Gas Sensor for Hazardous Nitrogen Dioxide Based on TiO₂ Nanotube Synthesis via Electrochemical Method

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Abstract

Because of the quick growth of electrical instruments used in noxious gas detection, the importance of gas sensors has increased. X-ray diffraction (XRD) can be used to examine the crystal phase structure of sensing materials, which affects the properties of gas sensing. This contributes to the study of the effect of electrochemical synthesis of titanium dioxide (TiO₂) materials with various crystal phase shapes, such as rutile TiO₂ (R-TiO₂NTs) and anatase TiO₂ (A-TiO₂NTs). In this work, we have studied the effect of voltage on preparing TiO₂ nanotube arrays via the anodization technique for gas sensor applications. The results acquired from XRD, energy dispersion spectroscopy (EDX), and field emission scanning electron microscopy (FE-SEM) elucidate that TiO₂ was created. In addition, systematically examining the gas detection properties was also done. The gas sensor was produced from TiO₂ nanotubes, and the gas-detecting features were directed at nitrogen dioxide (NO₂), which is a hazardous gas. The sensor formed from TiO₂ nanotubes detects NO₂ gas at various temperatures, from room temperature to 300 °C, and it has good sensitivity to this gas. The results exhibit that the gas sensor that was synthesized at 30 V has good sensitivity and a short response time at room temperature for NO₂ gas sensing.

1. Introduction

The development of portable and low-cost gas sensors with high sensitivity, selectivity, and low working temperatures is highly desirable and still a great challenge. Because of their clear benefits, including their low cost, manufacturing freedom, and excellent thermal and chemical stability, metal oxides appeal as materials for the creation of gas sensing devices [1-3]. For the production of gas monitors, particularly hierarchical nanostructured metal oxides with various shapes are suitable materials.

Utilizing dye-sensitized solar cells, photocatalytic water filtration, capacitive performance, and water splitting to produce hydrogen are just a few examples of how titanium dioxide (TiO₂) is successfully used in environmental and energy production [4-10]. N-type semiconductors are commonly regarded as potential materials for gas detection applications in sensor technology [11-13]. For many distinct gases, including H₂ [14, 15], NO₂ [16, 17], NO₃ [18], CO [19], NH₃ [20], H₂S [21-23], and VOCs, they exhibit outstanding sensitivity and selectivity. (i.e., methanol, ethanol, propanol [24, 25], and acetone [26]. It is also commonly noted and researched that useful surface area affects the gas-detecting capabilities of TiO₂ thin films [27]. TiO₂ has a wide band gap and a very high resistivity that can reach 10⁸ Ω. However, n-type semiconducting properties can be caused by even a small deviation from stoichiometry due to too many titanium ions [28]. These findings indubitably support the notion that defect disorder and oxygen-to-titanium content ratio stoichiometry play a significant part in the electrical characteristics of TiO₂ [29].

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Sol-gel processes [30-32], flame spray synthesis [33], hydrothermal processes [34], electrospinning techniques [35], chemical and physical vapor deposition [36, 37], and thermal, chemical, and electrochemical (anodization) oxidation [38-41] are a few of the different ways TiO$_2$ can be produced. The phrase "anodization" is a blanket term encompassing a variety of material-treatment procedures, frequently done to produce oxide coatings that enhance the performance of a surface. Nanotubular TiO$_2$ forms that are completely aligned and self-organized can be produced by anodizing or anodic oxidizing titanium metal sheets.

Although TiO$_2$ is typically produced as a thin layer, more advanced nanostructures like nanowires, nanorods, nanotubes, and nanoplates have lately been used [35-43]. Microstructural elements such as grain size and surface morphology, which are among the most significant factors affecting a gas sensor's sensitivity, are the source of this research's path.

The large surface area and the shape of tubular structures can increase gas sensitivity. The production of highly ordered nanostructures is another crucial element for the consistency of the functional characteristics of gas sensors. Studies have revealed that titania nanotubes are primarily responsive to hydrogen [42, 43]. The conductance of TiO$_2$ in air, the sensing signal, the reaction, and the recovery periods are some of the factors that need to be improved in order to broaden the uses of titania nanostructures in the construction of chemical sensors.

Therefore, the present research is focused on the recent synthesis, modifications, and gas sensing properties of titania nanotubes synthesized by an anodization method and fabricated for NO$_2$ sensing. TiO$_2$ nanotubes exhibit a good sensing at ambient temperature; therefore, these results contribute to enhanced durability and decreased energy consumption.

