Influence of Exposed Facets and Acid Treatment on the Sensitivity and Selectivity of Room Temperature TiO$_2$ Semiconductor Gas Sensing Properties

By

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ABSTRACT

Due to the demands of the current age gas sensing devices to satisfy humanity and environmental requirements, sensors with arrangement of excellent sensitivity and selectivity, prompt response-recovery times, low operating temperature, reproducibility, insignificant interference from ambient humidity, and long-term stability are desired. This is motivated by the global gas sensor market estimated at USD 2.19 billion in 2019 and a compound annual growth rate of 8.3% increase expected form 2020-2027. Moreover, according to studies, more than 5 million deaths related to air pollution are reported annually. In South Africa alone, more than 20000 deaths are reported yearly.

Therefore, this study investigates the low and room temperature (RT) gas sensing properties of pure TiO$_2$ nanostructures such as nanotubes, nanowires and hierarchical spheres and that doped with various Mn concentrations towards detection of toxic gases and volatile organic compounds for indoor and outdoor air quality monitoring for health and security purposes. Our findings show that designing and tuning of nanostructure morphology has significant impact on the structural, optical and sensing properties of TiO$_2$. Thus, herein through a simple hydrothermal method and followed by washing with various concentrations of Hydrochloric acid (HCl) and distilled water (DW) we achieved a notable surface area of 1375 m$^2$/g with a change in morphology from nanoparticles to nanotubes.

The gas sensing characteristics, such as response, sensitivity and selectivity conducted towards CH$_4$, NH$_3$, CO and NO$_2$ gases at different operating temperatures, demonstrated higher selectivity towards CH$_4$ gas at 23 °C. This was behaviour was
attributed to the high surface area and crystallinity of displayed by the multi-dimensional nanotubes acting as nanochannels for gas diffusion. Furthermore, through annealing we tuned the selectivity of TiO$_2$ towards NO$_2$, the sensor displayed an enhanced sensitivity of 29.44 ppm$^{-1}$ and admirable selectivity towards NO$_2$, among other interfering gases, ensuring adequate safety in monitoring NO$_2$ in automobiles and households.

This study has further afforded a breakthrough to design for the first time the dual-functionality sensor for detection of toluene (C$_7$H$_8$) and xylene (C$_8$H$_{10}$) from TiO$_2$ nanowires operating at room and low temperature, for low power consumption purpose and such sensor is a striking platform for economic and indoor air quality monitoring. To the best of our knowledge, a temperature-dependent selectivity dual sensor operating a room temperature and 125 °C has never been reported. By testing the sensor in various relative humidity, the findings validated that the current sensor can be used for detection of C$_7$H$_8$ and C$_8$H$_{10}$ in a vastly sensitive and selective way with insignificant interference from ambient humidity.

Besides, through annealing, we further showed that the selectivity of the nanostructures can be tuned, due to exposed facets containing plentiful active oxygen species which are more activity for adsorption. Thus, the superior sensitivity towards toluene and ethylbenzene among other aromatic hydrocarbon VOCs, was exhibited by thermally treated sea-urchin like TiO$_2$ hierarchical spheres. The T5 sensor (i.e. annealed at 500 °C) displayed temperature-dependent selectivity towards ethylbenzene at 75 °C. The T7 sensor (i.e. annealed at 700 °C) revealed the highest response of 13 towards toluene at 150 °C, which could be justified by exposed high surface energy {001} facets. The sensor illustrated a robust stability towards relative
humidity (10-90%), which is very vital for practical and real-time applications in ambient conditions.

In addition, by utilizing a simple synthesis strategy that permits easy and reproducible results, we prepared manganese (Mn) doped TiO\textsubscript{2} hierarchical structure having recorded a highest surface area reported. This process indicated that the improvement of the surface area with an increase in Mn doping concentration shows a clear dependency on the doping concentration, resulting to a record surface area of $4347\pm14$ m\textsuperscript{2}/g and pore volume of 27.85 cm\textsuperscript{3}/g. A gas sensor based on optimized Mn-doped TiO\textsubscript{2} established a poor response towards reducing gases (CO and CH\textsubscript{4}), volatile organic compounds (C\textsubscript{7}H\textsubscript{8}, C\textsubscript{3}H\textsubscript{7}OH, C\textsubscript{6}H\textsubscript{6}, E-C\textsubscript{6}H\textsubscript{6} and C\textsubscript{8}H\textsubscript{8}), while tested to C\textsubscript{2}H\textsubscript{5}OH vapour, unprecedented response, improved sensitivity and selectivity was witnessed at 100 °C. This was due to a remarkable surface and abundant porosity allowing more gas adsorption. The Mn4 sensor showed a strong repeatability over 10 cycles at 100 ppm C\textsubscript{2}H\textsubscript{5}OH after 20 days, without showing any drift, confirming its robust stability, which could be useful for detection of C\textsubscript{2}H\textsubscript{5}OH in real applications. Finally, this work has been adopted for intellectual property and an innovation disclosure has been granted (Disclosure number: T18/19-00029), while a United States patent is currently being filed.
I, Zamaswazi Portia Tshabalala, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature: .................................................................

Date: .................................................................
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“Ungumafunga angajiki.”

2nd Corinthians 1: 20

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**INTELLECTUAL PROPERTY (IP)**


*Intellectual Property, Innovation Disclosure (Disclosure number: T18/19-00029) and US Patent is currently being filed.*

**CONFERENCES ATTENDED**

- SACPM 2017-Amanzi
  - Poster Presentation: Structural transformation and enhanced gas sensing characteristics of TiO₂ nanostructures induced by annealing.
- The 7th Annual World Congress Nano Science and Technology- Japan 2017
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- South African Institute of Physics 2018
  - Oral Presentation: Enhanced selectivity of NH₃ by TiO₂ nanoparticles induced by band narrowing.
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- Oral Presentation: The Influence of Morphology on Surface to Volume ratio of TiO$_2$ nanostructures and their CO gas sensing Properties.

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CHAPTER 1: Introduction

1.1 Background and Rationale

The presence of harmful and toxic substances in vapourous form deteriorates the quality of air in working and living environments leading to detrimental health and safety effects [1-2]. Gases such as volatile organic compounds (VOCs) i.e. aromatic hydrocarbons, alcohols, aldehydes, and non-organic gases such as carbon monoxide (CO), nitric oxide (NO, NO$_2$), hydrogen sulphide (H$_2$S) and ammonia (NH$_3$) are major air pollutants with extreme risk factors as they could be flammable, explosive and poisonous to human health with long term effects that can result into death [3-6]. Developing countries have high level of these pollutants due to human activities driven by urbanization and industrialization as the countries’ economy is dependent on it [7, 8]. These activities include combustion of biomass or fossil fuels such as wood, charcoal, coal, crude oil and gasoline for power generation, heating, automotive industry, mining, and manufacturing [7, 10].

Majority of the people spend most of their time in confined spaces, be it homes, offices, hospitals, warehouses and factories, even in beauty salons, where they get exposed to harmful gases through household products and poor ventilation [3, 4, 11, 12]. The European Commission and the United States Environmental Protection Agency branded CO, NO$_2$ and VOCs as high priority in door pollutants that should be monitored for indoor Air quality [13, 14]. CO which is loosely termed the “silent killer”, is a colourless and odourless poisonous and flammable gas. Headache, dizziness and fatigue are early symptoms of exposure to CO concentration above the 9 ppm indoor exposure limit. Prolonged exposure may result to CO poisoning and death [13, 14]. At concentration levels greater than 35 ppm it binds with hemoglobin resulting in oxygen
deprivation and a person suffocates therefore, the occupational safety and health administration (OSHA) of the USA and the National Institute for Occupational Safety and Health (NIOSH) recommended a 35 ppm permissible exposure limit (PEL) for an eight-hour time-weighted average (TWA) shift [13-16].

In South Africa (SA), gas stoves, paraffin (Kerosene) heaters, wood and coal combustion are the major sources of indoor CO emission with concentration levels above 18, 7, and 30 ppm respectively (see Fig. 1.1a) [17, 18]. The mortality and cause of death report published by Statistics South Africa (STATS SA) in 2018 [19] illustrated that deaths due to smoke inhalation, fire and flames made 6.5 % of top 10 causes of death in SA. This was greater than deaths caused by diseases such as tuberculosis, diabetes and HIV/AIDS [19-21]. Moreover, the results shown in Fig. 1.1b were published in 2015 by the Africa Progress Panel (APP) and the statistics illustrate deaths caused by household air pollution from solid biomass between 2004 and 2010 and further show the 2030 projections. It can be clearly seen that the cause of deaths due diseases such as malaria, tuberculosis and HIV/AIDS declines over the years where else more lives are expected to be lost due to CO (“Africa’s hidden killer” as they refer to it) emitted during use of biomass [18].

Among the VOCs, the alcohol group such as ethanol, propanol, butane and aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX) are extremely hazardous and are carcinogenic, teratogenic and mutagenic in nature [5, 11, 21, 22]. Household products such as adhesives, paints, paint thinners, pharmaceutical products, cosmetic and cleaning products, printers, carpet, foam and furniture are common sources of VOCs that contribute to pollution of indoor air [1, 11, 12]. Even though benzene (C₆H₆) is colourless it has a distinct smell and has extreme
side effects to exposure and causes bone marrow abnormalities and leukemia. A 1 ppm airborne concentration of 8-hour (TWA) limit was set by the OSHA and a 5 ppm short term limit over 15 min period [23].

![Fig.1: (a) Household sources of CO and VOCs, (b) Deaths caused by household air pollution from solid biomass in Africa between the years 2004-2010 and 2030 projections.](Reprinted with permission from [18] 2015, Power People Planet: The Africa Progress Panel).

Ethylbenzene (C₆H₅CH₂CH₃) is a benzene derivative and has a 100 ppm PEL set by the OSHA and the American conference of governmental industrial hygienists (ACGIH) [24]. Xylene (C₆H₄(CH₃)₂), has as sweet smell and may cause damage to the kidneys and liver above 200 ppm therefore a 100 ppm TWA limit is set [24]. Toluene (C₆H₅CH₃) has teratogenic properties i.e. it may induce termination of pregnancy in females and has 20 ppm 8 hour TWA set by the ACGIH and 100 ppm PEL by OSHA [25]. Since ethanol and propanol are central nervous system depressants, exposure may result to dizziness, nausea and vomiting, and loss of coordination and have 1000 ppm and 200 ppm PEL [26]. Air pollutants are more hazardous in confined spaces as concentration may be high due to poor ventilation. Therefore, air quality monitoring in living and work spaces is of great importance to
timely detect the presence of VOCs even at low concentrations in order to minimize exposure.

1.2 Chemiresistive Gas Sensors for Indoor Air Quality Monitoring

Although the human nose can detect some of the gases due to smell however, it is not safe or reliable due to the fact that some gases are odourless, or can be detected through sense of smell at concentration level above exposure limit. A number of analytical techniques/instruments can be used to detect VOCs such as cathodoluminescence, photoacoustic spectroscopy and optical parametric oscillator, gas chromatography coupled with mass spectrometer and flame ionized detectors [27-30]. However, these are inconvenient in the field as they are very expensive to purchase and maintain, they are also bulky (desktop size) and have long analysis time. A study on the risks of BTEX concentrations emitted due to combustion of coals was conducted by Masekameni et al. [30]. Near field measurements were carried out over 3 hour periods using a gas chromatographer with an inlet feeder additionally, for enhanced sensitivity it was coupled with a photoionizer detector. Moreover, a traditional kitchen found in informal settlements in South Africa was replicated. A cancer risk factor of 1.1 and 1.2 was found in adult males and females which was 110 and 120 times higher than the stipulated risk indicator by the Unites States Environmental Protection Agency.

Semiconductor metal oxides (SMOXs) have been extensively used in chemiresistive gas sensors research due to advantages such as high sensitivity, rapid response time, easy fabrication, portability and affordability [1-6]. The first demonstration was done in 1952-1953 by Brattain and Bardeen [31] where they observed change in electrical resistivity of germanium (Ge) due to surface interaction
with different gas molecules. In 1962 Seyama et al. [32] observed changes in electrical conductivity of zinc oxide (ZnO) thin films exposed to propanol. It has now been over half a century since the pioneering work by Seiyama and Taguchi [33] led to the first invention of chemiresistive gas sensor to be fabricated and practically used with tin dioxide (SnO$_2$) as a sensitive layer. Figaro Inc. owned by Taguchi, commercialized the gas sensor in 1968 and the devices were used as fire alarms by monitoring the presence of combustible and explosive gases. Later, Shaver et al. [34] in 1967 studied the effects of noble metal additives on the electric properties of the MOXs with the aim to improve response and sensitivity.

Extensive studies have been done over the years on different metal oxides (TiO$_2$, SnO$_2$, In$_2$O$_3$, WO$_3$, Cu$_2$O$_4$ and ZnO) for gas sensing [1-6, 12-15]. Titanium dioxide (TiO$_2$) is the most attractive material due to its unique properties such as excellent catalytic activity, chemical stability, wide band gap, low cost and biocompatibility that enable potential technological applications in solar cells, photoelectrodes, antimicrobial additive and gas sensors [10, 35-37]. More than one polymorph can be found presenting different properties; however, the mostly studied polymorphs for gas sensor applications are anatase and rutile phases due to their high photocatalytic activity and thermodynamic stability, respectively [38-40]. Nanoscience and nanotechnology have enabled significant progress in the gas sensing research field. Nanostructured TiO$_2$ samples have enhanced properties compared to their bulk counterparts due to alteration and manipulation of properties such as grain size, dimension and structure one can achieve high specific surface area and surface to volume ratio, enhanced defects, fast electron transport, and tailored facets of enhanced surface activity resulting to novel fabrication of highly sensitive, stable, portable and multi system sensor devices [4, 38-41].
1.2.1 CO Gas Sensing

Surface area and porosity are important properties of a SMOX gas sensor as they highly influence gas adsorption. Moon et al. [42] reported on a highly sensitive CO sensor with a response of 4220 % measured at 250 ºC towards 500 ppm gas concentration with response and recovery times of 9 and 11 s, respectively. The authors attributed the enhanced response to a network of nanostructured TiO$_2$ hollow hemispheres on a thin film achieved via room temperature sputtering. Additionally, CO sensing properties of TiO$_2$ xerogel thin films achieved by vacuum and solvothermal drying process displayed a dependent relationship between response and porosity. The conventionally dried thin film had high surface area and porosity consequently sensitivity increased from 2.53 to 6.81 as porosity increased from 15 to 62 % when exposed to 50 ppm CO at 350 ºC [43]. The micro-arc oxidized porous TiO$_2$ film was tested between 5-100 ppm CO at 350 ºC. A concentration dependent response behavior was observed with a maximum response of 4.02 at 100 ppm. Moreover, the sensor was responsive even at 10 ppm (1.68) which is an adequate gas concentration for indoor CO monitoring [44].

However, the surface area and porosity are not the only influencing factors to enhanced CO sensing, crystallinity and phase also play a role as demonstrated by Seeley et al. [45] where an increase in response from 7.5 to 8.9% was recorded towards 500 ppm CO at 600 ºC operating temperature. Even though authors observed the loss of surface area as the TiO$_2$ nanoparticles were thermal treatment between 700 -900 ºC they attributed the improved sensing to improved crystallinity from amorphous to anatase and phase stability of samples thermally treated at 800 ºC. Furthermore, computational studies on the effect of rutile TiO$_2$ surface orientation on CO and H$_2$S sensing were undertaken by Zhang et al. [46]. The {100} rutile facet was
more prone to CO detection whereas the \{001\} showed enhanced H\textsubscript{2}S dissociation forming hydroxyl radicals on the surface.

Elemental doping and surface sensitization are some of the explored options to enhance sensitivity towards CO. The use of reduced graphene oxide as an additive on the surface of Nb-doped TiO\textsubscript{2} microsphere improved sensor conductivity consequently improving the response even at high CO concentrations (100-1000 ppm). Maximum response value of 6.2 was displayed by the 5wt% rGO/TiO\textsubscript{2}:Nb composite while response of TiO\textsubscript{2}:Nb was about 3.7 at 400 °C operating temperature in the presence of 1000 ppm CO\textsuperscript{[47]}.

1.2.2 BTEX Gas Sensing

The chemical structure of methyl group (-CH\textsubscript{3}-) among BTEX is similar and follow a similar dissociation/sensing mechanism. Therefore, a highly selective material is required for low concentration detection of BTEX such as, the thin films made of hydrothermally synthesized TiO\textsubscript{2} nanotube examined in the presence of 500 ppm H\textsubscript{2}, 500 ppm CO, 47 ppm ethanol and 50 ppm toluene. Maximum response of about 25 was observed towards toluene at 50 ppm and was attributed to larger pore diameter of 201.3 nm dominated by macrospores which effortlessly allow toluene to diffuse at high operating temperature\textsuperscript{[48a]}. Additionally, in \textsuperscript{[48b]} balling milling increased the surface area without degrading the porosity which in turn increased the response to ~50 at 50 ppm toluene. Moreover, due to surface modification enhanced response of 42.9% towards 500 ppm toluene vapour at room temperature was reported by Seekaew \textit{et al.}\textsuperscript{[49]} using graphene-carbon nanotubes loaded with TiO\textsubscript{2} nanoparticles achieved via chemical vapour deposition and sparking methods. Pure and Au-loaded TiO\textsubscript{2} hedgehog-like hierarchical architectures synthesized via hydrothermal method
were prepared by Zhang et al. [37] for detection of xylene at temperatures between 320-400 °C. At a working temperature of 375 °C the sensors displayed optimum response of 3.19 and 6.49 for pure and Au-TiO$_2$ towards 100 ppm of xylene.

**1.2.3 Alcohol Gas Sensing**

Even though TiO$_2$ has excellent photo-chemical properties, wide band gap, porosity and facets {001} with high surface energy. However due to poor selectivity in the presence of interfering gases addition of dopants and heterostructures have been explored to enhance sensitivity, improve selectivity and decrease power consumption for VOCs sensing [5, 6, 12, 37-39]. Mesoporous Ag-doped TiO$_2$/SnO$_2$ nano-hybrid achieved via wet impregnation followed by nano-casting displayed ultra-sensitivity and selectivity towards ethanol with acetone, isopropanol, methanol, and ethyl acetate as interfering gases [5]. The authors observed an exceptional response value above 300 towards 500 ppm ethanol concentration at optimum operating temperature of 275 °C. More interestingly, the nano-hybrids displayed good sensitivity at low concentration less than 50 ppm. Room temperature detection of ethanol by TiO$_2$/Pt/TiO$_2$ sandwich showed a linear increase in response with concentration (10-100 ppm) with fast response and recovery times. However, the sensor illustrated poor selectivity to ethanol when compared to methanol, and 2-propanol as interfering gases and the recovery was assisted by UV-irradiation [50]. Temperature dependent sensitivity was observed using Nb-TiO$_2$/ZnO hierarchical nanostructures between ethanol and methanol [51]. While varying the temperature between 250 and 400 °C at constant gas concentration of 100 ppm, an optimum response value of 225.2 at 400 °C was observed upon exposure to ethanol whereas, methanol reached maximum at 350 °C with a response value of 649 by sensor 3ZT-2 (indicating 3 layers of ZnO coating).
However, the sensor displayed longer recovery time of 11.09 and 2.86 minutes upon exposure to ethanol and methanol respectively [51].

1.2.4 Sensing Mechanism

Gas sensing is a surface phenomenon and metal oxides are favourable for this process because they are non-stoichiometric with oxygen vacancies as dominant defects and also the interaction between target gas and oxide surface is reversible [1, 52]. The sensing mechanism of metal oxide gas sensors was first reported by Wolkestein [53] in 1961 based on electron theory of chemisorption and catalysis. The conditions for electric charge transportation in a semiconductor exposed to target gases were later reported by Morrison in 1982 [54], Yamazoe et al. in 1983 [55] and Gopel et al. in 1995 [56] and following their theories we can explain the gas sensing mechanism in semiconductor metal oxides.

The working principle of a resistive semiconductor gas sensor is related to the variation of surface conductivity as a function of the surrounding gas atmosphere. Two types of MOXs are available being, the n-type (with electrons as dominant charge carriers) and p-type (with holes as majority charge carries) [52]. The adsorption of gas molecules on a MOXs surfaces often leads to redox reactions by serving as an electron donor or acceptor which is determined by the reductive or oxidative nature of the analyte gas. The interaction between gas molecules and materials mainly takes place on the surface; hence the number of atoms residing at a material's surface are critical for controlling the sensor performance. Due to the large surface-to-volume ratio provided by nanostructured materials, they have a much larger portion of surface atoms than bulk atoms.
Gas sensing mechanism of MOXs can be categorized into two, the ionosorption model and the oxygen vacancy model. The ionosorption model is the most familiar and is mostly used as the proposed sensing mechanism. For TiO$_2$, an n-type MOX, atmospheric oxygen adsorbed on the surface traps electrons from the conduction band and form oxygen species (O$_2^-$, O$^-$ and O$^{2-}$) dependent on working temperature as expressed in equations 1.1-1.3 [1, 49, 57].

\[
O_2(\text{ads}) + e^- \rightarrow O_2^- (T<100 \, ^\circ C) \tag{1.1}
\]

\[
O_2^- (\text{ads}) + e^- \rightarrow O^- (100 \, ^\circ C < T< 300 \, ^\circ C) \tag{1.2}
\]

\[
O^- (\text{ads}) + e^- \rightarrow O^{2-} (T> 300 \, ^\circ C) \tag{1.3}
\]

As seen on the sensing mechanism schematic in Fig 2 an electron depletion region is formed on the MOX surface resulting to an increase in resistance of the MOX. In the presence a reducing gas (electron donor) such as VOCs, H$_2$, CO, and CH$_4$, the adsorbed oxygen species reacts with the gas molecules and donate an electron back into the conduction band therefore decreasing the depletion layer resulting to the decrease in sensor resistance. With oxidising gases O$_3$, CO$_2$, and NO$_2$ the opposite occurs. The target gas reacts with the chemisorbed oxygen ions on the surface and extracts electrons. The depletion layer increases as there is less electron flow and the electrical resistance increases further.

1.2.5 Experimental Procedure

1.2.5.1 Synthesis Method: Hydrothermal

As mentioned above, one of the many advantages of using SMOXs as sensing material/layer is the easy synthesis presented by various methods such as
physical/chemical Vapour deposition, combustion, microemulsion, sol-gel, co-precipitation and hydrothermal/ solvothermal method. Among many, hydrothermal method is the most convenient technique for the synthesis of SMOXs.

