



# Incorporating N Atoms into SnO<sub>2</sub> Nanostructure as an Approach to Enhance Gas Sensing Property for Acetone

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**Abstract:** The development of high-performance acetone gas sensor is of great significance for environmental protection and personal safety. SnO<sub>2</sub> has been intensively applied in chemical sensing areas, because of its low cost, high mobility of electrons, and good chemical stability. Herein, we incorporated nitrogen atoms into the SnO<sub>2</sub> nanostructure by simple solvothermal and subsequent calcination to improve gas sensing property for acetone. The crystallization, morphology, element composition, and microstructure of as-prepared products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Electron paramagnetic resonance (EPR), Raman spectroscopy, UV–visible diffuse reflectance spectroscopy (UV–vis DRS), and the Brunauer–Emmett–Teller (BET) method. It has been found that N-incorporating resulted in decreased crystallite size, reduced band-gap width, increased surface oxygen vacancies, enlarged surface area, and narrowed pore size distribution. When evaluated as gas sensor, nitrogen-incorporated SnO<sub>2</sub> nanostructure exhibited excellent sensitivity for acetone gas at the optimal operating temperature of 300 °C with high sensor response ( $R_{air}/R_{gas} - 1 = 357$ ) and low limit of detection (7 ppb). The nitrogen-incorporated SnO<sub>2</sub> gas sensor shows a good selectivity to acetone in the interfering gases of benzene, toluene, ethylbenzene, hydrogen, and methane. Furthermore, the possible gas-sensing mechanism of N-incorporated SnO<sub>2</sub> toward acetone has been carefully discussed.

**Keywords:** acetone gas sensor; nitrogen incorporating; mesoporous structure; tin oxide

## 1. Introduction

Gas sensor has many important applications such as environment monitoring, industrial and personal safety, and medical diagnostics, etc. In recent years, the indoor pollutions of volatile organic compounds (VOCs) have been much concerned as the inhalation of the slowly released VOCs could induce chronic toxic effects to human health. Acetone is one of the typical VOCs, which has been frequently applied in scientific labs and industries. High concentration of acetone (>173 ppm) can anaesthetize the central nervous system and cause damage to important organs of the human body. Consequently, some major environmental safety agencies including National Institute of Occupational Safety and Health (NIOSH) and European Agency for Safety and Health at Work (EU-OSHA) have established guidelines to limit the exposure of human to acetone in indoor and workplace air [1]. For example, the cumulative exposure limits of acetone gases measured in an average user-adjusted period of 4–16 h is 250 ppm and 1000 ppm prescribed by NIOSH and EU-

OSHA, respectively. Therefore, high sensibility with a ppm-level detection limit and good selectivity towards acetone are required for acetone gas sensor applied in indoor and workplace. Among the versatile candidate materials for gas sensor towards acetone, metal oxides such as  $\text{SnO}_2$  [2],  $\text{WO}_3$  [3],  $\text{ZnO}$  [4], and  $\text{In}_2\text{O}_3$  [5] are most commonly used due to their good sensitivity and low power consumption. In particular,  $\text{SnO}_2$  shows excellent gas sense performance and has been intensively investigated, because of its low cost, high electron conductivity, and good thermal and chemical stability [6,7]. It has been widely known that the sensitivity is an important parameter for the gas sensor, besides other parameters such as selectivity and response-recovery time [8]. The higher sensitivity means better capability to detect the target gas. However, the sensitivity towards acetone of the above-mentioned metal oxides materials is still to be improved for practical applications [9].

One feasible way for increasing the sensitivity is to choose the materials with large surface area to provide more active sites [10]. In this regard, many ingenious synthetic strategies have been used to prepare various types of nanostructured  $\text{SnO}_2$  such as porous hierarchical flower-like nanomaterials [11], hollow microcubes [12], porous microtubules [13], nanorods [14], nanowires [15], hierarchical micro-nanostructures [16]. Theoretically speaking, the improvement of the sensitivity by utilizing large surface area materials is limited as the properties of gas sensors are dependent primarily on the electronic and structural properties of the materials [17]. From this perspective, as a common method for modulating the electronic and structural properties of a semiconductor, the extrinsic ion incorporation is considered as an important competitive method. For instances, Singh et al. synthesized Er-doped  $\text{SnO}_2$  [18] and Gd-doped nanostructures [19] with enhanced sensor response resulted from large surface area and enormous oxygen vacancies [20]. Li et al. pointed that oxygen vacancies were beneficial to the adsorption of surface oxygen species, which was attributed to the enhanced gas sensitivity of Pr-doped  $\text{SnO}_2$  [21]. Gao et al. studied the acetone sensing properties of La-doped  $\text{SnO}_2$  nanoarrays [22]. Patil et al. reported the acetone gas sensing properties of Co-doped  $\text{SnO}_2$  thin films [23].

Despite the tremendous researches on the influence of cationic incorporation on  $\text{SnO}_2$  gas-sensing properties, researches on anion incorporation are rather limited. Guo et al. reported that the sensitivity of  $\text{SnO}_2$  gas sensor towards  $\text{H}_2$  was significantly improved by Fluorine (F) doping because of the increased conductivity [24]. Basu et al. studied the enhanced gas sensing behaviour of F-doped  $\text{SnO}_2$  towards alcohol [25]. When compared with F element, nitrogen (N) is another ideal dopant for  $\text{SnO}_2$  because of the similar ionic radii of nitrogen and oxygen [26]. It is reported that the intrinsic electrical resistance and signal noise level could be well reduced by nitrogen (N)-incorporation of metal oxides [27]. Sun et al. showed that the N-doping would result in a reduction in band gap and it was energetically favourable for substituting O with N [28]. In bulk N-incorporated  $\text{SnO}_2$ , significantly enhanced conductivities were observed [29]. However, there is no gas sensor implication for N incorporated  $\text{SnO}_2$  nanostructure and it is still unclear whether N incorporation can effectively enhance the gas-sensing property of  $\text{SnO}_2$ .

Here, we report our first step toward this direction and show that the incorporation of nitrogen into the  $\text{SnO}_2$  nanostructure enhances its gas sensing properties towards acetone. The relevant acetone gas-sensing mechanism of N-incorporated  $\text{SnO}_2$  gas sensor was discussed.

## 2. Materials and Methods

### 2.1. Sample Preparation

In the experiment, the samples were prepared by simple solvothermal and subsequent calcination. For the synthesis of N-incorporated  $\text{SnO}_2$  sample, 1.0518 g  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was dissolved in 32 mL ethanol (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and then 1.2608 g hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ , Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was added to the transparent solution with vigorous stirring, which formed a white suspension. The suspension was put into a 45 mL Teflon-lined stainless-steel autoclave, which was heated at 180 °C for 24 h and cooled naturally. The resultant product was washed by water and ethanol several times, and then dried in air at 80 °C for 12 h.

Finally, the dried product was calcined at 550 °C for 2 h to obtain N-incorporated SnO<sub>2</sub> nanostructure. For the synthesis of pure SnO<sub>2</sub> sample, no C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> was used, while the other experiment conditions were the same. The key synthesis process of N-incorporated SnO<sub>2</sub> nanostructure is shown in Figure 1.



