolution TEM (HRTEM) imaging was further employed to reveal the lattice fringes and interfacial structures of the materials. Raman spectra were recorded using a LabRAM Soleil Nano spectrometer with a 532 nm Ar-ion laser as the excitation source to investigate the molecular vibration modes, chemical structures, and bonding characteristics. Fourier transform infrared spectroscopy (FTIR, Bruker INVENIO) was performed to analyze intermolecular interactions and functional groups, providing further insight into the chemical properties of the samples. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific K-Alpha spectrometer, and all binding energies were calibrated using the C 1s peak at 284.8 eV as the reference. XPS was used to determine the surface elemental compositions and chemical states of the samples.

### 2.4 Sensor fabrication and performance testing

The as-prepared samples were mixed with anhydrous ethanol in an agate mortar to form a homogeneous paste. The paste was then uniformly coated onto a ceramic substrate equipped with Au–Pd interdigitated electrodes with a size of 7 × 13.4 mm<sup>2</sup> to form a uniform gas-sensing layer. Subsequently, the fabricated gas sensors coated with the samples were annealed in ambient air at 200 °C for 2 h to improve their thermal stability and repeatability. Unless otherwise specified, all gas-sensing measurements were conducted at 23 °C and 23% relative humidity, which was adjusted using an air humidifier and monitored with a hygrometer. The real-time resistance of the sensor was recorded using a Keithley 6500 digital multimeter. The sensor response (*S*) was defined as follows.

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

Here, ( $R_g$ ) and ( $R_a$ ) represent the resistance values of the gas sensor upon exposure to the target gas and air, respectively. In addition, the response time ( $T_{res}$ ) and recovery time ( $T_{rec}$ ) were used to evaluate the gas adsorption and desorption rates of the sensor, respectively. The response time was defined as the time required for a stabilized sensor to reach 90% of the total resistance change after exposure to the target gas. The recovery time was defined as the time required for the resistance to recover by 90% of the total resistance variation during the recovery process.

### 3. Results and Discussion

#### 3.1 Structural analysis

Figure 1 shows the TEM images, high-resolution lattice fringes, and SAED patterns of pristine  $WS_2$  and  $WS_2/rGO$  composites prepared under different conditions. As shown in Fig.

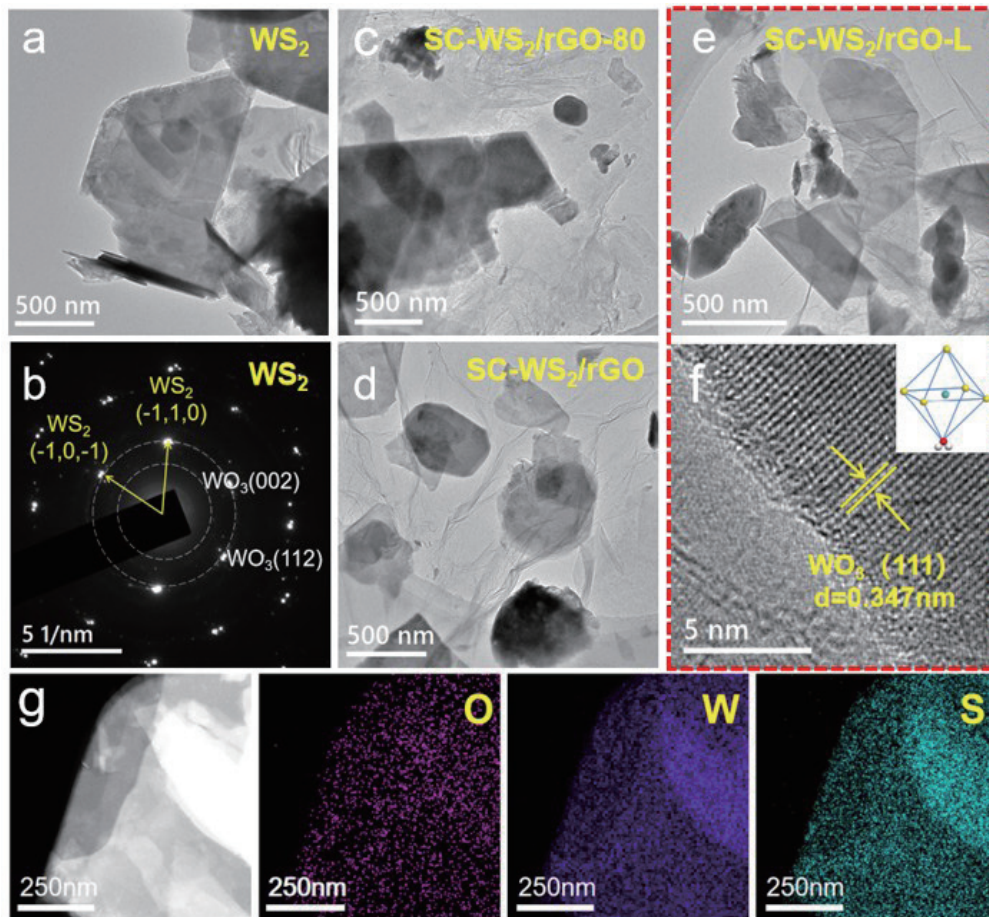


Fig. 1. (Color online) (a) Low-magnification TEM image of pristine  $WS_2$ . (b) SAED pattern of pristine  $WS_2$ . (c) Low-magnification TEM image of SC- $WS_2/rGO$ -80. (d) Low-magnification TEM image of SC- $WS_2/rGO$ . (e) Low-magnification TEM image of SC- $WS_2/rGO$ -L. (f) HRTEM image of SC- $WS_2/rGO$ -L. (g) EDS elemental mapping images of pristine  $WS_2$ .

1(a), pristine WS<sub>2</sub> displays a typical multilayer-stacked morphology with relatively thick nanosheets and well-defined edges. The sharp diffraction spots in the SAED pattern [Fig. 1(b)] indicate high crystallinity. In addition to the characteristic diffraction spots of hexagonal WS<sub>2</sub>, extra diffraction features corresponding to the (112) and (002) planes of monoclinic WO<sub>3</sub> are observed, as marked by the white dashed circles.<sup>(18)</sup> This suggests that tungsten oxide impurities are already present in the pristine WS<sub>2</sub> raw material. The pronounced O signal detected in the energy-dispersive X-ray spectroscopy (EDS) spectrum [Fig. 1(g)] further confirms this result. Figure 1(c) presents the TEM image of the SC-WS<sub>2</sub>/rGO-80 sample. After SC CO<sub>2</sub> treatment at 80 °C, the WS<sub>2</sub> sheets remain relatively large, and their hybridization with rGO is nonuniform. The poor dispersion and loose interfacial contact indicate that the relatively low treatment temperature is insufficient to promote effective WS<sub>2</sub> exfoliation and the formation of a well-developed WS<sub>2</sub>/rGO heterointerface.

