Improved ppb-level NO$_2$ conductometric sensor induced by trace Au on SnO$_2$ nanosheet

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ABSTRACT

As a main exhaust emission from vehicles, nitrogen dioxide is harmful to environment and human health. Gas sensors with high performance for nitrogen dioxide detection is essential. In this work, SnO$_2$ nanosheet aggregates loaded with Au were used to fabricate a NO$_2$ gas sensor. Pristine SnO$_2$ was synthesized via a solvothermal method. Subsequently, the ultraviolet (UV) light-assisted reduction method was utilized to load Au nanoparticles and improve the sensing properties. The SnO$_2$ modified with a trace of Au nanoparticles (0.5 wt%) shows high response to ppb-level NO$_2$ (35–100 ppb) at a low temperature (90 °C). Besides excellent selectivity and long-term stability, the 0.5% Au/SnO$_2$ based sensor can detect 2 ppb NO$_2$ with the response value of 1.2. The enhanced sensing properties can be attributed to the interface interaction between Au and SnO$_2$, causing the enhanced absorption capability for oxygen and NO$_2$ molecules. Additionally, trace amount of loading Au can maintain small size of Au nanoparticles, making the active sites on SnO$_2$ more effective. This work provides a convenient method for preparing a ppb-level NO$_2$ gas sensor with high performance.

1. Introduction

Nitrogen dioxide (NO$_2$) is the main exhaust emission from vehicles, aggravating the formation of acid rain and photochemical smog with the surge of vehicles in these years [1,2]. Undesirable consequences such as the reduction of atmospheric visibility [3], acidification of surface water [4], potential eutrophication [5] and the increasing content of toxins in waters can be witnessed. Besides the damage to environment, NO$_2$ can cause direct harm to human health. Even low concentration of NO$_2$ (53 ppb) may increase the incidence of acute respiratory diseases in children as announced by the US Environmental Agency [6]. Therefore, it is essential to monitor the concentration of NO$_2$ in our surrounding environment.

There are a few technologies to detect NO$_2$, including gas chromatography [7], electrochemistry method [8] and spectrophotometer [9], but their shortcomings, such as the complicated operation steps and bulky volume limit their widespread application. However, gas sensors made of metal oxide semiconductor (MOS) have attracted researchers'

attention in recent years because of their low cost, miniaturization and intriguing sensing performance [10,11]. NO$_2$ sensors based on typical MOS, including n-type semiconductors (SnO$_2$ [6,12,13], In$_2$O$_3$ [14,15]) and p-type semiconductors (NiO [16,17], CuO [1,18]), have been fabricated. Among them, n-type SnO$_2$ with a wide band of 3.59 eV is a potential material for detecting NO$_2$ [19]. However, the sensing performances of pure SnO$_2$ based gas sensors cannot completely satisfy the application requirement, especially selectivity and limit of detection (LOD) remaining problems to be solved. Several methods have been reported to improve the properties of gas sensing materials. Among them, noble metal (Au, Ag, Pd and Pt et al.) loading is an effective method, because noble metal nanoparticles have high catalytic activity [20–27]. Yu et al. fabricated H$_2$S sensor based on Pt-decorated ZnO nanorods and the obtained LOD was as low as 1.1 ppb [25]. Zhao et al. prepared Pd-In$_2$O$_3$ to detect methane and proved the significantly improved sensing properties with Pd loading [26]. Saito et al. prepared Au-loaded pyramid-shaped ZnO particles with a response value of 1371–1 ppm isoprene, which was 45 times higher than that of pristine

ZnO particles [21]. Wang et al. synthesized ZnO flowers functionalized by Au nanoparticle with outstanding sensing performance to acetone [24].

In this work, a trace of Au nanoparticles loaded SnO_2 was used to fabricate a NO_2 sensor. Compared to the pure SnO_2, the Au/SnO_2 exhibited higher sensitivity and faster response to ppb-level NO_2, especially reduced the LOD to 2 ppb. The effect brought about by Au nanoparticles was evaluated via multiple characterization methods. The increased concentration of oxygen vacancy and improved NO_2 adsorption property are attributed to the interface interaction between Au and SnO_2. The ameliorative NO_2 sensing performance was also given reasonable explanation.

2. Experimental section

All the chemical reagents used were analytically pure, they are listed in Table S1 in the Supplementary data.

2.1. Preparation of sensing materials

2.1.1. Preparation of SnO_2 nanosheet aggregates
In a typical preparation process, 2 mmol tin chloride dihydrate ($SnCl_2 \cdot 2 H_2O$), 1 mmol hexamethylene tetramine ($C_6H_{12}N_4$) and 10 mmol sodium hydroxide (NaOH) were dissolved into a mixture solution with 20 mL of deionized water and 20 mL of absolute alcohol. The above solution was stirred for 90 min, and then transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 18 h. After cooling down to RT naturally, the solid precipitates were collected by centrifugation and washed with deionized water and ethanol several times. After being dried in 80 °C for 12 h, the obtained powder was annealed at 500 °C for 3 h in a muffle furnace (heating rate was 1 °C min^{-1}).

