



# Article Indium Oxide Decorated WS<sub>2</sub> Microflakes for Selective Ammonia Sensors at Room Temperature

Qiyilan Guang<sup>1</sup>, Baoyu Huang<sup>1</sup>, Jun Yu<sup>2</sup>, Jianwei Zhang<sup>2,\*</sup> and Xiaogan Li<sup>1,\*</sup>

- <sup>1</sup> Liaoning Key Lab of Integrated Circuit and Biomedical Electronic System, School of Microelectronics, Dalian University of Technology, Dalian 116024, China
- <sup>2</sup> School of Biomedical Engineering, Dalian University of Technology, Dalian 116024, China
- \* Correspondence: jwzhang@dlut.edu.cn (J.Z.); lixg@dlut.edu.cn (X.L.)

**Abstract:** Tungsten sulfide decorated with indium oxide nanoparticles  $(In_2O_3/WS_2)$  was studied for a chemiresistive-type NH<sub>3</sub> sensor at room temperature. It was found that the responses of the developed In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub> heterostructure nanocomposite-based sensors are significantly improved to 3.81 from 1.45 for WS<sub>2</sub>. The response and recovery time of the heterostructure-based sensor was found to significantly decrease to 88 s/116 s (10 ppm) from 112 s/192 s for the WS<sub>2</sub>-based one. The sensor also exhibits excellent selectivity and signal reproducibility. In comparison to WS<sub>2</sub> decorated with both ZnO and SnO<sub>2</sub> in similar ways, the In<sub>2</sub>O<sub>3</sub>-decorated WS<sub>2</sub> has overall better sensing performance in terms of sensitivity, selectivity and response/recovery speeds for NH<sub>3</sub> from 1 ppm to 10 ppm at room temperature. The improved sensing properties of WS<sub>2</sub> incorporating In<sub>2</sub>O<sub>3</sub> could be attributed to the joint enhancement mechanisms of the "electronic and catalytic" sensitizations.

Keywords: WS<sub>2</sub>; WS<sub>2</sub>-In<sub>2</sub>O<sub>3</sub>; heterostructure nanocomposites; ammonia; gas sensor



Citation: Guang, Q.; Huang, B.; Yu, J.; Zhang, J.; Li, X. Indium Oxide Decorated WS<sub>2</sub> Microflakes for Selective Ammonia Sensors at Room Temperature. *Chemosensors* **2022**, *10*, 402. https://doi.org/10.3390/ chemosensors10100402

Academic Editors: Andrea Gaiardo, Barbara Fabbri and Vincenzo Guidi

Received: 8 September 2022 Accepted: 4 October 2022 Published: 8 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

# 1. Introduction

Ammonia is a natural, colorless and corrosive gas that is potentially toxic to human health and the environment [1]. It comes from the decomposition of feces and dead animals and plants and exists in the atmosphere at low concentrations [2]. Ammonia is mainly used as a fertilizer to increase crop yields. It is also widely used in refrigeration, fuel, textile production and other industrial fields [3]. As a carbon-free hydrogen carrier, ammonia contains 17.6 wt.% hydrogen. It can be used as a green fuel for internal combustion engines and gas turbines which play an indispensable role in addressing the chemical fuel depletion crisis [4,5]. However, a high level of ammonia exposure can cause damage to human health; therefore, the upper exposure concentration of ammonia within 8 h is limited to 25 ppm [6]. Excessive ammonia emissions can subsequently lead to environmental acidification which needs to be monitored in real time [7,8].

To fulfill the demand for monitoring ammonia, sensors working at room temperature with low cost, low power consumption, high sensitivity, fast response, and good selectivity need to be developed [9]. Metal oxides such as SnO<sub>2</sub>, ZnO, TiO<sub>2</sub>, WO<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> are widely explored as the sensing materials for detecting ammonia. However, they are usually operated at high temperatures between 100 °C and 550 °C, which requires high power consumption [10–16]. To fabricate low-temperature chemiresistive-type gas sensors, graphene with a two-dimensional (2D) network of carbon has become a promising candidate material due to its advantages of high specific surface area and excellent electrical conductivity [17]. However, its application is limited by the zero band gap feature, and graphene is not very responsive to ammonia at room temperature. Therefore, graphene was usually functionalized with metal nanoparticles, metal oxides, organic molecules and conductive polymers to enhance its functionality [18].

As analogs to graphene, metal dichalcogenides such as MoS<sub>2</sub>, SnS<sub>2</sub> and WSe<sub>2</sub> have also become potential candidate materials for fabricating nanoelectronic devices [19]. Singh et al.

synthesized a p-MnS<sub>2</sub>/n-WO<sub>3</sub> heterostructure for a chemical ammonia sensor and found it displayed an improved response to ammonia at 200 °C compared to the pure p-MnS<sub>2</sub>-based one [20]. Xia et al. reported a WS<sub>2</sub>/SnO<sub>2</sub>-based sensor with 2D/0D heterostructure and noticed the response to NO<sub>2</sub> could be further improved under UV at room temperature [21]. Wang et al. found that the (2D/2D) rGO/WS<sub>2</sub> heterostructure-based ammonia sensor showed improved response/recovery at room temperature. The reasons are attributed to the extra active sites introduced by the secondary 2D phase [22]. Kim et al. fabricated a Au-decorated WS<sub>2</sub>-SnO<sub>2</sub> core–shell nanosheet-based gas sensor and demonstrated that it has enhanced sensing properties for CO at 3.4 V [23].

