Porous NiO–WO₃ heterojunction nanofibers fabricated by electrospinning with enhanced gas sensing properties

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A series of NiO–WO₃ composite nanofibers with different molar ratios (Ni/W = 0%, 1%, 3% and 5%) were fabricated based on an electrospinning and calcination technique. The gas sensing performances of sensors based on the as-produced nanofibers were studied towards acetone in detail. Compared with the pure WO₃ nanofibers, the porous NiO–WO₃ composite nanofibers exhibited higher sensitivity, faster response, and shorter recovery time towards acetone. Particularly, the 3 mol% NiO–WO₃ heterojunction nanofibers demonstrated the largest sensitivity, exhibiting a prominent value of 22.5 under 100 ppm acetone at the operating temperature of 375 °C, which is almost 2.1 times larger than that of the pure WO₃ nanofibers. Moreover, the 3 mol% NiO–WO₃ heterojunction nanofibers also exhibited excellent selectivity and long-term stability to acetone. The combined effects including the formation of p–n heterojunctions between NiO and WO₃, high oxygen species absorbing capacity, and special porous structural features with high surface area and small grain size, contributed to the enhanced sensing properties of the 3 mol% NiO–WO₃ composite nanofibers. These attractive gas sensing properties enable the NiO–WO₃ heterojunction nanofibers to be a promising material for application in gas sensors.

For the purpose of improving the gas sensing performances of WO₃, several approaches have been developed in recent years. The first is the construction of WO₃ nanostructures with special morphologies by a variety of methods, such as vacuum deposition, spin-coating, sputtering, and electrospinning. Compared with other methods, electrospinning is an inexpensive and versatile technique for the fabrication of ultra-long one dimensional (1D) organic or inorganic nanofibers with diameters ranging from the nano to the micrometer scale. As we all know, the 1D functional nanomaterials have many good characteristics, such as high surface-to-volume ratio and outstanding carrier transport performance. The second approach is the surface modification of WO₃ by noble metals, such as Au/Pt and Pd. However, morphology-induced improvement of gas sensor performances is still limited, and the high cost also hinders the practical application potential of noble metal modified WO₃.

Thirdly, formation of WO₃-based composite nanomaterials by adding other metal oxides is a popular strategy to improve gas sensor performances. Among the various oxide additives, NiO is a p-type semiconductor with an energy gap of 3.5–4.2 eV. Importantly, compared with other metal oxides, NiO has obviously higher oxygen species absorbing ability, which is very useful for improving gas sensing performance. Gas sensors based on pure NiO nanostructures, such as NiO nanoparticles, polycrystalline nanowires, and nanoflowers, have been demonstrated. Furthermore, NiO can form useful...
heterojunctions with n-type semiconductors, including SnO$_2$ (ref. 7–9) and WO$_3$, to further modulate the width of depletion layer. NiO p-type catalysts were employed to enhance the sensing performances of SnO$_2$ towards VOCs, and the results showed that enhanced sensing performances including higher response and selectivity, shorter response–recovery time were obtained through the NiO additive. Nevertheless, only several articles on NiO–WO$_3$ composite sensing nanomaterials have been reported up to now. Bao et al. synthesized the plate-like heterogeneous NiO–WO$_3$ nanocomposites by the annealing method. Their results showed that the p–n heterogeneous nanocomposites provided the benefits of fast response, improved sensitivity and outstanding selectivity towards NO$_2$ at room temperature. Noh et al. prepared the NiO–WO$_3$ composite thick films by the screen-printing technique, and showed that the sensitivity for NO$_2$ increased distinctly for the composite samples with 1.0 mol% NiO.

In this paper, for further improving the sensing performances of WO$_3$ nanostructures, an electrospinning and calcination method was used to fabricate 1D p–n heterogeneous NiO–WO$_3$ composite nanofibers with porous structure. The gas sensing behaviors of the sensors fabricated by the as-prepared WO$_3$ and NiO–WO$_3$ heterojunction nanofibers were systematically explored. The NiO–WO$_3$ heterojunction nanofibers were demonstrated to have markedly higher acetone sensing characteristics than that of the pure WO$_3$. Moreover, the enhanced mechanism in sensing performance of the heterojunction nanofibers was also explained.

