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Article

Synthesis and Characterization of TiO_2 Nanotubes for High-Performance Gas Sensor Applications

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Abstract: In this present work, we investigated the fabrication, properties, and sensing applications of TiO_2 nanotubes. A pure titanium metal sheet was used to demonstrate how titanium dioxide nanotubes can be used for gas-sensing applications through the electrochemical anodization method. Subsequently, X-ray diffraction indicated the crystallization of the titanium dioxide layer. Scanning electron microscopy and transmission electron microscopy then revealed the average diameter of the TiO_2 nanotubes to be approximately 100 nm, with tube lengths ranging between 3 and 9µm and the thickness of the nanotube walls being about 25 nm. This type of TiO_2 nanotube was found to be suitable for NO_2 gas sensor applications. With an oxidation time of 15 min, its detection of NO_2 gas showed good result at 250 °C, especially when exposed to a NO_2 gas flow of 100 ppm, where a maximum NO_2 gas response of 96% was obtained. The NO_2 sensors based on the TiO_2 nanotube arrays all exhibited a high level of stability, good reproducibility, and high sensitivity.

Keywords: titanium dioxide; electrochemical anodization; TiO_2 nanotubes; gas sensors

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1. Introduction

In recent years, significant attention has focused on advancing NO_2 sensors by employing metal oxide semiconductors, such as SnO_2, In_2O_3, ZnO, and WO_3, [1–4]. TiO_2 nanotube arrays [5,6], however, offer several distinct advantages over these materials for NO_2 sensing beyond their large surface-to-volume ratio. Indeed, TiO_2 nanotubes have tunable physical and electronic properties [7,8] that allow for more precise control over a sensor's sensitivity through modifications in the TiO_2 nanotubes' crystallinity, diameter, length, and wall thickness. Furthermore, TiO_2 nanotubes show excellent electron mobility, which can improve sensor response times and overall sensitivity when compared to other metal oxides. Such properties make TiO_2 nanotubes very promising for various applications in a number of fields. They also have enormous potential for development compared with other nanostructure forms in fields like photocatalysis [8] and energy storage [9]. Moreover, TiO_2 nanotubes exhibit outstanding sensitivity and selectivity for many distinct gases, including H_2 [10,11], NO_2 [12], NO_x [13], CO [14], NH_3 [15], and H_2S [16,17], as well as Volatile Organic Compounds (VOCs). Various techniques have been applied to fabricate TiO_2 nanotubes [18], such as electrochemical anodization [19–21]. The production of TiO_2 nanotubes on a titanium sheet through anodization is the best process for yielding highly ordered and organized nanostructures. Toxic gases like CO, SO_2, H_2S, NO_x, and so on are harmful to human life and the environment, so there is a need for gas detectors to detect and subsequently control leaks of these unsafe gases. Extending the lifetime of sensors based on TiO_2 also provides more opportunities for developing new high-quality sensors.

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To expand the use of titania nanostructures in fabricating gas sensors, some physical parameters need to be improved, namely the sensing signal, the response, and the recovery times. Several nanostructures have been used to fabricate gas detectors, one of them being vertical TiO_2 nanotube arrays prepared using electrochemical anodization, which have numerous oxygen vacancies that provide effective gas diffusion and more asset sites. They are considered an ideal platform for gas sensing due to their fast response, high sensitivity, low cost, and long-term stability [22].

In this present study, a TiO_2 nanotube array was used for NO_2 gas sensing. A simple electrochemical anodization on a titanium sheet yielded layers of self-organized TiO_2 nanotubes. X-ray diffraction (XRD) and other analytical methods were then used to characterize the properties of the nanomaterials. The morphology and microstructure of these layers were then determined using a scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively.

Outdoor pollutants like NO and NO_2 can result in serious human harm when their concentration exceeds certain exposure limits. Above regulatory limits, these gases increase the likelihood of cardiovascular, respiratory, and cancerous diseases. Gas sensors are therefore vital for detecting dangerous pollutant levels, so developing gas monitoring systems that can sensitively and selectively track these pollutants is a priority [23–26].