**Figure 1.** Scheme of the synthesis process of N-incorporated SnO<sub>2</sub> nanostructure.

## 2.2. Sample Characterization

X-ray diffraction (XRD, MiniFlex II, Rigaku, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan) were used to characterize the phase structures and microstructures of the samples, respectively. Scanning electron microscopy (SEM, JSM-6700-F, JEOL, Tokyo, Japan) and energy dispersive spectrometer (EDS, Oxford INCA Energy 250, Oxford Instruments, Abingdon, UK) were employed to study the elements distribution. X-ray photoelectron spectroscopy (XPS, ESCA-LAB250XI, Waltham, MA, USA) was used to characterize chemical compositions and valence states of the samples with a monochromatic Al Ka X-ray source. Electron paramagnetic resonance (EPR, Bruker-BioSpin E500, Rheinstetten, Germany) was performed to study the defects of the samples. Raman spectroscopy (Horiba, Labram HR800 Evolution, Kyoto, Japan) was employed to characterize structural information of the samples. UV–visible diffuse reflectance spectroscopy (UV-vis DRS, UV-2600) was measured to study the band-gap energies of the samples. The surface area and porosity analyzer (ASAP2460, Micromeritics, Norcross, GA, USA) were used to investigate the pore size distribution and specific surface area by Barrett–Joyner–Halenda (BJH) model and Brunauer–Emmett–Teller (BET) method, respectively.

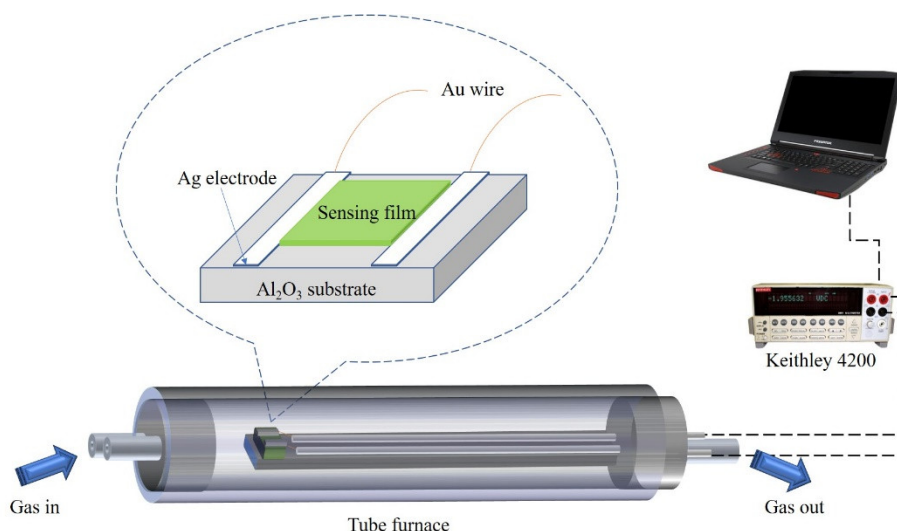
## 2.3. Sensor Fabrication and Test

A home-made system [30] was used to characterize the sensor. In brief, the sensing film of N-incorporated or pure SnO<sub>2</sub> samples were formed by drop-coating on the substrate of Al<sub>2</sub>O<sub>3</sub> with two Ag electrodes, whose two ends were connected with Au wires. The structure of the sensor and test device are shown in Figure 2. For the fabrication of Ag electrode, Ag paste was first printed on the Al<sub>2</sub>O<sub>3</sub> substrate and Au wires and then dried by irradiation under an infrared lamp, which made Au wires, Ag powder, and the Al<sub>2</sub>O<sub>3</sub> substrate stick together. All of them were heated at 550 °C for 30 min to sinter together. Since the work function of SnO<sub>2</sub> studied in this work is ~3.1–3.6 eV, Ag seems to be the best electrode for conductive contact due to the high work function of Au and Pt. The obtained sensor was then put in to a quartz chamber for the test of the sensitivity. Before the test, the sensor was preheated and stabilized at 400 °C for 20 h to achieve good ohmic contact. The linear V-I curves of the N-incorporated sample on Ag electrodes coated Al<sub>2</sub>O<sub>3</sub> substrate at 300 °C clearly imply good ohmic contact of the sensing film and the metal electrode (Figure S1). When the test began, the quartz chamber was fulfilled with target gas for ~0.65 min with 600 mL min<sup>−1</sup> gas flow. The target gas was introduced into the quartz tube by mixing the certified gas “mixtures” (Beijing Hua Yuan Gas Chemical Industry Co., Ltd., Beijing, China) and dry air in a proper ration controlled by the mass

flow controllers (CS-200C, Beijing Sevenstar Qualiflow Electronic Equipment Manufacturing Co., Ltd., Beijing, China). The bias on the sensor was set to 5 V. Keithley 4200 Sourcemeter was used to record the current. The response was defined as the ratio of sensor resistance in air and in the detected gas ( $R_{\text{air}}/R_{\text{gas}} - 1$ ), in which  $R_{\text{air}}$  and  $R_{\text{gas}}$  represent the electrical resistance of the sensor in air and test gas, respectively. The response/recovery time is defined as the time required for the resistance of the sensor to change to 90%/10% of the saturation value after exposure to the test gas/air. The coefficient of variation (CV) is used to represent the repeatability of the sensor, which is defined as

$$C_v = R_{SD}/R_{\text{average}} \times 100\%, \quad (1)$$

where  $R_{SD}$  and  $R_{\text{average}}$  are the standard deviation (SD) and average value of responses, respectively.



