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Cross-Linked SnO₂ Nanosheets Modified by Ag Nanoparticles for Formaldehyde Vapor Detection

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Abstract: Ag@SnO₂ nanosheets were prepared through a hydrothermal method followed by heat treatment and a liquid reduction process. Many Ag nanoparticles (Ag NPs) were dispersed uniformly over the surface of the SnO₂ nanosheets. The thickness of the SnO₂ nanosheets was approximately 10 nm. After decoration with Ag NPs, the Ag@SnO₂ nanosheet sensors exhibited improved gas-sensing behaviors compared to the pure SnO₂ nanosheet sensor. The response of cross-linked SnO₂ nanosheets decorated by Ag NP sensors for 100 ppm formaldehyde vapor was up to 101.4, which was double that (45.5) of the pure SnO₂ nanosheet sensor. The response and recovery times of the Ag@SnO₂ sensor were 21 s and 23 s, respectively. The Ag@SnO₂ nanosheet sensors showed reasonable cycling stability, as demonstrated by testing with 100 ppm formaldehyde 10 times. The superior gas-sensing behaviors of the Ag@SnO₂ sensor were due to the large specific surface area, cross-linked nanostructure, and synergistic effect of the Ag NPs with huge sensitizing active sites and numerous SnO₂ nanosheets.

Keywords: SnO₂; Ag nanoparticles; nanosheet; gas sensor; formaldehyde



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1. Introduction

Formaldehyde is an important chemical raw material often used in the chemical, textile, and wood industries [1–3]. However, formaldehyde is toxic, flammable, and volatile. Repeated exposure to even low formaldehyde concentrations (e.g., 0.08 ppm) can harm the nervous and immune systems of humans [4,5]. Therefore, a gas sensor with high sensitivity and a low detection limit is needed to detect formaldehyde gas.

In recent years, researchers reported that gas sensors based on metal oxide semiconductors (MOS) have higher sensitivity, better selectivity, and lower manufacturing cost. Common gas-sensing materials include ZnO [6], SnO₂ [7], MoO₃ [8], NiO [9], and In₂O₃ [10]. Among these MOSs, SnO₂ is an *n*-type semiconductor with a bandgap of 3.6 eV, a rapid electron transmission rate (160 cm²/V s), and desirable physicochemical properties [11–13].

Controlling the morphology of the SnO₂ to improve the sensor response is a viable strategy. Based on the sensing mechanism, the sensing property is also related to its morphology and the size of the nanocrystals. SnO₂ materials with uniform morphology and adequate size would improve the performance of gas sensors. Therefore, SnO₂ materials with different morphologies, such as nanosphere [14], nanowire [15], nanorod [16], nanotube [17], nanosheet [12], and micro/nanoflower [18], were constructed to enhance their sensing properties. Li et al. constructed a sensor using SnO₂ nanospheres prepared through a hydrothermal method [19]. The sensor showed a strong response (38.3) for

100 ppm formaldehyde at 200 °C, and the response/recovery times were 17 s/25 s, respectively. The exceptional sensing performance was ascribed to the favorable porous nanosphere structure providing numerous surface-active sites and convenient channels for the easy adsorption and diffusion of gas molecules. Hu et al. utilized flower-like SnO₂ as a sensing material [20]. The sensor response to 100 ppm formaldehyde reached 34.6 with response/recovery times of 64 s/10 s. The flower-like structure can supply many active sites for accelerating the diffusion and transport of gas molecules and electrons. Among these morphologies, 2D nanosheets have a large specific surface area, suitable surface energy, and stable structure, which can significantly improve the response, shorten the response/recovery times, and reduce the detection limit [21]. Xu et al. prepared SnO₂ nanosheets using a hydrothermal method [12]. The nanosheet sensor displayed a strong response to 79.5 to 100 ppm formaldehyde at 200 °C, with response and recovery times of 42 s and 112 s, respectively. Yu et al. synthesized SnO₂ nanosheets using a solvothermal method [22]. In addition, Meng et al. used the stepwise recognition method of qualitative classification and quantitative regression to improve the recognition rate, the resolution, and the generalization performance of the SnO₂ sensor, which is a new way of on-line rapid sensor detection for drug-producing chemicals [23]. The SnO₂ sensor exhibited a response of 7 to 100 ppm formaldehyde at 200 °C, with short response/recovery times (1 s/6 s). Many researchers have made progress in improving the sensor performance by synthesizing various morphologies of tin dioxide. Nevertheless, it is still necessary to synthesize hierarchical SnO₂ with a large specific surface area to further enhance the sensor performance.

The following methods are often used to improve the practicality of SnO₂-based gas sensors by reducing the working temperature and shortening the response/recovery times: element doping [24], construction of heterojunctions [25,26], and noble metal modification [27]. Among them, the decoration of noble metals on sensing material is an effective strategy to promote the sensing properties. The commonly used noble metals include Pd [28], Au [29], Pt [30], and Ag [31]. For example, Li et al. modified SnO₂ nanosheets with Pd/Au nanoparticles [32]. The Pd NPs-modified SnO₂ sensor exhibited a strong response of 125 and a response time of 68 s toward 100 ppm formaldehyde at 110 °C. Tang et al. synthesized Pt-modified SnO₂ nanospheres with a mean diameter of 30–50 nm [14]. As sensing materials, it achieved a response of 70.1 toward 100 ppm formaldehyde with an extremely short response time (5 s) at 200 °C. The enhanced sensing property was mainly ascribed to two reasons. First, the electron transfer speed can be accelerated because of the electron sensitization effect. Second, the synergistic effect of noble metals and SnO₂ promotes the redox reactions on the surface of the materials [33]. Ag is relatively inexpensive with stable chemical properties compared with other noble metals. Therefore, Ag is a promising alternative to modify sensing materials and improve the sensing performance. For example, Liu et al. [34] attached Ag NPs to the surface of SnO₂ using a liquid reduction method. The resulting sensor exhibited a strong response to volatile organic compounds (VOCs). The response of the Ag@SnO₂ sensor was 14.4 for 10 ppm formaldehyde at the optimal operating temperature (150 °C), while the response of pure SnO₂ was only 3.2 at the same working temperature. Many strategies to decorate SnO₂ with noble metals have been developed. Despite many achievements in the preparation of Ag@SnO₂ sensing materials, there is a considerable focus on SnO₂ hierarchical structures modified by Ag NPs with improved sensing performance for VOCs.

In this study, numerous cross-linked SnO₂ nanosheets loaded with uniform Ag NPs were prepared via a hydrothermal method combined with a heat treatment and liquid reduction process. Compared with pure SnO₂ nanosheets, Ag@SnO₂ nanosheets showed enhanced sensing properties towards VOCs. This paper discusses the effect of Ag NPs on the sensing performance, including the sensing mechanism of the Ag@SnO₂ nanosheets.

