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Xanthate sensing properties of Pt-functionalized WO_3 microspheres synthesized by one-pot hydrothermal method

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ABSTRACT

WO_3 microspheres in a hierarchical nanorod-assembled architecture were prepared by using a facile one-pot hydrothermal method. The morphology and structure of pure, and 1, 3, and 5 mol% Pt-functionalized WO_3 microspheres were characterized by means of SEM, TEM, XRD, XPS and FTIR measurements. Structural characterizations demonstrated that these WO_3 microspheres assembled by numerous one-dimensional WO_3 nanorods were approximately 2–5 μm in diameter. The nanorods with their diameters in the range of 70–90 nm showed a single crystal hexagonal structure. Gas sensors based on pure and Pt-functionalized WO_3 microspheres showed reversible response and outstanding selectivity to xanthate gas at the operating temperature range of 75–175 °C. The sensor response increased with the increase of xanthate gas concentration. The highest response of 102.7 was obtained for the sensor based on 3 mol% Pt-functionalized WO_3 microspheres to 100 ppm xanthate gas at an operating temperature of 100 °C, which could be ascribed to the large effective surface area and high porosity of WO_3 microspheres as well as the catalytic effect of Pt nanoparticles.

1. Introduction

With the rapid development of mining industry over the past few decades, much more attention has been paid to safety issues relating to mineral processing reagent. To meet the urgent need for gas sensors which are capable of detecting environmentally harmful gases and odors in ore-dressing plants, the development of high-performance gas sensors for mining gas detection is essential. As an important flotation reagent, xanthate plays a key role in the flotation beneficiation of precious metal and base metal sulfide ores as well as in the additive or reactant in rubber, pesticides and pharmaceuticals [1–4]. However, xanthate is easily hydrolyzed to carbon disulfide (CS_2) and corresponding alcohols in aqueous solution and flotation pulps, which will be accumulated continuously in the flotation plants and subsequently bring about the harm for the worker health. For example, butyl xanthate ($C_5H_9NaOS_2$) reacts with H_2O to form CS_2 and butanol (C_4H_9OH), as expressed in the following equation [3,5]:

$$(CH_3)_2CHCH_2OCS_2Na+H_2O = CS_2 + (CH_3)_2CHCH_2OH + NaOH \quad (1)$$

CS_2 is a kind of toxic volatile organic compound, which can cause various health risks such as atherosclerosis, nervous system and coronary artery diseases [6]. Moreover, it is of an inflammable nature with a spontaneous combustion point of 100 °C. On the other hand, butanol is another toxic volatile organic compound generated by xanthate decomposition, which can cause symptoms such as dizziness, headache somnolence and dermatitis. In addition, when the temperature is higher than the flash point 35 °C of butanol, the air mixture may cause an explosion or flash fire [7]. Therefore, the development of an accurate and effective sensor is necessary for detecting xanthate gas during its production and usage in domestic and industrial applications.

In the recent times, various types of gas sensors, such as electrochemical [8], optical [9], and resistive gas sensors [10], have played a key role in homeland security and environment monitoring. Among these gas sensors, metal oxide semiconductors, such as WO_3 [11], SnO_2 [12,13], ZnO [10,14] and TiO_2 [15], have been widely developed because of their structural simplicity and low cost. As a key n-type semiconductor with a wide band gap of 2.6–3.2 eV, tungsten oxide (WO_3) has received significant attention in the past few years due to its unique physiochemical and remarkable gas sensing properties. Gas sensors based on WO_3 materials have exhibited excellent sensing performances to many target gases, such as volatile organic compounds (VOC) [16–18], NO_x [19,20], H_2S [21], O_3 [22,23], NH_3 [24], H_2 [25,26] and so on. Up to now, WO_3 sensing materials have been synthesized by various methods, such as chemical vapor deposition [27],

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magnetron sputtering [28–31], thermal evaporation [11,32], sol-gel [33,34], pyrolysis [25,35] and hydrothermal [36]. Especially, hydrothermal route is one of the most attractive methods because of its simplicity, low process temperature, low-cost mass production, precise control of product microstructure, and easy addition for catalyst in metal oxide microstructures through the reaction [37]. So far, the hydrothermal method has been used to successfully fabricate WO_3 sensing materials with different morphologies such as films [36], nanorods [38,39], nanoplates [40,41], hollow microspheres [42], hierarchical urchin-like and flower-like WO_3 nanostructures [37,43].

Up to now, several efforts have been made to improve the gas sensing properties of WO_3 gas sensors by using many methods, namely, the use of composites [44,45], the addition of noble metal [20,32,37,46], and surface modification [47–49], of which the addition of noble metal has been confirmed to be the most effective method for improving the chemisorption process and enhancing response/recovery speed, which is due to their attractive catalytic properties. As an effective catalyst, Pt can greatly improve gas sensing performances of the sensors to reducing gases, such as carbon monoxide, hydrocarbon and hydrogen, by chemical sensitization via the well-known spillover effect [36]. It can be effectively used in order to increase the response and selectivity as well as decrease the response/recovery time by reducing the activation energy [31,50]. For example, Shen et al. [13] reported that Pt-doped SnO_2 nanowires showed a high response to H_2 at an operating temperature of 100 °C. Liu et al. [51] reported that Pt-functionalized WO_3 nanorods exhibited fast response and recovery speeds as well as high response to ethanol and methanol gases compared to the pure WO_3 nanorods. Samerjai et al. [25] investigated the H_2 sensing performance of Pt-loaded WO_3 films. They reported that a high response and outstanding selectivity to H_2 could be achieved at a relatively low operating temperature of 150 °C. D'Arienzo et al. [24] reported that the combination between mesoporous WO_3 architecture and Pt doping can effectively promote the response to ammonia.

