Enhanced toluene sensing performance of gold-functionalized WO$_3$·H$_2$O nanosheets

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**Abstract**

Au nanoparticle-functionalized composites have been proven to be promising materials for gas sensing applications. We successfully synthesized tungsten oxide (WO$_3$·H$_2$O) nanosheets by a facile and effective hydrothermal process and decorated Au nanoparticles on their surface for ultra-high sensitivity levels to toluene gas. The structure and morphology of the samples were characterized by X-ray diffraction (XRD), Energy Dispersive X-ray Spectrometer (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Gas-sensing measurements revealed superior toluene sensing properties of Au nanoparticle-functionalized WO$_3$·H$_2$O nanosheets (Au-WO$_3$·H$_2$O) compared with bare WO$_3$·H$_2$O. The maximum response value of Au-WO$_3$ reached 50–100 ppm toluene at 300°C, which was nearly four times as high as that of bare WO$_3$. Meanwhile, Au-WO$_3$·H$_2$O exhibited the shorter response/recovery time, better selectivity and lower operating temperature to toluene gas than those of bare WO$_3$·H$_2$O. Also, the mechanism involved in improving the toluene sensing properties of WO$_3$·H$_2$O by Au nanoparticle-functionalization was discussed.

**1. Introduction**

Toluene is a common solvent used either singly or in solvent mixtures in many industrial processes. It is a colorless, volatile liquid and its vapor is flammable and explosive. The transformation of toluene in ozone in atmosphere is responsible of green-house effect. The narcotic and neurotoxic properties of toluene represent the main health hazards. High concentrations of toluene vapor may cause fatigue, weakness, confusion, dizziness, drowsiness, and unconsciousness in short-term occupational exposure. Long-term occupational exposure may result in impairment of the central nervous system. The LOAEL for effects on the central nervous system from occupational studies is approximately 88 ppm [1–4].

Due to rapid growth of industry and academia, there has been an increasing attention on fabricating high-performance sensors for hazardous and poisonous gases [5–8]. To realize ultra-high gas sensing levels which are regulated by sensitivity, selectivity, response/recovery time and stability of gas sensors, significant efforts have been made in fabrication of active sensing materials [9–12]. Among different kinds of sensing materials, including polymers, carbon nanotubes, and moisture absorbing materials, nanostructural metal oxide semiconductors are discovered to prevent possible disasters caused by harmful gases for their advantages such as low cost, controllable preparation, good selectivity and biological and chemical stability [13], desirable surface activity and high response.

Tungsten oxide (WO$_3$) is an indirect band gap n-type semiconductor [14] and has been intensively investigated in a variety of fields including gas sensors [15,16], electrochromic and photochromic devices [17], optical emitters [18], lithium ion batteries [19,20], photocatalysts [21,22] and solar energy devices in past decades. However, enhancing the gas sensing performance to meet the practical application requirements is still a challenge.

To further improve the gas sensing performance of metal oxide semiconductor sensors, many researchers have made tremendous efforts. It is well known that metallic catalysts such as Ag, Au, Pd, Pt nanoparticles decorated onto the surfaces of metal oxide could greatly improve gas sensing response, response/recovery speed and selectivity, and decrease the optimal operating temperature [9,23–25]. Recently, Vallesjos et al. deposited gold nanoparticles onto nanostructured material WO$_3$ via the Aerosol Assisted Chemical Vapour Deposition (AACVD) [25]. Chávez et al. functionalized Pd particles onto the surface of WO$_3$ nanowires via a drop-casting method using a saturate PdCl$_2$ solution [26]. Tao He et al. deposited...
gold nanoparticles onto the surface of a vacuum-evaporated WO3 thin film through a spin-coating technique [27].

In this work, we successfully synthesized WO3·H2O nanosheets by a hydrothermal method and decorated Au nanoparticles onto their surface through a facile solution process. To demonstrate the potential applications, the as-prepared materials were used to fabricate gas sensors. The measuring results revealed that the Au-functionalized WO3·H2O nanosheets sensor exhibited higher response, faster response/recovery speed, better selectivity and lower optimum operating temperature to toluene compared with bare WO3·H2O. The possible mechanism involving in the enhanced toluene sensing properties induced by Au nanoparticles functionalization was also discussed.

2. Materials and methods

2.1. Chemical reagents

All the starting materials (AR grade): Na2WO4·2H2O, citric acid were purchased from the Sinopharm Chemical Reagent Co. Ltd., and no subsequent purification processes were carried out.

2.2. Preparation of gold-functionalized WO3·H2O nanosheets

Firstly, synthetic process of WO3·H2O was as follows: 0.5 g of Na2WO4·2H2O was dissolved in 30 ml distilled water and stirred for 20 min at room temperature. Then 4 ml of 3 M HCl aqueous solution was introduced. After 10 min of stirring, 0.6 g citric acid was added. Then the resulting yellow suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave, sealed and treated at 120 °C for 24 h. After the hydrothermal reaction was completed, the resulting product was washed with distilled water for three times to remove the ions, and finally dried in air at 60 °C overnight to obtain nanocrystalline WO3·H2O.