2. Experimental

2.1. Materials

Tungsten(vi)chloride (WCl$_6$), nickel acetate Ni(CH$_3$COO)$_2$·4H$_2$O and N,N-dimethylformamide (DMF) were bought from Sinopharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (PVP, $M_w = 1\,300\,000$) were purchased from Alfa Aesar. All chemical reagents were of analytical grade and used directly.

2.2. Synthesis of pure WO$_3$, pure NiO and NiO–WO$_3$ composite nanofibers

A series of NiO–WO$_3$ composite nanofibers with different Ni/W molar ratios (0%, 1%, 3% and 5%) were synthesized based on a versatile electrospinning technique combined with subsequent calcination. Typically, the precursor solution for electrospinning process was prepared by dissolving 1.5 g WCl$_6$, 1.2 g PVP and a desired amount of Ni(CH$_3$COO)$_2$·4H$_2$O (Ni/W molar ratios = 0%, 1%, 3% and 5%) in DMF solvent (10 mL) under vigorous stirring at 80°C for 6 h. The above solution was then stirred overnight at room temperature to obtain a homogeneous mixture sol. Afterwards, the prepared homogeneous mixture sol was carefully sucked into a 20 mL plastic syringe. The feeding rate of the precursor solution was fixed at 0.8 mL h$^{-1}$. The high voltage was 21 kV, and the distance between the needle of the syringe and grounded aluminum foil was set to be 15 cm. Finally, NiO–WO$_3$ nanofibers were obtained by calcination of the primary nanofibers at 500°C for 2 h in air to remove organic constituents. In addition, pure NiO

Fig. 1 The CGS-4TP intelligent gas sensing analysis system: (a) test chamber; (b) test system in the chamber; (c) probe, sensor and heating plating platform; (d) ceramics substrate.
nanofibers were also prepared by dissolving 0.5 g Ni(CH₃COO)₂·4H₂O and 1.2 g PVP in DMF solvent and the above-mentioned electrospinning procedure was repeated.

2.3. Characterization

The phase purity and crystalline structures of the as-prepared samples were characterized by X-ray diffractometer (XRD: Bruker, Germany, Cu-Kα radiation, λ = 1.5406 Å). The morphologies and sizes of the as-prepared nanofibers were observed by a field emission scanning electron microscope (FE-SEM: Nova NanoSEM450, Czech) equipped for energy-dispersive X-ray spectroscopy (EDX), and field emission transmission electron microscope (FE-TEM: Tecnai G2 F20). X-ray photoelectron spectroscopic (XPS: VG Scientific, UK) was performed to analyze the surface composition and oxidation state of the samples. The Brunauer–Emmett–Teller (BET) surface area and porosity of the samples were determined from nitrogen adsorption analysis by an ASAP 2020 instrument (Micromeritics).

2.4. Sensor fabrication and gas sensing test

The gas sensing properties of the samples were investigated by using a CGS-4TP intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China). The sensor was pressed firmly with two probes, as can be seen in Fig. 1(a), (b) and (c), respectively. For device fabrication, the obtained samples were first grounded slightly together with several drops of water. The formed slurry was coated onto an Ag–Pd interdigitated electrodes [Fig. 1(d)]. The aging treatments of the obtained sensors were carried out at 200 °C for 2 h. The external temperature controller under heating ceramic plate [Fig. 1(b) and (c)] was employed as a heater to adjust the operation temperature from room temperature to 500 °C. Finally, the test gas was added into the 1.8 L test chamber [Fig. 1(a)] by using a micro-syringe. The sensors were exposed to the atmospheric air again by opening the sensing chamber. The relative humidity of the atmospheric air was regulated ranging from 40% to 45% by the dehumidification of air conditioner. Here, sensor response (Sₐ) is described as $S_\alpha = R_\alpha / R_g$, where $R_\alpha$ and $R_g$ are the corresponding sensor resistances in air and test gas atmosphere, respectively. The response and recovery times were defined as the time for the sensor to achieve 90% of the total response change for test gas adsorption and desorption, respectively.