**Figure 2.** Illustration of gas sensor structure and test device.

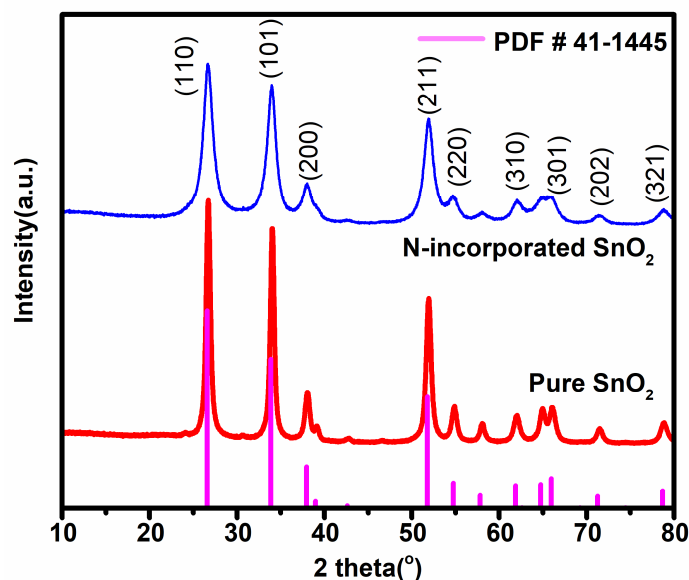
### 3. Results and Discussion

#### 3.1. Morphology and Structural Characterization

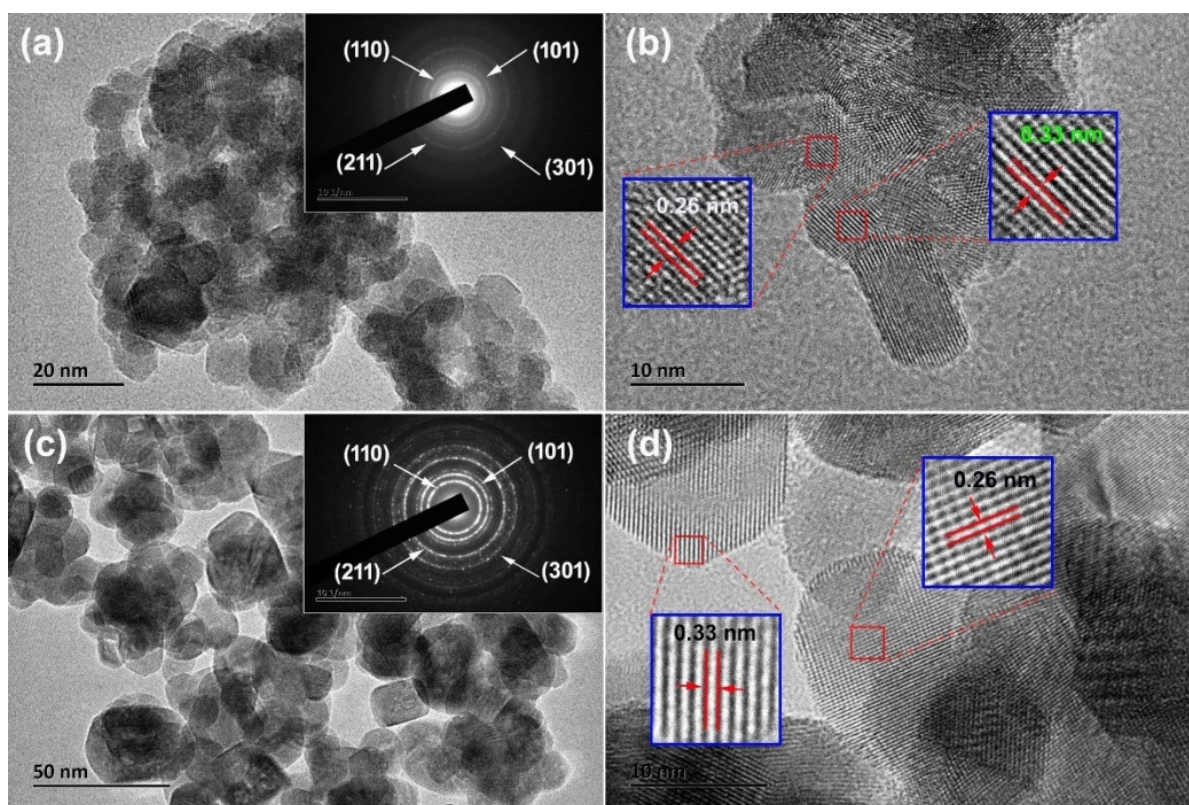
The XRD patterns of N-incorporated  $\text{SnO}_2$  and pure  $\text{SnO}_2$  samples were shown in Figure 3. All diffraction peaks of N-incorporated  $\text{SnO}_2$  sample matched well with the standard diffraction data (PDF. No. 41-1445) for rutile structure  $\text{SnO}_2$ . Comparatively, the diffraction peak positions of the pure  $\text{SnO}_2$  sample remained unchanged, while the diffraction peaks were apparently sharpened and the peak intensity became stronger. It indicates relatively higher crystallinity and larger crystallite size of the pure  $\text{SnO}_2$  sample than those of the N-incorporated  $\text{SnO}_2$  sample. In both samples, no other diffraction peaks of impurities phase were found. Based on the data of the (101) diffraction peaks, the average crystallite sizes of both samples were calculated by Scherrer's formula [31]; these were 12 nm for the N-incorporated  $\text{SnO}_2$  sample and 30 nm for the pure  $\text{SnO}_2$  sample, respectively.

To study the morphology and microstructures of N-incorporated  $\text{SnO}_2$  and pure  $\text{SnO}_2$  samples, TEM, high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) patterns were measured, as shown in Figure 4. Figure 4a shows that the N-incorporated  $\text{SnO}_2$  sample was composed of nanoparticles of 10–20 nm in diameter, which were aggregated together to form porous structure. Comparatively, as shown in Figure 4b, the particle size of nanoparticles of the pure  $\text{SnO}_2$  sample was increased to 15–40 nm in diameter. The pore sizes of the pure  $\text{SnO}_2$  sample were also apparently larger than that of the N-incorporated  $\text{SnO}_2$  sample. The phenomenon of particle size reduction in  $\text{SnO}_2$  nanoparticles induced by nitrogen incorporation was also reported by Wang et al., which could be due to the suppression role of nitrogen atoms in the long-range order formation of host lattices [32]. The SAED pattern of the N-incorporated  $\text{SnO}_2$  sample (inset in Figure 4a) was featured by diffuse diffraction rings, as compared with distinct polycrystalline diffraction rings with some bright spots in the pure  $\text{SnO}_2$  sample (inset in Figure 4b). HRTEM images (Figure 4c,d) of both samples reveals

distinct lattice lines with spacings of 0.33 and 0.26 nm, which are attributed to the (110) and (101) planes of rutile structure  $\text{SnO}_2$  [33]. Thus, both samples were well crystallized, which is consistent with the XRD results.



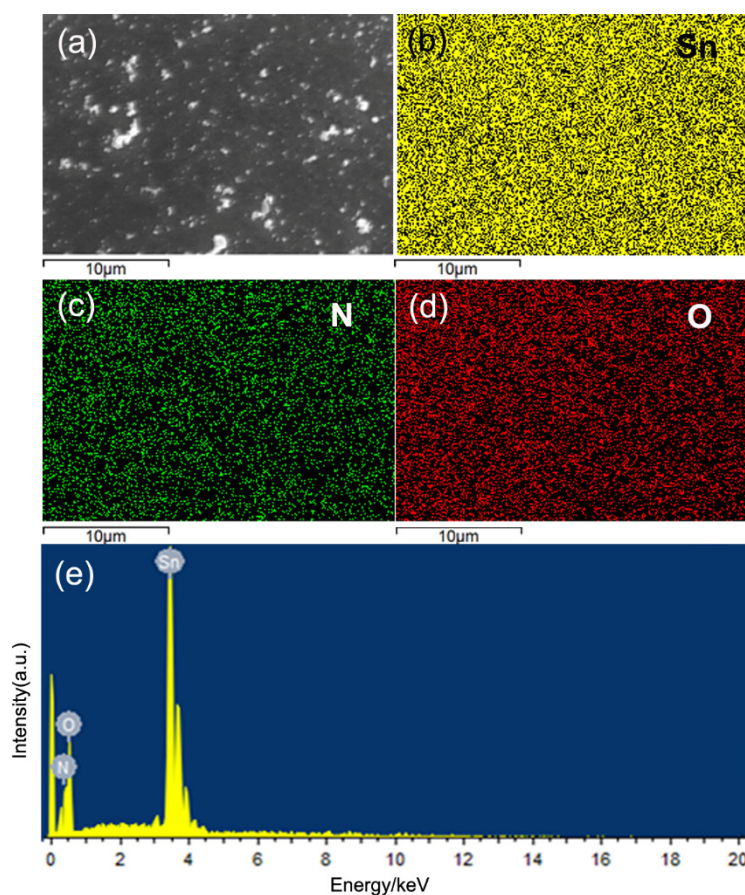
**Figure 3.** The XRD patterns of N-incorporated  $\text{SnO}_2$  and pure  $\text{SnO}_2$  samples.



