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Fabrication of Highly Sensitive Gas Sensor Based on Au Functionalized WO₃ Composite Nanofibers by Electrospinning

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Abstract

A highly sensitive and selective gas-sensing material based on gold (Au)-functionalized tungsten oxide (WO₃) composite nanofibers (NFs) has been fabricated under mild conditions by electrospinning (ES). Au nanoparticles (NPs)-decorated WO₃ composite NFs were obtained by ES of the tungsten precursor (ammonium metatungstate hydrate) (AMT) and polyvinyl alcohol (PVA) solution followed by a two-step annealing treatment. The chemical and structural characterizations of the resulting composite nanofibers have been performed with various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and inductively coupled plasma optical emission spectrometry (ICP-OES). The gas-sensing properties of the WO₃-Au composite NFs with different Au contents (0.01 M and 0.1 M) toward volatile organic compounds (VOCs) (such as *n*-butanol) have been studied. A discussion concerning the role of Au content and the operating temperature is given to optimize the sensitivity, the dynamic response-recovery behaviors and consequently the efficiency of the WO₃-Au composite sensor.

Keywords: tungsten oxide; gold; electrospinning; gas sensor; nanofibers

1. Introduction

Metal-oxide semiconductors are considered as an important class of materials because of their potential applications in photocatalysis, solar cells and gas sensors [1]. In particular, WO_3 , an n-type semiconductor with a wide band-gap of 3.7 eV, has recently attracted much interest in gas sensors. Currently, a low-cost approach to fabricate gas sensor materials with excellent sensitivity and selectivity is highly desired [2]. Several effective methods, including doping, dimension control and phase structure design, are increasingly being adopted by researchers to further improve the gas sensing performance [3-5]. Size reduction of the sensing material is a well-known method to increase the gas-sensing performance. This is mainly due to a large surface to volume ratio achieved in this case leading to more available surface reaction sites for the absorption of gas species. As a consequence, many research efforts have been focused on the fabrication of gas sensors based on micro/nano-structured amorphous WO_3 films [6-8], and various shapes of WO_3 nanostructures, including nanoplates [9], nanoneedles [10], nanorods [11] and nanoparticle (NPs) [12].

Many of previous studies on WO_3 -based sensors were focused on the detection of NO, NO_2 , H_2 , H_2S and NH_3 [13-15], and only a few studies have investigated the gas-sensing performance toward volatile organic compounds (VOCs), such as *n*-butanol, methanol, ethanol and acetone [16]. VOCs are numerous, varied, ubiquitous and some of them are dangerous to human health or cause harm to the environment [17]. Therefore, it is necessary to fabricate sensitive and selective gas-sensing materials for the detection VOCs. Compared to the widely used approaches of vacuum deposition [18], spin-coating [19], sputtering [20], sol-gel synthesis [21] and thermal evaporation [22] for the synthesis WO_3 -based materials, electrospinning technique is a cost-effective and versatile method for large-scale production of one-dimensional composite materials with high surface areas. Another advantage of this

technique is that the self-supporting material is made of entangled fibers giving a huge accessible porosity which can be interesting for the above-mentioned targeted applications. Moreover, the generated foam-like morphology allows open pores and large voids to be generated by the consecutive heat treatment, resulting in enhanced sensing performances. Indeed, rapid response/recovery behaviors are facilitated by the good gas accessibility onto the surface for reaction [23]. In addition, the catalytic functionalization of noble metal nanoparticles onto oxide NFs has been introduced to promote gas sensing reactions by reducing the activation energy, and thereby increasing the sensing response and selectivity while also decreasing the maximum working temperature of the sensors. Noble metals such as Pd, Pt and Au are known to be used as catalysts for gas activation [24]. Therefore, the WO₃ NFs functionalized by Au NPs is an effective method for enhancing the sensing response of WO₃ nanofibers and electrospinning is a highly attractive method for the large scale synthesis of such composite nanofibres.