2.1.2. Preparation of Au/SnO_2 nanosheet aggregates
Typically, 100 mg of the obtained SnO_2 powder was dispersed in ethanol and magnetically stirred. Then, a certain amount of $HAuCl_4$ aqueous solution (0.01 M) was added. Its mass ratios to SnO_2 were respectively 0.3%, 0.5%, and 1.0% for three samples. The solution was irradiated by ultraviolet (UV) light ($\lambda = 365$ nm, 10 mW/cm^2) for 5 min at room temperature with stirring. For comparison, another 0.5% Au/SnO_2 (S) was also obtained by impregnation reduction method. Sodium borohydride ($NaBH_4$) as well as $HAuCl_4$ were added into the SnO_2 aqueous suspension and stirred for 90 min. Subsequently, the Au/SnO_2 product was centrifugated with deionized water several times and dried for several hours. Finally, the collected powder was calcined at 400 °C for 2 h in a muffle furnace (heating rate was 1 °C min^{-1}). The synthetic process is schematically illustrated in Fig. 1.

2.2. Characterization

X-ray powder diffraction (XRD Rigaku D/Max 2550) with Cu Kα radiation ($\lambda = 0.15418$ nm) was used to analyze the crystalline phases of samples. The angle scanning range was from 20° to 70°. The field-emission scanning electron microscopy (FESEM JEOL JSM-7500 F) was utilized to observe the samples' morphologies, operated at an acceleration voltage of 10 kV, the attached energy dispersive X-ray spectrometry (EDS) was adopted to investigate the samples' elemental composition. The morphology details of the samples were obtained by transmission electron microscopy (TEM; JEOL JSM-2100 F) and high-resolution transmission electron microscopy (HRTEM; JEOL JSM-2100 F). To analyze the surface composition and element valence, X-ray photoelectron spectra (XPS) were carried out with Al Kα as the excitation source and corrected with respect to the standard peak of C 1 s at 284.3 eV. The desorption properties of the materials to NO_2 were measured by the NO_2 temperature programmed desorption (NO_2-TPD, AMI-300, USA) with a mass spectrometer for gas analysis (Omnistar, Pfeiffer, Germany).

2.3. Sensor fabrication and property testing

The schematic illustration of a chemiresistive gas sensor is shown in Fig. S1. Its fabrication process and measurement method on gas sensing were detailedly described in our previous work [28,29]. For the device fabrication, the mixture of sample powder and ethanol was made into slurry in an agate mortar and brushed uniformly onto a ceramic tube having a pair of gold electrodes at its two ends. To control the operating temperature of a sensor, a Ni-Cr alloy coil heater was inserted through the ceramic tube. Resistances of the as-fabricated device in air or target gas were measured by using a multimeter (Fluke 8864 A), whose maximum range is up to 1 GΩ. The traditional static testing system was adopted, different NO_2 concentration was obtained by diluting different volume of standard NO_2 gas with air in 1 L of the gas chamber. The sensitivity is defined as $S = R_a/R_g$ for reducing gas or $S = R_g/R_a$ for oxidizing gas, where R_a and R_g are the resistances in air and in certain test gas atmosphere, respectively. Gas response and recovery time are defined as the time required for 90% of the total resistance change throughout adsorption and desorption process. The effect of humidity on sensing performance was studied. The various relative humidity was set at 25 °C by using the humidity chamber (Shanghai ESPC Environment Equipment Corporation, China).
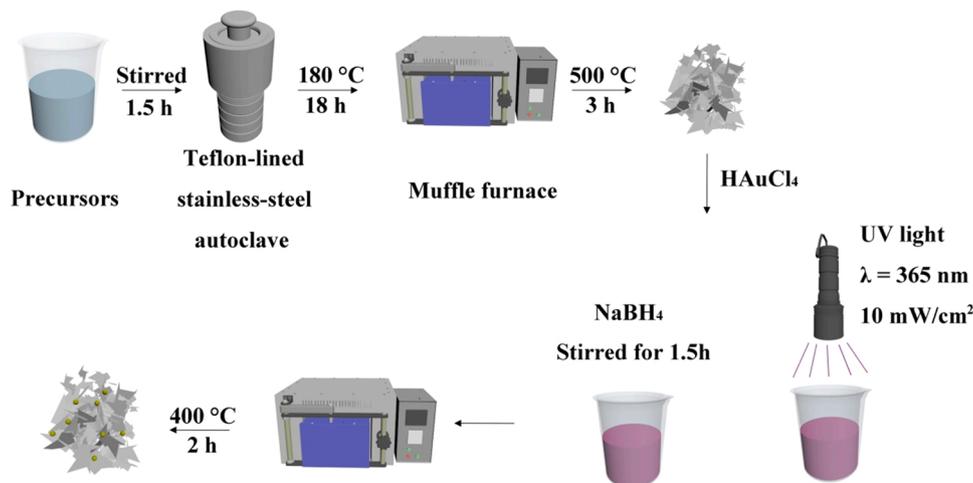
Fig. 1. Schematic diagram of the preparing process of Au loaded SnO_2.

