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Gas-Sensing Performance of TiO_2 Nanorod Arrays Synthesized by Solvothermal Method

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ABSTRACT

In this study, titanium dioxide (TiO_2) nanorods formed through by solvothermal growth on a glass substrate coated with FTO (fluorine-doped tin oxide) are synthesized in order to fabricate an Al/TiO_2-based gas sensor. This is valuable due to the morphology and nanostructure of the sensing film have an important effect on gas sensors' abilities for operation. Investigation using XRD and FESEM demonstrated the synthesized TiO_2 nanorods' crystal nanostructure. Perfectly ordered and uniform TiO_2 nanorods synthesized in an aqueous solution by varying the volumetric ratio of HCl to Ethanol and the acidity. At room temperature, the current–voltage (I–V) characteristic and the sensor's sensitivity to various reducing (ethanol and methanol) and oxidizing (oxygen, and carbon monoxide) gases were studied. For O_2, CO, methanol, and ethanol gases, the corresponding relative sensitivity (Response) to a bias voltage (V) of 0.5 V is 53.758, 91.248, 108.298 and 144.689 %. While the gas sensor was in the dark and at room temperature, it was more sensitive to ethanol than other gases with good response and stability by the relative deviation of the gas response sensitivity was less than 2%. As a result, when compared to oxygen, carbon monoxide, and methanol gases, which have strong response sensitivity and stability, the study shows that TiO_2 nanorods are a suitable method of enhancing ethanol sensing abilities.

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1.Introduction

A device that uses sensors is an appliance which recognizes and detects signals, physical conditions, and chemical molecules. It also changes the form of signals (Hotovy et al., 2004) (Chang et al., 2010). A chemically sensitive gas sensor is a device that uses chemical reactions in order to convert a variety of gases in different environments into signals that can be detected analytically, such as changes to voltage, frequency, or current (Kohl, 1989). There are five main types of commonly used gas sensors: calorimetric gas sensors, metal oxide gas sensors, gas acoustic wave sensors, and gas capacitance sensors (Rzaij and Abass, 2020). The majority of these sensor devices have structures based on semiconducting metal oxide layers, which, when exposed to gases, adapt their resistance to electric current (Goel et al., 2023). SnO_2, MOS_2, WO_3, ZnO, NiO, CuO and TiO_2 semiconductors are the main building materials of these sensing layers, that possess a number advantages like high sensitivity, broad gas detection range, simplicity of use, and facilitate of fabrication and low cost (Liu et al., 2015, Kumar et al., 2020, Dong et al., 2020, Kang et al., 2021, Chou et al., 2015, Lupan et al., 2016, Tian et al., 2021). Among them, TiO_2 is a promising candidate for the application of ethanol gas sensor owing to its low cost, high stability, wide band gap (3.1 eV) and environmental friendliness (Krishna et al., 2022) Also, the physical characteristics of layers (nanostructures) can be influenced by the methods for preparation and deposition procedures employed to produce them, which may have an impact on their intended use. One strategy to dealing with these important concerns is the development of gas sensors utilizing nanostructures used; however, as of currently, nothing nanostructures have demonstrated excellent sensitivity and selectivity, making their use in useful real-world applications based on single gas detection for quantitative purposes impractical (Krishna et al., 2022). Due to its special qualities, which include astounding catalytic activity, chemical stability, a wide band gap, low cost, and biocompatibility, titanium dioxide (TiO_2) is especially useful of the semiconducting metal oxides. These characteristics wide up the potential uses for it in solar cells, photoelectrodes, antimicrobial activity, and gas sensors (Noman et al., 2019). To deal with the issue at hand, the size-specific structural characteristics of the structures need to exist in the nanodomain for the purpose to have a wide surface area for gas entry from the environment (Machín et al., 2021). Therefore, one-dimensional or two-dimensional forms like nanorods, nanotubes, nanobelts, and nanoplates are the most attractive (Machín et al., 2021) TiO2 nanorods arrays' potential is increased by these configurations (Khizir and Abbas, 2022). A variety of techniques including hydrothermal, solvothermal, electrochemical, sol-gel, co-precipitation, chemical vapor deposition, sonochemical, atomic layer deposition, and microwave-assisted hydrothermal, are currently used for the preparation and synthesis of TiO_2 nanomaterials (Khizir and Abbas, 2021). The solvothermal approach stands out among them because to its excellent material purity, improved control over size and shape, minimal processing temperature, ease of variation of experimental parameters, and reduced manufacturing costs (Arthi et al., 2023).

