NH₃ Sensing Performance of Pt-Doped WO₃·0.33H₂O Microshuttles Induced From Scheelite Leaching Solution

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Abstract

$\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ microshuttles (WMSs) self-assembled by numerous nanorods along the same direction were prepared based on a cheap tungsten-containing metallurgical raw material by combination processes of NaOH leaching and one-step hydrothermal method. The microstructures and gas sensing properties of various concentrations (0, 0.7, 1.0, and 1.3 mol%) of Pt-doped WMSs were investigated to improve their performance. The microstructural characterizations demonstrated that the WMSs assembled by one-dimensional $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ nanorods were approximately 0.8–1.9 μm in diameter. Such nanorods exhibited a single hexagonal structure with their diameters ranging from 17 to 62 nm. The gas sensing properties indicated that Pt-doped WMSs showed superior gas sensing performance in terms of the sensor response and NH_3 selectivity in the operating temperature range of 25–225 $^\circ\text{C}$ as compared with pure one, and simultaneously Pt doping could significantly reduce the detection limit of NH_3 . Especially, 1.0 mol% Pt-doped WMSs exhibited highest response of 28.2 to 1000 ppm NH_3 at 175 $^\circ\text{C}$, which was 4 times higher than pure one at 50 $^\circ\text{C}$. The remarkably enhanced gas sensing performance of Pt-doped WMSs to NH_3 could be ascribed to the electronic and chemical sensitization mechanisms of noble metal nanoparticles.

1. Introduction

With the rapid development of society and economy, human health problem has gradually become an increasing topic. Ammonia (NH_3) with a strong pungent odor is a toxic and colorless gas, and easy to dissolve in water [1, 2]. It is a very important chemical product and industrial raw material, which is widely used in decoration, chemical fertilizer, medicine, industrial refrigeration and other important fields [3–8]. In addition, NH_3 is also a kind of indoor air pollutant with great harmfulness, which is prevalent in our daily life, such as protein rich corruption, interior decoration materials and home adhesives, etc., which could cause serious harm to human health even under a low concentration by damaging throat, lungs, eyes, and skin [9–11]. NH_3 is also explosive, and there is a potential risk of explosion when mixed with air [12]. According to the relevant reports of some safety and health institutions, long-term inhalation or exposure of high concentration (more than 5000 ppm) of NH_3 can seriously endanger human health, and even cause death. The immediately dangerous to life or health concentration (IDLH) towards NH_3 is 300 ppm [13–16]. When the human body is in the low concentration of NH_3 environment such as 35 ppm for a long time, it will also cause the increase of blood ammonia concentration, which will lead to a serious of pathological changes of organs such as liver and kidney [14, 17, 18]. Therefore, it is very important to develop a new NH_3 gas sensor with high response and selectivity.

WO_3 is a common transition-state semiconductor metal oxide, which is recognized as a sensing material with good application prospects in the field of gas sensors due to its many excellent physical and chemical properties, such as unique non-stoichiometric, narrow band gap, strong acid resistance and high temperature resistance [19]. Tungsten trioxide hydrate ($\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$) is a kind of hydrate of WO_3 , which is widely applied as gas sensing material because of its excellent physical and chemical properties. At present, there are relatively few researches focusing on $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ sensing materials. Single-component $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ sensing materials often have some drawbacks in the field of gas sensors, such as poor selectivity, low response, high operating temperature, slow response/recovery speed, etc., so that they cannot be well applied to monitor the toxic and harmful gases. For the sake of improving the gas-sensing performance, a variety of morphologies and structures of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ nanomaterials have been synthesized, including 0-D nanoparticles [20], 1-D nanorods [21], 2-D nanosheets [22], and 3-D microspheres [23]. In addition, it is also an effective way to enhance their gas-sensing performance by adding noble metal elements into the sensing materials. Ganesh et al. [24] reported that some noble metal doping in the nanomaterials could change their

morphology and energy band structure, which resulted in the increase of specific surface area and the formation of more active reaction center of gas molecules on the nanomaterial surface, thereby leading to the enhancement in the gas sensing properties of nanomaterials. Thai et al. [25] demonstrated that some noble metal catalysts such as Pt or Pd possessed strong reactivity to some gaseous molecules, especially some containing-hydrogen atoms molecules, such as NH_3 , ethanol, H_2 , and liquefied petroleum gas. Chen et al. [26] synthesized a Pt/NiO thin film-based gas sensor for monitoring NH_3 . They indicated that NH_3 molecules could be effectively and directly dissociated into nitrogen and hydrogen molecules by introducing Pt in the sensing materials.

Heretofore, the tungsten sources used for synthesizing functional WO_3 nanomaterials are mainly some analytical reagents or extremely high-purity tungsten metals, such as Na_2WO_4 [27], H_2WO_4 [28], $(\text{NH}_4)_{10}\text{H}_2\text{W}_{12}\text{O}_{40}$ [29], $\text{H}_3\text{O}_{40}\text{PW}_{12}\cdot x\text{H}_2\text{O}$ [16], WCl_6 [30], etc., which not only have high production costs, but also show low plasticity in terms of purity, particle size, etc. Thus, these disadvantages will affect the microstructure and physic-chemical properties of WO_3 nanomaterials prepared later. Therefore, it is of great significance to find a tungsten source material with low price and good plasticity to prepare WO_3 functional nanomaterials.

Scheelite is a kind of tungsten mineral with tetragonal crystal system, which is the main raw material for tungsten smelting. Some noble metal elements are often associated with scheelite, and these noble metal elements may be conducive to improving the gas sensing performance of nanomaterials. In this paper, a tungsten-containing metallurgical raw material was selected as the tungsten source, and the optimized alkali extraction process of tungsten was adopted to obtain a test-grade tungsten-containing leaching solution with low impurity content. Subsequently, the $\text{WO}_3\cdot 0.33\text{H}_2\text{O}$ microshuttles (WMSs) with stable crystal phase, excellent purity and good dispersivity were prepared by a one-step hydrothermal method with the leaching solution as the precursor solution. For the sake of further investigating the influence of noble metal elements on the microstructure and gas sensing performance of WMSs, the in-situ doping of Pt was used to simulate the associated noble metal elements in scheelite. The results showed that Pt doping could significantly improve the performance of the $\text{WO}_3\cdot 0.33\text{H}_2\text{O}$ sensing materials to NH_3 , and the relevant gas sensing mechanism was also discussed.