**Fig.1. 2:** Schematic diagram of sensing mechanism of TiO$_2$ nanorods when exposed to a reducing gas (CH$_4$).

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The reaction (nucleation and growth) takes place in a liquid medium (water or any other solvent) which hydrolysis and condenses the metal salts within the vessel. Moreover, this method has advantages such as homogeneity in particle size and
morphology, phase, chemical composition and reproducibility which can be controlled by pressure, temperature and time [58-60].

Here in, the conventional oven and microwave assisted hydrothermal method were used to achieve pure and doped TiO₂ nanostructures. Teflon lined vessels are used in the conventional oven and/or microwave to maintain the temperature as the reaction progresses. Even though during hydrothermal method temperature can go as high as 500 °C, in this work synthesis was carried out under mild conditions i.e. temperature < 200 °C. The microwave assisted route is convenient as it accelerates the reaction and shortens the reaction time and the process is simple and energy efficient. The use of reactor in a conventional oven may be time consuming however homogeneity and various morphologies can be achieved. Using both routes TiO₂ nanoparticles, nanotubes, nanowires and nanowires arranged hierarchically into sea-urchin like architectures were achieved by varying the reducing agent and reaction time.

1.2.5.2 Materials and Chemicals

The reagents used in the experimental chapters were purchased from Sigma-Aldrich and were used without any purification. Reagents include P25 TiO₂ Degussa (99.9 % purity), sodium hydroxide (NaOH, 99.9 % purity), potassium hydroxide (KOH, 99.9 % purity), manganese (II) nitrate tetrahydrate (Mn (NO₃)₂ 4H₂O, 99%), Hydrogen peroxide (H₂O₂, 35 %), hydrochloric acid (HCl, 37 % purity).

1.2.5.3 Sensor Fabrication and Gas Testing

To investigate the sensing performance of the various TiO₂ nanostructures, the nanostructures were homogenously dispersed and sonicated in ethanol to form a slurry which was then uniformly coated on the alumina substrates (size: 0.5 mm x 2
mm) with two Pt electrodes (on its top surface) and a micro-heater (on its bottom surface). The deposited sensing layers were heated in a furnace at 200 °C for 30 min in order to eliminate the undesirable organic solvent used and to achieve proper adhesion, as well as to stabilize the sensor. The sensor resistances to various concentrations (5-100 ppm) of different gases (chapter dependent) and operating temperature were measured by switching between the mixture gases and synthetic dry air using a KSGAS6S gas testing apparatus (KENOSISTEC Model, Italy).

The gas testing instrument set-up used in this work is shown in Fig. 1.3a The system consists of a sensing chamber with sample stages, mass flow controllers, gas and a dry air inlet carrying it into the chamber, gas outlet including a vent outlet, two thermostatic baths, one supplies wet air into the mixer during humidity measurements and the second is for volatile gas measurements. In addition, there are six KEITHLEY picoammeters for the conductance measurement and six heaters that supply voltage across the sample. Different gases can be connected based on the experimental design.

1.3 Problem Statement and Novelty

The mandate for detection and monitoring of various toxic and volatile organic compounds in a selective routine is of high demand globally. This is due to the accelerated air pollution that results in a large number of deaths and costs the economy trillions of rands according to World Bank [61]. Despite all the work that has been done on MOX gas sensors, there are few reports on pure TiO$_2$ sensing material with higher sensing response, improved sensitivity and selectivity at low temperatures (< 200 °C) and an understanding of facets and surface chemistry that governs gas sensing. High working temperatures, instability and cross- sensitivity are the most
pressing challenges faced by researchers on improving gas sensing performance of MOXs materials. Moreover, the synthesis of MOX with controlled and reproducible morphologies still remains a challenge in the gas sensing field and this limits fabrication of sensors devices and commercialization.

**Fig. 1. 3:** Sensing schematic diagram and the BTEX vapour used in this work.

Therefore, this study is aimed at addressing these problems by preparing MOX based sensors with controlled morphology, exposed planes with high index facets that create the surfaces that are very reactive for the adsorption of oxygen species in order to enhance the sensitivity and selectivity. Moreover, we report on dual functionality of TiO$_2$ hierarchical structures with sensing governed by defects and operating temperature. Furthermore, we report for the first time, to the best of our knowledge selectivity of ethanol driven by modified structural and surface properties of TiO$_2$. 
1.4 Thesis Outline

This thesis is made of eight chapters:

**Chapter One:** Background and rationale on gas sensing

- This chapter focuses on the background and need of study. Furthermore, the body of work that has been done for VOCs and CO sensing using TiO$_2$ nanostructures is highlighted based on the effect of different properties such as structure, particle size, morphology, defects, and surface area and pore dominance.

**Chapter Two:** Tools and techniques for characterization and evaluation of nanosensors

- This chapter is a review of characterization techniques used to evaluate different types of gas sensors. Moreover, the advantages of synthesis methods used in this thesis are discussed.

**Chapter Three:** Fabrication of TiO$_2$ nanotubes based sensors for enhanced CH$_4$ performance induced by notable surface area and acid treatment

- In this chapter TiO$_2$ nanotubes were achieved via microwave assisted hydrothermal method using KOH as reducing agent and after were washed with deionized water, 0.5 and 1.0 M HCl. The effect of acid, morphology, and surface area on sensitivity selectivity was studied.
Chapter Four: Structural transformation and enhanced gas sensing characteristics of TiO\textsubscript{2} nanostructures induced by annealing.

- In this chapter TiO\textsubscript{2} nanostructures were achieved via microwave assisted hydrothermal method using NaOH as reducing agent and after were washed with 1.0 M HCl. The samples were further annealed at 450, 700 and 900 °C for 4 hours to investigate the effect of structure and morphology transformation induced by thermal treatment.

Chapter Five: Designing of vastly sensitive and selective dual-functionality of toluene and xylene gas sensors based on TiO\textsubscript{2} nanowires

- In this chapter three morphologies of TiO\textsubscript{2} nanostructures were synthesized by varying the reaction time. The sensing properties of the nanostructures were investigated at low temperature (< 200 °C) and each morphology showed selectivity towards a different target gas. Moreover, a dual selectivity induced by operating temperature was observed.

Chapter Six: Improved BTEX gas sensing characteristics of thermally treated TiO\textsubscript{2} hierarchical spheres manifested by high-energy \{001\} crystal facets.

- In this chapter the effect of crystal facets of the detection of BTEX was studied using sea-urchin like TiO\textsubscript{2} hierarchical architecture annealed at 300, 500, 700 and 900 °C for 2 hours.
**Chapter Seven:** An approach for realization of astonishing surface area and porosity in Mn doped TiO$_2$ hierarchical nanostructures: selective detection in ethanol Vapour

- In here the sea-urchin like TiO$_2$ hierarchical architecture were doped with manganese to improve sensitivity and selectivity towards VOCs.

**Chapter Eight:** Executive Summary

- Conclusion and remarks
1.5 References


[61] https://ca.news.yahoo.com/air-pollution-costs-global-economy-221508082.html
[Access: 30 January 2020].
CHAPTER 2: Tools and Techniques for Characterization and Evaluation of Nanosensors

2.1 Introduction

Nanosensors are electronic devices designed at nanorange in order to measure slight changes in physical or chemical quantities, analyse and convert the information into a signal [1]. A sensor device consists of a sensor element, which is a fundamental transduction component that transforms one form of energy into another (e.g. a nanostructured material), the detector or signal processing hardware (analogue or digital), and the physical packaging for the sensor itself. The sensing element plays a significant role in the characteristics of the sensor and therefore nanotechnology allows the use of nanomaterials (less than 100 nm), which provide new physical and chemical properties of the material systems through molecular and atomic level manipulation [2]. As a result, nanosensors are smaller and lightweight, with a larger reactive surface area, improved sensitivity, and greater selectivity and improved response times compared to existing sensor technologies [3].

Generally, engineered nanoscale materials exhibit numerous exceptional and anticipated physical characteristics, such as increased catalytic efficiency, optical absorption, reactivity, electrical conductivity, strength and magnetic features, compared to bulk matter of the same composition [2]. The difference is due to the increased chemical reactivity of nanomaterials, provided by their large surface area, compared to bulk and quantum confinement effect at nanoscale [4]. These changes in physiochemical properties can fundamentally enhance the sensor performance related to sensitivity and specificity (selectivity) by orders of magnitude, while offering further opportunities to scale down devices in order to achieve pervasive sensing.
Different kinds of nanosensors exist based on their sensing materials and working principle such as optical sensors, chemical sensors, physical sensors and biosensors, which lead to a wide range of application of sensors such as in industrial, medical, safety and security, aeronautical and automobile, agricultural and environmental sectors [1]. The development of nanosensors involves material preparation, property characterization and device fabrication. Nonetheless, the fabrication of nanosensors is still established on probationary and inaccuracy instead of a know-how strategy that facilitates a coherent design of sensing nanomaterials based on fundamental progressions. The ultimate know-how encompasses a comprehensive understanding of the association of the structures, characteristics, and functionality. A clear link of the synthesis methods and attained nanostructures should also be considered and linked to the sensing performance. Therefore, this chapter discusses the different techniques for characterization of nanomaterial and nanosensor performance evaluation.

2.2 Generic Techniques and Tools for the Characterization of Sensing Materials

Different nanomaterials can be used as sensing elements such as carbon based, metal based, dendrimers and composites. These nanomaterials can be characterized based on two methods, namely, microscopic imaging and spectroscopic analysis. Microscopic methods allow scientists to view the nanostructures and study the shape and size, surface structure, and interparticle interaction, whereas the chemical, structural, and optical properties can be studied using spectroscopic analysis. A detailed description of different characterization techniques used for the study of the nanomaterials is given here.
2.2.1 Electron Microscopy

In order to study the morphology of nanostructures, scientists need tools that can observe the shape and size at high magnification. This is impossible with optical microscopes due to limitation of wavelength; therefore, electron microscopes are used. Electron microscopes use electrons energy instead of photons in order to observe matter at atomic resolution. This is due to the fact that electrons have smaller wavelength, which can give information at nanoscale. Scanning electron microscope (SEM) and transmission electron microscope (TEM) are the two types of microscopy that will be discussed.

2.2.1.1 Scanning Electron Microscope

The SEM technique can be used to study the topography and surface structure as well as the cross-sectional view of the various sensing layers. It provides researchers with an opportunity to know the prepared morphology. This technique has been extensively used to study the surface morphology of various metal oxide–based sensors [5–10]. For instance, Fig. 2.1a displays experimentation of the hybrid cantilever for gas sensor applications, wherein one senses the gas density by the alteration of the resonance frequency of the cantilever [11]. The cantilever employed in this presentation contains a beam sort of tip, which is roughly 30 and 160–200 μm in width and length, respectively. The broader ends of the cantilever beam are altered with zeolite crystals as a gas detector, as observed in Fig. 2.1a. The extra mass stacking by adsorption of the gas molecules are perceived by measuring the variation of the beam resonance frequency. Fig. 2.1b and c displays the SEM micrograph of MQ-3 sensor, based on the Taguchi design [11]. A thick semiconducting metal oxide (SMOX) film is deposited around the alumina ceramic tube employing a platinum
electrode wire on top and a coiled nickel–chromium heating element inside the tube. The layer of the sensing material is porous containing small SnO$_2$ nanoparticles, which are roughly 50 nm in diameter developing into bigger agglomerates [12]. The MiCS-5914 sensor, revealed in Fig. 2.1d-h, displays improved sensing design. It has Si/SiO$_2$ substrate where the four gold–platinum electrodes (two designed for current–voltage measurement and two for sensing heating) and the SMOX-sensing layer are deposited. The higher SEM magnification (Fig. 2.1g and h) of the sensing layer demonstrates that it is made of tungsten nanoplates, which are roughly 100 nm wide and 20 nm thick [13].

### 2.2.1.2 Transmission Electron Microscope

TEM is a major technique in the scientific field, both in physical and biological sciences, due to its phenomenal ability to characterize the internal structure of the nanomaterials used for various applications, to obtain information about the particle size, shape, crystallinity, and interparticle interactions [4, 14, 15]. Several studies have applied TEM analyses to carry out, mostly, ex situ analyses for sensing applications [6, 15–20]. For instance, Fig. 2.2 displays the TEM micrographs of various n-type gas sensors decorated with p-type SMOX, that is, ZnO nanowires decorated with Co$_3$O$_4$ and SnO$_2$ nanowires decorated with Cr$_2$O$_3$ [21–25]. Usually, decoration by discrete p-type SMOX nanostructures on n-type nanowires (NWs) offers several ways to modify their gas-sensing features. Fig. 2.2a displays a schematic diagram of p–n junctions, which form the increase of the electron depletion layer in n-type NWs below the p-type nanoclusters. Recent studies have shown that through in situ TEM analyses, the electron beam (e-beam) exposure induces enhanced disorder activation and noticeable stress relaxation in aluminium and gold films straddling a range of thicknesses (80–400 nm) and grain sizes (50–220 nm). The e-beam prompts irregular
sample necking that strangely relies further on the diameter of the e-beam instead of its intensity [26].

![Image of SEM micrograph of the cantilever, where the end is selectively altered by zeolite microcrystals [11].](image1)

**Fig. 2.** (a) SEM micrograph of the cantilever, where the end is selectively altered by zeolite microcrystals [11], (b and c) SEM image related to the practical parts in MQ-3 and MiCS-5914 sensor, respectively [12], and (d–h) SEM images of a gas sensor structure, displaying profound trenches close to macropores recognized by photo-electrochemical etching (PECE). (d) Cross-section view of the cleaving edge via the macropores array. (e) Top view of lithographically restructured n-Si wafer. (f) Trench and neighbouring macropores array after PECE. (g) Cross-section view of the cleaving edge perpendicular to the trench, where the trench is emphasized by the red dotted line. (h) Cross-section view of the cleaving edge parallel to the trench [13].

2.2.1.3 Transmission Electron Microscope

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With the recent works of Pt-loaded SnO$_2$, scanning transmission electron microscopy (STEM) showed the existence of metallic Pt clusters on the surface of SnO$_2$ as shown in Fig. 2.3. Constantly using STEM to measure on the same area, a solid increase of the metallic Pt clusters represent that they are formed during the measurements [27]. Tofighi et al. [28] carried out STEM on Au, Pd, and Au-Pd nanoparticles decorated on SnO$_2$ after gas-sensing analyses and found that a solid
increase of the metallic clusters is formed during analyses, confirming the analyses of the previous results [27-30].

![Diagram of electron depletion layer schematic in n-type SMOX NWs loaded with p-type SMOX nanoclusters](image)

**Fig. 2.** (a) Electron depletion layer schematic in n-type SMOX NWs loaded with p-type SMOX nanoclusters [21] and (b and c) TEM micrographs of ZnO NWs decorated with Cr$_2$O$_3$ [22]. (d) SnO$_2$ NWs decorated with Cr$_2$O$_3$ [23]. (e and f) ZnO nanowires decorated with Co$_3$O$_4$ [21]. ZnO NWs decorated with (g) NiO [24] and (h) Mn$_3$O$_4$ [25].


### 2.3 Scanning Probe Microscope

The scanning probe microscope (SPM) has become one of the vital techniques for nanomaterial characterization because of its various versatile applications. SPM
enables analysis of surface properties, such as friction, thermal conductivity, mechanical, magnetic, electrical, and adhesion at nanoscale resolution. The analysis can be carried out through two probe–sample interactions, where the probe scans the sample and sample scans the probe at a 100 nm setup. The first SPM was the scanning tunnelling microscope, and advances in technology have allowed specialized SPM, such as the atomic force microscope (AFM), magnetic force microscope, electric force microscope, and can work in different environments such as in ambient condition and ultrahigh vacuum.

Fig. 2. 3: (a) High-angle annular dark-field imaging (HAADF) -STEM images and (b) High-resolution transmission electron microscopy (HR-TEM) image of unused SnO$_2$ loaded with Pt [27]. STEM micrographs of SnO$_2$-1000 loaded with (c) Au (0.1 wt.%), (d) Au-Pd (0.1 wt.%), and (e) Pd (0.1 wt.%), and SnO$_2$-450 loaded with (f) Au (1.0 wt.%), (g) Au-Pd (1.0 wt.%), and
(h) Pd (1.0 wt.%) after sensing analyses at an operating temperature of 300°C [28]. Arrows shown in (c-h) signifies the presence of noble-metal nanoparticles.


Furthermore, in a recent work, STEM, for the first time, was used to study the surface during a catalytic process [31]. According to Bandarenka et al [31] they were able to regulate, in detail, the locations in which the reaction speed, and henceforth the activity of the catalysts, is the best. A distinctive association between the intensity of the noise and surface defects of the catalysts was witnessed. When the number of defects improves, the noise also does, due to more electron flow and therefore more current as well. Therefore, this technique may be suitable for gas-sensing application, since the sensing properties are somehow considered to be defect-dependent.

Among the SPM techniques, AFM is the most popular microscopic-analysis tool, owing to its versatile ability in analysing both conductive and nonconductive matter, and can operate in environments such as ambient, liquid, and vacuum (even ultra-high vacuum, UHV). The details of the operation of the technique are reported in Refs. [32–35]. For instance, this technique has been utilized to probe into the topography of various sensing layers [36]. Fig. 2.4 a and b presents the titanium oxide nanodots (ND) sensors formed by AFM nanolithography. As seen in these AFM topography micrographs, two ND-based gas sensors have different sizes, and their cross-sections are depicted in Fig. 2.4 c and d, respectively [36]. Fig. 2.4 e–g presents the relative-humidity (RH) sensor fabricated employing the definite printed circuit board (PCB) technology. A flawed square shape was attained because of the manual deposition of poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS)
close to the gap region. The PEDOT: PSS layer was disconnected as well once the polyimide film was removed. The AFM descriptions illustrated that the PEDOT: PSS is uniformly deposited on the substrate [37].

Fig. 2. 4: (a and b) AFM topographic micrographs of the two ND sensors. (c and d) Cross-sectional plots of the two NDs [36]. (e) Developed humidity sensor associated with a 5-cent US coin. (f) Optical microscope micrographs of the sensor at the sensing area. (g) 2D AFM topography micrographs of the PEDOT: PSS surface placed on the substrate [37].

2.4 X-Ray Diffraction

Among many spectroscopic methods for nanomaterial characterization, the X-ray diffraction (XRD) technique is a popular and powerful non-destructive tool. It is widely used in studying crystallography including structure, phase, grain size, lattice strain, and lattice parameters of materials. Numerous work has been carried out in the past using an XRD for characterization of nanomaterials used for sensing, mostly ex situ analyses [5, 10, 19–21]. Although some of the in situ analyses do exist, for instance, a recent study carried out in situ XRD analysis to probe into the crystal phase formation of these quasimetallic species at the surface of NiO–WO₃ nanorods heterojunction random networks [38].

2.4.1 Energy-Dispersive X-Ray Spectroscopy

In order to study elemental composition and distribution (mapping) in nanomaterials, energy-dispersive X-ray spectroscopy (EDS) is commonly used. The EDS detector is incorporated in both SEM and TEM systems and the measurements are carried out at high energy. The material surface is bombarded by high-energy electrons, where an electron will be knocked out from the inner shell and will thus leave a vacancy. When the high energy level is transferred to lower levels, an X-ray photon is released as shown in Fig. 2.5a [39] and detected by the EDS detector. The emitted X-rays are assigned according to each element present in the sample and represented in a form of a spectrum or mapping. Fig. 2.5 b and c shows a typical EDS spectrum and mapping of ZnO doped with Au. EDS is a qualitative technique for elemental composition. For quantitative analysis, X-ray photoelectron spectroscopy (XPS) should be used [40].
Fig. 2.5: (a) Schematic of X-ray emission during electron–atom interaction [39]. A typical (b) EDS spectrum and (c) elemental mapping of Au-doped ZnO rose–like hierarchical nanostructures [40].

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2.4.2 X-Ray Photoelectron Spectroscopy

XPS is a versatile technique used for surface analysis of a wide range of nanomaterials such as conducting, insulating and biological materials of up to 10 nm thickness and at 0.1%–1% for all elements excluding H and He [4, 41]. Current developments of the XPS allow in situ analysis. Quantitative information can be obtained from XPS, such as elemental composition, chemical and electronic state of the elements, within the sample (see Fig. 2.6 a). The XPS survey spectra display
peaks centered at specific binding energies, which can be used to identify elemental species due to the fact that each element has a characteristic binding energy.

Moreover, from the position and shape of the high-resolution core-level peaks, one can obtain the chemical/oxidation state, binding energy stoichiometry adsorbed species, and surface contamination of the analyzed sample. Most of the literature of XPS is based on ex situ [5, 6, 42]. Some of the initial ex situ started around the year 1990 by Mockert et al. [43] using lead phthalocyanine–based sensor film. In situ XPS and near-edge X-ray absorption fine-structure spectroscopy techniques were employed to observe the relation of the molecules with the graphene films [44]. The findings showed that before and after exposure of the films, to a NOx mixture, caused sensing of the identical concentrations of the adsorbed NO2 and NO species on the graphene oxide.

XPS analysis for metal oxides was carried out by Shingange et al. [45] for surface-functionalized ZnO nanorods with Au nanoparticles of 2 wt.%. Fig. 2.6b shows the survey spectra confirming the presence of Zn, O, and C for the nanorods. Furthermore, high-resolution core-level spectra were carried out for Zn, Au, and O. Fig. 2.6c shows the core-level spectra for Zn with duplets attributed to Zn 2p1/2 and Zn 2p3/2, suggesting oxidation state of Zn2+. A metallic form of Au was reported with photoelectron peaks at Au 4f7/2 and 4f5/2. O 1s core-level spectra were reported with and deconvoluted into specific peaks, namely, Oa peak on the lowest binding energy, which arises from O2− ions on the wurtzite structure of hexagonal Zn2+ ion array, and Ob peak on the medium binding energy, which is attributed to O2− ions that are in oxygen-deficient regions, which further the intensity quench on the Au–ZnO,
suggesting change in oxygen-related defects. At high binding energy, the O\textsubscript{c} peak is associated with loosely bound chemisorbed species on the surface.