This study also focuses on the sensing behavior of TiO_2 nanotube array sensors toward NO_2 through a homemade gas-detection cell. The aim was to develop a sensitive NO_2 sensor for low-concentration detection to assure the safety, health, and wellbeing of people by limiting the presence of NO_2 in the air. The results of this study will help inform future research based on using TiO_2 nanotubes for gas detection, as well as other potential applications. The synthesis process for the TiO_2 nanotubes in this work is simpler and less costly than that of other methods like metal oxide elaboration. Thus, a gas sensor based on TiO_2 nanotubes is more suitable for daily use.

2. Preparation of the Titania Nanotubes

To fabricate a TiO_2 nanotube layer, we took a 1-mm-thick titanium metal sheet with 99.7% purity and subjected it to electrochemical anodization in an electrochemical unit. This process, as presented in Figure 1, is a relatively simple and efficient way to fabricate well-aligned and highly ordered TiO_2 tubular structures. It involves two electrodes, a working electrode in titanium and the second counter electrode in platinum. The electrolyte solution in which the two electrodes are immersed is a mixture of 100 mL of ethylene glycol (EG), 1% ammonium fluoride (NH_4F), and 2% ultrapure water, as presented in Figure 1.

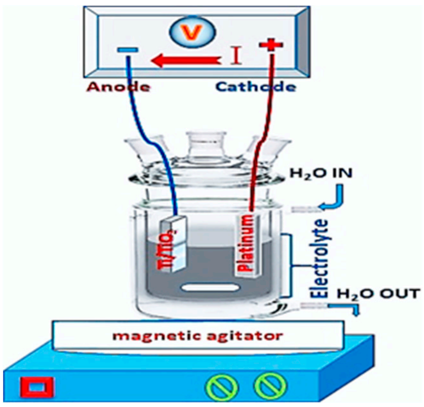

Figure 1. Schematic of anodization cell.

The TiO_2 nanotubes are prepared in two steps, the first step involves polishing titanium at 120 V for 45 min., while the second step consists of preparing the TiO_2 nanotubes at 60V for 15, 30, and 60 min. for the samples used in this study. Only porous structures were prepared on the sample surface at a lower anodization voltage, but when the anodization voltage was higher, the tubes started to form on the titanium metal surface. The applications of TiO2 nanotubes are closely related to their electrical, chemical, and optical properties. The obtained anodized TiO_2 nanotubes are typically amorphous, and the conductivity of native TiO_2 is very low, thus hampering applications

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like gas sensing. In this study, we focused on modifying the TiO_2 nanotubes to improve their electrical, chemical, and optical properties through thermal treatment. As such, the TiO_2 nanotubes were annealed at 400 °C for 3 hours in air to induce a phase transition from the amorphous structure to a crystalline anatase phase. X-ray diffraction scanning electron microscopy and transmission electron microscopy were then used to examine the nanotube array samples.

3. Characterization

Once the TiO_2 nanotubes were prepared through anodization on metallic titania, we crystallized them through thermal annealing at 400 °C for three hours in the air. The crystal structure of the produced TiO_2 nanotubes was obtained through X-ray diffraction (XRD). The resulting crystal phases possessed better properties than amorphous TiO_2.

Claire modifications were observed on the TiO_2 nanotubes before and after the heat treatment, as shown in Figure 2a,b. Definite XRD peaks at 25.3°, 37.7°, 47.7°, 53.8°, 54.9°, 62.5°, 68.6, 70.5°, and 74.9° can be seen in Figure 2, these correspond to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) diffraction peaks of anatase TiO_2 (JCPDS anatase card #21-1272), thus justifying the crystallization of the TiO_2 layer through the formation of the anatase phase.