In this work, the structural and morphological properties of TiO_2 nanorods were investigated after they were easily and efficiently synthesized by the solvothermal process using titanium tetrachloride ($TiCl_4$) as a precursor. The hydrolysis of $TiCl_4$ has been regulated by certain inorganic acids to produce transparent sols that act as precursors to solvothermal processing. Also, to achieve a controlled hydrolysis, ethanol and HCl combination were used as the solvent in a different ratio. The corresponding TiO_2 nanorod-based gas sensor's sensing capabilities and sensitivity are proven.

2. Experimental details

2.1 Materials

Before being employed, none of the chemicals underwent additional purification; they were all of analytical-level purity. 99.9% pure titanium tetrachloride ($TiCl_4$) and 97% pure ethanol (EtOH) grade were purchased from Sigma-Aldrich Chemistry.

2.2 Synthesis of TiO2 nanostructures

TiO_2 nanorod arrays were grown on FTO-coated glass using the solvothermal technique. The solvothermal method and the hydrothermal method are comparable in several aspects; the main distinction is that this technique requires the use of a non-aqueous solvent. Due to the possibility of using organic solvents with high boiling points, the process's temperature could rise above that of the hydrothermal technique (Malekshahi Byranvand et al., 2013). In the first, the FTO-coated glass was divided into 2.5 cm × 2.5 cm pieces to be put as substrates. After being cleaned by sonication in acetone, ethanol and deionized water the substrates were dried using N_2 flow. The substrates were put into a 100 mL Teflon reactor that was sealed and contained 0.65 ml of titanium tetrachloride ($TiCl_4$) as a titanium precursor as well as a variety of volume ratios of ethanol to HCl. Selecting an appropriate solvent is essential when using a solvothermal technique. Ethanol are a few demonstrations of common organic solvents. To get a translucent and clear solution, the mixture was quickly stirred for 25 minutes using a magnetic stirrer. Afterward, the solution mentioned was put in a Teflon-lined stainless-steel autoclave with a capacity of 100 ml at room temperature. After that, an autoclave was air-cooled to room temperature after being heated to 170 °C for 6 hours. afterwards cooling, the samples were cleaned with deionized water and dried for one hour at 70 °C to dry them out. The subsequent formula explains the TiO_2 production reaction (Al-Algawi et al., 2017):

$$TiCl_4 + 3CH_3CH_2OH + H_2O \xrightarrow{\text{ice bath/stirring}} Ti(OCH_2CH_3)_3(OH) + 4HCl \quad (1)$$

$$Ti(OCH_2CH_3)(OH) \xrightarrow{\text{autoclave}} Ti(OH)_4 + 3CH_2CH_2 \quad (2)$$