In previous studies, WS<sub>2</sub> has been reported to show promise in detecting harmful gases at room temperature [24]. Metal oxides such as SnO<sub>2</sub> and ZnO and noble metals such as Pt and Au have been strategically used to improve the sensing properties in terms of sensitivity, selectivity and response/recovery speeds. In<sub>2</sub>O<sub>3</sub> is also a good semiconducting material for gas sensing because it has a lower resistance and a good response to HCHO [25], NO<sub>2</sub> [26] and CO [27]. Therefore, in this work, the 2D WS<sub>2</sub> heterostructured by indium oxide nanoparticles was examined. Indium oxide was selected as the secondary phase to improve the sensing properties of a WS<sub>2</sub>-based chemiresistive-type sensor at room temperature for the following two reasons: We found that the synthesized sensors all displayed higher responses and faster recovery to ammonia than the pure WS<sub>2</sub> microflake-based one at room temperature. Comparing the response rates of the developed sensors to the pure sensor, In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub> heterostructure nanocomposite-based sensors exhibited a much faster response, The improved performance of the In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub>-based sensors could be mainly attributed to the electronic sensitization between In<sub>2</sub>O<sub>3</sub> and WS<sub>2</sub>. Sensors based on WS<sub>2</sub> heterostructured with ZnO/SnO<sub>2</sub> were also characterized and compared.

# 2. Experimental Method

#### 2.1. Synthesis of In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub> Nanocomposites

The WS<sub>2</sub> powders used in this study were purchased from Aladdin Co., Shanghai, China. In<sub>2</sub>O<sub>3</sub> powders were purchased from Macklin Biochemical Co., Ltd., Shanghai, China. ZnO and SnO<sub>2</sub> powders were obtained from Aladdin Co., Shanghai, China. All chemicals were of analytical grade and used as received. First, 50.0 mg WS<sub>2</sub> powders and 55.5 mg In<sub>2</sub>O<sub>3</sub> powders were added to 15 mL and 20 mL deionized (DI) water, respectively, followed by the sonication in an ultrasound water bath for 15 min. Different amounts of In<sub>2</sub>O<sub>3</sub> solutions (0.1 mL, 0.2 mL, 0.6 mL and 1 mL) were added drop-wise to the WS<sub>2</sub> dispersion solution with vigorous stirring for half an hour to obtain the WS<sub>2</sub> suspensions with different concentrations of In<sub>2</sub>O<sub>3</sub> (0.5%, 1%, 3% and 5%). WS<sub>2</sub> suspensions with different ZnO contents and SnO<sub>2</sub> contents (0.5%, 1%, 3% and 5%) for comparisons were obtained by the same method. Then the obtained mixtures were washed with absolute alcohol and DI water three times in sequence and dried at 60 °C overnight in a drying oven.

#### 2.2. Characterization

X-ray diffraction (XRD, D8 Advance, Bruker Corporation, Billerica, MA, USA) was used to investigate the chemical information and crystal structure of indium oxide decorated tungsten sulfide (IO/WS<sub>2</sub>) heterostructure nanocomposite-based samples. A field emission scanning electron microscope (FESEM, Gemini 300, ZEISS Corporation, Jena, Germany) and a transmission electron microscope (TEM, Tecnai G2 F20, FEI Corporation, Hillsboro, OR, USA) were used to study the surface morphologies of the prepared IO/WS<sub>2</sub> samples. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific Corporation, Waltham, MA, USA) was performed to explore the elemental compositions and chemical oxidation states of the IO/WS<sub>2</sub> samples.

# 2.3. Fabrication and Measurement of the Gas Sensors

A printable paste was formed by grinding a small amount of the obtained  $IO/WS_2$  materials and DW in an agate mortar. Then the paste was spread on the gold interdigital

electrodes pre-printed on the ceramic substrate, which were dried at 60 °C for 12 h in a drying oven to develop the IO/WS<sub>2</sub>-based chemiresistive-type sensor. To measure the sensing properties of the fabricated sensor, the sensor was placed in a testing chamber with a volume of 50 L, and the resistance of the sensor was recorded using a digital multimeter (Keysight 34465A). A corresponding amount of liquid solutions including ammonia, formaldehyde, toluene, methanol, ethanol and acetone, which were purchased from Kermel Co., Tianjin, China, was vaporized to achieve different gas vapors by heating after being injected into the small crucible at the corner of the testing chamber. The gas vapor concentrations were calculated by the following formula [28]:

$$C = (22.4 \times \rho \times d \times V_1 / (M \times V_2))$$
(1)

where C (ppm) represents the targeted gas concentration,  $\rho$  (g/mL) represents the liquid density, d represents the liquid purity, M (g/mol) represents the liquid molecular weight, V<sub>1</sub> (L) represents the liquid volume and V<sub>2</sub> (L) represents the volume of the testing chamber (50 L). The sensor response (S) was defined by the resistance ratio of R<sub>g</sub>/R<sub>a</sub>, where R<sub>g</sub> is the resistance of the sensor in target ammonia and R<sub>a</sub> is the resistance of the sensor in air. The response time and recovery time were measured by the time course of 90% of the maximum response amplitude.