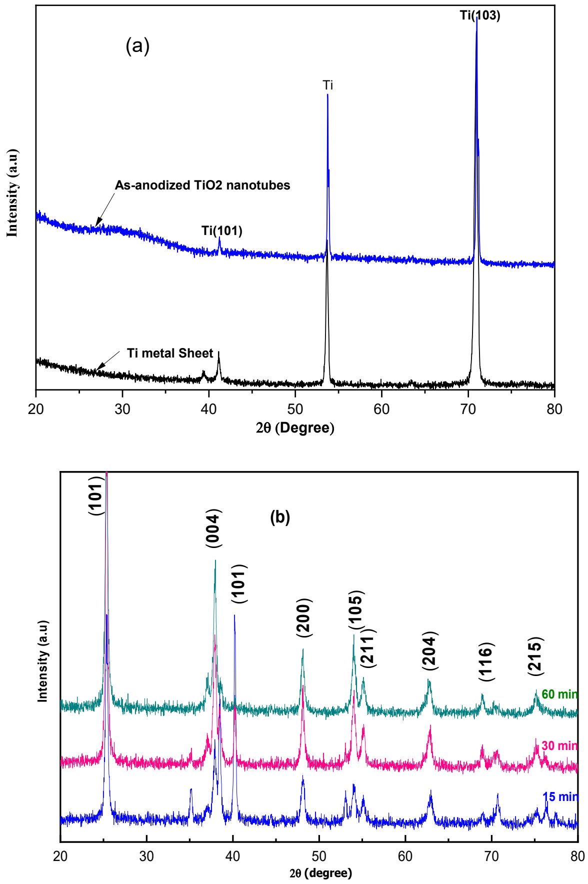

Figure 2. X-ray diffraction of (a) Ti metal sheet and as-anodized TiO_2 nanotubes (b) TiO_2 nanotubes formed at 15, 30 and 60 min and annealed at 400 °C for 3 hours in air.

Figure 3 shows SEM images of the pure TiO_2 nanotubes formed at 15, 30, and 60 min. and annealed at 400 °C for 3 hours in air, and these show a highly ordered and organized nanostructure layer on the Ti substrate. Images of the cross-sectional SEM morphology indicate the elaboration of ordered and vertical titanium nanotubes, with the tube length varying at 3, 7, and 9 µm for 15, 30, and 60 min. anodization times, respectively. With a short anodization time, the nanotubes are short because the pore formation process has just started and the walls of the nanotubes are relatively thick. As the anodization time increases, the length of the nanotubes grows substantially. The electric field drives the oxidation of the metal at the bottom of the nanotube, while the electrolyte dissolves the

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oxide at the top. This process allows for the vertical growth of the nanotubes and continued etching of the walls of the tubes, causing them to thin out and the pore diameter to widen. At extremely long anodization times, the tube length reaches a saturation point where growth stops or becomes negligible and leads to minimal changes in diameter compared to the growth in length.