![Fig. 1. XRD pattern of bare WO3·H2O.](image1)

![Fig. 2. SEM images of WO3 nanostructures: (a), (b) bare WO3·H2O, (c), (d) Au nanoparticle-functionalized WO3·H2O.](image2)
Fig. 3. EDX image of Au nanoparticle-functionalized WO3·H2O.

Secondly, functionalization process of the WO3·H2O nanosheets was as follow: The prepared WO3·H2O nanosheets (0.067 g) were suspended in 20 ml distilled water. Then 0.2 ml of 0.05 M HAuCl4 solution and 1 ml of 4 M NH3 solution were added into the WO3·H2O suspension followed by stirring for 6 h at 50 °C.

Fig. 4. (a) Typical TEM image of the Au-functionalized WO3·H2O nanosheet, (b) HRTEM image taken from (a).

2.3. Characterization

The crystalline phase was analyzed by X-ray diffraction (XRD) using a Scintag XDS-2000 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images were performed on a SHIMADZU SSX-550 (Japan) instrument to observe the morphologies and sizes of the samples. Transmission electron microscope (TEM) images and Energy dispersive X-ray spectrogram (EDX) were obtained on a JEM-ARM200F.

2.4. Fabrication and measurement of sensors

The fabrication of the sensors has been reported by other groups [28,29]. The as-prepared material was mixed with deionized water in a weight ratio of 100:25 and ground in a mortar to form a paste. The paste was then coated uniformly on an Al2O3 ceramic tube with a couple of parallel Au electrodes (each electrode contact with two platinum wires) to form a sensing film (a thickness of about 300 μm). A Ni–Cr heating wire was placed through the alumina tube as a heater to provide an operating temperature for the gas sensor. The electrical contact was made through connecting four platinum wires and the heating wire with the sensor pedestal by welding.

Gas sensing characteristics were measured by CGS-8 intelligent gas sensing analysis system (Beijing Elite Tech Co. Ltd., China).
3. Results and discussion

3.1. Characterization

The XRD pattern of bare WO$_3$·H$_2$O was shown in Fig. 1. The XRD spectrum showed that the obtained peaks could be indexed to the (0 2 0), (1 1 1), (0 3 1), (0 4 0), (2 0 0) and (0 0 2) planes of WO$_3$·H$_2$O, which was in consistent with No. 46-0379 of the Joint Committee on Powder Diffraction Standards card (JCPDS). The diffraction peaks of WO$_3$·H$_2$O nanosheets were sharp and intense, indicating the highly crystalline character of the samples. Moreover, no additional peaks related to impurities were observed. The broadening of the peaks could be ascribed to the small size of the nanocrystals. Combined with SEM and EDX analysis of the Au-functionalized WO$_3$·H$_2$O product, it can be deduced the successful synthesis of Au-functionalized WO$_3$·H$_2$O nanosheets.

The size and shape of samples were further analyzed by SEM technique. Fig. 2(a) and (c) showed the low magnification SEM images of the bare WO$_3$·H$_2$O and the Au nanoparticle-functionalized WO$_3$·H$_2$O representatively; (b) and (d) showed the corresponding high magnification SEM images representatively. It was observed that both products are composed of a large quantity of nanosheets distributed uniformly with a thickness of $\sim 35$ nm.

Fig. 3 showed a typical EDX spectrum of Au-functionalized WO$_3$·H$_2$O which confirmed the existence of the catalytic metallic particles. The results showed that the atomic gold concentration was 1.42%.

Further detailed structural analysis of the Au-functionalized WO$_3$·H$_2$O nanosheets were carried out using TEM. Fig. 4a depicts a single Au-functionalized WO$_3$·H$_2$O nanosheet. It can be noted that many dark spots (partly marked by the red arrows) were dotted over the surface of nanosheet. HRTEM result confirms that the dark spots were Au nanoparticles with a lattice spacing of about 0.236 nm, corresponding to the (1 1 1) plane of Au, while the spacing between adjacent lattice planes marked was 0.347 nm and 0.292 nm, which can be indexed to the (0 2 0) and (0 3 1) plane of WO$_3$·H$_2$O (Fig. 4b).
3.2. Gas sensing properties

The responses of the sensors based on bare WO3·H2O and Au-functionalized WO3·H2O nanosheets to 100 ppm toluene (C7H8) at different operating temperature were tested to determine the optimum operating temperature, as shown in Fig. 5. Response of gas sensor which is significantly influenced by operating temperature can achieve the maximum value at the optimal operating temperature. When operating temperature is below the optimal operating temperature, chemical adsorption and reaction between gas molecules and chemisorbed oxygen which are related to the response of gas sensors can’t obtain enough activation energies. Nevertheless continuing increasing the temperature will accelerate gas desorption and results in a decrease in response [30].