By contrast, the SC-WS<sub>2</sub>/rGO sample treated at 180 °C under 20 MPa CO<sub>2</sub> exhibits a much thinner nanosheet morphology [Fig. 1(d)]. The WS<sub>2</sub> nanosheets are uniformly dispersed and intimately coupled with rGO sheets, forming a compact “ultrathin nanosheet-conductive network” heterostructure. Such a structure is expected to provide abundant accessible surface sites and continuous charge transport pathways, which are favorable for room-temperature gas sensing. Figures 1(e) and 1(f) show the TEM image and high-resolution lattice fringes of the SC-WS<sub>2</sub>/rGO-L sample, respectively. After liquid-phase pre-exfoliation followed by SC CO<sub>2</sub> treatment, the WS<sub>2</sub> sheets are significantly thinned [Fig. 1(e)], demonstrating the effectiveness of the pre-exfoliation process. However, lattice fringes with an interplanar spacing of 0.347 nm are observed in the high-resolution image [Fig. 1(f)], which can be assigned to the (111) plane of WO<sub>3</sub>. This indicates that although the two-step strategy enhances WS<sub>2</sub> exfoliation, it fails to fully suppress oxidation side reactions, leading to residual tungsten oxide species at the heterointerface.

The microstructure, lattice characteristics, and elemental distribution of SC-WS<sub>2</sub>/rGO were systematically investigated by HRTEM, SAED, and EDS elemental mapping. As shown in the HRTEM image in Fig. 2(a), two regions with distinctly different contrasts can be observed. The darker regions are assigned to WS<sub>2</sub> nanosheets, whereas the low-contrast wrinkled regions correspond to rGO sheets. Notably, the WS<sub>2</sub> nanosheets are tightly anchored on the rGO surface, forming an intimate heterointerface between the two components. This closely coupled structure is expected to facilitate efficient interfacial charge transfer during gas-sensing reactions. After fast Fourier transform filtering of the red-circled region in Fig. 2(a), well-resolved lattice fringes of WS<sub>2</sub> can be clearly observed, as shown in Fig. 2(c). The measured interplanar spacing is 0.266 nm, which agrees well with the theoretical value of the (101) plane of hexagonal WS<sub>2</sub> (JCPDS No. 08-0237). This result indicates that the crystalline structure of WS<sub>2</sub> is well preserved during the supercritical treatment, without obvious lattice distortion or structural damage.<sup>(19)</sup> The lattice structure of WS<sub>2</sub> was further verified by SAED analysis. As shown in Fig. 2(b), the diffraction pattern exhibits well-defined diffraction spots, which can be indexed to hexagonal WS<sub>2</sub>. Among them, the (−1, 0, −1) plane is consistent with the (101) lattice plane observed in the HRTEM image. The sharp and clear diffraction spots demonstrate that WS<sub>2</sub> maintains good crystallinity

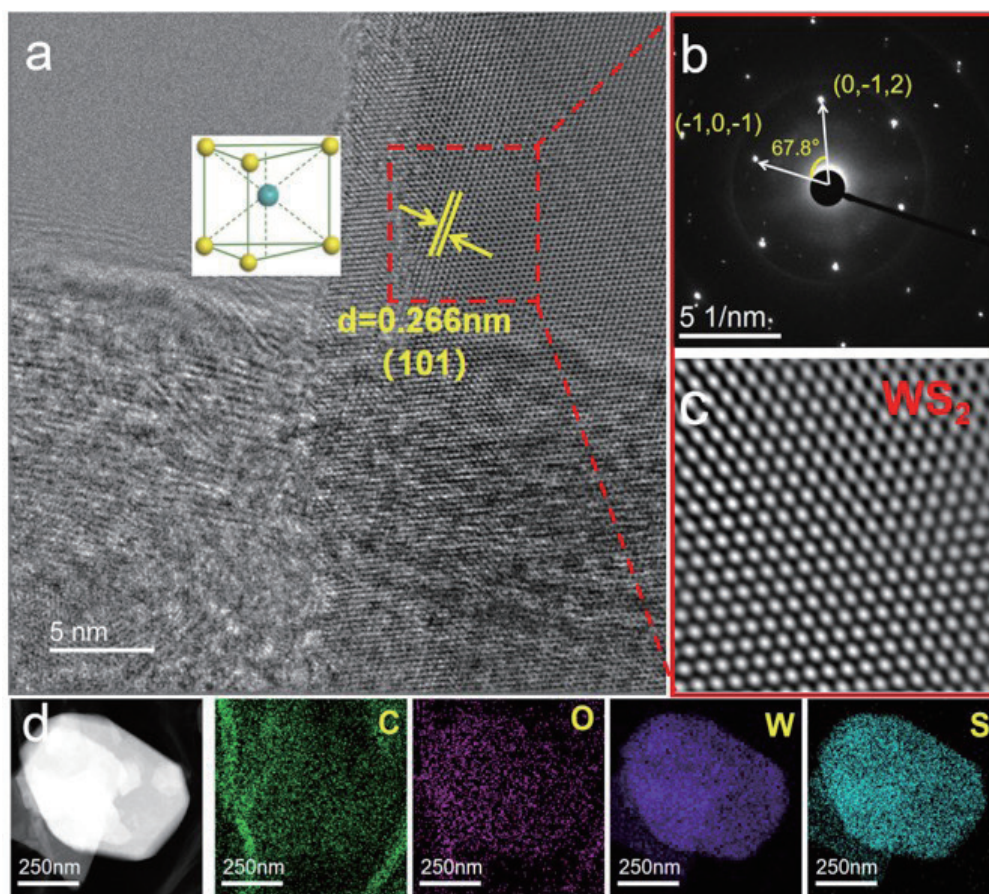


Fig. 2. (Color online) (a) HRTEM image of SC-WS<sub>2</sub>/rGO. (b) Diffraction pattern of SC-WS<sub>2</sub>/rGO. (c) Filtered image of the red region in (a). (d) EDS elemental mapping images of SC-WS<sub>2</sub>/rGO.

after SC treatment, which provides a structural basis for stable electrical behavior during NH<sub>3</sub> sensing. The EDS elemental mapping images of the SC-WS<sub>2</sub>/rGO sample are presented in Fig. 2(d). The spatial distributions of W and S elements are highly overlapped, confirming the presence of WS<sub>2</sub> nanosheets and their homogeneous distribution in the composite. Moreover, the overlapping distributions of W, S, and C elements provide direct evidence that WS<sub>2</sub> nanosheets are successfully anchored onto the rGO sheets, leading to the formation of a compact heterostructure rather than a simple physical mixture.

