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# $TiO_2$ Nanotubes for Room Temperature Toluene Sensor*

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## Abstract

**$TiO_2$ nanotubes were used to prepare gas sensor and the gas sensing properties towards toluene were analyzed. Titania nanotube arrays were fabricated via electrochemical anodization method in glycerol electrolytes containing $NH_4F$. The sensor fabricated from these nanotubes exhibits a good response to toluene at room temperature with good sensitivity. The toluene sensing properties were tested from 20 to 150 ppm concentrations.**

## Keywords

**$TiO_2$, Nanotubes, Toluene, Gas Sensing, Room Temperature**

**Subject Areas:** **Environmental Chemistry, Nanometer Materials**

## 1. Introduction

Toluene is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent, and is sometimes also used as an inhalant drug for its intoxicating properties; however, inhaling toluene has potential to cause severe neurological harm [1] [2]. It is harmful to human beings even at very low concentrations [3] [4].

It is therefore important to develop instruments for environmental control of this class of compounds. In this sense, the use of thick film sensors of the metaloxide semiconductor (MOX) type is well known. Further in recent years the synthesis of nanostructured materials which enhance the sensitivity to gases because of the increased specific surface area was incorporated.

Nevertheless, it needs a high operating temperature, which increases the power consumption and decreases the suitability and reliability of the sensor.

Recently the study of the sensitivity of MOX sensors at low temperature has been proved attractive. A possible strategy to improve the sensors sensitivity at room temperature is to produce nanostructures, such as nano-

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tubes. However, most of metal oxide semiconductors gas sensors focus your attention on detecting traces concentration of gases including $H_2$, CO, $H_2S$, $C_3H_8$, $C_2H_5OH$, $CH_2O$, and $NO_x$ [5]-[12]. We have previously studied the detection of ethanol, ammonia and chloroform at room temperature from $TiO_2$ nanotubes [13] [14].

In recent years, studies have been undertaken concerning the toluene sensing characteristics. Deng *et al*. reported that C-doped $WO_3$ gas sensors exhibited high sensitivity and selectivity toward toluene and xylene at 320˚C [15]. Wang, *et al.* developed an Au-ZnO NW-based sensor for the detection of benzene or toluene with good selectivity and high sensitivity at the working temperature of 340˚C [16]. Song *et al*. proposed a novel toluene sensor based on ZnO-$SnO_2$ nanofiberweb operating between 200˚C and 400˚C [17]. Qi *et al*. described the toluene sensing properties at 350˚C of $SnO_2$ nanofibers synthesized through an electrospinning method [18].

Zeng *et al*. reported the toluene sensing properties of the pure ZnO and $TiO_2$-doped ZnO nanostructures at operating temperatures from 160˚C to 390˚C [19].

But there are few articles related to the detection of toluene at low temperature [20]. Nowadays, Kim *et al.* successfully measured toluene gas at room temperature using nanoporous thin film of titania ($TiO_2$) in a device microfabricated by a nanoimprinting method [21].

In this work, we prepared large-scale $TiO_2$ nanotubes by electrochemical anodization technique and investigated its application in detecting toluene vapor. The prepared gas sensor exhibits desirable sensing characteristics including good sensitivity and reproducibility at room temperature.

## 2. Experimental Procedure

The electrochemical anodization was performed in a two-electrode cell with the Ti sheet as the anode and the platinum foil as the cathode [22]-[27]. The samples of commercially pure grade titanium (99.8%) have dimensions of 15 mm × 10 mm × 0.5 mm thick. Prior to the anodization, the titanium sheets were firstly smoothed and cleaned using sandpaper, then the samples were ultrasonically cleaned in isopropyl alcohol and acetone solution, afterwards rinsed with deionized water and finally dried in a nitrogen stream. The distance between the cathodic and anodic electrodes was approximately 1.5 cm. The electrolyte consisted of a glycerol solution with 0.6 wt% ammonium fluoride ($NH_4F$). All the experiences were carried out under magnetic agitation at room temperature (20˚C). The anodization was conducted applying a ramp from 0 to 50 V during 30 min and finally holding the voltage constant for 3 hs using a Keithley 6517B electrometer. A Keithley 2000 multimeter was used to measure the current as a function of time. After the anodization was finished the Ti sheet was cleaned with deionized water, dried with a nitrogen stream and finally was annealed in air at 550˚C for 2 hours.

The samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Scanning electron microscope (Fei model Quanta 200) was employed for the morphological characterization of the $TiO_2$ nanotubes samples. X-ray diffraction (XRD) patterns were recorded at room temperature with CuK$\alpha$ radiation of 0.15418 nm in a diffractometer (PANalytical model Empyrean) having theta-theta configuration and a graphite secondary-beam monochromator, using a generator voltage of 40 kV and current of 40 mA. The data were collected for scattering angles ($2\theta$) ranging from 20˚ to 55˚ with a step of 0.026˚ for 2 s per point. Measurements of the electrical responses to toluene were performed in a dynamic flow system. The gas-sensing properties were proved in a chamber of 250 $cm^3$ volume with a controlled atmosphere. The sample under test was placed inside the chamber and exposed to 20, 40, 80 and 150 ppm toluene concentration of flowing gas, at atmopheric pressure and room temperature, chamber and exposed to 20, 40, 80 and 150 ppm toluene concentration of flowing gas, at atmopheric pressure and room temperature. The gas injection was performed using a system based on the permeation tube technology (Owlstone OVG-4 Vapor Generator). Synthetic air with humidity content lower than 3 ppm of water was used as carrier and reference gas. A flow rate of 100 sccm was stablished with a mass-flow controller. Two stainless steel crocodile clips were attached on $TiO_2$ nanotubes and served as the electrodes for sensor testing. The distance between the two electrodes was around 2 - 3 mm. A personal computer with GPIB interface board was used to acquire the data of the sensor's electrical response. The electrical resistance of the nanotubes was measured by a Keithley sourcemeter 2612A with data acquisition capability. A schematic of experimental set up for gas sensor measurement is shown in **Figure 1**.

## 3. Results and Discussion

### 3.1. Microstructure Characterization

**Figure 2** shows the XRD patterns of the sample calcined at 550˚C obtained for 50 V. It can be seen that the

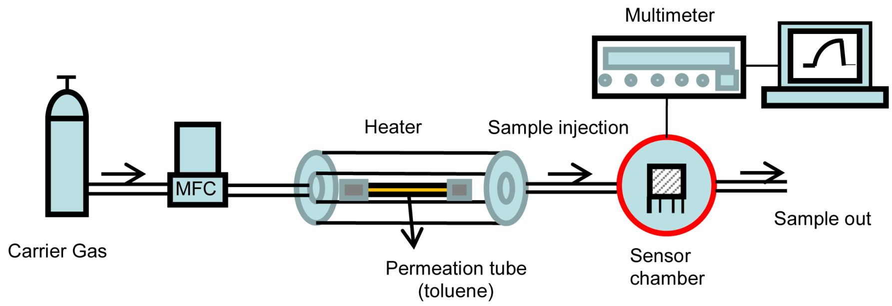


**Figure 1.** Schematic of experimental set up for gas sensor measurement.

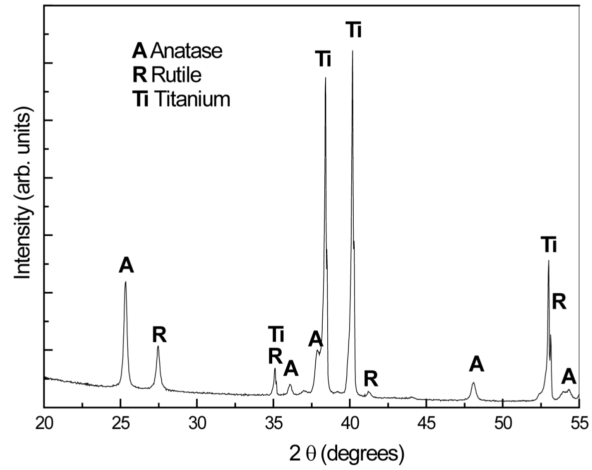


**Figure 2.** X-ray diffractogram of the $TiO_2$ obtained with a 50 V anodizing voltage.

phases present are rutile (01-077-0446), anatase (01-071-1169) and titanium (00-044-1294) according to the literature [28] [29]. Typical peaks of body-centered tetragonal-structured anatase phase at $2\theta$ near 25˚, 37˚ and 48˚ are observed in the XRD pattern, which correspond to the characteristic planes (101), (004) and (200), respectively with lattice constants of $a$ = 0.3804 nm and $c$ = 0.9614 nm and peaks of body-centered tetragonal-structured rutile phase at $2\theta$ near 27˚, 36˚, 41˚ and 54˚ are observed in the XRD pattern which correspond to the planes (110), (101), (111) and (211), respectively with lattice constants of $a$ = 0.46325 nm and $c$ = 0.29912 nm.