In this context, the gas-sensing performance of Au-functionalized WO₃ composite NFs toward different gases (methanol, ethanol, acetone and *n*-butanol) has been investigated. Particularly, *n*-butanol, which is often used in perfumes and fragrances, repellents, petroleum refineries and frequently used as a solvent for paints, coatings and natural synthetic resins, have been rarely studied comparing to others [25]. Long-term exposure to *n*-butanol may be hazardous as it can act as a depressant to the central nervous system. For all these reasons, we have focused our efforts to develop a facile approach to fabricate WO₃-Au composite NF gas sensor by electrospinning for the sensitive and selective detection of volatile *n*-butanol, and to understand the mechanisms behind the enhanced performance of the WO₃-Au composite NFs.

2. Experimental details

2.1 Chemicals

Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\geq 99.9\%$, Sigma Aldrich), Ammonium metatungstate hydrate (AMT, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $\geq 99.9\%$, Sigma Aldrich), Polyvinyl alcohol (PVA, $[\text{C}_2\text{H}_4\text{O}]_n$, $M_w \sim 72\,000 \text{ g}\cdot\text{mol}^{-1}$, $\geq 99\%$, Sigma Aldrich), 1-methyl-2-pyrrolidinone ($\text{C}_5\text{H}_9\text{NO}$, 99.5%), polyvinylidene fluoride ($(\text{CH}_2\text{CF}_2)_n$, 99.5%), methanol (CH_4 , 99.9%), absolute ethanol ($\text{C}_2\text{H}_6\text{O}$, 99.9%), *n*-butanol ($\text{C}_4\text{H}_{10}\text{O}$, 99.9%), and acetone ($\text{C}_3\text{H}_6\text{O}$, 99.9%) were used as received without further purification. Deionized water was used in all the synthesis processes. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and AMT were used as gold and tungsten precursors, respectively. PVA was used as a polymer matrix since it excellent good spinnability by electrospinning, and it possesses a good solubility in H_2O , which can co-dissolve the tungsten precursor.

2.2 Fabrication of WO_3 and WO_3 -Au composite nanofibers

An electrospinning method was used to synthesize WO_3 NFs. In a typical procedure, 10 g of PVA were dissolved in 90 g of H_2O , and stirred at 80 °C for 12 h to get PVA/ H_2O homogenous solutions. Then AMT (1 g) was mixed with 10 ml of the previous solution, to get the weight ratio of PVA:AMT 1:1. To ensure good mixture homogeneity, the resulting solution was then stirred at room temperature for 6 h.

A typical electrospinning setup is composed of a collector, a plastic syringe, with a 21 gauge stainless steel needle, and a high-voltage power supply (HV supply from Iseg Co., T1CP 300 304 p, 0~30 kV). The prepared electrospinning solution was loaded into the syringe. The working distance was 10 cm from the needle tip to the collector. The feeding rate was 0.2 $\text{ml}\cdot\text{h}^{-1}$ and was controlled by a syringe pump (KDS-100, Bioseb Co.). Under these working

conditions, an electric field of $1 \text{ kV}\cdot\text{cm}^{-1}$ led to a stable jet. The as spun AMT-PVA composite NFs were collected on aluminium film, and then collected NFs were annealed at $500 \text{ }^\circ\text{C}$ for 2 h in ambient air with the heating rate of $3 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and cooled in furnace to obtain pure WO_3 NFs.

The WO_3 -Au composite NFs were achieved using a facile method by electrospinning combining a two-step annealing treatment including the gold salt reduction. The schematic diagram of the experimental procedure allowing the formation of WO_3 -Au composite NFs is shown in Fig.1. First, the as spun AMT-PVA composite NFs were stabilized at $200 \text{ }^\circ\text{C}$ for 2 h in ambient air. Secondly, the stabilized composite NFs were impregnated with gold solution either by depositing a volume of solution or dipping the sample within the solution. The latter concentration is adjusted at two values 0.01M and 0.1M. The exact volume remaining in the sample was not determined. The exact content of gold was measured by inductively coupled plasma optical emission spectrometry (ICP). Finally, a calcination step at $500 \text{ }^\circ\text{C}$ for 2 h is performed, not only to remove the polymer part, but also to reduce the gold salt and obtain Au NPs. The samples of pure WO_3 and WO_3 -Au with various Au contents were named as WO_3 , WO_3 -Au-0.01M and WO_3 -Au-0.1M, respectively.