As shown in Fig. 3(a), the XRD pattern of pristine WS<sub>2</sub> exhibits a series of sharp characteristic diffraction peaks at  $2\theta \approx 14.3, 28.9, 43.9,$  and  $58.4^\circ$ , which can be assigned to the (002), (004), (006), and (110) planes of hexagonal WS<sub>2</sub>, respectively (JCPDS No. 08-0237). These well-defined diffraction peaks confirm the good crystallinity of pristine WS<sub>2</sub> and its typical layered structure. After SC CO<sub>2</sub> treatment assisted by the reductant, the XRD pattern of the SC-WS<sub>2</sub>/rGO composite shows notable changes. The intrinsic diffraction peaks of WS<sub>2</sub> become sharper

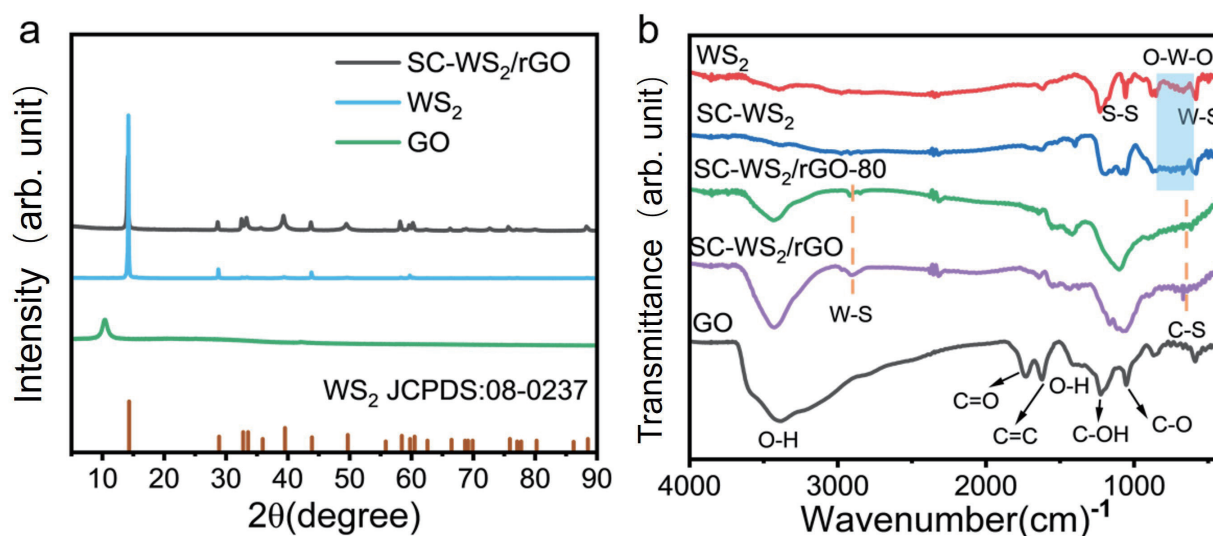


Fig. 3. (Color online) (a) XRD patterns of GO, pristine WS<sub>2</sub> and SC-WS<sub>2</sub>/rGO samples. (b) IR spectra of GO, pristine WS<sub>2</sub>, SC-WS<sub>2</sub>, SC-WS<sub>2</sub>/rGO-80, and SC-WS<sub>2</sub>/rGO samples.

and more intense, accompanied by a reduced full width at half-maximum (FWHM), indicating that the crystallinity of WS<sub>2</sub> is well preserved and even improved during the composite formation process. More importantly, in addition to the diffraction peaks observed in pristine WS<sub>2</sub>, several new peaks appear in the SC-WS<sub>2</sub>/rGO sample, which can be indexed to the (100), (101), (102), (103), (105), (008), and (112) planes of WS<sub>2</sub>. This phenomenon can be attributed to the penetration and exfoliation effects of high-pressure CO<sub>2</sub> fluid during the SC process, which promotes the interlayer separation and dispersion of WS<sub>2</sub>. As a result, crystal planes that were originally masked or weakened by preferential stacking become more exposed and detectable in the XRD pattern. Meanwhile, the introduction of the reductant effectively suppresses possible oxidation side reactions during SC treatment, thereby protecting the lattice integrity of WS<sub>2</sub> and allowing more diffraction signals from different crystal planes to be clearly resolved. These results demonstrate that the hexagonal crystal structure of WS<sub>2</sub> is well retained after composite formation, while its structural ordering is enhanced to some extent. In addition, no obvious characteristic diffraction peak of GO, typically located at around 10°, is observed in the SC-WS<sub>2</sub>/rGO composite. This suggests that GO is partially reduced to rGO and that rGO is uniformly dispersed in the composite without obvious restacking.

FTIR was further employed to analyze the chemical bonding states and evolution of functional groups in the samples, as shown in Fig. 3(b). The spectrum of pristine GO displays several characteristic absorption bands. The peaks located at 1214, 1397, 1634, and 1730 cm<sup>-1</sup> can be assigned to C–O stretching vibration, C–OH bending vibration, O–H bending vibration/C=C skeletal vibration, and C=O stretching vibration, respectively, confirming the successful preparation of GO.<sup>(20)</sup> In addition, the broad absorption band in the range of 2986–3606 cm<sup>-1</sup> is

attributed to O–H stretching vibration, mainly originating from adsorbed water molecules and hydroxyl groups on the GO surface. After supercritical treatment assisted by the reductant, the absorption bands associated with oxygen-containing functional groups in the SC-WS<sub>2</sub>/rGO composite are significantly weakened. This indicates that hydrazine hydrate effectively removes most oxygen-containing groups from the GO surface, leading to the successful reduction of GO to rGO.<sup>(21)</sup> For pristine WS<sub>2</sub> and the SC-WS<sub>2</sub> sample prepared without the reductant, a broad absorption band in the range of 500–1000 cm<sup>−1</sup> can be observed, which is assigned to O–W–O stretching vibration, confirming the presence of tungsten oxide impurities.<sup>(22)</sup> In contrast, this band is markedly weakened or almost disappears in the SC-WS<sub>2</sub>/rGO composite, suggesting that the introduction of the reductant effectively suppresses the oxidation side reactions of WS<sub>2</sub> and removes tungsten oxide impurities from the precursor, thereby producing a higher-purity WS<sub>2</sub>/rGO heterostructure. Notably, a new absorption peak appears near 620 cm<sup>−1</sup> in both SC-WS<sub>2</sub>/rGO and SC-WS<sub>2</sub>/rGO-80, which can be attributed to C–S stretching vibration. The appearance of this peak provides evidence for chemical bonding between WS<sub>2</sub> and rGO, rather than simple physical mixing. Meanwhile, the absorption peaks near 609 and 1097 cm<sup>−1</sup> correspond to the stretching vibrations of W–S and S–S bonds in WS<sub>2</sub>, respectively, indicating that the intrinsic structure of WS<sub>2</sub> is well preserved during composite formation. In addition, the broad band around 3400 cm<sup>−1</sup> is mainly associated with adsorbed hydroxyl groups from the atmosphere, whereas the weak band near 2920 cm<sup>−1</sup> may be tentatively related to the bending vibration of W–S bonds.<sup>(23)</sup>

