



Communication TiO₂ Nanotubes Membrane Flexible Sensor for Low-Temperature H₂S Detection

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Abstract: This paper presents the fabrication and characterization of a flexible gas sensor based on TiO_2 nanotubes membrane, onto which array interdigitated gold electrodes in one side and a common heater in the backside were obtained using conventional microfabrication techniques. This was used to detect hydrogen sulphide within a concentration range of 6–38 ppm. The response to low concentrations of H₂S at low temperature and good stability make the sensor a promising candidate for practical applications. These results support the proposal that the TiO_2 nanotubes membrane flexible sensors are promising in portable on-site detection based on low cost nanomaterials.

Keywords: TiO₂ nanotubes membrane; flexible sensor; Kapton; H₂S

1. Introduction

Hydrogen sulphide (H_2S) is a colorless, toxic, corrosive and flammable gas which smells like bad eggs [1]. Is often produced in coal, coal oil or natural gas manufacturing, crude petroleum, volcanic gases, coils, natural gas, hot springs [2]. Other sources from industrial activities include food processing, cooking ovens, craft paper mills, tanneries, and petroleum refineries [3]. Produced during anaerobic digestion of organic matter, wastes or recyclable polymeric materials [4,5]. The threshold limit value (TLV) is 10 ppm [6]. Thus, real time detection in the concentration range (<15 ppm) is the most important for the human health safety. Produces damage in breathing system to human and animals. Further, it can cause a malodor-nuisance problem even at relatively low concentrations [7]. H_2S is an intermediate in the synthesis of organothiol compounds and elemental sulphur. The use of metal oxide semiconductor (MOX) to detect toxic gases has attracted considerable interest [8–12]. A method for measuring the quantity of H_2S using a MOX gas sensor is desirable. In recent years, great efforts have been devoted to the development of portable gas sensor device. These devices require new features such as low-power consumption, low-cost and low-weight in addition than good sensitivity, selectivity and stability. In particular, the use of substrates flexible for manufacturing gas sensors could be a potential alternative to the more expensive silicon technology [13–16].

Among the various reported flexible substrates, polymers including polyimide (PI), polyethylene terephthalate (PET), poly-dimethylsiloxane (PDMS), and polyethylene naphthalate (PEN). PI has attracted immense interest because of its extraordinary thermal, mechanical, and chemical properties. Particularly among the various flexible substrate, we selected Kapton[®] for its excellent thermal stability, solvent resistance, low cost, electronic and mechanical properties including high Young's modulus (2.5 GPa), wide operating work temperature (-269 to 400 °C), high resistivity ($1.0 \times 10^{17} \Omega \cdot cm$), low coefficient of thermal expansion (20 ppm·°C⁻¹), and low thermal conductivity ($0.12 \text{ Wm}^{-1} \cdot \text{K}^{-1}$) [17].

In the present paper, a new approach for developing flexible gas sensors based on TiO_2 nanotube membrane is presented, which is used to research gas sensor tests on H_2S at low temperature.

2. Experimental Methods

2.1. TiO₂ Membrane Preparation

The highly ordered uniform TiO_2 nanotubes membrane array was grown by a two-step electrochemical anodization method of a Ti metal sheet. The detailed preparation of TiO_2 nanotubes membrane was reported in our previous work [18].

The samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman Spectroscopy and BET. Scanning electron microscope (Zeiss Supra40 Gemini) was employed for the morphological characterization of the TiO₂ nanotubes samples. Transmission electron microscopy (TEM) observation was carried out on a Philips CM200 microscope operating at an accelerating voltage of 160 kV. ImageJ software was used to determine the diameter and length of the TiO₂ nanotubes.

XRD patterns were recorded at room temperature with Cu K α 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 θ) ranging from 20° to 55° with a step of 0.026° for 2 s per point.

Raman measurements were carried out using a LabRAM HR Raman system (Horiba Jobin Yvon) spectrometer equipped with a microscope objective and a charge coupled device detector (CCD). The Raman spectra were recorded in a backscattering configuration using 514.5 nm line of an Ar⁺ laser as an excitation line.