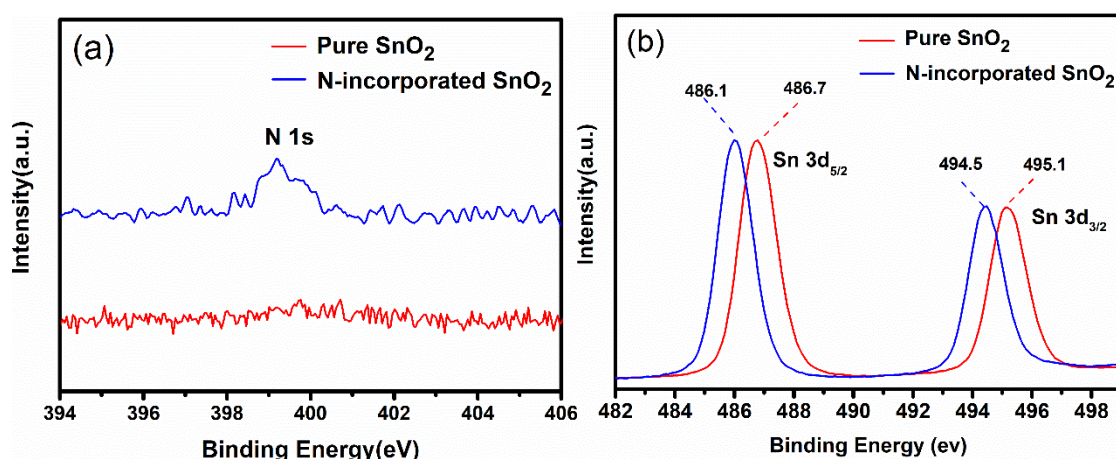
**Figure 4.** Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the samples: TEM image (a) and HRTEM image (b) of N-incorporated  $\text{SnO}_2$  sample; TEM image (c) and HRTEM image (d) of pure  $\text{SnO}_2$  sample. The insets in (a) and (c) show the SAED patterns of the samples.

In order to verify the existence of the nitrogen incorporation in  $\text{SnO}_2$  nanoparticles, we carried out a detailed study on elements distribution and chemical compositions by EDS and XPS. As shown by EDS mapping results in Figure 5, only elements Sn, N, and O were found and they were

homogeneously distributed in the N-incorporated  $\text{SnO}_2$  samples. Since no impurity phases were found in XRD detection, it indicates that nitrogen atoms could be incorporated into  $\text{SnO}_2$ . The nitrogen incorporation is also confirmed by XPS analyses (Figure 6). A peak at 399.3 eV of N1s was only observed in N-incorporated  $\text{SnO}_2$  sample (Figure 6a), which confirmed the nitrogen incorporation into the surface of the sample [34]. Quantitative results show that the N content was 1.79 at% in N-incorporated  $\text{SnO}_2$  sample. Figure 6b shows the Sn 3d spectra of N-incorporated and pure  $\text{SnO}_2$  samples. For pure  $\text{SnO}_2$  sample, the peaks at 486.7 eV and 495.1 eV were identified to the standard Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> peaks of rutile  $\text{SnO}_2$ , respectively. It indicates the existence of  $\text{Sn}^{4+}$  [35]. The difference of Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> peaks is 8.4 eV, which is in agreement with that in the literatures [36]. However, for N-incorporated  $\text{SnO}_2$  sample, the core binding energy of Sn 3d<sub>5/2</sub> and Sn 3d<sub>3/2</sub> peaks shifted toward lower binding energy by 0.6 eV. Such blueshift to lower binding energy has been reported in nitrogen-incorporated  $\text{SnO}_2$  films [37] and defective black  $\text{SnO}_2$  [38]. It could be ascribed to (i) the shift of 3d orbital energy level resulted from  $\text{N}^{3-}$  that has higher coulombic potential than  $\text{O}^{2-}$  [37]; and (ii) the formation of oxygen vacancies caused by charge compensation effect, which resulted in fewer O neighbours around Sn on average [38].

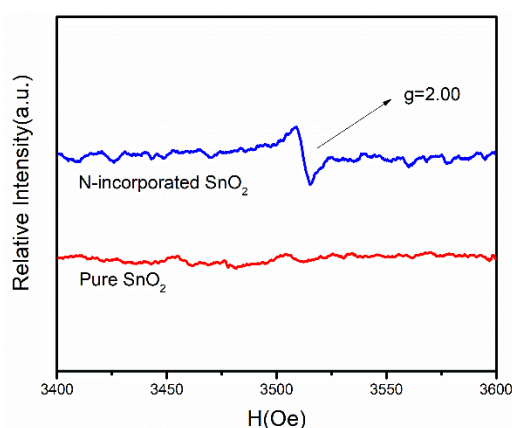


**Figure 5.** (a) Scanning electron microscopy (SEM) image and X-ray mapping of (b) Sn, (c) N, (d) O, and (e) energy dispersive spectrometry (EDS) spectrum of the N-incorporated  $\text{SnO}_2$  sample.



**Figure 6.** X-ray photoelectron spectroscopy XPS spectrum of (a) N 1s and (b) Sn 3d of N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples.

The existence of oxygen vacancies in N-incorporated SnO<sub>2</sub> sample was confirmed by the EPR signals. As shown in Figure 7, N-incorporated SnO<sub>2</sub> sample exhibited a strong signal at  $g = 2.00$ , which is attributed to the electrons trapped on oxygen vacancies. In contrast, no apparent signal for pure SnO<sub>2</sub> sample was observed. Thus, nitrogen incorporation is indicated to promote the formation of oxygen vacancies. Because the radius of nitrogen atom is close to that of the oxygen atom, the nitrogen atom can replace the oxygen atom. Since the nitrogen atom is trivalent and the oxygen atom is divalent, the doping of two nitrogen atoms will theoretically form an oxygen vacancy. Moreover, it is reported that nitrogen doping also reduces the formation energy of oxygen vacancies [39], which is also beneficial to the increase in oxygen vacancy concentration.



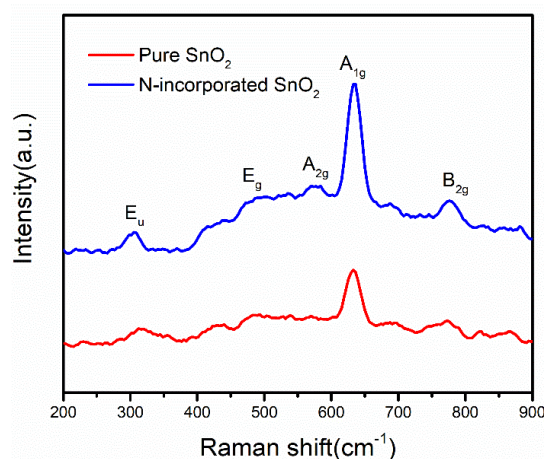
**Figure 7.** Electron paramagnetic resonance (EPR) signals of N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples.