$$Ti(OH)_4 \xrightarrow{\text{annealing}} TiO_2 + 2H_2 \quad (3)$$

2.3 Gas Sensor Construction and Measurements

Initially, TiO_2 nanorods grown using solvothermal processes were used to fabricate a gas sensor. The metal was deposited on the front side of TiO_2 nanorods/FTO coated glass, whereby the electric current travels across to the contacts, in order to achieve ohmic contacts for the electrical electrodes that transmit electrical current using a thermal evaporation coating system type (JEE-4B/4 C). The system's main components are a rotary pump that is used to evacuate the chamber from atmospheric pressure to a level where the diffusion pump can maintain the chamber's pressure. The pressure in the chamber has been reduced to around 10^{-5} Torr. To heat the tungsten basket for evaporation, the current (0 - 40 mA) was transmitted through it. The Al metal was deposited through a typical mask on the front-end sides of the TiO_2 nanorods sensing membrane where the current flows laterally to the contacts. Since Al work function is suited for producing good ohmic characteristics with TiO_2, a proper mask is designed to make a front metal contact on pH-sensor operation. Under a vacuum pressure of $2{\times}10^{-5}$ torr, high purity Al was deposited on the sample's surface to form a metal contact. In Figure 3.4, the thermal evaporation coating system (PVD) and mask utilized for the sensing membrane of gas sensor (Al/TiO_2) are illustrated. The front side Al contact was constructed using a mask made of an interdigitated electrode with a 12-finger pattern as shown in Figure (1). The two probes coupled to Keithley (6487) Picoammeter/Voltage source unit were used to record the current and voltage of the samples in a vacuum chamber under dark conditions in order to measure the voltage-current curves of the sensing device at various controlled environments. A personal computer was linked to an ExceLINKX-based software program that made use of Keithley (6487) source device with a GPIB interface. The vacuum chamber coverage, the gas tank, a bottle source that produces gas vapor by heating a liquid (ethanol and methanol) on a plate-type heater and the vacuum pump constitute the major components of the set up system. The process in this scenario begins with measuring I-V curves in air within the chamber, followed by creating a low vacuum (10^5 Pa) in the chamber by taking out air molecules when the gas control is closed and the vacuum valve is open, and finally by introducing gas (O_2, CO, Ethanol and Methanol) into the inside of the chamber. Figure (2) illustrates a design diagram of the gas sensing the setup process.

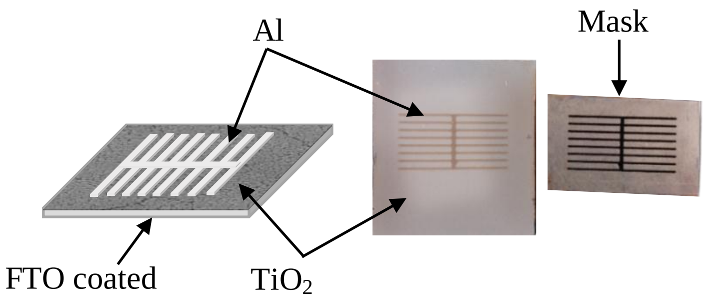

Figure 1: Schematic illustration with photographic of the fabricated single layer device and mask used for the gas sensing of gas-sensor (Al/TiO_2)

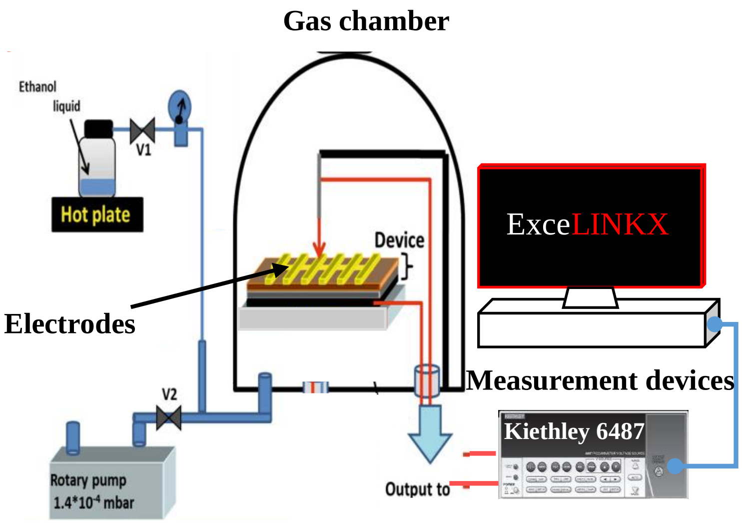

Figure 2: Schematic diagram of experimental setup for gas sensor measurements.