In our previous study, we have proposed the complexing surfactants-mediated hydrothermal synthesis of WO_3 microspheres for NO_2 sensing applications [52]. The WO_3 microspheres obtained by this way showed a higher porosity and larger effective surface area, in addition to showing excellent NO_2 sensing properties. To the best of our knowledge, there have been no reports on xanthate gas detection associated with the metal oxide semiconductors previously. Therefore, in the present study, the gas sensors based on Pt-functionalized WO_3 microspheres were investigated, with the aim of enhancing their gas sensing properties to xanthate gas generated from ore dressing in the mining industry, which will provide a possible direction for developing high-performance gas sensors used in the mining industry as safety devices.

In this work, a series of gas sensors based on WO_3 microspheres functionalized with different amounts of Pt (0, 1, 3 and 5 mol%) were prepared by a facile one-pot hydrothermal method, which can provide a simple and versatile route to prepare microspheres with a higher porosity and larger effective surface area for improving surface functionalities. Various characterizations were performed to investigate the crystal structure and morphology of the as-synthesized samples. Subsequently, the response of the four types of WO_3 microspheres to xanthate gas was evaluated. Further, the possible gas sensing mechanism was also discussed for the Pt-functionalized WO_3 sensor.

2. Experimental

2.1. Synthesis

All chemical reagents used in the experiments were of analytical grade and thus, employed directly without further purification. On the other hand, xanthate used here was composed of butyl xanthate ($C_5H_9NaOS_2$) with a content of 84 wt%, and was of laboratory grade (LR). A facile one-pot hydrothermal process was used to synthesize the pure and Pt-functionalized WO_3 microspheres. In a typical experimental procedure, 6 mmol of sodium tungstate ($Na_2WO_4{\cdot}2H_2O$), 6 mmol of citric acid ($C_6H_8O_7{\cdot}H_2O$), 6 mmol of oxalic acid ($C_2H_2O_4$) and 6 mmol of potassium sulfate (K_2SO_4) were dissolved into 120 mL of deionized water to obtain a transparent solution under stirring for 10 min. Subsequently, a certain amount of $H_2PtCl_6{\cdot}6H_2O$ was added into the above solution under stirring for 15 min. After that, 3 M HCl aqueous solution was added dropwise to the above mixture solution under continuing stirring until the pH value of the solution was 1. Then the above mixture solution was transferred to a Teflon-lined stainless-steel autoclave of 200 mL capacity, and heated at 160 °C for 12 h. After cooling down to room temperature naturally, the resulting products were separated from the solution by washed with deionized water for five times, and subsequently dried at 60 °C for 4 h in air. Then, the obtained products were annealed at 400 °C for 4 h in a quartz tube furnace to stabilize the microstructure and gas sensing properties of the obtained samples. The four samples with the molar ratios of Pt to WO_3 of 0, 1, 3, and 5 mol% were labeled as S1, S2, S3 and S4, respectively.

2.2. Structural characterization

The crystalline phase, morphological and microstructural properties of pure and Pt-functionalized WO_3 microspheres were characterized by means of following methods/techniques: X-ray diffraction (XRD, PANalytical X'Pert Pro, Cu Kα , λ = 1.54056 Å), field emission scanning electron microscopy (FESEM, ZEISS Ultra Plus, operating voltage of 20 kV), high-resolution transmission electron microscopy (TEM, FEI G^2-20, operating voltage of 200 kV) equipped with an energy dispersive X-ray spectrometer (EDX), X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Al Kα), and Fourier transform infrared spectroscopy (FTIR, NICOLET 380).

2.3. Gas sensing measurements

Gas sensors were prepared as follows: the desired amount of the synthesized powder was ground softly with several drops of deionized water in an agate mortar to obtain a homogeneous paste. As shown in Fig. 1(a), the obtained paste was directly brush-coated onto the alumina substrates to form a gas sensing layer with a thickness of about 100 μm. The top of the alumina substrate was coated with a pair of Au electrodes attached with Pt lead wires. A resistance heater was equipped on the bottom of the alumina substrate to control the operating temperature, as shown Fig. 1(b). After drying for 30 min at room temperature, the four lead wires of the alumina substrate were welded onto the sensor holder to fabricate the gas sensor device, as shown Fig. 1(c). Finally, the gas sensor device was placed in an aging equipment to stabilize the gas sensing layer by heating it at 300 °C in air for 8 h at a heating rate of

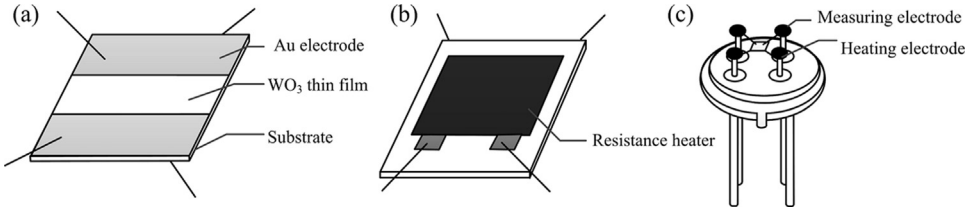

Fig. 1. Schematic diagram of the gas sensor device based on Pt-functionalized WO_3 microspheres. (a) Top surface of gas sensor. (b) Bottom surface of gas sensor. (c) Gas sensor device.