2. Experimental Details

2.1. Preparation of Cross-Linked SnO₂ Nanosheets

First, 1.0 g of SnCl₂·2H₂O was dissolved in 20 mL deionized water with stirring, followed by adding 10 mL NaOH (1.5 mol l^{−1}) solution. Subsequently, 0.3 g cetyltrimethyl ammonium bromide (CTAB) was placed into a mixed solution. After stirring for 30 min, 0.8 mL hydrazine hydrate was added to the mixture. Subsequently, the mixture was maintained at 150 °C for 24 h. The precursor was obtained after drying at 70 °C for 10 h. Finally, the cross-linked SnO₂ nanosheets were achieved by annealing the precursor at 700 °C for 30 min at a constant heating rate (5 °C min^{−1}).

2.2. Preparation of Cross-Linked Ag@SnO₂ Nanosheets

The prepared SnO₂ powder (0.5 g) was dispersed in 15 mL of deionized water with constant stirring. Subsequently, 1 mL of a 20 mM AgNO₃ solution and 2 mL of a 10 mM ascorbic acid solution were added to the mixture solution with stirring for another 60 min. Finally, the product was collected after washing three times and dried at 70 °C for 5 h.

2.3. Characterization

The related information is shown in the Supporting Information (SI).

3. Results and Discussion

3.1. Characterizations

Figure 1a exhibits the X-ray diffraction (XRD) pattern of the precursor and annealed product. Before calcination, all the XRD peaks of the precursor were assigned to SnO₂ (JCPDS No. 06-0395) and Sn₃O₄ (JCPDS No. 16-0737). After calcining the precursor at 700 °C, all the peaks at 26.1°, 33.9°, 37.9°, 51.8°, 54.7°, 61.8°, 64.7°, 65.9°, and 71.2° 2θ were indexed to the (110), (101), (200), (211), (220), (310), (112), (301), and (202) lattice planes of tetragonal rutile SnO₂ (JCPDS No. 41-1445), respectively. No impurity peaks were detected. Moreover, the high crystallinity of the final product was obtained by observing the sharp and strong XRD peaks. The XRD pattern of Ag@SnO₂ exhibited the peaks for SnO₂ and peaks at 38.1°, 44.2°, 64.4°, and 77.5° 2θ corresponding to the (111), (200), (220), and (311) planes of Ag (JCPDS Card No. 04-0783), respectively, indicating that the product contained Ag and SnO₂. Figure 1b exhibits energy-dispersive X-ray spectroscopy (EDS) analysis, confirming the existence of Sn, O, and Ag in the final product.

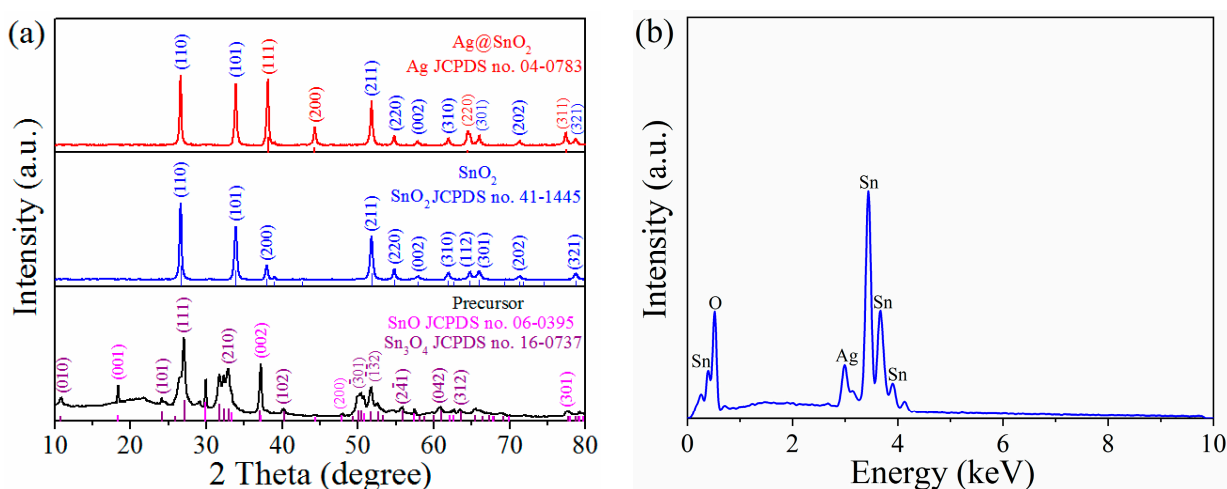


Figure 1. (a) XRD pattern; (b) EDS analysis of the cross-linked Ag@SnO₂ nanosheets.

The morphologies of the samples were studied by scanning electron microscopy (SEM). Figure 2a,b shows the sheet-linked morphology of the precursor. The nanosheets had a smooth surface. Many cross-linked nanosheets formed a hierarchical structure by self-

assembly. Some pores formed among the cross-linked nanosheets. Synthesis of cross-linked SnO_2 nanosheets from an aqueous solution containing Sn^{2+} ions may be explained via the following mechanism:

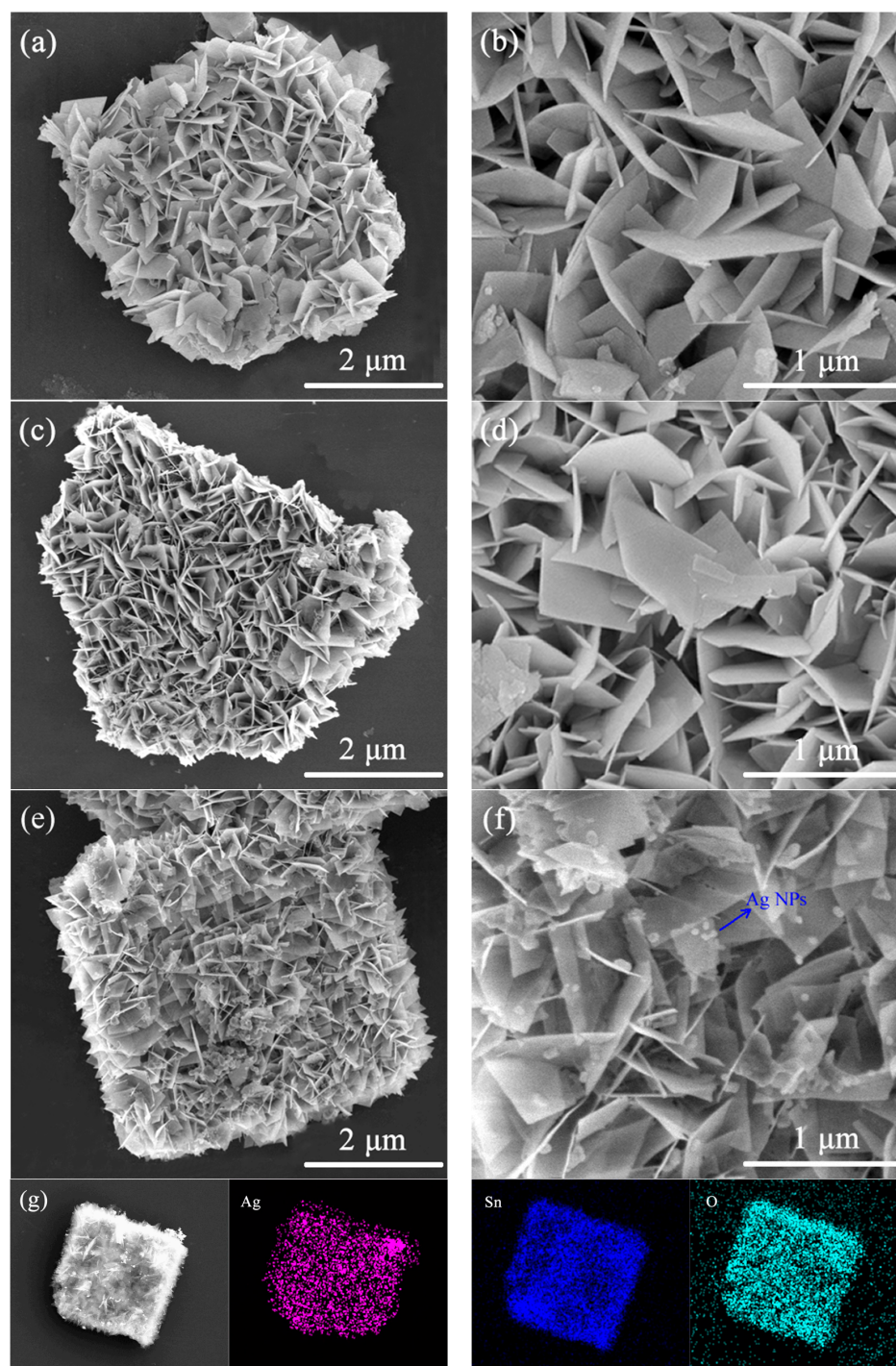
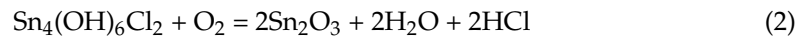
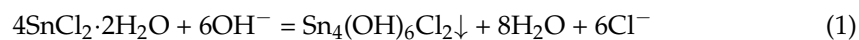


Figure 2. SEM images of (a) the precursor; (b) the precursor; (c) cross-linked SnO_2 nanosheets; (d) cross-linked SnO_2 nanosheets; (e) cross-linked Ag@SnO_2 nanosheets; (f) cross-linked Ag@SnO_2 nanosheets. (g) Elemental mapping images of Ag@SnO_2 nanosheets.

The reaction (1) could be easily observed when adding NaOH to the Sn^{2+} solution, resulting in some $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ microplates. After that, the $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ microplates were gradually oxidized, forming some Sn_2O_3 nuclei on the surface of the microplates. Upon increasing the time further, Sn_2O_3 nuclei formed from the oxidation of $\text{Sn}_4(\text{OH})_6\text{Cl}_2$, followed by crystal growth. In liquid medium, the growth habit of Sn_2O_3 crystal is mainly determined by its intrinsic structure. Therefore, the cross-linked nanosheet-like precursor was obtained. Finally, the cross-linked SnO_2 nanosheets were obtained via calcination of the precursor in air. Figure 2c,d presents SEM images of the precursors after high-temperature calcination. The morphology maintains the structure of cross-linked nanosheets. The thickness of the nanosheets was ca. 10 nm, as shown in Figure S3. As displayed in Figure 2e,f, after being decorated by Ag NPs, abundant Ag NPs were attached uniformly to the surface of each nanosheet, and no obvious aggregation of Ag NPs occurred. Figure S4 presents the size of the Ag NPs with 80 nm. The loaded Ag NPs can supply many active sites for gas adsorption and accelerate the transfer of electrons. Figure 2g presents the mapping images of the Ag@SnO_2 nanosheets, confirming the presence of Ag, Sn, and O. The Ag NPs were modified uniformly on the nanosheet surface.

The morphology of the composites was explored further by transmission electron microscopy (TEM). Figure 3a,b shows TEM images (low/high magnification, respectively) of the SnO_2 nanosheets modified by Ag NPs (Ag@SnO_2). The sample maintained a cross-linked nanosheet morphology. Abundant Ag NPs were scattered uniformly over the SnO_2 nanosheet surface, with no serious aggregation of Ag NPs. As shown in Figure 3c, the lattice spacing of 0.176 nm matches the crystal plane (211) of rutile SnO_2 in the TEM image with high-resolution TEM (HRTEM). From Figure 3b,c, the crystallographic orientation of the SnO_2 nanosheet is the (211) plane. The nanosheet grows along the (211) direction, but the basal plane cannot be determined. Moreover, the lattice spacing (0.236 nm) corresponded to the crystal plane (111) of Ag [35]. From the SAED pattern of Ag@SnO_2 (Figure 3d), five distinct diffraction rings corresponded to the (100), (101), (200), (211), and (301) crystal planes of the tetragonal SnO_2 , indicating that the nanosheet was polycrystalline [36]. The diffraction ring could be attributed to the crystal plane (311) of Ag [35].

Figure 4a presents the nitrogen adsorption/desorption isotherms of the Ag@SnO_2 nanosheets. The specific surface area of the nanocomposites is $11.9 \text{ m}^2 \text{ g}^{-1}$. The pore size ranged from 0.86 nm to 24.65 nm, with an average pore size of 12.86 nm. By comparison, the specific surface area of pure SnO_2 nanosheets was only $8.1 \text{ m}^2 \text{ g}^{-1}$. The pore sizes were between 0.89 and 28.12 nm, averaging 11.78 nm. The cross-linked nanosheets contributed to the formation of numerous pores. The Ag@SnO_2 nanosheets had a larger specific surface area than the pure SnO_2 nanosheets. The higher specific surface area was favorable for providing more available active sites for the gas molecules. The porous structure helped improve the diffusion efficiency of gas molecules by shortening the diffusion distance.