3. Results and discussion

3.1 Effect of precursors: ratios of (ethanol/water)/HCl

The FE-SEM morphologies of the TiO_2 nanorods syntheses on FTO coated glass with varying volumetric ratios of HCl:(H_2O/Ethanol) are shown in Figure (3). As seen in Figure (3-a), the sample at 30ml:(0ml/30ml) of the HCl:(H_2O/Ethanol) consisted of attached nanorods uniformly dispersed across the FTO surface. The average diameter of the nanorods has been found to be (62.64) nm. The sample's shape looked like that of a sample formed with just ethanol as solvent after adding 15 ml replacement of ethanol for water in the solvent, as seen in Figure (3-b), with the nanorods approximately perpendicular to the surface with decrease in average diameter of nanorods about (52.44). As the volumetric ratios of HCl:(H_2O/Ethanol) varied to 40ml:(15ml/5ml), it was demonstrated in Figure (3-c) that the distances between the nanorods increased as the nanorods the density of the packs developed and decrease in average diameter of nanorods about (45.40) nm. This resulted in densely packed TiO_2 sample that was composed of roughly unevenly spaced and aggregation of nanorods.

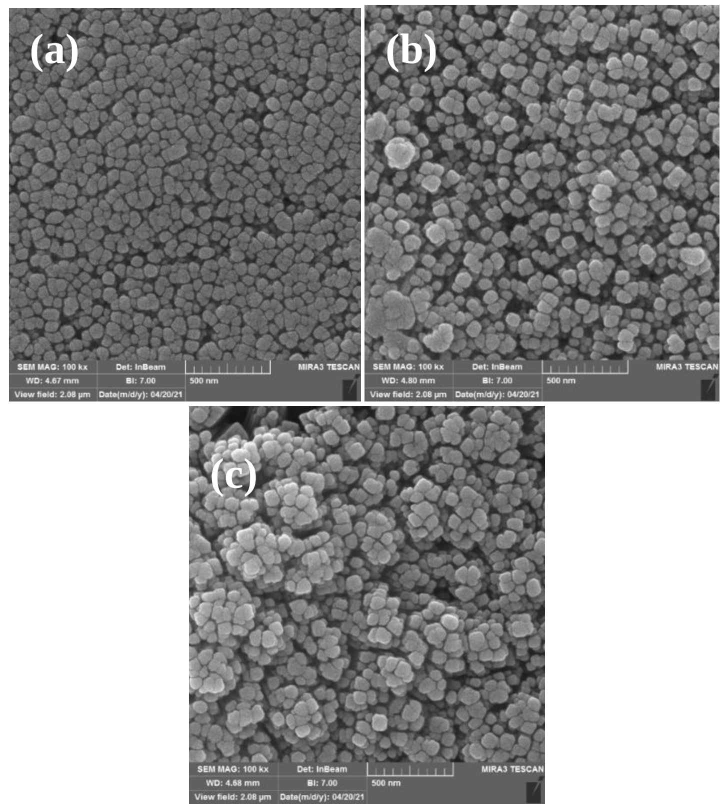

Figure 3: Surface SEM images of the samples prepared at 170°C for 6-hours with HCl:(H_2O/Ethanol) volume ratios of (a) 30ml:(0 ml/30ml), (b) 30ml:(15ml/15ml), (c) 40ml:(15ml/5ml)

3.2 The Effect of Acids

Figure (4) shows the FE-SEM (Field Emission Scanning Electron Microscopes- (TESCAN, Instrument model: MIRA III Made in Czech Republic)) images of TiO_2 synthesized via a solvothermal process at various acids for 6 hours at 170 °C. The morphology of the TiO_2 nanorods shows that they are spherical in shape and become regular in array when HCl is used as an alternative to HNO_3. The nucleation and growth of the rutile phase were facilitated by Cl-ions' strongest mineralizing action (Wu et al., 1999).

Also, the fact that NO_3^- anion has a lower affinity for a titanium atom in a solution that is aqueous has long been established (Wu et al., 1999). It has also been commonly published that, in solvothermal processes, rutile production can be grown in a highly acidic medium (Zhou et al., 2012). Wide accessible surface can give more possibility for target gas adsorption, resulting in increased gas response or sensitivity. Regularly arranged nanords with rough surfaces and reduced diameter offer potential for gas sensor applications. Therefore, the elevated sensitivity (i.e., variation in conductivity) of the sensor naturally requires a high surface-to-volume ratio, even though the gas sensing process is closely associated with surface responses as previously described. The enhanced TiO_2 samples were then chosen to serve as membranes, and they subsequently developed into a gas sensor.