2. Experimental

2.1 Materials

The tungsten-containing metallurgical raw material used in this study was mainly composed of scheelite minerals, which was provided by Gansu Xinzhou Mining Co., Ltd. In all the experiments, the as-used reagents were analytical grade (AR) without further purification, and the as-used water was deionized water. In this study, an X-ray Fluorescence spectrometer (XRF) was used to determine the main components of the metallurgical raw material, and the corresponding results are illustrated in Table 1. As observed in Table 1, the main component in the metallurgical raw material is WO_3 (62.36%), and the main gangue compositions are CaO (19.11%), SiO_2 (5.55%), P_2O_5 (3.99%), MgO (2.82%), and Fe_2O_3 (1.55%). Subsequently, the sieve water analysis test was also carried out to further clarify the particle size distribution of the metallurgical raw material. As observed in Table 2, the part with the particle size of less than $38\text{ }\mu\text{m}$ accounts for 89.13% of the total mass of the metallurgical raw material. It demonstrates that the particle size of the metallurgical raw material is very fine, which can meet the test requirements and be directly used in the subsequent leaching experiments.

2.2 Preparation of the samples

The preparation process of the functional WMSs by adopting a cheap tungsten-containing metallurgical raw material as the tungsten source is different from that of the conventional nanomaterials, which mainly consists of the following two steps.

Firstly, the tungsten-containing leaching solution was prepared from a tungsten-containing metallurgical raw material by a NaOH leaching process. This step plays an important role in the WMSs preparation. It could not only convert solid-phase tungsten into liquid-phase tungsten, but also could remove most of impurities in the tungsten-containing metallurgical raw material. During the NaOH leaching process, most of the alkaline harmful impurities, such as iron, calcium, and magnesium, etc., remained in the leaching residue in the form of precipitates, while most of tungsten introduced into the leaching solution in the form of tungstate, realizing the effective separation of impurities and tungsten. The leaching experiments of the metallurgical raw material by NaOH as the leaching reagent were carried out in a 250 mL micro-high pressure autoclave (Shanghai Yanzheng Co., Ltd) equipped with a temperature sensor and a magnetic rotor. The specific operation steps are as follows: the metallurgical raw material (5.0 g) and NaOH (3.5 g) were firstly put into the above autoclave in turn. Secondly, according to the pre-set liquid-solid ratio of 1:1 (quality ratio of deionized water to metallurgical raw material), a certain amount of deionized water was added into the above equipment. Then, the leaching experiment was carried out at 180 °C for 2 h, and the stirring speed was set as 400 rpm. After the reaction, the leaching slurry was transferred into a beaker, and some cleaning and filtering operations were carried out to get the tungsten-containing leaching solution. Subsequently, the content of main elements in the leaching solution was examined by an inductively coupled plasma atomic emission spectrometer (ICP-AES), and the relevant results are illustrated in Table 3. It can be observed from Table 3 that the content of tungsten in the leaching solution is relatively high and the contents of other impurities are low, and no other new impurities that are difficult to remove are introduced in the leaching process. The as-obtained tungsten-containing leaching solution could meet the requirements of the experimental-purity standard, so it could be directly used as the precursor solution for the preparation of $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ sensing materials in the future.

Secondly, using the as-obtained tungsten-containing leaching solution as the precursor solution, the WMSs were synthesized by a one-step hydrothermal method with the assistance of Na_2SO_4 surfactant. The leaching solution contains a large amount of Na^+ ions and OH^- ions, and Na^+ ions always acts as an important component of structure modifier in the synthesis process of WO_3 sensing materials. If its content is too high, it will directly affect the microstructure of the nanomaterials. Therefore, the Na^+ ions in the leaching solution should be removed first in the preparation process. The detailed experiment process is as follows. Firstly, 10 mL of leaching solution was placed into a beaker with the capacity of 250 mL, and 3 M of HCl solution with a volume of 24 mL was slowly added into the above beaker with strongly stirring for 2 min to obtain tungstic acid precipitate. The as-obtained precipitation product was washed and filtered for 5 times with deionized water to remove the metal cations from the leaching solution. Then, NaOH (0.27 g) and deionized water (50 mL) were mixed with the pre-treated tungstic acid precipitate, and continuous stirring was carried out until the as-obtained white tungstic acid was dissolved completely. Subsequently, 0.6 g of Na_2SO_4 was added into the above mentioned mixture, and kept strongly stirring for 10 min. For the sake of obtaining the WMSs with different Pt concentrations, a certain amount of chloroplatinic acid (H_2PtCl_6) solution based on the molar ratio (0, 0.7%, 1.0%, and 1.3%) of Pt to W was placed into the above mixed solution under continuously stirring for 10 min. The pH value of the mixture was adjusted to 2.2 using 3 M of HCl solution under intensely stirring for 10 min. Then, the as-obtained mixed solution was transferred to a 100 mL hydrothermal autoclave, and reacted at 140 °C for 12 h. When the hydrothermal reaction was completed, the as-obtained precipitation product was collected by washing and filtering with deionized water for 5 times, and then dry treatment was performed in an oven at 60 °C.

Finally, the grayish-white WMSs with stable crystal form were obtained by annealing the resultant product in a tube furnace at 400 °C for 4 h.

2.3 Characterization of the samples

An X-ray Fluorescence spectrometer (XRF, Shimadzu XRF-1800) was adopted to examine the elemental compositions of the tungsten-containing metallurgical raw material. An inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Fisher Scientific) was used to investigate the main elemental compositions of the as-prepared tungsten-containing leaching solution. An X-ray diffractometer (XRD, PANalytical X'Pert Pro, Cu-K α radiation $\lambda=1.5406$ Å) was applied to investigate the main component and crystal structure of the WMSs powder. A field-emission scanning electron microscope (FESEM, ZEISS Ultra Plus) was used to observe the surface morphology of the Pt-doped WMSs with different Pt concentrations. A high-resolution transmission electron microscope (TEM, FEIG²-20) was used to characterize the microstructure of the as-prepared nanomaterials. An energy-dispersive spectroscope (EDS) attached to TEM equipment was used to investigate the elemental distribution state of the WMSs. An X-ray photoelectron spectroscope (XPS, ESCALAB 250 Xi, Al K α radiation) was adopted to characterize the elemental compositions and relevant valence state of the sensing materials. An infrared spectrometer (FTIR, NICOLET380) was used to analyze the functional groups and chemical bonds of the as-synthesized samples.