Figure 5a presents the UV-vis spectra of cross-linked Ag@SnO_2 and pure cross-linked SnO_2 nanosheets. The maximum absorption peak of the as-prepared samples occurred around 300 nm. The absorption band (350–280 nm) of Ag-SnO_2 composite is red-shifted compared with pristine SnO_2 , which can be attributed to the charge transition between Ag and SnO_2 , leading to the enhancement of gas-sensing performance [34]. Figure 5b presents the calculated bandgap of Ag@SnO_2 and the SnO_2 using the Tucker model. The calculated bandgaps for SnO_2 and Ag@SnO_2 were 2.81 eV and 2.66 eV, respectively. The bandgap of Ag@SnO_2 was smaller than that of SnO_2 , possibly due to Ag NPs accelerating the electron transfer rate, improving the surface electron concentration of Ag@SnO_2 , so that more electrons were injected into the conduction band of Ag@SnO_2 , inducing the Burstein–Moss effect [37,38].

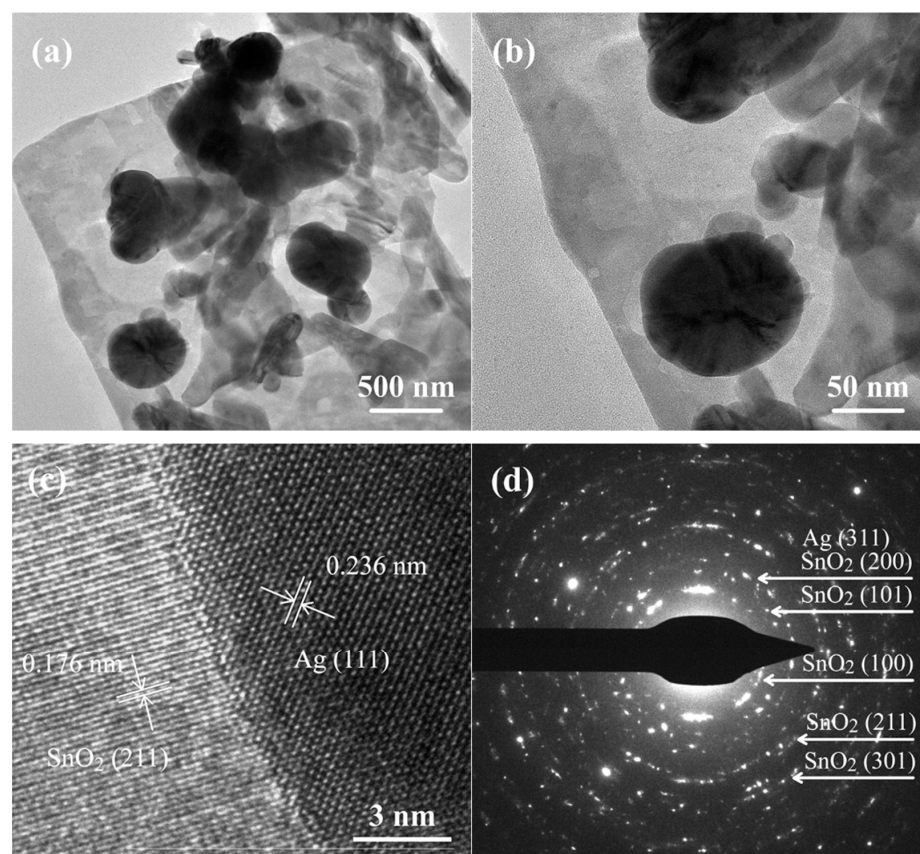


Figure 3. (a) TEM image; (b) HRTEM image; (c) lattice-resolved HRTEM image; (d) selected area electron diffraction (SAED) pattern of Ag@SnO₂ nanosheets.

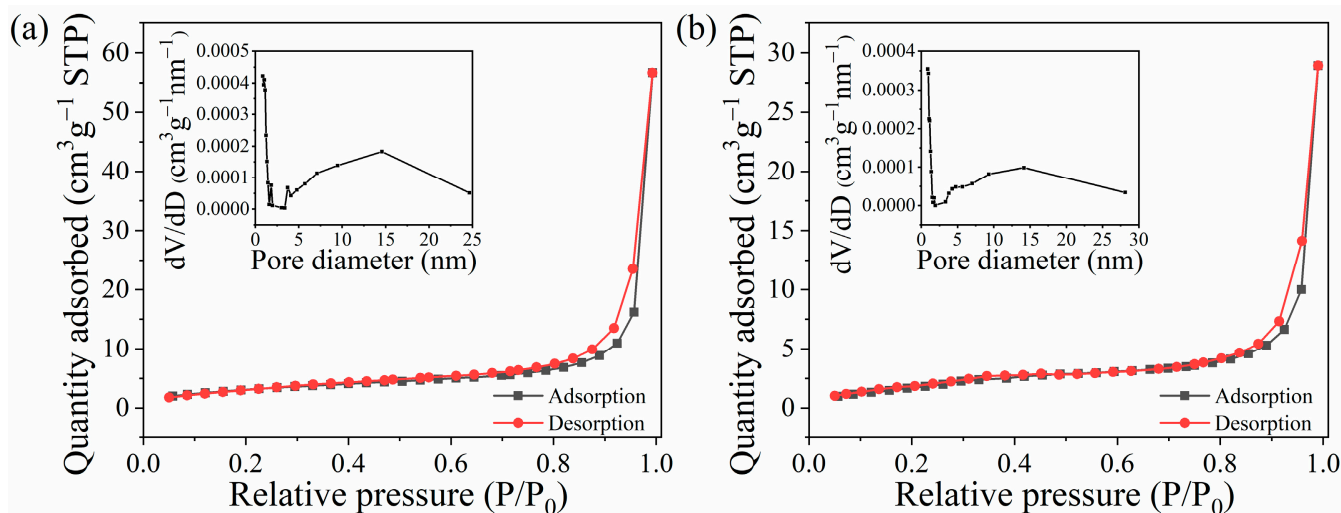


Figure 4. Nitrogen adsorption/desorption isotherms of (a) Ag@SnO₂; (b) pure SnO₂ nanosheets. The inset image is the pore size distribution.