2.3 Characterization

WO_3 -Au NFs were characterized using scanning electron microscopy (SEM, FEI Guanta 250), and high resolution transmission electron microscopy (HRTEM, JEOL 2100F). Each NF mean diameter and NPs size were determined from measurements performed on 100 filaments or particles, using the software Nano Measurer. The formation of WO_3 NFs by thermal annealing was characterized by X-ray diffraction (XRD, Phillips, PW 1830/40 wide-angle goniometer using $\text{Cu K}\alpha 1 \lambda=1.54056\text{\AA}$) from 10° to 120° for 2θ . The Au contents of WO_3 -

Au-0.01M and WO₃-Au-0.1M samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX). N₂ sorption isotherms for WO₃ were determined using a sorptomatic system (Thermo Electron Corporation). The specific surface area of powdered samples was estimated by applying the Brunauer - Emmet - Teller (BET) equation in the $0.05 \leq P/P_0 \leq 0.35$ intervals of relative pressure and using a value of 16.2 \AA^2 for the cross-sectional area of molecular N₂. A non-linear regression by the least-squares method was performed to fit the interval data (*nads* vs. *P/P0*) in the experimental isotherms.

2.4 Gas sensor fabrication and measurements

The gas sensors were fabricated as follows: (i) mixing the powder of NFs with the binder (polyvinylidene fluoride (PVDF)), and grinding in an agate mortar homogenously; (ii) adding some drops of the solvent (1-methyl-2-pyrrolidone) to the agate mortar to form a slurry; (iii) coating the slurry on an alumina ceramic tube, which equipped with a pair of Au electrodes and four Pt wires for resistance measurements; (iv) annealing in air at 350 °C for 3 h of the alumina ceramic tube to remove the organic binder and to improve the stability of the sensor. Prior to the test, a Ni-Cr resistor was inserted into the ceramic tube for controlling the working temperature, by adjusting the working voltage. A reference resistor was placed in series with the sensor to form a complete measurement circuit. The test gas was injected into the testing chamber using a micro-syringe. The response (*S*) of the sensor is defined as $S = R_{\text{air}}/R_{\text{gas}}$, the ratio of the electrical resistances measured in air (*R_{air}*) and in the tested gas atmosphere (*R_{gas}*). The gas-sensing performance of WO₃ and WO₃-Au composites NFs was tested using a commercial WS-30A gas-sensing measurement system (Zhengzhou Winsen Electronics Technology Co., Ltd., Zhengzhou, China), at a relative humidity of 50~65%. The response time (τ_{res}) is defined as the time required by the sensor to achieve 90% of its

maximum response after the gas injection, whereas the recovery time (τ_{rec}) is the time taken by the sensor to reach 10% of its initial resistance after removal of the gas.

3. Results and Discussion

3.1 Morphology and Composition

The crystal structures of the samples were determined by XRD. Fig. 2 displays XRD patterns of the as-prepared WO_3 and WO_3 -Au composite products. As shown in Fig. 2a, the XRD pattern of the sample WO_3 can be well-indexed to tungsten oxide (JCPDS Card No. 32-1395), with lattice parameters $a = 7.309 \text{ \AA}$, $b = 7.522 \text{ \AA}$, and $c = 7.678 \text{ \AA}$. In comparison, the XRD pattern of the sample WO_3 -Au-0.1M (Fig. 2b) shows the diffraction peaks of both WO_3 and cubic gold with lattice parameters $a = 4.0786 \text{ \AA}$ (JCPDS No. 04-0784). In Fig. 2b, peaks at $2\theta = 23.1^\circ$, 23.6° , 24.4° , 33.6° , and 34.1° are indexed to the (002), (020), (200), (-202) and (202) planes of WO_3 , respectively. Additionally, the three more peaks at $2\theta = 38.2^\circ$, 44.4° , and 64.6° correspond to the (111), (200) and (220) planes of the cubic gold phase (JCPDS No. 04-0784).