Fig. 2. 6: (a) An illustration of an XPS system showing the setup and information that can be extracted from measurements [46]. (b) XPS survey spectra of the ZnO and Au/ZnO nanorods. (c and d) core-level spectra of Zn 2p peaks, (e and f) O 1s spectra for the ZnO and Au/ZnO nanorods [45].
2.5 Optical Spectroscopy

Optical spectroscopy techniques are mostly used to study optical properties of nanomaterials. Studying and understanding these properties enable the vast application of nanomaterials such as in optical detectors, laser, sensor, phosphor, solar cell, photocatalysis, photoelectrochemistry, and biomedicine imaging [47]. Techniques, such as ultraviolet–visible (UV–Vis) spectroscopy, photoluminescence (PL), and Raman and Fourier-transform infrared (FTIR) spectroscopy, are generally based on detection of light after interacting with matter. Light can be transmitted, absorbed, scattered, or emitted from the sample containing information about the material of interest. Samples can be analysed at solid or liquid state, making these techniques versatile such as semiconductors, degradation of dye under UV lamp. In this section, we report on few optical techniques, experimental setup, and how to carry out analysis utilizing these techniques. It is necessary to indicate that UV–Vis and FTIR spectroscopy are discussed in the following subsection, since they are linked in operando methods.

2.5.1 Photoluminescence Spectroscopy

PL spectroscopy is an important technique in the study of the surface-defect states, donor and acceptor states, and induced trapping states present within the band gap of materials. PL spectroscopy is a type of electromagnetic spectroscopy, which analyses fluorescence and phosphorescence from a sample. This technique measures/detects photons emitted during molecular relaxation (deexcitation) from an excited state, similar to UV–Vis spectroscopy (photon absorption). Fluorescence
refers to the rapid emission of light shortly after photoexciting the material, whereas in phosphorescence, light emission lasts longer (may even last hours), even after photoexcitation has stopped [48, 49].

The nature of the electronic transition produces two types of luminescence, namely, intrinsic and extrinsic [48, 49]. Intrinsic luminescence is produced if influenced by the band-gap structure of the material. There are various kinds of luminescence, such as band-to-band luminescence, exciton luminescence, and cross-luminescence. When an excited electron transition from the valence band recombines with a hole in the conduction band, a band-to-band luminescence is observed, whereas exciton luminescence is due to radiative recombination of bound electron-hole pairs within the band gap of the materials. Cross-luminescence is due to electron-hole recombination in the outermost energy level; however, this occurs when the band-gap energy is greater than the energy difference between the valence band and the outermost energy band. Extrinsic luminescence is due to defect states and impurities (doping) in the host lattice.

Mhlongo et al. [50] studied luminescence properties of pure and transitional metal-doped ZnO nanostructures, and the PL of both is shown in Fig. 2.7. The nanostructures were analysed at 320 nm excitation wavelength and an asymmetric broad emission peak was observed in the low UV–Vis range (350–750 nm). The addition of Cu into ZnO lattice displays significant intensity quench of the violet–blue region, whereas the addition of Co quenched the intensity of the green region. Intensity quench can be attributed to formation of oxygen vacancies and zinc-related defects by addition of Cu and Co, respectively. By deconvolution, authors assigned various emissions to intrinsic and extrinsic transitions (see Ref. [50] for more details).
Fig. 2. 7: (a) PL spectra of undoped and Mn, Co, and Cu-doped ZnO nanostructures obtained at 320 nm excitation wavelength. (b–e) Deconvoluted peaks by Gaussian fit [50].

2.6 Physisorption Analysis

Physisorption is a phenomenon where gas molecules are physically adsorbed (adhere) to a surface at a pressure less than the Vapour pressure and less to no change occurs on the electron structure of the molecule. This is a surface-based process mostly used to investigate surface properties such as surface area and porosity (both pore diameter and volume) [51]. Physisorption is governed by the Van der Waals forces due to the relatively weak attraction between the adsorbate gases and the materials surface. The adsorbed amount is dependent on temperature, pressure and interaction potential between the gas and surface. Usually measurements are carried out at constant temperature therefore the adsorption isotherm is a function of adsorbed weight against pressure at constant temperature. Physisorption analysis favours low temperatures and the absence of strong chemisorption [51, 52].

Nanomaterial are widely known for high surface to volume ratio and a porosity range including micropores (less than 2 nm), mesopores (between 2-50 nm), and macropores (above 50 nm) [52]. Porous nanomaterials have applications such as gas storage by metal organic frameworks (MOFs), gas sensing by semiconductors and filters [53]. Therefore, physisorption analysis is important in order to acquire information about such properties. The Brunauer-Emmett-Teller (BET) theory explains multilayer physisorption on solid surface, where gas molecules are adsorbed on already adsorbed molecules and it is given by equation (2.1):

\[
\frac{1}{V_a(P/P_0 - 1)} = C \frac{(P/P_0)}{V_m C} + \frac{1}{V_m C}
\]  

(2.1)
Where \( V_a \) is the volume of adsorbed gas, \( V_m \) is the volume of gas adsorbed into the monolayer, \( P \) and \( P_0 \) are the equilibrium and saturation pressures of the adsorbate at the temperature of adsorption and \( C \) is a dimensionless constant which is related to the enthalpy of adsorption [53, 54].

Kortidis et al. [55] conducted physisorption analysis using BET system under nitrogen gas for NiO, Mn₃O₄, and CuO nanostructures prepared using a hydrothermal method. The \( \text{N}_2 \) adsorption-desorption isotherms are presented in detail in Fig. 2.8a-c. Fig. 8a presents a type II isotherm showing gradual increase at lower pressure (\( P/P_0 < 0.2 \)). A monolayer form on the knee, as relative pressure increases a multilayer is formed and reaches maximum at higher pressure (\( P/P_0 > 0.7 \)). These are characteristics of a macroporous material which was reported as 52.5 nm with a very low surface area of 1.22 \( \text{m}^2/\text{g} \). An upward shift is observed in Fig. 2.8b with a type IV isotherm which is similar to type II. However, there is a H3 hysteresis loop due to deviation in adsorption and desorption process.

This behaviour is attributed to mesoporosity as reported by authors with the pore diameter of 18.6 nm and surface area of 21.31 \( \text{m}^2/\text{g} \). Interestingly, Fig. 2.8c presents a type I isotherm which is unexpected from BET as it follows Langmuir theory. Type I isotherms represent materials dominated by micropores and high adsorption energy. This leads to maximum adsorption occurring at low relative pressure, a drastic increase and plateau is observed as pressure approached \( P/P_0 \sim 1 \) and thus only monolayer adsorption is measured. These observations are in agreement with the values reported in [55] with the pore diameter and surface area of 1.29 nm and 0.0032 \( \text{m}^2/\text{g} \), respectively.
2.7 Thermal Characterization Techniques

Thermal-analysis techniques allow one to explore various properties of a nanomaterial against time and temperature, such as structural/phase transformation, melting, crystallization point, mass degradation, heat capacity, and thermal expansivity [56]. The nanomaterials can be heated or cooled at a desired environment while varying or keeping temperature constant. One of the advantages of such techniques is that the samples can be analysed at any physical state (solid, liquid, and
gel) and a small amount is needed. Later, we discuss thermal-analysis techniques used for different analysis purposes.

2.7.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) investigates the rate of change in weight of a material as a function of time or temperature. The measurements can be taken under cooling or heating conditions in air, vacuum, or under a flux of inert or flammable gases (nitrogen, helium, argon) [4, 56]. Two modes/settings can be used to carry out analysis, namely, isothermal mode and scanning mode, where measurements are carried out as a function of time and temperature, respectively. Generally, with preparation or synthesis of SMOX nanofiber materials, a polymer is used during electrospinning; therefore, to completely remove the polymer and decompose the metal acetate to an oxide, TGA is used to study the crystallinity of the materials. For instance, considering the study done by Park et al. [57] on pure ZnO nanofibers, using the TGA, findings showed that calcination temperature of >420 °C was required to eliminate the solvent and polymer in order to completely decompose the zinc acetate to the form of a pure ZnO phase.

2.8 Types of Nanosensors

Scientists have been focusing on designing smaller and precise sensors in order to enhance sensitivity, accuracy, and the ability to embed these nanosensors within other systems such as microelectromechanical systems (MEMS) and nanoelectromechanical systems. MEMS can be imbedded in a number of electronic devices, such as home and office appliances, automobiles, smartphones, laptops, and tablets, making MEMS easily available to use. Typically, nanosensors consist of two
components, the receptor and transducer. The receptor transforms physical/chemical input information into a form that can be measured by the transducer. The transducer converts the information into a functional analytical signal. Therefore, sensors can be classified based on the receptor function (physical, chemical, and biochemical), based on transducer function (optical, electrical, electrochemical, etc.). Other classifications are based on the type of sensing material (polymer, inorganic, carbon nanotubes, and metal oxides), field of application (medical, environmental), and fabrication methods (screen printing, vapour deposition, electrospinning).

2.8.1 Mechanical Sensors

In the case of a mechanical sensor, the signal is due to physical changes such as mass, pressure, velocity, and displacement. Among these sensors, there are motion-based sensors that depend mainly on Newton’s law of motion to transduce any measurands, while some sensors are based on changes in vibrations, caused by the presence/change in mass, in order to detect measurands such as in an oscillating cantilever [58, 59]. Such sensors can be used in medical monitoring for patients with heart malfunction where the physical movement of a patient’s chest can be correlated to the heart rate [60]. Some mechanical sensors (pressure sensor) measure change in resistance (piezoresistive effect) or electricity (piezoelectric effect) of a given material, in a presence of strain, as a result of tension or compression. The mostly used materials for piezoresistive and piezoelectric transducers are crystalline semiconductors and quartz, respectively [59].
2.8.2 Thermal Sensors

These types of sensors have transducers that measure changes in electrical parameters with temperature. For example, in a thermocouple, two metal wires, in direct contact with two or more junctions with receptor, measures changes in temperature and converts to DC voltage [61]. The linear relationship between temperature difference and output voltage makes the thermocouple a good sensor at higher temperatures. However, sensitivity decreases at lower temperatures, high noise ratio, and the need of reference junction for calibration are some of the disadvantages of a thermocouple. A thermistor is a temperature-sensitive resistor, which nonlinearly decreases in resistance as the temperature increases. This sensor is mostly used for low temperatures to prevent self-heating by passing minimum current.

2.8.3 Optical Sensors

Optical sensors have the ability to detect light, typically at a specific range of the electromagnetic spectrum (ultraviolet, visible, and infrared). The sensor detects either wavelength, frequency, or polarization of light and converts it into electric signal due to photoelectric effect. The presence of an analyte causes change in absorbance, luminescence, or refractive index of the material resulting in a change in the output signal [58]. Vacuum, gas tube photosensors, photovoltaic solar cells, semiconductor light sensor (photodiode), and infrared sensors are some of the mostly used sensors. Thermoelectric optical sensors convert light to heat by absorbing the incident radiation and producing a temperature output related to light intensity.
2.8.4 Biosensors

Biosensors are an extension of chemical sensors where the receptor is a biomaterial. The bioreceptor detects the target chemical substance and the transducer converts it into an electrical signal. Biomolecules, such as DNA and antibodies, are mostly used as bioreceptors. Biosensor devices are carefully designed and developed to be implanted inside the body as health monitors, and into wearable devices. Biosensors are widely used in blood glucose analysis for diabetic patients [62] and in capacitor-based immunosensors for the determination of human immunoglobulin G antibody [63].

2.8.5 Chemical Sensors

A chemical sensor is a device that transforms chemical information into an analytical signal. The chemical interacts with the receptor as the concentration of the analyte (either liquid, gas, or volatile substance) increases. The chemical or physical changes measured by the transducer are then presented in a form of a useful electrical signal. Chemiresistive gas sensors based on SMOX are widely used due to the advantages they possess such as excellent sensitivity, cost effectiveness, easy synthesis and integration, and simple sensing mechanism. When the analyte gas interacts with the SMOX surface, there is a change in charge carrier concentration of the material and the output signal is observed as an electrical resistance. Among its many applications, chemiresistive gas sensors are used for monitoring toxic and explosive gases in mines such as CO and CH$_4$, respectively [64, 65].

Another example of chemical sensors based on physical interaction is the infrared gas sensor. The sensing mechanism is based on the changes in vibrational
frequency of the gas molecules as they interact with the incident infrared radiation, and the output signal is observed as change in temperature with the gas concentration. Fig. 2.9 shows the micrographs of different sensors, such as sensor temperature, acceleration sensor, and UV sensor. As shown in Fig. 2.9a–c, the device contains two sheets. The details of how the device was fabricated are discussed in Ref. [61]. It should be pointed out that the disposable sensing element for straight interaction with the skin involves a three-axis acceleration, an ECG sensor, and temperature sensors with a silver interconnection. They are all printed on a not-reusable polyethylene terephthalate sheet with a kirigami structure [22], permitting it to easily stretch on the human body [61].

2.9 Evaluation of Nanosensors

2.9.1 Tools and Techniques for the Evaluation of Nanosensor Performance

In order to evaluate the performance of a nanosensor system, a relevant performance criterion should be chosen based on the specific application. Some of these criteria include the following:

- *Response and recovery times* are defined as the essential time taken by the sensor to achieve 90% of its highest response once the target gas is injected, and the time needed by the sensor to obtain about 10% of its original resistance after the introduction of synthetic air in the chamber, respectively (see Fig. 2.10a).

- *Detection limit or Resolution* is considered as the least physical change, which can be detected by the sensor.
Fig. 2. 9: Representative of (a) the entire structure of the sensor device, which involves the disposable and recyclable constituents, (b) EGaIn and Ag contact area among the sheets, and (c) three-axis acceleration sensor. (d) Micrograph of the invented device. Optical microscopy micrographs displaying the carbon nanotube-TFT designs utilized in (e) the ultraviolet sensor and (F) temperature sensor. (g) AFM micrograph of the carbon-nanotube network film employed for the TFT channel. (h) Device micrograph, which is emphasized on the EGaIn–Ag contact area among the sheets. (I) IDS–VGS and (J) IDS–VDS features of a CNT–TFT characteristic of the devices. (K) EGaIn–Ag contact graph of electrical resistance versus temperature. The insert associates I–V features at temperatures of 25.3°C and 55.6°C [61].

- **Sensitivity** is the ratio of sensor output to the variation in the value of the measured, (see Fig. 2.10b).

- **Repeatability** is the capability of a sensor to show the same value on the independent application of the same input (see Fig. 2.11c).

- **Selectivity** is related to properties that define whether a sensor can selectively respond to a number of analytes or even precisely (discriminate) to a particular analyte (see Fig. 2.11b).

- **Working temperature** is usually the temperature at which maximum response is observed (see Fig. 2.11a).

- **Reproducibility** denotes the nearness of agreement in results attained from identical tests conducted under similar conditions of measurements (see Fig. 2.11d).

- **Dynamic range** is the total range of the sensor from minimum to maximum. It is the ratio of the largest and the smallest possible values of a changeable quantity. It is typically measured as a ratio or as a base-10 or base-2 logarithmic value.

- **Robustness** relatively insensitive to temperature, electrical noise, physical shock, vibration, etc.

- **Usable lifetime (stability)** is the period of time over which the sensor will continuously operate.

- **Speed and ease** of use by nontechnical personnel.
Fig. 2. 10: (a) Dynamic response–recovery behaviour and (b) Responses versus ethanol concentration for In$_2$O$_3$ gas sensors at 185 °C [66].

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2.9.2 Specialized Techniques and Tools for the Characterization of Nanosensors

Although several nanosensors have been mentioned and discussed, we will only focus on techniques used to characterize the gas sensors. With the purpose of comprehending the gas-sensing mechanism of SMOX nanosensors, in operando techniques that have been developed. These in operando techniques allow for secondary analyses, for instance, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), to take place during gas-sensing analyses.
Fig. 2. 11: (a) Response versus temperature graph for the ZnO nanostructures at 40 ppm H₂S for determining working temperature [67]. (b) Selectivity investigation of gas sensors exposed to different gases at constant concentration (40 ppm) [55]. (c) Repeatability measurements of ZnO nanostructures toward 20 and 40 ppm H₂S concentrations kept constant per four cycles [67] and (d) stability test of TiO₂ nanostructures toward 60 ppm CH₄ measured over 30 days [65].

2.9.2.1 Ex situ, in situ, and operando apparatus

The expressions: in situ, ex situ, and operando are extensively used to differentiate methods that are utilized to probe into functional materials by the experimental settings concerning their counterpart with genuine working conditions. These terms “in situ, ex situ,” and “operando” are derived from the heterogeneous catalysis field [68–72], wherein in situ spectroscopy signifies instrumentations and measurements for catalyst analysed during reaction environments [69]. Ex situ experiments comprise all kinds of materials, which are analyzed in any environment, such as temperature, pressure, and atmospheric composition, which are not associated with the real operation settings of the resultant sensing material. Whereas, the tenure operando spectroscopy was announced only lately to define instrumentations, which are capable of analyzing a working catalyst. The use of operando to probe into the gas sensors during operation, employing spectroscopic techniques, arose in the late 1990s [73–76].

Currently, the operando methods for gas sensor investigation compromise numerous spectroscopic and electrical characterization systems, as shown in the schematic later (Fig. 2.12), which will be discussed in the section later. The coupling of paired tools in the characterization of sensing layers during operating settings is a very influential instrument for a precise and in-depth understanding of the system probed. Specifically, X-ray absorption spectroscopy (XAS) combined with DRIFTS and mass spectroscopy (MS) comprise a dominant combination as XAS characterizes the focal elements of the material system, choosing the absorption edge, and DRIFTS observes the surface adsorbates, while MS allows product identification and quantification. The spectroscopy methods include Raman [76, 77], FTIR [78–80], UV–Vis [81], X-ray absorption and emission spectroscopies [82–84], and DRIFTS [77, 79,
While, electrical techniques comprise Kelvin probe setup [88, 89], AC impedance spectroscopy [80, 90], and Hall effect measurements [91, 92]. Further understanding on operando studies is provided in Refs. [73–75].

2.9.2.2 Operando diffuse reflectance infrared Fourier-transform spectroscopy

DRIFTS is one of the most appropriate operando spectroscopic methods for the analyses of the metallic centers, detection of surface adsorbates, and quantification of reaction products, which are accomplished during gas sensing. Generally, DRIFT spectra illustrate the similar qualitative characteristics observed in transmission spectra, although the quantifiable investigation of DRIFT spectra entails the usage of the Kubelka–Munk theory for diffuse reflectance spectroscopy [93, 94]. The original work carried out on operando techniques, on gas sensing, was in 1995 by Benitez et al. [95] using the DRIFTS methods with real-time resistance measurements on CdGeON sensors that operated at ~200 °C under atmospheric pressure, exposed to various concentrations of nitrogen. However, considering others such Lenaerts et al. [96], Baraton et al. [97–102], Pohle et al. [103–105], Harbeck et al. [106,107], Weimar et al. [108–110], and Hess et al. [76] huge progress has been achieved using DRIFTS.
Fig. 2. 12: Collection of existing in situ and operando techniques used to characterize SMOx gas sensors, which compromise various spectroscopic, diffractive, and electrical measurements [75].

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Fig. 2.13a displays DRIFTS bands of the Pt-doped SnO$_2$ materials disclosing a resilient overall surface reduction that includes metal-oxygen species allocated to SnO$_2$ and to the Pt oxide clusters. This enhanced surface reduction during the CO exposure, which suggests an active gas reception and consequently results in substantial sensor signals. The recent work of Barsan and Weimar et al. [90] showed that the pure SnO$_2$ bands associated with surface oxygen and hydroxyl groups reduced, while the Au nanoparticle–doped SnO$_2$ nanostructures revealed the same behaviour, indicating that CO gas reception occurs on the surface of SnO$_2$. However, no changes were noticed in the SnO$_2$ surface for Au-Pd and Pd nanoparticles (NP)–
loaded samples, denoting that gas reception does not occur on the surface of SnO$_2$, and is moved to the Au-Pd or Pd NPs in 10% RH (see Fig. 2.13).

Fig. 2.13: (a) DRIFT spectra of doped SnO$_2$ with Pt exposed to 300 ppm CO in dry (red) and 10% RH at 25°C (blue). The temperature of the sensor was set at 300°C. Operando DRIFT bands of SnO$_2$-1000 structure exposed to 50 ppm CO in dry air, shown in the upper images and in 10% RH shown in the images at 300°C [28].
2.9.2.3 Ultraviolet–Visible Spectroscopy

The UV–Vis spectroscopy can be used to analyze different materials, such as metal oxides, organic and inorganic bioconjugates, used for different applications such as gas sensing and catalysis. The technique is based on the absorption of the UV region (200–400 nm) and visible region (400–800 nm) of the electromagnetic radiation by molecular species. The absorbed energy results in the excitation of ground state electrons. The sample can be in solid form or solution form mostly dissolved in water or ethanol. In that case the spectrum for ethanol alone should be used and subtracted as a reference. Measurements can be made in transmittance, absorbance and reflectance. Reflectance/transmittance could be attributed to stronger optical absorption.

In the case of an inorganic material such as phosphors and semiconductors, as shown by Ogugua et al. [111], the energy band gap \( (E_g) \) can be estimated from plotting the intensity of reflected light against wavelength from which absorption spectra can be obtained using:

\[
F(R) = \frac{(1-R)^2}{2R}
\]  

(2.2)

The Kubelka–Munk as shown in equation (2.2), \( R \) is the reflectance of the material and \( F(R) \) is proportional to absorption coefficient \( \alpha \) in the equation:

\[
(\alpha h\nu)^{1/n} = A(h\nu - E_g)
\]  

(2.3)

Where \( n = 1/2, 3/2, 2, 3 \) dependent on the transition and \( A \) is proportionality constant which is independent of the material chemical composition therefore the Tauc plot will
be given by equation 2.2. In this case the band gap values were extrapolated from the linear part of the expression

\[(F(R)hv)^{1/n} = A(hv - E_g)\]  

(2.4)

If the measurements are taken in absorbance mode one can skip equation 2.2 and use 2.3 directly for band gap estimation [111].

2.9.2.4 X-Ray Absorption Spectroscopy

The realization of X-rays has induced them to be an essential analysis technique to probe into the structure and composition of solids. Currently, X-ray-related techniques comprise different techniques based on diffraction, scattering, absorption, or emission of X-rays. XAS, extended X-ray absorption fine structure, and X-ray absorption near-edge structure have been employed to analyze the structure and the electronic features of the nanomaterials, and as a result, have been considered to be a perfect system for operando investigation [112]. XAS has also been found to be an appropriate characterization tool in gas-sensing nanomaterials for noble-metal loadings (Pt, Au) to study the oxidation states of elements and structural properties [113]. Although XAS has been employed to study several nanomaterials, however, limited work in in-situ or operando has been carried out. For instance, in-situ XAS, employing the high energy resolution fluorescence detection mode, was applied to a monolayer Pt/ Rh (111) sample.