2.4 Fabrication of gas sensor device

The WMSs powder and an appropriate amount of absolute ethanol were placed in a 1.5 mL of centrifuge tube, and dispersed it for 15 min under ultrasonic to obtain a uniformly viscous slurry. Then, the slurry was evenly brushed on the ceramic tube surface, so that a pair of pre-plated annular Au electrodes was completely covered by the slurry to obtain a gas sensing film. Among them, a pair of Pt leads was connected to each Au electrode, and a Ni-Cr alloy heating coil was traversed through the whole hollow ceramic tube to adjust operating temperature by changing the heating voltage. After the paste coated on the Au electrode was completely dried, the four Pt leads and the two ends of the heating coil were respectively welded to the corresponding terminal on the hexagonal base. Finally, the assembled gas sensor was aged at 300 °C for a week to strengthen the contact between the sensing particles and enhance the surface stability of the gas sensing material.

2.5 Gas sensing measurements

In this study, a static gas distribution system (WS-30A, Weisheng Electronics Co., Ltd) was used to investigate the performance of pure and Pt-doped WMSs sensing materials. The measurements were carried out in a fume hood with a relative humidity ranging from 28% to 30%, and the operating temperatures of all sensor samples were in the range of 75–225 °C. The target gas was NH₃, and the other interference gases mainly included NO₂, acetone, toluene, methanol, methanal, and SO₂. For the preparation of NH₃ and other interfering gases, a micro-syringe was firstly adopted to extract the required volume of liquid reagents. Then, the liquid reagents were placed on the evaporation device in the test chamber, and the mixed gases could be obtained by mixing the evaporated gas and the air using a fan. The functional relationship between the needed liquid volume and the as-obtained gas concentration is shown as follows:

$$V_x = \frac{V \times C \times M}{22.4 \times \rho \times d} \times 10^{-9} \times \frac{273 + T_R}{273 + T_B} \quad (1)$$

Here, V_x represents the volume of the required liquid reagent (mL), V refers to the volume of the test chamber (mL), C is the concentration of the detected gas, M is the molecular weight of the liquid reagent (g), P is the density of the

liquid reagent (g/cm^3), d represents the purity of the liquid reagent, T_R is the test ambient temperature ($^{\circ}\text{C}$), and T_B is the temperature in the test chamber ($^{\circ}\text{C}$).

The response of the gas sensor to the detected gas is calculated according to the two formulas of $S=R_a/R_g$ (for reducing gas) and $S=R_g/R_a$ (for oxidizing gas), in which R_a and R_g refer to the resistance values of the gas sensor in clean air and detected gas atmosphere, respectively. The response time (T_{res}) refers to the time required for the resistance change of the gas sensor to achieve 90% of the final balance value after injecting the detected gas, while the recovery time (T_{rec}) refers to the time required for the resistance of the gas sensor to recover to 90% of the initial resistance value after releasing the detected gas [31].

3. Results And Discussion

3.1. Structural and morphological characteristics

The crystal structure and phase purity of the WMSs with different Pt concentrations were investigated by XRD technology, and the results are illustrated in Fig. 1. As seen in this figure, the pure and Pt-doped WMSs have obvious characteristic peaks at the diffraction angle between 10° and 70° , which are consistent with those of the standard data file (JCPDS No. 35-1001), indicating that all the as-synthesized products are $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ with hexagonal crystal structure. There are no other diffraction peaks related to impurity components in the XRD patterns, reflecting that the as-synthesized products show high purity. It can also be observed that the main diffraction peaks of all samples are strong and narrow, demonstrating that the as-synthesized samples are in good crystallinity, and grow along (200) plane preferentially. By comparison, it is found that the diffraction peak intensities of (200) planes of all Pt-doped samples are greater than that of the pure one. The diffraction peak intensity gradually increases with the increase of Pt concentration in the range of 1–1.0 mol%, and then decreases with further increasing the concentration, indicating that Pt doping can promote its growth along the main crystal plane. In addition, the relevant diffraction peaks of Pt are not found in all XRD patterns, which maybe mainly due to the low amount of Pt in the WMSs samples.

Fig. 2 shows the SEM images of the WMSs with different Pt concentrations. It can be seen that the pure and Pt-doped WMSs with the diameter of 0.8–1.9 μm are composed of well-dispersed microshuttles, which are self-assembled from numerous nanorods. These nanorods with the diameter of 17–62 nm are closely packed in the same direction, and the length of the nanorods is gradually shortened from the middle position to the outer position, eventually resulting in the formation of the microshuttles. Moreover, with increasing Pt concentration, the surface of the obtained microshuttles becomes smoother, indicating that Pt doping may promote the growth of nanorods in a more dense direction to a certain extent.

The microstructure, crystallinity and elemental distribution of 1.0 mol% Pt-doped WMSs were further measured by TEM and EDS technologies, and the corresponding results are illustrated in Fig.3. Figs. 3(a-c) are the low-resolution TEM images of this sample, which further prove that the as-synthesized sample with good dispersion is composed of WMSs self-assembled by nanorods. The nanorods are closely packed in the same direction, and the nanorods existed at the middle of the microshuttles are obviously longer, which is consistent with the observation results of SEM images. Such kind of coarse structure can effectively increase the specific surface area of the sensing material, which will be beneficial to the chemisorption of gaseous molecules as well as the subsequent reactions with the material surfaces. Fig. 3(d) is the high-resolution TEM image of the WMSs. Some very clear lattice fringes can be found, indicating a high crystallinity of the sample. Among them, the lattice spacing of 0.365 nm can match well with the (110) crystal plane of hexagonal $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$, and the lattice spacing of 0.227 nm can match well with the (020)

crystal plane of PtO_2 . Fig. 3(e) illustrates the selected area electron diffraction (SAED) image of the WMSs. As observed in this figure, there are many neat and regular diffraction spots in the entire field of view, indicating that the microshutters with excellent crystallization are composed of single-crystal nanoparticles. Figs. 3(f-i) are the distribution images of main elements of Pt-doped WMSs. As observed in these figures, the three elements of W, O and Pt are the main elements of the WMSs, and each element is uniformly distributed in the microshutters, indicating that Pt element is successfully doped into the microshutters by the in-situ hydrothermal method in the form of its oxide.