As shown in the Raman spectra of the SC-WS<sub>2</sub>/rGO composite in Fig. 4(a), two characteristic peaks located at 348 and 417 cm<sup>−1</sup> can be assigned to the in-plane (E<sub>2g</sub>) mode and the out-of-plane (A<sub>1g</sub>) mode of hexagonal WS<sub>2</sub>, respectively. The presence of these two peaks confirms that

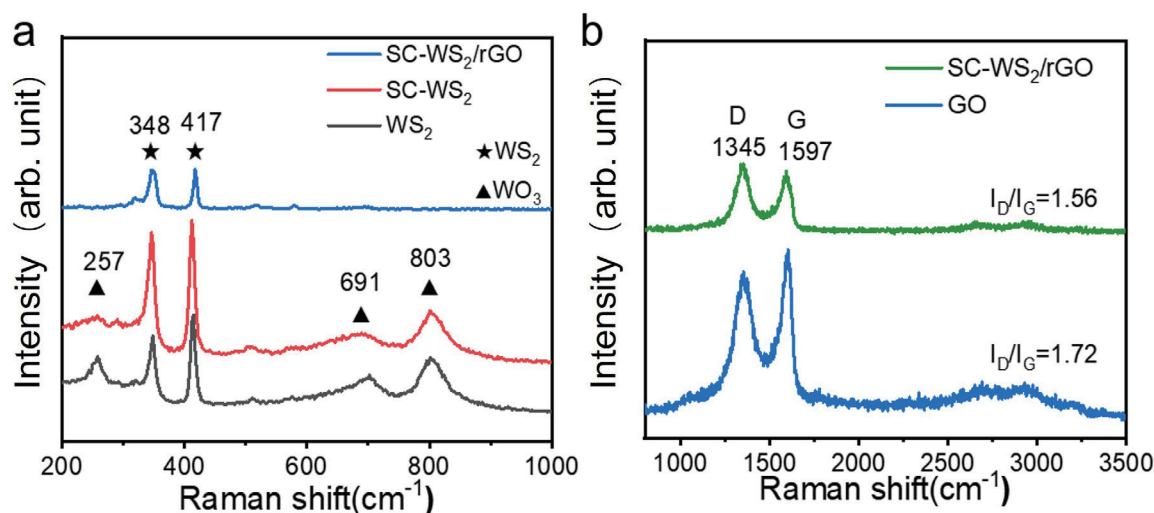


Fig. 4. (Color online) (a) Raman spectra of SC-WS<sub>2</sub>/rGO, SC-WS<sub>2</sub>, and WS<sub>2</sub> in the 200 to 1000 cm<sup>−1</sup> Raman shift range. (b) Raman spectra of SC-WS<sub>2</sub>/rGO and GO in the 1000 to 3500 cm<sup>−1</sup> Raman shift range.

the intrinsic crystal structure of WS<sub>2</sub> is well preserved during the composite formation process. In the low-wavenumber region, the Raman peak observed at 257 cm<sup>-1</sup> can be attributed to the W–O–W bending vibration involving bridging oxygen atoms. In addition, the peaks at 691 and 803 cm<sup>-1</sup> correspond to the W–O–W vibration mode and the stretching vibration of crystalline WO<sub>3</sub> associated with bridging oxygen atoms, respectively.<sup>(24)</sup> These tungsten oxide-related Raman signals are clearly observed in pristine WS<sub>2</sub>, confirming the existence of WO<sub>3</sub> impurities in the raw material. For the SC-WS<sub>2</sub> sample prepared without the reductant, the WO<sub>3</sub>-related Raman peaks are still present, indicating that supercritical CO<sub>2</sub> treatment alone cannot effectively remove tungsten oxide impurities. In contrast, these peaks are significantly weakened or even disappear in the reductant-treated SC-WS<sub>2</sub>/rGO composite, demonstrating that the introduction of the reductant effectively suppresses the oxidation side reactions of WS<sub>2</sub> and removes pre-existing tungsten oxide impurities. As a result, a higher-purity WS<sub>2</sub>/rGO heterostructure is obtained. Figure 4(b) shows the characteristic Raman region of carbonaceous materials. All samples exhibit two typical peaks at 1345 and 1597 cm<sup>-1</sup>, corresponding to the D and G bands of carbon materials, respectively.<sup>(25)</sup> The intensity ratio I<sub>D</sub>/I<sub>G</sub> is calculated to be 1.72 for pristine GO, whereas it decreases to 1.56 for the SC-WS<sub>2</sub>/rGO composite. This decrease suggests that the reductant-assisted SC treatment effectively repairs structural defects in the carbon framework of GO and improves the ordering degree of the carbon structure. Such structural restoration helps recover the sp<sup>2</sup>-conjugated network of rGO, thereby enhancing carrier mobility and improving its role as a conductive network. Meanwhile, the reduced defect density in the carbon skeleton favors more uniform and intimate interfacial contact between rGO and WS<sub>2</sub>, thus strengthening the electronic coupling within the heterostructure.

XPS was employed to investigate the surface chemical compositions and valence states of pristine WS<sub>2</sub>, SC-WS<sub>2</sub>, SC-WS<sub>2</sub>/rGO-80, SC-WS<sub>2</sub>/rGO, and SC-WS<sub>2</sub>/rGO-L, as shown in Fig. 5. Figure 5(a) presents the high-resolution W 4f spectra. For pristine WS<sub>2</sub>, the two peaks located at 32.8 and 35.2 eV are assigned to W<sup>4+</sup> 4f<sub>7/2</sub> and W<sup>4+</sup> 4f<sub>5/2</sub>, respectively, corresponding to the intrinsic W species in WS<sub>2</sub>.<sup>(26,27)</sup> In contrast, the peaks at 35.8 and 38.2 eV are attributed to W<sup>6+</sup> 4f<sub>7/2</sub> and W<sup>6+</sup> 4f<sub>5/2</sub>, indicating the presence of tungsten oxide impurities in the raw WS<sub>2</sub>, consistent with the Raman and TEM results. For SC-WS<sub>2</sub> prepared without the reductant, the W<sup>6+</sup> content increases markedly, suggesting that SC CO<sub>2</sub> treatment alone induces the partial oxidation of WS<sub>2</sub> and promotes the conversion of W<sup>4+</sup> to W<sup>6+</sup>. By comparison, SC-WS<sub>2</sub>/rGO exhibits the lowest W<sup>6+</sup> content among all samples, with W<sup>4+</sup> remaining dominant, demonstrating that hydrazine hydrate effectively suppresses oxidation side reactions during the supercritical process and enables the formation of a high-purity WS<sub>2</sub>/rGO heterostructure. The effects of reaction temperature and pre-exfoliation treatment are also reflected in the W valence state. The W<sup>6+</sup> content in SC-WS<sub>2</sub>/rGO-80 decreases to 16.1% compared with pristine WS<sub>2</sub>, indicating that the reductant can partially inhibit oxidation even at a relatively low temperature. However, this effect is less pronounced than that achieved at 180 °C. Notably, SC-WS<sub>2</sub>/rGO-L shows the highest W<sup>6+</sup> content of 20.1%, in agreement with the WO<sub>3</sub> lattice fringes observed by TEM. This result suggests that liquid-phase pre-exfoliation promotes the thinning of WS<sub>2</sub> sheets but simultaneously increases edge-active sites and oxidation susceptibility. Figure 5(b) shows the