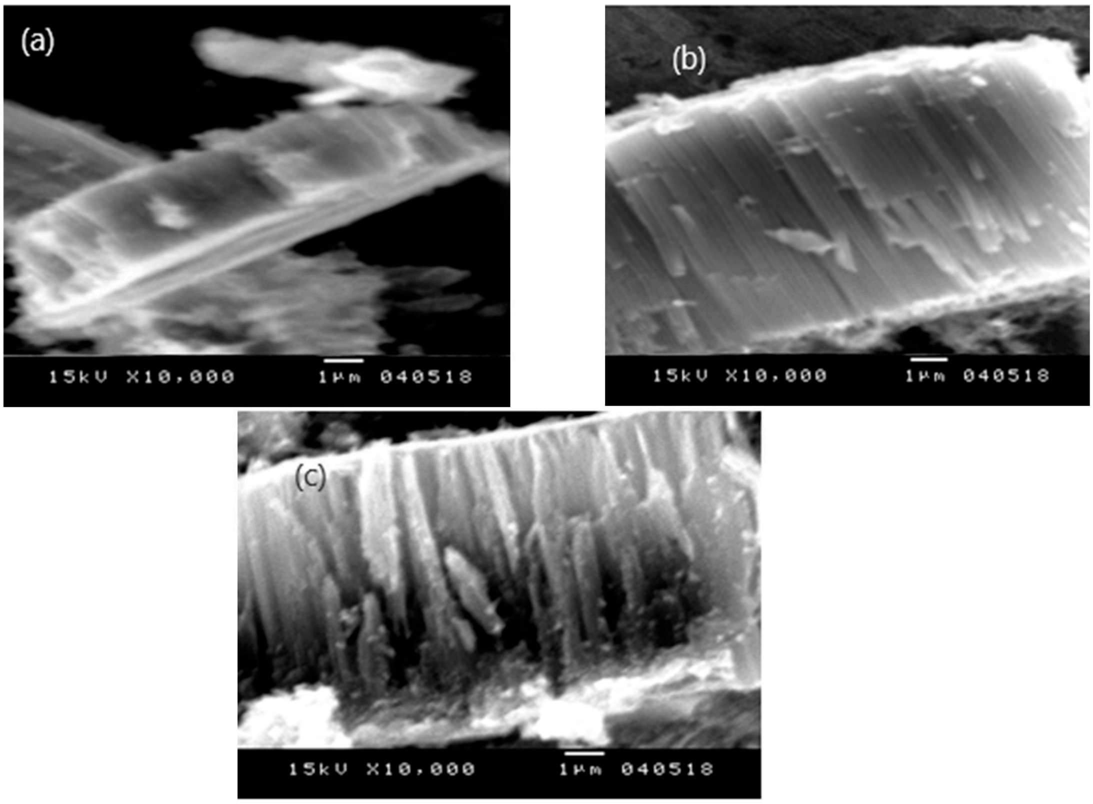

Figure 3. SEM cross-section of TiO_2 nanotubes formed at three different anodization times (a) 15, (b) 30, and (c) 60 min.

Transmission electron microscopy (TEM) was used to examine the morphology and uniformity of the TiO_2 nanotubes. Thus, a Philips CM30 transmission electron microscope was used to obtain accurate information about the morphology and size distribution of the pure TiO_2 nanotubes. Figure 4 shows the sample images obtained from the transmission electron microscope, thus confirming the nanomaterial structure of the TiO_2. The TEM images (Figure 6) reveal that the followed methodology results in the fabrication and growth of highly ordered, structured nanotubes with an average inner diameter of about 100nm and a thickness in the nanotube walls of about 25nm.

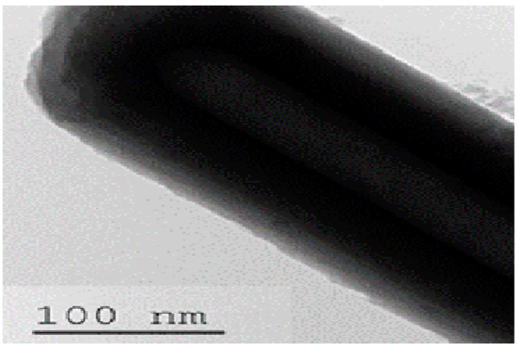

Figure 4. TEM image of TiO_2 nanotubes formed anodically at 60 min and annealed at 400 °C for 3 hours in air.

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The impacts of the anodization time and nanotube length on the gas sensor's sensitivity are shown in Figure 5. From this, we can see that the shorter anodization cycles and shorter nanotube lengths result in enhanced sensitivity. For instance, a sensor with 3 μm nanotubes anodized for 15 minutes exhibited a sensitivity of 99.62%. On the other hand, a sensor with a longer anodization time of 60 minutes had a sensitivity of only 24.12%. Thus, this study revealed that the length of a titanium nanotube is a crucial factor affecting the sensitivity of gas sensors in that shorter nanotubes are typically associated with improved sensitivity. In summary, the various characteristics of shorter titanium nanotubes—such as their increased surface area, low mass loading, and reduced diffusion path—contribute to their enhanced sensitivity and recovery potential.

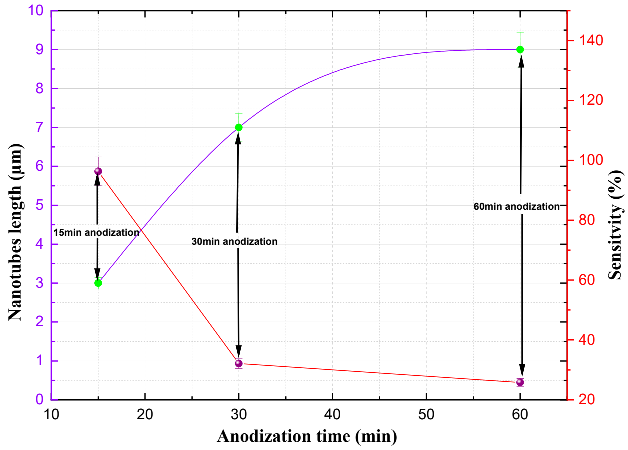

Figure 5. Nanotubes length and sensitivity as a function of anodization time.