The chemical valence state and elemental compositions of the 1.0 mol% Pt-doped WMSs characterized by XPS technology are presented in Fig. 4. The C 1s peak (284.8 eV) was regarded as a reference to calibrate the binding energies of the Pt-doped sample. The full scanning XPS spectrum of this sample shown in Fig. 4(a) indicates that the surface elements are comprised of primarily C and some W and O. As observed in Fig. 4(b), the peak located at 531.05 eV corresponds to O 1s, confirming the presence of lattice oxygen (O^{2-}), which can be bonded with W [32]. As seen in Fig. 4(c), the W 4f spectra of the WMSs can be deconvoluted into two strong peaks of W 4f_{5/2} (37.43 eV) and W 4f_{7/2} (35.33 eV), demonstrating that the tungsten in $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ crystal mainly exists in the form of W^{6+} state [33]. In addition, a single peak at 40.98 eV can be observed, which originates from a weak emission of W 5P_{3/2} [34]. Fig. 4(d) shows the XPS spectrum of Pt 4f. There is an obvious absorption peak located at 79.46 eV, and its binding energy is corresponding to Pt 4f, indicating the presence of PtO_2 in the Pt-doped WMSs [31].

The main functional groups and chemical bonds of pure and Pt-doped WMSs were investigated by FTIR technology, and the results are shown in Fig. 5. It is found that the four samples have similar FTIR spectrum, namely that the positions and intensities of the characteristic peaks are basically same. For each sample, two characteristic peaks appear at 713 and 881 cm^{-1} , both of which are ascribed to the stretching vibration of the bridging oxygen (W-O-W) [32]. A weak peak can be found at 1389 cm^{-1} , which can be contributed to the stretching vibration of W-OH [35]. The bending vibration band of O-H can be found at 1619 cm^{-1} for the sample [36]. The stretching vibration band of -OH appears at 3452 cm^{-1} [37]. In addition, the characteristic peaks of other impurities are not found, which further indicates that the four samples have higher purity. Simultaneously, there are no characteristic peaks related to Pt in the FTIR spectra, which may be attributed to the low amount of Pt in the samples.

3.2. Gas sensing characteristics

Fig. 6 illustrates the responses of the WMSs with various Pt concentrations to 1000 ppm NH_3 gas in the temperature range of 25–225 °C. As seen in Fig. 6, except for the pure one, the responses of all Pt-doped WMSs show an obvious trend of “first rising and then descending” with increasing operating temperature. This is mainly ascribed to the chemical activities of the gas sensing materials and gas molecules, and the adsorption-desorption process of the gaseous molecules on the nanomaterial surfaces is greatly affected by the operating temperature [38–43]. The responses of all Pt-doped WMSs increase as the temperature increases in the range of 25–175 °C, and then decrease as the temperature value exceeds 175 °C. Therefore, the optimal operating temperature of Pt-doped WMSs towards NH_3 gas is 175 °C. Compared with Pt-doped WMSs, the pure one exhibits higher response at a lower temperature ranging from 25 to 100 °C, and the response reaches the maximum value at 50 °C. However, the response stability of the pure sample is relatively poor, and there is basically no response to NH_3 gas in the high temperature range. The responses of pure, 0.7, 1.0 and 1.3 mol% Pt-doped WMSs to 1000 ppm NH_3 gas at optimal operating temperatures are 7.8, 21.2, 28.2 and 3.8, respectively. Obviously, although the pure WMSs can obtain the maximum response at a relatively lower temperature, the response is far less than those of 0.7 and 1.0 mol% Pt-doped ones. The enhanced response of the WMSs by Pt doping may be ascribed to the excellent catalytic activity of PtO_2 nanoparticles [44, 45].

When Pt concentration is low, the catalyst dispersed on the surface of sensing material can only catalyze a part of NH_3 molecular. As Pt concentration further increases, the finely dispersed PtO_2 nanoparticles will trap more electrons, leading to the improvement in the N-H bond dissociation.

Fig. 7 shows the response-recovery curves of the WMSs to 1000 ppm NH_3 gas at their optimal operating temperatures. As seen in Fig. 7, when the four gas sensors are placed in the NH_3 gas atmosphere, the resistance values of the gas sensors drop sharply, and then trend to be stable. When the NH_3 gas is released, the resistance values of all the gas sensors can be completely recovered to their initial values, demonstrating that the WMSs are n-type MOS materials. According to the analysis, the response and recovery times of pure WMSs to 1000 ppm NH_3 gas at 50 °C are 45 and 74 s, respectively. The response times of 0.7, 1.0 and 1.3 mol% Pt-doped WMSs to the same concentration of NH_3 gas at 175 °C are 54, 39 and 42 s, respectively, while the recovery times are 401, 300 and 182 s, respectively. The results show that a certain amount of Pt doping can not only shorten the response time of the gas sensing material, but also greatly improve the response value, which will be very beneficial to the real-time detection of NH_3 gas.

Fig. 8 presents the response-recovery curves of the WMSs to various concentrations (10, 30, 50, 100, 300, 500, and 1000 ppm) of NH_3 gas at optimal operating temperatures. As observed in Fig. 8, the amplitude changes of the resistance values of the four gas sensors obviously show a similar stepwise increasing trend with increasing NH_3 concentration, indicating that the responses also show the same increase trends. Among them, the pure WMSs have almost no response to the low concentration of NH_3 gas. In the case of in-situ Pt doping, the gas sensing materials show a greater response to low-concentration NH_3 gas, indicating that Pt doping can detect lower concentration of NH_3 gas. In addition, the amplitude change of the resistance value of 1.0 mol% Pt-doped WMSs for various concentrations of NH_3 gas are significantly higher than those of pure and other Pt-doped ones.