2.9.2.5 Operando Raman and Surface-Enhanced Raman Spectroscopy studies (SERS)

Although significant results exist for ex-situ Raman analyses, some extensive analyses have been performed on in-situ and operando Raman analyses. For
instance, Sanze *et al.* [76, 77]. Through operando, revealed that when In$_2$O$_3$ is tested toward ethanol (EtOH), the sensor response can be openly associated with the nature of the adsorbates, the existence of surface hydroxyl groups, and the oxidation state of In$_2$O$_3$ [76,77]. In addition, Sanze *et al.* [77] indicated through operando Raman (i.e., once changing from synthetic air to 250 ppm EtOH at 190 °C) the vanishing of hydroxyl groups around 3639 and 3656 cm$^{-1}$ (related to O–H stretch) is supplemented by the creation of acetate at 871 cm$^{-1}$, related to C–C stretch and 2935 cm$^{-1}$ related to C–H stretch.

When exposed to 250 ppm EtOH in air, an intense reversible alteration, linked to the modification in the Ag state in the course of EtOH sensing, was observed at the low frequency. The intense intensity-enhancement in the In$_2$O$_3$ phonons, in Fig. 2.14, is ascribed to the EtOH surface reduction of oxidized to metallic Ag, resulting in a Raman improvement established on SERS. This allows the metal oxidation state to be revealed during operating environment of the gas sensor. Furthermore, through operando Raman and IR spectroscopy, Sanze *et al.* [77] showed that at an operating temperature of 190°C toward acetaldehyde (CH$_3$CHO) in N$_2$, the In$_2$O$_3$ is reduced and surface acetate is created by hydroxyl group reaction with adsorbed CH$_3$CHO (Fig. 2.14b) (see Ref. [77] for more details).

### 2.9.2.6 Mössbauer Spectroscopy

Mössbauer spectroscopy has been used previously to probe into the oxidation states as well as to trail the reaction kinetics of sensing nanostructures. Mössbauer spectroscopy can only be applied to a limited number of elements, which display the Mössbauer Effect, such as $^{57}$Fe, $^{119}$Sn, and $^{182}$W isotopes.
Fig. 2. 14: (a) Operando Raman spectra of 1 wt.% Ag/In$_2$O$_3$-based sensor toward EtOH at 190°C. (b) Temporal relationship of IR, Raman, and sensor resistance data of the operando experiments in exposure of CH$_3$CHO to In$_2$O$_3$ [77].

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Therefore, studies may be accomplished on Fe$_2$O$_3$, SnO$_2$, and WO$_3$; thus for Mössbauer Effect application, only materials containing the isotopes should be considered for gas-sensing application. Although, only limited work exists on in-situ Mössbauer spectroscopy, studies have also shown the importance of a combination of Mössbauer spectroscopy with other techniques, for instance HR-TEM and electron diffraction have facilitated the core characteristics to be expansively analysed. Moreover, few studies have performed in-situ transmission Mössbauer spectroscopic examinations on SnO$_2$ powders [114]. The in-situ studies on ($^{119}$Sn) were extracted at 173 °C using the conversion electron Mössbauer spectroscopy studies of sensors [115–117].

2.9.2.7 Electron Paramagnetic Resonance Spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy is valuable instrumentation for gas-sensing analysis [118–121]. It is used to detect the superoxide radical, which forms owing to the transfer of electrons, trapped in oxygen vacancies (V$_O$), to the adsorbed oxygen molecules in the SnO$_2$ surface and atomic adsorbed oxygen (O$^-$), also as paramagnetic V$_O$, which are alleged to be significant species in the gas response of SMOX. Nonetheless, the paramagnetic species are not observable during operando [122,123]. Previous studies have carried out EPR ex-situ analyses on several SMOX to detect superoxide radical, V$_O$, and O$^-$ and link these properties with the gas-sensing performances [52,118–121,124]. However, with regard to catalysis, differentiation between the synergetic and direct mechanisms, which may be appropriate in redox reactions and their comparative contributions, is executed through in-situ EPR spectroscopic investigations that facilitate the classification of the valence states of the metal ions/atoms.
2.9.2.8 Electrical Characterization

The comprehensive understanding of the effect of noble and transitional metal dopants, surface additives as well as the mixed oxide heterostructure, on the electrical characteristics of gas-sensing layers, is required for getting a deeper insight in the link between the sensor behaviour and its chemical composition, the structure, and functionality.

2.9.2.9 Hall Effect Measurements

The Hall Effect measurement system has been used to characterize both the free carrier concentration and Hall mobility, and in this manner, to differentiate between a thermally activated mobility from an activated carrier density. In addition, the association of Hall Effect and resistivity measurements has been reported as an influential way of obtaining information correlated to the mechanisms of electrical conduction in polycrystalline SMOX layers [91,125,126]. This is the foundation to understanding semiconductor gas sensors. Detailed information related to this technique could be found in Ref. [91].

2.9.2.10 Kelvin Probe Microscopy and Work Function Measurements

Kelvin probe microscopy (KPM) technique is used to obtain a profound quantifiable comprehension of the sensing mechanism of SMOX. KPM is considered as a dual-pass AFM technique [127–129]. Typically, during the first line scan, the AFM tip obtains the sample topography profile in tapping mode. During the second line scan, the tip moves at a pre-set height directly above the surface of the sample. In the succeeding pass the cantilever of the AFM is electrically excited by applying a direct current (DC) voltage $V_{DC}$ together with an alternating current (AC) element with an
amplitude $V_{AC}=1$ V and frequency that is equal to the cantilever oscillation resonant frequency. The DC element is regulated by a feedback loop in a way that the cantilever amplitude at $\omega_0$ equals zero. In these circumstances the DC tip voltage $V_{DC}$ equals the surface potential $\Phi(x,y)$ underneath the tip [128,129]. Consequently, by mapping $V_{DC}$ against the tip position, the KPM appearance accounts the surface potential distribution $\Phi(x,y)$ alongside the surface of the sample by the means of very high spatial resolution.

KPM has previously been used by several researchers to probe into the surface potential and local charge distribution of sensing films. For instance, in a previous study [130], the authors combined the electronic transport together with KPM experimental to investigate differences in the surface potential and local charge distribution for reduced graphene oxide (RGO) sensor once exposed to acetone and ammonia. Some representative AFM-topography micrographs of RGO sample, comprising the two electrodes and the KPM setup drawing, are depicted in Fig. 2.15a and b. The inset of Fig. 2.15a reveals the KPM analyses carried on the RGO regions amid the two electrodes as dented by the red dotted square. In Fig. 2.15c–e the sample was exposed to dry air, acetone, and dry air again. While the graphs in Fig. 2.15f–h correspond to the surface potential [130]. With regard to work-function measurements for sensing, they can be carried out using a KPM setup. The measured signal represents the difference in the work function between the oscillating gold paddle and the sensing layer. The gold paddle must be insensitive to the analyte used, so that the signal represents the changes of the sample electronic structure under investigation [131,132].
Fig. 2.15: (a) AFM topography micrograph of an RGO sensing device. The red dotted square streaks the area between the electrodes employed for the KPM analyses and is depicted in the magnified image in the inset. From the inset, blue lines highlight the location of the Au electrodes. (b) KPM representations showing the coinciding RGO platelets gathered between the Au electrodes. Potential mappings of an RGO sensor once exposed to (c) dry air, (d), acetone, and (e) dry air. Note that the image of (d) was extracted while the sample was exposed to acetone (see details in Ref. [130]), while the image in (e) was extracted when the sample was exposed to dry air for 15 min, (f-h) Surface potential histograms of the micrographs depicted in (c-e) [130].

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2.9.2.11 Alternating Current Impedance Spectroscopy

The DC analyses provide information on the global sensor response, while AC impedance analyses provide the understanding of the nature of the conduction processes and the mechanism of gas/solid interactions [133]. Previous studies have used the AC impedance spectroscopy to investigate the transient response of a WO₃ gas sensor to O₃ where the analyses were carried in dry air and in the presence of gas. They found that the impedance evolution is different in the presence of gas than under dry air without gas. Further details on the impedance analyses on gas sensing have been provided in Ref. [73].

2.10 Conclusion

The application of various analytical techniques for gas-sensing characterization ranging from ex-situ, in-situ and operando studies were evaluated and it was found that employing of corresponding techniques in a multiprobe method permits investigation of various material features and processes that exists in similar experiments. A clear link of the synthesis methods and attained nanostructures should also be considered and linked to the sensing performance. Although the understanding of sensing mechanism is influenced by more than one factor the usage of proper experimental work and advanced characterization techniques makes it possible close the gap between the theory and applications.
2.11 References


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CHAPTER 3: Fabrication of TiO₂ Nanotubes Based Sensors for Enhanced CH₄ Performance Induced by Notable Surface Area and Acid Treatment

Abstract

We report on the notable surface area and gas sensing properties of TiO₂ nanotubes synthesized following a microwave assisted hydrothermal method followed by washing with various concentrations of Hydrochloric acid (HCl) and distilled water (DW). The sample washed with DW only had narrow nanotubes in diameter. Structural analyses showed that the TiO₂ nanotubes are made of 55 % of anatase phase, while the 45 % is associated to rutile phase. Moreover, at higher HCl concentration, increased crystallite sizes and nanotubes diameter were observed from the X-ray diffraction and scanning electron microscopy analyses, respectively. A remarkable increase in surface area of 1375.238 m²/g was observed with a change in morphology from nanoparticles to nanotubes (i.e. the sample washed with 1.0 M HCl). The gas sensing properties, such as response, sensitivity and selectivity were tested towards CH₄, NH₃, CO and NO₂ gases at different operating temperatures. The TiO₂ nanotubes washed with 1.0M HCl presented higher selectivity and sensitivity (0.62 ppm⁻¹) towards CH₄ gas at 23 °C. This was attributed to the exceptionally high surface area and crystallinity provided by the one dimensional nanotubes acting as nanochannels for gas diffusion. The improved sensitivity and selectivity at room temperature for the 1.0M HCl treated sample suggest that it could be applied as a low-power consumption CH₄ gas sensor. The gas sensing mechanism is also discussed in detail.
3.1. Introduction

Monitoring combustible gases in the working environment is essential to prevent incidents such as explosions during production and mining [1]. Nanostructured semiconducting metal oxides (SMO), such as SnO$_2$, ZnO, V$_2$O$_5$, CuO and TiO$_2$ are widely used as chemoresistive gas sensors, due to the change in resistance when in contact with the target gases [1-5]. TiO$_2$ is known for its high photocatalytic activity and widely used in water splitting. However, because of its high stability, nontoxicity, corrosion resistance and affordability [4], TiO$_2$ has attracted a lot of researcher’s attention in gas sensing application for detection of gases, such as hydrogen, ammonia and nitrogen dioxide [4-6].

One dimensional (1-D) nanostructures (nanotubes, nanorods, nanobelts, nanowires, etc.) have attracted great attention due to their application in vast nanotechnology devices, such as solar cells, spintronics and gas sensors to name a few [6-8]. 1-D nanostructures provide a path way for electron transportation and high surface to volume ratio, allowing a high rate of gas adsorption and diffusion on the entire material [3-5]. Studies have shown that the sensitivity of the gas sensing materials is dependent on the defects states (structural vacancies, surface state and oxygen adsorption sites). TiO$_2$ nanostructures containing high concentration of vacancy type defect demonstrate improved gas sensing performances [4]. For instance, Tshabalala et al. [4] demonstrated an enhanced sensitivity in TiO$_2$ samples synthesised following the microwave assisted hydrothermal method and attributed the improvement to the high presence of Ti$^{3+}$ oxygen vacancies. Among the gases, methane (CH$_4$) is a colourless, odourless and flammable gas, which can cause explosion at high concentrations in air. It is also a key element of nature gas and it has been extensively
utilized as a source of energy for domestic and industrial applications [9]. Usually CH$_4$ is not harmful; however, it can cause asphyxiation by reducing the percentage of O$_2$ in a sealed room. This may explain the reason why the patient loses consciousness [10]. Therefore, recognizing an efficient detection and monitoring of CH$_4$ through modest and convenient approach is very vital to inhibit health risks and safeguard the safety of industrial workers and the worldwide population [11]. Most of the metal oxide based sensors operate at high temperature, which result in unwarranted power consumption and limited lifetime of the gas sensor devices [12, 13]. As a result, developing CH$_4$ sensors based on semiconductor metal oxide (SMO) materials is vital to minimize fabrication costs and maintain long-term stability. Furthermore, limited studies exist that report on the remarkable surface area higher than 1375.238 m$^2$/g in SMO based sensors, more specifically TiO$_2$. Therefore, herein, we report on the synthesis of TiO$_2$ nanotubes with the significant surface area, and high sensitivity towards CH$_4$ gas at room temperature prepared using the hydrothermal method. Moreover, it is explained in detail that the annealing temperature affects the surface area, defect states and sensing capabilities of the TiO$_2$ nanostructures.

3.2. Experimental Details

3.2.1. Synthesis Procedure

TiO$_2$ nanotubes were synthesized following hydrothermal method. A commercial P25 Degussa TiO$_2$ was dispersed in a potassium hydroxide (KOH, 85% purity) solution and stirred to maintain homogeneity. The mixture was then subjected to microwave irradiation (Perkin-Elmer/Anton Paar Multiwave 3000) for 10 min at a power of 150 W. Subsequently, it was cooled to room temperature and then washed
with distilled water (DW), 0.5 M and 1.0 M hydrochloric acid (HCl, 37% purity)) molarity until pH 7. Note that the HCl treated samples were initially washed with various HCl concentrations, thereafter with DW as to reach the desired pH. The mixture was centrifuged and dried at 120 °C for 14 hrs. The samples were further annealed at 450 °C. The commercial TiO$_2$ (P25 Degussa) used as received was labelled as S1, while those washed with DW, 0.5 M HCl and 1.0 M HCl were labelled as S2, S3 and S4, respectively.

3.2.2. Characterization

The surface morphology of the TiO$_2$ nanostructures were carried out using scanning electron microscopy equipped with energy dispersive x-ray spectroscopy (Zeiss Auriga). Structural analysis was carried out using a Panalytical X’ pert Pro PW 3040/60 XRD equipped with a Cu $K_\alpha$ ($\lambda = 0.154056$ nm) monochromatic radiation source and for Transmission electron microscope (TEM) analysis, TiO$_2$ powders were placed on holey-carbon-coated Cu grids from ethanol suspensions and evaluated using a JOEL HR-TEM operated at 200 kV. The specific surface area and the pore volume of the samples were measured by nitrogen (N$_2$) physisorption using a Micromeritics TRISTAR 3000. The photoluminescence (PL) measurements were characterized using a Horiba Jobin-Yvon NanoLog spectrometer at an excitation wavelength of 325 nm.

3.2.3. Gas Sensing Fabrication and Testing

First, gas sensors were developed using the same procedure as in our previous work [4]. Where the TiO$_2$ powder was dispersed in ethanol and drop-coated on alumina substrates (size: 2 mm × 0.5 mm) containing two Pt electrodes (on their top
surfaces) and a micro-heater (on its bottom surface). The response of the sensors was examined by monitoring the variation of the electrical resistance of the sensors using a commercial KSGAS6S gas sensing station (purchased from KENOSISTEC, Italy). The desired concentrations were controlled by changing the mixing ratio of the CO, CH₄, NH₃ and NO₂ gases and dry synthetic air. The gas concentrations ranged from 5 to 100 ppm, while the operating temperatures of the sensors were set at 23, 100, 150, 200 and 250 °C by adjusting the voltages. The response-recovery times were estimated as follows: \( t_{\text{res}} \) or \( t_{\text{rec}} = t_{90\%\text{total}} - t_{\text{initial}} \), where the response time \( t_{\text{res}} \) denotes the time required to obtain 90% variation in resistance when exposed to gas and recovery times \( t_{\text{rec}} \) denotes the time needed to reach 90% of the current variation in air. The gas sensing response was calculated using the following formula:

\[
\text{Response} = \frac{R_a}{R_g} \text{ for reducing gas} \quad \text{and} \quad \text{Response} = \frac{R_g}{R_a} \text{ for oxidizing gas}
\]

where \( R_a \) is the resistance in air and \( R_g \) is the resistance during test gas exposure.

### 3.3. Results and Discussion

#### 3.3.1. Surface Morphology Analysis

Fig. 1 shows the SEM micrographs of TiO₂ nanostructures. As depicted in Fig. 1a, the P25 Degussa (i.e. S1) shows nanoparticles with an average diameter of 20-30 nm. After hydrothermal process and washing using DW, the nanotubes and some nanoparticles are observed on the surface (see Fig. 1b). However, after washing with 0.5 M and 1.0 M HCl, the nanotubes that are entangled together are observed across the surface, as shown in Fig. 1(c and d). The energy dispersive x-ray spectroscopy
(EDX) spectrum in Fig. 1e confirms that the prepared TiO₂ contains no impurities, only Ti and O elements are observed.

Fig. 3. 1: SEM micrographs of the TiO₂ nanostructures (a) S1, (b) S2, (c) S3 and (d) S4. Note (e) corresponds to EDX spectrum of S4.
3.3.2. Structural Analysis

XRD patterns of the TiO$_2$ nanostructures in Fig. 2a display a mixture of anatase and rutile phase with anatase phase dominating ≥ 60%. The diffraction peaks at angle of $2\theta = 25.32^\circ$, $37.90^\circ$, $48.22^\circ$, $53.94^\circ$, and $62.75^\circ$, corresponding to an anatase phase crystallographic structure (TiO$_2$, JCPDS card #84-1286), with the presence of rutile phase at $27.50^\circ$, $36.04^\circ$, and $54.41^\circ$ (TiO$_2$, JCPDS card #75-1753), were indexed. After hydrothermal treatment, narrow peaks were observed and were attributed to the growth in crystallite sizes (see Fig. 2b), while the lattice strain decreased. The crystallite sizes were calculated using Williamson Hall [14]. Moreover, at higher HCl concentration (S3 and S4), the rutile 110 peak at $27.50^\circ$ intensified and a growth in diameter of the nanotubes was observed. We should point out that the percentage of anatase and rutile phase in TiO$_2$ from the XRD spectra were calculated using an empirical equation used by Depero et al. [15]:

$$W_R = \frac{1}{1 + \left(1.26 \frac{I_R}{I_A}\right)^{-1}}$$  \[1\]

where $W_R$ is the fraction of rutile phase, $I_R$ is the most intense rutile peak and $I_A$ is the most intense anatase peak.
Fig. 3. 2: (a) XRD patterns of TiO$_2$ nanostructures and (b) correlation of crystallite sizes and lattice strain of samples S1-S4.

TEM images display a change in morphology from nanoparticles to nanotubes after hydrothermal treatment, as seen in Fig. 3(a-i). The S1 sample in Fig. 3(a and b) shows nanoparticles in the range of 15 nm in diameter, while the SAED patterns (Fig. 3c) shows that the dispersion is monocrystalline. Indexing of the main rings are in agreement with the presence of anatase phase with crystal planes of (101), (004), (200), (105) and (204), and are in relation with the XRD analyses (Fig. 2a) [16]. At 0.5 acid treatment (i.e. S3), the nanoparticles transform to “nanotube-like” structure. The SAED patterns of the S3 show slightly diffused Debye ring showing (101) and (004) planes, probably due to a contribution from both nanoparticles and nanotubes. By introducing a 1.0 M HCl (S4), more nanotubes were formed with an average diameter of 16.3 nm. The SAED patterns demonstrated that the nanotubes are mono-crystalline with dominance of {110} facets [17].
Fig. 3. HR-TEM micrographs of TiO$_2$ samples (a-c) S1 nanoparticles, (d-f) TiO$_2$ nanoparticles with nanotubes S3, and (g-i) S4 nanotubes after hydrothermal treatment.
3.3.3. Surface analysis

Nitrogen adsorption-desorption isotherms of TiO$_2$ nanotubes synthesized via hydrothermal method and washed with DW, and various concentrations of HCl are shown in Fig. 4. All the samples in Fig. 4 display a type IV hysteresis loop with mesoporous structure and a broadening towards higher relative pressure. However, for S3 a limited adsorption (quick saturation) at high relative pressure was observed, which can be attributed to capillary condensation. The Brunauer, Emmett and Teller (BET) surface area ($S_{\text{BET}}$) increases with a change in morphology from nanoparticles (S1) to nanotubes (S2-S4) after hydrothermal treatment. S1 sample shows a $S_{\text{BET}}$ of 40.512 ± 0.051 m$^2$/g. Interestingly, a remarkable increase in $S_{\text{BET}}$ is observed for S2, S3 and S4 to 184.628 ± 0.402, 120.266 ± 0.143 and 1375.238 ± 53.395 m$^2$/g, respectively. It is important to mention that a $S_{\text{BET}}$ as high as 1375.238 ± 53.395 m$^2$/g has never been reported before for pure TiO$_2$ nanostructures. Such behaviour was due to the hollow tubular structure providing a larger surface area (as seen in TEM results). Moreover, in Fig. 4, the pore area of S3 is lower than that of S2, while the pore diameter of S4 is by far the smallest of all four samples. Thus, varying the washing method and acid concentration influence the crystallinity, pore structure and specific surface area of the nanotubes, which can be explained by etching phenomenon.
Fig. 3.4: Nitrogen adsorption and desorption isotherms for TiO$_2$ nanostructures, (a) S1, (b) S2, (c) S3 and (d) S4. The insets correspond to the pore diameter of the various TiO$_2$ nanostructures (i.e. S1-S4).

The adsorption of the oxygen species is associated to the structural defects on the metal oxides surface, particularly the oxygen vacancies, which are mostly
influential in the sensing performance of TiO$_2$. Thus, to study the efficiency of trapping, immigration and transfer charge carriers, the PL study was carried out. Fig. 5(a) displays the room temperature PL spectrum of the TiO$_2$ nanostructures synthesised following the hydrothermal method and washed with various HCl concentrations. A quench in PL intensity was observed as the morphology transforms from nanoparticles to nanotubes after the hydrothermal method. Moreover, a shift to higher energy and peak broadening on the TiO$_2$ nanotubes samples (S2-S4) was observed. The original PL spectra were deconvoluted into four Gaussian peaks as shown in Fig. 5(b-e). Peaks centred between 3.2 and 3.0 eV attributed to direct electronic transition from the bottom of the conduction band to the top of the valence band were observed for all the samples [6, 18]. The broad visible PL emission is due to an increase in the oxygen vacancies. Electronic transitions from defects levels within the band gap resulted in additional peaks located at 2.8 eV, which are attributed to self-trapped excitons in the octahedral [18-20], while peaks around 2.6 eV and 2.4 eV correspond to shallow and deep oxygen vacancy related trap states (i.e. Ti$^{3+}$ and F$^+$ centres, respectively) [19-21].