4. The Fabrication and Performance of the Sensing Device

After preparing the titanium dioxide nanotubes with the anodization method, their integration into an NO_2 gas-sensing device was needed to ensure their effectiveness. For this purpose, front metal contacts were needed to measure electrical properties, so the choice and design of the front grid's contacts would affect the response of the final device in practical applications.

Figure 6 illustrates the design of the transducer on the TiO_2 substrate with a tubular structure, and it shows the metallic electrodes evaporated on the front side of the nanotubular array substrate.

Additionally, a heater was integrated onto the back of the device in order to reach and maintain the desired operating temperature on the titania nanotubes' surface.

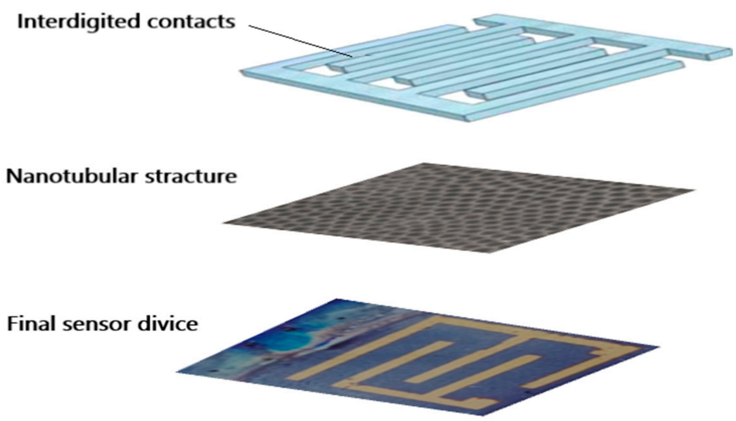

Figure 6. Design of a gas sensor device and TiO_2 nanotubes array gas detector.

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NO_2 and TiO_2 nanotubes have numerous mechanisms that affect their electrical conductivity. NO_2 can adsorb on a TiO2 surface through either physical or chemical means. The former is triggered by the Van der Waals effect, while the latter is achieved by the formation of bonds between the two. NO_2 is a strong oxidant, meaning it readily grabs electrons from other substances. When NO_2 comes into contact with a TiO_2 surface, it snatches electrons away from the nanotube. This process is expressed in Equation (1):

$$NO_2(\mathrm{g}) + \mathrm{e}^- \rightarrow NO_2{}^- \tag{1}$$

At a low temperature, a reduction in conductivity is caused by the adsorption of NO_2. This phenomenon is accompanied by an increase in the transfer of electrons, but the elevated temperatures caused by the chemical reaction can speed up the process and increase the likelihood of NO_2 molecules separating from the TiO_2 nanotubes, thus reducing the impact of the NO_2 on the nanotubes' conductivity.

Temperature can have a significant impact on how certain sensors function. In addition to the NO_2 molecules' attachment and detachment, it can also influence the chemical reactions occurring on the nanotube surface.

To validate the response of a TiO_2 nanotube device toward NO_2 gas, a homemade gas-detection cell for NO_2 gas sensing was made using the TiO_2 nanotube material.

The optimization of the working temperature is illustrated in Figure 7, such that the experiment revealed that the sensor showed the best response at 250°C.