## 3. Results and Discussion

#### 3.1. Microstructure Characterizations

Figure 1 shows the XRD patterns of the pure WS<sub>2</sub> and IO/WS<sub>2</sub> with 1% In<sub>2</sub>O<sub>3</sub> (IO/WS<sub>2</sub>-1) heterostructure nanocomposite-based samples. The main peaks in the XRD pattern of WS<sub>2</sub> (red) correspond to 2H-WS<sub>2</sub> (PDF # 87-2417). The peaks in the XRD pattern of the IO/WS<sub>2</sub>-1 heterostructure nanocomposite-based sample contain the diffraction peaks of both WS<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> (PDF # 71-2194) without other impurities. The size of In<sub>2</sub>O<sub>3</sub> particles can be calculated by the Scherrer equation as follows [29]:

$$D = K\lambda/(\beta \cos\theta)$$
(2)

where D is the size of the particle,  $\lambda$  is the X-ray wavelength (1.54178 Å),  $\beta$  is full width at half maximum (FWHM) of the diffraction peak,  $\theta$  is the angle of diffraction and K is Scherrer's constant (K = 0.943). The size of the In<sub>2</sub>O<sub>3</sub> particles estimated from XRD by the Scherrer equation is 61 nm. However, the size of WS<sub>2</sub> microflakes cannot be calculated by the Scherrer equation because it does not meet the required condition (D < 100 nm).

As shown in Figure 2a,b, the morphology of WS<sub>2</sub> microflakes did not exhibit much change after being incorporated with  $In_2O_3$ . The WS<sub>2</sub> microflakes are 0.4–4.3 µm in diameter. The  $In_2O_3$  nanoparticles show a cube shape with particle size around 30 nm distributed on WS<sub>2</sub> microflakes as shown in Figure 2c. Compared to the size calculated by the Scherrer equation, the size of  $In_2O_3$  particles observed in the TEM was smaller. This may be caused by the strained lattice in the crystals of  $In_2O_3$ . The  $In_2O_3$  particles and WS<sub>2</sub> microflakes were physically mixed without further heating; as a result, the size and morphology of  $In_2O_3$  particles remained unchanged. Figure 2d shows the high-resolution TEM (HRTEM) image of the  $IO/WS_2$ -1 heterostructure nanocomposite-based sensor. The lattice spacing of 0.273 nm corresponds to the (100) plane of WS<sub>2</sub>, and the lattice spacing of 0.292 nm corresponds to the (222) plane of  $In_2O_3$  nanoparticles, which confirmed the heterostructure formed between  $In_2O_3$  and WS<sub>2</sub>. The SEM elemental mapping images of  $IO/WS_2$ -1 heterostructure nanocomposites are shown in Figure S1 in the Supplementary Materials. The synthesized sample contains four elements: *W*, *S*, In and O. The relative concentrations of each element are summarized in Table S1.



Figure 1. XRD patterns of WS<sub>2</sub> and IO/WS<sub>2</sub>-1 samples.



Figure 2. SEM images of (a) WS<sub>2</sub> and (b) IO/WS<sub>2</sub>-1; (c) TEM image of IO/WS<sub>2</sub>-1; (d) HRTEM image of IO/WS<sub>2</sub>-1.

Figure 3a shows the survey of the XPS spectra of WS<sub>2</sub> microflakes, In<sub>2</sub>O<sub>3</sub> nanoparticles and IO/WS<sub>2</sub>-1 heterostructure nanocomposites. As shown in Figure 3b, the peaks centered at 531.3 eV and 532.4 eV correspond to the adsorbed oxygen and  $SO_4^{2-}$  of WS<sub>2</sub>, respectively [30]. The peaks at 531.3 eV, 532.4 eV, 530.1 eV and 533.32 eV shown in Figure 3c correspond to the adsorbed oxygen,  $SO_4^{2-}$ , lattice oxygen and hydroxyl in the IO/WS<sub>2</sub>-1 heterostructure nanocomposites, respectively [28,31]. The concentrations of the adsorbed

oxygen contents estimated from the integrated areas under each peak for the adsorbed  $O_2^-$  on both WS<sub>2</sub> and IO/WS<sub>2</sub>-1 samples were found to increase from 25.57 at.% in the WS<sub>2</sub> sample to 54.65 at.% in the IO/WS<sub>2</sub>-1 sample. However, the amount of SO<sub>4</sub><sup>2-</sup> in the IO/WS<sub>2</sub>-1 sample was reduced, which may be due to the reduction reaction with the hydroxyl groups. The refined core spectra of W 4f and S 2p of both WS<sub>2</sub> and IO/WS<sub>2</sub>-1 samples are shown in Figure S2. The binding energies of both W and S shift to the lower binding energy direction by 0.05 eV after the incorporation of In<sub>2</sub>O<sub>3</sub> nanoparticles. This could be attributed to the electronic equilibrium effect between WS<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, in which WS<sub>2</sub> obtained the electrons transferred from In<sub>2</sub>O<sub>3</sub>. In a comparison of Figure S3 (shown in the Supplementary Materials) and Figure 3d, the refined core spectra of In 3d of In<sub>2</sub>O<sub>3</sub> and IO/WS<sub>2</sub>-1 samples demonstrate that the binding energy of In 3d shifts to a higher energy by 1.1 eV after the incorporation with WS<sub>2</sub> microflakes, indicating the loss of electrons.



