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Synthesis and Sensing Properties to NH_3 of Hexagonal WO_3 Metastable Nanopowders

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WO_3 is an important kind of wide-bandgap semiconducting metal oxides, which has a very promising property in gas-detection behavior. It has several polymorphs with triclinic, monoclinic, orthorhombic structures being the stable forms of this oxide. However, by a method known as *acid precipitation*, new metastable open crystalline forms with hexagonal structure have been successfully synthesized. The nanopowders were characterized by SEM, TEM, and XRD, and their sensing response to reducing gases (NH_3) was measured and compared to monoclinic WO_3, showing a much better sensing property of the hexagonal WO_3.

Keywords Acid precipitation; Ammonia; Hexagonal; Metastable; Monoclinic; Nanopowder; Open structure; SEM; Sensitivity; Sensor; Synthesis; TEM; Thin film; Tungsten oxide; XRD.

1. Introduction

Metal oxides are polymorphic compounds and controlled chemical processing may stabilize oxide polymorphs that would otherwise be energetically unstable. Recent studies by the authors' group, [1–3] led to the hypothesis that the ability for selective detection of a particular gaseous analyte in the presence of interfering gas mixtures (i.e., sensor selectivity) is largely determined by the chosen crystalline polymorph (specific crystallographic phase) of a stoichiometric and pure metal oxide used for sensing. Transition metal oxide such as MoO_3 and WO_3 were used as model systems in those studies.

Orthorhombic (α-phase) MoO_3 was found to exhibit high specificity to the detection of ammonia and amines. MoO_3 has a layered structure with (010) basal plane that is built up of double chains of edge-sharing [MoO_6] octahedral units connected through vertices. Thus the α-phase is selective to ammonia and highly sensitive to amines (which are moderate bases) because their sensing mechanism involves the reduction of MoO_3 and the formation of ordered phases (reaction-based sensing process) as it has confirmed in the works of Gouma using XPS studies, [2, 3]. It is suggested that transition metal oxides with "loosely-bound" and open structures are necessary in order to achieve selective amine detection, as they enable the reaction of lattice oxygen with the gas and provide easy mechanisms for accommodating the off-stoichiometric M:O ratio [4]. Issues of structural stability due to the high volatility of this material, however, limit its use in high temperature sensing applications. The search for alternative materials that are isostructural with MoO_3 identified WO_3 as promising candidates.

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WO_3 has been used to detect various gases due to its excellent semiconducting properties. Since Shaver reported the first WO_3gas sensor for the detection of hydrogen [5], there has been numerous reports on WO_3 sensors for detecting NO_2 and NH_3 and other gases such as ozone, CO, CH_4, and H_2S, esp. during the last 5 years. Xu et al. [6] have reported their studies of selective detection of NH_3 over NO in combustion exhausts by using Au and MoO_3 doping on WO_3 elements. The effects of dopants [7], substrate dependence [8], calcining and operating temperatures [9, 10], stoichiometry and microstructure [11], film thickness [12] on WO_3 based films were studied respectively by different groups. The enhanced response of Pt, Au Cr [13], Cu or V [14]-doped WO_3 nanocrystalline powders to NH_3 were also studied. Tomchenko et al. [15] designed and fabricated semiconducting metal oxide sensor array for the selective detection of combustion gases. Teoh et al. [16] and Kim et al. [17] have even developed room-temperature WO_3 based gas sensors. Recently, multi-wall carbon nanotube modified WO_3 thin films were obtained and proved to highly improve gas sensing properties [18]. In addition, tungsten oxide sensing layers on highly ordered nanoporous alumina template has been synthesized by Khatko et al. [19].