Fig. 9 illustrates the responses of the WMSs with different Pt concentrations towards 10–1000 ppm NH_3 gas at the optimal operating temperatures. As observed in this figure, the responses of the four sensing materials are continuously enhanced with increasing NH_3 concentration. Especially, 1.0 mol% Pt-doped WMSs show higher response values to different concentrations of NH_3 gas, while 1.3 mol% Pt-doped WMSs show poor response to NH_3 gas, indicating that the appropriate concentration of Pt doping is helpful to improve the response of gas sensing material. The high concentration of Pt doping may inhibit the gas sensing reactions on the material surface to a certain extent, thus reducing the sensor response. As observed in this figure, 1.0 mol% Pt-doped WMSs does not reach the saturation stage for the chemisorption of NH_3 molecules when the NH_3 concentration is 1000 ppm, indicating that the as-prepared gas sensing material can supply more active sites for the chemisorption of gaseous molecules, and has a wider detection range for NH_3 gas. The responses of 1.0 mol% Pt-doped WMSs to the above different concentrations of NH_3 gas are 1.9, 3.7, 5.0, 8.9, 13.2, 16.8 and 28.2, respectively.

Fig. 10(a) shows the reproducibility of 1.0 mol% Pt-doped WMSs to 1000 ppm NH_3 at 175 °C. It can be seen that after the introduction of 1000 ppm NH_3 gas in five cycles, the Pt-doped WMSs exhibit approximately the same amplitude change of the resistance values, reflecting good reproducibility. In addition, when the NH_3 gas is released, the Pt-doped WMSs can completely recover the initial resistance value, showing excellent detection reversibility. The long-term stability illustrated in Fig. 10(b) demonstrates that the response values of the as-synthesized sensing material to 1000 ppm NH_3 gas has been fluctuating around 28 in the whole test period of 30 days, indicating that the present gas sensor has a good long-term stability.

Fig. 11 illustrates the selectivity of pure and 1.0 mol% Pt-doped WMSs towards NH_3 gas in different kinds of gas atmospheres, such as methanol, NO_2 , acetone, methylbenzene, SO_2 and methanal. As seen in Fig. 11, the response of Pt-doped WMSs towards 1000 ppm NH_3 at 175 °C is as high as 28.2, while the response values are relatively low and not higher than 3 to 1000 ppm methanol, 5 ppm NO_2 , 100 ppm methylbenzene, 100 ppm methanal, 100 ppm acetone and 100 ppm SO_2 , demonstrating that Pt doping can significantly improve the response of the sensing material to NH_3 gas, but it has no obviously enhanced effect on the responses of other interfering gases.

In order to further clarify the superiority of the present sensor, the gas sensing properties of the as-synthesized WMSs was compared with those of other WO_3 -based gas sensors, mainly including the peak response, the response/recovery time and the optimal operating temperature, and the corresponding results are shown in Table 4. It can be seen that most of NH_3 gas sensors based on WO_3 sensing materials have the optimal operating temperature in a higher temperature range of 250–350 °C, while the WMSs-based gas sensors prepared in this study show lower operating temperature, especially the Pt-doped WMSs gas sensors. In addition, the as-synthesized Pt-doped WMSs sensing material has lower operating temperature and higher response to the same concentration of NH_3 gas compared with the Pt-decorated WO_3 thin film in the literature. Although the as-prepared Pt-doped WMSs exhibit a lower response to a higher concentration of NH_3 gas compared with the WO_3 flower-like nanostructures, the operating temperature of the as-prepared sensing material is far lower than that of the reported sensing materials. Therefore, the as-synthesized Pt-doped WMSs show good comprehensive performance.

3.3. Gas sensing mechanism

The WMSs belong to a kind of surface-controlled gas sensing material. The gas sensing properties of the WMSs is greatly affected by the type and quantity of the chemisorbed oxygen on the material surface. The gas sensing reaction process of the WMSs mainly includes the following two stages. In the first stage, oxygen molecules in air adsorb on the surface of the WMSs at a certain operating temperature, capturing electrons from the conduction band of the sensing material, and forming a variety of chemical adsorbed oxygen ions on the material surface, such as O_2^- (less than 100 °C), O^- (100–300 °C), and O^{2-} (more than 300 °C) [50, 51]. At this time, the depletion layer width of the WMSs increases, so the resistance value of the material increases. In the second stage, when the WMSs are placed in the NH_3 atmosphere, the highly reactive oxygen anions will react with the NH_3 molecules to produce smaller group molecules such as N_2 , NO and NO_2 , and release free electrons [52]. These free electrons are transferred to the conduction band of the WMSs, and the depletion layer width of the sensing material becomes narrow, thus the resistance value of the material decreases significantly [47, 53].

On the basis of the gas sensing performance results of the as-synthesized WMSs, the appropriate concentration of Pt doping can significantly enhance the gas sensing performance to NH_3 gas. The enhancement in gas sensing properties of the semiconductor materials induced by the noble metal nanoparticles is mainly ascribed to the electronic sensitization and chemical sensitization mechanism of the noble metal nanoparticles, which can play a catalytic role in the electron transport and transfer on the material surface, thereby improving the gas sensing properties to the reducing NH_3 gas [46]. In the process of electron sensitization, noble metal oxide nanoparticles can act as effective electron acceptors to capture free electrons from the surface of the WMSs and form electron depletion layer at the contact interface of the two materials. When the reducing NH_3 molecules contact with the noble metal nanoparticles, the noble metal oxides are reduced and the extra electrons are released and returned to the material surface, which is shown as the enhancement in the response. The chemical sensitization process is mainly due to the catalytic oxidation of noble metal nanoparticles on the material surface. The noble metal nanoparticles can supply

active adsorption and reaction sites for NH_3 molecules on the WMSs surface. On the one hand, the introduction of noble metal element will accelerate the formation of chemisorbed oxygen on the material surface. On the other hand, it will make it easier for electrons to transfer from the active adsorption sites to the surfaces of the sensing materials, and react with the oxygen anion on the surfaces of the sensing materials, so as to enhance the gas sensing performance to NH_3 gas.