3. Results and discussion

The phase composition and crystal structures of the synthesized pure WO₃ nanofibers and NiO–WO₃ heterojunction nanofibers were studied using XRD, as displayed in Fig. 2(a). A series of strong diffraction peaks are observed for all curves, which are agreed well with the crystalline monoclinic WO₃ phase (JCPDS, no. 43-1035), indicating that all samples show a high degree of crystallinity after calcination. Not only in the pure WO₃, but also in all the samples, there are no other crystal phases or impurities detected within XRD detection limit (5%). The absence of NiO signals in XRD for the NiO–WO₃ nanofibers is probably attributed to the low concentration and high dispersion of NiO in WO₃ body. Moreover, for all NiO–WO₃ composite nanofibers, the diffraction peaks are broadened compared with those of the pure WO₃, indicating the decreased crystallite sizes for composite nanofibers. The mean grain sizes of different products were calculated through Scherrer equation. As demonstrated in Fig. 2(b), the mean grain sizes of pure WO₃, 1%, 3% and 5 mol% NiO–WO₃ composite nanofibers are 13.4, 8.5, 8.0, and 10.0 nm, respectively. Obviously, the NiO–WO₃ composite nanofibers have a smaller grain size compared with pure WO₃. This should be ascribed to that NiO phase inhibits the grain growth of WO₃ during the heat treatment process. This inhibition effect is expected to increase with increasing Ni content. Nonetheless, at high Ni content, the aggregation of NiO nanocrystallites is unavoidable, leading to the decline of the inhibition effect. Consequently, the 5 mol% NiO–WO₃ nanofibers have larger grain size than that of 1% and 3% nanofibers. Smaller of the mean grain size, more oxygen species can be adsorbed on the surface of nanofibers. This will be further supported by the subsequent XPS results in Fig. 3, where the 3 mol% NiO–WO₃ nanofibers have much higher oxygen species absorbing capacity, which may be benefit to the sensor performance.

The XPS spectra were measured to further investigate the chemical states of W and Ni, and analyze the surface oxygen

![Fig. 2](attachment:image_url) (a) XRD patterns of pure WO₃ nanofibers and NiO–WO₃ composite nanofibers and (b) the size distributions of different samples.
species of pure WO\(_3\) and NiO–WO\(_3\) heterojunction nanofibers. A wide survey scan clearly indicates that the main constituent elements are W, O, C and Ni in the 3 mol% NiO–WO\(_3\) heterojunction nanofibers [see Fig. 3(a)]. The peaks of W 4f spectrum at 37.8 eV and 35.6 eV correspond to W 4f\(_{5/2}\) and W 4f\(_{7/2}\), respectively [Fig. 3(b)], suggesting a normal state of W\(^{6+}\) in the heterojunction nanofibers.\(^{36,45}\) In addition, the O 1s peaks of pure and heterojunction nanofibers are asymmetric and can be deconvoluted into two main components located at 530.5 and 532.0/532.1 eV by fitting with the Gaussian function, as shown in Fig. 3(c)–(f). The intense peak with lower binding energy can be associated with the O 1s core level of the lattice oxygen (O\(_{\text{lattice}}\)) in the metal oxides (WO\(_3\) or NiO). The peak with higher binding energy is proposed to be the chemically adsorbed...
oxygen (O$_{\text{ads}}$) on the grain surfaces. Moreover, we can assess the oxygen species absorbing capacity according to the intensity of O$_{\text{ads}}$ component in the O 1s peak. The O$_{\text{ads}}$ component relative percentages of the pure WO$_3$, 1 mol%, 3 mol%, and 5 mol% NiO–WO$_3$ are 20.5%, 34.0%, 41.2% and 35.4%, respectively. Apparently, upon NiO introduction, the content of O$_{\text{ads}}$ component is markedly increased. In particular, 3 mol% NiO–WO$_3$ heterojunction nanofibers have the highest content of O$_{\text{ads}}$. As we all know, the gas sensing performance of nanomaterials is related to the capability of chemisorbed oxygen. Thus, such a high percentage of O$_{\text{ads}}$ content in the NiO–WO$_3$ heterojunction nanofibers will undoubtedly benefit the enhancement of sensing performance. Fig. 3(g) shows the high resolution XPS spectrum of Ni 2p in the 3% NiO–WO$_3$ nanofibers, where two groups of peaks located at 851–867 and 868–885 eV are revealed, corresponding to the characteristic peaks of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$, respectively. It is seen that the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ main peaks are centered at 855.8 and 873.5 eV, respectively. Moreover, two extra Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ satellite peaks are also observed at 861.9 and 879.9 eV, respectively. The above results are consistent with the previous reports, further confirming the presence of NiO in the heterojunction nanofibers.