2. Experimental Work

2.1. Material

Titanium foils (Flow Serve Company, USA) with a thickness of 0.8 mm and a purity of 99.9% and ethylene glycol (EG) and ammonium fluoride (NH$_4$F) (AnalR Chemical Co.) with a purity of 99.5% and 98.0%, respectively, were used. Furthermore, deionized water (DI) (Nanopure Water System, 18 M-cm at 25 °C) was used to yield all of the solutions during the experiment. The voltage source used was a power supply (Laboratory DC Power Supply, TM-605).

2.2. Synthesis Process

In this study, TNT was produced utilizing the electrochemical anodization method. The anodization electrochemical cell's two electrodes are a titanium anode and a graphite cathode (see Fig. 1a). A nanotubular oxide layer is formed on the anode surface when a constant voltage is placed between the anode and cathode due to oxidation, reduction, and field-driven ion diffusion. The anodization parameters influence the characteristics of the produced nanotubes, and the composition of the electrolyte has a significant impact on nanotube production. Fig. 1 depicts the experimental setup utilized for anodization, the titanium plate before anodization, and the titanium plate following anodization. The Ti foil was cleaned by sonication in acetone, isopropanol, and deionized water (DI) for 15 min. Then, 6 M of HNO$_3$ was used to be chemically etched for 10 min in order to form a smooth surface. After that, the Ti foil was rinsed with DI water and left to dry in the air. The amorphous nanotubes are transformed into crystalline ones by annealing for 2 hrs thermal at 500 °C [6].
Figure 1: (a) The setup used to create TiO$_2$ nanotubes, (b) titanium foil before electrochemical anodization, and (c) the formation of TiO$_2$ nanotubes on the titanium foil after electrochemical anodization.

2.3. Characterization of TiO$_2$ Nanotube

X-ray diffractometry (XRD) (X’Pert Pro, Philips) was executed in order to determine the structures of the prepared samples. Field emission scanning electron microscopy (FE-SEM) was applied to recognize the morphologies of the TiO$_2$ nanotube, and the energy dispersive x-ray (EDX) spectrometer was used to analyze the elements. In addition, the Scherrer equation was used to calculate the crystallite sizes of TiO$_2$ nanotubes:

$$D = \frac{0.89 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $\cos \theta$ and $\lambda$ are the incident angles of the X-rays and the wavelength of the X-rays, respectively, while $\beta$ is the full width at half the maximum of the maximum diffraction peak.

2.4. Gas Sensor System

Fig. 2 represents the sensing test system. It mainly consists of a cylindrical chamber for the test and is made of stainless steel; a gate to allow the gas flow during the test, valve for air flow; electrical connection pins for the heater beneath the chamber base; electrodes with the sensor; a heater with a hot plate; a thermocouple is required for controlling the sensor operation temperature; a digital meter interfaced with a PC for recording the sensor current when the sensor is under dry air fed by a needle valve and flow meter; and current variation when the sensor is subjected to NO$_2$ gas-air fed by a tube over the sensing film to measure the sensitivity. Response time and recovery time are two significant factors in a gas sensor. The response time is known as the time required by the sensor to acquire 90% of the response on exposure to the target gas. The recovery time is realized as the time required to attain 90% recovery when gas is turned
off [44]. The response and recovery times can be calculated using the following equations:

\[
\text{Response time (sec.)} = |t_{\text{gas (on)}} - t_{\text{gas (off)}}| 	imes 0.9
\]

(2) \hspace{1cm}

\[
\text{Recovery time (sec.)} = |t_{\text{gas (off)}} - t_{\text{gas (recovery)}}| 	imes 0.9
\]

(3)

3. Results and Discussion

3.1. Structural and Morphological Characteristics

Fig. 3 (a, b, c, and d) depicts the FESEM images of titanium oxide nanotube arrays (TiO$_2$ NTs) produced at various voltages (10, 20, 30, and 40 V) after 2 hrs of annealing. Fig. 3 shows that as the voltage increases, the titanium nanotubes (TNTs) become clearer and the nanotubes become longer. It is possible to detect an improvement in the tubes' diameter and length by changing the anodization voltages [39]. Fig. 4a demonstrates that under this oxidation voltage (10 V), TiO$_2$ nanotubes have not formed. The form of the tubes becomes more apparent when the voltage is increased. The mechanism of the response shows the start of the growth phase of TiO$_2$ NTs. However, Fig. 3 shows the top view and cross-section of TNT nanotubes produced at different voltages. The lengths and inner and outer diameters of TiO$_2$ nanotubes may be calculated using the images. Under anodization circumstances, TiO$_2$ nanotubes had diameters of 26 to 49 nm, respectively, and a length of 2.6 to 3.37 µm. EDX was also used to analyze the components of TiO$_2$ NTs produced at various anodization voltages after 2hrs of annealing. The TNT elemental weight percentages were stated, as may be seen in Table 1. The elemental mapping and EDX spectra of TiO$_2$ NTs are also shown in Figs. 4 and 5, which confirm the presence of titanium and oxygen elements. The anodizing electrolyte also contains carbon and nitrogen.
Figure 3: Top view FE-SEM images of TNTs prepared at: (a) 10 V; (b) 20 V; (c) 30 V, and (d) 40 V at 2hr of annealing. Cross-sectionals of the TiO$_2$NTs are displayed in inset of the figure.