3. Results and discussion

3.1. Characterization of the Samples

To investigate the phase information of the samples, the powder XRD patterns of the pristine SnO_2, 0.3% Au/SnO_2, 0.5% Au/SnO_2, 0.5% Au/SnO_2 (S) and 1.0% Au/SnO_2 were measured and shown in Fig. 2 (a). For the first four samples, their diffraction peaks can be completely matched with those of rutile SnO_2 (JCPDS PDF 41–1445) without extra characteristic diffraction peaks from Au. For 1.0% Au/SnO_2, an additional peak at around 44.5° (Fig. 2 (b)), which corresponds to (200) diffraction of Au (JCPDS PDF 1–1174) can be observable. The increased loading amount of Au for 1.0% Au/SnO_2 brings about the detectable signal from Au.

The FESEM images of pure SnO_2, 0.3% Au/SnO_2, 0.5% Au/SnO_2, 0.5% Au/SnO_2 (S) and 1.0% Au/SnO_2 are presented in Fig. S2. It can be seen that all these SnO_2 samples are made up of nanosheet aggregates with the size of a few microns. Au loading does not have significant effect on the morphology of SnO_2. And the Au particles could be only discerned from FESEM pictures of 0.5% Au/SnO_2 (S) and 1.0% Au/SnO_2 (Fig. S2 (h) and Fig. S2 (j)). The contents of Au were analyzed by EDS (Fig. S3) and listed in Table S2, which are roughly consistent with desired results. To explore the detailed microstructure, the TEM and HRTEM images of all samples were obtained (Fig. 3, Fig. S4 and Fig. S5). The samples are composed of aggregated nanosheets, in agreement with their FESEM images. For Au loaded SnO_2, Au nanoparticles with distinct contrast can be apparently observed on the surface of the nanosheets. The size of Au nanoparticles is about 8–10 nm for 0.3% Au/SnO_2 and 0.5% Au/SnO_2. Their HRTEM images (Fig. 3 (c) and Fig. S4 (f)) further show the lattice spacing of 0.235 nm and 0.335 ± 0.001 nm, corresponding to the (111) lattice plane of Au and (110) lattice plane of SnO_2, respectively. But for 1.0% Au/SnO_2, the dimension of the Au nanoparticles is roughly 40 nm (Fig. S4 (g-i)), indicating the agglomeration of Au with the increasing amount of added $HAuCl_4$. As for 0.5% Au/SnO_2 (S), different sizes (10–60 nm) of Au nanoparticles can be observed, exhibiting the size inhomogeneity by impregnation reduction method (Fig. S5 (a-c)). Also, the elemental mapping images of 0.5% Au/SnO_2 (Fig. 3 (d-g)) and 0.5% Au/SnO_2 (S) (Fig. S5 (d-g)) describe the even dispersion of Sn, O, and Au elements throughout the sample. The above results verify that the Au nanoparticles are loaded on the SnO_2 nanosheets.

The surface atomic compositions and element chemical state of the samples were analyzed by X-ray photoelectron spectroscopy (XPS). The corresponding spectra of all the samples are shown in Fig. 4. All the signals from Sn, O, C and Au can be observed from their full spectra (Fig. 4 (a)). For pristine SnO_2, the peaks of Sn $3d_{3/2}$ and $3d_{5/2}$ are located at 494.53 and 486.13 eV (Fig. 4 (b)). However, with the amount of loaded Au increasing, these characteristic peaks shifted in the direction of high binding energy (Sn $3d_{3/2}$: from E (SnO_2) = 494.53 eV to E (1.0% Au/SnO_2) = 494.93 eV; Sn $3d_{5/2}$: from E (SnO_2) = 486.13 eV to E (1.0% Au/SnO_2) = 486.48 eV). This implies that electron density of Sn^{4+} in outer shell decreases by interaction of Au with SnO_2. The high resolution XPS of Au 4 f electron is shown in Fig. 4 (d). The binding energy at around 83.20 and 86.85 eV, is attributed to 4 $f_{7/2}$ and 4 $f_{5/2}$, respectively. Their energy positions are little lower than 84.00 and 87.71 eV of metallic Au [30,31], which is opposite to the above of Sn 3d XPS spectra. Combining the XPS spectra of Sn and Au, it is inferred that there exists electron transfer from SnO_2 to Au, which might be caused by the difference between their work functions. Additionally, the high-resolution spectra of O 1 s (Fig. 4 (c)) for all the samples can be fitted into three characteristic peaks, which are related to three kinds of oxygen species. The peaks at 529.8 ± 0.30, 530.8 ± 0.30, 532.2 ± 0.30 eV are attributed to the lattice oxygen (O_L), deficient oxygen (O_V) and surface-adsorbed oxygen (O_C), respectively [11]. The percentages of these oxygen species are listed in the Table S2. It shows that 0.5% Au/SnO_2 has the highest ratio of O_V/O_L and O_C/O_L among all the Au loaded SnO_2 samples.

The NO_2 temperature programmed desorption (NO_2 -TPD) curves of pure SnO_2 and 0.5% Au/SnO_2 were measured and compared (Fig. 5). As seen from them, there are several peaks which are related with desorption of two different nitrato species [32]. The start-up temperatures for desorption of pure SnO_2 and 0.5% Au/SnO_2 are about 80 °C. Meanwhile, the area under TPD curve is a little larger for 0.5% Au/SnO_2, presenting higher amount of adsorbed NO_2 molecules caused by more active sites. The above results verify the interfacial interaction between Au nanoparticles and SnO_2 has a positive effect on the NO_2 absorption properties.