The element components and valences of the Ag@SnO₂ nanosheets were examined by X-ray photoelectron spectroscopy (XPS). Figure 6a exhibits the survey spectrum of the product, demonstrating the existence of Sn, O, and Ag. As shown in Figure 6b, there were two peaks at ca. 486.1 eV and 494.5 eV in the Sn 3d spectrum, which could be ascribed to Sn 3d_{5/2} and Sn 3d_{3/2} [39], respectively. This result suggests the formation of Sn⁴⁺ in SnO₂. Figure 6c exhibits the Ag 3d spectrum, where two peaks at 367.1 eV and 373.1 eV are ascribed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively [22,40]. From the O 1s spectrum in

Figure 6d, three peaks at ca. 529.8 eV, 530.6 eV, and 531.9 eV were ascribed to lattice oxygen (O_L , 53.4%), vacancy oxygen (O_V , 27.8%), and chemisorbed oxygen (O_C , 18.8%), respectively. Abundant chemisorbed oxygen formed in the composites, which improved the sensing performance. Figure S5 shows the C 1s spectrum of cross-linked Ag@SnO₂ nanosheets, which may come from the adsorbed CTAB on the sample. Furthermore, the weight percentage of Ag among the Ag@SnO₂ composites was calculated to be 9.7 wt % through the XPS results.

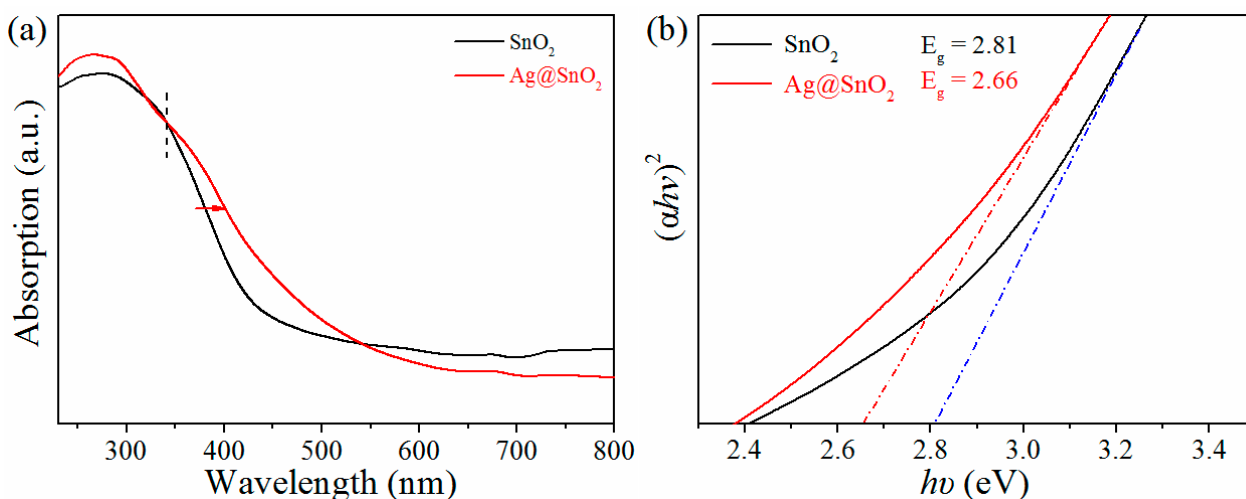


Figure 5. (a) UV-vis absorption spectra of pure cross-linked SnO₂ and cross-linked Ag@SnO₂ nanosheets. (b) Bandgap determinations using $(\alpha h\nu)^2$ vs. $h\nu$ of cross-linked SnO₂ nanosheets and Ag@SnO₂ nanosheets.

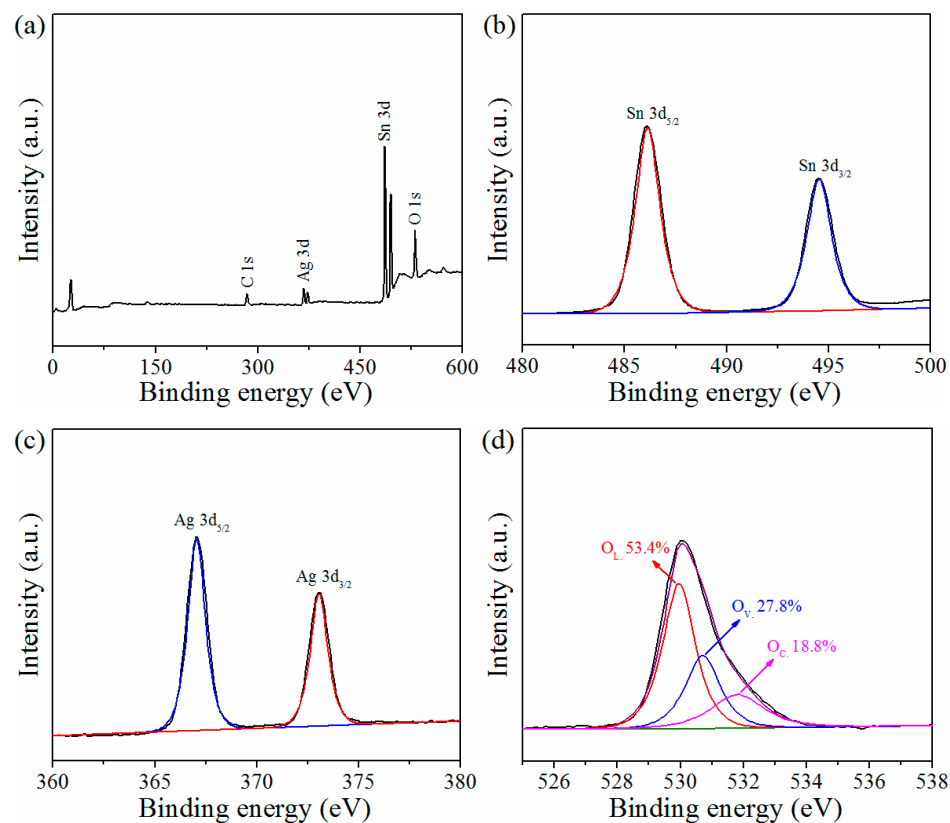


Figure 6. XPS spectra of cross-linked Ag@SnO₂ nanosheets of (a) survey spectrum; (b) Sn 3d; (c) Ag 3d; (d) O 1s spectra.