In order to obtain more detailed information of oxygen vacancies, Raman spectra were further performed to study the structure difference between N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples, as shown in Figure 8. It is well known that the normal lattice vibration modes of rutile structure SnO<sub>2</sub> at the  $\Gamma$  point of the Brillouin zone are given by

$$\Gamma = 1A_{1g} + 1A_{2g} + 2A_{2u} + 1B_{1g} + 1B_{2g} + 2B_{1u} + 1E_g + 4E_u, \quad (2)$$

Among these lattice vibration modes, three modes of  $A_{1g}$ ,  $B_{2g}$ , and  $E_g$  are Raman active. Other modes including  $A_{2g}$ ,  $A_{2u}$ ,  $B_{1g}$ ,  $B_{1u}$ , and  $E_u$  are Raman inactive because they do not appear in the single-crystal SnO<sub>2</sub> according to symmetry analysis [40]. It was observed that both N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples clearly exhibited three characteristic vibration modes of  $A_{1g}$ ,  $B_{2g}$ , and  $E_g$ , which confirmed the rutile structure of SnO<sub>2</sub>. We noticed that the Raman inactive vibration modes of  $E_u$  and  $A_{2g}$  were also observed, which were located at around 300 and 578 cm<sup>-1</sup>, respectively. The appearance

of these inactive vibration modes has been ascribed to the existence of oxygen vacancies in rutile SnO<sub>2</sub> [41]. Notwithstanding similar spectral features in both samples, the intensities of A<sub>1g</sub>, A<sub>2g</sub>, and E<sub>u</sub> peaks appeared to be much stronger in N-incorporated SnO<sub>2</sub> sample in comparison with the pure SnO<sub>2</sub> sample. It is well documented [42] that oxygen vacancies in SnO<sub>2</sub> could be classified as three types of subbridging, bridging, and in-plane oxygen vacancies, which are responsible for E<sub>u</sub>, A<sub>1g</sub>, and A<sub>2g</sub> modes, respectively. The peak intensities of these modes are proportional to the density of oxygen vacancies [43]. Thus, the incorporation of N atoms into SnO<sub>2</sub> apparently increased the concentration of these oxygen vacancies, which is well consistent with EPR result. Additionally, it is noted that the E<sub>u</sub> peak exhibits a decrease in wavenumber (redshift) in N-incorporated SnO<sub>2</sub> sample. It has been widely accepted that oxygen has a Pauling electronegativity of 3.5, which is larger than that of 3 for nitrogen. Thus, the ability of an oxygen nucleus to attract electrons from the Sn atom is stronger than that of N atom. Therefore, the substitution of N<sup>3−</sup> for O<sup>2−</sup> would result in the increase of electron density around Sn atom in the O–Sn–O structure, as well as the formation of oxygen vacancies ascribed to the charge compensation effect. In consequence, the spatial charge between O and Sn could be redistributed to weaken the strength of the Sn–O bond, leading to the redshift of the E<sub>u</sub> peak. Thus, above results provide an insight into the impact of nitrogen incorporation in the Raman behaviour of oxygen vacancies in SnO<sub>2</sub> nanomaterials.



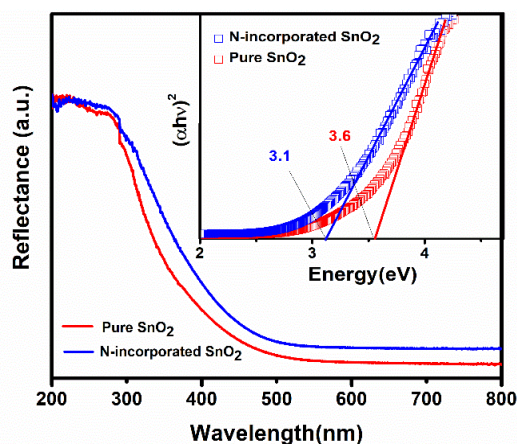
**Figure 8.** Raman spectra of the N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples.

To investigate the influence of nitrogen incorporation and oxygen vacancies on the band-gap width of rutile SnO<sub>2</sub>, UV–visible diffuse reflectance spectroscopy of N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples were performed. As shown in Figure 9, the absorption edge of N-incorporated SnO<sub>2</sub> sample shifts to a longer wavelength as compared to that of pure SnO<sub>2</sub> sample. Such a red-shift phenomenon is consistent with other experimental findings [37]. The band-gap energy can be calculated by the following equation:

$$\alpha h\nu = A (h\nu - E_g)^n, \quad (3)$$

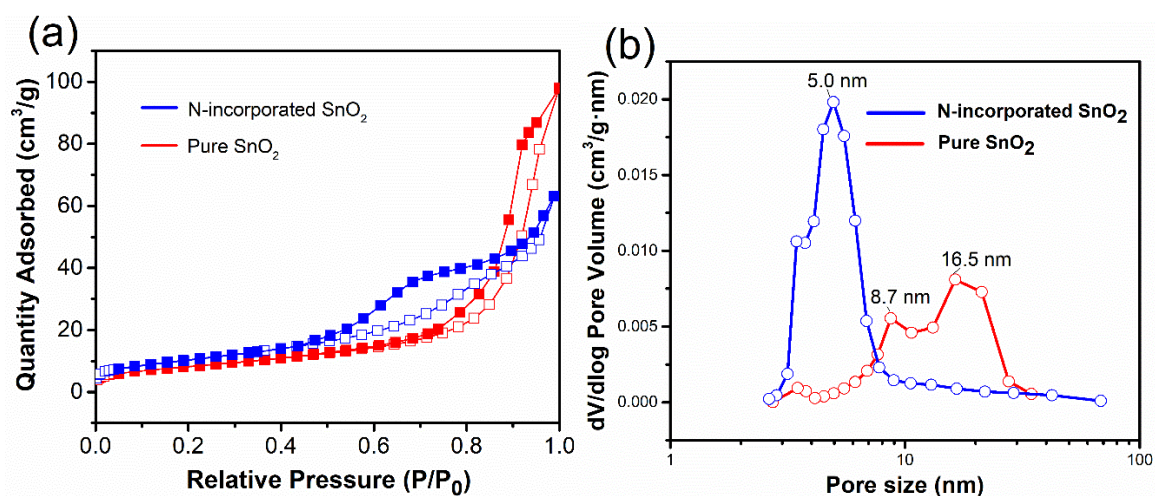
where  $\alpha$  is the absorption coefficient,  $E_g$  is the band-gap energy,  $h\nu$  is the photon energy,  $n$  equals 0.5 for direct allowed transition or 2 for indirect allowed transition, respectively. Since SnO<sub>2</sub> is a direct type semiconductor,  $n$  equals 0.5 in this case. Thus, the value of  $E_g$  can be obtained through extrapolating the linear portion towards zero absorption by fitting the plot of  $(\alpha h\nu)^2$  as a function of  $h\nu$ , as shown in the inset in Figure 9. It is seen that the value of  $E_g$  for pure SnO<sub>2</sub> is 3.6 eV, similar to the reported value for bulk SnO<sub>2</sub> [44], while the value of  $E_g$  for N-incorporated SnO<sub>2</sub> was decreased to 3.1 eV. Since it was well documented that the reduction of particle size could increase the band gap of SnO<sub>2</sub> [45], we believe that the nitrogen incorporation is the main reason for the decrease of the band-gap of N-incorporated SnO<sub>2</sub> sample. In this regard, Sun et al. [28] have performed the density functional theory (DFT) calculations of nitrogen doping behaviours on the single-crystalline rutile SnO<sub>2</sub>. Their calculation has drawn a conclusion that the N atom is energetically favourable to be

incorporated to the O site. As N atom is incorporated, the N 2p states are delocalized and contributory to the formation of some gap states hybridized by O 2p states and Sn 3d states, which results in a band to gap states transition and causes the reduction of the band-gap.