**Figure 3.** (a) XPS spectra of WS<sub>2</sub>,  $In_2O_3$  nanoparticles and  $IO/WS_2$ -1 heterostructure nanocomposites; (b) O 1s refined core spectra of WS<sub>2</sub> microflakes; (c) O 1s refined core spectra of  $IO/WS_2$ -1 heterostructure nanocomposites; (d) In 3d refined core spectra of  $IO/WS_2$ -1 heterostructure nanocomposites.

## 3.2. Electrical and Sensing Performance

Figure 4 shows the I–V curves with applied voltages between -5 V and +5 V of the WS<sub>2</sub> microflake-based sensor and the IO/WS<sub>2</sub> heterostructure nanocomposite-based sensors. It is found that the resistances of the fabricated IO/WS<sub>2</sub> heterostructure nanocomposite-based sensors increased with the increase in the In<sub>2</sub>O<sub>3</sub> nanoparticle content. The resistance values of WS<sub>2</sub>, IO/WS<sub>2</sub>-0.5, IO/WS<sub>2</sub>-1, IO/WS<sub>2</sub>-3 and IO/WS<sub>2</sub>-5 sensors estimated from Figure 4 are 2.7 M, 3.6 M, 6.6 M, 10.4 M and 31.3 M, respectively. The I–V curves are linear in an ohmic connection between the sensing materials and gold electrodes.

The responses of sensors based on WS<sub>2</sub> and IO/WS<sub>2</sub> heterostructure nanocomposites with different In<sub>2</sub>O<sub>3</sub> concentrations to 10 ppm ammonia at room temperature are shown in Figure 5a. The IO/WS<sub>2</sub> heterostructure nanocomposite-based sensor exhibited higher responses than the pure WS<sub>2</sub> microflake-based one. With an increase in the In<sub>2</sub>O<sub>3</sub> content, the response of IO/WS<sub>2</sub> heterostructure nanocomposite-based sensors firstly increases as the In<sub>2</sub>O<sub>3</sub> percentage increases from 0.5% to 1% and then decreases above 3% In<sub>2</sub>O<sub>3</sub>. It achieves the maximum response of 3.81 with 1% In<sub>2</sub>O<sub>3</sub> content. However, as shown in Figure 5b, the response and recovery time of IO/WS<sub>2</sub> heterostructure nanocomposite-based



sensors continue to decrease as the concentration of  $In_2O_3$  increases from 0.5% to 5% with  $In_2O_3$  introduction.

Figure 4. I-V curves of samples based on WS2 microflakes and IO/WS2 heterostructure nanocomposites.



**Figure 5.** (a) Responses of  $WS_2$  and  $IO/WS_2$  heterostructure nanocomposite-based sensors to 10 ppm ammonia at room temperature; (b) corresponding response time and recovery time.

The gas-sensing mechanism of the IO/WS<sub>2</sub> heterostructure nanocomposite-based sensor is illustrated in Figure 6. As shown in Figure 6a, as the WS<sub>2</sub> is in contact with In<sub>2</sub>O<sub>3</sub>, the electrons will move from the conducting band of In<sub>2</sub>O<sub>3</sub> to the conducting band of WS<sub>2</sub> while the holes will move from the valence band of WS<sub>2</sub> to the valence band of In<sub>2</sub>O<sub>3</sub> due to the work function of In<sub>2</sub>O<sub>3</sub> (4.28 ev) being lower than that of WS<sub>2</sub> (4.9 ev). The transfer of the electrons and holes creates a hole depletion layer (HDL) on the WS<sub>2</sub> side and a hole accumulation layer (HAL) on the In<sub>2</sub>O<sub>3</sub> side, which leads to an increase in the resistance on the WS<sub>2</sub> and a decrease in the resistance on the In<sub>2</sub>O<sub>3</sub> side. As a p-type semiconductor, the total resistance of the fabricated IO/WS<sub>2</sub> heterostructure nanocomposite-based sensor increased for the WS<sub>2</sub> determination. When the Fermi levels reach equilibrium, the IO/WS<sub>2</sub> heterostructure is formed, as shown in Figure 6b. Figure 6c explains the reason for the improved gas-sensing performance of the IO/WS<sub>2</sub> heterostructure nanocomposite-based sensor. As the IO/WS<sub>2</sub> heterostructure formed, WS<sub>2</sub> obtained the electrons transferring from In<sub>2</sub>O<sub>3</sub>, leading to more oxygen molecules adsorbed on WS<sub>2</sub> (reaction 4) with more oxygen ions produced. The result is consistent with the XPS result. Reaction 5 is thus



promoted. When exposed to ammonia, the generated oxygen ions would react with the ammonia to produce more nitric oxide, water and electrons [32].

Figure 6. (a) Band diagram of the IO/WS<sub>2</sub> heterostructure before contact; (b) band diagram of the IO/WS<sub>2</sub> heterostructure after contact; (c) illustration of redox reaction occurring at the interface of WS<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>.