4. Conclusions

Pure and Pt-doped $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ microshuttles were prepared from a tungsten-containing metallurgical raw material by combination processes of NaOH leaching for obtaining test-grade leaching solution containing tungsten and one-step hydrothermal method for synthesizing sensing materials. The WMSs with the diameter of approximately 0.8 – 1.9 μm were self-assembled by many one-dimensional nanorods along the same direction. These nanorods with a single hexagonal crystal structure had different lengths, and their diameters were in the range of 17 – 62 nm. A certain concentration of Pt doping not only could improve the gas sensing performance towards NH_3 in terms of the response, reproducibility, and selectivity in the operating temperature range of 25 – 225 $^\circ\text{C}$, but also could significantly reduce the detection limit of NH_3 gas. Especially, the 1.0 mol% Pt-doped WMSs exhibited highest response value of 28.2 towards 1000 ppm NH_3 at 175 $^\circ\text{C}$, which was about 4 times higher than pure one at 50 $^\circ\text{C}$. The enhancement in gas sensing performance of Pt-doped WMSs to NH_3 gas could be ascribed to the catalysis of noble metal nanoparticles.

Declarations

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References

1. Albaris H, Karuppasamy G (2020) Investigation of NH_3 gas sensing behavior of intercalated PPy-GO- WO_3 hybrid nanocomposite at room temperature. *Materials Science Engineering: B* 257:114558
2. Meng W, Dai L, Zhu J, Li Y, Meng W, Zhou H, Wang L (2016) A novel mixed potential NH_3 sensor based on TiO_2/WO_3 core-shell composite sensing electrode. *Electrochim Acta* 193:302–310
3. Xiong Y, Xu W, Ding D, Lu W, Zhu L, Zhu Z, Wang Y, Xue Q (2018) Ultra-sensitive NH_3 sensor based on flower-shaped SnS_2 nanostructures with sub-ppm detection ability. *J Hazard Mater* 341:159–167
4. Das M, Sarkar D (2017) One-pot synthesis of zinc oxide-polyaniline nanocomposite for fabrication of efficient room temperature ammonia gas sensor. *Ceram Int* 43:11123–11131
5. Soleimanpour AM, Jayatissa AH, Sumanasekera G (2013) Surface and gas sensing properties of nanocrystalline nickel oxide thin films. *Appl Surf Sci* 276:291–297
6. Dhivya P, Prasad AK, Sridharan M (2014) Nanostructured TiO_2 films: Enhanced NH_3 detection at room temperature. *Ceram Int* 40:409–415

7. Yan H, Song P, Zhang S, Zhang J, Yang Z, Wang Q (2016) A low temperature gas sensor based on Au-loaded MoS₂ hierarchical nanostructures for detecting ammonia. *Ceram Int* 42:9327–9331
8. Li S, Liu A, Yang Z, Zhao L, Wang J, Liu F, You R, He J, Wang C, Yan X, Sun P, Liang X, Lu G (2019) Design and preparation of the WO₃ hollow spheres@ PANI conducting films for room temperature flexible NH₃ sensing device. *Sens Actuators B* 289:252–259
9. Fedoruk MJ, Bronstein R, Kerger BD (2005) Ammonia exposure and hazard assessment for selected household cleaning product uses. *Journal of Exposure Analysis Environmental Epidemiology* 15:534–544
10. Björn, Timmer, Wouter, Olthuis, Albert, van, den, Berg], Ammonia sensors and their applications – a review, *Sensors and Actuators B: Chemical*, (2005)
11. Wagh MS, Jain GH, Patil DR, Patil SA, Patil LA (2006) Modified zinc oxide thick film resistors as NH₃ gas sensor. *Sens Actuators B* 115:128–133
12. Timmer B, Olthuis W (2005) A.v.d. Berg, Ammonia sensors and their applications – a review. *Sens Actuators B* 107:666–677
13. Mani GK, Rayappan JBB (2013) A highly selective room temperature ammonia sensor using spray deposited zinc oxide thin film. *Sens Actuators B* 183:459–466
14. Guernion N, Ewen RJ, Pihlainen K, Ratcliffe NM, Teare GC (2002) The fabrication and characterisation of a highly sensitive polypyrrole sensor and its electrical responses to amines of differing basicity at high humidities. *Synth Met* 126:301–310
15. Li P, Wang B, Qin C, Han C, Sun L, Wang Y (2020) Band-gap-tunable CeO₂ nanoparticles for room-temperature NH₃ gas sensors. *Ceram Int* 46:19232–19240
16. Wang Y, Liu J, Cui X, Gao Y, Ma J, Sun Y, Sun P, Liu F, Liang X, Zhang T, Lu G (2017) NH₃ gas sensing performance enhanced by Pt-loaded on mesoporous. *Sens Actuators B WO₃*:473–481 238)
17. Travlou NA, Badosz TJ (2017) Nanoporous carbon-composites as gas sensors: Importance of the specific adsorption forces for ammonia sensing mechanism. *Carbon* 121:114–126
18. Jang WK, Yun JM, Kim HI, Lee YS (2012) Improvement in ammonia gas sensing behavior by polypyrrole/multi-walled carbon nanotubes composites. *Carbon Letters* 13:88–93
19. Kulkarni SB, Navale YH, Navale ST, Stadler FJ, Ramgir NS, Patil VB (2019) Hybrid polyaniline-WO₃ flexible sensor: A room temperature competence towards NH₃ gas. *Sens Actuators B* 288:279–288
20. Li J, Huang J, Yu C, Wu J, Yanagisawa K (2011) Hierarchically structured snowflakelike WO₃·0.33H₂O particles prepared by a facile, green, and microwave-assisted method. *Chem Lett* 40:579–581
21. Liu X, Su X, Yang C, Ma K (2019) Hydrothermal synthesis of WO₃·0.33H₂O nanorod bundles as a highly sensitive cyclohexene sensor. *Sensors* 19:1257
22. Gao X, Chao Y, Feng X, Ying Z, Wang J, Su X (2012) WO₃·0.33H₂O nanoplates: Hydrothermal synthesis, photocatalytic and gas-sensing properties. *Mater Lett* 84:151–153
23. Wang H, Yang H, Chu D, Ge G, Sun J, Hu W, Chen X, Wang W, Xue Y (2017) Synthesis of 3D hierarchical WO₃·0.33H₂O microsphere architectures with enhanced visible-light-driven photocatalytic activity. *Mater Lett* 193:5–8
24. Ganesh RS, Durgadevi E, Navaneethan M, Patil VL, Ponnusamy S, Muthamizhchelvan C, Kawasaki S, Patil PS, Hayakawa Y (2018) Tuning the selectivity of NH₃ gas sensing response using Cu-doped ZnO nanostructures. *Sensors Actuators A: Physical* 269:331–341