3.2. Sensing performance

The responses of all these sensors based on pristine SnO_2, 0.3% Au/SnO_2, 0.5% Au/SnO_2 and 1.0% Au/SnO_2 toward 100 ppb NO_2 were measured at different operating temperature (Fig. 6 (b)). It can be seen that as the temperature goes up, the response values of the four sensors increase firstly and then decrease. The maximum response values for all sensors locate consistently at 90 °C. The relationship of response versus operating temperature was also discussed in pervious literature [30]. Compared to the pure SnO_2, Au-loaded SnO_2 shows a higher response to 100 ppb NO_2 at 90 °C. Among them, 0.5% Au/SnO_2 shows the maximum value of 35, which is 8.2 times higher than that of the pure SnO_2 (3.8). Continuing to increase Au content sharply decreases the response. The resistance values of the Au-loaded SnO_2 in fresh air also change because of Au loading. As shown in Fig. 6 (a), the Au-loaded SnO_2 samples
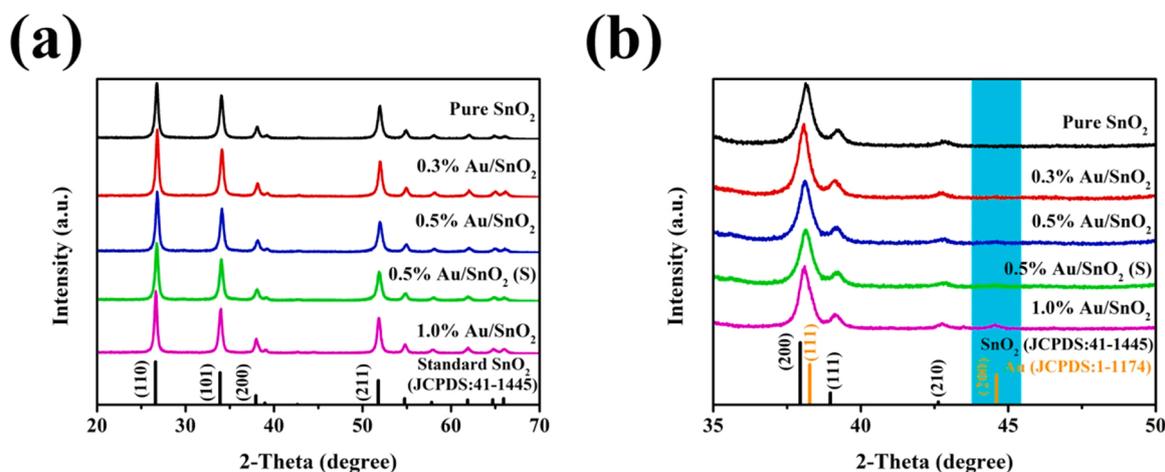
Fig. 2. (a) XRD patterns of the Au loaded SnO_2 samples with different Au loading amount. (b) Comparison of partial peaks from XRD spectra.
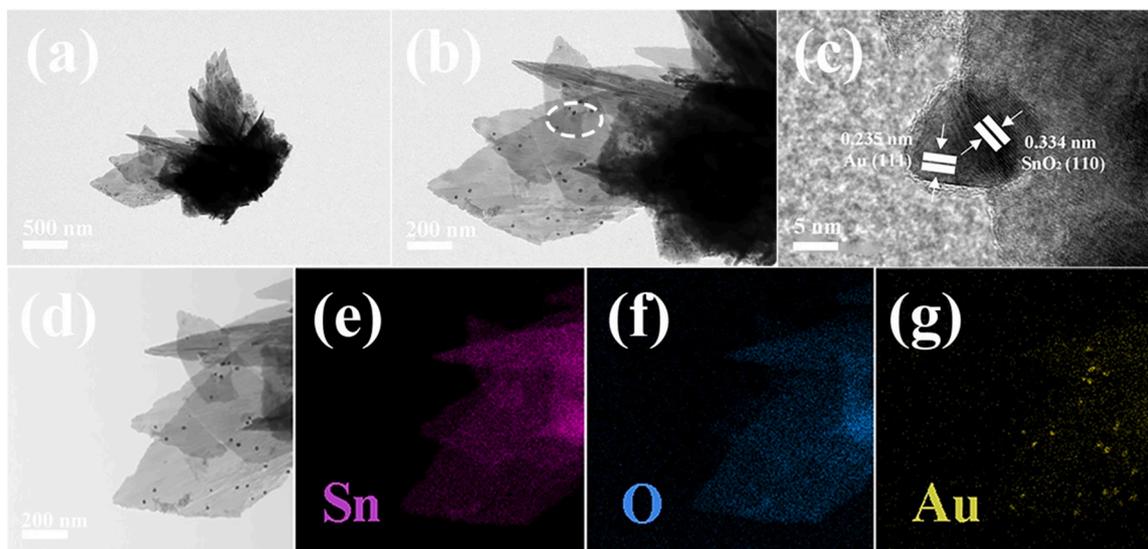
Fig. 3. (a, b) TEM and (c) HRTEM images; (d-g) sample and corresponding elemental mapping images of Sn, O and Au, respectively for 0.5% Au/SnO₂ sample.
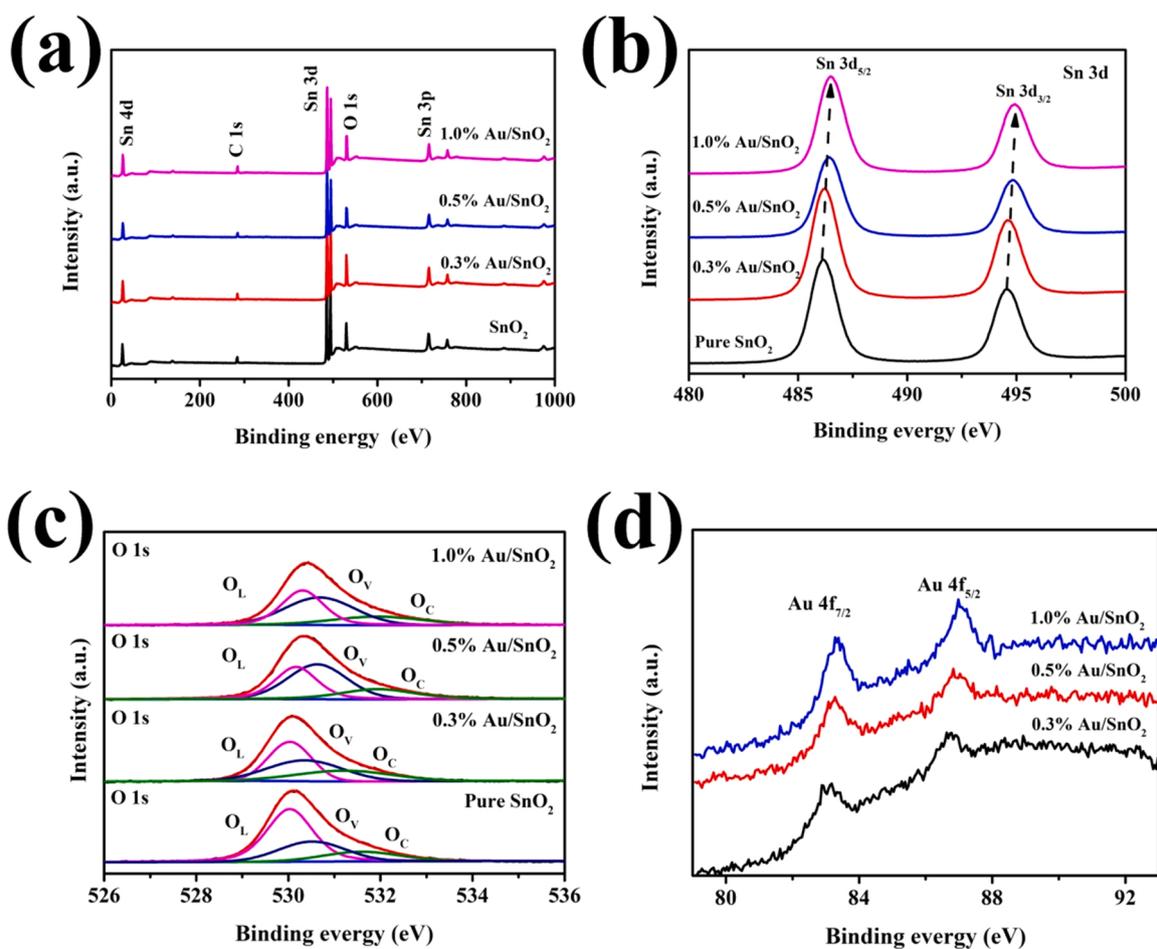
Fig. 4. XPS spectra of the samples: (a) full range, (b) Sn 3d (c) O 1 s, and (d) Au 4 f.

