Acetone gas sensor based on α-Ag2WO4 nanorods obtained via a microwave-assisted hydrothermal route

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1. Introduction

Over the past decades, inorganic semiconducting nanostructures have drawn interest from the research community driven by their physical and chemical properties, which enable their use in light-emission/detection devices, gas sensors, biomedical devices, and battery electrodes [1–6]. Among different nanostructures, one-dimensional (1D) semiconducting materials, such as nanorods, nanowires, and nanotubes must be highlighted because of their distinctive geometries and fascinating properties [7,7–11]. Their synthesis has been carried out by various chemical and/or physical methods [7,12–14], among which the microwave-assisted hydrothermal (MAH) method has proven efficient, fast and versatile for the obtaining of organic and inorganic materials [2,7,15–17].

Silver tungstate (Ag2WO4) compounds have attracted widespread scientific and technological interest, especially regarding their multifunctional applications [2,16,18–25]. In a previous study, we reported the gas-sensing performance of such 1D α-Ag2WO4 nanorod-like structures obtained by MAH route, which detected lower concentrations of ozone, i.e., 80 ppb [2]. Regarding gas sensing applications, the main advantage of 1D nanostructures is their high surface-to-volume ratio, which favors the adsorption of gases on their surface [26], enhances their sensing performance and enables the detection of lower gas concentrations [26–28].

Over the past years, breath analysis has been utilized as a useful tool for the noninvasive diagnosis and monitoring of a broad range of diseases [29–31]. Acetone is a specific breath marker for diabetes, therefore, gas sensors have been used for the detection of acetone levels in the human breath [29,30,32]. Its concentration ranges between 0.3 and 0.9 ppm for healthy humans, whereas it is found in higher concentrations, i.e., >1.8 ppm in diabetic patients [29,30,33]. Efforts have been devoted towards the discovery of novel acetone-sensing compounds, or enhancement of the gas sensing performance of traditional acetone gas sensor devices [1,29–32,34–41]. As shown in Table 1, different semiconducting metal oxides have been investigated as acetone gas sensor, as displayed in Table 1.

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This manuscript addresses the gas sensing properties of 1D α-Ag2WO4 nanorod-like structures obtained by MAH route. The morphological characteristics of as-prepared nanorods were analyzed by field emission scanning electron microscopy (FE-SEM). The α-Ag2WO4 nanorods were tested for the detection of acetone, ethanol, and ammonia. The gas sensing experiments performed at 350 °C revealed their higher sensitivity to acetone in comparison to other gases, fast response-recovery time and excellent repeatability.

2. Experimental

2.1. Preparation and characterization of α-Ag2WO4 nanorods

The synthesis of silver tungstate (α-Ag2WO4) nanostructures was accomplished using the urea prepared by the microwave-assisted hydrothermal (MAH) treatment method, using AgNO3 (99.8%), Na2WO4·2H2O (99.5%), and PVP40 ((C6H10NO)n; 99%) as reagents. The precursor α-Ag2WO4 solution was heat-treated in microwave hydrothermal equipment for 1 h at 160 °C. Further details of the synthesis procedure may be found in Ref. [2]. The sample was structurally characterized by X-ray diffraction (XRD) using CuKa radiation (Rigaku diffractometer, model D/Max-2500PC) in a 2θ range from 10° to 60° with a step of 0.02° at a scanning speed of 2° min⁻¹. The morphological features of the α-Ag2WO4 nanostructures were analyzed under a field emission scanning electron microscope (FE-SEM; FEI INSPECT F50) operating at 20 kV and by transmission electron microscopy (TEM) on a JEM 2010 UR operating at 200 kV.