Typical peaks of hexagonal close-packed titanium phase at $2\theta$ near 35˚, 38˚ and 40˚ are observed in the XRD pattern which correspond to the planes (100), (002) and (101), respectively with lattice constants of $a$ = 0.295 nm and $c$ = 0.4682 nm. The average crystal grain size was calculated by Scherrer equation from full width at half maximum of $TiO_2$ anatase (101) diffraction peaks. The crystal grain size has an average size of 30 nm.

From SEM images, the microstructure of titania nanotubes was observed. **Figure 3** shows the morphology of the $TiO_2$ nanotubes grown at 50 V. Self ordered arrays of titanium oxide nanotubes were obtained. The size of the nanotubes has a diameter of 150 nm, the wall thickness has a dimension of 30 nm and the tube length has 2 μm. As reported by the XRD analysis and SEM characterization, the nanotubes are indeed polycristalline composed of numerous nanocrystallites with an average size about 30 nm.

## 3.2. Gas Sensor Characteristics

The relative resistance is calculated as $R/R_0$, were R is the sensor resistance in the gas and $R_0$ is the sensor resistance in ambient air. The responses of the $TiO_2$ nanotube array sensors were quite stable and reproducible for repeated testing cycles. **Figure 4** shows the response to different toluene concentrations of the sensor done with the $TiO_2$ sheet.

$TiO_2$ is an n-type semiconductor and therefore when exposed to air the oxygen molecules are adsorbed on the

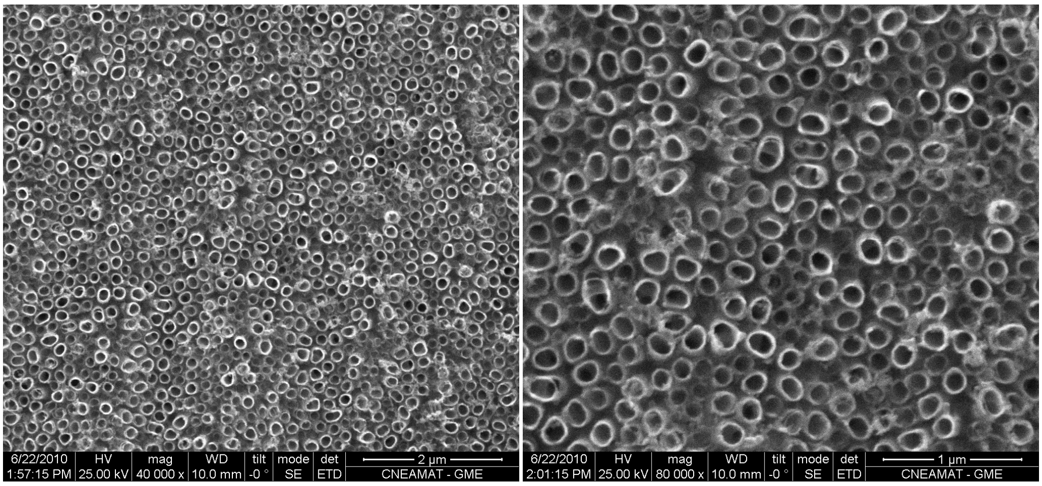


**Figure 3.** SEM micrographs of the anodised $TiO_2$ at 2 magnification levels.

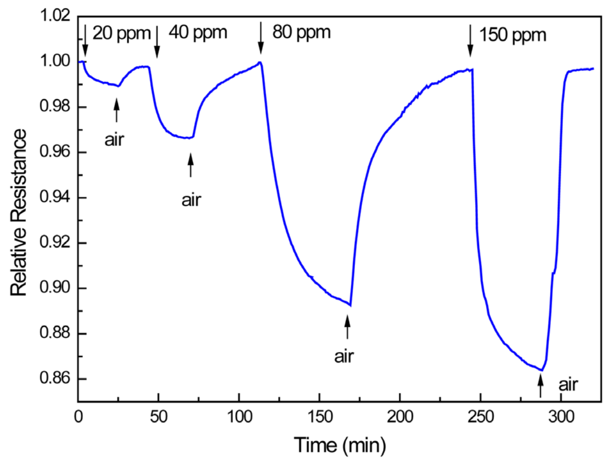


**Figure 4.** Response of the $TiO_2$ nanotubes versus toluene concentrations at room temperature.

surface and form $O_2^-$ ions at room temperature by capturing electrons from the conduction band (**Figure 5(a)**) according with Equations (1) and (2) [30]. When the sensor is exposed to a reductive gas, for instance, toluene, the gas reacts with the surface oxygen species (**Figure 5(b)**) according with Equation (3) and releases the trapped electrons back to the conduction band, which decreases the surface concentration of $O_2^-$ ions and increases the electron concentration, which leads to a further decrease of the resistance of the sensor.