The morphologies of WO_3 and WO_3 -Au NFs investigated by SEM are shown in Fig. 3. It can be observed that the 1-dimensional NF morphology of WO_3 and WO_3 -Au composite NFs remains after the heat treatment. However, the smooth and continuous surface of the as-spun AMT-PVA composite NFs becomes rough after the annealing process, due to the crystal growth of WO_3 and the decomposition of PVA polymer (as seen in Supporting Information Fig. S1). Fig. 3a shows a typical structure of the WO_3 NF, which is composed of small WO_3 particles with an average size of 50 nm. This typical polycrystalline structure has generated a porosity characterized by a specific surface area of $3 \text{ m}^2 \cdot \text{g}^{-1}$ and a mean size of 34.6 nm measured by BET. Fig. 3b and 3c show the SEM images of the WO_3 -Au composite NFs with different Au contents. The bright dots observed on the NF surface could correspond to Au

NPs. Indeed, this hypothesis is strengthened by XRD results and by the number of bright dots that is larger for the sample WO₃-Au-0.1M.

The size measurements of the as-prepared WO₃ nanofibers and the decorated Au NPs are summarized in Table 1. The average diameters of the WO₃, WO₃-Au-0.01M, and WO₃-Au-0.1M composite NFs are 315 nm, 350 nm, and 370 nm, respectively (as seen in Supporting Information Fig. S2). After functionalized with Au NPs, the mean diameter of the NFs increases slightly from 315 nm to 350 nm, which may be due to the presence of Au NPs on the surface of WO₃ NFs. Another possible reason is that gold atoms present during the annealing treatment can act as seeds for the WO₃ crystallization and growth. Moreover, the gold aqueous solution may have introduced water into the fibers. This water is then released as steam, thus increasing the fiber porosity. The gold contents of WO₃-Au-0.01M and WO₃-Au-0.1M composite NFs were measured by ICP as 0.47% and 1.65%, respectively. Slightly discrepancy between concentration and the gold content is attributed to impregnated volume variation, but content qualitatively increased with gold concentration. A simple image analysis allowed us to check that composition obtained by ICP was in qualitative agreement with the number of NPs observed by SEM on the WO₃ NFs, indicating that gold NPs are mostly located on the fiber surface (the details as shown in Supporting Information S3). The average sizes of Au NPs in the two samples are 8 nm (WO₃-Au-0.01M) and 7 nm (WO₃-Au-0.1M), respectively, by SEM image analysis with software Nano Measurer (as seen in Supporting Information Fig. S4).

The ICP results show that the final Au content could be tuned by adjusting the initial concentration of the gold aqueous solution and the impregnated volume. This is important as the content of the noble metal largely influences the gas-sensing performance as seen in previous studies [26]. In the proposed method, the first thermal stabilization at 200 °C plays

an important role in keeping the fiber structure intact. Without this preliminary step, the polymer PVA would be partly dissolved by water of the Au aqueous solution thus leading to the structural destruction of the NFs. Moreover, as Au ions can be dissolved in water, they are more easily dispersible onto the WO₃ surface. Finally, the thermal treatment process allows the Au ions to be reduced and transformed into Au NPs. This simple annealing treatment allows for the decoration of Au NPs and the transformation to WO₃ to be simultaneously achieved at the same low temperature. All these advantages demonstrate that the proposed synthesis strategy is a facile and effective method for producing well-controlled WO₃-Au composite NFs.

Fig. 4 shows TEM images of WO₃-Au-0.1M composite NFs. From Fig. 4a, it can be observed that the prepared WO₃ NF is well-decorated with Au NPs with an average particle size of ~7 nm (Fig. S3c). A typical HRTEM image of the WO₃-Au composite NF is shown in Fig. 4b. The crystallographic planes (111), (200), and (220) of gold (JCPDS No. 04-0784) are observed clearly with the corresponding lattice distances were 2.389 Å, 2.036 Å, and 1.435 Å, respectively. Moreover, the crystallographic plane (002) of WO₃ is also present confirming the orthorhombic structure of WO₃. Previous studies by Jiang et al. have shown that the interaction energies of Ag, Pd or Pt NPs deposited on α -Fe₂O₃ were much higher with a porous/rough surface than with a smooth one, leading to an easier deposition on the α -Fe₂O₃ surface [27, 28]. As the prepared WO₃ NFs are relatively porous, the total potential energy of the Au NPs can be significantly decreased when deposited on such porous surfaces. Hence, the Au NPs were more likely to nucleate and grow on the surface of the WO₃ NFs via heterogeneous nucleation than forming separate nuclei by homogeneous nucleation during the synthesis process.

