



The correlation between the ethylene response and its oxidation over TiO₂ under UV irradiation

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ABSTRACT

The anatase and rutile TiO₂ film sensors were prepared by drop-coating method with calcination at 450 and 600 °C, respectively. After tested the ethylene sensing property over the as-prepared TiO₂ sensors under UV irradiation, it was found that the anatase TiO₂ as well as the rutile sensor exhibited a response to ethylene in the dry nitrogen atmosphere, but with anatase showing a much lower response to ethylene (almost no response) than rutile in the dry air atmosphere (containing oxygen). Moreover, this difference to the ethylene response between the anatase TiO₂ sensor and the rutile one was also observed in a wet air atmosphere under UV irradiation. Based on the results of photocatalytically oxidizing ethylene over anatase and rutile TiO₂, it is proposed that the weak gas response to ethylene over the anatase TiO₂ under UV irradiation can be attributed to the oxidation of ethylene itself. This also suggests that a good photo-assisted semi-conductor sensor should have a strong photoresponse property but a weak photocatalytic performance for the sensed gas.

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1. Introduction

It is well known that UV irradiation can exert an effect on the gas detection over the metal oxide semiconductors: On the one hand, UV irradiation can stimulate the generation of carriers to increase the density of the free electron–hole pairs, and change the inter-grain potential barrier to decrease the depletion layer between the semiconductor and the adsorbed gas [1]. On the other hand, UV irradiation can lead to the photodissociation of the gas targets and the subsequently formed chemical species adsorbed on the surface of semiconductor [2–4]. These physical–chemical phenomena allow for the possibility of utilizing gas sensing at room temperature over these photo-responded metal oxides and then the implementation of the corresponding sensors as the portable devices with low power consumption.

TiO₂, as a semiconductor, has been well investigated as a gas sensing material because of its high chemical stability, high electrochemical activity, high catalytic activity, and low cost. Most studies are mainly focused on how to enhance the gas chemisorption or the inner charge transfer of the TiO₂-based materials, structured in a variety of forms such as nanotube [5–8], nanorod [9–11], nanobelt [12,13], and nanowire [14] synthesized by hydrothermal, anodization, chemical vapor deposition sol–gel methods, and other methods. These nano-TiO₂ materials may be in an anatase

[5,8,12,14] or rutile phase [10] which depended on the synthetic methods. Moreover, the ultraviolet light had been also introduced into the gas sensing system to promote the gas sensing performance of the semiconductor sensors [4]. However, this attention was mainly paid to the promotion effect of the gas sensing properties of TiO₂ but little to the difference of the gas response behaviors between anatase and rutile TiO₂ induced by UV irradiation.

It is widely accepted that the chemisorption of the gas target and subsequently its catalytic reaction on the surface of the metal oxides are the two main factors which lead to the gas response [15]. With this viewpoint, the gas response over TiO₂ under UV irradiation should be related with the photocatalytic reaction behavior of the gas over TiO₂. That is to say, the influence of the photocatalytic reaction of the gas target on its response over TiO₂ should be considered while investigating the ultraviolet-assisted TiO₂ gas sensor response. Since anatase TiO₂ generally shows a higher photocatalytic activity than rutile TiO₂ [16], the gas response under UV irradiation over the anatase TiO₂ may be different from that over the rutile one provided that the gas can be photocatalytically oxidized.

To investigate the correlation between the gas response and its oxidation over TiO₂ under UV irradiation, in this work, two nano-structured TiO₂ thick film (30–50 μm) sensors in an anatase and rutile phase were prepared, respectively. Ethylene was acted as the gas target, and its response over the two sensors under UV irradiation in the atmosphere with or without oxygen was studied. Correspondingly, the photocatalytic performances of the anatase and rutile TiO₂ for oxidizing ethylene were compared.

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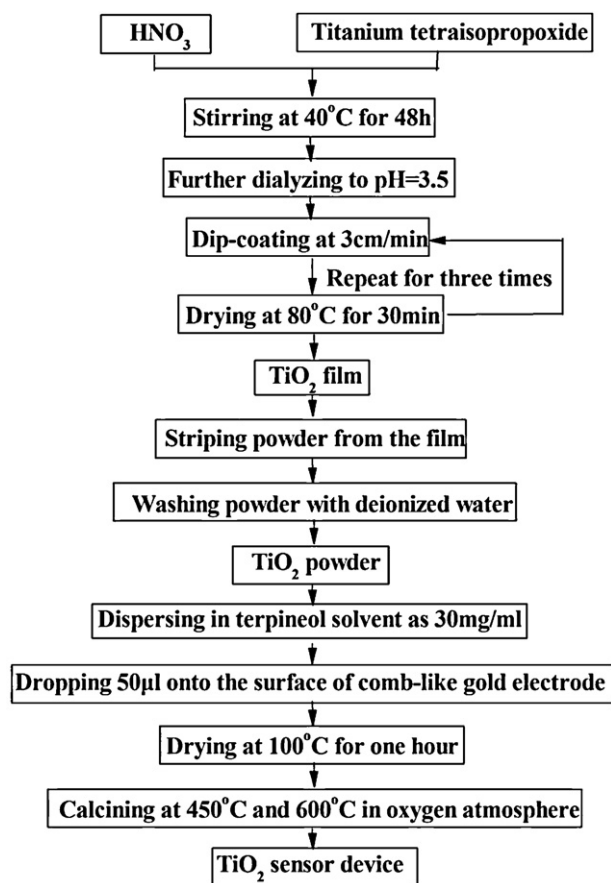


Fig. 1. The schematic diagram of preparing the TiO_2 sensor device.