$$O_{2(g)} \leftrightarrow O_{2(ads)} \tag{1}$$

$$O_{2(ads)} + e^- \rightarrow O^-_{2(ads)} \tag{2}$$

$$C_7H_{8(g)} + O^-_{2(ads)} \rightarrow C_7H_8O_{(g)} + H_2O + e^- \tag{3}$$

The total response of the sensor depends on the surface reaction and also on the rate of gas diffusion. The rate of gas diffusion is limited by the microstructure of the nanotubes, the size of toluene gas molecules and the operating temperature. As shown in **Figure 4** the response and recovery times are long probably by the slowness of the reaction of the toluene gas with the adsorbed oxygen ions, and also by the low diffusion rate.

The sensitivity is defined as $\left(R_{gas} - R_{air}\right)/R_{air}$, where $R_{air}$ is the resistance of sensor in air and $R_{gas}$ is the steady resistance of sensor in the presence of the tested gas. The sensitivity of the sample is plotted as a function of toluene concentration in **Figure 6**, indicating a linear characteristic value of the sensor.

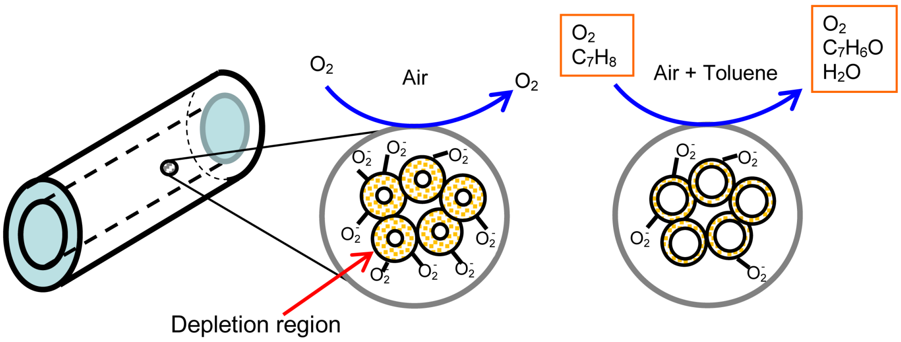


**Figure 5.** Sketch illustrating the chemisorption of oxygen ions over the $TiO_2$ in (a) air (b) air and toluene.

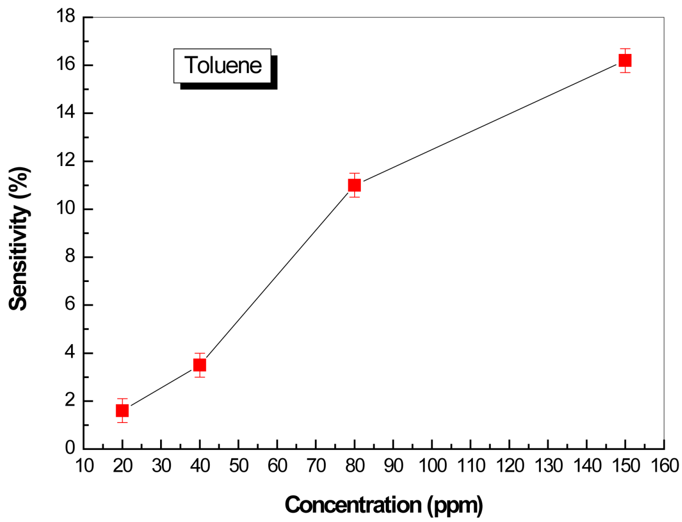


**Figure 6.** Sensitivity of the $TiO_2$ nanotubes sensor to different concentrations at room temperature.

$TiO_2$ gas sensor exhibits an unusual good response at room temperature. This can be probably attributedto-$TiO_2$ nanotubes consist of small nanocrystals joined together into 1D tubular structure, resulting in many more active sites for gas chemisorption. In addition, both the inner and outer walls of $TiO_2$nanotubes can adsorb a large number of gas molecules, therefore the nanotubes behave as nanochannels for the gas diffusion [31]. In summary, $TiO_2$ nanotubes gas sensors show a singular sensitivity compared to the corresponding conventional metal oxide semiconductors whose optimal operation temperature range is from 200˚C to 400˚C.

## 4. Conclusion

$TiO_2$ nanotubes are synthesized through an electrochemical anodization method and the sensor fabricated from these nanotubes exhibits good toluene sensing properties at room temperature. The linear relationship between the response and the gas concentration is found in the range of 20 - 150 ppm for toluene. Moreover, the low cost and easy route to synthesize sensing materials ($TiO_2$ nanotubes) may also be useful for the development of miniaturized devices.

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