3.2 Gas-sensing performance

It is well known that the operating temperature highly influences the response of semiconductor-based gas sensors, as it governs the mobility of electrons and the electrical conductivity from the metal oxide material [29, 30]. Therefore, the responses of the WO_3 and WO_3 -Au composites NFs toward 100 ppm of *n*-butanol were tested at different operating temperatures in order to find the optimum operating temperature of these sensors, as a compromise between electrical conductivity and molecules desorption. Fig. 5a shows the variation in responses of the WO_3 , WO_3 -Au-0.01M, and WO_3 -Au-0.1M composite NF sensors toward 100 ppm of *n*-butanol with increasing operating temperatures. The response curves of these sensors show a typical bell-shape in the entire temperature range from 175 to 325 °C. Further observation of Fig. 5a reveals that both WO_3 -Au sensors exhibit a lower optimum operating temperature at 250 °C compared to pure WO_3 sensor which displays the highest response toward *n*-butanol gas at 300 °C. The maximum response values of these three sensors toward 100 ppm of *n*-butanol are 7.3 for WO_3 at 300 °C, 34.7 for WO_3 -Au-0.01M and 152.7 for WO_3 -Au-0.1M at 250 °C. In comparison to the pure WO_3 sensor, the two WO_3 -Au sensors show much higher response toward *n*-butanol at a lower optimum operating temperature (250 °C), indicating the benefit of the Au decoration.

The dynamic response-recovery curves of the three sensors toward to 100 ppm *n*-butanol at 250 °C are given in Fig. 5b. It reveals the *n*-type sensing behaviours of all the fabricated sensors, whereby the output voltage of each of these sensors increases as the *n*-butanol gas is injected into the test chamber but gradually decreases as the sensors are exposed to air. However, it is clear that the increase in the output voltage upon exposure to *n*-butanol is greater for both WO_3 -Au sensors than for pure WO_3 sensor, indicating the higher response of the WO_3 functionalized with Au NPs. The response is highly enhanced as the Au content is

increased further from 0.47% to 1.65% by weight. Furthermore, it can be observed from Fig. 5b that the WO₃-Au-0.01M and WO₃-Au-0.1M sensors show 5 and 20 times higher response, respectively, compared to the pure WO₃ sensing material.

The content of noble metal has a significant influence on the sensing performance, thus we first investigated the response of the pure WO₃, WO₃-Au-0.01M, and WO₃-Au-0.1M sensors as a function of *n*-butanol concentration (10, 20, 50, 100, 200, 500 ppm) at 250 °C. The results in Fig. 5c show that the WO₃-Au-0.1M composite NF sensor exhibits a high response of $S = 63.6$ toward 10 ppm of *n*-butanol, whereas the response values of WO₃-Au-0.01M composite NF and pure WO₃ sensors are 9.5 and 1.55, respectively. Increasing the *n*-butanol concentration to 100 ppm, the response significantly increases to 229.7 for WO₃-Au-0.1M, 34.7 for WO₃-Au-0.01M and 4.5 for pure WO₃.

For WO₃ and WO₃-Au-0.01M sensors, the response initially rises quickly with increasing concentration of *n*-butanol before eventually reaches saturation at a higher concentration of *n*-butanol. In comparison, the pure WO₃ sensor experiences only a slight increase in response with increasing *n*-butanol concentration. This result demonstrates that the Au additive generates a promotion effect on the sensor response. Furthermore, it can be observed that different Au contents result in a large difference in the sensing response. The response of the WO₃-Au-0.1M sensor keeps increasing sharply and reaches as high as 515.2 at an *n*-butanol concentration of 500 ppm, which is ~60 times higher compared to the response of pure WO₃ sensor ($S = 8.5$) and also 8 times higher than the response of WO₃-Au-0.01M sensor ($S = 68.1$). All these results clearly indicate the beneficial addition of Au NPs on the surface of WO₃ NFs.

