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Acetone sensing performances based on nanoporous TiO_2 synthesized by a facile hydrothermal method

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ABSTRACT

Nanoporous titanium dioxide was synthesized by a hydrothermal method without using of surfactant or template. The structure, morphology, surface chemical states and specific surface area were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and N_2 adsorption-desorption isotherms, respectively. The as-synthesized products are anatase-TiO_2 with small grain size (about 12.27 nm) and high surface area (147.17 $m^2\,g^{-1}$). The as-synthesized porous TiO_2 powder was used to fabricate indirect-heating gas sensor whose gas-sensing characteristics toward acetone were investigated. At its optimal operation temperature, the sensor possesses a good sensitivity, selectivity, linear dependence, low detection limitation, and response/recovery, repeatability as well as long-term stability. Especially for the high sensitivity and fast response/recovery, its response reaches 25.97 for 500 ppm acetone, which is several times higher that of the reported TiO_2-based sensors. The response and recovery times are only 13 and 8 s, respectively. Those values demonstrate the potential of using as-synthesized TiO_2 for acetone gas detection, particularly in the dynamic monitoring. Apart from these, the mechanism related to the advanced properties was also investigated and presented.

1. Introduction

With the development of the world's economy, issues of environment become the subject of widespread concern. Volatile organic compounds (VOCs) are primary sources of environmental pollutants and considered seriously harmful to human body. For example, acetone (CH_3COCH_3), a widely used chemical reagent in industrial processes, can anesthesia human central nervous system, which would cause a series of negative influence. When the concentration is higher than 173 ppm, it can cause damages to eyes, noses, and central nervous system [1]. Human's exposure to high levels of acetone may cause respiratory irritation, mood swings, and nausea. Likewise, breathing high levels of acetone (in industrial area) can cause respiratory tract irritation, dizziness, and loss of strength [2]. Meanwhile, acetone gas also shows extreme flammability. Explosion or flash fire may occur with volume content between 2.5% and 12.8% at a temperature higher than its flash point (−20 °C). The high effumability also increases the risk. On the other hand, acetone was known to be the final product for other ketone bodies' metabolism [3]. In blood, acetone may be freely transported through alveolus walls and easily mix with alveolus air. Hence, the acetone concentration in the breath exhaled by diabetics is proportional to the acetone content in the blood. Thus its concentration in blood may be used as a measure of ketoacidosis. Therefore, fabricating acetone gas sensor with high sensitivity possesses important meaning for the field of occupational safety and human health. And the key for the reliable gas sensor is the sensing material.

As an important, wide-energy-gap (E_g = 3.0–3.4 eV) semiconductor, titanium dioxide (TiO_2) has been intensively studied as a key material for fundamental research and technological applications in the fields of semiconductors, lithium-ion batteries [4–7], photocatalytic decomposition [8–10] and solar cell [11–13], because of its good chemical stability, non-toxicity, abundance and low cost [14]. It is also reported that TiO_2, as a semiconductor, also shows certain gas sensing character, especially for acetone. However, the sensitivity, even for acetone, is still un-ideal. For instance, Bhowmik et al. [15] reported the response of the sensor based on TiO_2 nanotubes only reaches 3.35 toward 1000 ppm acetone. Deng et al. [16] reported that the response of the gas sensor fabricated

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from TiO_2 nanofibers can not reach 3 toward 50 ppm acetone. From the mentioned limitation of the concentration, the reported sensitivity obviously can not meet the practical applications. Hence, a further design for higher sensitivity is urgently needed.

As we know, the gas sensing of metal oxide sensors generally are based on the catalytic reaction between the target gas and the adsorbed oxygen on the surface of the sensing materials [17]. That is to say, the gas sensing property highly relies on the exposed surface area. In another words, a high specific surface area could provide more active sites and consequent higher sensitivity. From this point of view, fabricating porous TiO_2 could be a good choice to enhancing the sensitivity toward acetone for practical use. Pang et al. [18] prepared porous TiO_2 nanobelts by an alkali hydrothermal process with a temperature of 200 °C for 72 h, then immersing the product in HCl aqueous for 72 h and finally annealing at 600 °C for 3 h. The waste sludge templated TiO_2 with a surface area of 130 $m^2\ g^{-1}$ was synthesized through a calcination process [19]. Yu et al. [20] synthesized porous TiO_2 films with the surface area ranged from 35 to 43 $m^2\ g^{-1}$ by a complicated procedure with template of silica. Obviously, these processes were multistep, long-playing and power-wasting. For practicing purpose, the economy effect also should be taken into consideration. In addition, Lechuga et al. [21] reported that anionic and non-ionic surfactant had an acute toxicity to aquatic organisms. Hence, a simple, convenient and surfactant-free method to porous TiO_2 is urgent to appear.