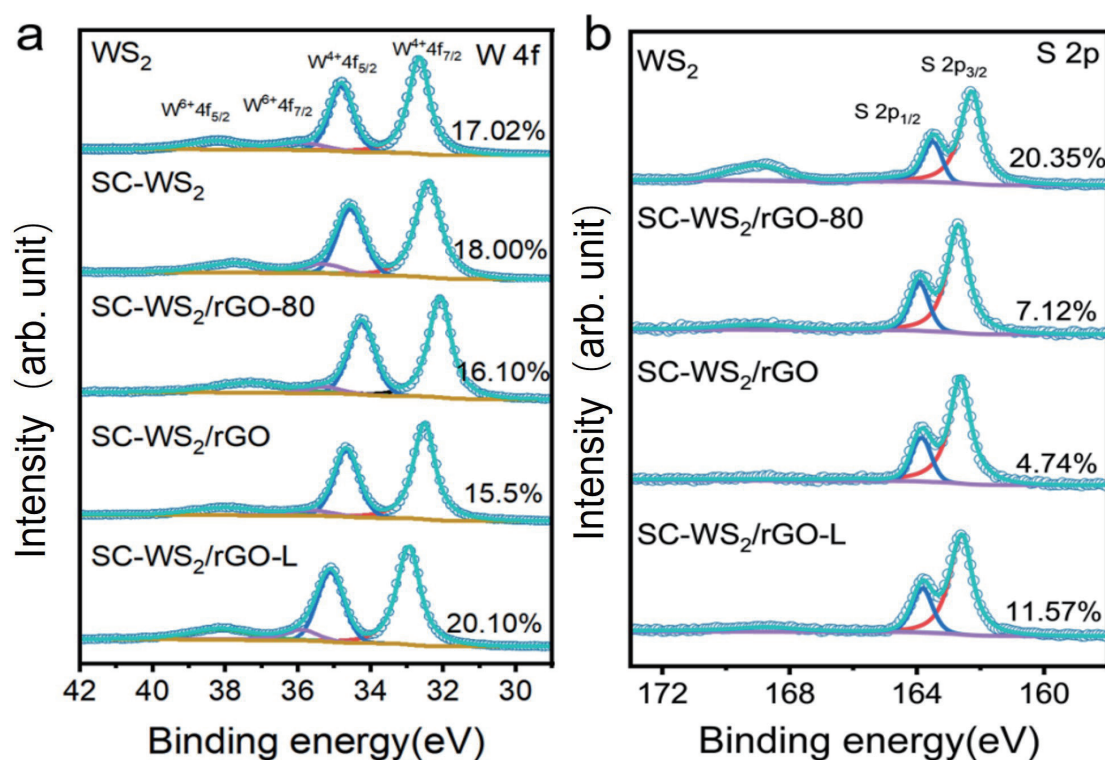


Fig. 5. (Color online) (a) High-resolution W 4f spectra of pristine WS<sub>2</sub>, SC-WS<sub>2</sub>, SC-WS<sub>2</sub>/rGO-80, SC-WS<sub>2</sub>/rGO, and SC-WS<sub>2</sub>/rGO-L. (b) High-resolution S 2f spectra of pristine WS<sub>2</sub>, SC-WS<sub>2</sub>/rGO-80, SC-WS<sub>2</sub>/rGO, and SC-WS<sub>2</sub>/rGO-L.

high-resolution S 2p spectra. All samples exhibit two characteristic peaks at approximately 162.5 and 163.7 eV, corresponding to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> of S<sup>2-</sup> in WS<sub>2</sub>, respectively. In addition, the peak near 169 eV can be assigned to sulfate species, which are associated with deeply oxidized sulfur species.<sup>(28)</sup> A detectable sulfate signal is observed in pristine WS<sub>2</sub>, confirming the presence of minor sulfur oxide impurities in the raw material. For SC-WS<sub>2</sub>/rGO, the sulfate-related peak intensity decreases to the lowest level, with a relative content of only 4.74%, indicating that the reductant effectively suppresses deep oxidation of sulfur species and preserves the dominant S<sup>2-</sup> state. In contrast, the sulfate content in SC-WS<sub>2</sub>/rGO-80 remains higher than that in SC-WS<sub>2</sub>/rGO, while SC-WS<sub>2</sub>/rGO-L exhibits the highest sulfate content, further confirming that liquid-phase pre-exfoliation aggravates the oxidation of WS<sub>2</sub>.

The high-resolution C 1s XPS spectra of GO and SC-WS<sub>2</sub>/rGO are shown in Fig. 6. The C 1s spectra can be deconvoluted into three main components located at 284.8, 286.8, and 288.0 eV, which are assigned to sp<sup>2</sup>-hybridized carbon (C–C/C=C), hydroxyl/epoxy groups (C–O/C–OH), and carboxyl groups (O–C=O), respectively. A clear difference in the carbon chemical states can be observed after the SC CO<sub>2</sub>-assisted composite process. For SC-WS<sub>2</sub>/rGO, the relative content of sp<sup>2</sup>-hybridized carbon increases significantly from 51.8 to 61.1%, whereas the total content of