The response-recovery properties of the WO₃-Au composite NF sensors were also compared to the pure WO₃ NF sensor, as depicted in Fig. 5d. The response time values of the WO₃-Au-0.1M sensor toward 10, 20, 50, 100, 200 and 500 ppm of *n*-butanol are 31, 33, 34, 55, 71 and 84 s, respectively. These response values are significantly lower than those of pure WO₃ sensor (61, 76, 71, 76, 96 and 101 s, respectively). This shows that the response time of the WO₃-Au-0.1M sensor is accelerated by 5 to 43 s compared to the pure WO₃ sensor. Moreover, the recovery time values of the WO₃-Au-0.1M sensor toward 10, 20, 50, 100, 200 and 500 ppm of *n*-butanol are only slightly increased by 9 to 15 s as the concentration of *n*-butanol increases, which is highly accelerated compared to pure WO₃ sensors recovery time changing from 10 to 122 s.

The details of response-recovery properties of the WO₃-Au-0.1M composite NFs sensor are shown in Fig. 6. The variation in the voltage of the WO₃-Au-0.1M sensor toward 10 ppm of *n*-butanol at 250 °C is shown in Fig. 6a. It presents fast response and recovery time values of about 31 and 9 s, respectively. Fig. 6b shows the response and recovery time curves of the WO₃-Au-0.1M sensor with different concentration of *n*-butanol at 250 °C. It can be observed that the response time increases as the *n*-butanol concentration is increased. In contrast, the recovery time the WO₃-Au-0.1M sensor remains very (~13 s) fast, regardless of the concentration of *n*-butanol.

Selectivity is another important parameter of a gas sensor. A good gas sensor can selectively detect a particular gas when it is exposed to an environment containing multiple gases with similar physicochemical properties. The selectivity tests of the WO₃, WO₃-Au-0.01M and WO₃-Au-0.1M sensors were carried out by comparing their response to *n*-butanol against other VOCs with nearly identical physicochemical properties, such as methanol, ethanol, and

acetone. From Fig. 7a, it is noted that the $\text{WO}_3\text{-Au-0.1M}$ sensor clearly exhibits the highest response toward volatile *n*-butanol gas, with $S = 229.7$ at a concentration of 100 ppm. This is around 2 to 28 times higher than the response to other gases, indicating its excellent selectivity toward *n*-butanol vapour. In comparison, the selectivity of the pure WO_3 sensor is much poorer than the $\text{WO}_3\text{-Au}$ composite NF sensors as it could not distinguish the different organic vapours.

The modulation model of depletion layer by oxygen adsorption is the most commonly accepted model to explain the sensing mechanism of metal oxide based sensor. According to literature, the response from a sensor increases with an increase in the alkyl (carbon-carbon) chain length from methanol (CH_4O) to *n*-butanol ($\text{C}_4\text{H}_{10}\text{O}$). When the adsorbed oxygen species react with higher alkyl chain length alcohols such as *n*-butanol as opposed to shorter ones such as methanol, the enhancement of gas sensitivity can be attributed to the higher increase in electron concentration (and therefore a higher increase in conductivity) [31]. Moreover, heavier molecules will vibrate and/or rotate less than lighter molecules, and therefore, they tend to have lower diffusivities, in this case gas molecules are more likely to react on the surface of metal oxide sensing materials. As the number of carbons in the alkyl chain for *n*-butanol is larger compared to other alcohol molecules with smaller molecular weight (methanol 1, ethanol 2, and acetone 3 as shown in Table 2), the response of the $\text{WO}_3\text{-Au-0.1M}$ sensor toward *n*-butanol is much higher than toward other gases.

The reproducibility of the response for this particular sensor toward 100 ppm of *n*-butanol was also investigated as shown in Fig. 7b. The output voltage value remains more or less similar with the continuous cycling tests. For practical applications, gas sensors not only need to exhibit high sensitivity and selectivity toward the target gases, but also good stability to

ensure their long-term reliability. Fig. 7c shows the stability evaluation of the WO₃-Au-0.1M sensor toward 50 ppm of *n*-butanol over a total period of 30 days. It is clearly shown that the WO₃-Au-0.1M sensor exhibits excellent stability toward *n*-butanol gas as the *S* value remains equal to around 150 during the 30 days testing period.