The surface area was calculated using the Brunauer–Emmett–Teller (BET) method based on the adsorption data. The BET specific surface area and pore distribution of the samples which were degassed at 150 °C for 8 h were determined by N₂ adsorption/desorption method, which were carried out on a Micromeritics Accelerated Surface Area and Porosimetry System ASAP 2020 v 3.01 instrument.

2.2. Sensor Fabrication

Kapton[®] HN film (poly(4,4'-oxydiphenylene-pyromellitimide), commercially available from DuPont, with thickness of 150 μ m was used as a flexible substrate. The fabrication of the interdigitated gold electrodes were made by sputtering evaporation for about 250 nm thick on one side of the substrate, using conventional microfabrication procedures. There is an array of 5 interdigitated electrodes with their connection pads. The width of the electrodes and the gap in between them are 0.15 mm and 0.27 mm, respectively (Figure 1a).

On the backside of the flexible substrate a thin film of titanium was deposited by sputtering evaporation. Titanium (600 nm thick) was selected as heating material because of low electrical conductivity and good adhesion. The width of the heater was 150 μ m. A voltage of 20 V was applied across the titanium heaters to achieve an operation temperature of 70 °C. In Figure 1b, we can see the circuit design used in this work.



Figure 1. Schematic diagram of the flexible sensor (**a**) Top part of the sensor consisting of gold interdigitated electrodes; (**b**) Titanium heater deposited at the bottom part of the Kapton substrate.

Finally, the TiO_2 membrane nanotubes was supported on the interdigitated gold electrodes. The manufacturing detailed of the process was reported in our previous work [18]. As shown in Figure 2 no visible detachment of the TiO_2 membrane is displayed when the device is bent.



Figure 2. Optical image of the fabricated sensor.

2.3. Sensor Characterization

The gas sensing characterizations were carried in a Teflon chamber with a volume of 50 mL under dynamic flow conditions. The target gas concentration inside the chamber was controlled by the mass flow controllers (MFC) connected to bottles of dry synthetic air (79% nitrogen and 21% oxygen) as gas carrier and gas parent. We used the parent H_2S gas with calibrated concentration of 50 ppm in dry air balance. Prior to each measurement, the sensor was exposed to dry synthetic air for about 2 h to reach a stable state. Afterwards, the gas mixture (synthetic air and H_2S) was delivered on one side of the sensor device at a constant total flow rate of 80 sccm (standard cubic centimeters per minute) with different H_2S flow rate.

The gas concentration was controlled and measured using the following equation:

$$Conc_{(ppm)} = Conc \ gas \ parent_{(ppm)} \frac{Flow \ rate \ gas \ parent}{Total \ flow \ rate}$$
(1)

To achieve different humidity (10%–65%), the dry synthetic air was mixed at certain proportions with the synthetic air flowing through a bubbler filled with water and thus saturated to 100% relative humidity (RH). The RH was measured with an electronic hygrometer (Sensirion SHT 71).

A Keithley sourcemeter 2612 A with a bias voltage fixed at 2 V was used to collect real-time data from the sensor. The electrical resistance of the sensor was monitored and recorded as a function of the operating time.

The time dependent electrical resistance is measured at various gas concentrations from 6 ppm to 38 ppm, using a computer-based data acquisition system.

The resistance decreased and reached to a minimum value and after several minutes, resistance back to its initial value.

The sensor response defined as $S = (R_0 - Rg)/Rg$ where Rg denote the sensor resistance under the influence of a test gas and R_0 the sensor resistance in synthetic air.

The response time is defined as the time needed for the variation in electrical resistance to reach 90% of the equilibrium value after injecting the gas, and the recovery time is defined as the time needed for the sensor to return to 90% of the original resistance in air after removing the gas.

3. Results and Discussion

3.1. Microstructure Characterizations

Figure 3 shows the XRD patterns of the sample (calcined at 480 °C for 40 min to detach easily the TiO₂ membrane from the Ti substrate) obtained for 70 V anodizing voltage. It can be seen that the phase present is anatase (01-071-1169). The diffraction peaks at $2\theta = 25.1^{\circ}$, 37.4° , 47.8° are identified to be the (101), (004) (200) crystal faces respectively. The other phases (*) emerge presumably associated

to the chemical intermediates (e.g., TiF_4) of the electrochemical anodization. The average crystal grain size was 34 nm calculated by Scherrer equation from full width at half maximum of TiO_2 anatase (101) diffraction peaks. Crystallite size has a significant effect on sensor performance.



