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Abnormal p-type sensing response of TiO_2 nanosheets with exposed {001} facets

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ABSTRACT

TiO_2 nanosheets with exposed {001} high-energy facets were used as gas sensing materials. Interestingly, the sensor displayed a regular n-type response to alcohol with high sensitivity at high temperatures above 250 °C, but abnormal p-type sensing behavior over a wide temperature range from room temperature to 120 °C. Such an unusual p-type sensing response, unprecedented for n-type TiO_2 nanomaterials, was attributed to the proton transfer between alcohol molecules and adsorbed water molecules on the surface of TiO_2 nanosheets. The present work provides a new insight into the gas sensing mechanism of metal oxide nanostructures.

1. Introduction

Gas sensor technology plays a major role in healthcare, pollution control and environmental monitoring. The resistive gas sensor usually utilizes an electrical response by the adsorption of gas molecules on the surface of the active layer, which results in a large change in its electrical resistance. With special shapes and chemical properties, metal oxide nanostructures have been demonstrated to be important candidates as building blocks for resistive sensing applications in recent years. In general, semiconducting metal oxide sensors are classified into two kinds: n-type (e.g., SnO_2, ZnO, TiO_2, WO_3, In_2O_3, Fe_2O_3) [1] and p-type (e.g., NiO, CuO, Cr_2O_3, Co_3O_4, Mn_3O_4) [1,2], depending on the nature of the majority carriers at the material surface. In most cases, n-type semiconducting oxides display typical n-type sensing response, showing a resistance decrease after exposure to reducing gases. Rarely, p-type sensing response (n-p transition) was also demonstrated for urchin-like α-Fe_2O_3 nanostructures [3], In_2O_3-Fe_2O_3 mixture [4], Pt@SnO_2 nanorods [5], TeO_2 nanowires [6] and noble metal doped TiO_2 [7,8]. The mechanism of the n-p transition sensing behavior is still a matter of debate. Some authors attributed this phenomenon to the strong absorption of oxygen species and formation of a surface inversion layer [3,4]. Others ascribed the phenomenon to catalyst-induced morphological changes of ionsorbed oxygen [5], concentration-controlled transition mechanism [6], or p-type doping with noble metals [7,8]. In spite of some explanations reported, the n-p transition is still not absolutely understood and needs to be further investigated.

Being an important n-type semiconducting oxide with a wide band gap of 3.2 eV [9], anatase TiO_2 has been extensively researched as catalysts, electrode materials, and gas sensors, due to its low cost, nontoxicity, chemical stability and high catalytic activity [10–12]. It has been known that the {001} facets of anatase TiO_2 exhibit the highest photocatalytic activity than the other ones [13]. Unluckily, the majority of the exposed surface of anatase TiO_2 crystals is {101} facets because of their lowest surface energy (0.44 J/m^2) than that of {001} facets (0.90 J/m^2). Since the pioneering work of the synthesis of anatase TiO_2 with exposed high-energy {001} crystal facets by Yang et al. [13], numerous works have contributed to the synthesis of anatase TiO_2 with exposed {001} facets. Nevertheless, most of the reported works have been concentrated on the controllable preparation and application in photocatalysis [14–17], and the gas sensing application of TiO_2 nanostructures with exposed {001} facets is rarely reported. Since gas-sensing properties of metal oxides are largely dependent on the surface atom structure of exposed facets, TiO_2 nanostructures with

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high-energy {001} facets should be in favour of exploring the gas-sensing properties and related mechanism.

In this work, by using TiO_2 nanosheets with exposed {001} high-energy facets as gas sensor active layer, abnormal p-type sensing behavior is revealed to alcohol at a wide temperature range (room temperature to 120 °C), which can be switched to regular n-type response with high sensitivity at increasing operation temperature (≥250 °C). Surprisely, the abnormal p-type sensing response is not consistent with the previously accepted mechanisms, but results from the proton transfer between alcohol and adsorbed water molecules on the surface of TiO_2 nanosheets. The present work enriches the research of TiO_2 sensing material and provides a new insight into the gas sensing mechanism of metal oxide nanostructures.

2. Experimental

Anatase TiO_2 nanosheets with exposed {001} facets were fabricated by the hydrothermal approach similar to that reported by Yuan et al. [16]. In a typical procedure, 3 mL of HF was added dropwise into a Teflon-lined stainless steel autoclave containing 25 mL $Ti(OC_4H_9)_4$ under magnetic stirring. The autoclave was kept at 180 °C for 24 h in an electric oven. After cooling down naturally to room temperature, the anatase TiO_2 samples were collected by centrifugation, washed thoroughly with deionized water and absolute ethanol 3 times, and then dried in vacuum at 80 °C for 6 h.

The morphology and crystalline structure of the samples were characterized by field emission scanning electron microscopy (SEM, FEI, Nova NanoSEM 450) equipped with energy-dispersive x-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM, FEI, Tecnai G^2 F20 S-TWIN), and high-resolution transmission electron microscopy (HRTEM). The Raman spectrum was recorded on a Raman microspectroscope with a 532 nm Ar^+ laser as an excitation source. Mott Schottky measurement was performed using a standard three-electrode electrochemical cell, where the electrolyte was Na_2SO_4 (0.2 M), reference electrode was Ag/AgCl, and counter electrode was a Pt-coated glass slide. The gas sensing tests were conducted by a CGS-4TP intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China). The obtained TiO_2 nanosheets were ground slightly together with several drops of distilled water in an agate mortar. The gas sensor was then obtained by coating the formed TiO_2 paste onto an Ag-Pd substrate. The test gas was injected into the chamber (1.8 L in volume) by using a syringe and sensitivity of the sensor is defined as $S = R_g/R_a$ or $S = R_a/R_g$ ($S > 1$), where R_a and R_g are treated as the resistance in air and in test gas, respectively.