The intra-band gap states in the TiO$_2$ crystal structure in Fig. 5(e) demonstrate the presence of electron and hole trap states that result to the broad visible emission peak. As the electrons are excited (320 nm) from the valence band ($V_b$) to the conduction band ($C_b$) some electrons get trapped by the Ti associated states. The green emission at higher energies (3-2.3 eV) is due to the recombination of free electrons with holes trapped by oxygen vacancies above the valence band edge. The red emission is due to the radiative recombination of trapped electrons with valence band holes [20-22].
Fig. 3. 5: (a) PL spectra of the synthesized TiO₂ nanostructures, (b)-(e) correspond to deconvoluted graphs of the S1-S4 samples. (f) Schematic diagram of the electronic transitions in TiO₂ nanotubes.
3.4.4. Gas Sensing Analysis

To study the optimal temperature of the TiO$_2$ based sensors, the sensors were exposed to various gases NH$_3$, CH$_4$, NO$_2$, and CO at 80 ppm, while the operating temperatures were varied from 23 to 250 °C. The sensor response as a function of operating temperature for the S1-S4 samples is presented in Fig. 6a. As shown in Fig. 6, the S4 based sensor reveals a higher response to CH$_4$ gas at room temperature (23 °C) compared to its counterparts. Its response decreases when the operating temperature increases. This higher response is related to a remarkable surface area provided by the hollow tubular structure.

Fig. 6b presents the values of the resistance in air (R$_a$) for the S1-S4 based sensors. It is clear that the R$_a$ of all the sensors decreases with the increase in the operating temperature from 23 to 250 °C. However, the R$_a$ values of the S2 and S3 sensors increase slightly at 100 °C, displaying R$_a$ values of 4.3×10$^8$ kΩ and 1.0×10$^9$ kΩ, respectively, in comparison to those observed at 23 °C (2.0×10$^8$ kΩ and 7.5×10$^8$ kΩ for S2 and S3, respectively). This increase at 100 °C is probably due to the number of free electrons within S2 and S3 decreases at 100 °C, and therefore, the sensing materials display high resistance state. Kim et al. [23] and Kortidis et al. [24] have shown that the R$_a$ decreases with an increase in operating temperature. Moreover, it is evident that the S1 sensor shows higher R$_a$ of 1.9×10$^9$ kΩ at 23 °C, in comparison to its counterparts, such higher R$_a$ could be due to the fact that the S1 has less free electrons, since the PL confirmed that the S1 has less V$_\text{O}$.

Fig. 6c displays the response of various sensors (S1-S4) versus the CH$_4$ gas concentrations at an operating temperature of 23 °C. It is clear that the corresponding responses of the sensors increase almost linearly from 5 ppm to 60 ppm. The quick
saturation at 60 ppm CH$_4$ gas concentration could probably be associated to low operating temperature, 23 °C. The S4 based sensor reveals the highest response of 57 at 60 ppm, which is roughly 0.64 higher than other sensors. Interestingly, a response of approximately 4.3 is observed at 5 ppm. The higher sensing response is due to superior active surface area derived from nanotubes, allowing the sensor to be active at low operating temperature towards CH$_4$ gas. Additionally, the nanotubes also offer multiple channels for adsorption and desorption of chemisorbed O ions and gas molecule species; and can trap and release a large number of free electrons and provide abundant pathways for the gas molecules to alter the resistances of the sensor and enhance the gas sensing responses [25]. Additionally, Zhou et al. [26, 27] have reported that the 1-D aligned porous nanowires gas sensors are appropriate for gas diffusion and contain efficient specific surface area that result in rapid gas response and improved sensitivity.

\[ \text{RMS}_{\text{noise}} = \sqrt{\frac{S^2}{N}} \]

The linear relationship between the S1-S4 responses and CH$_4$ gas concentrations point out the reliable operation of the sensors over a tested concentration. Upon using the linear least-squares fit to the data, the sensitivity of the S1-S4 based sensors is estimated as 0.23, 0.30, 0.35 and 0.62 ppm$^{-1}$, respectively as shown in Fig. 6d. The higher sensitivity (0.62 ppm$^{-1}$) of the S4 is due to superior surface area, resulting to large amount of surface active sites for both gas adsorption and surface reaction [28-30]. The theoretical detection limit ($D_L$) was estimated using the following formula, $D_L = 3 \left( \frac{\text{RMS}_{\text{noise}}}{\text{Slope}} \right)$ [31, 32] (where RMS is the room mean square, which is calculated using the following formula, ). Therefore, the estimated $D_L$ values were 0.5, 0.3, 0.9 and 0.25 ppm for S1, S2, S3 and S4, respectively. The
sub-ppm level detection limit (0.25 ppm) for S4 towards CH$_4$ gas proves the potential for high performance CH$_4$ sensors at 23 °C.

Fig. 3. 6: (a) The Sensors response versus operating temperature towards CH$_4$ gas, (b) resistance in air (R$_a$) versus operating temperature for S1-S4, (c) response versus CH$_4$ gas concentration, and (d) linear least-squares fit versus CH$_4$ gas concentration.

The response and recovery times are one of the considered parameters to assess the characteristics of the gas sensors. Fig. 7a shows a single cycle response-recovery graph of the S1-S4 based sensors exposed to 60 ppm CH$_4$ gas at 23 °C. It
is evident from the plot that all the sensors show a clear response when the gas is introduced in the chamber and recovers well when exposed to air. Fig. 7b-c illustrates a response ($t_{res}$) and recovery ($t_{rec}$) times plot as a function of CH$_4$ gas concentration. At lower gas concentration (5-10 ppm), the $t_{res}$ increases, while at higher concentration, a $t_{res}$ decreases for all the sensors, showing a lowest $t_{res}$ of 66 s for the S1 and S4 at 60 ppm. In Fig. 7c, the $t_{rec}$ increases with gas concentration up to 40 ppm, then decreases. The lowest response time point out that our S4 based gas sensor covers some of the criteria (such as rapid response-recovery times, high selectivity and sensitivity, low detection limit, etc.) required for the real-time applications.

![Fig. 3. 7:](image)

**Fig. 3. 7:** (a) Resistance curves of the S1-S4 sensors to 60 ppm CH$_4$ at 23 °C, (b and c) response and recovery times of the S1-S4 sensors to various CH$_4$ gas concentrations.

The comparison with CH$_4$ sensors of various metal oxides morphology is shown in Table 1. From the table, the current TiO$_2$ nanotubes sensors display the comparatively low optimum functioning temperature and improved response. Thus, the sensor might be capable to show good CH$_4$ sensing characteristics and reach practical application needs to detect CH$_4$ gas at low operating temperature.
<table>
<thead>
<tr>
<th>Sensing materials</th>
<th>Synthesis procedure</th>
<th>Conc. (ppm)</th>
<th>Temp. (°C)</th>
<th>Res. ($R_a/R_g$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ Nanoparticles</td>
<td></td>
<td>500</td>
<td>600</td>
<td>0.92</td>
<td>Seeley et al. [33]</td>
</tr>
<tr>
<td>n-SiNWs/TiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-SiNWs/TiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ nanoparticles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$_2$O$_3$-decorated In$_2$O$_3$</td>
<td>Sputtering deposition and arc-discharge</td>
<td>200</td>
<td>350</td>
<td>2.1</td>
<td>Vuong [36]</td>
</tr>
<tr>
<td>nanostructures</td>
<td>deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb-implanted SnO$_2$ thin film</td>
<td>r.f. sputtering</td>
<td>1000</td>
<td>250</td>
<td>0.214</td>
<td>Rastomjjee et al. [37]</td>
</tr>
<tr>
<td>(dose= $3\times10^{16}$ ions/cm$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb-doped and Pd-functionalized SnO$_2$</td>
<td>Flame spray pyrolysis</td>
<td>500</td>
<td>300</td>
<td>30</td>
<td>Großmann et al. [38]</td>
</tr>
<tr>
<td>ZnO thin film</td>
<td>Electrochemically</td>
<td>100</td>
<td>220</td>
<td>2.22</td>
<td>Basu et al. [39]</td>
</tr>
<tr>
<td>SnO$_2$-based powders</td>
<td>Sonication–assisted simultaneous precipitation</td>
<td>1000</td>
<td>350</td>
<td>10</td>
<td>Das et al. [40]</td>
</tr>
<tr>
<td>ZnO nanowalls</td>
<td>Thermal evaporation</td>
<td>100</td>
<td>300</td>
<td>2.00</td>
<td>Chen et al. [41]</td>
</tr>
<tr>
<td>Ni$_2$O$_3$-decorated SnO$_2$</td>
<td>Sputter deposition</td>
<td>200</td>
<td>400</td>
<td>2.2</td>
<td>Vuong [42]</td>
</tr>
<tr>
<td>ZnO microstructure</td>
<td>Solvothermal</td>
<td>100</td>
<td>140</td>
<td>1.05</td>
<td>Aghagoli et al. [43]</td>
</tr>
<tr>
<td>1wt.% Co/ZnO microstructure</td>
<td>hydrothermal</td>
<td>100</td>
<td>140</td>
<td>3.55</td>
<td>Hu et al. [44]</td>
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<tr>
<td>ZnO thin film</td>
<td>Sol-gel method</td>
<td>100</td>
<td>250</td>
<td>3.89</td>
<td>Bhattacharyya et al. [45]</td>
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<tr>
<td>1at.% Pd/ZnO nanosheets</td>
<td>Hydrothermal</td>
<td>100</td>
<td>200</td>
<td>8.65</td>
<td>Wang, et al. [46]</td>
</tr>
<tr>
<td>TiO$_2$ nanotubes</td>
<td>Hydrothermal</td>
<td>60</td>
<td>23</td>
<td>57</td>
<td>Current work</td>
</tr>
</tbody>
</table>

Conc.: Concentration (ppm); Temp.: Temperature (°C); Res.: Response, Ref.: References. *% refers ($R_a/R_g) \times 100$ or ($R_g/R_a) \times 100$. 

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Selectivity is one of the important parameter that is required for fabrication of gas sensing materials for real application. Therefore, the selectivity results carried out at room temperature with the sensors exposed to 60 ppm of CH₄, including the NH₃, CO, and NO₂ gases are displayed in Fig. 8a. The S₄ based sensor shows the highest response of 57 towards CH₄ gas at 23 °C in comparison to other gases. The response is more than three times higher in comparison to other gases and this indicates a substantial selectivity. The higher sensing response to CH₄ in comparison to other gases could be due to smaller binding energy of the CH₄, as shown in Table 2 when associated to the other gases that makes it possible to break down and contribute in the reaction. Previous study ascribed the improved sensing response to polarization of CH₄ molecules allowing it to be easily adsorbed by the sensing surface, resulting to increased conductivity [47]. Since the S₄ sensor only showed higher surface area, with limited pore diameter and volume, the response of the S₃ based sensor to almost all the gases could be due to better pore volume and active surface area in comparison to S₄, allowing easier gas adsorption.

For quantification, we evaluated the gas selectivity values \(S_{CH4}/S_{NH3}\), \(S_{CH4}/S_{CO}\) and \(S_{CH4}/S_{NO2}\) toward CH₄ over NH₃, CO and NO₂ interference gases at 23 °C for S₄ based sensor [48, 49]. The \(S_{CH4}/S_{NH3}\), \(S_{CH4}/S_{CO}\) and \(S_{CH4}/S_{NO2}\) demonstrated maximum values of 93.67, 10.02 and 100.24, respectively. This is clear evidence that the S₄ based sensor is a favourable sensor for highly selective and sensitive detection of CH₄ gas at 23 °C.

To substantiate the sensing findings, further considerable analyses were done by associating the 60 ppm CH₄ sensing response with the changes in the TiO₂ phase induced by acid treatment and the BET surface area. As displayed in Fig. 8b, the sensing response towards 60 ppm CH₄ gas increases with an increase in rutile phase,
except the S2, which shows higher increase in rutile phase. Furthermore, we compared the response versus crystallite sizes. As shown in Fig. 8c the response increases with crystallite sizes. Katoch et al. [50] have reported that ZnO nanofibers with enhanced crystallinity disclose smaller carrier concentration that lead in a more noticeable change in sensor resistance. Such behaviour was also noticed by Oosthuizen et al. [51] using CuO nanoplatelets based sensor when exposed to CO gas.

The correlation between the BET surface area and gas sensing response (measured at 60 ppm) reveals that the response increases with the BET surface as a function of acid treatment concentration, as demonstrated in Fig. 8d. Furthermore, it is well-intentioned to declare that their behaviour is dependent on the acid treatment, since larger surface area was observed at higher HCl concentration, which became favourable for gas-ion/species adsorption in the gas-sensing analyses, and thus response and recovery kinetics were quick, and sensitivity/response was high.
Fig. 3.8: (a) Selectivity plot, (b) Response versus rutile content and (c) Response versus crystallite sizes and (d) Response versus BET surface area for S1-S4.
Table 3. 2: Properties of the gases tested in this work [52, 53]

<table>
<thead>
<tr>
<th>Gas type</th>
<th>Bond</th>
<th>Bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>H−CH₃</td>
<td>431</td>
</tr>
<tr>
<td>NH₃</td>
<td>H−NH₂</td>
<td>435</td>
</tr>
<tr>
<td>CO</td>
<td>C=O</td>
<td>1079</td>
</tr>
<tr>
<td>NO₂</td>
<td>O−N−O</td>
<td>473</td>
</tr>
</tbody>
</table>

3.4.5. Gas Sensing Mechanism

The superior CH₄ gas sensing performance of the S4 based sensor was attributed to the unique surface area. With regards to sensing mechanism, usually, when the sensing layer (in this case TiO₂ nanotubes) is in air, it adsorbs the oxygen molecules easily since they have high electron affinity (0.43 eV) and then the O₂⁻ molecules adsorption will ultimately receive free electrons [4, 51], see equations (2 and 3):

\[ O_2 \rightarrow O_2(ads) \]  \hspace{1cm} (2)

\[ O_2(ads) + e^- \rightarrow O_2^- \]  \hspace{1cm} (3)

It is well known that the quantity of the chemisorbed oxygen molecules is significantly governed by the operational temperature, surface conditions of the gas sensor, surface defects and the active surface area of the sensing layer [4, 15, 51, 54, 55]. It is expected that the current TiO₂ nanotubes with a superior surface area will adsorb a significant amount of O₂⁻ at 23 °C and thus contribute to superior sensing. Therefore, abundant reaction sites are provided for CH₄ reactions, resulting to improved sensing performance. The dimensional nanotubes acting as nanochannels also promotes the
adsorption and desorption of gas species. The extraction of electrons from TiO$_2$ surface layer will lead to the creation of an electron depletion layer on the TiO$_2$ surfaces. Thus, when the TiO$_2$ sensing layer is exposed to CH$_4$ gas at 23 °C, the electrons will be unconfined to the TiO$_2$ conduction band and the electron depletion layer thickness will reduce because of the redox reaction occurring among the methane molecules and oxygen ions. Basically, the potential barriers in the nanorods control the electrons transport in the course of the adsorption/desorption of the gas molecules, and consequently result in a decrease of the sensor resistance [56] and the following reactions (see equations 3 and 4) will occur [4]:

$$\text{CH}_4^- \rightarrow \text{CH}_3^+(\text{ads}) + \text{H}^- (\text{ads}) \quad [4]$$

$$\text{CH}_4(\text{ads}) + 4\text{O}^-(\text{ads}) \rightarrow \text{CO}_2(\text{gas}) + 2\text{H}_2\text{O} + 4\text{e}^- \quad [5]$$

### 3.5. Conclusion

In conclusion, we have prepared highly porous TiO$_2$ nanotubes with a remarkable specific surface area via hydrothermal method. A change in morphology from nanoparticles to nanotubes after hydrothermal treatment was observed. The S4 (i.e. TiO$_2$ nanotubes) structure displayed an extraordinary specific surface area (1375.238 ± 53.395 m$^2$/g). The gas sensing features of different gases were studied at different operating temperatures and gas concentrations. The gas sensing characteristics of S4 showed improved response and selectivity to CH$_4$, with a value of 57 at 23 °C, signifying its significant use for low power consumption in gas sensor applications. The improved gas response of the S4 based sensor can have attributed to the increased crystallinity and enhanced surface area provided by the one dimensional nanotubes.
behaving as nanochannels for gas diffusion. Viable morphology-fine-tuning strategy and improved CH₄ gas sensing performances further point out the advantage of utilizing fabricated TiO₂ nanotubes in future for CH₄ real-time monitoring.
3.6. References


towards LPG sensing capabilities, Materials Chemistry and Physics 242 (2020) 122452.


CHAPTER 4: Structural Transformation and Enhanced Gas Sensing Characteristics of TiO$_2$ Nanostructures Induced by Annealing

Abstract

The improved sensitivity, selectivity, and admirable stability are fundamental features required for modern gas sensing devices to satisfy human and environmental requirements. Therefore, herein, we report on the room temperature gas sensing behaviour of TiO$_2$ nanotubes with significant response and sensitivity towards 60 ppm NO$_2$ gas. Improved sensitivity of 29.44 ppm$^{-1}$ and admirable selectivity towards NO$_2$, among other gases ensures adequate safety in monitoring NO$_2$ in automobile and food industries. The improved sensitivity of TiO$_2$ nanotubes was attributed to larger surface area provided by the hollow nanotubes resulting to improved gas adsorption and the relatively high concentration of oxygen vacancies.

4.1 Introduction

To date, fabrication of low-cost, ultra-sensitive and selective chemiresistive sensors that are able to detect toxic, flammable and explosive gases have become indispensable for environmental monitoring, industrial and biomedical applications [1]. Some of the challenges are to attain ultra-sensitive gas sensors that can operate at low temperature with high selectivity to detect the harmful gases. The current promising materials are semiconductor metal oxides (MOXs) which have displayed a substantial potential by their noticeable change in electrical resistance upon exposure to either reducing or oxidizing gases [2]. Moreover, MOXs are very stable and can be
easily synthesized in various forms using different synthesis routes (e.g. chemically or in the Vapour phase) [2-4].

TiO$_2$ nanotubes synthesized via hydrothermal method in alkali solution have attracted a number of researchers’ interest since first demonstrated by Kasuga et al. in 1998 [5]. This is due to the improved photocatalytic properties; charge transport properties and the large specific surface area provided by the tube-like structure increasing the number of potential active sites for the gas adsorption as compared to their bulk form [6-8] enabling potential application in gas sensing [3], lithium ion battery [8], hydrogen storage [7] and environmental cleaning [9]. TiO$_2$ nanostructures can be achieved in different phases such as anatase, rutile, and TiO$_2$(B), all owing to the synthesis conditions such as post heat treatment by annealing at low (<300 ºC), to elevated temperatures (400-900 ºC) [10, 11]. These TiO$_2$ polymorphs have different effects on the performance of the sensor, such as the high photocatalytic activity of anatase than that of rutile [11, 12]. From our previous studies we found that upon annealing at elevated temperature (700 ºC), our nanoparticles prepared using 18 M NaOH transformed to “rod-like” structure. Moreover, the sensing properties toward NO$_2$ and CH$_4$ gases improved due to a transformation of morphology and phase (from pure anatase to 30 % rutile) [3].

However, in the current work, we elucidate that a higher sensing response towards NO$_2$ gas is dependent on the morphology. Rengaraj et al. [13] has indicated that the performance of the inorganic materials can be significantly improved by controlling the size, morphology and structure. In addition, there are few studies which reported high sensing response towards NO$_2$ gas at room temperature after annealing without assistance of UV light or dopants. Therefore, herein, we report on the effect of
annealing temperature on the gas sensing properties of TiO$_2$ nanotubes prepared following the microwave assisted hydrothermal and annealing at various temperatures. Furthermore, the enhanced sensitivity and selectivity towards NO$_2$ gas are correlated with the morphology, crystal structure, and optical properties.

4.2 Experimental Details

4.2.1 Synthesis Procedure

To prepare the TiO$_2$ nanotubes the microwave assisted hydrothermal method was followed. As a starting material commercial TiO$_2$ powder, P25 Degussa (mixture of anatase and rutile) was dispersed in 10 M sodium hydroxide (NaOH) solution and stirred for homogeneity. The mixture was transferred into microwave Teflon lined vessels and microwave irradiated at 150 °C for 15 min (Perkin Elmer/Anton Paar Multiwave 3000). After being cooled to room temperature the products were centrifuged and washed with 1.0 M hydrochloric acid (HCl) aqueous solution (37 % purity) and distilled water till pH 7. The final powder was dried at 100 °C for 12 hours. It should be pointed out that the samples were labelled as S1, S2, S3 and S4 for the as-prepared, 450 °C, 700 °C and 900 °C annealed samples for 4 hours, respectively.

4.2.2 Material Characterization

The morphology and structure were confirmed using the ZEISS scanning electron microscope (SEM) and JOEL-2100 high resolution transmission electron microscope (HR-TEM) with monochromatic radiation source operated at 200 kV in conjunction with the X-ray diffraction (XRD) patterns obtained by a Panalytical X’pert Pro PW 3040/60 diffractometer equipped with Cu Kα radiation operated at 45 kV and 40 mA. The specific surface area and the pore volume of the samples were measured
by nitrogen (N\textsubscript{2}) physisorption using a Micromeritics TRISTAR 3000. The photoluminescence (PL) measurements were characterized using a Horiba Jobin-Yvon NanoLog spectrometer at an excitation wavelength of 320 nm.

4.2.3 Gas Sensing Fabrication and Testing

Gas sensing measurements were carried out by homogenously dispersing TiO\textsubscript{2} nanostructures in ethanol and drop-coated on alumina substrates. The response of the samples was examined by monitoring the variation of the electrical resistance of the sensors using a KSGAS6S gas sensing station (KENOSISTEC, Italy) under a constant flux of synthetic air used as gas carrier into which the desired concentrations (5-100 ppm) of CH\textsubscript{4} and NO\textsubscript{2} gases were added.