The released electrons would return to  $WS_2$ , leading to the improved sensing response of the IO/WS<sub>2</sub> heterostructure nanocomposite-based sensor. However, beyond the optimum concentrations of 1%, the concentration of IO/WS<sub>2</sub> heterostructures decreased because the formed IO/WS<sub>2</sub> heterostructures were fully covered by the introduced In<sub>2</sub>O<sub>3</sub> particles, leading to a lower sensor response [33]. The involved chemical reaction equations are as follows [30]:

$$O_2(air) \rightarrow O_2(ads),$$
 (3)

$$O_2 (ads) + e^- \rightarrow O_2^- (ads) \text{ (below 100 °C)}$$
(4)

$$4NH_3 + 5O_2^- \to 4NO + 6H_2O + 5e^-$$
(5)

The sensing properties of the WS<sub>2</sub> microflake-based sensor and the IO/WS<sub>2</sub> heterostructure nanocomposite-based sensors in response to different concentrations of ammonia from 1 ppm to 10 ppm at room temperature are displayed in Figure 7a. It can be seen that all the IO/WS<sub>2</sub> heterostructure nanocomposite-based sensors have much higher responses than the pure WS<sub>2</sub> microflake-based sensor. The IO/WS<sub>2</sub>-1 sample with 1% In<sub>2</sub>O<sub>3</sub> content exhibited the maximum response to different concentrations of ammonia. The calibration plots of the sensors are shown in Figure 7b. The response of the sensors to NH<sub>3</sub> from 1 ppm to 10 ppm indicates a typical tendency as reported in most studies. Figure 7c demonstrates that the fabricated IO/WS<sub>2</sub>-1 sensor exhibits good repeatability at room temperature. The good long-term stability of the IO/WS<sub>2</sub>-1 sample is evidenced in Figure 7d. This sample has small baseline fluctuation under the same conditions.



**Figure 7.** (**a**,**b**) Response curves and values of WS<sub>2</sub> microflake-based sensor and IO/WS<sub>2</sub> heterostructure nanocomposite-based sensors upon exposure to different concentrations of ammonia at room temperature; (**c**) repeatability of IO/WS<sub>2</sub>-1 heterostructure nanocomposite-based sensor at room temperature; (**d**) long-term stability and baseline of IO/WS<sub>2</sub>-1 heterostructure nanocomposite-based sensor.

Figure 8a exhibits the selectivity of the WS<sub>2</sub> microflake-based sensor and the IO/WS<sub>2</sub>-1 heterostructure nanocomposite-based sensor for ammonia, formaldehyde, toluene, methanol, ethanol and acetone at room temperature. It indicates that the synthesized IO/WS<sub>2</sub>-1 heterostructure nanocomposite-based sensor has an obvious response to ammonia. However, this sensor has no obvious response to other test gases, showing good selectivity at room temperature. Based on a previous report for WS<sub>2</sub>, the WS<sub>2</sub> matrix phase has good response to ammonia [24]. However, it does not have responses to other gases such as formaldehyde, toluene, methanol, ethanol and acetone at room temperature. With the introduction of  $In_2O_3$ , the formed IO/WS<sub>2</sub> heterostructure improved the performance of WS<sub>2</sub> in response to ammonia while not changing the non-responsive function of WS<sub>2</sub> for other gases.

Figure 8b shows the influence of the relative humidity on the response/baseline of the  $IO/WS_2$ -1 sensor for 10 ppm  $NH_3$  at room temperature. The  $IO/WS_2$ -1 sensor attained its maximum response when the humidity was about 50%. When the humidity was lower or higher than 50%, the response of the sensor decreased. The corresponding baseline resistance also had the minimum value at 50% RH, which became larger when the humidity was above or below 50% RH.

In comparison, the ZnO/WS<sub>2</sub> and SnO<sub>2</sub>/WS<sub>2</sub> heterostructure nanocomposites were also examined in this work. The detailed sensing characterizations are provided in Figures S4–S8 in the Supplementary Materials. The preparation and testing methods for the two materials are basically the same as those for the  $In_2O_3/WS_2$  heterostructure nanocomposites. The major merits of each type of WS<sub>2</sub>-based sensor are summarized in Table 1 together with the comparisons to more results reported in the literature. The  $In_2O_3$ -incorporated WS<sub>2</sub> nanocomposites show more advantages in detecting NH<sub>3</sub> at room temperature in terms of the sensitivity and response/recovery speeds. This indicates that the special "chemical catalytic" properties of the  $In_2O_3$  in response to ammonia may play a role in this difference in performance. It is reported that  $In_2O_3$  nanoparticles could provide more hydroxide species, resulting in the promotion of ammonia electro-oxidation [34].



**Figure 8.** (a) Gas-sensing selectivity of  $WS_2$  microflake-based sensor and  $IO/WS_2$ -1 heterostructure nanocomposite-based sensor for different gases (10 ppm); (b) response and baseline resistance of  $IO/WS_2$ -1 heterostructure nanocomposite-based sensor to 10 ppm ammonia under different humidities.

	able 1. A comparison of the	performance of NH <sub>3</sub> sensors	based on WS <sub>2</sub> materials.
--	-----------------------------	--	-------------------------------------

Sensitive Material	NH <sub>3</sub> Concentration	Temperature (°C)	Response (%)	Response/ Recovery (s/s)	Ref.
WS <sub>2</sub> nanoflakes	5 ppm	RT	217 <sup>a</sup>	120/150	[24]
rGO/WS <sub>2</sub>	10 ppm	RT	71	240/600	[35]
2:1 CuO/WS <sub>2</sub> nanohybrids	60 ppm	RT (30 °C)	59.5	35/213	[36]
$WS_2/WO_3$	10 ppm	150 °C	400	~150/~100	[37]
$Au/WS_2$	1 ppm	RT	191.54	968/788	[30]
$IO/WS_2$	1 ppm	RT	129.84	160/44	This work
$ZnO/WS_2$	1 ppm	RT	133.63	288/44	This work
$SnO_2/WS_2$	1 ppm	RT	117	224/24	This work

<sup>a</sup>: data obtained by conversion of data in the literature.