3.2. Sensing Performance of Ag@SnO₂ Nanosheet Sensors

The working temperatures are always considered an important factor of a gas sensor for wide applications. At different working temperatures, the responses of cross-linked Ag@SnO₂ and pure cross-linked SnO₂ nanosheet sensors exposed to 100 ppm formaldehyde vapor were recorded, as shown in Figure 7a. In the temperature range of 80–200 °C, the responses of the composites increased as the working temperature was increased. As for reductive gases, the response was defined as R_a/R_g , where R_a is sensor resistance in dry air, and R_g is sensor resistance in dry air containing test gas. At 140 °C, the response reached the maximum value of 101.4, with a decrease at higher temperatures. As a result, 140 °C is the optimal working temperature of the Ag@SnO₂ sensor. For the pure SnO₂ sensor, the maximum response was 45.5 at temperatures up to 180 °C. Thus, 180 °C is considered the optimal working temperature of the SnO₂ sensor, which is higher than that of the Ag@SnO₂ sensor. Due to the introduction of Ag NPs in the Ag@SnO₂, the strong catalytic effect enables formaldehyde molecules to be oxidized at a lower temperature. As shown in Figure 7b, formaldehyde, ethanol, isopropanol, acetone, methanol, toluene, ammonia, and benzene vapors are detected based on the Ag@SnO₂ and pure SnO₂ nanosheets sensors at 140 °C. The responses of the Ag@SnO₂ sensor to these seven vapors were 101.4, 66.8, 60.5, 42.8, 17.2, 12.2, 7.5, and 5.1, respectively. The corresponding responses of the pure SnO₂ sensor were 45.5, 42.2, 35.2, 29.3, 15.7, 9.8, 6.5, and 4.8, respectively. The results suggest that the sensing performance of the cross-linked Ag@SnO₂ nanosheet sensor is superior to that of the pure cross-linked SnO₂ nanosheet sensor. The high response of formaldehyde is mainly because different gases have different dissociation energies. The dissociation energy of formaldehyde (364 kJ mol^{−1}) is lower than that of ethanol (436 kJ mol^{−1}), methanol (439 kJ mol^{−1}), benzene (431 kJ mol^{−1}), acetone (393 kJ mol^{−1}), and toluene (368 kJ mol^{−1}). The low dissociation energy of formaldehyde is conducive to the reaction with the absorbed oxygen on the sensing material, thus showing strong response and high selectivity.

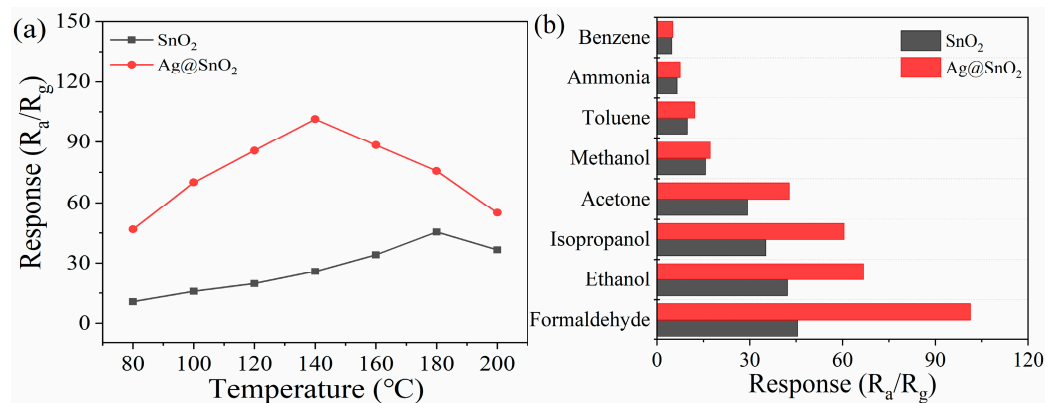


Figure 7. (a) Sensor responses of Ag@SnO₂ sensor and SnO₂ sensor to 100 ppm formaldehyde at various working temperatures; (b) response curves of two sensors to eight kinds of vapors (100 ppm) at 140 °C.

The gas sensors fabricated by the cross-linked Ag@SnO₂ and pure cross-linked SnO₂ nanosheets were applied to detect some VOCs at an optimal working temperature of 140 °C. Figure 8a exhibits the real-time response curve of the Ag@SnO₂ sensor and the pure SnO₂ sensor after exposure to formaldehyde vapor at different concentrations (1–400 ppm). The output current increased rapidly when the gas sensor was exposed to the formaldehyde vapor and maintained a stable condition. When the formaldehyde vapor broke away from the gas sensor, the output current quickly returned to the original value and maintained a stable current. Thus, the Ag@SnO₂ sensor possesses a distinct gas-sensing response and recovery. In Figure 8, the Ag@SnO₂ sensor exhibited an overshoot at a high concentration, which is the sensor response just after exposure to the target gas was highest, followed by a signal decay up to the end of the pulse. Particularly, the overshoot is drastic in ethanol and

isopropanol detection. This was mainly caused by uneven gas diffusion concentration after injecting the target gas. The local concentration of the target gas was high at the beginning of injection, and then diffused to the surrounding area. The Ag@SnO₂ sensor exhibits a fast strong response due to the catalytic effect of the Ag nanoparticles, resulting in an overshoot at high concentrations and signal decay, which cannot be obviously observed in the slow, weak response of the pure SnO₂ sensor. From the response curve of the sensor (insets), the response increased gradually as the formaldehyde concentration was increased. The calculated responses at a very low (1 ppm) and high concentrations (100 ppm) were 6.4 and 101.4, respectively. Figure 8b–d shows the real-time response curves of the Ag@SnO₂ sensor for ethanol, isopropanol, and acetone vapors, respectively. The insets present the respective response curves. Exposure to a fixed concentration of vapors (100 ppm) revealed responses to ethanol, isopropanol, and acetone vapors of 66.8, 60.5, and 42.8, respectively. Furthermore, for the pure cross-linked SnO₂ nanosheet sensor, the corresponding responses for formaldehyde, ethanol, isopropanol, and acetone vapors were 45.5, 42.2, 35.2, and 29.3. In addition, after exposure to 100 ppm formaldehyde, the response and recovery times of Ag@SnO₂ sensor were 21 s and 23 s, respectively, as shown in Figure S6. The response and recovery times of the SnO₂ nanosheet sensor were 28 s and 26 s, respectively, which are longer than those of the Ag@SnO₂ sensor. Compared with the SnO₂ nanoparticles [13], SnO₂ nanoflowers [20], flower-like SnO₂ microspheres [41], Pt-SnO₂ nanospheres [14], Ag-SnO₂ nanoparticles [34], hollow PdO/ZnO/SnO₂ nanospheres [42], and flower-like Bi-SnO₂ nanostructures [43], the cross-linked Ag@SnO₂ nanosheets showed exceptional sensing performance, including a higher response, quicker response, and short recovery times, as shown in Table S1. Two additional sensors were fabricated with the cross-linked Ag@SnO₂ nanosheets under the same process. Similar gas-sensing properties were obtained, which suggests the reproducibility of the sensors.