25. Thai NX, Van Duy N, Van Toan N, Hung CM, Van Hieu N, Hoa ND (2020) Effective monitoring and classification of hydrogen and ammonia gases with a bilayer Pt/SnO₂ thin film sensor. *Int J Hydrogen Energy* 45:2418–2428
26. Chen H-I, Hsiao C-Y, Chen W-C, Chang C-H, Chou T-C, Liu IP, Lin K-W, Liu W-C (2018) Characteristics of a Pt/NiO thin film-based ammonia gas sensor. *Sens Actuators B* 256:962–967
27. Hung CM, Dat DQ, Van Duy N, Van Quang V, Van Toan N, Van Hieu N, Hoa ND (2020) Facile synthesis of ultrafine rGO/WO₃ nanowire nanocomposites for highly sensitive toxic NH₃ gas sensors. *Mater Res Bull* 125:110810
28. Fan G, Chen D, Li T, Yi S, Ji H, Wang Y, Zhang Z, Shao G, Fan B, Wang H, Xu H, Lu H, Zhou Y, Zhang R, Sun J (2020) Enhanced room-temperature ammonia-sensing properties of polyaniline-modified WO₃ nanoplates derived via ultrasonic spray process. *Sens Actuators B* 312:127892
29. Ji H, Zeng W, Xu Y, Li Y (2019) Nanosheet-assembled hierarchical WO₃ flower-like nanostructures: Hydrothermal synthesis and NH₃-sensing properties. *Mater Lett* 250:155–158
30. Jeevitha G, Mangalaraj D, Ammonia sensing at ambient temperature using tungsten oxide (WO₃) nanoparticles, *Materials Today: Proceedings*, 18 (2019) 1602–1609
31. Li T, Shen Y, Zhong X, Zhao S, Li G, Cui B, Wei D, Wei K (2020) Effect of noble metal element on microstructure and NO₂ sensing properties of WO₃ nanoplates prepared from a low-grade scheelite concentrate. *J Alloy Compd* 818:152927
32. Wang M-D, Li Y-Y, Yao B-H, Zhai K, Li Z-J, Yao H-C (2019) Synthesis of three-dimensionally ordered macro/mesoporous C-doped WO₃ materials: Effect of template sizes on gas sensing properties. *Sens Actuators B* 288:656–666
33. Yuan K-P, Zhu L-Y, Yang J-H, Hang C-Z, Tao J-J, Ma H-P, Jiang A-Q, Zhang DW, Lu H-L (2020) Precise preparation of WO₃@SnO₂ core shell nanosheets for efficient NH₃ gas sensing. *J Colloid Interface Sci* 568:81–88
34. Kolhe PS, Mutadak P, Maiti N, Sonawane KM (2020) Synthesis of WO₃ nanoflakes by hydrothermal route and its gas sensing application. *Sensors Actuators A: Physical* 304:111877
35. Zhou P, Shen Y, Zhao S, Li G, Yin Y, Lu R, Gao S, Han C, Wei D (2019) NO₂ sensing properties of WO₃ porous films with honeycomb structure. *J Alloy Compd* 789:129–138
36. Li T, Shen Y, Zhao S, Zhong X, Zhang W, Han C, Wei D, Meng D, Ao Y (2019) Sub-ppm level NO₂ sensing properties of polyethyleneimine-mediated WO₃ nanoparticles synthesized by a one-pot hydrothermal method. *J Alloy Compd* 783:103–112
37. Shen Y, Li T, Zhong X, Li G, Li A, Wei D, Zhang Y, Wei K (2020) Ppb-level NO₂ sensing properties of Au-doped WO₃ nanosheets synthesized from a low-grade scheelite concentrate. *Vacuum* 172:109036
38. Zhang Z, Yates JT (2012) Band bending in semiconductors: chemical and physical consequences at surfaces and interfaces. *Chem Rev* 112:5520–5551
39. Ionescu R, Llobet E, Vilanova X, Brezmes J, Correig X (2002) Quantitative analysis of NO₂ in the presence of CO using a single tungsten oxide semiconductor sensor and dynamic signal processing. *Analyst* 127:1237–1246
40. Chen Y, Zhu C, Shi X, Cao M, Jin H (2008) The synthesis and selective gas sensing characteristics of SnO₂/α-Fe₂O₃ hierarchical nanostructures. *Nanotechnology* 19:205603
41. Chen Y, Xiao G, Wang T, Zhang F, Ma Y, Gao P, Zhu C, Zhang E, Xu Z, Li Q (2011) Synthesis and enhanced gas sensing properties of crystalline CeO₂/TiO₂ core/shell nanorods. *Sensors Actuators B-chemical* 156:867–874
42. Wang C, Yin L, Zhang L, Xiang D, Gao R (2010) Metal oxide gas sensors: Sensitivity and influencing factors. *Sensors* 10:2088–2106