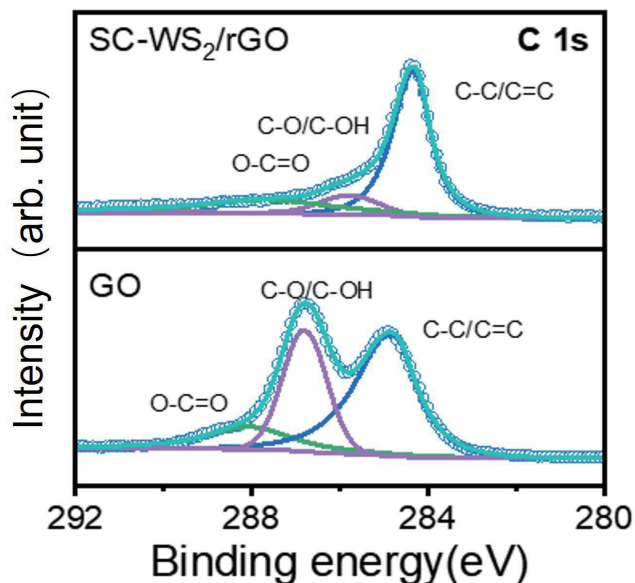


Fig. 6. (Color online) High-resolution C 1s spectra of GO and SC-WS<sub>2</sub>/rGO samples.

oxygen-containing groups, including C–O/C–OH and O–C=O, decreases markedly from 32.7 to 14.1%. In addition, the C/O atomic ratio increases from 1.6 for GO to 7.6 for SC-WS<sub>2</sub>/rGO, further confirming the substantial removal of oxygen-containing species from the carbon framework. These results demonstrate that the reductant-assisted SC CO<sub>2</sub> treatment effectively reduces GO to rGO, as evidenced by the increased sp<sup>2</sup> carbon content and the pronounced decrease in oxygen-containing functional groups. This observation is consistent with the reduced I<sub>D</sub>/I<sub>G</sub> ratio in the Raman spectra. The restored sp<sup>2</sup>-conjugated network of rGO provides favorable pathways for interfacial charge transfer, thereby contributing to the enhanced electronic coupling within the WS<sub>2</sub>/rGO heterostructure.

### 3.2 Gas-sensing performance toward ammonia

The dynamic response–recovery curves and concentration-dependent sensing results of the SC-WS<sub>2</sub>/rGO sensor toward NH<sub>3</sub> of different concentrations are shown in Fig. 7(a). The sensor exhibits typical response and recovery behavior upon exposure to and removal of NH<sub>3</sub>. As the NH<sub>3</sub> concentration increases from 6 to 900 ppm, the response value increases monotonically, clearly indicating a concentration-dependent sensing behavior. Notably, the sensor shows different response characteristics in the low-concentration range of 6–60 ppm and the high-concentration range of 120–900 ppm, as shown in Figs. 7(b) and 7(c). In the low-concentration region, the response displays a good linear relationship with NH<sub>3</sub> concentration, with a relatively well-fit slope, demonstrating the excellent sensitivity of the sensor toward trace NH<sub>3</sub>. On the basis of the linear calibration curve, the theoretical limit of detection (LOD) of the sensor is calculated to be as low as 13.11 ppb using the following equation.<sup>(29)</sup>

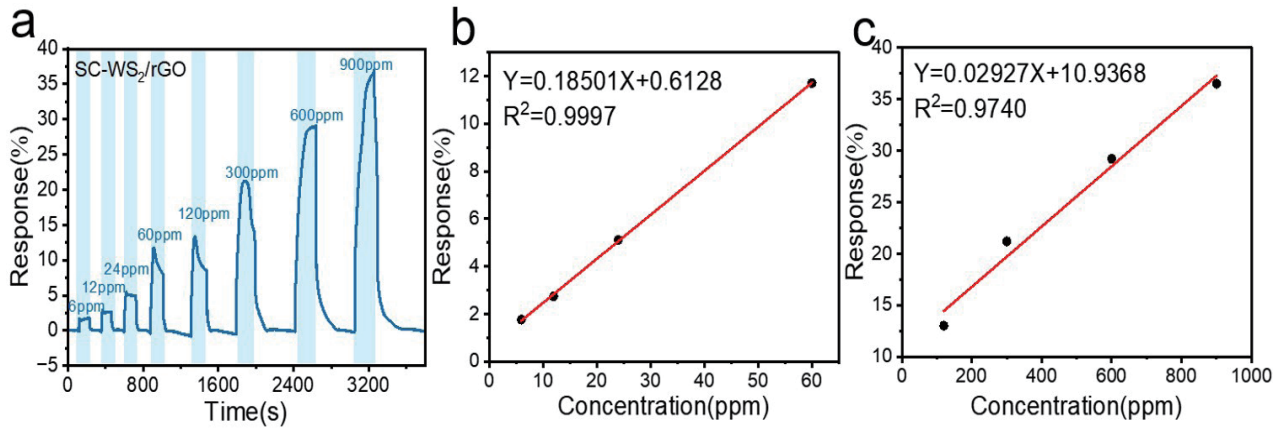


Fig. 7. (Color online) Gas sensing performance of the SC-WS<sub>2</sub>/rGO sensor. (a) Sensor response as a function of ammonia concentration over the range of 6–900 ppm. (b) Linear fit of the sensor response to ammonia at low concentrations. (c) Linear fit of the sensor response to ammonia at high concentrations.

$$LOD = 3 \frac{\sqrt{S^2/N}}{\text{slope}} = 13.11 \text{ ppb} \quad (2)$$

In the high-concentration range, the response continues to increase with increasing NH<sub>3</sub> concentration; however, the incremental response gradually decreases and tends toward saturation, exhibiting typical Langmuir-type adsorption behavior. Linear fitting of this concentration region yields another calibration line, which can be used to describe the sensing response under high-gas-loading conditions. The segmented fitting strategy provides a more comprehensive understanding of the sensor response over the entire concentration range. Specifically, the low-concentration region reflects the efficient capture of NH<sub>3</sub> molecules by active adsorption sites, whereas the high-concentration region reveals the evolution of the adsorption–desorption equilibrium on the material surface.

The dynamic NH<sub>3</sub> sensing responses of the SC-WS<sub>2</sub>/rGO-80 and SC-WS<sub>2</sub>/rGO-L composites shown in Fig. 8 were further compared. The results reveal that both samples exhibit markedly lower NH<sub>3</sub> responses than the SC-WS<sub>2</sub>/rGO sensor prepared at 180 °C. Referring to the structural characterization discussed above, the inferior performance of SC-WS<sub>2</sub>/rGO-80 can be attributed to the insufficient reaction temperature, which limits the reducing effect of the reductant, resulting in incomplete WS<sub>2</sub> exfoliation, nonuniform hybridization with rGO, and residual tungsten oxide impurities at the interface. Although SC-WS<sub>2</sub>/rGO-L achieves the effective thinning of WS<sub>2</sub> sheets, the abundant edge-active sites introduced during liquid-phase pre-exfoliation are more susceptible to oxidation side reactions during subsequent processing, thereby compromising the interfacial purity of the heterostructure.