**Figure 9.** Optical diffuse reflectance spectra of the N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples. The inset shows the energy dependence of  $(\alpha h\nu)^2$  for the samples.

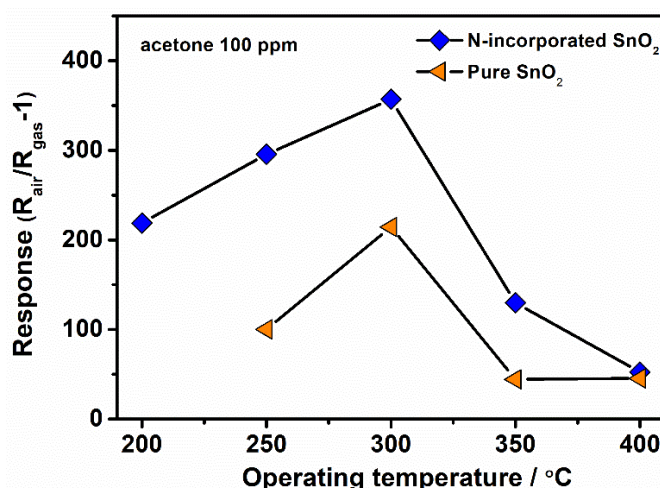
The impacts of N incorporating on the surface areas and pore distribution of the samples were investigated by the surface area and porosity analyzer. The surface area of N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples were calculated by BET method, which are 38.2 and 29.7 m<sup>2</sup>/g, respectively. The absorption–desorption isothermals of N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples are shown in Figure 10a. As can be seen, N-incorporated sample shows a typical IV type isotherm with a H2 hysteresis loop as classified by International Union of Pure and Applied Chemistry (IUPAC) [46], which is a characteristic of mesoporous system [47]. The sharp inflection of the hysteresis loop is located at a range of  $P/P_0 = 0.6–0.8$ . Comparatively, pure SnO<sub>2</sub> samples show a similar type isotherm, while the sharp inflection of hysteresis loop shifted toward higher  $P/P_0$  value. It indicates that the pore diameter of the mesoporous system increased. The pore size distribution curves for the mesoporous structures were determined from the desorption branches using the BJH model [48], as shown in Figure 10b. The N-incorporated SnO<sub>2</sub> sample exhibited a narrow pore size distribution centered at about 5 nm, while pure SnO<sub>2</sub> sample showed a broad pore size distribution centered at 8.7 and 16.5 nm. Therefore, the N-incorporated SnO<sub>2</sub> sample exhibits larger surface area and smaller mesopores than pure SnO<sub>2</sub> sample does, which may be beneficial to accelerating the adsorption and diffusion of target gas.



**Figure 10.** (a) N<sub>2</sub> adsorption-desorption isotherm curves and (b) pore size distribution curves of the N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> samples.

### 3.2. Gas sensing Properties

According to the increased oxygen vacancies concentration and mesoporous structure of the N-incorporated SnO<sub>2</sub> sample, we anticipate that it may probably possess good gas sensing properties. Sensor measurements were explored by using acetone as the target gas. We firstly studied the influence of working temperature on the sensor response of the N-incorporated SnO<sub>2</sub> sample to 100 ppm acetone gas, as well as that of pure SnO<sub>2</sub> sample for comparison, as shown in Figure 11. It can be seen that the sensor response of N-incorporated SnO<sub>2</sub> sample initially increased with the increasing of working temperature, and reached to a maximum response ( $R_{\text{air}}/R_{\text{gas}} - 1 = 357$ ) at 300 °C, and finally decreased with further increase of working temperature. Comparatively, the pure SnO<sub>2</sub> sample showed similar temperature dependent responses to 100 ppm acetone, except that its maximum response is only 215 at 300 °C. As shown in Figure S3, the poor response speed (>3 min) and the failure to recover to 10% of the resistance change clearly indicate that temperature higher than 200 °C is necessary for the N-SnO<sub>2</sub> sample. It has been reported that higher temperature can provide thermal energy for the reaction of the target gases and oxygen ions on the surface of SnO<sub>2</sub>, which is responsible for the increase of gas response with the increasing working temperature. At the same time, higher temperature can promote the desorption of oxygen ions from the surface of SnO<sub>2</sub>, which reduce the gas response of SnO<sub>2</sub>. In this work, the role of thermal energy is dominant below 300 °C, while the desorption of oxygen ions plays more significant role above 300 °C. In addition, it seems that nitrogen incorporation has no apparent impact on the optimal working temperature of SnO<sub>2</sub>. Thus, the optimal working temperature of 300 °C is applied in the subsequent gas sensing measurements.



**Figure 11.** Temperature dependent responses comparison of N-incorporated SnO<sub>2</sub> and pure SnO<sub>2</sub> gas sensors.

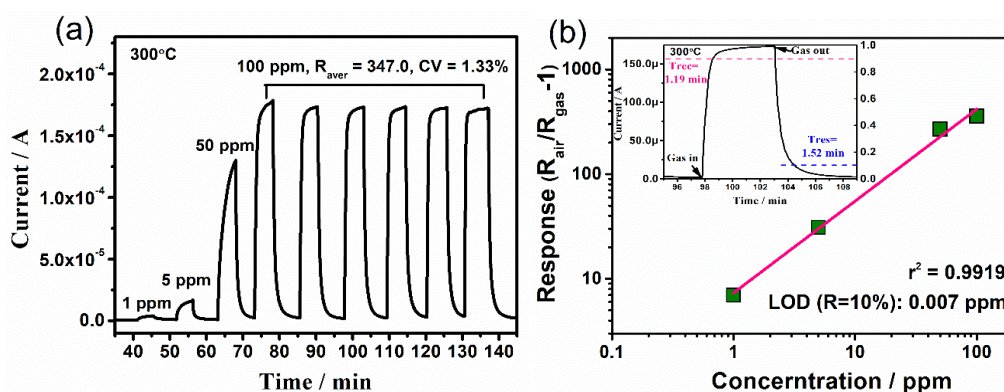
Figure 12a shows the dynamic responses of N-incorporated SnO<sub>2</sub> sample to acetone gas with different concentrations in dry air (1 ~ 50 ppm) and to 100 ppm acetone with six successive assays. The current curve presents good response-recovery to a broad range of the acetone concentrations (1 to 100 ppm) and typical behaviours of n-type semiconductor chemiresistor gas sensor. Notably, low  $C_v$  (1.33%) of six circles can be estimated, implying excellent repeatability of the device. According to the response equation of grain-based gas sensors and  $R = R_{\text{air}}/R_{\text{gas}} - 1$ , we can obtain the following equation (for resistance decrease) [49]:

$$\log R = \log(R_{\text{air}}/R_{\text{gas}} - 1) = \log A_g + \beta \log p_g \quad (4)$$

where  $p_g$  is the gas partial pressure,  $A_g$  is a prefactor, and the exponent  $\beta$  is the response order.