In this paper, nanoporous TiO_2 with a high surface area of 147.17 $m^2\ g^{-1}$ was obtained by a simple hydrothermal method without using of any surfactant or template. The nanoporous TiO_2 was then used as a sensing material for indirect heating sensor. Its acetone gas sensing properties were measured, and a remarkable enhanced sensitivity toward acetone that the reported TiO_2-based sensor is gained. To get further understanding on the related mechanism including formation and enhanced acetone gas sensing, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and the Brunner-Emmett-Teller (BET) were carried out.

2. Experimental details

2.1. Preparation of nanoporous TiO_2

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification.

Nanoporous TiO_2 was prepared by a simple low temperature hydrothermal method. The reaction can be described as follows:

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4 \quad (1)$$

$$TiO(OH)_2 \xrightarrow{\text{dehydrate}} TiO_2 + H_2O \quad (2)$$

In a typical synthesized experiment, 4.899 g titanyl sulfate was added to 50 mL deionized water with stirring until a homogenous solution was obtained. Then the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 80 mL and reacted under hydrothermal conditions at a temperature of 180 °C for 4 h. The autoclave was cooled down to room temperature in a standard atmosphere. The resulting products were centrifuged, and the white precipitates were thoroughly washed with deionized water and dried at 60 °C.

2.2. Characterization of as-synthesized nanoporous TiO_2

X-Ray diffraction (XRD, Rigaku D/MAX-3B powder diffractometer) with a copper target and $K\alpha_1$ radiation (λ = 1.54056 Å) was used for the phase identification, where the diffracted X-ray intensities were recorded as a function of 2θ. The sample was scanned from 10° to 90° (2θ) in steps of 0.01°. Transmission electron microscopy (TEM) measurement was performed on a Zeiss EM 912 Ω instrument at an acceleration voltage of 120 kV, while high-resolution transmission electron microscopy (HRTEM) characterization was done using JEOL JEM-2100 Electron Microscope (with an acceleration voltage of 200 kV). The samples for TEM were prepared by dispersing the final dry samples in ethanol, and this dispersing was then dropped on carbon–copper grids covered by an amorphous carbon film. The nitrogen adsorption isotherm was measured at 77.3 K with a Micromeritics ASAP 2010 automated sorption analyzer. Prior to the measurement, the sample was degassed at 300 °C for 6 h under a vacuum. X-ray photoelectron spectroscopy (XPS) was carried out at room temperature in an ESCALAB 250 system. During XPS analysis, an Al Kα X-ray beam was adopted as the excitation source and the vacuum pressure of the instrument chamber was 1×10^{-7} Pa as read on the panel. Measured spectra were decomposed into Gaussian components by a least-square fitting method. Bonding energy was calibrated with reference to the C1s peak (284.6 eV).

2.3. Preparation and test of gas sensor

The fabrication of indirect-heating structure sensor was described in the literature [22,23]. TiO_2 oxide was mixed with deionized water to form paste, and then coated onto the outside of an alumina tube (4 mm in length, 1.2 mm in external diameter, and 0.8 mm in internal diameter) with a pair of Au electrodes and platinum wires installed at each end. The thickness of the sensitive body, which was dried and calcined in air at 400 °C for 2 h, was about 0.5 mm. A Ni–Cr alloy wire crossing the alumina tube was used as a resistor to ensure both substrate heating and temperature control. In order to improve their stability and repeatability, the gas sensor was aged at operating temperature 320 °C for 120 h in air. The sensor's resistance was measured by using a conventional circuit in which the element was connected with an external resistor in series at a circuit voltage of 5 V. Then, the sensor was well connected to a bakelite base through platinum wires to perform electrical measurements using a WS-30A system, which structure was shown in Fig. S1. During the testing process, the needful amounts of the target substance were injected into the chamber by a microinjector when the resistance of the sensor was stable. The liquid was evaporated quickly in the chamber (18 L in volume). The electrical response of the sensor was measured with an automatic test system, controlled by a personal computer. The gas response β was defined as the ratio of the electrical resistance in air (R_a) to that in gas (R_g), namely $\beta = R_a/R_g$ [24,25]. In addition, the response time was defined as the time required for the gas response to reach 90% of the final equilibrium value after a test gas was injected, and the recovery time was the time needed for gas response to decrease by 90% after the gas sensor was exposed in air again.

3. Results and discussion

The structural features of the as-synthesized nanoporous TiO_2 particles were analyzed by XRD. The initial assignment was further confirmed by the refinement of the diffraction pattern with the Rietveld method. The experimental pattern, together with the calculated pattern obtained from the Rietveld refinement and difference profile are shown in Fig. 1. The structural parameters calculated from the Rietveld profile refinement are presented in Table 1. The difference curve between the calculated and experimental XRD patterns reveals an excellent agreement. The experimental diffraction peaks can be perfectly indexed to anatase TiO_2 (JCPDS No. 21-1272), space group: $I4_1/amd$ (141). The results indicated the high purity of the obtained product. The volume-