### 4. Conclusions

Compared to the pure WS<sub>2</sub> microflake-based sensor, the sensors based on In<sub>2</sub>O<sub>3</sub>incorporated WS<sub>2</sub> heterostructure nanocomposites exhibited a significantly improved response to ammonia at room temperature. In comparison to the ZnO/WS<sub>2</sub> and SnO<sub>2</sub>/WS<sub>2</sub> nanocomposites, In<sub>2</sub>O<sub>3</sub>-decorated WS<sub>2</sub> has better sensing features overall, including a better response with a faster response speed. The WS<sub>2</sub> with 1 wt.% In<sub>2</sub>O<sub>3</sub> nanocomposites achieve the highest response and the fastest response/recovery speeds. The sensor exhibited excellent signal repeatability and good long-term stability. It also possesses a good selectivity for formaldehyde, toluene, methanol, ethanol and acetone and is thus a promising candidate for detecting low-concentration NH<sub>3</sub> at room temperature.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/chemosensors10100402/s1, Figure S1. Elemental distribution of IO/WS<sub>2</sub>-1 heterostructure nanocomposites based sensor; Figure S2. (a,b) W 4f and S 2p refined core spectra of WS<sub>2</sub>, (c,d) W 4f and S 2p refined core spectra of IO/WS<sub>2</sub>-1 heterostructures nanocomposites based sensor; Figure S3. In 3d refined core spectra of In<sub>2</sub>O<sub>3</sub>; Figure S4. Elemental distribution of SnO<sub>2</sub>/WS<sub>2</sub>-1 heterostructure nanocomposites based sensor; Figure S5. (a,b) Response curves and response values of WS<sub>2</sub> and ZnO/WS<sub>2</sub> heterostructure nanocomposites based sensors to different concentrations of ammonia at room temperature, (c) response/recovery time of WS<sub>2</sub> and ZnO/WS<sub>2</sub> heterostructure nanocomposites based sensors to 10 ppm ammonia at room temperature, (d) relationship between ZnO/WS<sub>2</sub>-1 heterostructure nanocomposites based sensor's response/baseline resistance and humidity; Figure S6. (a). The response curve of the prepared ZnO/WS<sub>2</sub> heterostructure nanocomposites based sensors to 0.47 ppm ammonia at room temperature, (b) the selectivity of the WS<sub>2</sub> and ZnO/WS<sub>2</sub> heterostructure nanocomposites based sensors to different gases at room temperature; Figure S7. (a,b) Response curves and values of WS<sub>2</sub> microflakes based sensor and SnO<sub>2</sub>/WS<sub>2</sub> heterostructure nanocomposites based sensors to different concentrations of ammonia at room temperature, (c) response/recovery time of the SnO<sub>2</sub>/WS<sub>2</sub> heterostructure nanocomposites based sensors to 10 ppm ammonia at room temperature, (d) repeatability of SnO<sub>2</sub>/WS<sub>2</sub>-1 heterostructure nanocomposites based sensor; Figure S8. (a) The relationship between the response/baseline resistance and humidity of SnO<sub>2</sub>/WS<sub>2</sub>-1 heterostructure nanocomposites based sensor, (b) selectivity of the WS<sub>2</sub> microflakes based sensor and SnO<sub>2</sub>/WS<sub>2</sub> heterostructure nanocomposites based sensors to different gases; Table S1. The relative concentrations of each element in IO/WS<sub>2</sub>-1 heterostructure nanocomposites based sensor.