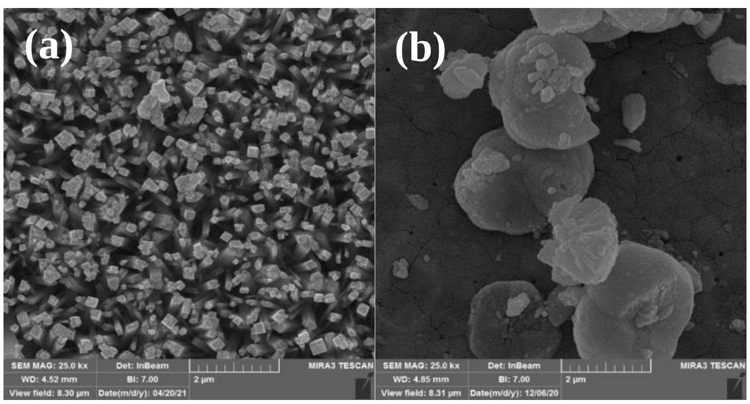

Figure 4: SEM images of TiO_2 nanorods thin films synthesized with different type of acidity (a) HCl, and (b) HNO_3.

X-ray diffraction (XRD) was used to study the crystalline structure of TiO_2 nanorod samples. The XRD structures of TiO2 nanorods at various aqueous solution amounts of either HCl or HNO_3 for the sample of 30ml:(30ml) of the HCl:Ethanol at 170 °C can be seen in Figure (5). The strongly peaks pointed to the crystalline TiO_2 nanorods that were highly produced. When using HCl as an aqueous solution, the obtained sample's greatest peak is likely located at 2θ = 27.27°, which is in line the corresponding (110) plane. The 2θ = 27.27° peak's strong intensity suggests that nanorods develop more strongly in the (110) direction. We can obtain phase-pure rutile in an aqueous solution of either HCl or HNO_3. As a result, pure rutile could be synthesized more readily in an HCl medium than in an HNO3 one because Cl^- anions have a lower affinity for a titanium atom than NO_3^- anions do. The Cl^-anions, or strong acidity, rapids up crystal formation. Even so, in Figure (5-b) the XRD pattern of TiO_2 shows additional peaks of the FTO substrate in an HNO_3 media. As a result, larger rutile nanorods are typically seen in stronger acidic solutions.

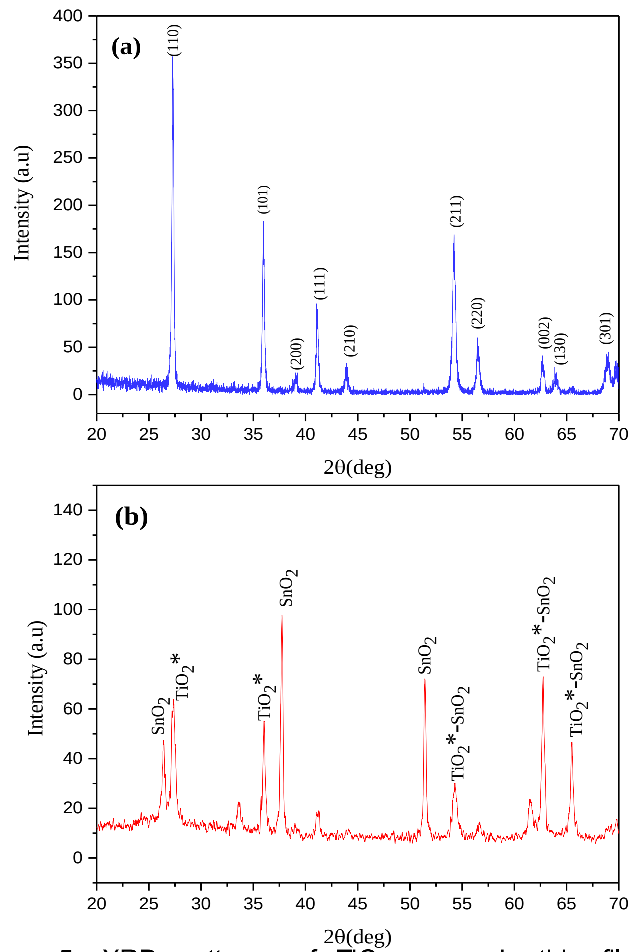

Figure 5: XRD patterns of TiO_2 nanorods thin films synthesized with different type of acidity (a) HCl and, (b) HNO_3

