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Gas sensor application of hydrothermally growth TiO$_2$ nanorods

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Abstract

This study focuses on TiO$_2$ nanorod-based gas sensor. TiO$_2$ nanorods were fabricated on fluorine doped tin oxide (FTO) substrate by hydrothermal method. The hydrothermal solution was prepared with titanium but-oxide, hydrochloric acid and deionized water (volume ratio 1:30:30). The morphologies and structure of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Highly ordered and homogenous TiO$_2$ nanorods obtained has a diameter of ca. 100 nm. Gas sensing properties of these structures were investigated against VOCs and different concentrations of H$_2$ at 200ºC. Sensor response was 200 (%) for 1000 ppm H$_2$. Among measured VOCs, TiO$_2$ nanorods are only sensitive to isopropanol at 200ºC.

Keywords: Metal oxide nanotube, TiO$_2$, hydrothermal method, gas sensor.

1. Introduction

Gas sensors based on metal oxide such as ZnO, NiO, CuO TiO$_2$ have attracted considerable attention because of low cost, wide range detectable gases, easier to use, and easy production [1-4]. The sensing mechanism of metal
Oxide is based on surface reaction with the gases in the atmosphere which changes its conductivity. Oxygen can be adsorbed on the surface of the metal oxide according to following equation [5];

\[
O_{2(gas)} + 2e^- \leftrightarrow 2O_{(ads)} \tag{1}
\]

\[
H_2_{(gas)} + O_{(ads)} \rightarrow H_2O_{(des)} + e^- \tag{2}
\]

For the n-type semiconductor, adsorbed oxygen decreases the conductivity of metal oxide by trapping electrons from the surface and depletion layer is formed. Oxygen can be desorbed during exposure the gas according to the equation (2). In this reaction trapped electrons turn back to the conductive band fully or partly. With the production of the nanostructures, the surface reactions increase on the surfaces because of the higher surface-volume ratio, so it can improve sensor parameters [6]. In this study, TiO\textsubscript{2} nanorods were fabricated by hydrothermal method in order to investigate gas sensing properties against different gases.

2. Experimental

2.1. Preparation and sensor output

TiO\textsubscript{2} nanorods have been prepared on FTO glass by hydrothermal method. Firstly, FTO substrates were cleaned with acetone, isopropanol and deionized water, subsequently. Then FTO substrates were placed vertically into Teflon beaker containing 1 ml titanium but-oxide, 30 ml hydrochloric acid and 30 ml deionized water. The Teflon beaker was sealed with stainless steel autoclave. Fig. 1 (a) shows a schematic of autoclave system. Hydrothermal process conducted for 18 hours at 150°C with a temperature controlled furnace. After hydrothermal process, the samples were cleaned with acetone and deionized water.

After fabrication of TiO\textsubscript{2} nanorods, Au electrodes were coated on the nanorods by thermal evaporation system in order to make electrical contacts. The thickness of Au electrodes was about 150 nm. A schematic illustration of TiO\textsubscript{2} nanorods sensor device are shown in Fig. 1 (b).

![Fig. 1. A schematic illustration of (a) hydrothermal growth system; (b) TiO\textsubscript{2} nanorods device.](image-url)
2.2. Structural and morphological characterization

In order to investigate structural and morphological properties of the nanorods X-ray diffraction (XRD, Rigaku Smartlab X-ray diffractometer with Cu-Kα radiation, λ = 0.15418nm) and scanning electron microscope (SEM, Philips XL 30 SFEG) was used.

According to the Fig. 2 (a), the diffraction peaks 27.4º, 36.1º, 41.2º, 54.3º, 62.7º and 69.8º were appointed to (110), (101), (111), (211), (002) and (112) crystal planes, respectively. The peaks belong to the rutile phase of TiO₂ [7]. SEM image shows that the nanorods are vertically aligned and homogenously covered entire surface of substrate as seen in Fig 2. (b). The nanorods have a diagonal shape and average diameter is about 100 nm. The length of the TiO₂ NRs is about 5 μm.

2.3. Gas measurements

The sensing element was placed into the home-made chamber (1L). The experimental procedure was performed by heating the device up to 200°C and waiting for to obtain steady state under high purity dry air. A constant bias voltage of 5 mV is applied to the TiO₂ nanorods sensor device, and the changes in the DC current versus time is recorded upon exposure to 250 - 2000 ppm H₂ and 5000 ppm volatile organic compounds (isopropanol, ethanol, methanol, chloroform, CCl₄, acetone) in dry air at 200°C.

3. Result and Discussion

Gas sensing properties of highly ordered nanorods were tested towards different concentrations of H₂ and 5000 ppm VOCs at 200°C. The sensor response to 250, 500, 1000 and 2000 ppm H₂ at operation temperature of 200°C is collected in Fig. 3 (a). Introducing of the reducing gas causes enhancement of the electrical current, proving the n-type behavior of the TiO₂ nanorods. The saturation and the recovery take approximately 20 minutes for each concentration of H₂. The sensor response of the TiO₂ NRs to the hydrogen was calculated as the ratio of the change in the current caused by the introduced gas to the base-current of the TiO₂ NRs [8].

\[
\text{Response} = \frac{I_{\text{gas}} - I_{\text{air}}}{I_{\text{air}}} = \frac{\Delta I}{I} \quad (3)
\]

The value of ΔI corresponded to increase of the current when H₂ was introduced into the chamber. This increase of the current is given by reduction of the depleted surface layer and increase of number of charge carriers caused by
the chemical reaction (2). Furthermore, there is direct ratio between H$_2$ concentration and sensor response as seen in Fig. 3 (a).

TiO$_2$ nanorod device measured against 5000 ppm ethanol, isopropanol, methanol, chloroform, CCl$_4$ and acetone. Among these gases TiO$_2$ NRs device was only able to sense isopropanol. Fig. 3 (b) shows a comparison for sensor responses of TiO$_2$ nanorods against 5000 ppm isopropanol and various concentrations of H$_2$.

![Fig. 3. (a) I-t measurement of TiO$_2$ nanorods against 250 – 2000 ppm H$_2$; (b) Comparative sensor response results.](image)

4. Conclusion

TiO$_2$ NRs were synthesized on FTO substrate by hydrothermal method. Vertically aligned TiO$_2$ NRs have a diameter about 100 nm and a length about 5 μm. TiO$_2$ nanorods also have rutile phase crystal structure. H$_2$ measurements of TiO$_2$ nanorods show that there is a linear relation between H$_2$ concentration and sensor response. Moreover, among measured VOCs TiO$_2$ NRs are only sensitive to isopropanol but only high concentrations. According to sensor measurements, TiO$_2$ nanorods fabricated by hydrothermal method can be useful for hydrogen detection and monitoring.

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