**Author Contributions:** Conceptualization, J.Y.; methodology, X.L.; validation, B.H.; formal analysis, Q.G.; investigation, Q.G.; resources, J.Z.; data curation, Q.G. and B.H.; writing—original draft preparation, Q.G.; writing—review and editing, X.L.; supervision, X.L.; project administration, X.L.; funding acquisition, B.H. and X.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors highly appreciate the financial support from the National Key R&D Program of China (No. 2021YFB3201302), National Natural Science Foundation of China (No. 61971085, 61874018, 62201117, 62111530055), the Fundamental Research Funds for the Central Universities (No. DUT19RC(3)054) and Dalian Science and Technology Innovation Fund Project (No. 2019J12GX048).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- 1. Negwamba, T.; Dinka, M.O. Assessing the performance of Trichardt Wastewater Treatment Plant (South Africa). *Phys. Chem. Earth* **2019**, *114*, 102784. [CrossRef]
- Cecilia, C.; Federica, B.; Marcella, G. Ammonia concentration and recommended threshold values in pig farming: A review. In Proceedings of the IEEE International Workshop on Metrology for Agriculture and Forestry, Trento-Bolzano, Italy, 3–5 November 2021; pp. 162–166.
- 3. Macedonio, F.; Frappa, M.; Bamaga, O. Application of a membrane condenser system for ammonia recovery from humid waste gaseous streams at a minimum energy consumption. *Appl. Water Sci.* **2022**, *12*, 90. [CrossRef]
- Berwal, P.; Kumar, S.; Khandelwal, B. A comprehensive review on synthesis, chemical kinetics, and practical application of ammonia as future fuel for combustion. *J. Energy Inst.* 2021, 99, 273–298. [CrossRef]
- Mallouppas, G.; Ioannou, C.; Yfantis, E.A. A Review of the Latest Trends in the Use of Green Ammonia as an Energy Carrier in Maritime Industry. *Energies* 2022, 15, 1453. [CrossRef]
- 6. Gardner, R. Use of the reciprocal calculation procedure for setting workplace emergency action levels for hydrocarbon mixtures and their relationship to lower explosive limits. *Ann. Occup. Hyg.* **2011**, *55*, 326–339.
- 7. Pedersen, J.M.; Feilberg, A.; Kamp, J.N.; Hafner, S.; Nyord, T. Ammonia emission measurement with an online wind tunnel system for evaluation of manure application techniques. *Atmos. Environ.* **2020**, 230, 117562. [CrossRef]
- 8. Orozco, J.L.; Caneghem, J.V.; Hens, L.; González, L.; Lugo, R.; Díaz, S.; Pedroso, I. Assessment of an ammonia incident in the industrial area of Matanzas. *J. Clean. Prod.* **2019**, 222, 934–941. [CrossRef]
- 9. Kwak, D.; Lei, Y.; Maric, R. Ammonia gas sensors: A comprehensive review. *Talanta* 2019, 204, 713–730. [CrossRef]
- 10. Aarya, S.; Kumar, Y.; Chahota, R.K. Recent Advances in Materials, Parameters, Performance and Technology in Ammonia Sensors: A Review. J. Inorg. Organomet. Polym. 2020, 30, 269–290. [CrossRef]
- 11. Tsymbalov, A.V.; Kalygina, V.M.; Maksimova, N.K.; Chernikov, E.V. Ammonia sensors based on resistive structures M–SnO<sub>2</sub>: Sb–M. J. Phys. Conf. Ser. 2020, 1499, 012037. [CrossRef]
- 12. Kathwate, L.H.; Umadevi, G.; Kulal, P.M.; Nagaraju, P.; Dubal, D.P.; Nanjundan, A.K.; Mote, V.D. Ammonia gas sensing properties of Al doped ZnO thin films. *Sens. Actuators A Phys.* **2020**, *313*, 112193. [CrossRef]
- 13. Yamazoe, N.; Tamaki, J.; Miura, N. Role of hetero-junctions in oxide semiconductor gas sensors. *Mater. Sci. Eng. B* **1996**, *41*, 178–181. [CrossRef]
- 14. Chen, Y.; Wu, J.; Xu, Z.; Shen, W.; Wu, Y.; Corriou, J.P. Computational assisted tuning of Co-doped TiO<sub>2</sub> nanoparticles for ammonia detection at room temperatures. *Appl. Surf. Sci.* **2022**, *601*, 154214. [CrossRef]
- 15. Büyükköse, S. Highly selective and sensitive WO<sub>3</sub> nanoflakes based ammonia sensor. *Mater. Sci. Semicond. Process.* **2020**, 110, 104969. [CrossRef]