2.2. Sensor preparation and gas-sensing measurements

The α-Ag2WO4 powder was dispersed in isopropyl alcohol for 30 min by an ultrasonic cleaner and the suspension was dried onto an SiO2/Si substrate containing 100 nm thick Pt electrodes separated by a 50 mm distance. The sample was then annealed in an electric furnace for 2 h under air atmosphere at 500 °C. The sensor sample was inserted into a gas sensing chamber for the control of both temperature and gas flow. The working temperature, which ranged from 250 °C to 350 °C, was maintained by an external heating source driven by a regulated power supply. A 1 V dc voltage was applied to the device while the electrical resistance was being monitored by a Keithley (model 6514) electrometer.

The acetone concentration was controlled through the mixing of acetone vapor with synthetic air at different ratios for the gas-sensing measurements. The desired gas concentration was obtained through the injection of the amount of liquid acetone required (Quemis, 99.5%) into a sealed glass container by a syringe. Dry air was used as both a reference (baseline) and a carrier gas and 8.3 cm² s⁻¹ constant total flow was maintained by mass flow controllers. The relative humidity inside the chamber was monitored by a commercial sensor (INSTRUTHERM, HT-700) and held at approximately 85%.

The sensor response, S, was defined as $S = R_{air}/R_{gas}$, where $R_{air}$ and $R_{gas}$ are the electrical resistances of the sensor device exposed to dry air and acetone gas. The response time of the sensor was defined as the time required for a change in the sample’s electrical resistance to reach 90% of the initial value when exposed to acetone. Similarly, the recovery time was defined as the time required for the electrical resistance of the sensor to reach 90% of the initial value after the acetone has been turned off.

3. Results and discussion

3.1. Structural, microstructural and gas-sensing properties

Fig. 1 shows the X-ray diffraction (XRD) patterns of α-Ag2WO4 nanostructures obtained via MAH route. All diffraction peaks were indexed to an orthorhombic structure with a Pn21n space group, according to ICSD file 4165, as expected [22]. FE-SEM image confirms the morphology of the α-Ag2WO4 sample, which consists of uniform and one-dimensional (1D) rod-like structures, as illustrated in the inset of Fig. 1(b) and (c). The average width and length of the nanorods were approximately 100 nm and 1.5 μm, as reported in our previous work [2]. The presence of Ag nanoparticles on the α-Ag2WO4 nanorods’ surfaces (Fig. 1c) is due to their exposition to electron irradiation under an SEM microscope [20–22]. Nevertheless, the as-prepared nanorods used in the gas sensor tests were not exposed to electron irradiation.

First, the sensor response of α-Ag2WO4 nanorods was investigated for 10 ppm of acetone at a fixed operating temperature of 300 °C and different exposure times (15 s, 60 s, 90 s, and 5 min), as shown in Fig. 2a. Upon exposure to acetone vapor, the electrical resistance of the nanorods quickly decreased, which is a typical response of n-type semiconductors exposed to reducing gases [29]. Additionally, the nanorods showed a good sensor response for short periods of time and tended toward saturation only for longer exposure times (>90 s), as shown in Fig. 2a. This behavior can be explained by the limited number of adsorption sites on the nanorods’ surface.

The α-Ag2WO4 sample was then exposed to 10 ppm of acetone at a fixed temperature of 60 s, so that the best operating temperature could be found. Such exposition time was chosen because the sensor response did not vary significantly for longer times. The results in Fig. 2b show an increase of the sensor response in function of the operating temperature — the maximum response was obtained at 350 °C, which is the limit of our gas sensing system. Righettoni and co-workers investigated the acetone gas-sensing properties of Si-doped WO3 nanoparticles prepared via flame spray pyrolysis method and observed the highest sensor response at 350 °C [30]. The gas sensing measurements performed at various operating temperatures are displayed in Fig. 51.

Fig. 3 shows the dynamic sensor resistance of the α-Ag2WO4 nanorods under exposure to various concentrations of acetone (0.5–20 ppm) at 350 °C. The reversible cycles of the response curves indicate a stable and reproducible response, as seen in Fig. 3a. The sensor response gradually increases with the increase in the concentration of acetone, which suggests the nanorods have not reached saturation, even for higher concentrations of up to 20 ppm, Fig. 3b. Additionally, the response time and recovery time ranged between 30–32 s and 46–130 s, respectively, towards various acetone concentrations.