Fast response and recovery are critical for the real-time monitoring of trace toxic and hazardous gases. Figures 9(a) and 9(b) show the dynamic response–recovery characteristics of

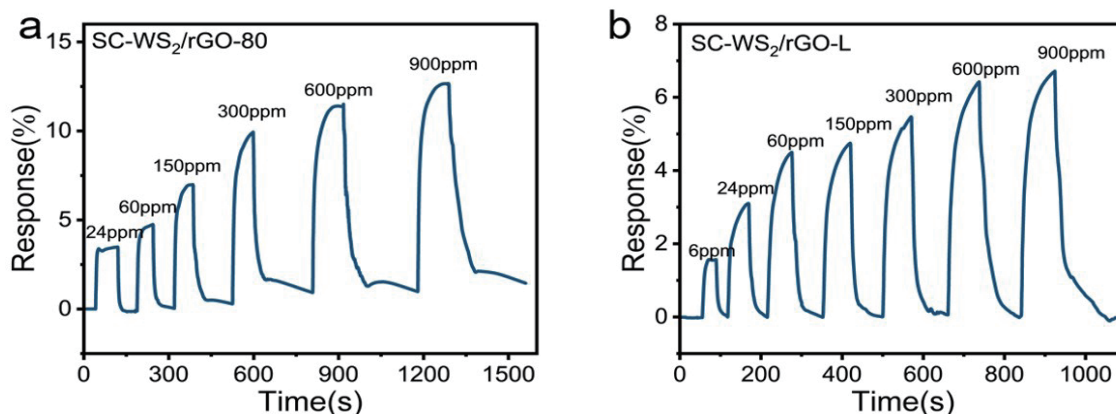


Fig. 8. (Color online) (a) Response of the SC-WS<sub>2</sub>/rGO-80 sensor as a function of ammonia concentration. (b) Response of the SC-WS<sub>2</sub>/rGO-L sensor as a function of ammonia concentration.

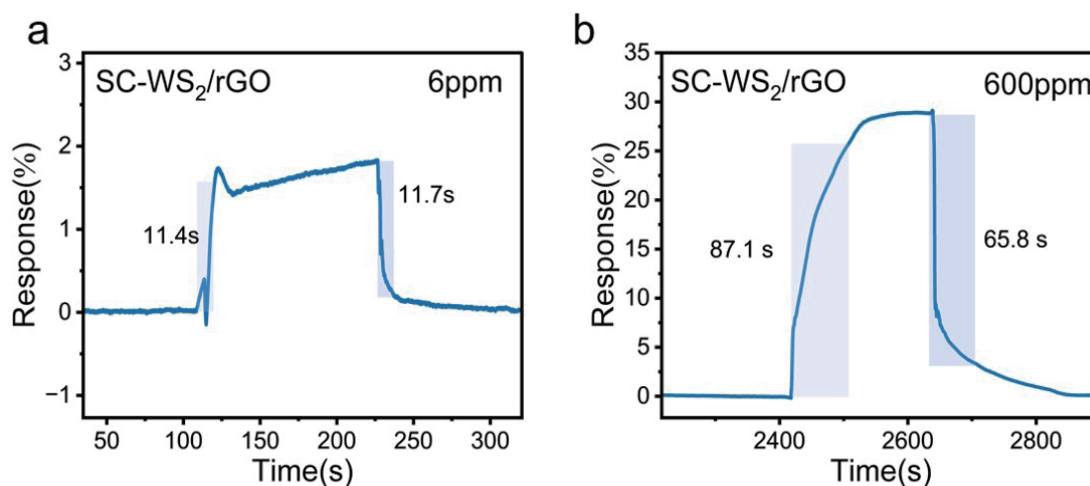


Fig. 9. (Color online) (a) Dynamic response and recovery time of the SC-WS<sub>2</sub>/rGO sensor when exposed to low-concentration (6 ppm) ammonia gas at 23 °C. (b) Dynamic response and recovery time of the SC-WS<sub>2</sub>/rGO sensor when exposed to high-concentration (600 ppm) ammonia gas at 23 °C.

the SC-WS<sub>2</sub>/rGO composite toward low-concentration (6 ppm) and high-concentration (600 ppm) NH<sub>3</sub>, respectively. Upon exposure to 6 ppm NH<sub>3</sub>, the SC-WS<sub>2</sub>/rGO sensor exhibits a response time of approximately 11.4 s and a recovery time of approximately 11.7 s, demonstrating its rapid response capability toward trace NH<sub>3</sub>. When the NH<sub>3</sub> concentration increases to 600 ppm, the response and recovery times are prolonged to 87.1 and 65.8 s, respectively. This behavior is consistent with the kinetic process at high gas concentrations, where longer times are

required for molecular diffusion and the establishment of adsorption–desorption equilibrium. Notably, the sensor maintains complete, stable, and reversible response behavior over a wide concentration range of 6–900 ppm. This excellent dynamic sensing performance can be attributed to the synergistic effects of the abundant active sites provided by ultrathin WS<sub>2</sub> nanosheets, the efficient conductive network of reduced graphene oxide, and the clean heterointerface between WS<sub>2</sub> and rGO.

As shown in Fig. 10(a), the sensor was repeatedly exposed to 6 ppm NH<sub>3</sub> for nine consecutive cycles at 23 °C. The response signals remain highly consistent, without obvious attenuation or baseline drift, demonstrating excellent reversibility and cycling stability. The robust heterointerface between WS<sub>2</sub> and rGO, together with the clean surface obtained through reductant-assisted treatment, ensures highly reversible gas adsorption and desorption processes. Long-term stability is another key parameter for practical sensor applications. As shown in Fig. 10(b), the sensor maintains a nearly unchanged response over 30 days of continuous testing, indicating excellent long-term operational stability. The selectivity results in Fig. 10(c) show that the response of the sensor toward 150 ppm NH<sub>3</sub> is approximately five times higher than that toward ethanol and about 25 times higher than those toward interfering gases such as acetone, toluene, and isopropanol, demonstrating its outstanding target-gas recognition capability. The high selectivity can be attributed to the strong electron-donating ability of NH<sub>3</sub> molecules and their specific interaction with active sites on the WS<sub>2</sub> surface. In contrast, the interfering gases are less likely to effectively occupy the active sites or induce significant charge transfer because of differences in molecular size, polarity, and adsorption energy. Overall, the SC-WS<sub>2</sub>/rGO sensor exhibits excellent repeatability, long-term stability, and selectivity, and its comprehensive sensing performance is superior to that of many previously reported sensors of similar types, as summarized in Table 1.