The morphologies of synthesized products investigated by SEM are shown in Fig. 4(a)–(e). It can be observed that all products are composed of a large number of continuous 1D nanofibers. Compared with pure WO$_3$ nanofibers [Fig. 4(a)], the NiO–WO$_3$ composite nanofibers have smaller mean diameter, as can be seen from Fig. 4(b)–(d) for 1 mol%, 3 mol%, 5 mol% NiO–WO$_3$ nanofibers, respectively. Moreover, one can see that the NiO–WO$_3$ heterojunction nanofibers are obviously rougher compared with the pure WO$_3$, which suggests that the NiO–WO$_3$ heterojunction nanofibers are beneficial to the gas adsorption and diffusion. The SEM image of pure NiO are also described in Fig. 4(e), showing the fiber-like morphology. EDX spectroscopy [Fig. 4(f)] indicates that W, O, Ni, and Al elements are detected in the 3 mol% NiO–WO$_3$ heterojunction nanofibers, where Al element in EDX spectrum is from Al substrate. The 3 mol% heterojunction nanofibers are confirmed to have the smallest mean grain size and highest percentage of O$_{\text{ads}}$ content. Accordingly, an enhanced sensing performance of the 3 mol% heterojunction nanofibers may be expected. Therefore, TEM and high-resolution TEM (HRTEM) measurements were performed to further investigate the microstructure of the 3 mol% heterojunction nanofibers. Fig. 5(a) displays the TEM image of an individual NiO–WO$_3$ nanofiber. The nanofiber is composed of many nanoparticles. Rough morphology and porous structure are also clearly revealed. HRTEM [Fig. 5(b)] observation reveals that the measured fringe spacing is about
0.24 nm, corresponding to the (111) plane of the cubic NiO. The fringe spacings of 0.36 nm and 0.38 nm, corresponding to the (200) and (222) crystal planes of monoclinic WO3, respectively, are also recognized.

The surface areas and porous structures of the pure WO3 and 3 mol% NiO–WO3 heterojunction nanofibers were examined by the nitrogen adsorption–desorption measurements. As shown in Fig. 6(a), a clear hysteresis loop is observed, suggesting the existence of abundant mesoporous structures in the nanofibers. The BET surface areas of the pure WO3 and 3% NiO–WO3 nanofibers are calculated to be 11.40 and 19.49 m² g⁻¹, respectively. Fig. 6(b) shows the corresponding pore-size distribution curves of the two samples. The pure WO3 nanofibers have a pore-size distribution centered at 7.95 nm, while the 3 mol% NiO–WO3 nanofibers exhibit an increased pore-size distribution at 15.26 nm. These results together with the TEM analysis indicate that the 3 mol% NiO–WO3 heterojunction nanofibers possess higher specific surface area and more porous structure, which are beneficial to the efficient gas absorption and diffusion.

It is well accepted that the gas sensing properties of semiconductors are significantly affected by the working temperature, because the content of ionized oxygen species (O²⁻, O⁻, O₂⁻) on the surfaces of semiconductors is greatly related to the temperature, accordingly resulting in the change of sensor resistance. Fig. 7 shows sensing response towards acetone as a function of working temperature for all sensors. One can see that NiO–WO3 heterojunction nanofibers exhibit higher response (Rₐ/R₉) than that of pristine WO3 and NiO nanofibers in all temperature range. Particularly, the largest sensitivity to acetone is demonstrated for the sensor based on the 3 mol% NiO–WO3 nanofibers at almost all measured temperatures. In addition, the temperature dependent response characteristic for all sensors exhibits a typical mountain-shaped curve. The responses of all sensors increase to maximum values at 375 °C, and then decrease as the operating temperature increases further. Accordingly, the optimum operating temperature is determined to be 375 °C for all sensors in the following sensing tests.