WO_3 has several polymorphs with triclinic, monoclinic, orthorhombic, and tetragonal structures being the stable forms of this oxide, and a metastable hexagonal structure (h-WO_3). However, all these previous works used stable structures to fabricate the sensors and they haven't discussed the structure influence on the gas sensing properties, esp. the sensing properties of h-WO_3 haven't been reported. H-WO_3 was first synthesized and reported in 1979 by Figlarz's group [20] by the dehydration of a tungsten oxide hydrate compound ($WO_3 \cdot 1/3H_2O$). Its structure is built up of WO_6 octahedra arranged in layers normal to the hexagonal c-axis, forming hexagonal tunnel structures [21]. Furthermore, h-WO_3 has attracted attention as an electrochromic material [22, 23] thus that it might be possible to produce sensors

that change color in the presence of reducing gases, such as CO.

In this paper, by a method called acid precipitation, new metastable open h-WO_3 crystalline forms can be synthesized. This work refers to the ammonia sensing properties of two polymorphs of WO_3, the stable monoclinic and the metastable hexagonal phase.

2. Experimental

To synthesize the hexagonal structured WO_3 powders, 1.17 g of $Na_2WO_4 \cdot 2H_2O$ of analytical grade was dissolved in 17 ml of water and the solution was cooled to 10°C. To this 8.4 ml of normal hydrochloric acid solution (analytical grade, 18% in excess of equimolar reaction) cooled to the same temperature was added in one dose. The mixture was put back into the refrigerator and allowed to stay for about 20 h. After this time the whole mixture turned to a whitish gel. Then 110 ml of water was added to the vessel and the gel and water were lightly stirred manually. After centrifuging the supernatant liquid was removed. Then 130 ml of water was added to the precipitate and the steps of light manual stirring, centrifuging and removal of supernatant liquid were repeated several times to obtain $H_2WO_4 \cdot H_2O$, the precursor of final h-WO_3 powders. $H_2WO_4 \cdot H_2O$ suspensions were passed to hydrothermal dehydration, carried out in Parr acid digestion bombs at autogeneous pressure at 125°C ± 5°C. Dehydration under air: furnace temperature: 300–330 °C, annealing time: 90 min. [24].

To prepare for the h-WO_3 gas sensor, 0.1 g of such h-WO_3 powders were weighed into 3 ml of heptanol and the suspension was ultrasonically stirred for at least 1 h. Two drops of the suspension were removed to drip on an Au electrode-coated Al_2O_3 substrate. The substrate is left at the room temperature for 1 h until the solution evenly spread on the substrate. Then the substrate was dried at 75°C for 10 min to remove the liquid. Such process was repeated for 3 times and then a uniform h-WO_3 thin film gas sensor was successfully prepared.

3. Results and discussion

The color of h-WO_3 powders is gray, different from that of common monoclinic WO_3 (γ-WO_3), which is yellowish green. The scanning electron microscopic (SEM) morphology of h-WO_3 powders is shown in Fig. 1(a).

In this image there are two typical shapes of WO_3 powders in the product. One shape is nanoparticles and the other is nanorods. The two shapes of powders are mixed together. Fig. 1(b), (c) are transmission electron microscopic (TEM) images of WO_3 nanoparticles and nanorods, respectively. The nanoparticles are about 10–50 nm in diameter while the nanorods are about 30–100 nm in diameter and 100–300 nm in length.