3.3 Sensing Performance

3.3.1 Current–Voltage Characterization of the Sensor

The current-voltage (I-V) measurement results for the two produced sample of TiO_2 nanorods with various metal contact materials of **Al** and **In** have been shown in Figure (6). It has been seen in Figure (6), just the sample that has been treated with Al metal exhibits an almost linear (I - V) characteristic over a wide range of applied voltage; this suggests that Al /TiO_2 nanorod have an ohmic contact behavior. For the samples in this investigation, it is the best choice for metal contact materials. On the other hand, as can be seen in the Figure (6), the I-V plots for the In/TiO_2 structure demonstrated non Ohmic (Schottky) contact behavior even in the voltage that was applied range.

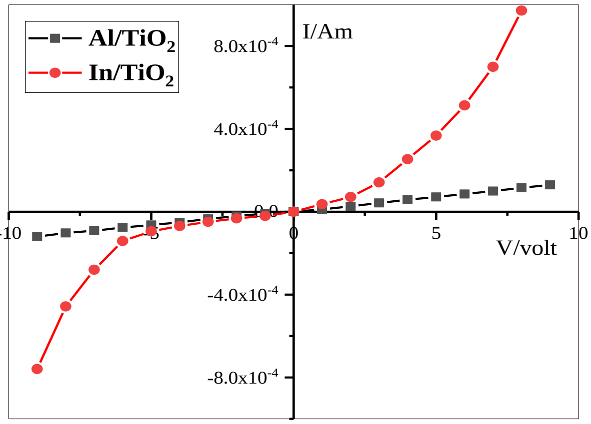

Figure 6: I-V measurement plots of TiO_2 nanorods thin films.

In Figure (7), various effects in the dark with and without gas exposed are studied, based on measurements of the I–V characteristics of the a synthesized TiO_2 nanords gas sensor structure made at ambient temperature. Investigations have been performed on the effects of reducing (ethanol and methanol) and oxidizing (oxygen, and carbon monoxide). The Al/TiO_2 device's gas sensing capabilities were assessed by measuring the variation in current across interdigit electrodes in various environmental conditions. A variety of variables, like the ion adsorption of gas molecules, the surface reactivity of a target gas with adsorbed oxygen or lattice oxygen, and nanocrystalline TiO_2, might result in a change in sensor responsiveness (Wu et al., 2022). The I-V curves show that, at identical bias voltages, the sensor's interaction with ethanol gas raised the current in comparison to the other gases. The reason for this is that the adsorbed oxygen and the exposed gas interact chemically, causing the oxygen species to reassert its electron and raise the current. Hence, the state of the current variation or disparity will depend on the kind of semiconductor. Consequently, the freed or released electrons reduce resistance in an n-type semiconductor. The TiO_2 nanorods' superior resistance to variation and higher ethanol-sensing abilities are mostly due to their larger surface area.

As consequently, the sensor may be used to detect oxidizing gases (carbon monoxide and oxygen) with selectivity, particularly when it is exposed to oxygen. It is most probably so that the covering of oxygen exceeds that in TiO_2 film with O_2 exposed, mainly because the variation in current is proportional to the whole surface area and the quantity of negative-charged chemical species, such as O_2^-, O^{-2}, and O^-, absorbed on the surface. As a result, a rise in charge carrier (electron) concentration in the n-type TiO_2 leads to a raised in current. This reaction also causes an exchange and transfer of charges between oxygen molecules and the titanium oxide thin films. The previously described results showed that the Al/TO_2 device has strong reactions to both reducing and oxidizing gases.