exhibit better conductivity than pristine SnO₂ and the 0.5% Au/SnO₂ has the lowest resistance. Deficient oxygen can be the main causes for it. For these samples, it is noteworthy that the concentration of oxygen vacancy, electric resistant and response value to NO₂ have the same change trend with increasing amount of loaded Au. Au nanoparticles with small size and well distribution are vital to this phenomenon.

Furthermore, the responses of the 0.5% Au/SnO₂ based sensor to various gases, including NO₂, CO, SO₂, NH₃, benzene, acetone, toluene and ethanol at 90 °C are compared in Fig. 6 (c). The respective concentration of NO₂, CO, SO₂ and NH₃ is 1 ppm, while it is 100 ppm for other VOCs. As seen for it, the response to NO₂ is far higher than those to the other gases by two orders of magnitude. It can be concluded that the 0.5%
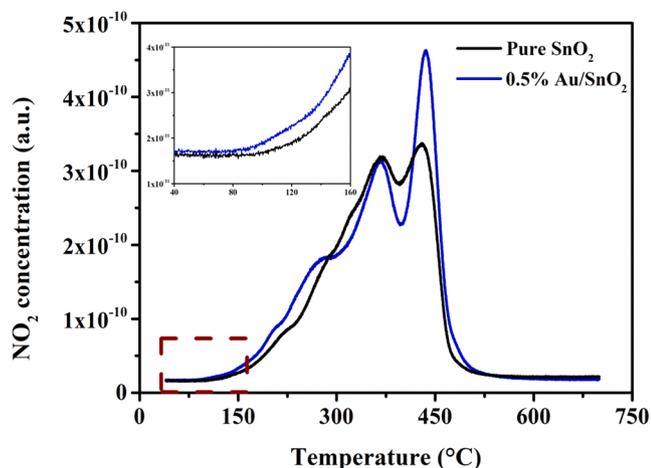
Fig. 5. NO₂ temperature-program desorption (TPD) curves of pure SnO_2 and 0.5% Au/SnO_2.

which S and C represents the sensor response and NO_2 concentration, respectively [33]. The slope of 0.5% Au/SnO_2 (1.41) is higher than that of pure SnO_2 (0.85), indicating a more promising sensing performance for detecting NO_2 [34]. In addition, 0.5% Au/SnO_2 based sensor have more excellent linearity (R^2 =0.99) in logarithmic form than pure SnO_2 (R^2 =0.94), illustrating the 0.5% Au/SnO_2 are more suitable to be used as sensing material in practical application [35]. Meanwhile, the transient response curve of the 0.5% Au/SnO_2 based sensor to 100 ppb NO_2 is shown in Fig. 7 (a). Compared to pure SnO_2 (Fig. S6), it displays faster response/recovery to NO_2. The response/recovery time of the 0.5% Au/SnO_2 based sensor is 484/286 s, while it is 740/2295 s for pure SnO_2. The dynamic response curves and response/recovery time of the 0.5% Au/SnO_2 based sensor with 20, 50, 100 and 200 ppb concentration of NO_2 were recorded (Fig. S7). The recovery time decreases with NO_2 concentration. It is not the case for response time. Given the high resistance value, which is beyond the upper measurement limit of Fluke 8864 A (1 GΩ) at NO_2 concentration higher than 200 ppb, the resistance was measured by using resistance meter SM-8213 (HIOKI). The dynamic process cannot be displayed at this situation.

Au/SnO_2 based sensor exhibits super selectivity toward NO_2 over these interference gases.

The relationship between response values of the sensors and gas concentration was investigated. Fig. 6 (d) provides the fitting function curves of pure SnO_2 and 0.5% Au/SnO_2 based sensors under different concentrations of NO_2 gas (20–1000 ppb). For these two sensors, it can be represented empirically by the function of Log(S-1) = aLogC + b,

To explore the LOD of the 0.5% Au/SnO_2 based sensor, the performance to several ppb NO_2 is investigated and the dynamic response curves are shown in Fig. 7 (b), 2 ppb NO_2 can be detected with the response value of 1.2. The corresponding response value versus NO_2 concentration is plotted in Fig. S8. It is worth emphasizing that simulated air was used in place of ambient air in the testing system to eliminate the impacts of NO_2 in air and ensure the correct detection at very low concentration of NO_2. Also, the dynamic response curves with

Fig. 6. (a) Resistance values of sensors based on Au loaded SnO_2 samples with different Au loading amount in fresh air at various temperatures; (b) The responses of sensors to 100 ppb NO_2 at different operating temperatures; (c) Responses of 0.5% Au/SnO_2 based sensor to various gases at 90 °C; (d) The fitting function curves of pure SnO_2 and 0.5% Au/SnO_2 based sensors under different concentrations of NO_2 gas (20–1000 ppb).

Fig. 7. (a) Transient curve of 0.5% Au/SnO$_2$ based sensor at 90 °C to 100 ppb NO$_2$; (b) The dynamic response curves of 0.5% Au/SnO$_2$ based sensor to NO$_2$ in low concentration (2–10 ppb), the insert shows the transient response curve to 2 ppb NO$_2$ (the LOD); (c) Long-term stability of 0.5% Au/SnO$_2$ based sensor to 100 ppb NO$_2$ at 90 °C in 150 days; (d) Four-cycle test curve of 0.5% Au/SnO$_2$ based sensor to 100 ppb NO$_2$.

20, 50, 100 ppb concentration of NO$_2$ were recorded in Fig. S9. It can be seen that the response to different concentration of NO$_2$ in simulated air has an unconspicuous increasement compared to that in ambient air. Also, the sensor displayed a tardier response/recovery without the interaction with water molecules. Additionally, long-term stability is a necessary factor for evaluating the sensing performance. The sensor based on 0.5% Au/SnO$_2$ was tested within 150 days. Its steady responses to 100 ppb NO$_2$ in Fig. 7 (c) exhibited its outstanding long-term stability. Good repeatability is also manifested in four cycle measurement (Fig. 7 (d)).