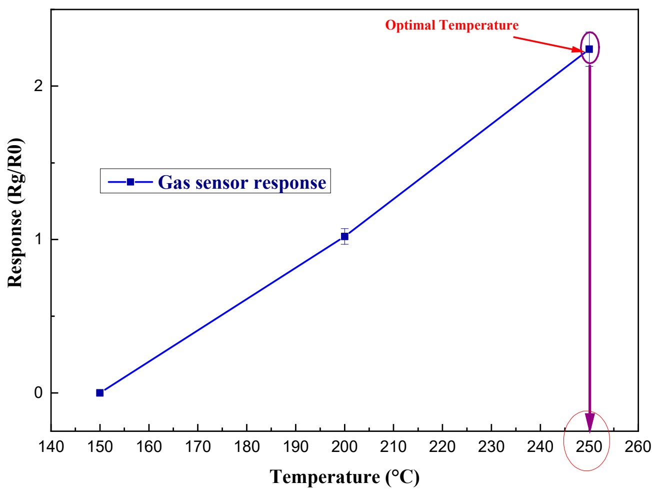

Figure 7. Optimization of the working temperature.

Nevertheless, to expand the applicability of titania nanostructures as gas sensors, several parameters need to be improved, namely the conductance of TiO2 in air, the sensing signal, the response, and the recovery times [27]. In this case, the dynamic response curve of the sample was measured in a range of 100 ppm. Figure 8 shows the gas-sensing measurements of TiO_2 nanotubes within a 100 ppm NO_2 gas atmosphere at 250°C.

The gas-sensing response (R) is defined as the ratio of the resistance values of the sensor to the detected gas to the resistance in air, as follows:

$$R = \frac{\mathrm{Rg}}{\mathrm{R}a} \tag{1}$$

Meanwhile, the gas sensitivity of the p-type sensor under NO_2 oxidizing gas is calculated through the following equation, with more details being available in Refs. [28,29].

$$S\ (\%) = \frac{(\mathrm{Rg}-\mathrm{Ra})}{\mathrm{R}a} * 100 \tag{2}$$

Where Ra represents the resistance of the film when exposed to air, and Rg denotes the resistance of the film when exposed to the analyte gas. The response time (τ_r) is the time for the resistor to change from Ra to Ra+90%*(Rg−Ra). Similarly, the recovery time (τ_c) is defined as the time required for the resistor to decrease from Rg to Rg−90%*(Rg−Ra).