Table 2 compares the gas-sensing performance of pure WO₃ and WO₃-Au-0.1M NF sensors prepared in this work with the best performances of previously reported sensors based on different nanostructures of oxide materials functionalized with noble metal NPs. The WO₃-Au composite NFs sensor fabricated in this work exhibit better sensing performance compared to Ag-WO₃ nanoplates [33], i.e. the response value increases from 1.2 to 8.1 and 7.5 to 22.3 toward methanol and acetone, respectively. Additionally, the response of the fabricated WO₃-Au-0.1M NF sensor toward *n*-butanol is much higher compared to previous sensors based on α -Fe₂O₃-ZnO-Au nanocomposites and α -Fe₂O₃-Au nanospindles [32-34]. All the above comparisons indicate the good sensing capability of the WO₃-Au composite NF sensor, not only toward *n*-butanol but also toward other gases (e.g. methanol, ethanol and acetone) compared to previous noble metal functionalized WO₃ nanostructures, including nanorods, nanoneedles or nanoplates modified with Au, Pt, or Ag NPs.

3.3 Sensing Mechanism

The sensing mechanisms of WO₃ and WO₃-Au composite sensors are relatively different from each other due to the oxide crystals and metal NPs components. For pure WO₃ sensor, the gas-sensing mechanism is similar to other semiconductor oxide sensors [35]. Indeed, oxygen molecules are adsorbed on the surface of the WO₃ nanocrystals when the sensor is exposed to air and are ionized to O⁻ or O²⁻ by capturing free electrons from the conduction band of WO₃. Thus, an electron depletion layer is formed by reducing the free charge carrier (electron)

concentration. In our case, the *n*-butanol molecules react with the adsorbed oxygen species (O^{2-}), which release the trapped electrons back into the conduction band of WO_3 . As a consequence, the concentration of free electron increases and ultimately decreases the resistance of the WO_3 sensor.

By comparison, the enhanced response of the WO_3 -Au composite sensor toward *n*-butanol could be attributed to both chemical and electronic sensitization effects induced by the Au NPs. The adsorbed oxygen can diffuse faster to the surface vacancies and capture electrons from the conduction band of WO_3 . The amount of active oxygen ions (O^- or O^{2-}) increases significantly with the present of Au NPs, due to its better oxygen dissociation properties than WO_3 . Due to both the increase in adsorbed oxygen and the molecules to ions rate of conversion, the degree of electron depletion at the Au/ WO_3 interface is higher than that at the pure WO_3 surface. Furthermore, a Schottky barrier is formed by the presence of Au NPs on the surfaces of the WO_3 nanocrystals [36]. It generates a layer depleting electron region at the Au/ WO_3 interface, which further increases the resistance of the sensor. The size of Au NPs plays also an important role since a NP small size, of a few nanometers, leads to an increase of the surface-to-volume ratio. The oxygen atoms have consequently more potential to adsorb on NPs and to react efficiently. A high and fast degree of electron depletion occurs in the WO_3 -Au sensor, which can also significantly enhance its resistivity. As a result, by combining the semiconductor and noble metal properties, WO_3 -Au sensors show higher sensitivity and faster response/recovery properties toward the target gases.

4. Conclusions

This study reports a facile and low-cost method to produce WO_3 -Au composite NFs based on electrospinning. WO_3 NFs were first synthesized through electrospinning of a mixture

solution containing PVA and AMT, followed by calcination at 500 °C. Uniformly sized Au NPs (5-10 nm) were then decorated on the surface of the WO₃ NFs as catalysts for improving the sensing response. The gas-sensing results demonstrate the excellent response of the WO₃-Au composite NF sensor, particularly the WO₃-Au-0.1M sensor, which exhibits ~60 times higher response and significantly improved selectivity toward *n*-butanol than the pure WO₃ sensor. In addition, they also show a decreased optimum operating temperature at 250 °C compared to 300 °C for pure WO₃ sensor. Furthermore, the Au-decoration also improves the response and recovery time of the WO₃ sensor by 5-43 s and 10-122 s, respectively. The enhanced response of the WO₃-Au composite NF sensor toward *n*-butanol may be attributed to the excellent catalytic activity of Au NPs which enhances the oxygen molecule to ion conversion rate and the existence of multiple depletion layers at the surface of the WO₃-Au composite NFs, which results in a greater change in resistivity upon exposure to *n*-butanol. This study will benefit for the design and construction of WO₃-based composite gas sensors with high performance toward VOCs for diverse sensing applications.