Table 1: EDS analysis for TiO$_2$ NTs at different voltages at 2hr of annealing.

<table>
<thead>
<tr>
<th>Applied voltage (V)</th>
<th>Element</th>
<th>Weight %</th>
<th>Weight % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>C</td>
<td>3.9</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>4.8</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>30.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>60.9</td>
<td>0.3</td>
</tr>
<tr>
<td>20</td>
<td>C</td>
<td>4.7</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>4.7</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>26.5</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>64.1</td>
<td>0.2</td>
</tr>
<tr>
<td>30</td>
<td>C</td>
<td>4.0</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>3.9</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>30.9</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>61.2</td>
<td>0.3</td>
</tr>
<tr>
<td>40</td>
<td>C</td>
<td>4.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>29.3</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>65.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Figure 4: EDX of TiO$_2$NTs prepared at: (a) 10 V; (b) 20 V; (c) 30 V, and (d) 40 V at 2h of annealing.

Figure 5: EDX-elemental mapping of TiO$_2$NTs prepared at: (a) 10 V; (b) 20 V; (c) 30 V, and (d) 40 V at 2hr of annealing.

Fig. 6 displays the XRD patterns of the synthetic samples at various anodization voltages after 2hrs of annealing. Four diffraction peaks were found for all of the produced samples; these peaks, referred to as anatase, were placed at 24.59°, 37.60°, 47.32°, and 75.55°. According to reference code 00-021-1272, the diffraction peaks were specified in the lattice planes (101), (004), (200), and (215). While Ti has three diffraction peaks, which found in all of the produced samples, these peaks were placed at 39.36°, 53.44° and 70.15°. According to reference code 00-044-1294, the diffraction peaks were specified in the lattice planes (101), (102) and (103). Moreover, no other peaks were detected for rutile TiO$_2$, implying that the as-prepared sample was of high purity for anatase TiO$_2$.

Also, the TiO$_2$ NTs nanotubes are polycrystalline, as shown in Fig. 6. Equation 1 was used to determine the average crystallite size (16.7 nm) from the total width at half the maximum of the TiO$_2$ anatase (101) diffraction peaks and 20.
3.2 Performance of Gas Sensing

Fluctuations in their resistance, which are caused by interactions between semiconductors and ambient gases, provide the foundation for semiconductors' sensing efficiency. The feature of gas sensing is referred to as the dynamic fluctuation of resistance. The sensitivity of the gas sensor for reducing gas is often expressed as the ratio of the resistance in air to the resistance when the gas is present \((R_{on}(\Omega) - R_{off}(\Omega)) / R_{on}(\Omega)\). In contrast, the definition of an oxidizing gas's response is its resistance in air to resistance in the absence of the gas \((R_{off}(\Omega) - R_{on}(\Omega)) / R_{off}(\Omega)\) [45]. The results of the interaction of gases and TiO₂ nanotubes revealed that the NO₂ gas decreased the resistance of the TiO₂ nanotube sensor when it was introduced. Air exhibits more resistance than NO₂ gas as a result of an oxide's (n-type) interaction with the oxidation gas, as seen in Figs. 7–10 [46].

Figure 6: XRD diffractograms of TiO₂ prepared at: (a) 10 V; (b) 20 V; (c) 30 V, and (d) 40 V at 2hrs of annealing.

Figure 7: Variation in TiO₂NTs resistance to NO₂ gas at various operating temperatures.
Figure 8: Variation in TiO$_2$ NTs resistance to NO$_2$ gas at various operating temperatures.