4.3 Results and discussion

4.3.1 Morphology and Structural analysis

The morphology study presented by the SEM images in Fig. 4.1 displayed a change in both size and shape as the annealing temperature increased up to 900 °C. A web of nanotubes with average diameter of 7.8 nm was observed on the as-prepared TiO\textsubscript{2} sample (S1 in Fig. 4.1a). Upon annealing at 450 °C the nanotubes grew in diameter to 22.2 nm (S2 in Fig. 4.1a). However, at 700 °C (S3 in Fig. 4.1a), a transformation to “nanorods-like” structures with average diameter of 87.2 nm was observed. This transformation was attributed to the collapsed walls of the tubular structure. Further growth and transformation was realized at 900 °C as the nanotubes transformed to thick nanorods or one dimensionally connected nanoparticles with an average diameter of 120 nm and become shorter in length (in S4). A complete transformation of tubular structure to irregular particles when annealed at 900 °C was
reported by Qamar et al. [14] and in our previous study [3], where TiO$_2$ nanoparticles annealed at 700 °C transformed to irregular connected nanoparticles forming dense rod-like nanostructures. It was observed that the higher annealing temperature promotes formation of nanorods because of the enhanced thermal stability as compared to that of the nanotubes.

Structural analyses carried out using HR-TEM and XRD demonstrated an improvement in crystallinity and structural transformation from anatase to a mixture of both anatase and rutile phase upon annealing as depicted by the selected area electron diffraction (SAED) and XRD patterns in Fig. 4.1b and c respectively. TEM images in Fig. 4.1b confirmed the change in morphology from nanotubes to nanorods observed as the annealing temperature increased. From the XRD spectra in Fig. 1c broad peaks were observed and attributed to smaller crystallite size and the formation of H$_2$Ti$_3$O$_7$ after hydrothermal treatment. Moreover, the SAED patterns displayed diffused Debye rings confirming the presence of an amorphous structure and validating that the nanotubes were really small in diameter. Using the JCPDs 21-1272 the peaks at $2\theta$ = 25.3, 38.1, 47.9, 54.6 and 62.5 ° were assigned to (101), (112), (200), (105) and (204) corresponding to anatase phase.

Upon annealing the TiO$_2$ nanotubes improved the crystallinity which was shown by bright rings in the SAED pattern of S2 and S3 in Fig. 4.1b. However, new reflection peaks/planes at $2\theta$ = 26.5, 29.7 and 45.2 ° emerged in sample S3 as the annealing temperature increased to 700 °C. According to Yoshida et al. [10] and Feist et al. [15], they can be assigned to the metastable TiO$_2$ (B) and H$_2$Ti$_3$O$_7$ intermediate phases. Highly crystalline mixture of TiO$_2$ polymorphs, metastable anatase and stable rutile phase were observed for S4 at higher annealing temperatures. Similar behaviour was
reported by Suzuki et al. [11] and the significant peaks at $2\theta = 27.6, 34.8, 40.2, 55.4$ and 60.7 corresponding to (110), (101), (200), (211) and (220) rutile phase were assigned using JCPDs 82-0514. Moreover, the rutile percentage improved with annealing temperature from 0.05% in S1 to 61% in S4 annealed at 900 °C.

Fig. 4. 1: (a) SEM micrographs, (b) HR-TEM with corresponding SAED patterns (inserts) and (c) XRD patterns of TiO2 nanostructures.
4.3.2 Surface Analysis

The Brunauer-Emmet-Teller (BET) surface area analysis of the TiO$_2$ nanostructures is shown in Fig. 4.2a. A significant decrease in BET surface area was observed as the annealing temperature increased from 124.86 m$^2$g$^{-1}$ to 81.73, 13.08 and 2.71 m$^2$g$^{-1}$ for samples S1, S2, S3 and S4, respectively. The desorption branch of the isotherm was used to determine the Barrett–Joyner–Halenda (BJH) pore size distributions of the nanostructures, displaying an increase in the pore diameter from 15.14 nm for S1 to 23.85, 39.25 and 74.51 nm for S2, S3 and S4. The trend was observed in Fig. 4.2a by the downwards shift of the isotherms and broader pore size distribution at high pressure with capillary condensation of the mesopores occurring above 0.6 P/Po. Based on Fig. 4.2a, samples S3 and S4 display no clear hysteresis loop. This can be assigned to the transformation of the hollow nanotubes to nanorods, resulting to loss of the internal surface provided by nanotubes.

To study the defect states, present on the surface of the TiO$_2$ nanostructures Photoluminescence (PL) analysis was carried out at room temperature. Fig. 4.2b displayed the PL spectra for as prepared TiO$_2$ nanotubes (S1) and those annealed at various temperatures resulting to nanorods (S3 and S4). The PL spectra displayed two major emission bands composed of a blue band centred at 415 nm and green band centred at 550 nm. The peak intensity increased with the increase in annealing temperature which was in agreement with the XRD results, where high crystallinity was observed at higher annealing temperatures. However, as the annealing temperature increased the number of defects (relative intensity) decreased as shown in Fig. 4.3f and this behaviour was attributed to phase and morphology transformation.
Similar observations were made by Jin et al. [16] and Seeley et al. [17] during the study of thermal stability of defects. Multiple Gaussian peaks were fitted to deconvolute the emission bands in Fig. 2b. The peaks were centred at 405 nm (peak 1), 421 nm (peak 2), 448 nm (peak 3), 553 nm (peak 4) and 590 nm (peak 5). According to the literature, peaks 1 and 2 originate from self-trapped excitons located in the TiO$_6$ octahedral [3, 18] while peaks 3 and 4 are due to the shallow trapped oxygen vacancies associated with the Ti$^{3+}$ and deep trap states of oxygen vacancies associated with F$^+$ centre [12, 16, 18]. Peak 5 is related to intrinsic defect states such as electron transition from F$^+$ centre to acceptor level above valence band [12, 18-20].

![Fig. 4. 2: (a) Nitrogen adsorption isotherms and (b) Photoluminescence spectra for the TiO$_2$ nanostructures.](image)

4.3.3 Gas sensing properties

To study the gas sensing properties of the TiO$_2$ nanostructures, samples S1-S4 were exposed to different environments including various concentrations of NO$_2$ and CH$_4$. The measurements were carried out at room temperature with gas concentration ranging from 5 to 100 ppm. Fig. 4.3a and b displayed the response and recovery dynamics of the sensors exposed to NO$_2$ and CH$_4$ analyte gases, respectively. The
sensors responded to the presence of a gas and recovered back to equilibrium when the gas was released. S2 demonstrates a high response towards both gases compared to other sensors with a maximum response of 1889 and 1147 towards 60 ppm NO$_2$ and CH$_4$ gases, respectively. Sensor response decreased for S3 and S4 due to a loss of surface area as displayed by the BET results in Fig. 4.2a, as the nanotubes transform to nanorod like structures.

As demonstrated in Fig. 4.3c and d, we observed a linear change in response as the gas concentration increased up to 60 ppm then the sensors saturated and the responses started decreasing. Sensor S2 displayed enhanced sensitivity (change of response per concentration) of 29.4 ppm$^{-1}$ toward NO$_2$ and 25.9 ppm$^{-1}$ towards CH$_4$ followed by S1 with 12.5 and 10.7 ppm$^{-1}$ towards NO$_2$ and CH$_4$, respectively. The presence of new peaks in the TiO$_2$ (B) structure in S3 resulted to poor response towards CH$_4$ as observed in Fig. 4.3b. Further poor sensitivity was observed in Fig. 4.3d for S3 and this behavior was in agreement with the observations made in XRD and BET results. S3 and S4 depicted higher ordering in the crystal structure and lower point defects (see XRD and PL results). Therefore, poor sensing response was anticipated. Besides no clear N$_2$ adsorption hysteresis loop was observed in the isotherms. S3 easily saturated and may result to sensor poisoning thus it cannot be used as CH$_4$ gas sensor (Fig. 4.3d).

Table 4.1 and Fig. 4.3e displayed the response and recovery times of the sensors when exposed to 60 ppm NO$_2$ and CH$_4$ target gases. As displayed in Fig. 4.3f the response time was taken from the baseline to 90% of response in the presence of gas and the recovery time was taken from maximum response to 10% when the gas was released. S2 demonstrated fast response and recovery time towards both gases.
At higher annealing temperatures, the sensor was more stable displaying shorter/quicker response and recovery times of 34 and 24 s, respectively. The relationship between annealing temperature and the relative PL intensity is shown in Fig. 4.3f.

The relative PL intensity was calculated from Fig. 4.2b where the PL spectra showed two broad emission bands centered at 415 nm (blue band) and at 550 nm (green band). Where, the relative intensity is the ratio of the green band to the blue band. The decrease in sensor response and relative PL intensity as the annealing temperature increased (Fig. 4.3f) was attributed to a decrease of the relative concentration of the oxygen vacancies and surface area as evident from the PL and BET analyses [19, 20]. The formation of nanorods resulted in agglomeration and formation of dense particles opposing the interparticle electron transportation in the grain boundaries therefore delaying the sensor response.

**Table 4.1**: Response ($T_{res}$) and Recovery ($T_{rec}$) time towards 60 ppm NO$_2$ and CH$_4$ gases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NO$_2$ (60 ppm)</th>
<th>CH$_4$ (60 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{res}$ (s)</td>
<td>$T_{rec}$ (s)</td>
</tr>
<tr>
<td>S1</td>
<td>114</td>
<td>90</td>
</tr>
<tr>
<td>S2</td>
<td>93</td>
<td>43</td>
</tr>
<tr>
<td>S3</td>
<td>107</td>
<td>125</td>
</tr>
<tr>
<td>S4</td>
<td>34</td>
<td>24</td>
</tr>
</tbody>
</table>
Fig. 4.3: TiO$_2$ nanostructures gas sensor response and recovery curve towards (a) NO$_2$ and (b) CH$_4$. The Response against (c) NO$_2$ and (d) CH$_4$ gas concentration. (e) The response and recovery times and (f) Response against annealing temperature curve the sensors when exposed to 60 ppm NO$_2$. 
4.4 Conclusion

In conclusion, TiO$_2$ nanotubes annealed at 450 °C exhibited enhanced response towards NO$_2$ with a response time of 93 s and recovery time of 43 s and relatively higher sensitivity of 29.44 ppm$^{-1}$ at room temperature due to their higher surface area of 81.73 m$^2$g$^{-1}$ and pore diameter of 39.2 nm. The PL relative intensity and sensing response decreased with annealing temperature emphasizing loss of surface defects. Our findings demonstrated that the sensing properties were dependent on the annealing temperature. Moreover, the structural transformation, from anatase to rutile was observed at higher annealing, justifying the low sensing response observed for S4. Thus, based on these findings, we conclude that our sensing material can be used to monitor NO$_2$ gas in automobile and food industries at low concentration and with low power consumption.
4.5 References


CHAPTER 5: Designing of Vastly Sensitive and Selective Dual-Functionality of Toluene and Xylene Gas Sensors Based on TiO$_2$ Nanowires

Abstract

The dual-functional sensors derived from semiconductor metal oxides operating at low temperature for low power consumption and robust stability towards humidity is a striking platform for economic and indoor air quality monitoring. Therefore, in this work, temperature-dependent selectivity and robust stability towards carbon monoxide (CO), toluene (C$_7$H$_8$) and p-xylene (C$_8$H$_{10}$) was displayed by various TiO$_2$ nanostructures synthesized following a facile hydrothermal method. The X-ray diffraction patterns confirmed tetragonal structure of anatase TiO$_2$. Surface studies confirmed the different morphologies, such as nanoparticles (TNP), nanowires (TNW) and sea-urchin like hierarchically (HHC) arranged TiO$_2$ nanostructures. Relatively high surface area and interconnected pore distribution were witnessed for TNWs and HHC nanostructures as compared to TNP. In-situ photoluminescence and X-ray photoelectron spectroscopy analyses confirmed the defect states of the nanostructures and the TNW nanostructure possessed the highest concentration of oxygen vacancies and Ti$^{3+}$ which influenced the dual selectivity functionality of TNW towards C$_7$H$_8$ and C$_8$H$_{10}$ at 25 °C and 125 °C, respectively. Additionally, at optimum working temperature of 25 °C, a response of 2.46 towards 20 ppm CO was witnessed for the HHC based sensor and was attributed to the available surface area and active sites presented by the hierarchically arranged nanostructures. Cross sensitivity measurements were conducted in the presence of interfering gases, which showed negligible cross-
responses. The long-term stability in the presence of relative humidity and the sensing mechanism underlying the fascination of dual-functionality for C$_7$H$_8$ and C$_8$H$_{10}$ Vapour detection were discussed in detail. These findings showed that the current sensors can be employed for detection of C$_7$H$_8$ and C$_8$H$_{10}$ in a vastly robust and selective way with insignificant interference from ambient humidity.

5.1 Introduction

Emissions of gaseous volatile organic compounds (VOCs) presents a great threat to the environment and human health. Developing countries have high levels of these pollutants, since their economy directly depends on industrial manufacturing/processing, mining, automobile industry and power plants burning crude oil and gasoline [1-3]. Gases such as carbon monoxide (CO), toluene (C$_7$H$_8$) and xylene (C$_8$H$_{10}$) have extensive health effects that can lead to death as they are either toxic, explosive or combustive [4-7]. CO is a poisonous gas as motivated by low concentration of 9 ppm indoor limit. A headache and dizziness may be experienced at low concentrations, whereas prolonged exposure may result to death. Occupational Safety and Health Administration (OSHA) has set a 35 ppm exposure limit for an eight-hour work shift [1, 3]. Toluene and xylene are aromatic hydrocarbons with long term health effects and besides exposure through inhalation, they can also be adsorbed through the skin. These VOCs attack the respiratory organs, central nervous system and are also flammable [3, 5-7]. Therefore, detection and monitoring of these gases is imperative for air quality and workplace safety.

Various analytical techniques such as Fourier Transform Infrared spectroscopy (FTIR) and Gas Chromatography coupled with Mass Spectrometry (GC-MS) can be used for gas detection. However, these are inconvenient in the field as they are very
expensive to purchase and maintain, bulky (desktop size) and have long analysis times. Thus, semiconductor metal oxides (SMOx) based sensors have attracted huge attention due to their promising properties, such as change in conduction resistance in the presence of an analyte gas. Moreover, they are affordable, easy to synthesize, mechanically flexible and portable and mostly have good sensitivity. Among the SMO’s, titanium dioxide (TiO₂) is the most attractive material, due to its unique properties such as excellent catalytic activity, chemical stability, large band gap, low cost and biocompatibility enabling potential technological applications in solar cells, photoelectrodes, anti-microbial activity and gas sensors [5,8-10]. More than one polymorph can be found presenting different properties, however the mostly studied polymorphs for gas sensor applications are anatase and rutile phases, due to their high photocatalytic activity and thermodynamic stability, respectively.

TiO₂ nanostructures can be synthesized via various methods and different morphologies can be achieved from zero to three dimensional nanostructures, such as nanoparticles (NP) [11], nanowires (NW) [12], nanorods (NR) [13], nanotubes (NT) [14], nanoribbons [15], and nanoplate [16], etc. These nanostructures are known for high surface to volume ratio which is beneficial for gas adsorption. Moreover, the hierarchical architectures made of assembled low dimensional building blocks present large specific surface area and large interconnected pore structures (voids) acting as distribution channels for the gas. Whereas, the nanoparticle agglomerates and reduce their efficiency as the gas transfer to the inner parts of the agglomerates is hindered, thus morphology has an extensive influence on the sensor performance [5, 10, 17].

Pozos et al. [18], carried out gas sensing measurements of CO using TiO₂ thin film deposited by ultrasonic spray pyrolysis and an optimum response of 300 was
recorded towards 300 ppm at a working temperature of 300 °C. Whereas, Hsu et al. [19] employed electrochemically grown TiO$_2$ nanotubes on LSCNO perovskite film forming a p-n heterojunction for CO detection. The sensors displayed improved response of about 38.41% at 200 °C towards 400 ppm. While several studies have reported toluene and xylene gas sensing using TiO$_2$ based sensors. For instance, enhanced response of 42.9% towards 500 ppm toluene vapour at room temperature was reported by Seekaew et al. [20] using graphene-carbon nanotubes loaded with TiO$_2$ nanoparticles achieved via chemical Vapour deposition and sparking methods. Pure and Au-loaded TiO$_2$ hedgehog-like hierarchical architectures synthesized via hydrothermal method were prepared by Zhang et al. [5] for detection of xylene at temperatures between 320 and 400 °C. At a working temperature of 375 °C, the sensors displayed optimum response of 3.19 and 6.49 for pure and Au-TiO$_2$ towards 100 ppm of xylene respectively. Most recently, a study by Kim et al. [21] showed a dual-mode selectivity of Nb-doped NiO hollow spheres-based sensor towards p-xylene and toluene Vapours at higher operating temperatures of 350 °C and 400 °C, respectively. Nonetheless, to our best of our knowledge no studies have reported a dual selectivity at low operating temperatures using a single sensor, more specially undoped metal oxide for detection of VOCs with a robust stability under relative humidity.

Therefore, herein we report on a dual-functionality of TiO$_2$ NW based sensor towards C$_7$H$_8$ and C$_8$H$_{10}$ at low operating temperatures of 25 and 150 °C, respectively, prepared by a simple hydrothermal method. The key focus of this work is based on the fabrication of dual-functionality of TiO$_2$ NW based gas sensors with enhanced response and robust stability to humidity changes. This is the first study reporting on low operating temperature dual-functionality of a single sensor for detection of VOCs
and this propose a prospective application as a low-power consumption \( C_7H_8 \) and \( C_8H_{10} \) Vapour sensor. In-situ photoluminescence (PL) studies were carried out to investigate the intrinsic defects states (oxygen vacancy \( (V_o) \) and \( Ti^{3+} \)) contributing to the temperature-dependent selectivity. The long-term stability under various relative humidity conditions and the fundamental sensing mechanism related to the appeal of dual-functionality for \( C_7H_8 \) and \( C_8H_{10} \) vapour detection are discussed in detail.

5.2 Experimental Details

5.2.1 Synthesis Procedure of the Various TiO\(_2\) morphologies

For the sea-urchin like hierarchical nanostructures (HHC), 6 g of TiO\(_2\) P25 Degussa was added to 10 M NaOH solution and stirred for a homogenous mixture. Hydrogen peroxide (\( H_2O_2 \)) was later added dropwise under vigorous stirring before transferring the solution to a Teflon-lined autoclave. For TiO\(_2\) nanoparticles (TNP) and nanowires (TNW) \( H_2O_2 \) was not added. The autoclave was heated at 150 \( ^\circ C \) for 2, 6 and 24 h to achieve HHC, TNP and TNW, respectively. The products were then allowed to cool down to room temperature and washed with 0.2 M HCL and distilled water (DW) until a pH 7 and then finally dried at 80 \( ^\circ C \) for 10 h and annealed at 450 \( ^\circ C \) for 4 h. The samples obtained were in powder form and were referred to as HHC, TNP and TNW, throughout the chapter.

5.2.2 Material Characterization

The crystal structure of TiO\(_2\) was examined using a Panalytical X'pert PRO PW 3040/60 X-ray diffractometer (XRD) equipped with a Cu-K\( \alpha \) (\( \lambda = 0.154 \) nm) monochromatized radiation source. High-resolution transmission electron microscopy (HR-TEM) was used to examine the morphology and crystalline structure of the
samples using a JEOL-TEM 2100 instrument operated at 200 kV. The powders were dispersed in ethanol and were deposited on holey-carbon-coated Cu grids. Surface morphology analyses were examined using an Auriga ZEISS scanning electron microscopy (SEM) at an accelerating voltage of 3 kV. The Brunauer-Emmett-Teller (BET) technique was used for surface area and pore volume analysis of the samples using a Micromeritics TRISTAR 3000 surface area analyzer using nitrogen (N\textsubscript{2}) as the probe gas. Prior to analysis, the samples were degassed at 60 °C for 12 h under a continuous flow of N\textsubscript{2} gas to remove adsorbed contaminants. The optical properties were determined using a Photoluminescence (PL) spectrometer. The PL spectra were measured using a Horiba Jobin Yvon iHR 320 Fully Automated Imaging Spectrometer with Kimmon IK Series 325 nm Laser and a PHI 5000 Versaprobe-Scanning ESCA Microprobe was used to carry out the X-ray photo-electron spectroscopy (XPS) analysis.

### 5.2.3 Sensing Films Characterization

To investigate the sensing performance of the various TiO\textsubscript{2} nanostructures (morphologies) a similar preparation method as described in chapter one was followed using the alumina substrates. The sensing resistances of the sensors to various concentrations (5-100 ppm) of different gases (i.e. toluene (C\textsubscript{7}H\textsubscript{8}), Xylene (C\textsubscript{8}H\textsubscript{10}), ammonia (NH\textsubscript{3}), methane (CH\textsubscript{4}), and carbon monoxide (CO)) were measured by switching between the mixture of gases and synthetic dry air using a KSGAS6S gas testing apparatus (KENOSISTEC Model, Italy). For all the tested target gases, the sensing measurements were carried out at temperatures between 25 and 150 °C. The relative humidity (RH) effect was tested by utilizing the programmable temperature and humidity test chamber in the range of 10-50 % RH.
5.3 Results and discussion

5.3.1 Structural and Morphological analysis

X-ray diffraction patterns for the synthesized TiO$_2$ nanostructures are presented in Fig. 5.1(a). The diffraction peaks in the patterns were ascribed to crystalline TiO$_2$ nanostructure of the anatase and rutile phases, according to JCPDS cards 21-1272 and 86-0147, respectively and no peaks corresponding to impurities were observed. It was also observed that as the reaction time increased from 2 to 24 h, the TiO$_2$ nanostructures completely transform from mixed-phase P25 Degussa to the pure anatase phase. The sample synthesized within 2 h presented peaks centred at $2\theta = 27.8$, 36.5 and 41.6$^\circ$ corresponding to (110), (101) and (111) diffraction planes of rutile phase TiO$_2$, respectively, as shown in Fig. 5.1(b). Using the Spurr Myers equation \[22\] on the mixed phase HHC, the crystalline particles contained 20% rutile and 80% anatase phase. It should be pointed out that the P25 Degussa showed a rutile phase of 21.3%. The broadening of the diffraction peaks was witnessed, due to the decrease in crystallite sizes as reaction time increased and morphology was transformed \[23\]. Moreover, a shift to higher Bragg’s angle occurred to all three samples (see Fig. 5.1b) and was recognised as lattice contraction, due to the increased microstrain as crystallite size decreased (see Fig. 5.1c).