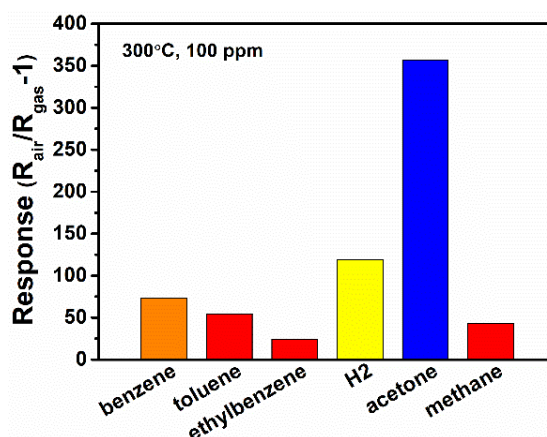
The limit of detection (LOD) as low as 0.007 ppm (7 ppb) of acetone was estimated according to Equation (4) by setting  $R = 0.1$  for N-SnO<sub>2</sub> (Figure 12b). Satisfying values of response time and recovery time can be obtained, which were calculated to be 1.19 min and 1.52 min, respectively. It is

found that recovery time obviously decreased with the increasing temperature, as shown in Figure S2. It is because that the additional thermal energy facilitates the adsorption/desorption of target gas molecules, thus good recovery at higher temperature can be accordingly observed.



**Figure 12.** (a) Typical response-recovery current curves toward acetone gas with different concentration, (b) log-log plots of concentration-responses of N-incorporated  $\text{SnO}_2$  gas sensor (the inset is the response and recovery time for the curve toward 100 ppm of acetone).

Furthermore, the selectivity of the sensor is evaluated by the cross-sensitivity measurement for a series of reducing gas (100 ppm for each) at 300 °C, as shown in Figure 13. For the indoor air monitoring and breath analysis, benzene and alkanes are two typical interferences for acetone sensing. Thus, we choose other reducing gas including benzene, toluene, ethylbenzene, hydrogen, and methane as the interfering gases. It can be found that the N-incorporated  $\text{SnO}_2$  sample shows much higher sensibility to acetone than other reducing gas including benzene, toluene, ethylbenzene, hydrogen, and methane, which indicate good selectivity of the N-incorporated  $\text{SnO}_2$  sample toward acetone gas. The stability of the N-incorporated  $\text{SnO}_2$  sample towards 100 ppm acetone at 300 °C was evaluated over a week period, as shown in Figure S4 in supporting information. The results show that the gas sensor maintains 97% of its original response to acetone. Thus, the N-incorporated  $\text{SnO}_2$  sample is expected to have good long-term stability. The repeatability within a batch of three samples is good with the relative standard deviation (RSD) of 2%, as shown in Table S1.



**Figure 13.** Cross-sensitivity toward 100 ppm of various reducing gas at 300 °C of N-incorporated  $\text{SnO}_2$  gas sensor.

For comparison, the sensing abilities of as-prepared N-incorporated  $\text{SnO}_2$  and other reported  $\text{SnO}_2$  nanostructures are listed in Table 1. It can be seen that N-incorporated  $\text{SnO}_2$  in this work exhibits outstanding gas sensing performance with the highest sensor response ( $R_{\text{air}}/R_{\text{gas}} - 1$ ) value of 357 and the lowest LOD value as 0.007 ppm (7 ppb) at 300 °C, demonstrating more superiority than those reported in the literature. Considering the low power consumption towards practical application, further experiments on developing low-temperature (<200 °C) N-incorporated  $\text{SnO}_2$  gas sensors still

need to be done in our future work. There are several good strategies such as the introduction of heterostructures [50], morphologies controlling [51], surface synergy [52,53], and molecule sieving layer coatings [49], etc.

**Table 1.** Gas responses to acetone of as-prepared N-incorporated SnO<sub>2</sub> and other reported SnO<sub>2</sub> nanostructures.

Sensing Materials	Acetone Concentration (ppm)	Working Temperature (°C)	Sensor Response ( $R_{air}/R_{gas} - 1$ )	LOD	Ref.
SnO <sub>2</sub> nanoparticles	100	240	17	0.2 ppm <sup>E</sup>	[54]
SnO <sub>2</sub> hollow microspheres	160	200	30	5 ppm <sup>E</sup>	[55]
SnO <sub>2</sub> nanopolyhedrons	100	370	29	1 ppm <sup>E</sup>	[56]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub> composites	100	250	15.8	10 ppm <sup>E</sup>	[57]
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @SnO <sub>2</sub> nanoparticles	100	370	5	10 ppm <sup>E</sup>	[58]
Fe-incorporated SnO <sub>2</sub>	100	200	29	0.1 ppm <sup>E</sup>	[59]
Eu-incorporated SnO <sub>2</sub> nanofibers	100	280	31.2	0.3 ppm <sup>E</sup>	[60]
Ca <sup>2+</sup> /Au co-incorporated SnO <sub>2</sub>	100	200	61	NM	[61]
cone-shaped SnO <sub>2</sub>	100	325	174	NM	[62]
Ce-incorporated SnO <sub>2</sub>	100	270	99	NM	[63]
Pd loaded Sm incorporated SnO <sub>2</sub>	100	200	15.7	NM	[64]
SnO <sub>2</sub> nanospikes arrays	100	320	39	0.5 ppm <sup>E</sup>	[65]
SnO <sub>2</sub> Hollow nanospheres	100	400	7.5	NM	[66]
Rh-incorporated SnO <sub>2</sub> nanofibers	100	200	132	NM	[67]
C <sub>3</sub> N <sub>4</sub> -SnO <sub>2</sub>	100	380	28 <sup>a</sup>	0.067 ppm <sup>C</sup>	[68]
In loaded WO <sub>3</sub> /SnO <sub>2</sub>	100	200	129	NM	[69]
SnO <sub>2</sub> /Au-incorporated In <sub>2</sub> O <sub>3</sub>	100	280	11.4	NM	[70]
Ag/SnO <sub>2</sub> hollow nano fibers	100	200	74	NM	[71]
Nanofibrous Pd-loaded SnO <sub>2</sub>	100	275	97.8	NM	[72]
N-incorporated SnO <sub>2</sub>	100	300	357	0.007 ppm <sup>C</sup>	TW

<sup>a</sup> Response calculated as  $V_g/V_a$ ; <sup>C</sup> Calculated value; <sup>E</sup> measured value; NM: not mentioned; TW: this work.