Fig. 8(a) illustrates the dynamic gas-sensing characteristics for all sensors upon exposure to different acetone concentrations.
concentrations (20–800 ppm) at 375 °C. Fig. 8(b) shows the corresponding response value as a function of acetone concentration for all sensors. We can see clearly that the response of all sensors is increased distinctly as the acetone concentration increases. For example, when the acetone concentrations are 20, 50, 100, 300, 500, and 800 ppm, the response values of the sensors constructed by the 3 mol% NiO–WO3 heterojunction nanofibers are 6.6, 13.7, 22.5, 33.5, 48, and 73, respectively. Generally, the sensor response ($S_g$) and the target gas concentration ($C_g$) have the following relationship:

$$S_g = 1 + a[C_g]^b$$

where $a$ is the prefactor, and $b$ is the surface species charge parameter.\(^{58}\); It is reported that when the adsorbed surface oxygen species is O\(^{2-}\), the parameter $b$ is about 1, while it approaches to 0.5 when the adsorbed surface oxygen species is O\(^{=}\).\(^{59}\) For a given temperature, the above equation can be changed into a linear form:

$$\log(S_g - 1) = b \log(C_g) + \log(a)$$

It can be seen that $b$ can be easily calculated from the slope of the corresponding $\log(S_g - 1) \sim \log(C_g)$ curve. The inset in Fig. 8(b) shows the good linear relation between the $\log(S_g - 1)$ and $\log(C_g)$ for all sensors. The values of the slope $b$ are determined to be about 0.63, 0.64, 0.60, and 0.64 for the pure WO\(_3\), 1 mol%, 3 mol%, and 5 mol% NiO–WO\(_3\) nanofibers, respectively. All the $b$ values are relatively close to 0.5, indicating that O\(^{2-}\) is the dominating oxygen species absorbed on the pristine WO\(_3\) and NiO–WO\(_3\) heterojunction nanofibers.

The response–recovery curves of the four kinds of sensors towards 100 ppm acetone at 375 °C are further described in Fig. 9(a). The response times are calculated to be 10, 7, 6, and 6 s, while the recovery times are evaluated to be 15, 12, 11, and 11 s, for the pure WO\(_3\), 1 mol%, 3 mol%, and 5 mol% NiO–WO\(_3\) sensors, respectively, as displayed in Fig. 9(b). This demonstrates that compared with the pure WO\(_3\), the NiO–WO\(_3\) heterojunction nanofibers have shorter response and recovery times. These improved response and recovery times may be ascribed to the special porous structure of the NiO–WO\(_3\) nanofibers, which is beneficial to a fast absorption and desorption of gas molecules.

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**Fig. 8** (a) Dynamic gas-sensing characteristics of the sensors based on different samples under various gas concentrations and (b) the corresponding response value on acetone gas concentration at 375 °C.

**Fig. 9** (a) Response–recovery curves of the pure WO\(_3\) and NiO–WO\(_3\) gas sensors to 100 ppm acetone at 375 °C and (b) the response and recovery times of all sensors to acetone.
Fig. 10 exhibits the selectivity of the pristine WO₃ and NiO–WO₃ sensors to other interfering gases, such as ethanol (C₂H₅OH), methylbenzene (C₇H₈), acetic acid (CH₃COOH), isopropyl alcohol (C₃H₈O), ammonia (NH₃), and methyl alcohol (CH₃OH) at 100 ppm concentration. Obviously, the sensor based on 3 mol% NiO–WO₃ heterojunction nanofibers exhibits the highest response value of 22.5 to 100 ppm acetone, whereas the responses to other gases are less than 9. In addition, the relative increase of response value to acetone upon the introduction of NiO is 93.04%, which is also the highest. These results demonstrate the prominent selectivity to acetone of the 3 mol% NiO–WO₃ sensor. It is noted that the relative increase to NH₃ is up to 81.82%, indicating that the adding of NiO also improves the selectivity of NH₃. The excellent selectivity may be due to the different gas reaction processes and different energies needed to react with the adsorbed active oxygen species (O²⁻) on the surface of NiO–WO₃ nanofibers. At the optimum operating temperature of 375 °C, some gases may escape from the surface of NiO–WO₃ nanofibers and other gases may not react fully with adsorbed O²⁻ species because of insufficient energy.⁶