Figure 9: Variation in TiO$_2$ NTs resistance to NO$_2$ gas at various operating temperatures.
The primary concerns for gas sensing characteristics, particularly at low working temperatures, are response and recovery times. As illustrated in Fig. 11, the responses of the gas sensors to 45 ppm NO\textsubscript{2} were tested at operating temperatures ranging from ambient temperature to 300°C in order to determine the best temperature for the manufactured TNT gas sensor to function at varied anodizing voltages. In contrast to the TiO\textsubscript{2} NTs sensors created at 10, 20, and 40 V, Fig. 10 shows that the reaction times of NO\textsubscript{2} gases via the TiO\textsubscript{2} NTs prepared at 30 V were faster. Additionally, at the working temperature (room temperature), all the produced samples that were employed as gas sensors exhibited satisfactory reaction times for NO\textsubscript{2} sensing of less than 30 sec. All the gas sensors were manufactured at 10, 20, 30, and 40 V had recovery durations calculated from Eq. (3) that were, respectively, 88.2, 73.8, 92.7, and 66.6 sec at a lower operating temperature. Due to its embedded properties of a large surface area, an improved rate of electron transport, a powerful capacity for adsorption [47], and numerous hollow locations for the gas to diffuse more quickly [48-50], TNTs at 30 volts may be the ideal nanostructure for gas disclosure.
Fig. 11: Response and recovery times of TiO$_2$ NTs prepared at various voltages.

Fig. 12 illustrates the TiO$_2$ NTs sensor's gas sensitivity to NO$_2$ at various working temperatures, from room temperature to 300 °C at a 45 ppm NO$_2$ concentration. The sensitivity of TNTs sensors ranged from roughly 6.060 to 16.903%, with the TiO$_2$ NTs sensor manufactured at 30 V (for 2 hrs of annealing) have the maximum sensitivity at room temperature at 16.903%. This indicates that the sensitivity of the sensor is significantly impacted by the operating temperature. The TiO$_2$ NTs sensor had the highest sensitivity at room temperature due to the hollow structures, which helped enhance the gas exposure and made it easy to adsorb and desorb gas molecules [50].

The way TiO$_2$ NTs gas sensors detect gases strongly impacted by the nanomaterial's surface properties. The process starts when oxygen from the atmosphere is absorbed. Conduction band electrons are drawn to the surface of the TiO$_2$ NTs grains by the adsorbed oxygen, leaving behind positively charged donor ions. The electrical field becomes stronger when negatively charged oxygen ions like O$^-$ or O$_2$$^-$ interact with positively charged donor ions. Therefore, when the amount of oxygen ions on the surface rises, the potential barrier's size also rises, increasing resistance. As a result of interactions with gas molecules in the environment, less O$^-$ or O$_2$$^-$ is produced, which lowers resistance [42]. As a result, the TiO$_2$ NTs gas sensor functions very well at ambient temperature. Since TiO$_2$ nanotubes are composed of small nanocrystals that have been bonded together to form a 1D tubular structure, this is most likely the case. This suggests that there are a lot of gas chemisorption active sites. TiO$_2$ nanotubes may also have broad surfaces that can store gas molecules in addition to acting as gas diffusion nanochannels [42].
Figure 12: Sensitivity of TiO$_2$NTs prepared at: (a) 10 V (b) 20 V, (c) 30 V, and (d) 40 V.

4. Conclusions
In summary, the anodization process was used to produce highly ordered TiO$_2$ nanotube arrays (TiO$_2$ NTs). Additionally, this study examined how voltages impacted TiO$_2$ NTs surface characteristics before having an influence on their capacity to serve as gas sensors. The findings of the gas sensing test showed that TiO$_2$ NTs at 30 V could detect NO$_2$ at room temperature with significantly better sensitivity and a quicker response time. The TiO$_2$ NTs extraordinary efficiency at detecting gases may be primarily attributable to the geometry of their highly ordered nanotubes and the size of their surface area. This study provides the chance to investigate NO$_2$ sensing by observing the response and recovery durations of NO$_2$ gas at varied operating temperatures at a constant concentration of 45 ppm. This study shows that the TiO$_2$ NTs sensor may be improved to detect NO$_2$ gas with high sensitivity at room temperature.

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Conflict of Interest
Authors declare that they have no conflict of interest.

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توليف الأنابيب الثنائية TiO\textsubscript{2} كمستشعر لغاز ثنائي أوكسيد النتروجين بالطريقة الكهروكيميائية

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الخلاصة

تستخدم الأنابيب الثنائية TiO\textsubscript{2} كمستشعر لغاز ثنائي أوكسيد النتروجين (NO\textsubscript{2}) بشكل ناجح. وتم توصيف التأثير الكيميائي للأنابيب الثنائية TiO\textsubscript{2} من خلال تحليل الطاقة الفوكس (XRD)، والنماذج الإلكترونية (EDX) والتجارب الإضاءة (SEM). يتم استخدام الأنابيب الثنائية TiO\textsubscript{2} كمستشعر لغاز ثنائي أوكسيد النتروجين (NO\textsubscript{2}) بشكل ناجح.

الكلمات المفتاحية: أنابيب TiO\textsubscript{2} الثنائية، الطريقة الكهروكيميائية، غاز ثاني أكسيد النتروجين (NO\textsubscript{2}), استشعار الغاز، الحساسية.