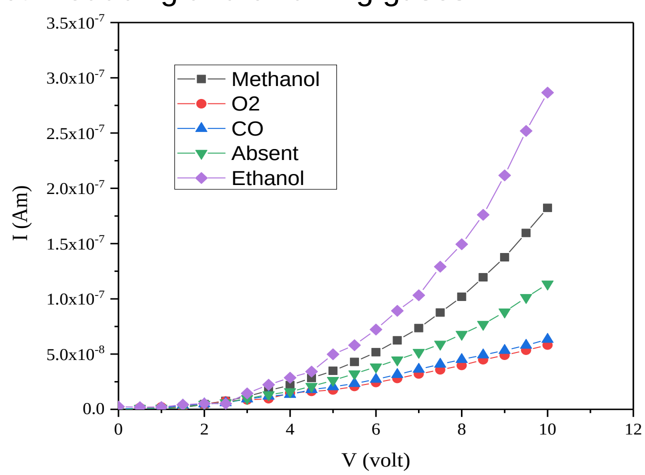

Figure 7: I–V curves of Al/TiO_2/Al sensor measured at room temperature when exposed to oxidizing gases and reducing gases.

3.3.2 Sensitivity of the Sensor

A sensor's gas sensitivity (S) can be defined as the percentage of the current's output variation that occurs after the sensor is exposed to a gas to the current that occurs at dark without any gas input. Using Equation (4), one can determine the sensor sensitivity (S_g) for gas exposure (Govardhan and Nirmala Grace, 2016).

$$S_g = \frac{I_g - I_d}{I_d} \quad (4)$$

where Id is the current measured in the absence of gas and Ig is the current measured in the presence of gas in the dark. When faced with both oxidizing and reducing gases, the Al/TiO_2

gas detector's gas sensitivity was measured as an estimate of the bias voltage, which is in a range of 0–10 V. Figure (8) illustrates the TiO_2 nanorods devices' relative sensitivity to different exposed gases as a function of bias voltage. The increased ratio of surface to volume of the TiO_2 nanorods, which offers stronger effective detecting regions, is responsible for the sensor's excellent sensitivity. The relative sensitivity (Response) for the bias voltage (V) of 0.5 V are 53.758, 91.248, 108.298 and 144.689 % for O_2, CO, Methanol and Ethanol gases, respectively. Studies show that, in comparison to oxygen, and carbon monoxide gases, the application of TiO_2 nanorods is a successful strategy for enhancing ethanol and methanol sensing capability.

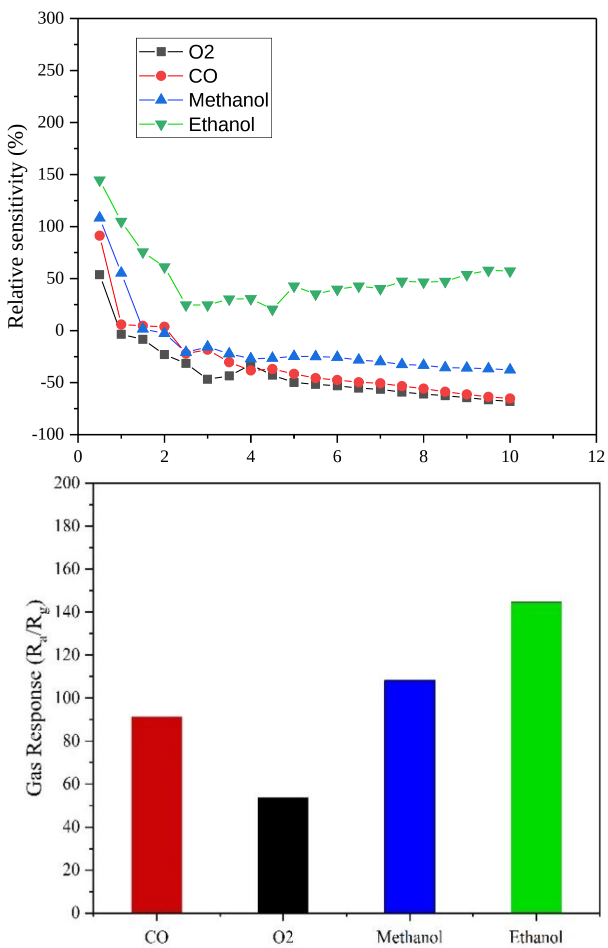

Figure 8: Comparison of the relative sensitivity and gas response at room temperature as a function of bias voltage for the Al/TiO_2/Al device measured in the dark with towards Ethanol and Methanol vapors, Oxygen, and Carbon monoxide gas.