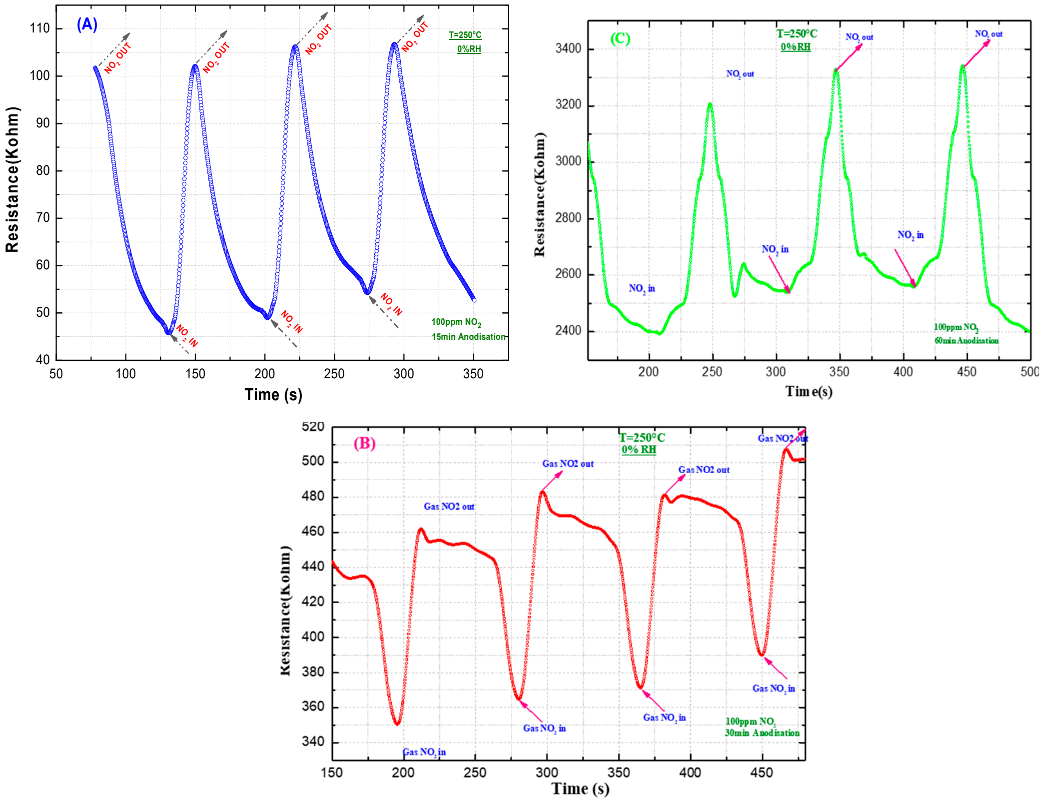

Figure 8. Sensor response characteristics and the dynamic response peak of TiO_2 nanotubes sensor against 100ppm NO_2 gas at 250°C for anodization times: (A) 15min, (B) 30min and (C) 60min.

The resistance response of TiO_2 nanotubes formed through 15, 30, and 60 min. of anodization were measured in 100 ppm NO_2 gas at a 250 °C working temperature. Good sensing performance was observed for the TiO2 nanotubes anodized for 15 min, compared with anodized for 30 and 60 min., as indicated in Figure 8 and Table 1. In addition, the long-term stability of the TiO2 sensor (anodized for 15 min) was verified, remaining stable for 40 cycles.

Table 1. The Sensing performance, response, and recovery times sensitivity and nanotube length of TiO2 nanotubes operating at 15, 30, and 60min anodization for 100-ppm NO2 gas concentration at 250°C working temperature.

Sensor-based TiO_2	Response Time(s)	Recovery Time(s)	Sensitivity%
15 min Anodization	3.6±0.2	34±1.7	96.3±4.8
30 min Anodization	15.6±0.8	68.2±3.5	32.1±1.6
60 min Anodization	65±	132.8±6.6	25.8±1.3

The variation in the response of TiO_2 nanotubes at different anodization times for a 100 ppm NO_2 gas concentration is shown in Figure 9a. The NO_2 gas response was found to drop from 96% to 32% with an increase in anodization time from 15 to 30 min. before dropping further to 25.8% for a 60 min. anodization time. These lower response values are due to there being insufficient thermal energy to release the electrons from the trap defect levels and participate in the adsorption on the surface of the sensor film. In contrast, at an anodization time of 15 minutes, the maximum NO_2 gas response of 96% is obtained due to there being sufficient thermal energy to release the maximum number of electrons to overcome the trap levels below the conduction band and participate in the gas adsorption phenomenon. The response and

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response-recovery times of TiO_2 nanotubes operating at different anodization times for a 100 ppm NO_2 gas concentration are summarized in Table 1 and Figure 9b. From these, it can be seen how both the response and recovery times increase with an increasing anodization time.