Both the TNP and HHC showed a (103) plane and this plane is not observed for the TNW. Therefore, these observations were verified using Williamson-Hall (W-H) and Debye Scherrer (D-S) equations for the analysis of crystallite size and micro-strain and the results are displayed in Fig. 5.1c and Table 5.1. Small variations were observed from the crystallite size ($D_w$ and $D_s$) calculated following the W-H and D-S analyses, as shown in Fig 5.1c. Negative slopes were observed from the W-H


analysis, and according to previous studies, such behaviour is due to compressive stress in the lattice. Besides, in Table 5.1 the experimental interplanar (d) spacing given by the expression of tetragonal structure, were less than the theoretical values, consequently indicating lattice contraction.

increased. (b) Broadening of the (004) peak and (c) crystallite sizes calculated using Williamson –Hall and Scherrer equation.
Table 5.1: Crystallite size and lattice parameters for the synthesized TiO$_2$ nanostructures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>d-spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W-H analysis</td>
<td>Scherrer analysis</td>
</tr>
<tr>
<td>HHC</td>
<td>11.60</td>
<td>11.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TNP</td>
<td>11.41</td>
<td>11.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TNT</td>
<td>7.74</td>
<td>4.26</td>
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<tr>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>
The micrographs from scanning electron microscopy (SEM) in Fig. 5.2a-c displayed various morphologies of the synthesized TiO$_2$ nanostructures achieved through varying the reaction time. As displayed in Fig. 5.2a, after 2 h hierarchically arranged TiO$_2$ nanowires forming sea-urchin like macrospheres (HHC) were achieved with interconnected voids and non-uniform diameter estimated between 1.5-2.5 μm, whereas the nanowires have average diameter of 12.4 nm. At 6 h, uniformly distributed TiO$_2$ nanoparticles (TNP) were achieved with an average particle diameter of 11.2 nm and a porous surface (with holes/cracks) as observed in Fig. 5.2b inset (see Fig S1, in appendix A). The nanowires (TNW) with average diameter 7.6 nm were obtained over prolonged reaction time of 24 h. The nanowires displayed a loosely packed web-like arrangement, creating channels for gas adsorption, indicating their potential application in gas sensing.

Fig. 5.2g-i displayed the HR-TEM images and selected area electron diffraction (SAED) patterns of the synthesized nanostructures. Well defined lattice fringes were observed, and interplannar spacing were measured, which corresponded well to planes of anatase TiO$_2$ HHC, TNP and TNW. The SAED patterns observed in Fig. 5.2g-i are in agreement with the inter-planner spacing and compressive strain (in Table 5.1) calculated from XRD. The low resolution SEM and TEM images confirming a clear reproducible morphology for all three nanostructures are shown in Appendix A (Fig. S1 and S2)

The Brunauer-Emmett-Teller (BET) nitrogen (N$_2$) adsorption-desorption analysis as well as the pore structures for the synthesized TiO$_2$ nanostructures are presented in Fig. 5.3. Type IV isotherms were observed in Fig. 5.3a-c for all the samples, which was indicative of capillary condensation in the mesopores. The BET
surface areas of $68.23 \pm 0.12$, $100.47 \pm 0.08$ and $125.79 \pm 0.23$ m$^2$.g$^{-1}$ were observed for TNP, HHC, and TNW, respectively.

Fig. 5. 2: SEM images of TiO$_2$ nanostructures synthesized via hydrothermal method by varying reaction time (a) hierarchical nanowires (b) nanoparticles and (c) nanowires were achieved. (insets: shows the SEM low magnification and particle size/diameter distribution of the nanostructures). (d-f) HR-TEM micrographs and (g-i) SAED patterns of TiO$_2$.

Additionally, Type H2 hysteresis loops were witnessed, which are characteristics of pores with non-uniform size and shape [24, 25]. Intense adsorption at higher relative pressure ($P/P_o$) was displayed by the isotherm as shown in the insets
of Fig. 3a-c, showing a broadening between 0.85-1.0 for TNP and 0.9-1.0 for TNW and HHC. This behavior was attributed to interconnected pore structure of micro-mesopores with pore size distribution of [2-60] nm with average 14.6 nm for sample TNP. Fig. 5.3e suggests the dominance of ink bottle pores with narrow diameter less than 10 nm and wider bodies with volume 0.269 cm$^3$.g$^{-1}$, hence capillary condensation occurs at pressures less than 0.9 relative pressure followed by saturation as the pores are filled.

Pore size distribution of [4-120] nm with average 14 nm, indicating that interconnected pore structure of meso–macropores was measured for TNW thus maximum adsorption occurred above 0.9 relative pressure. As seen from Fig. 5.3f pores with diameters less than 20 nm have larger volume of about 0.425 cm$^3$.g$^{-1}$ and as the pore size increased (> 30 nm) the volume decreased to less than 0.1 cm$^3$.g$^{-1}$. Moreover, sample HHC due to its morphology, an interconnected pore structure of meso–macropores with a distribution of 6-120 nm and an average of 26.3 nm were observed. It can be clearly seen from Fig. 5.3d that HHC possessed slit-like mesopores and funnel shaped macropores with wider diameter and larger bodies. However, as the diameter increased the pore volume decreased forming shallow pores. These types of pores influenced the steep increase in adsorption and the capillary condensation occurring at higher relative pressures above 0.95 and longer recovery times [25].
Fig. 5. 3: $N_2$ adsorption-desorption isotherms for the synthesized TiO$_2$ nanostructures (a) HHC, (b) TNP (c) TNW and their corresponding (d-f) cumulative volume and pore distribution plot.
5.3.2 Optical and Elemental Composition State

Fig. 5.4a-i displays the PL spectra of the synthesized TiO$_2$ nanostructures with various morphologies. For clear comparison, in-situ PL measurements were carried out at temperatures corresponding to sensor working temperature from 30-150 °C at an excitation wavelength of 320 nm. A visible luminescence band was observed centred at 423, 425, and 423 nm for HHC, TNP and TNW, respectively. It was clearly observed from Fig. 5.4a-c that the PL intensity drastically quenched as the working temperature increased. Moreover, the peaks full width at half maximum (FWHM) become narrower. PL is a surface dependent phenomenon, and the emission originates from excitons, V$_o$ and surface states, therefore any change in the surface environment due to temperature has a substantial impact on the luminescence observed [8, 11, 14, 26, 27]. Due to the use of hydrothermal method for synthesis, V$_o$ and surface hydroxyl groups are dominant sites for trapped charges and this was later confirmed by XPS analysis.

Within the broad peak, a number of emission peaks are superimposed therefore the peaks were deconvoluted as shown in Fig. 5.4d-i. The broad emission peaks measured at 30 °C were fitted with Gaussian bands centered at 410, 429, 448, 490 and 556 nm for HHC and 411, 432, 444, 477 nm for TNP and TNW (see Fig. 5.4d-f). No band edge emission was observed due to indirect band gap of anatase TiO$_2$. The near band edge emissions were observed at 411 nm [14, 27]. The violet-blue emissions at 432, 446, 474 and 490 nm originate from de-excitation from lower levels in Ti$^{3+}$ 3d states of TiO$_2$ lattice to the deep levels (acceptor) created by (OH$^-$) [11,26,27]. Whereas, the green emission 550 nm is due to de-excitation from lower levels in the V$_o$ of TiO$_2$ lattice to the ground state [11, 27-30].
Fig. 5.4: Photoluminescence spectra of TiO₂ nanostructures with different morphology (a) HHC, (b) TNP (c) TNW measured at 30 °C. (d-f) fitted emission spectra at 30 °C and (g-i) 150 °C.

Fig. 5.4a-c and Fig. S3 in the appendix A displayed that as the PL measurement temperature increased up to 150 °C the emission intensity decreased and peaks became narrow such that they were deconvoluted into 3 peaks. Fig. 5.4g-i displays the emission spectra of the TiO₂ nanostructures measured at 150 °C fitted with
Gaussian bands centred at 412, 435, and 474 nm for HHC, 410, 444 and 476 nm for TNP and 465 nm for TNW. Due to the samples non-stoichiometric Ti-O bonding in the lattice the loss of an oxygen atom resulted to an electron pair trapped in the $V_o$ which then generated an F centre.

\[
V_o + 2e^- \rightarrow F^- \quad (1)
\]

\[
F + Ti^{4+} \rightarrow Ti^{3+} + F^+ \quad (2)
\]

\[
Ti^{3+} + V_o + e^- \rightarrow F^+ \quad (3)
\]

\[
Ti^{4+} + e^- \rightarrow Ti^{3+} \quad (4)
\]

An electron in the F-centre may occupy the nearest Ti$^{4+}$ ion resulting to Ti$^{3+}$ and F$^+$ centre, which is a single electron associated with $V_o$. The F$^+$ centre forms shallow and deep trap states as shown in equations (1)–(47) [26-30].

The variations in the relative intensities of the emission bands of HHC, TNP, and TNW samples at the various PL operating temperatures have been analyzed by Commission International de l’Eclairage (CIE) chromaticity diagrams and the results are presented in Fig. 5.5. As illustrated in Fig. 5.5a–c all samples confirmed blue emission, validating the formation of structural defects. However, in Fig. 5.5a the emission was tuned from violet to blue by different PL operating temperatures, indicating that the HHC at room temperature contains different defects in comparison to its counterparts. While in Fig. 5.5b and c the blue emissions were not tuned by various operating temperatures, denoting that both materials contain almost the same defects. In addition to the CIE diagram, at elevated temperatures above 100 °C the CIE x-y coordinates were not captured within CIE colour gamut (refer to Table 5.2), this is due to the relatively less blue emission that was noticed from PL spectra.
**Fig. 5.5:** CIE chromaticity diagram of (a) HHC, (b) TNP and (c) TNW samples at the various PL operating temperature. (Note: HHC/TNP/TNW-30, HHC/TNP/TNW-70 and HHC/TNP/TNW-100 represent CIE x-y coordinates at the operating temperature of 30, 50, and 100 °C, respectively.)

**Table 5.2:** CIE x-y coordinates of HHC, TNP and TNW samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>X</th>
<th>Y</th>
<th>Samples</th>
<th>X</th>
<th>Y</th>
<th>Samples</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHC-30</td>
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<td></td>
<td>TNP-30</td>
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<td>0.03</td>
<td>TNW-30</td>
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<td>0.04</td>
</tr>
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<td>TNP-70</td>
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<td>0.03</td>
<td>TNW-70</td>
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<td>0.03</td>
</tr>
<tr>
<td>HHC-100</td>
<td>0.13</td>
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<td>TNP-100</td>
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<td>0.02</td>
<td>TNW-100</td>
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<td>0.01</td>
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<td>HHC-120</td>
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<td>-0.02</td>
<td>TNP-120</td>
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<td>0.0</td>
<td>TNW-120</td>
<td>0.10</td>
<td>-0.03</td>
</tr>
<tr>
<td>HHC-150</td>
<td>-7.73</td>
<td>-10.93</td>
<td>TNP-150</td>
<td>0.07</td>
<td>-0.08</td>
<td>TNW-150</td>
<td>0.08</td>
<td>-0.06</td>
</tr>
</tbody>
</table>
5.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was conducted to confirm the chemical composition and elemental chemical state of the hydrothermally synthesized TiO$_2$ structures (HHC, TNP and TNW) with different morphology achieved as reaction time increased. The survey spectra shown in Fig. S4 (appendix A) confirmed the presence of Ti, O and C, which was consistent with chemical composition of the TiO$_2$ sensors. No contaminants were present and all the peaks were calibrated with respect to C1s peak, however the traces of C element on the surface of the nanostructures were due to exposure to ambient air.

The representative high-resolution core level spectra of Ti corresponding to HHC, TNP and TNW are shown in Fig. 5.6a-c. The Ti 2p spin orbit doublets peaks displayed the characteristic split of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$. A broadening at lower binding energies was observed as reaction time increased signaling an increase in vacancies as Ti$^{4+}$ is reduced to Ti$^{3+}$, moreover it is clear indication of non-stoichiometric (TiO$_{2-x}$) [31]. The separation energy was measured as 5.7, 5.75, and 5.76 eV for HHC, TNP and TNW sensors which is less than the standard value of 5.70 eV in anatase indicative of the shift to lower energy [28, 29]. The doublets were deconvoluted resulting into two subpeaks each. For HHC the subpeaks were centred at 457.1 eV and 459.0 eV for 2p$_{3/2}$ and at 462.8 eV and 464.6 eV for 2p$_{1/2}$; for TNP the subpeaks were centred at 457.1 eV and 458.9 eV for 2p$_{3/2}$ and at 463.1 eV and 464.7 eV for 2p$_{1/2}$. More interestingly on the TNW sensor, the Ti 2p$_{3/2}$ doublet encompassed 3 peaks centred at 455.1 eV, 457.4 eV and 458.8 eV for 2p$_{3/2}$ and Ti 2p$_{1/2}$ centred at 461.3 eV and 464.3 eV. For each doublet, the subpeaks at higher energies i.e. 459.0, 458.9 and 458.8 eV and 464.6, 464.7, and 464.3 eV, were attributed to Ti$^{4+}$ valence states of both 2p$_{3/2}$ and 2p$_{1/2}$ respectively [8, 28, 29]. Whereas, the low intensity
subpeaks at lower energies 457.1, 457.4 eV and 462.8. 463.1 and 461.3 eV were attributed to Ti$^{3+}$ valence state [8, 28, 29, 32]. The additional lower energy peak observed at 455.1 eV was attributed to the presence of lower valence states of Ti ions (Ti$^{2+}$) in the TNW sensor [29, 31].

Fig. 5.6d-f displays the O 1s core level spectra of the synthesized TiO$_2$ sensors. The curves display an asymmetric distribution with a tail extending towards higher binding energies which was indicative of the chemical state of oxygen on the surface. The curves were deconvoluted into 3 subpeaks centred at 530.1, 531.1 and 532.2 eV for HHC, 530.0, 531.1 and 532.1 eV for TNW where else the TNP show a shift to lower binding energies with peaks centred at 529.7, 530.4 and 531.8 eV. The intense subpeaks at about 530.1 eV were attributed to O$^{2-}$ ions in the TiO$_2$ crystal lattice, while the subpeaks at 531.5 eV were due to oxygen deficient regions (O$_{Ti^{3+}}$) and the peaks at 532.2 eV were assigned to hydroxyl groups absorbed on the surface [8, 28, 29, 32]. Zhang et al. [33] observed the peak at 529.7 eV and it was attributed to lattice oxygen combined with Ti$^{4+}$. As seen in Table S1, the quantitative analysis of Ti$^{3+}$ state was given by the area percentage and was found to be about 29.38% for hierarchical arranged nanostructures and 27.16% for the nanoparticles. However, the ratio drastically increased to 40.57% as the concentration of lower valence states of Ti ions (Ti$^{3+}$ and Ti$^{2+}$) increased in the nanowire (TNW) sensor.
Fig. 5.6: XPS spectra of Ti 2p core level of (b) HHC, (c) TNP and (d) TNW and O1s core level spectra of TiO₂ (d) HHC, (e) TNP and (f) TNW.
5.3.4 Gas Sensing Properties

Working temperature is a vital factor that affects the gas-sensing characteristics. Gas sensing characterization were carried out to determine the effect of morphology, surface structure and working temperature on the TiO$_2$ nanostructures sensing performance. The synthesized TiO$_2$ nanostructures possessing different morphology namely, TNP, TNW and HHC were tested towards various gases (CO, CH$_4$, NH$_3$), including volatile organic compounds (C$_7$H$_8$ and C$_8$H$_{10}$). As shown in Fig. 5.7a, all three samples displayed typical n-type behaviour of a chemiresistive sensor where the resistance decreased in the presence of a reducing gas and recovered upon exposure to dry synthetic air. Besides, there was a change in resistance with an increase in gas concentration. To find the optimum working conditions, the operational temperature was varied between 25-150 °C. Fig. S5 displays the transient resistance plots of various TiO$_2$ nanostructures to CO, C$_7$H$_8$ and C$_8$H$_{10}$ at various working temperatures. The change in resistance of HHC sensor towards CO decreased with increasing the working temperature, while that of TNP and TNW increased with operating temperature towards C$_7$H$_8$ and C$_8$H$_{10}$, respectively.

Fig. 5.7b-d show the sensor response against temperature at a gas concentration of 40 ppm. The sensor response towards reducing gas was estimated by $(R_a/R_g)$-1, where $R_a$ was the sensor resistance in dry air and $R_g$ was the sensor resistance when exposed to target gas. It was observed from Fig. 5.7b that when HHC sensor was exposed to CO gas the sensor response decreased as temperature increased, whereas the opposite behaviour was witnessed for C$_8$H$_{10}$, where the response increased with operating temperature. According to In-situ PL analyses, the higher response of TNW sensor towards C$_7$H$_8$ at the operating temperature of 23 °C
(i.e. RT) is defect dependent, since this coincides well with higher relative concentration of defects observed at the same temperature. However, with regards to improved C₈H₁₀ response at 150 °C, it was clear that it was not defect dependent since at the same temperature the PL intensity related to defects decreased strongly.

**Fig. 5. 7:** (a) Resistance against time plot showing n-type chemiresistive sensor characteristics and the sensor response against temperature at 40 ppm of (b) CO, (c) C₇H₁₀ and (d) C₈H₁₀.
Fig. 5.8a and b a clear temperature-dependent selectivity of the TiO$_2$ TNW sensor is witnessed. The sensors were exposed up to 100 ppm analyte gas at each working temperature, however for comparison purposes the results presented in Fig. 5.8 correspond to 40 ppm gas concentration. When the sensors were exposed to CO, CH$_4$, NH$_3$, and C$_7$H$_8$ the sensors presented higher response at low temperatures (25 ºC) which then decreased as working temperature increased (75 ºC-150 ºC). The HHC sensor showed potential selectivity towards CO with a response of 2.38, whereas the TNW sensor displayed superior response of 6.57 and selectivity towards C$_7$H$_8$ at low temperatures. When the sensors were exposed to 40 ppm C$_8$H$_{10}$ as analyte gas, the sensor response increased with temperature and enhanced response of 9.69 was observed for TNW sensor at 125 ºC (see Fig. 5.8b). Similar behaviour was observed by Kim et al. [21], showing a dual-mode selectivity of a one sensor towards p-xylene and toluene vapours, however at higher operating temperatures of 350 ºC and 400 ºC, respectively, using Nb-doped NiO hollow spheres-based sensor. Additionally, Motsoeneng et al. [34] also observed a temperature-dependent selectivity towards C$_3$H$_7$OH at 75 ºC and C$_2$H$_5$OH at 150 ºC using SnO$_2$ hollow sphere and nanorods based sensors.

In the presence of CO, the HHC sensor presented a more pronounced response value than other sensors. The CO sensing was attributed to surface structure and surface area, although the TNW sensor possessed higher surface area (125.79 m$^2$. g$^{-1}$), the HHC has contribution of both surface area (100.47 m$^2$. g$^{-1}$) and larger amount of meso-macro pores (~26.31 nm). Additionally, the hierarchical architecture enables percolation of gas to penetrate into the entire layer, such that each individual grain is affected and more surface-active sites are exposed, hence the rapid response was observed. However, at elevated temperatures response...
decreased, due to the fact that the mean surface lifetime is inverse to temperature and there is less interaction between surface and gas molecules as desorption of gas is greater than adsorption [13, 35].

Fig. 5.8: Selectivity plot of the various sensors exposed to 40 ppm gas concentration at (a) 25 °C and (b) 150 °C.

In addition, it was observed that for the VOCs (Fig. 5.7c-d) sensing was not solely dependent on the surface area, but also on the decomposition and volatility of C7H8 and C8H10. The TNW sensor displayed enhanced response towards the VOCs (i.e. C8H10) followed by TNP sensor, even though it had a smaller surface area (68.23 m²g⁻¹) as compared to HHC, which showed a noisy signal. Recent reports have indicated that anatase TiO₂ with high-energy {001} crystal facets containing plentiful active oxygen species are more conducive for the gas adsorption in comparison to that of the usually exposed {101} crystal facets [36, 37]. The {001} crystal facets contains surplus of unsaturated Ti5c atoms, which might behave as active sites for sensing [38] as a result, the reductive C8H10 molecules are considerably more favourable to be adsorbed on the oxidative {001} facets, instead of the reductive {110} facets. Since both sensors, i.e. TNW and TNP had high ratio {001} facets exposed, they displayed the highest response to 100 ppm C8H10 among the sensors. Thus, the higher response for both TNW and TNP is probably due to exposed high energy {001}
facets which have high activity to absorb organic gases. Lin et al. [39] justified their higher sensing response towards 100 ppm C₈H₁₀ and C₂H₆O vapour, due to high ratio {100} facets exposed of 3D flower-like Fe₂(MoO₄)₃. The room temperature sensing mechanism was proposed for toluene. Moreover, sensing mechanism towards C₈H₁₀ at 125 °C was explained and the dissociation energy of aromatic hydrocarbon groups at elevated temperatures results to increase the sensor response for xylene. Furthermore, the previous study associated this improved performance to C₇H₁₀ and C₈H₁₀ to the gases reformation with reasonable reactivity into more reactive species in the course of the transport of gas via the sensing film with catalytic activity [21]. This is due to the fact that C₇H₁₀ and C₈H₁₀ have adequate reactivity, and assimilated into smaller, and more active species, for example benzaldehyde, benzyl alcohol and benzoic acid, by fractional oxidation [40-44].

The sensor responses as a function of gas concentration plots are shown in Fig. 5.9a-c. In the presence of analyte gas the response increased with concentration and saturated at higher gas concentration when the sensors were exposed to CO and C₇H₈, showing maximum response of 2.46 and 7.65 towards 20 ppm (HHC) and 60 ppm (TNW) of the respective gases. When exposed to C₈H₁₀ at 125 °C, the responses linearly increased with concentration and no saturation occurred and the response of about 36.3 at 100 ppm was recorded for TNW sensor. The higher responses at 100 ppm fit well with the accepted Permissible Exposure Limit by OSHA for the concentration of xylene for breathing zone [45a]. According to the National Institute of Occupational Safety and Health (NIOSH), the endorsed airborne exposure limit is 100 ppm for C₇H₈, while based on American Conference of Governmental and Industrial Hygienists (ACGHI) the threshold limit value is averaged at 20 ppm over a 8-h work-shift for C₇H₈ [45b]. The sensors showed response signal from 10 ppm of C₇H₈ up to
100 ppm, while for C₈H₁₀ a signal was observed for as low as 5 ppm. It is important to note that even though sensor HHC displays good/competitive response (values) towards the VOCs, the sensor signal is extremely noisy making it an unreliable sensor. Furthermore, the sensitivity (i.e. slope) which is the change in response per analyte gas concentration was computed as the slope of the linear fit on the curves as seen in Fig. 5.9d-f. The HHC sensor demonstrated sensitivity (S) value of 0.151 ppm⁻¹ towards CO, while TNW exposed to C₇H₈ and C₈H₁₀, demonstrated values of 0.214 ppm⁻¹ and 0.0241 ppm⁻¹, respectively. Even though the HHC and TNW based sensors displayed higher sensitivity at low concentration, they are not stable at higher concentrations of CO and C₇H₈.