### 3.3. Gas-Sensing Mechanism

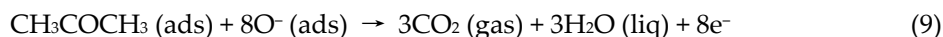
It has been known that the gas-sensing mechanism of SnO<sub>2</sub>-based gas sensor is primary ascribed to the resistance change of SnO<sub>2</sub> in different target gas atmospheres, which is caused by the adsorption and desorption of target gas molecules on the surface of SnO<sub>2</sub>. In air atmosphere, oxygen molecules are adsorbed on the surface of SnO<sub>2</sub> and capture the electrons from the conduction band of SnO<sub>2</sub>, forming the surface adsorbed oxygen species such as O<sub>2</sub><sup>-</sup> and O<sup>-</sup>. This progress could be described as follows:



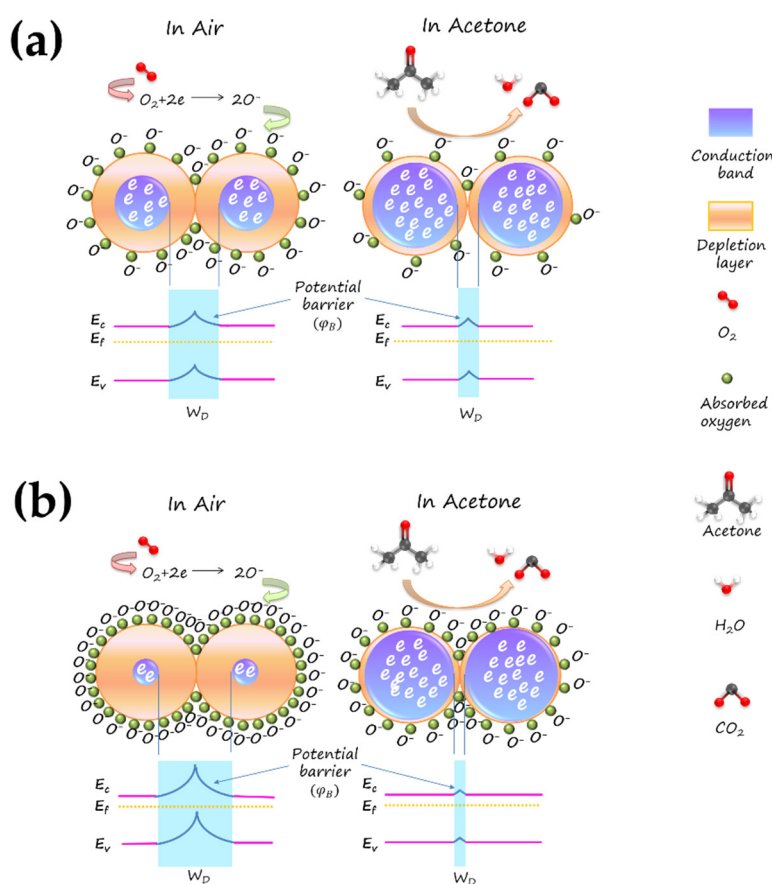
Under this condition, the concentration of free electrons in the conduction band of SnO<sub>2</sub> decreased, forming the electron depletion layer and potential barrier on the surface and at grain boundaries, respectively. As a result, the sensor resistance will increase vastly. The potential barrier could be described by Equation (8) [73]:

$$\varphi_B = AN_d W_D^2, \quad (8)$$

where  $\varphi_B$  is the potential barrier,  $N_d$  is the donor density,  $W_D$  is the width of depletion layer, and  $A$  is the constant. When in a condition of reducing gas of acetone, the surface oxygen species of SnO<sub>2</sub> would react with acetone and free the trapped electrons back into the conduction band of SnO<sub>2</sub>, which would reduce the width of the depletion layer and thus lower the height of potential barrier. Consequently, the sensor resistance will decrease. The possible reaction is shown in Equation (9) [74].



Having aforementioned discussion in mind, we believe that the significantly enhanced gas-sensing property of the N-incorporated sample should be mainly attributed to the following three main reasons. Firstly, the incorporation of nitrogen into  $\text{SnO}_2$  resulted in rich surface oxygen vacancies. These surface oxygen vacancies tend to adsorb oxygen molecules, because of the lower adsorption energy of oxygen molecules on the oxygen vacancy sites than that on the perfect sites [60,75]. Therefore, these surface oxygen vacancies can act as electron donors, making a great quantity of electrons in the conductive band captured in air and released in acetone atmosphere. It would greatly increase the difference of the width of depletion layer ( $W_D$ ) and the height of potential barrier ( $\varphi_B$ ) in different atmospheres, resulting in a higher response. Secondly, as N atom is incorporated, the N 2p states are delocalized and contributory to the formation of some gap states hybridized by O 2p states and Sn 3d states, which results in a band to gap states transition and causes the reduction of the band gap. It makes electrons more easily excited, which improves electron transport. Thirdly, the incorporation of nitrogen into  $\text{SnO}_2$  resulted in the reduction of particle size, along with the large surface area and unique mesoporous structure. These would provide more active sites on the surface of  $\text{SnO}_2$ , and facilitate acetone diffusion and mass transport within sensing material. Therefore, the N-incorporated  $\text{SnO}_2$  shows a superior gas sensing property. The gas-sensing mechanism of as-prepared N-incorporated  $\text{SnO}_2$  sensor is shown in Figure 14.



**Figure 14.** Schematic of acetone sensing mechanism of (a) pure  $\text{SnO}_2$  and (b) N-incorporated  $\text{SnO}_2$  samples.

#### 4. Conclusions

In summary, mesoporous N-incorporated  $\text{SnO}_2$  and pure  $\text{SnO}_2$  nanostructures have been prepared by simple solvothermal and calcination procedure. The XRD and TEM results showed that the N incorporating led to the decreased crystalline size of  $\text{SnO}_2$ , without changing the rutile crystal

structure. EDS and XPS analysis confirmed the presence of nitrogen in the N-incorporated SnO<sub>2</sub> nanostructure. It resulted in obviously increased surface oxygen vacancies, which has been revealed by EPR and Raman. It has been also observed that N-incorporated SnO<sub>2</sub> nanostructure exhibited reduced band-gap width, larger surface area, and smaller mesopore size, in comparison with pure SnO<sub>2</sub>. The gas sensor based on N-incorporated SnO<sub>2</sub> nanostructure exhibited excellent acetone gas-sensing property with high sensor response ( $R_{\text{air}}/R_{\text{gas}} - 1 = 357$ ) and low limit of detection (7 ppb) at the optimal operating temperature of 300 °C. Moreover, the N-incorporated SnO<sub>2</sub> gas sensor shows a good selectivity to acetone in the interfering gases of benzene, toluene, ethylbenzene, hydrogen, and methane. The enhancing role of N incorporation could be attributed to increasing the surface oxygen vacancies, reducing band-gap width, and lowering the crystal size of nanoparticles. Hence, N-incorporated SnO<sub>2</sub> nanostructure could be a promising candidate material for highly sensitive gas sensor toward acetone gas. Our future studies will focus on the low-temperature N-incorporated SnO<sub>2</sub> gas sensor to meet the demand of low power consumption towards practical application.

**Supplementary Materials:** The following are available online at [www.mdpi.com/xxx/s1](http://www.mdpi.com/xxx/s1), Figure S1: The V-I curve of the N-incorporated SnO<sub>2</sub> sample on Ag electrodes coated Al<sub>2</sub>O<sub>3</sub> substrate at 300 °C; Figure S2: Typical response-recovery current curves of the N-incorporated SnO<sub>2</sub> gas sensor toward acetone gas with different concentration at different temperatures: (a) 250 °C; (b) 350 °C; (c) 400 °C; Figure S3: The response and recovery curve for the N-incorporated SnO<sub>2</sub> sample toward 1 ppm of acetone at 200 °C; Figure S4: Stability response curve of the N-incorporated SnO<sub>2</sub> gas sensor toward 100 ppm of acetone at 300 °C. Table S1: The repeatability within a batch of three samples.

**Author Contributions:** X.G. conceived, designed, performed the experiments, and wrote the paper; Y.W., P.L., Y.Y., D.C., and X.L. analyzed the data.

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

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