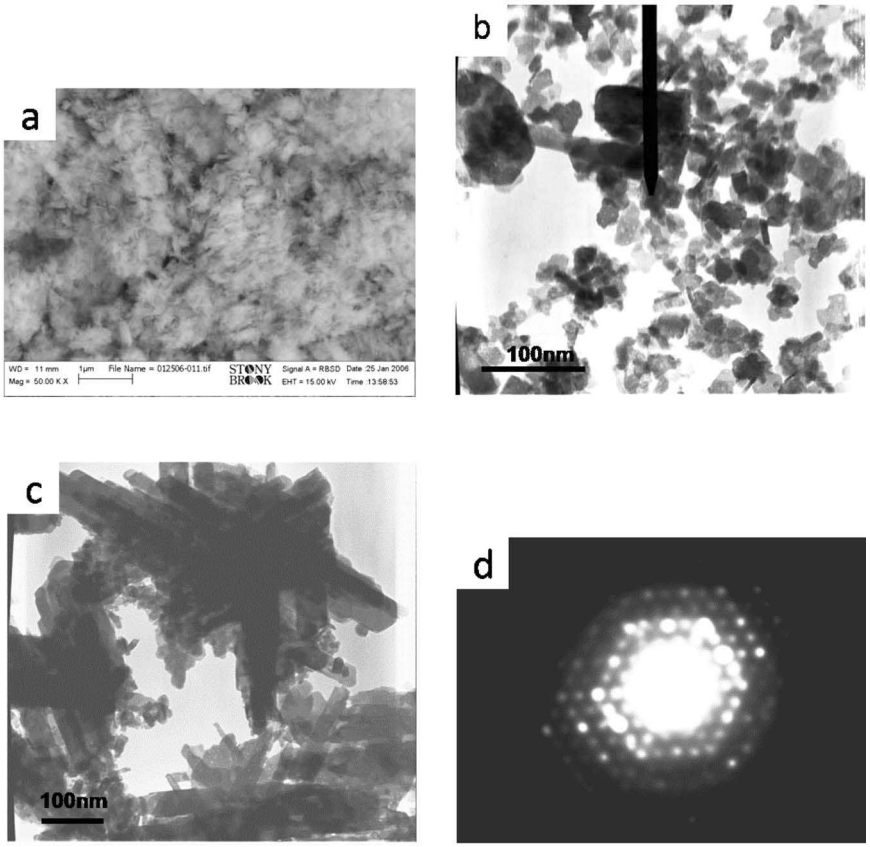

Figure 1.—Morphology and structure of h-WO_3 powders. a) SEM image showing two shapes; b) TEM image of WO_3 nanoparticles; c) TEM image of WO_3 nanorods; d) SAED pattern of WO_3 powders showing a hexagonal structure.

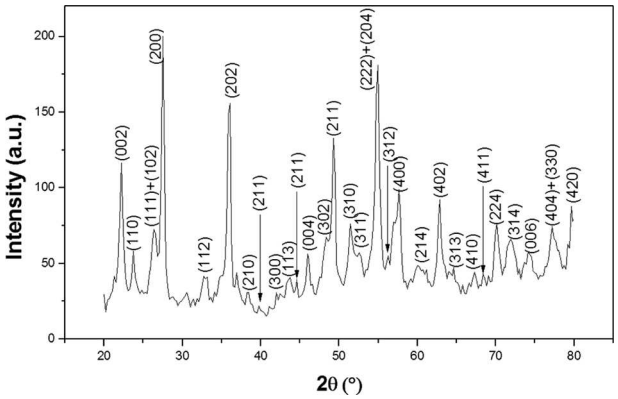

FIGURE 2.—XRD result of h-WO_3 powders.

Although the WO_3 nanoparticles and nanorods are different in shape, they share a same structure. Fig. 1(d) is selected area electron diffraction (SAED) pattern of the WO_3 powders. It shows that the powders have a hexagonal structure. Such result is confirmed by the following X-ray diffraction (XRD) result.

The XRD result of the metastable powders is shown in Fig. 2. According to the result, the product is in a high purity and can be indexed as a primitive hexagonal structure with the lattice parameter of $a = 0.7324\,\text{nm}$ and $c = 0.7662\,\text{nm}$, compared to the standard data file (JCPDS file No.: 852459).

To measure the sensing property of the h-WO_3 nanopowders, we prepared a thin film sensor using these powders as source material on Au electrode-coated Al_2O_3 substrate (shown in the "experimental method" chapter). The sensing test was carried on at 400°C and we used ammonia (NH_3) as the testing gas. When the concentration of NH_3 is 50 ppm, 100 ppm, and 200 ppm, the resistance has lowered down from 90 kΩ to about 11 kΩ, 7 kΩ and 4 kΩ (shown in Fig. 3(a)) and the sensitivity is up to 88%, 92%, and 96% (shown in Fig. 3(b)), respectively. This result indicates an outstanding sensing response of h-WO_3 nanopowders to NH_3 reducing gas. In addition, the sensitivity at a certain concentration of NH_3 is reproducible, showing that the sensing property of the h-WO_3 nanopowders is stable which can be regarded as an excellent candidate for detecting NH_3 gas.