- Bhardwaj, S.K.; Bhardwaj, N.; Kukkar, M.; Sharma, A.L.; Kim, K.H.; Deep, A. Formation of High-Purity Indium Oxide Nanoparticles and Their Application to Sensitive Detection of Ammonia. *Sensors* 2015, 15, 31930–31938. [CrossRef]
- 17. Sharieh, J.K.; Rahim, G.; Maryam, S. Attached two folded graphene nanoribbons as sensitive gas sensor. *Phys. B Condens. Matter* **2022**, *628*, 413630.
- 18. Tang, X.; Debliquy, M.; Lahem, D.; Yan, Y.; Raskin, J.P. A Review on Functionalized Graphene Sensors for Detection of Ammonia. *Sensors* **2021**, *21*, 1443. [CrossRef]
- Rani, S.; Sharma, M.; Verma, D.; Ghanghass, A.; Bhatia, R.; Sameera, I. Two-dimensional transition metal dichalcogenides and their heterostructures: Role of process parameters in top-down and bottom-up synthesis approaches. *Mater. Sci. Semicond. Process.* 2022, 139, 106313. [CrossRef]
- Sukhwinder, S.; Jyotirmoy, D.; Utpal, S.; Sandeep, S. MoS<sub>2</sub>/WO<sub>3</sub>Nanosheets for Detection of Ammonia. ACS Appl. Nano Mater. 2021, 4, 2594–2605.
- Xia, Y.; Xu, L.; He, S.; Zhou, L.; Wang, M.; Wang, J.; Komarneni, S. UV-activated WS<sub>2</sub>/SnO<sub>2</sub> 2D/0D heterostructures for fast and reversible NO<sub>2</sub> gas sensing at room temperature. *Sens. Actuators B Chem.* 2022, 364, 131903. [CrossRef]
- Wang, X.; Huang, B.; Wu, X.; Gu, D.; Li, X. Enhanced ammonia sensing properties of rGO/WS<sub>2</sub> heterojunction based chemiresistive sensor by marginal sulfonate decoration. *Sens. Actuators B Chem.* 2021, 337, 129776. [CrossRef]
- 23. Kim, J.H.; Mirzaei, A.; Kim, J.Y.; Yang, D.H.; Kim, S.S.; Kim, H.W. Selective CO gas sensing by Au-decorated WS<sub>2</sub>-SnO<sub>2</sub> core-shell nanosheets on flexible substrates in self-heating mode. *Sens. Actuators B Chem.* **2022**, 353, 131197. [CrossRef]
- Li, X.; Li, Z.; Wang, J.; Zhang, J. WS<sub>2</sub> nanoflakes based selective ammonia sensors at room temperature. Sens. Actuators B Chem. 2017, 240, 273–277. [CrossRef]
- 25. Tian, J.; Chen, X.; Wang, T.; Pei, W.; Li, F.; Li, D.; Yang, Y.; Dong, X. Modification of indium oxide nanofibers by polyoxometalate electron acceptor doping for enhancement of gas sensing at room temperature. *Sens. Actuators B Chem.* **2021**, 344, 130227.
- Yang, Z.; Zhang, D.; Chen, H. MOF-derived indium oxide hollow microtubes/MoS<sub>2</sub> nanoparticles for NO<sub>2</sub> gas sensing. *Sens. Actuators B Chem.* 2019, 300, 127037. [CrossRef]
- 27. Zhang, D.; Wu, J.; Cao, Y. Cobalt-doped indium oxide/molybdenum disulfide ternary nanocomposite toward carbon monoxide gas sensing. *J. Alloy. Compd.* **2019**, 777, 443–453. [CrossRef]
- Zhang, S.; Song, P.; Zhang, J.; Yan, H.; Li, J.; Yang, Z.; Wang, Q. Highly sensitive detection of acetone using mesoporous In<sub>2</sub>O<sub>3</sub> nanospheres decorated with Au nanoparticles. *Sens. Actuators B* 2017, 242, 983–993. [CrossRef]
- Zoleikha, H.; Reza, T.L.; Fereshteh, R.A. 3-Identification and analytical methods. In *Heterogeneous Micro and Nanoscale Composites* for the Catalysis of Organic Reactions; Elsevier: Amsterdam, The Netherlands, 2022; pp. 33–51.
- Guang, Q.; Huang, B.; Li, X. Au-Decorated WS<sub>2</sub> Microflakes Based Sensors for Selective Ammonia Detection at Room Temperature. Chemosensors 2022, 10, 9. [CrossRef]
- Huang, B.; Wang, Y.; Hu, Q.; Mu, X.; Zhang, Y.; Bai, J.; Wang, Q.; Sheng, Y.; Zhang, Z.; Xie, E. A low temperature and highly sensitive ethanol sensor based on Au modified In<sub>2</sub>O<sub>3</sub> nanofibers by coaxial electrospinning. *J. Mater. Chem. C* 2018, *6*, 10935. [CrossRef]
- Liu, Z.; He, T.; Sun, H.; Huang, B.; Li, X. Layered MXene heterostructured with In<sub>2</sub>O<sub>3</sub> nanoparticles for ammonia sensors at room temperature. Sens. Actuators B Chem. 2022, 365, 131918. [CrossRef]
- Liu, W.; Gu, D.; Li, X. Ultrasensitive NO<sub>2</sub> Detection Utilizing Mesoporous ZnSe/ZnO Heterojunction-Based Chemiresistive-Type Sensors. ACS Appl. Mater. Interfaces 2019, 11, 29029–29040. [CrossRef] [PubMed]
- Silva, J.C.M.; Piasentin, R.M.; Spinace, E.V.; Neto, A.O.; Baranova, E.A. The effect of antimony-tin and indium-tin oxide supports on the catalytic activity of Pt nanoparticles for ammonia electro-oxidation. *Mater. Chem. Phys.* 2016, 180, 97–103. [CrossRef]
- Wang, X.Y.; Gu, D.; Li, X.; Lin, S.; Zhao, S.; Rumyantseva, M.N.; Gaskov, A.M. Reduced graphene oxide hybridized with WS<sub>2</sub> nanoflakes based heterojunctions for selective ammonia sensors at room temperature. *Sens. Actuators B Chem.* 2019, 282, 290–299. [CrossRef]
- Zhao, C.; Wang, P.; Niu, G.; Luo, D.; Wang, Q.; Wang, F. Rapid and Efficient Detection of NH<sub>3</sub> at Room Temperature Using CuO/WS<sub>2</sub> Nanohybrids. *IEEE Sens. J.* 2022, 17, 3175827. [CrossRef]
- 37. Perrozzi, F.; Emamjomeh, S.M.; Paolucci, V.; Taglieri, G.; Ottaviano, L.; Cantalini, C. Thermal stability of WS<sub>2</sub> flakes and gas sensing properties of WS<sub>2</sub>/WO<sub>3</sub> composite to H<sub>2</sub>, NH<sub>3</sub> and NO<sub>2</sub>. *Sens. Actuators B Chem.* **2017**, *243*, 812–822. [CrossRef]