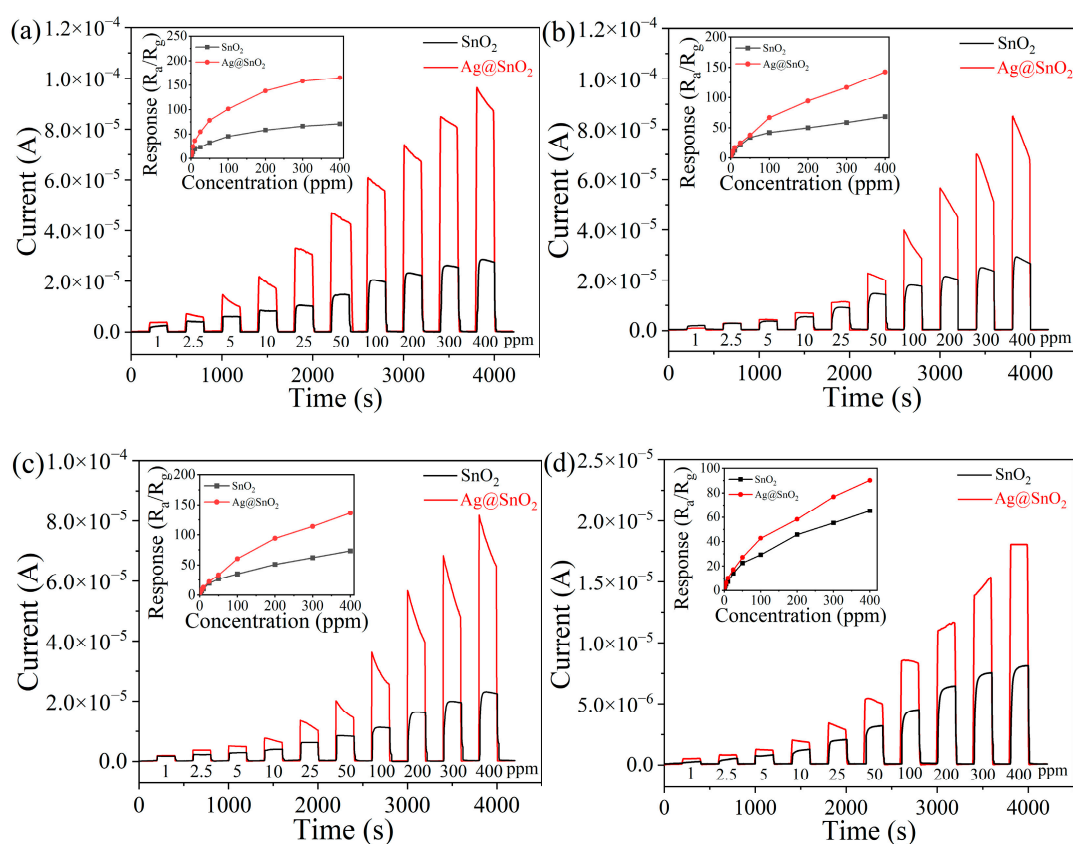


Figure 8. Real-time response curves of sensor devices upon exposure to different concentrations of (a) formaldehyde; (b) ethanol; (c) isopropanol; (d) acetone at 140 °C. The insets show the corresponding sensor response curves.

The repeatability of the Ag@SnO₂ sensor was assessed by conducting real-time response tests to 100 ppm formaldehyde ten times at the optimal working temperature, as shown in Figure 9a. The output current increased sharply when the sensor was exposed to the formaldehyde vapor. The output current quickly returned to the initial state when the formaldehyde vapor was away from the sensor. Over ten cycles, the sensor maintained a similar current to the first, indicating reasonable repeatability of the Ag@SnO₂ sensor for formaldehyde vapor detection. Figure S7 shows the long-term stability of the Ag@SnO₂ sensor towards 100 ppm formaldehyde vapor at the working temperature of 140 °C. The response of the sensor remained relatively stable within 14 days, and the sensor performance remained unchanged throughout the long-term testing process, indicating its stability. Figure 9b shows the response curves for different formaldehyde concentrations. The linear regression coefficients for Ag@SnO₂ and SnO₂ were 0.9642 and 0.9884, respectively.

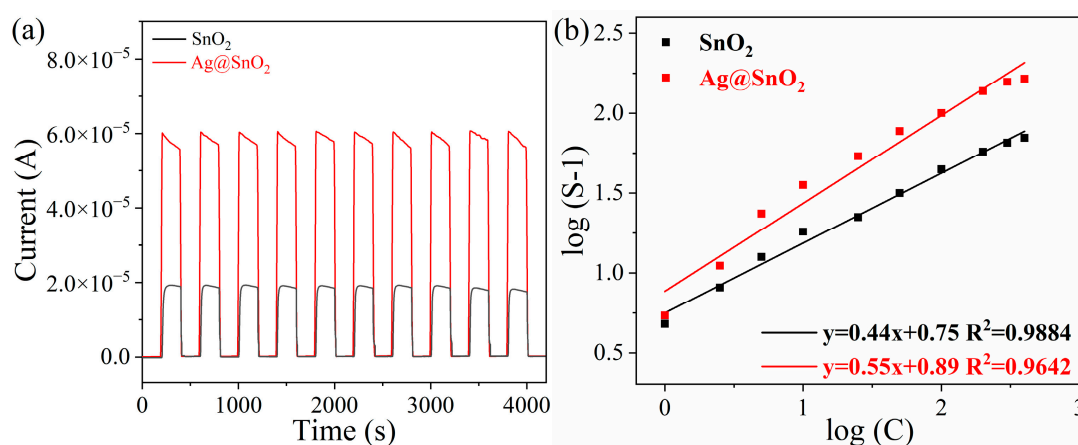
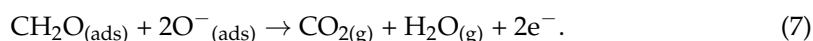


Figure 9. (a) Current change curves of Ag@SnO₂ sensor towards 100 ppm formaldehyde vapor for 10 tests at 140 °C; (b) the linear fitting curve of cross-linked Ag@SnO₂ and SnO₂ nanosheet sensors towards formaldehyde in the concentration range of 1–400 ppm.

3.3. Gas-Sensing Mechanism

The sensor based on SnO₂ abides by a gas-sensing mechanism with a typical *n*-type semiconductor material. Figure 10 presents a schematic illustration of the sensing mechanism of the Ag@SnO₂ nanosheet sensor. The internal resistance of the sensing material will change due to large differences in resistance when the sensors are exposed to air and reducing gases [44]. When the SnO₂ sensor is exposed to air, oxygen molecules will be adsorbed on the SnO₂ surface. At the working temperature, oxygen molecules transform to oxygen species (O₂⁻ and O⁻) with strong oxidation by capturing electrons from the conduction band (CB) of SnO₂. An electron-depleted layer (EDL) will form because of the loss of electrons in the CB of SnO₂, which leads to a rapid increase in sensor resistance [45,46]. When the sensor is exposed to formaldehyde vapor, the oxygen species on the material surface will quickly react with formaldehyde vapor to produce CO_x and H₂O(g). At the same time, the electrons captured by the oxygen anions are released back to the CB of the SnO₂, narrowing the EDL thickness. This contributes to a rapid decrease in sensor resistance. The reaction process is shown in the following formulae [47].