In order to investigate the selectivity of sensor, α-Ag2WO4 nanorods were exposed at 350 °C to acetone, ethanol, and ammonia at the concentration level of 10 ppm. The electrical measurements

| Compound | Acetone level (ppm) | Operating temp. (°C) | References |
|----------|---------------------|----------------------|------------|
| ZnO      | 1–500               | 350                  | [1]        |
| ZnO      | 1000–3000           | 325                  | [40]       |
| Zn–CuO   | 0.2–50              | 310                  | [41]       |
| WO3:Si   | 0.1–0.6             | 350                  | [33]       |
| ZnO:NiMn | 50–300              | 300                  | [34]       |
| ZnFe2O4  | 0.8–50              | 200                  | [39]       |
| α-Fe2O3  | 1–5                 | 350                  | [31]       |

Table 1

Brief summary of results reported for acetone gas sensors based on semiconducting metal oxides.
are displayed in the Fig. S2, respectively. According to Fig. 4, the nanorods were sensitive for all gases, exhibiting the highest sensitivity to acetone when compared to other gases under the same concentration. The sensor response obtained was, 2.77 $\pm$ 0.04 (acetone), 1.69 $\pm$ 0.02 (ethanol), and 1.57 $\pm$ 0.05 (ammonia).

Initially, when the sample is exposed to an air atmosphere, the oxygen molecules are adsorbed on the different $\alpha$-Ag$_2$WO$_4$ surfaces, resulting in the formation of oxygen ionic species, such as O$_2$/C0, O/C0, O$_2$/C0 [42]. In our experiments, the operating temperatures, $T_{opt}$, was varied from 250 °C to 350 °C, and thus the ionic species O$^-$ are dominant [43]. These O$^-$ species contribute to form a depletion layer in the nanorods surfaces, leading to high resistance [27]. In the sequence, upon exposure to acetone, CH$_3$COCH$_3$ molecules will react with the chemisorbed oxygen ions at the nanorods surfaces. As consequence, the charge carrier is increased and, the depletion layer is diminished, leading to a decrease in electrical resistance [43,31]. The acetone gas sensing mechanism of the $\alpha$-Ag$_2$WO$_4$ nanorods can be explained by:

$$\text{O}_2\,(g) + 2e^- \rightarrow 2\text{O}_2^{\text{ads}} \quad (1)$$

$$\text{CH}_3\text{COCH}_3\,(g) + 8\text{O}_2^{\text{ads}} \rightarrow 3\text{CO}_2\,(g) + 3\text{H}_2\text{O}\,(l) + 8e^- \quad (2)$$

3.2. Final remarks applying for future investigations

As the $\alpha$-Ag$_2$WO$_4$ compound is a potential gas sensor device, the way intrinsic factors, as type of crystalline structure (alpha, beta, and gamma) also affect the gas sensing performance in silver tungstate should be investigated. Future approaches on Ag$_2$WO$_4$ characteristics should also include analyses of the plasmonic effect on gas sensing properties, i.e., presence of Ag metallic nanoparticles grown on the nanorods surfaces due to their exposition to electron irradiation under an SEM microscope.
4. Conclusion

This paper reported on a fast and effective approach for the preparation of acetone gas sensors based on 1D \( \alpha\)-Ag\(_2\)WO\(_4\) nanostructures via a microwave-assisted hydrothermal method. XRD and FE-SEM analyses revealed the presence of a crystalline phase of \( \alpha\)-Ag\(_2\)WO\(_4\) that exhibits a rod-like morphology. Gas sensing measurements showed the good acetone sensing performance of such nanorods at an operating temperature of 350 °C. The nanorods detected different acetone levels that ranged from 0.5 ppm to 20 ppm and showed a fast response (of ca. 30 s), excellent repeatability, and great potential for practical applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.05.078.

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