43. Lu G, Wang X, Liu J, Qiu S, He C, Li B, Liu W (2013) One-pot synthesis and gas sensing properties of ZnO mesoporous architectures. *Sensors Actuators B-chemical* 184:85–92
44. Kim J, Wu P, Kim HW, Kim SS (2016) Highly selective sensing of CO, C₆H₆, and C₇H₈ gases by catalytic functionalization with metal nanoparticles. *ACS Appl Mater Interfaces* 8:7173–7183
45. Bing Y, Zeng Y, Feng S, Qiao L, Wang Y, Zheng W (2016) Multistep assembly of Au-loaded SnO₂ hollow multilayered nanosheets for high-performance CO detection. *Sensors Actuators B-chemical* 227:362–372
46. Liu IP, Chang C-H, Chou TC, Lin K-W (2019) Ammonia sensing performance of a platinum nanoparticle-decorated tungsten trioxide gas sensor. *Sens Actuators B* 291:148–154
47. Hieu NV, Quang VV, Hoa ND, Kim D (2011) Preparing large-scale WO₃ nanowire-like structure for high sensitivity NH₃ gas sensor through a simple route. *Curr Appl Phys* 11:657–661
48. Toan NV, Hung CM, Duy NV, Hoa ND, Le DTT, Hieu NV (2017) Bilayer SnO₂-WO₃ nanofilms for enhanced NH₃ gas sensing performance. *Materials Science Engineering: B* 224:163–170
49. Xiong Y, Zhu Z, Guo T, Li H, Xue Q (2018) Synthesis of nanowire bundle-like WO₃-W₁₈O₄₉ heterostructures for highly sensitive NH₃ sensor application. *J Hazard Mater* 353:290–299
50. Boudiba A, Zhang C, Navio C, Bittencourt C, Snyders R, Debligny M (2010) Preparation of highly selective, sensitive and stable hydrogen sensors based on Pd-doped tungsten trioxide. *Procedia Eng* 5:180–183
51. Belysheva TV, Bogovtseva LP, Kazachkov EA, Serebryakova NV (2003) Gas-sensing properties of doped In₂O₃ films as sensors for NO₂ in air. *J Anal Chem* 58:583–587
52. Chen Y, Zhang W, Wu Q (2017) A highly sensitive room-temperature sensing material for NH₃:SnO₂-nanorods coupled by rGO. *Sens Actuators B* 242:1216–1226
53. Zhang C, Kanta AF, Yin H, Boudiba A, D'Haen J, Olivier MG, Debligny M (2013) H₂ sensors based on WO₃ thin films activated by platinum nanoparticles synthesized by electroless process. *Int J Hydrogen Energy* 38:2929–2935

Tables

Table 1
Chemical multi-element analysis results of the tungsten-containing metallurgical raw material.

Component	WO ₃	CaO	SiO ₂	P ₂ O ₅	MgO	SO ₃	Fe ₂ O ₃	F	BaO	K ₂ O	MoO ₃	Others
Content/%	62.36	19.11	5.55	3.99	2.82	2.17	1.55	0.69	0.35	0.28	0.25	0.88

Table 2
Results of sieve water analysis test of the tungsten-containing metallurgical raw material.

Particle size / μm	Yield ratio / %
+ 75	3.41
-75 + 45	4.92
-45 + 38	2.54
-38	89.13
Total	100.00

Table 3
Analysis results of main components of leaching solution.

Element	W	Si	Mo	As	P
Content(g/L)	122.2	0.33	0.52	0.061	0.99

Table 4
Comparisons of NH₃ gas sensing properties of Pt-doped WMSs-based gas sensor with other WO₃-based gas sensors.

Materials	T _{op} (°C)	NH ₃ (ppm)	Response	T _{res} /T _{rec} (s)	References
Pt-decorated WO ₃ thin film	250	1000	26.9	~	[46]
WO ₃ nanowires	250	1500	9.7	7/8	[47]
Bilayer SnO ₂ -WO ₃ nanofilms	300	250	7.1	~	[48]
WO ₃ @SnO ₂ core shell	200	15	1.55	62/42	[33]
Nanosheet-assembled hierarchical WO ₃ flower-like nanostructures	350	100	36.3	~	[29]
WO ₃ -W ₁₈ O ₄₉ heterostructures	250	500	23.3	13/49	[49]
RGO/WO ₃ nanowire composites	300	100	11	37/711	[27]
Pure WO ₃ ·0.33H ₂ O micro-shuttles	225	1000	7.8	45/74	This work
Pt-doped WO ₃ ·0.33H ₂ O micro-shuttles	175	1000	28.2	39/300	This work

Figures

Figure 1

XRD spectra of the WMSs with different Pt concentrations. (a) Pure. (b) 0.7 mol%. (c) 1.0 mol%. (d) 1.3 mol%.

Figure 2

Low- and high-magnification SEM images of the WMSs with different Pt concentrations. (a-b) Pure. (c-d) 0.7 mol%. (e-f) 1.0 mol%. (g-h) 1.3 mol%.

Figure 3

TEM, EDS and SAED images of 1.0 mol% Pt-doped WMSs. (a-c) Low-resolution TEM images. (d) High-resolution TEM image. (e) SAED image. (f) TEM image. (g) Distribution image of O element. (h) Distribution image of W element. (i) Distribution image of Pt element.

Figure 4

XPS spectra of 1.0 mol% Pt-doped WMSs. (a) Full scanning XPS spectrum. (b) O 1s spectrum. (c) W 4f spectrum. (d) Pt 4f spectrum.

Figure 5

FTIR spectra of the WMSs with different Pt concentrations. (a) Pure. (b) 0.7 mol%. (c) 1.0 mol%. (d) 1.3 mol%.

Figure 6

Responses of the WMSs with different Pt concentrations to 1000 ppm NH₃ gas at different operating temperatures.

Figure 7

Response-recovery curves of the WMSs with different Pt concentrations to 1000 ppm NH₃ gas at their optimal operating temperatures.

Figure 8

Response-recovery curves of the WMSs to various concentrations of NH_3 gas at optimal operating temperatures.

Figure 9

Responses of the WMSs to various concentrations of NH₃ gas at optimal operating temperatures.

Figure 10

(a) Reproducibility curve and (b) long-term stability curve of 1.0 mol% Pt-doped WMSs to 1000 ppm NH₃ gas at 175 °C.

Figure 11

Selectivity of pure and 1.0 mol% Pt-doped WMSs to different types of gases at optimal operating temperatures.