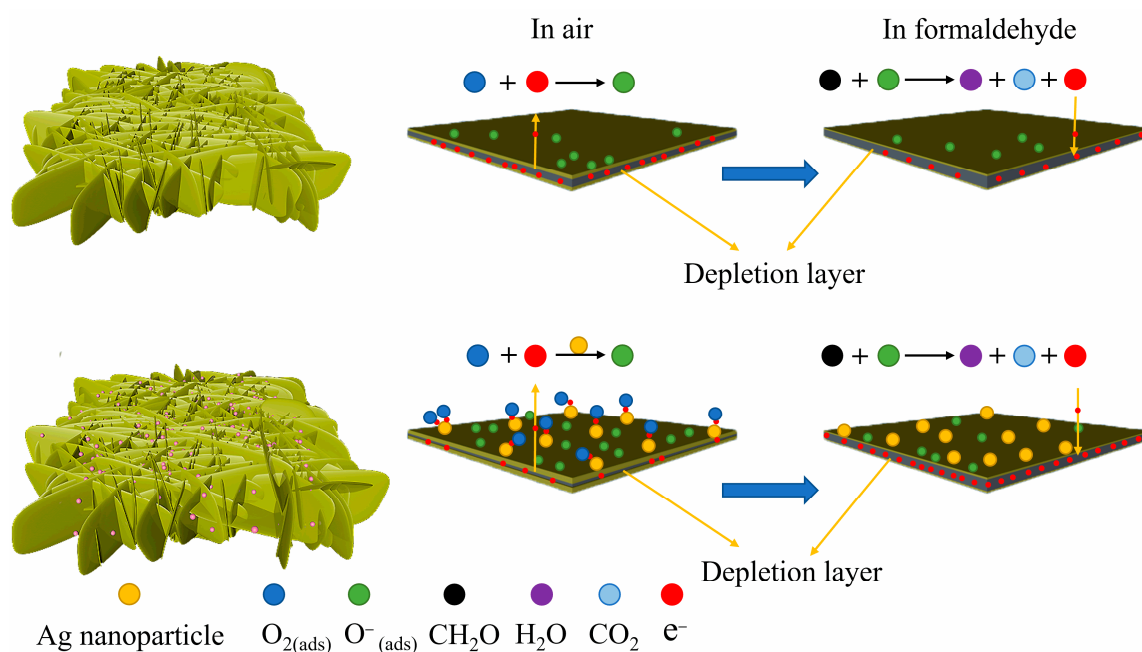


Figure 10. Schematic diagram of the sensing mechanism of cross-linked Ag@SnO₂ nanosheet sensor.

The mechanism for the enhanced sensing performance of the Ag@SnO₂ sensor can be described from the following aspects. After Ag nanoparticles are attached to the SnO₂ surface, the spillover and catalytic effects will show [34]. Ag NPs will increase the chemisorbed oxygen on the SnO₂ surface, which provides more reactive sites for redox reactions. Moreover, the barrier variation of the SnO₂-based sensors is greatly influenced by the amount and type of oxygen adsorbed on the material surface. The Ag@SnO₂ composites have more chemisorbed oxygen than the pure SnO₂, which is due to the spillover effect between Ag nanoparticles and the material surface, accelerating the decomposition rate of the oxygen. The faster oxygen decomposition rate provides more oxygen species on the material surface. Hence, the reaction rate between oxygen species and formaldehyde molecules is accelerated, and the resistance transition rate inside the sensor is also increased.

Furthermore, the work function of Ag (5.1 eV) is higher than that of SnO₂ (4.9 eV). When Ag NPs are modified on the surface of the SnO₂, electrons flow from the surface of the SnO₂ to the surface of the Ag NPs, and the Schottky junction is formed between them [48,49]. When the Ag@SnO₂ sensor is exposed to air, the electrons accumulating on the surface of the Ag nanoparticles react quickly with oxygen, which promotes the ionization of adsorbed oxygen. In addition, the amount of oxygen species converging on the surface of the Ag NPs will overflow to the material surface, resulting in an increasing number of oxygen species on the surface [50]. Finally, the electron depletion layer of Ag@SnO₂ is thicker than that of SnO₂, which further increases the resistance of sensing material in air. When the Ag@SnO₂-based sensor is exposed to formaldehyde gas, the large number of oxygen species adsorbed on the sensing material quickly react with formaldehyde molecules with the help of Ag catalysis. As the reaction progresses, many free electrons return, decreasing the thickness of the electron depletion layer and increasing the current of the Ag@SnO₂ sensor.

4. Conclusions

Numerous cross-linked SnO₂ nanosheets decorated with Ag NPs were prepared using a hydrothermal method, followed by a heat treatment and liquid reduction process. Many Ag NPs were dispersed uniformly over the surface of the cross-linked SnO₂ nanosheets with a thickness of ca. 10 nm. In contrast to the pure cross-linked SnO₂ nanosheet sensor, the Ag-decorated SnO₂ nanosheet sensor showed an enhanced sensing performance for VOC detection. For the 100 ppm formaldehyde vapor, the Ag@SnO₂ sensors exhibited a

stronger response than the pure SnO₂ sensor at a low optimal working temperature. The exceptional sensing behaviors of the Ag@SnO₂ sensors were attributed to the favorable cross-linked nanosheet structure, large specific surface area, and the synergistic effect of Ag NPs and cross-linked SnO₂ nanosheets.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemosensors11020116/s1>, Figure S1: Experimental setup; Figure S2: Photograph of the sensor; Figure S3: High-magnification SEM image of cross-linked SnO₂ nanosheets; Figure S4: High-magnification SEM image of cross-linked Ag@SnO₂ nanosheets; Figure S5: C 1s spectrum of cross-linked Ag@SnO₂ nanosheets; Figure S6: Response and recovery characteristics of cross-linked Ag@SnO₂ nanosheets and pure cross-linked SnO₂ nanosheet sensors to 100 ppm formaldehyde vapor; Figure S7: Long-term stability of the Ag@SnO₂ sensor towards 100 ppm formaldehyde vapor at the working temperature of 140 °C; Table S1: Responses of SnO₂-based gas sensors to different concentrations of formaldehyde vapor.

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