Figure 3. X-ray diffractogram of the TiO₂ after annealed at 480 °C.

Raman spectrum of annealed specimens is shown in Figure 4. Anatase phase of TiO_2 has six Raman active modes $(A_{1g} + B_{1g} + E_g)$ [19], which are observed at 143, 196–197, 393–395, 517–521, and 636–638 cm⁻¹. These spectral bands prove the presence of anatase TiO_2 . The strongest E_g mode at 143 cm⁻¹ is due to the symmetric stretching vibration of oxygen atoms in O–Ti–O bonds. The B_{1g} and A_{1g} modes are attributed to symmetric and anti-symmetric bending vibration of O–Ti–O bonds.



Figure 4. Raman spectrum of annealed TiO₂ nanotube arrays.

From SEM and TEM images (Figures 5 and 6), we observed the morphology of titania nanotubes array prepared by electrochemical anodization followed by thermal annealing. The measured pore diameter was around 100 nm and the tube length was 12 μ m. The wall thickness is approximately 30 nm (Figure 5b) and is similar with the average crystal grain size obtained by Scherrer equation. Probably the width of the wall is formed by one single nanocrystal.

As shown in Figure 6b, the nanotubular structure can be clearly seen, all the tubes are hollow and opened at both ends.

As seen in Figure 7, the specific surface area obtained by using the Brunauer–Emmett–Teller (BET) method for the TiO₂ is 52 m²·g⁻¹. The total pore volume (single point) (cm³·g⁻¹): 0.11. In addition, the pore size distribution curve (inset in Figure 7) calculated from the desorption branch of the N₂ isotherms by Barrett–Joyner–Halenda (BJH) method further indicate a main distribution range from 2 to 50 nm. The sample exhibited typical type IV isotherm, with distinct H₂-type hysteresis loops at P/P₀ ranging from 0.4 to 1.0 (IUPAC classification), indicating the existence of the mesoporous structure [20].

The large specific surface area is consistent with a nanotubular structure with a thin wall thickness. The results indicated that the TiO_2 nanotubes membrane were potential to exhibit excellent properties for gas sensor applications.



Figure 5. SEM micrograph of the TiO₂ nanotubes membrane at (a) low (b) high magnification.



Figure 6. TEM micrograph of the (a) bundles and (b) single TiO₂ nanotubes membrane.



Figure 7. Nitrogen adsorption–desorption isotherm of TiO_2 and its BJH pore size distribution desorption plot (inset image).

3.2. Gas Sensor Characteristics

Figure 8 shows the behavior of the flexible sensor in the presence of H_2S tested at low temperature in a range of operating concentrations from 6 to 38 ppm.

In the presence of a dry-air atmosphere, the electrical resistance of the sample was found to be 600 M Ω , which was fixed as the base line resistance.

The resistance decreased when the nanotube sensors were exposed to H_2S gas and recovered completely to the initial value when the gas supply was stopped.

To investigate the long term stability of the TiO_2 nanotube membrane sensor, the gas sensing performance was evaluated once again after 6 months and the sensor provided reproducible results, which indicates its great potential for practical application.

It is suggested that the components adsorbed in the film surface are removed successfully after each measurement.

The response time and the recovery time are about 146 s and 209 s, respectively, for 6 ppm of H₂S.



Figure 8. Resistance evolution in presence of several H₂S concentrations.

Figure 9 shows the response plot as a function of the H_2S concentration in ppm. These sensors are capable of detecting H_2S concentrations as low as 6 ppm. As it can be seen, the response increases with increasing concentration, which indicates a good sensitivity of the sensor.



Figure 9. Response of TiO_2 sensors vs. H_2S concentration.