The influence of humidity on sensing performance should be considered in practical application. So, the transient response curves of 0.5% Au/SnO$_2$ based sensor to 100/200 ppb NO$_2$ at 90 °C were measured in various relative humidity (RH) (15%, 30%, 45%, 60%, 75% and 90%) (Fig. S10). As shown in Fig. 8 (a, b), both the response to NO$_2$ and resistance values in air decrease with the humidity increasing. Compared to the response values in 30% RH (routine humidity condition in testing system), a reduction of 31.4% to 100 ppb and 24.8% to 200 ppb in 90% RH were measured. This phenomenon may be explained by the process of active sites being poisoned with hydroxyl groups [36–38]. At high humidity, more water molecules occupy the adsorption sites on the surface of Au/SnO$_2$, impeding the adsorption of NO$_2$ molecules and reducing the response value. Moreover, response/recovery kinetics of the fabricated sensor are also affected by humidity (Fig. 8 (c)). The response time decreases from 484 s at 30% RH to 257 s at 90% RH and recovery time reduces from 286 s to 62 s. Such results might be attributed to the increased electronic conductivity caused by the interaction of SnO$_2$ with water molecule. The enhanced interaction between
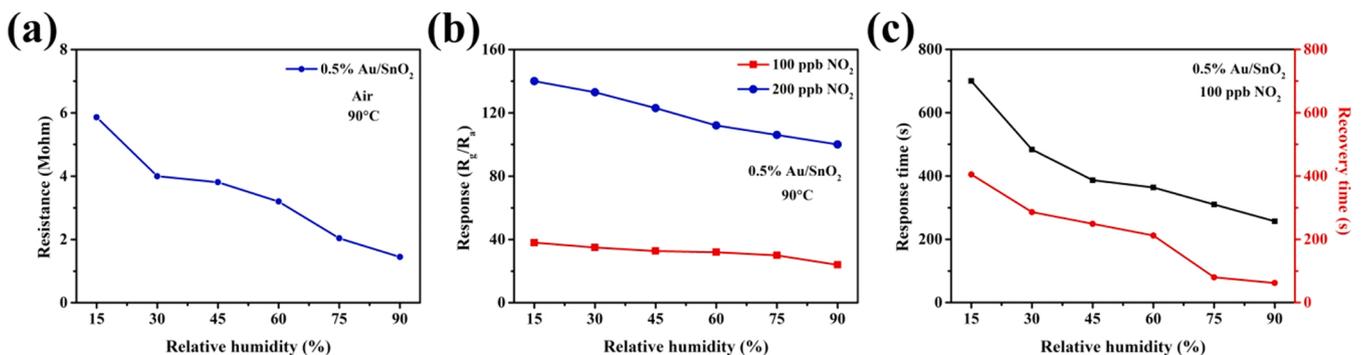
Fig. 8. (a) Resistance value in air, (b) response value and (c) response/recovery time of 0.5% Au/SnO$_2$ based sensor to 100/200 ppb NO$_2$ at various humidity (The setting temperature at humidity chamber was 25 °C).

water vapor and the target gas may also be one reason [39–41].

In order to compare the effect on the sensing performance of Au loaded SnO_2 with different reduction methods, the response values of 0.5% Au/SnO_2 (S) to NO_2 were investigated (Fig. S11). Under 100 ppb NO_2, the maximum response value is 17 at 90 °C, which is higher than that of pristine SnO_2 but lower than that of 0.5% Au/SnO_2, indicating that the gas sensing properties of the Au loaded SnO_2 obtained by different reduction methods are quite different [42]. The enhanced performance of Au loaded SnO_2 obtained by UV irradiation could be due to its uniform and appropriate Au nanoparticle size.

To appraise the sensing properties of 0.5% Au/SnO_2 to NO_2, other NO_2 sensors reported in the literature are listed in Table S3 and their sensing performances are compared. Among these devices, the 0.5% Au/SnO_2 based sensor exhibits high response to ppb-level NO_2 and the low LOD.

3.3. Sensing Mechanism

For a chemiresitive gas sensor, it is well accepted that adsorbed oxygen molecules play an important part in sensing process. They can capture electrons from the conduction band of sensing material and be ionized into O_2^- (lower than 150 °C) [6]. When the sensor contacts with oxidative NO_2 atmosphere, chemical reaction between the adsorbed NO_2 molecules and active O_2^- occurs with electrons involved [43]. The dissipated electrons from sensing material in this process bring about the increase of resistance. The above sensing mechanism is schematically illustrated in Fig. 9 and the involved sensing reactions are expressed in Eqs. (1)–(3) [44]:

$$O_2(absorbed) + e^- \rightarrow O_2^- \tag{1}$$

$$NO_2 + e^- \rightarrow NO_2^- \tag{2}$$

$$2NO_2 + O_2^- + e^- \rightarrow 2NO_3^- \tag{3}$$
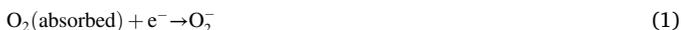
In our work, 0.5% Au/SnO_2 exhibits far higher response and faster response/recovery speed to NO_2 than pristine SnO_2. Obviously, loaded Au can be responsible for the performance enhancement. According to the analysis on element XPS, it is manifested that the concentration of oxygen vacancy increases for Au/SnO_2 samples compared to pure SnO_2. Among them, 0.5% Au/SnO_2 has the maximum oxygen vacancy concentration. Oxygen vacancy acts as an active site for oxygen absorption and is conducive to sensing process. It is reasonable that 0.5% Au/SnO_2 exhibits the highest response to NO_2 among these sensors. Besides, small size of Au nanoparticles may be another cause [45]. Appropriate amount of Au nanoparticles with small size can highlight its spillover sensitization. This is the case for 0.5% Au/SnO_2. On the contrary, large Au particle in 1.0% Au/SnO_2 weakens its spillover effect. Additionally, NO_2-TPD curves confirm that, 0.5% Au/SnO_2 occupies better absorption ability to NO_2. It is the case that the sensitivity characteristic is greatly ameliorated for 0.5% Au/SnO_2 based sensor. This result verifies the effect of Au loading on NO_2 adsorption. In addition, Schottky contact can be formed between Au and SnO_2. The work function of Au (5.1 eV) is larger than that of SnO_2 (4.9 eV) [46,47], and the band diagram is shown in Fig. S12. Co-electron flows from SnO_2 to Au until equilibrium of their Femi energy. The formation of depletion layer at SnO_2 side may contribute to improved sensitivity of SnO_2, but the phenomenon about the decrease in resistance of the Au/SnO_2 comparing to pure SnO_2 is dominated by the concentration of oxygen vacancy. On the whole, the interfacial reaction between SnO_2 and Au brings about comprehensive effect enhancing the NO_2 sensing performance of SnO_2.

4. Conclusions

Based on Au loaded SnO_2 nanosheet aggregates, a highly selective and sensitive NO_2 sensor was fabricated. It has a high response of 35–100 ppb NO_2 at a low operating temperature (90 °C), and the LOD can reach 2 ppb. Combined characterization results with measurement, the factors for the enhanced sensing property are investigated and analyzed. Apart from spillover effect and electron sensitization, the additional interfacial interaction between Au and SnO_2 may play an important role. This reaction brings about improved oxygen vacancy concentration and NO_2 absorption capability. The relative high concentration of oxygen vacancy provides more active sites for the selective adsorption reaction, endowing the Au/SnO_2 sensors with high sensitivity and good selectivity to NO_2 at a low operating temperature. The modulated NO_2 absorption property may make contribute to the sensitivity of 0.5% Au/SnO_2 based sensor. Overall, this work provides a facile method for preparing high-performance NO_2 sensors by loading trace amounts of Au on the SnO_2 nanosheets.
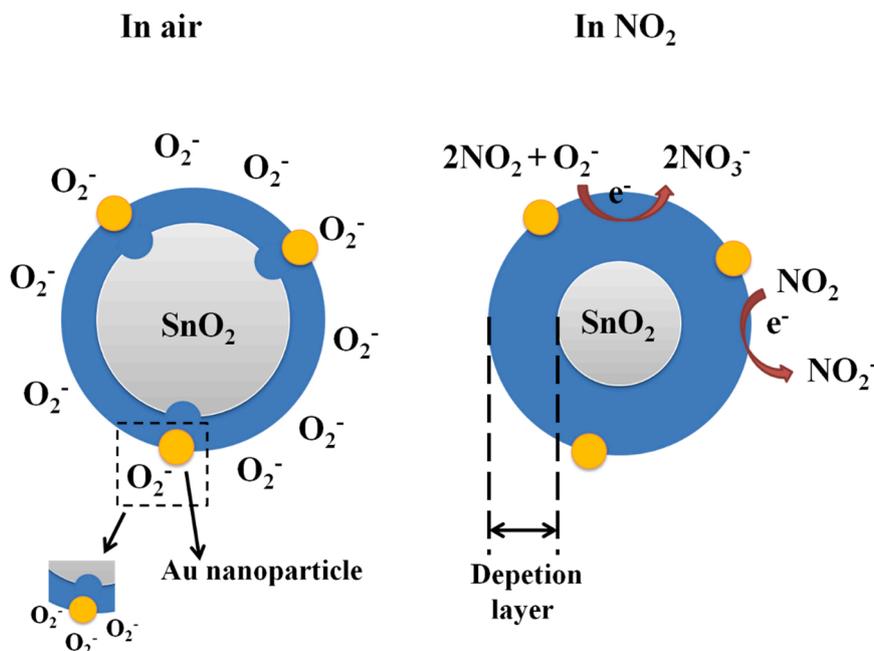
Fig. 9. Schematic illustration of the sensing mechanism.

CRediT authorship contribution statement

Weiyi Bu: Conceptualization, Methodology, Writing – original draft, Validation, Writing – review & editing. **Yan Zhang:** Resources, Investigation, Writing – review & editing. **Qixuan Qin:** Formal analysis, Writing – review & editing. **Yuliang Li:** Methodology, Writing – review & editing. **Xiaohong Chuai:** Conceptualization, Methodology, Resources, Project administration, Funding acquisition, Writing – review & editing. **ZhijieZhou:** Methodology, Writing – review & editing. **Changhua Hu:** Methodology, Writing – review & editing. **Tianshuang Wang**: Conceptualization, Methodology, Writing – review & editing. **Peng Sun:** Methodology, Writing – review & editing. **Fangmeng Liu:** Methodology, Writing – review & editing. **Geyu Lu:** Conceptualization, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2022.133237.

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