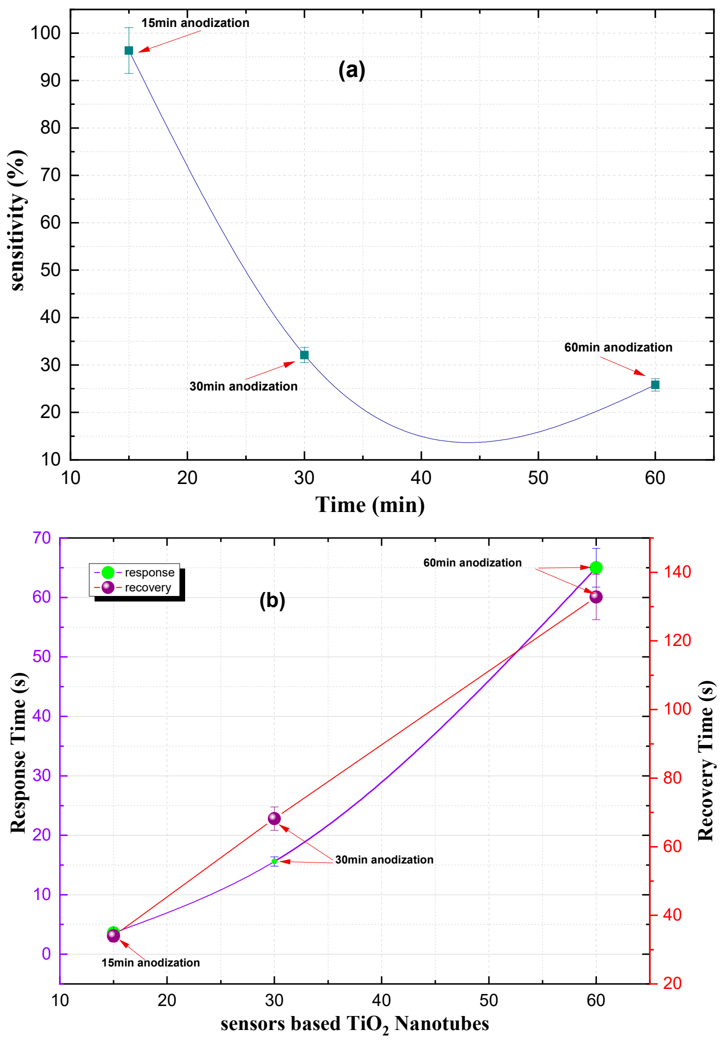

Figure 9. The Sensing performance (a) response, and (b) response-recovery times of TiO_2 nanotubes operating at 15, 30, and 60min anodization for 100 ppm NO_2 gas concentration at 250°C working temperature.

Figure 10 illustrates how the length of the titanium nanotubes affects the response time and recovery time of the gas sensor. It shows that sensors with shorter nanotubes have faster response and recovery times. For example, a sensor with 3-micrometer nanotubes has a response time of only 3.6 seconds, while a sensor with 9-micrometer nanotubes takes 65.5 seconds to respond. Additionally, the time it takes for the sensor to recover between measurements (i.e., the overlap time) also increases with nanotube length. These findings suggest that the length of the titanium nanotubes is a key factor in determining the overall performance of a gas detector.

Compared to long titanium nanotubes, they are therefore better suited for gas sensing. Investigations have also shown that doped and mixed titania structures are emerging as important materials for improving the conductometric properties of sensors [30–33].

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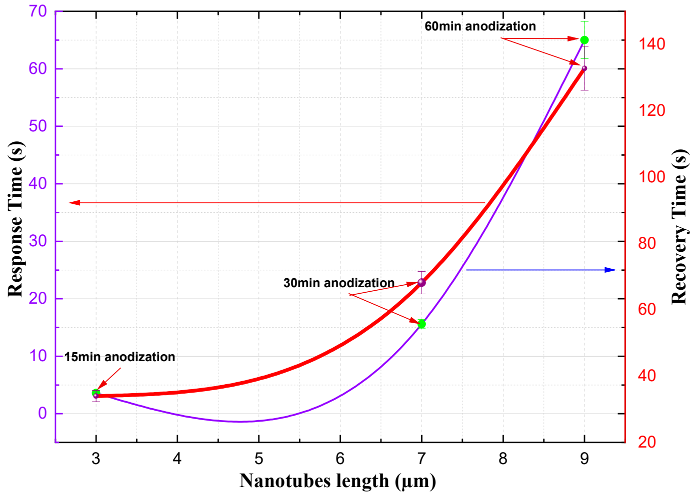

Figure 10. Response and recovery time as a function of nanotube length.

5. Conclusions

Titania nanotube arrays were synthesized in this study through a simple and relatively inexpensive electrochemical anodization method. XRD, SEM, and TEM characterizations demonstrated that this anodization process results in self-organized arrays of highly ordered vertical nanotubes on the Ti foil. Our research results also showed that the sensitivity of TiO_2 nanotubes for NO_2 gas detection is in the 24–99.6% range with a response time of 3.6 s at 250° C when exposed to a flow of around 100 ppm NO_2 gas. The preparation process is very simple and convenient, and the cost is relatively cheap. These advantages enhance the potential of TiO_2 nanotubes as excellent candidates for use in NO_2 gas detection. For instance, a sensor with 3-µm-long nanotubes after being anodized for 15 minutes exhibited a sensitivity of 99.62%.

To conclude, TiO_2 nanotubes exhibited high stability, good reproducibility, and high sensitivity for sensing NO_2, thus positioning them as a promising material for NO_2-sensing and other applications.

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