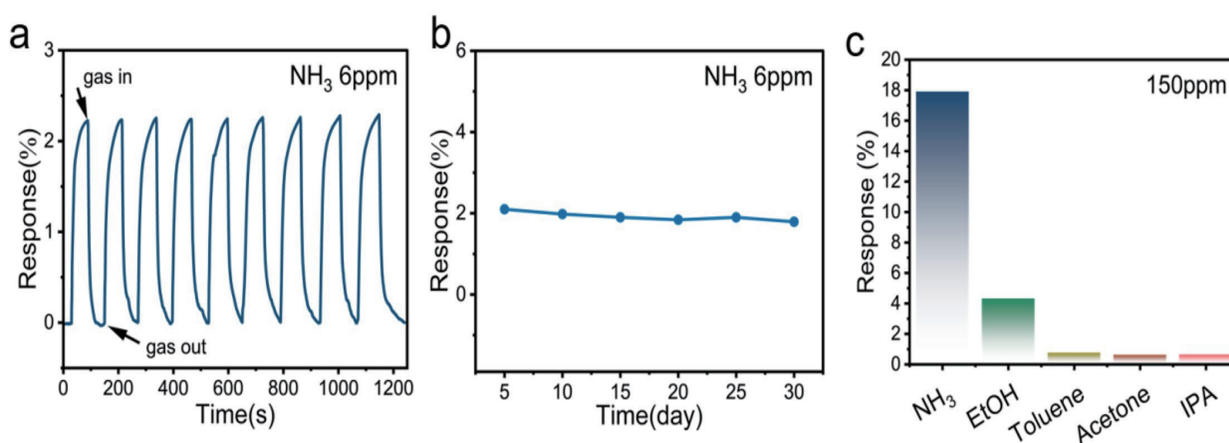


Fig. 10. (Color online) (a) Sensitivity consistency of the SC-WS<sub>2</sub>/rGO sensor after nine repeated exposure cycles to 6 ppm ammonia at room temperature. (b) Long-term stability of the SC-WS<sub>2</sub>/rGO sensor evaluated over 30 days. (c) Selectivity plots of the SC-WS<sub>2</sub>/rGO sensor for various interfering gases at 23 °C.

Table 1  
Performances of different gas sensors in detecting ammonia in dry air.

| Material                                 | $T(^{\circ}\text{C})$ | Concernturation | $S(\%)$    | $T_{res}(\text{s})/T_{rec}(\text{s})$ | Selectivity | Ref.             |
|------------------------------------------|-----------------------|-----------------|------------|---------------------------------------|-------------|------------------|
| <b>SC-WS<sub>2</sub>/go</b>              | <b>RT</b>             | <b>6</b>        | <b>2.1</b> | <b>11.4/11.7</b>                      | <b>High</b> | <b>This Work</b> |
| rGO/NiO                                  | RT                    | 100             | 4.14       | 290/166                               | Moderate    | Ref. 30          |
| WO <sub>3</sub>                          | 350                   | 100             | 3.32       | 150/210                               | Low         | Ref. 31          |
| rGO/Co <sub>3</sub> O <sub>4</sub>       | RT                    | 20              | 1.78       | 351/1199                              | Not tested  | Ref. 29          |
| SnO <sub>2</sub> QDs/MoS <sub>2</sub>    | RT                    | 100             | 8.6        | 6/121                                 | Moderate    | Ref. 32          |
| PANI/TiO <sub>2</sub>                    | RT                    | 100             | 5.4        | 100/232                               | Low         | Ref. 33          |
| WS <sub>2</sub> /TiO <sub>2</sub> QD     | RT                    | 250             | 43.72      | —/174                                 | High        | Ref. 8           |
| NiO/ZnO                                  | RT                    | 50              | 23         | 27/150                                | Moderate    | Ref. 34          |
| Mxene/SnO <sub>2</sub> /TiO <sub>2</sub> | 200                   | 100             | 2.5        | 6/9                                   | Moderate    | Ref. 35          |
| NiO-Bi <sub>2</sub> O <sub>3</sub>       | RT                    | 50              | 10         | 89.2/7.7                              | Not tested  | Ref. 36          |

### 3.3 Enhanced NH<sub>3</sub> sensing mechanism

When the SC-WS<sub>2</sub>/rGO gas sensor is exposed to ambient air, oxygen molecules are adsorbed on the active surfaces of WS<sub>2</sub> and rGO. These adsorbed oxygen molecules capture electrons from the conduction band of the sensing material and form ionized chemisorbed oxygen species.<sup>(37)</sup> The type of chemisorbed oxygen species strongly depends on the operating temperature of the sensing layer. Since the SC-WS<sub>2</sub>/rGO sensor operates at room temperature, oxygen molecules are mainly chemisorbed on the surface in the form of superoxide species by the following process.



This electron-withdrawing process increases the hole concentration on the WS<sub>2</sub> surface and thickens the hole accumulation layer, thereby placing the sensor in a relatively low-resistance state. When the sensor is exposed to reducing NH<sub>3</sub> gas, NH<sub>3</sub> molecules react with the adsorbed oxygen species through surface redox reactions. NH<sub>3</sub> can participate in the reaction through two possible pathways: direct reaction with O<sub>2</sub><sup>−</sup> or protonation to form NH<sub>4</sub><sup>+</sup> followed by reaction with O<sub>2</sub><sup>−</sup>. The possible reactions can be described as follows.



The electrons released during these reactions are injected back into the sensing material and recombine with holes in WS<sub>2</sub>. Consequently, the hole concentration decreases, and the hole accumulation layer becomes thinner, resulting in an increase in sensor resistance. This resistance variation is consistent with the experimentally observed response behavior of the SC-WS<sub>2</sub>/rGO sensor toward NH<sub>3</sub>.

#### 4. Conclusions

In this work, interface-purified WS<sub>2</sub>/rGO heterostructures were successfully fabricated through a reductant-assisted SC CO<sub>2</sub> one-step strategy for room-temperature NH<sub>3</sub> sensing. The optimized treatment at 180 °C enabled simultaneous WS<sub>2</sub> exfoliation, GO reduction, and heterointerface purification, producing an ultrathin nanosheet architecture with reduced W<sup>6+</sup> and sulfate impurities and strong electronic coupling between WS<sub>2</sub> and rGO. The resulting SC-WS<sub>2</sub>/rGO sensor exhibited excellent NH<sub>3</sub> sensing performance at room temperature, including rapid response/recovery times of 11.4/11.7 s toward 6 ppm NH<sub>3</sub>, stable reversible responses in the range of 6–900 ppm, a theoretical detection limit of 13.11 ppb, good long-term stability, and superior selectivity. A clean heterointerface facilitates active-site exposure, reduces carrier transport barriers, and accelerates interfacial charge transfer, thereby enabling fast, sensitive, and stable NH<sub>3</sub> detection. The outcomes of this study extend SC CO<sub>2</sub>-assisted heterointerface engineering to 2D transition metal sulfide-based sensing materials and highlights the “ultrathin nanosheet–clean interface–strong electronic coupling” design principle as a promising strategy for developing high-performance room-temperature gas sensors.

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#### Conflicts of Interest

The authors declare no conflicts of interest.

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