As shown in Fig. 5, Au-functionalized WO3·H2O exhibited lower optimum operating temperature (~300 °C) compared with that of bare WO3 (~325 °C) to toluene. The response values for both materials were 50 and 13 respectively at the corresponding temperature. It was obviously that the maximum response of Au-functionalized WO3·H2O is nearly four times as high as that of bare WO3·H2O.

The sensing transients of bare WO3 and Au-functionalized WO3 sensors to 10–500 ppm toluene at corresponding optimum operating temperature were given in Fig. 6. It clearly showed that introduction of Au nanoparticles improved the sensing performance in terms of response/recovery speed and sensitivity.

When exposed to reducing gases, the resistance of the sensor decreases for an n-type semiconductor as expected. The response time (τres) is defined as the time taken from Rs to Rs − 90% × (Rs − Ra) under the target gas environment; the recovery time (τrec) is defined as the time taken from Rs to Rs + 90% × (Rs − Rs) in the air environment [31]. In order to facilitate the comparison and analysis, the τres and τrec values to various toluene concentrations of both samples were summarized in Fig. 7. The τres and τrec values of the Au-functionalized WO3·H2O sensor were very short while those of the bare WO3·H2O sensor were relatively long. It was seen that the response time of both sensors increases with the increase of toluene concentration, which could be attributed to the restriction of gas diffusion. The τrec values of the Au-functionalized WO3·H2O sensor were also shorter than those of bare WO3·H2O sensor in the same toluene concentration. These may be attributed to that the noble nanoparticles could improve the modulation of nano-Schottky barriers during the oxidation of toluene due to the electron mechanism.

As shown in Fig. 8, the response increased with the increase of toluene concentration. The detection limit of both sensors could reach as low as 2 ppm for toluene. The responses of bare WO3·H2O sensor to 2–1000 ppm toluene ranged from 2.2 to 30, which ranged from 3.3 to 89 for Au-nanoparticles functionalized WO3·H2O sensor. Table 1 presents comparisons between the gas sensing performances of the Au-functionalized WO3·H2O and other reported results. Au-functionalized WO3·H2O in this paper exhibited shorter response/recovery time, better selectivity and lower operating temperature compared with other materials.

Fig. 9 showed the bar graph of the responses of sensors based on bare WO3·H2O and Au-functionalized WO3·H2O to a variety of gases with a concentration of 100 ppm, which were tested at their optimum operating temperatures. It could be observed that the response of the Au-functionalized WO3·H2O sensor to 100 ppm toluene at 300 °C was 50, which was higher than the responses to 100 ppm ethanol, formaldehyde, ammonia, acetone and methane. Thus, the Au-functionalized WO3·H2O sensor had better selectivity to toluene over other gases compared with bare WO3·H2O at optimum operating temperature.

3.3. Gas sensing mechanism

WO3 is an n-type semiconductor oxide with free electrons as the main carriers, and its sensing mechanism can be explained through the change in resistance of the sensor caused by the adsorption and desorption process of gas molecules on the surface of the gas sensing material [37]. When exposed to air at a moderate temperature, the oxygen molecules in air can form chemisorbed oxygen species (O2−, O− and O2−) [38] on the surface of sensing layer by capturing electrons from the conduction band of WO3·H2O (Eqs. (1)–(4)). This brings about the formation of a thick electron-depletion region which results in the increase of the resistance of the sensors [39].

When exposed to toluene, the target gas molecules are oxidized by oxygen species and electrons are released back to the conduction band of WO3·H2O, leading to the increase of the charge carrier density, the diminish of electron depletion layer and the decrease of the resistance of the sensors. In toluene environments, target gas reacts with chemisorbed oxygen anions. These reactions can be expressed as followed (Eqs. (5)–(7)) [40,41].

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\begin{align*}
\text{O}_2(\text{gas}) & \rightarrow \text{O}_2(\text{ads}) \quad (1) \\
\text{O}_2(\text{ads}) + e^- & \rightarrow \text{O}_2^{-}(\text{ads}) \quad (T < 100 ^\circ \text{C}) \quad (2) \\
\text{O}_2^{-}(\text{ads}) + e^- & \rightarrow 2\text{O}^{-}(\text{ads}) \quad (100 ^\circ \text{C} < T < 300 ^\circ \text{C}) \quad (3) \\
\text{O}^{-}(\text{ads}) + e^- & \rightarrow \text{O}_2^{-}(\text{ads}) \quad (T > 300 ^\circ \text{C}) \quad (4) \\
\text{C}_7\text{H}_8(\text{g}) & \rightarrow (\text{C}_7\text{H}_8)_\text{ads} \quad (5)
\end{align*}
\]
The excellent gas sensing performance of Au-functionalized WO3-H2O sensors has been observed in several studies. The detection limit of Au-functionalized WO3-H2O sensor is a potential candidate for high-performance toluene sensor.

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