The preliminary discussion about the correlation between the oxidation of ethylene and its response is given. Moreover, considering the existence of humidity in practical applications, the ethylene response over the anatase and rutile TiO_2 were also compared at atmospheres with the different relative humidity (RH) controlled by various kinds of saturated salt solutions [17].

2. Experimental

2.1. Preparation of TiO_2 film sensor device

The TiO_2 film sensor device sample was prepared according to the procedure shown in Fig. 1. The detailed process can be described as follows: (i) To prepare the TiO_2 sol: a 12.5 mL of titanium tetraisopropoxide (analytic grade from Shanghai Chemistry Reagent Co. Ltd., China) was slowly added into a HNO_3 solution (a 1.1 mL of 68% HNO_3 diluted with a 150 mL of H_2O) under vigorous stirring for hydrolysis. To prepare a clear TiO_2 sol, the obtained suspension solution was allowed to stay at 40°C under stirring for 48 h and was further dialyzed to $\text{pH} = 3.5$ [18]. (ii) To prepare the TiO_2 nano-powder with a very small size: a microscope slide (Sail brand, China) was pretreated with acetone, ethanol, and deionized water in sequence. Then, the as-prepared TiO_2 sol was coated onto the dried clear slide by a dip-coating process (with a withdrawing rate of 2 cm min^{-1}) and the subsequently dried process (100°C for 0.5 h). After repeating the above process three times, a TiO_2 powder as film was formed onto the surface of the microscope slide. Finally, TiO_2 powder with an average particle size of $1.5\ \mu\text{m}$ (measured by Zetasizer system, 3000 HAS, Malvern Instruments, UK) was obtained by stripping the as-prepared TiO_2 film from the slide surface. (iii) To prepare the TiO_2 sensor device: a commercial alumina

sheet with a comb-like gold electrode on one side surface was used as the substrate for TiO_2 sensor. After washed in acetone, ethanol, and deionized water in sequence and then dried in air, a $50\ \mu\text{L}$ TiO_2 suspension (30 mg of as-prepared TiO_2 powder was dispersed into a 1 mL terpineol solvent) was dropped onto the surface of the comb-like gold electrode of this substrate. Then, this substrate coated with TiO_2 suspension was dried at 100°C for 1 h and then calcinated in oxygen at 450 or 600°C for 2 h in a tube furnace with a heating rate of 2°C min^{-1} . After cooled down to the room temperature naturally, a TiO_2 film ($30\text{--}50\ \mu\text{m}$) sensor device was obtained named as T450F or T600F. Note that the terpineol solvent in T450F or T600F sample has been volatilized or decomposed during the treating process.

2.2. Characteristics of TiO_2 samples

X-ray diffraction (XRD) patterns were collected on Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation operated at 40 kV and 40 mA. The data were recorded in the 2θ range of $20\text{--}80^\circ$ with a step width of 0.02° . Scanning electron microscopy (SEM) investigations were carried out on an FEI Nova NanoSEM 230 field-emission scanning electron microscope. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}), pore diameter and pore volume were determined by nitrogen adsorption–desorption isotherm measurements at 77 K on a Micromeritics ASAP 2010 system. The samples were degassed in vacuum at 200°C until a pressure lower than 10^{-6} Torr before the actual measurements.

2.3. Gas sensing performances

The gas sensing properties of TiO_2 film sensors was conducted in a chamber shown in Fig. 2. The chamber with a total volume of 100 mL was made of stainless steel. Four UV lamps with a wavelength centered at 365 nm (4 W, Philips TL/05) were used as the irradiation source and the total light intensity on the surface of sensing film was $7.3\ \text{mW cm}^{-2}$. The response of TiO_2 sensor to the gas is described by the variation of its impedance.

A high purity N_2 or air was introduced into the chamber as the background atmosphere, and a 400–1600 ppm C_2H_4 (balance with the high purity N_2) as the probe gas. The total flow rate was kept at $250\ \text{mL min}^{-1}$. The resistance of the film sensor was measured by a JF02E gas sensing test system (Kunming GuiYanJinFeng Tech. Corp., Ltd.) and the applied voltage was controlled at 8.5 V. Prior to any measurement, the film sensor sample was maintained at 200°C for 1 h in a high purity N_2 to remove the water and the other gas adsorbates. The humidity of the atmosphere was controlled by making the dry mixture to pass through the different saturated salt solution such as LiCl , MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, NaCl , and KCl solutions [19]. Fig. 3 presents the detailed RH value in the wet atmosphere corresponding to the different salt solutions measured by Center 310 series humidity temperature meter. Note that all the above experiments were carried out at room temperature.

2.4. Photocatalytic performances

In our work, it is difficult to evaluate the photocatalytic performances of film sensor in the gas sensing system. To compare the photocatalytic performances of two TiO_2 film sensors, two TiO_2 powder samples with the same phase and textural properties as the two TiO_2 film sensors need to be prepared as catalysts. To obtain the TiO_2 powder samples, the prepared TiO_2 sol in Section 2.1 was dried at 80°C , and then calcinated at the same temperature (450 or 600°C) as the treating temperature of preparing TiO_2 film sensors. The obtained two TiO_2 catalyst samples were named as T450P and T600P, respectively.

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