The long-term stabilities of the sensors constructed by the pure WO₃ and 3 mol% NiO–WO₃ nanofibers were also investigated, as displayed in Fig. 11. The tests were performed at 375 °C to 100 ppm acetone over 20 days. The results indicate that the response values based on pure WO₃ and NiO–WO₃ sensors are fluctuated lightly around 22.5 and 11, respectively, confirming the good stabilities of both the pure and heterojunction nanofiber based sensors.

4. Proposed sensing mechanism

It is well known that the sensing mechanism of the metal oxides is in close relation to the resistance change caused by the adsorption of oxygen species and reaction with test gas molecules on the surface.¹⁰ As illustrated in Fig. 12(a), when the sensor is exposed to air, ionized oxygen species (O²⁻) is formed on the surface of the WO₃ nanofibers at high temperature (375 °C) by transferring the electrons from the conduction band of WO₃ to chemisorbed oxygen. This leads to the generation of an electron depletion layer near the surface of WO₃. When acetone is introduced, the surface reaction occurs between CH₃COCH₃ and active O²⁻ species on the surface of WO₃ nanofibers, according to the following equation:⁶

\[
\text{CH}_3\text{COCH}_3 (\text{gas}) + 8\text{O}^2₋ \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O} + 16\text{e}₋ \tag{3}
\]

This process results in a decrease of the sensor resistance because a large quantity of trapped electrons are released back to the conduction band of WO₃. This low resistance state goes back to the original high resistance state when the sensor is exposed to air again.

By comparison, our experimental results illustrate that compared with the pure WO₃, the NiO–WO₃ composite nanofibers possess obviously enhanced sensing performances towards acetone. The sensing enhancement mechanism here can be attributed to the several following reasons. The first one is the generation of p–n junctions at the interfaces between p-type NiO and n-type WO₃. This enhancement mechanism was also responsible for the improved gas response for NiO–SnO₂.⁸
CuO–SnO$_2$,$^6$ CuO–SnO$_2$,$^6$ and Co-doped SnO$_2$,$^6$ composites in previous reports. In our case, NiO is a p-type semiconductor and WO$_3$ is a n-type semiconductor.$^6$ When p-type NiO nanocrystals are introduced into n-type WO$_3$, many p–n junctions should be formed at the interfaces between the NiO and WO$_3$. The transferring of electrons from WO$_3$ to NiO occurs due to that the Fermi level of p-type NiO is much higher than that of n-type WO$_3$. Simultaneously, the migration of holes also happens from the Fermi level of p-type NiO is much higher than that of n-type WO$_3$. Simultaneously, the migration of holes also happens from the Fermi level of p-type NiO is much higher than that of n-type WO$_3$. Particularly, the 3 mol% NiO–WO$_3$ heterojunction nanofibers exhibited the largest response to 100 ppm acetone, showing an excellent response value of 22.5 at the operating temperature of 375 °C, which is almost 2.1 times larger than that of the pure WO$_3$ nanofibers. In addition, excellent selectivity and long-term stability to acetone were also demonstrated for the 3 mol% NiO–WO$_3$ sensor. The combined effects including the generation of p–n junctions between NiO and WO$_3$, high oxygen species absorbing capacity, and special porous structural features with high surface area and small grain size, were accountable for the enhanced sensing properties of the 3 mol% NiO–WO$_3$ heterojunction nanofibers.

**Conflicts of interest**

There are no conflicts to declare.

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