Another crucial component of the gas sensor is its long-term stability, which shows the sensor's dependability. At room temperature, the Al/TiO_2/Al sensor's stability in the presence of 50 parts per million ethanol was assessed. Figure 9 demonstrates this clear: during the first 15 hours, the relative deviation of the gas response sensitivity was less than 2%, and during the next 15 hours, it was almost 3%. The gas sensing characteristics of various dimensions TiO_2 nanostructures used for ethanol gas detection are compared with some previously published data in Table 1.

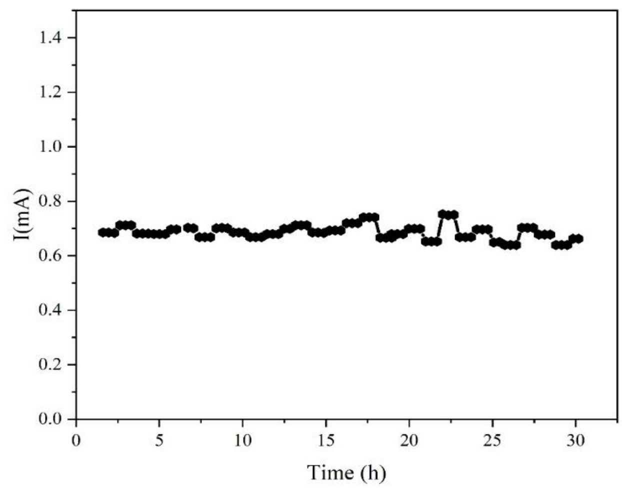

Figure 9: Al/TiO2/Al sensor's long-term stability with relation to ethanol vapor at ambient temperature.

Table 1: Comparison of the gas sensing properties of different dimensional TiO_2 nanostructures used for ethanol gas detection with some previous reported.

TiO_2 Morphology	Fabricated methods	Analyte detected	Concentration (ppm)	Response (Sensitivity) 100%	Ref.
Nanotubes	electrochemical anodization	Ethanol	100	74.5	(Gakhar and Hazra, 2020)
Nano-flowers	hydrothermal	Ethanol	400	22.9	(Gao et al., 2017)
Nano-flowers	hydrothermal	Ethanol	100	24	(Wang et al., 2020)
Pine-branch-like	hydrothermal	Ethanol	100	4	(Mei et al., 2020)
Nanorods	Solvothermal	Ethanol	50	108.298	**Present work**

Conclusions

By using a solvothermal technique, TiO_2 nanorods have been grown on an FTO substrate. The crystal structure of rutile phase is present in vertically aligned TiO_2 nanorods. The volumetric ratio of HCl to ethanol and the acidity were varied and resulted in exactly arranged and homogenous TiO_2 nanorods in an aqueous solution. Significant advances were observed in the reducing (ethanol and methanol) and oxidizing (oxygen and carbon monoxide) gas response at room temperature. Study indicates that using TiO_2 nanorods is an appropriate way of improving ethanol sensing ability when compared to oxygen, carbon monoxide, and methanol n gases with good stability. The comparable relative sensitivity (Response) for the gases O_2, CO, methanol, and ethanol is 53.758, 91.248, 108.298 and 144.689 percent, respectively, to a bias voltage (V) of 0.5 V. With a relative deviation of the gas response sensitivity of less than 2%, the gas sensor demonstrated superior sensitivity to ethanol compared to other gases, even while it was at ambient temperature and in the dark.

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Potential conflicts of interest. All authors report no conflicts of interest relevant to this article.

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