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Figure Captions

Fig. 1. Schematic diagram illustrating the formation of WO₃-Au composites NFs.

Fig. 2. XRD patterns of (a) WO₃ and (b) WO₃-Au-0.1M composites NFs.

Fig. 3. SEM images of the as-prepared samples: (a) WO₃ NFs annealed at 500 °C, (b) WO₃-Au-0.01M composites NFs, and (c) WO₃-Au-0.1M composites NFs.

Fig. 4. (a) TEM image of WO₃-Au-0.1M composites NFs; (b) High-resolution TEM image of Au NPs embedded WO₃ NFs showing the Au and WO₃ lattices.

Fig. 5. (a) The variation in responses of WO₃, WO₃-Au-0.01M and WO₃-Au-0.1M sensors toward 100 ppm of *n*-butanol as a function of the operating temperature; (b) Dynamic response-recovery behaviors of the WO₃, WO₃-Au-0.01M and WO₃-Au-0.1M sensors toward various concentrations of *n*-butanol at the optimum working temperature (250 °C); (c) Response vs. concentration curves of the WO₃, WO₃-Au-0.01M and WO₃-Au-0.1M sensors toward *n*-butanol at 250 °C; (d) Response-recovery time vs. *n*-butanol concentration plots of the WO₃, WO₃-Au-0.01M and WO₃-Au-0.1M sensors at 250°C

Fig. 6. (a) The dynamic response-recovery behavior of the WO₃-Au-0.1M sensor toward 10 ppm of *n*-butanol at 250 °C; (b) The response and recovery vs. concentration curves of the WO₃-Au-0.1M sensor toward *n*-butanol at 250°C.

Fig. 7. (a) Selectivity test of the WO₃, WO₃-Au-0.01M and WO₃-Au-0.1M sensors toward various VOCs at 250 °C; (b) Response of WO₃-Au-0.1M sensor to cycling toward *n*-butanol (100 ppm) at 250 °C; (c) Stability evaluation of the WO₃-Au-0.1M sensors toward 100 ppm of *n*-butanol over a period of 30 days.

List of Tables

Table 1 Measurement results of the mean diameter of fiber and Au nanoparticle size of WO₃-Au composites NFs

	as spun	WO ₃ -500 °C	WO ₃ -Au-0.01M	WO ₃ -Au-0.1M
Fiber diameter / nm	412 ± 42	315 ± 42	350 ± 32	370 ± 43
Au particle size / nm	---	---	8 ± 2	7 ± 2
Au contents	---	---	0.47%	1.65%

Table 2 Comparison of the gas-sensing performance of various WO₃ based sensors toward 100 ppm of different VOCs

Sensor Materials	Gases	T (°C)	C (ppm)	S (R _a /R _g)	Refs
WO ₃ nanofibers	C ₂ H ₆ O	250	100	3.43	This work
Au-WO ₃ nanofibers		250	100	90.8	This work
Pt-WO ₃ powder		190	100	40	[30]
Au-WO ₃ nanofibers	CH ₄ O	250	100	8.1	This work
Ag-WO ₃ nanoplates		200	100	1.2	[31]
Au-WO ₃ nanofibers	C ₃ H ₆ O	250	100	22.3	This work
Ag-WO ₃ nanoplates		200	100	7.5	[31]
Au-WO ₃ nanofibers	C ₄ H ₁₀ O	250	100	229.7	This work
α-Fe ₂ O ₃ -ZnO-Au nanorods		225	100	113	[32]
α-Fe ₂ O ₃ -Au nanospindles		300	100	7.2	[32]