3. Results and discussions

The morphology of obtained products was firstly examined by SEM. Fig. 1(a) displays a typical SEM image of TiO_2 sample prepared by hydrothermal method in the presence of HF. It is obvious that uniform sheet-shaped nanostructures are observed. These nanosheets possess a well-defined rectangular outline with an average side length of 67 nm and thickness of 8 nm. The phase characteristic of the TiO_2 nanosheets was identified from XRD pattern as presented in Fig. 1(b). The diffraction peaks can be well-indexed to the pure anatase phase of TiO_2 (JCPDS card no. 21-1272). Based on the XRD result, the intensity ratio of (200) to (004) peaks is 4.10. This value is distinctly larger than the standard value of 1.75, indicating that there is a special anisotropic growth along the [100] direction of the crystal, which is in good accordance with the nanosheet-like morphology of TiO_2 with exposed {001} facets. The percentage of {001} facets can be quantitatively measured by Raman spectroscopy according to the previous report [17]. As shown in Fig. 1(c), the peaks observed at 144, 394, 514, and 636 cm^{-1} belong to the typical anatase TiO_2 phase, coinciding with the XRD result. By measuring the peak area ratio of the E_g (144 cm^{-1}) and A_{1g} (514 cm^{-1}) modes, the percentage of {001} facets is thus determined to be about 76.3%.

TEM and HETEM images were carried out to give further insight into the morphology and structure of the TiO_2 nanosheets. Fig. 2(a) describes a typical TEM image of the obtained TiO_2 product, clearly showing the nanosheet-like morphology with rectangular outline. The HRTEM pattern taken from the flank of a single nanosheet is depicted in Fig. 2(b). The measured fringe spacing, which is parallel to the top and bottom lattice planes, corresponds well to the lattice spacing of the (001) planes (0.235 nm) of anatase TiO_2. In addition, the HRTEM image recorded from the top surface of an individual nanosheet is shown in Fig. 2(c). The lattice spacing of 0.19 nm agrees well with the distance of (200) planes of anatase TiO_2. These results clearly demonstrate that the exposed top and bottom surfaces are {001} facets.

Fig. 3(a) shows the normalized resistance response curves of the TiO_2 nanosheet-based sensor to 500 ppm alcohol as a function of the operating temperature ranging from room temperature to 400 °C. Upon exposure to alcohol gas, the evident decrease in resistance of the sensor is observed at the operation temperature above 250 °C, and the resistance returns to the initial state after exposure to air, corresponding to a typical n-type gas sensing behavior of TiO_2 semiconductor. This is reasonable since TiO_2 semiconductor is known to be an n-type gas sensing materials. However, the resistance of the sensor increases upon exposure to alcohol gas at the temperatures below 120 °C, showing a completely inverse gas sensing behavior. This abnormal p-type gas sensing response at low temperature is quite interesting and surprising. In addition, the corresponding gas sensitivities of the sensor upon exposure to 500 ppm ethanol at various operating temperatures are presented in Fig. 3(b). Clearly, a temperature-dependent sensing behavior is revealed. The p-type response increases firstly with the increase of temperature from room temperature (30 °C) to 70 °C, and decreases with the further increase of temperature to 150 °C. The maximum p-type response is 7.1 at the optimal operating temperature of 70 °C. Even at room temperature, the p-type response is still evidently identified with a value of 1.7. With the temperature above 250 °C, the gas sensing behavior converts into a normal n-type response, which increases firstly and then decreases with increasing operating temperature. The maximum n-type response can be up to 24.1 at the optimum operating temperature of 310 °C.

Generally, stoichiometric TiO_2 shows oxygen deficiency, resulting in an n-type conduction of the TiO_2. However, p-type TiO_2 can be achieved with Ti-defected preparation process or doping of foreign atoms [18,19]. To clarify the conduction type of the prepared TiO_2 nanosheets, Mott Schottky measurement was performed. Using the linear part of the Mott Schottky curve, it is possible to obtain the conduction type from the sign of the slope. Fig. 4 shows the Mott Schottky plot for the TiO_2 nanosheet sample at a frequency of 10 kHz. The Mott Schottky plot displays a positive slope, confirming the n-type conduction of the prepared TiO_2 nanosheets [18,20,21].

The n-type sensing mechanism of the TiO_2 nanosheets can be expressed by the modulation model of depletion layer [22]. When the TiO_2 sensor is exposed to air, O_2 can be adsorbed on the surface of TiO_2 nanosheets to form oxygen species (O_2^-, O^{2-} or O^-) by capturing electrons from the conduction band of TiO_2. As a result, an electron depletion layer is formed on the surface of TiO_2 nanosheets, leading to an increased sensor resistance. When ethanol is added, the adsorbed oxygen species react with the ethanol molecules, and release the captured electrons back into the conduction