Further, the influence of relative humidity, on the sensing performance of the sensor, was investigated for different relative humidity level (10% and 65%) at room temperature. Figure 10 shows the response of the sensor to 18 ppm H_2S at 10% and 65% RH. It can be clearly seen from the figure that the reaction between the surface oxygen and the water molecules conduces to a decrease in baseline resistance of the gas sensor. However, the response to H_2S is not appreciably affected by the change of RH.



Figure 10. Resistance evolution in presence of 18 ppm H₂S concentration at different RH.

In comparison with other metal oxide materials, Table 1 lists the gas sensing data of the sensors toward H_2S recently reported in the literature. The relatively low operating temperature of TiO_2 in this article is a suitable parameter for gas sensors because it minimizes the power needed to operate the practical devices. The relatively low operating temperature is probably due to the TiO_2 nanotubes behaving like nanochannels for the diffusion of gas.

Materials 9 wt% Fe-doped CaCu₃Ti₄O₁₂ CuO-ZnO

ZnO nanowires

C03O4-SWCNT

 α -Fe₂O₃ nanopart

Cu nanoparticles

SWCNT

ZnO nanorods

TiO₂ nanotubes

arc-discharge

hydrothermal

chemical route

vapor phase

transport

anodization

250

300

25

25

70

Gas-sensing response of recently reported metal oxide sensors toward H_2S .					
Method	Temperature °C	Concentration (ppm)	H ₂ S (Response)	Response Definition	Ref.
sol-gel	250	10	126	R_a/R_g	[21]
hydrothermal	100	100	40	R_a/R_g	[22]
hydrothermal	25	5	79	Ig/Ia	[23]

500

4

26

475

12 - 144

Table 1. Gas-sensing response of recently reported metal oxide sensors toward H₂S.

100

6

20

3

6 - 38

 TiO_2 is a n-type semiconductor. Like the most metal oxide semiconductor sensors, the sensing mechanism of the TiO_2 nanotubes-based sensors was proposed to be the adsorption and desorption of the gas molecules on the surface of the sensing film, which can induce the change of the film's resistance.

When it is exposed to air, oxygen would adsorb on its surface and form $O_2^{-}_{(ads)} O^{-}_{(ads)}$ [28,29] which act as acceptors by trapping electrons from the nanotube conduction band and creating a depletion region on the nanotube surface according to the following equations:

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

$$O_2^{-}_{(ads)} + e^{-} \rightarrow 2O^{-}_{(ads)}$$
 (3)

The chemisorbed oxygen species act as surface acceptors and trap electrons increasing the electron concentration, and hence decrease the resistance of the TiO_2 nanotubes.

The following reaction would take place at low temperature on the surface of the sensor [22,26]:

$$2H_2S + 3O_2^{-}_{(ads)} \rightarrow 2H_2O + 2SO_2 + 3e^{-}$$
(4)

The adsorbed oxygen species can play a crucial role in sensing H_2S gases and therefore the surface-to-volume ratio of the particular nanotubes structure, which can adsorb more oxygen species compared with nanorods and nanoparticles. At the same time, the hollow structure can enhance the diffusion of gas and achieve high sensitivity at H_2S even at low temperatures.

In a word, the superior gas sensing response of the nanotubular TiO_2 is due to the small nanoparticle size, large specific surface area and efficient gas diffusion access.

4. Conclusions

A flexible gas sensor based on TiO_2 membrane nanotubes was fabricated. The Kapton substrate was deposited by sputtering evaporation, one side with the interdigitated gold electrodes and the other one with the heater, using conventional microfabrication procedures. Finally, the TiO_2 membrane nanotubes was supported on the interdigitated gold electrodes.

The responsiveness to H_2S gas at low temperature contributes to significantly reduce the power consumption. The use of a flexible sensor is the most promising for portable on-site detection. These sensors have been tested in laboratory conditions and must be validated systematically to overcome harsh environmental conditions, e.g., determine the release of H_2S gas from the volcanos.

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Conflicts of Interest: The authors declare no conflict of interest.

[24]

[25]

[26]

[27]

This work

 $(-R_a)/R_a \times 100$

 R_a/R_g

 $(R_g - R_a)/R_a \times 100$

 R_a/R_g

 $(R_a - R_g)/R_g \times 100$

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