To compare the sensing property of h-WO_3 to other structured WO_3, we also prepared γ-WO_3 thin film gas sensor using the same method. The powders have similar morphology and sizes with h-WO_3, but have different structures. The sensing response and sensitivity of γ-WO_3 are shown in Fig. 4. At a NH_3 concentration of 50 ppm, 100 ppm, and 200 ppm, the sensitivity of γ-WO_3 is 67.5%, 75.5%, and 82%. Although it indicates a good sensing response of γ-WO_3 to NH_3, it is much lower than that of h-WO_3 nanopowders.

Therefore, we can conclude that h-WO_3 powders have a much better sensing property than γ-WO_3 nanopowders. As mentioned in the Introduction chapter, h-WO_3 has a

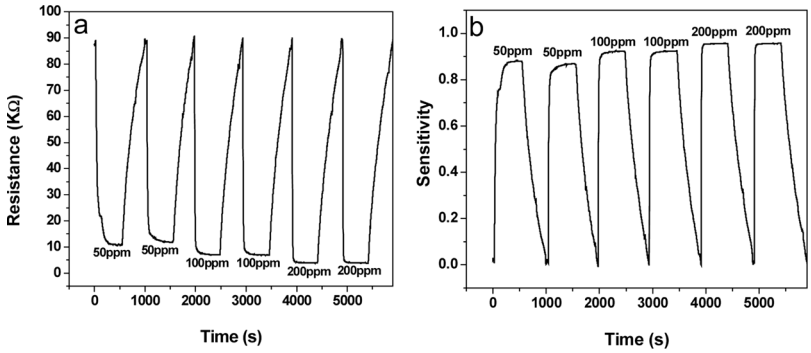

FIGURE 3.—The (a) response and (b) sensitivity to NH_3 gas of h-WO_3 powders at 400°C

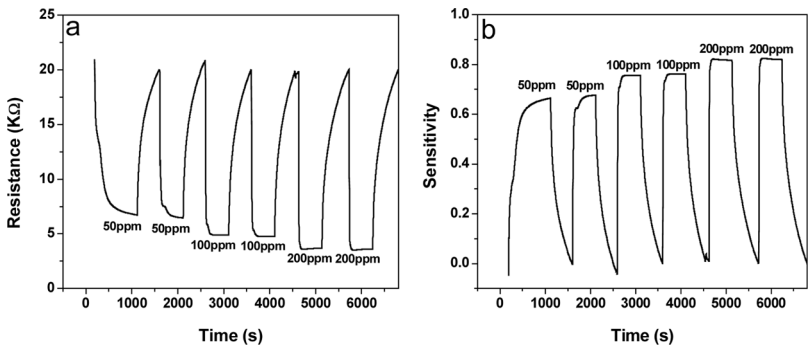

FIGURE 4.—The (a) response and (b) sensitivity to NH_3 gas of γ-WO_3 powders at 400°C

loosely-bound and more open layered structure. When it is exposed to NH_3, it is believed that NH_3 tend to remove oxygen from lattice and form ordered phases. Such reaction leads to the higher sensing properties of h-WO_3 to NH_3.

4. Conclusion

NH_3 selective gas sensor based on tungsten oxide nanopowder films were successfully synthesized using acid precipitation method. The product has a new hexagonal structured metastable phase rather than common stable phases of tungsten oxides, such as monoclinic etc. The synthesized h-WO_3 sensor has a very high sensitivity to NH_3 gas, up to 88%, 92%, and 96% responding to 50 ppm, 100 ppm, and 200 ppm of NH_3, respectively, which is much higher than that of γ-WO_3 sensor which has similar morphology and sizes. It is believed that it is the more open structure of h-WO_3 that improves its sensitivity compared to other stable phases.

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