In addition, the limit of detection (LOD) was projected from the experimental data by employing this equation \( LOD = 3 \times \frac{RMS_{\text{noise}}}{slopes} \) [46, 47], where RMS_{noise} is root-mean-square (rms) deviation of the baseline before the exposure to the target gas. The calculated LOD were 0.11, 0.49, 0.49 ppm for HHC sensor towards CO, C₇H₈ and C₈H₁₀, respectively. While TNP displayed LOD values of 2.33, 0.59, 0.26 ppm towards CO, C₇H₈ and C₈H₁₀, and TNW sensor revealed LOD of 0.11, 0.52 and 0.94 ppm towards CO, C₇H₈ and C₈H₁₀, respectively. The appealing low LODs are worthy for real time gas detection. Additionally, quantitative analysis was carried out for cross selectivity, given by the ratio between response of target and interfering gases [48, 49] as shown in Fig. 5.10a-c. The relatively maximum and minimum ratios of S_{C₇H₈}/S_{NH₃} and S_{C₇H₈}/S_{CH₄}, and S_{C₈H₁₀}/S_{CH₄} and S_{C₈H₁₀}/S_{C₇H₈}, respectively, were witnessed and this was an indication that NH₃ does not interfere much in comparison to CH₄ on C₇H₈ at 25 °C and while CH₄ does not interfere much in comparison to C₇H₈ on C₈H₁₀ at 125 C. The less differentiation on the CO (Fig. 5.10a) for HHC indicates that much interferences occur.
Fig. 5.9: Response against gas concentration towards (a) CO, (b) C\textsubscript{7}H\textsubscript{8} and (c) C\textsubscript{8}H\textsubscript{10} and (d-f) their corresponding linear fit.
One of the crucial properties of a sensor is its response ($T_{\text{res}}$) and recovery ($T_{\text{rec}}$) times. The response time is the time taken by the sensor to reach 90% of response in the presence of target gas whereas the time taken for the sensor to reach 90% recovery back to baseline as target gas is flushed out is called the recovery time [49]. As shown in Fig. 5.10a-b when exposed to the analyte gas the sensors show longer $T_{\text{res}}$ of about 2 min at lower concentration (< 20ppm) and decreased to < 1 min as concentration increases and longer $T_{\text{res}}$ were observed between 2-3 min. This behaviour can be attributed to the pore type, causing steep increase in adsorption as gas percolate through the hierarchical structure, due to capillary condensation early onset of recovery is observed hence longer response time. Table 5.2 compares the responses of the current sensors with those reported in literature focusing on CO, C$_7$H$_8$ and C$_8$H$_{10}$ gas sensor based on TiO$_2$. While our current sensors show better performances at low operating temperatures, nonetheless, those reported in the literature display improved performances at higher operating temperatures and some are incorporated with metal additives or heterostructures. Thus, this makes our sensors better candidates due to their advantage in low-power consumption.
Fig. 5.10: Cross-selectivity plots of the TiO$_2$ sensors as a ratio of (a) CO (b) C$_7$H$_8$ and (c) C$_8$H$_{10}$ and the interfering gases. (d) Response and (e) Recovery times of the sensors towards their respective gases.
Table 5.3: Comparison study based on TiO$_2$ gas sensors for CO, C$_7$H$_8$ and C$_8$H$_{10}$.

<table>
<thead>
<tr>
<th>Sensing element</th>
<th>Synthesis procedure</th>
<th>Concentration (ppm)</th>
<th>Operating Temperature ($^\circ$C)</th>
<th>Response (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>TiO$_2$ thin film</td>
<td>Spray pyrolysis</td>
<td>300</td>
<td>300</td>
<td>[18]</td>
</tr>
<tr>
<td>TiO$_2$/perovskite</td>
<td>electrochemical</td>
<td>400</td>
<td>200</td>
<td>38.41%</td>
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</tr>
<tr>
<td>Pd-TiO$_2$ film</td>
<td>flame stabling on a rotating surface</td>
<td>800</td>
<td>400</td>
<td>4.25</td>
<td>[51]</td>
</tr>
<tr>
<td>TiO$_2$ sea-urchin hierarchical</td>
<td>hydrothermal</td>
<td>20</td>
<td>25</td>
<td>2.46</td>
<td>In this work</td>
</tr>
<tr>
<td>C$_7$H$_8$</td>
<td>TiO$_2$ nanotubes</td>
<td>electrochemical</td>
<td>400</td>
<td>42%</td>
<td>[52]</td>
</tr>
<tr>
<td>Pt@ZnO-TiO$_2$ nanotubes</td>
<td>Electrospinning</td>
<td>5</td>
<td>300</td>
<td>11.1</td>
<td>[53]</td>
</tr>
<tr>
<td>3D TiO$_2$/G-CNT</td>
<td>chemical vapour deposition</td>
<td>500</td>
<td>25</td>
<td>42%</td>
<td>[20]</td>
</tr>
<tr>
<td>Au-loaded TiO$_2$ pecan-kernel</td>
<td>hydrothermal</td>
<td>100</td>
<td>375</td>
<td>7.3</td>
<td>[54]</td>
</tr>
<tr>
<td>TiO$_2$ Nanowires</td>
<td>hydrothermal</td>
<td>60</td>
<td>25</td>
<td>7.65</td>
<td>In this work</td>
</tr>
<tr>
<td>C$<em>8$H$</em>{10}$</td>
<td>TiO$_2$ nanotubes</td>
<td>electrochemical</td>
<td>400</td>
<td>42%</td>
<td>[53]</td>
</tr>
<tr>
<td>Hedgehog-like Ag-TiO$_2$ architectures</td>
<td>hydrothermal</td>
<td>100</td>
<td>375</td>
<td>6.49</td>
<td>[5]</td>
</tr>
<tr>
<td>Co$_3$O$_4$/TiO$_2$ composite</td>
<td>pyrolyzing sacrificial template</td>
<td>100</td>
<td>120</td>
<td>11.17</td>
<td>[55]</td>
</tr>
<tr>
<td>TiO$_2$ Nanowires</td>
<td>hydrothermal</td>
<td>100</td>
<td>125</td>
<td>36,26</td>
<td>In this work</td>
</tr>
</tbody>
</table>
5.3.5 Influence of Relative Humidity

Humidity is one of the main challenges towards reliability and stability of the chemiresistive sensors as it affects its electrical characteristics, resulting into poor sensing response to target gas, more especially at low operating temperatures. For comparison purposes, the influence of relative humidity (RH) on the HHC sensor was tested towards 40 ppm CO while the TNW was tested towards 40 ppm C7H8 and C8H10 concentration. The RH ranged between 10 and 50 %. For CO and C7H8 the measurements were conducted at an operating temperature of 25 °C and C8H10 at 125 °C and the results are displayed in Fig. 5.11. It is remarkable to show that when HHC and TNW sensors were exposed to CO and C7H8, respectively at low temperatures (25 °C) the sensors displayed drastic change in resistance (i.e. improved response, see Fig. S6) as RH increased from 10 % to 50%. This was indicative that the material is prone to water vapour as it reacts with adsorbed oxygen and release electrons, which result to an increase in sensor response (see Fig. S2) [56]. However, when the TNW sensor was tested towards 40 ppm C8H10 in the presence of various RH at elevated temperature (125 °C), the response decreased at low RH, suggesting physiosorbed water on active sites [48, 57] and as the RH increased the change in resistance increased up to 50 % compared to low RH. This behaviour relates that the CO, C7H8 and C8H10 do not compete with humidity for reaction partners on the HHC and TNW sensors surface, instead the sensors performance is promoted by humidity. Previous reports [58, 59] have indicated that by operando diffused-reflectance infrared Fourier transform infrared spectroscopy that the RH will generally interact with the metal surface and not be in competition with the adsorbed gas molecules for the pre-adsorbed oxygen ions, consequently its interfering effects in the sensing was noticeably reduced.
Fig. 5. 11: Dynamic resistance of (a) HHC sensors to 40 ppm CO at 25 °C, (b-c) TNW to 100 ppm C$_7$H$_8$ and C$_8$H$_{10}$ at 25 and 125 °C, respectively at various relative humidity.

To investigate the long-term stability analyses, we conducted the sensing performances towards C$_7$H$_8$ and C$_8$H$_{10}$ for three months in the presence of various relative humidity conditions, as displayed in Fig. 12. By comparing the resistance behaviour towards C$_7$H$_8$ and C$_8$H$_{10}$ of the fresh sensor with that stored for three in ambient conditions, while both being tested in the presence of RH, it clear that the change in resistance for the sensor stored for three months is significant in comparison to that of the fresh sensor. Furthermore, it is worthy to mention that by increasing the
RH, the resistance change becomes more significant. Thus, in terms of response as shown in Fig. 12c and d, when the sensors are tested towards \( \text{C}_7\text{H}_8 \) and \( \text{C}_8\text{H}_{10} \) the responses of the sensors stored for three months increased strongly with an increase in RH in comparison to the fresh sensor. At 50 % RH, the response increased 20 times more in relation to that tested in dry air. This behaviour clearly denote that the sensor is RH dependent, and to best of our knowledge this behaviour shown by the sensor stored for three months has never been reported. Detailed analyses are required to further understand the mechanism behind this behaviour and such analyses will fall as part of the future work.

**Fig. 5.12:** Real-time resistance of the (a) Fresh sensor and 3 months stored sensor, (c-d) Response versus RH of Fresh sensor and that stored for 3 months tested towards \( \text{C}_7\text{H}_8 \) and \( \text{C}_8\text{H}_{10} \) in the presence of various relative humidity conditions.
5.3.6 Sensing Mechanism

The detection ability of chemiresistive gas sensors is strongly dependent on the change in electrical properties of semiconductor material’s surface, due to the interaction with gas molecules. In the presence of dry air, the TiO$_2$ sensors surface interacts with atmospheric oxygen, which get adsorbed. The chemisorbed oxygen extracts electrons from the surface forming oxygen species such as $O_{2(ads)}^-$, $O^-$, $O_{2}^-$ which are dependent to the operating temperature as expressed in equation 5.5 and 5.6.

$$O_{2,ads} + e^- \rightarrow O_{2,ads}^- \quad (T< 100 \, ^\circ C)$$ (5.5)

$$O_{2,ads}^- + e^- \rightarrow O_{ads}^- \quad (100 \, ^\circ C < T< 300 \, ^\circ C)$$ (5.6)

Consequently, for n-type semiconductors a depletion region gets formed on the material’s surface (see Fig. 13a). In this layer the electron concentration is low and energy barrier is high, hence the sensor resistance increases [18, 60]. When the sensors are exposed to CO (reducing gas), the gas molecules react with the chemisorbed oxygen and oxidize CO forming CO$_2$ and an electron is released back to the surface as shown in the reaction in equation 5.7 and schematic in Fig. 13a.

$$2CO + O_{2,ads}^- \rightarrow 2CO_2 + e^-$$ (5.7)

The injected electrons narrow the depletion region and resistance thus the effect is observed as an increase in electrical conductivity. The reaction of CO with ionized oxygen species, decreases the TiO$_2$ surface negative charge, consequently lowering the energy barrier between the grains, therefore the electrons freely migrate. In an intrinsic semiconductor, morphology is highly influential to the change in surface charge and charge resistance [51]. Similar behaviour is expected for both C$_7$H$_8$ and
C₈H₁₀ vapours and the sensing reaction at 25 and 125 °C, respectively are expressed in equations 5.8 and 5.9 [61, 62].

\[
C₆H₅CH₃ + 9O²⁻_{ads} \rightarrow 7CO₂ + 4H₂O + 9e^{-} 
\]  

(5.8)

\[
C₆H₇(CH₃)₂ + 21O²⁻_{ads} \rightarrow 8CO₂ + 5H₂O + 21e^{-} 
\]  

(5.9)

As seen from equations (5.8 and 5.9) and schematic in Fig. 13b and c, there is a large number of electrons with potential to be donated to the surface and increase with the carbon chain. PL and XPS analyses confirmed that the TNW sensor has the highest concentration of V₀, which acts as electron donors to the surface adsorbed oxygen ions, resulting to oxidized gas molecules, hence a large amount of electrons was injected back to the sensor and electrical conductivity increased.
Fig. 5.13: Sensing mechanism related to (a) CO, (b) C\textsubscript{7}H\textsubscript{8} and (c) C\textsubscript{8}H\textsubscript{10} vapours detection at 25 and 150 °C.
5.4 Conclusion

In summary, TiO$_2$ nanostructures with different morphologies were successfully achieved via hydrothermal method. The nanowires and flower-like hierarchical architecture possessed relatively high surface area (100 and 125 m$^2$. g$^{-1}$, respectively) and interconnected pores with diameters ranging from meso-macro pores. Sensing characteristics of the fabricated sensors were assessed towards CO, C$_7$H$_8$ and C$_8$H$_{10}$ gases whose presence in an indoor environment can cause severe health risks. At optimum working temperature of 25 °C, a more pronounced response towards 20 ppm CO was presented by HHC with a response and recovery times of 85 and 124 seconds and was attributed to the available surface area and active sites presented by the morphology (hierarchically arranged nanowires). Additionally, our sensing tests using one sensor displayed an admirable temperature-dependent dual-functionality sensing performance to selectively detect C$_7$H$_8$ and C$_8$H$_{10}$ vapours in robust behaviour at low operating temperatures (25 and 150 °C), respectively, in comparison to any previously TiO$_2$-based sensors reported in the literature. Finally, we have shown that our current dual-selectivity sensor with a robust stability towards C$_7$H$_8$ and C$_8$H$_{10}$ vapours by tailoring operating temperature, could be attractive from the economic point of view due to low power consumption and appeal for air quality monitoring.
5.5 References


(b) https://www.cdph.ca.gov/Programs/CCDPHP/DEODC/OHB/HESIS/CDPH%20Document%20Library/xylene.pdf


CHAPTER 6: High Stability to Humidity Changes and Improved BTEX Gas Sensing Characteristics of Thermally Treated TiO₂ Hierarchical Spheres Manifested by High-Energy {001} Crystal Facets

Abstract

Aromatic hydrocarbons like benzene, toluene, ethylbenzene and xylene (BTEX) are lethal volatile organic compounds, which should be precisely monitored to maintain occupational safety and indoor air quality. Thus, herein, the superior sensitivity towards toluene and ethylbenzene, among other BTEX was exhibited by thermally treated sea-urchin like TiO₂ hierarchical spheres achieved via hydrothermal method. X-Ray diffraction patterns displayed improvement in crystallinity with annealing temperature and a total phase transformation to rutile phase, due to thermal instability of anatase phase. The Brunauer-Emmett-Teller surface area analyzer showed that porosity increased with annealing temperature, whereas a thermal quench after 500 °C was observed on the photoluminescence results. To demonstrate the uniqueness of hierarchical structure and the effect of annealing at different temperatures, the gas sensing performances towards BTEX vapours was evaluated at various conditions. The T5 sensor displayed temperature dependent selectivity towards ethylbenzene at 75 °C, with a detection limit of ~100 ppb. The T7 sensor revealed the highest response of 13 towards toluene at 150 °C, which could be justified by exposed high surface energy {001} facets, containing plentiful active oxygen species, which are more active for adsorption of toluene. The sensors displayed a clear stability towards relative humidity (10-90%), which is very vital for practical and real-time applications in
ambient conditions. The fundamental gas sensing mechanism associated to the
detection of BTEX vapour was discussed in detail.

6.1 Introduction

Based on its volatility, organic compounds can be classified into volatile organic
compounds (VOCs), semi-volatile organic compounds (SVOCs), and non-volatile
organic compounds (NVOCs) [1]. Among the VOCs there are aromatic hydrocarbons,
benzene, toluene, ethylbenzene and xylene and are mostly referred to as BTEX. BTEX
vapours are highly hazardous, and carcinogenic in nature. The major sources of BTEX
vapour emissions are refining of crude oil and burning of coal and followed by the use
in industrial processes (like paints, adhesives and pesticides), and human activities
such as transportation [1-5]. These gases have short-term effects such dizziness,
headaches, eye, throat and skin irritation. Additionally, they can induce long-term
effect on human health as they may affect the nervous and respiratory systems.
Exposure to ethylbenzene and benzene may cause bone marrow abnormalities and
leukaemia. Xylene may cause damage to the kidneys and liver. Whereas toluene may
induce termination of pregnancy in females [6-8]. Therefore, air quality monitoring in
living and work spaces is of great importance to timely detect the presence of BTEX
even at low concentrations and minimise exposure.

Among the many used devices (gas chromatography, mass spectroscopy,
cathodoluminescence, etc.) for monitoring BTEX vapour [9], metal oxides
semiconductor (MOS) gas sensors are highly used, due to advantages such as high
sensitivity, rapid response time, easy fabrication, portability and affordability [10, 11].
Extensive studies have been done on different metal oxides (TiO₂, SnO₂, In₂O₃, WO₃,
Cu₃O₄ and ZnO) for BTEX sensing. However, their short coming were the high
operating temperatures. Such as the work done by Woo et al. [5] on Co-ZnO branched nanowires synthesized via multiple step vapour phase reactions. The branched nanowires displayed ultra-selectivity and sensitivity to 5 ppm p-xylene at 400 °C compared to toluene and benzene. Seo et al. [12] reported high response to toluene at 500 °C using porous TiO$_2$ nanotubes thin films. To overcome the high working temperatures, addition of dopants and heterostructures have been employed, however this approach depends on the amount of dopants and metal incorporation. A 0.5% Au-loaded TiO$_2$ hedge-hog architectures achieved via hydrothermal method and isometric impregnation route exhibited enhanced response at 100 ppm Xylene at 375 °C operating temperature [3]. ZnO-SnO$_2$ core-shell nanowires synthesized via vapour-liquid-solid growth technique and atomic layer deposition were tested towards carbon monoxide, benzene and toluene by Kim et al. [13]. The authors reported enhanced response towards 10 ppm toluene at 300 °C. Seekaew et al. [14] achieved a room temperature toluene sensing using 3D TiO$_2$/ graphene–carbon nanotubes and optimal response was observed at 500 ppm. In addition, extreme sensitivity and selectivity were displayed by NiO/NiMoO$_5$ nanocomposite hierarchical spheres towards 5 ppm xylene, in the presence of toluene and benzene, at 375 °C [4].

TiO$_2$ is a promising metal oxide for BTEX detection, owing to highly active surface provided by anatase phase. Moreover, it can be easily synthesised following different procedures that promote defect states such as oxygen vacancies. Among the different morphologies that can be achieved, hierarchical architectures are more attractive, due to the enhanced surface to volume ratio and interconnected pore network. Besides, to best of our knowledge few studies exist on the detection of ethylbenzene. Most researchers study xylene which is a composition of isomers (m-p- and o xylene) [15, 16]. Additionally, limited reports on metal oxide based sensors exist
on the detection of benzene derivatives, such as ethylbenzene, triethylbenzene, and chlorobenzene. Mostly used materials are conducting polymers such as doped polypyrrole polymers [17, 18], polyaniline nanofibers [19] and polymerized n-octadecylsilane surface [20]. Thus, in the present work, we report on the low temperature gas sensing performance towards ethylbenzene and toluene vapours using thermally treated sea-urchin like hierarchical TiO₂ architectures synthesized via simple hydrothermal method. The hierarchical TiO₂ architectures (T7) sensor illustrated the best response towards toluene at 150 °C. Our findings further disclosed the possible detection of benzene at 5 ppm using T7 based sensor, and its response increased with relative humidity (RH) percentage (10-90%), displaying that it is susceptible to water vapour. Such behaviour was also witnessed for T5 sensor towards toluene in the presence of RH. The essential gas sensing mechanism associated to the detection of BTEX vapour was discussed in detail.

6.2 Experimental Details

6.2.1 Synthesis Procedure

The reagents used in this experimental work were purchased from Sigma Aldrich and used with no further purification. 2 g of TiO₂ P25 Degussa was added to sodium hydroxide solution and stirred to attain homogeneity. H₂O₂ was later added dropwise under vigorous stirring before transferring to a Teflon-lined autoclave. The product was then allowed to cool down to room temperature and separated by centrifugation. The solid product was washed with 0.2 M HCl and distilled water (DW) as to reach the desired pH of 7. The final product was dried at 80 °C and annealed at 300, 500, 700 and 900 °C for 2 hours at each temperature. The samples obtained
were in a powder form and were labelled as T0, T3, T5, T7, and T9, corresponding to the as-prepared, 300, 500, 700 and 900 °C annealing temperatures, respectively.

6.2.2 Material Characterization

The crystal structure of TiO$_2$ was examined using Panalytical X’pert PRO PW 3040/60 X-ray diffractometer (XRD) equipped with a Cu-K$_\alpha$ ($\lambda = 0.154$ nm) monochromatized radiation source. High-resolution transmission electron microscopy (HR-TEM) was used to examine internal structure using a JEOL-TEM 2100 instrument operated at 200 kV. Surface morphology analyses were examined using an Auriga ZEISS scanning electron microscopy (SEM) at an accelerating voltage of 3 kV. The Micromeritics TRISTAR 3000 Brunauer-Emmett-Teller (BET) surface area analyzer technique was used to probe the surface area and the pore volume analysis of the samples. The Photoluminescence (PL) spectra were measured using the Cary Eclipse fluorescence spectrophotometer and the PHI 5000 Versaprobe-Scanning ESCA Microprobe was used to carry out X-ray photo-electron spectroscopy (XPS) analysis.

6.2.3 Sensing Films Preparation and Characterization

Gas sensing films were fabricated by homogenously mixing TiO$_2$ hierarchical spheres using ethanol to form a slurry and the slurry was pasted on alumina substrates (size: 2 mm x 0.5 mm) containing interdigitated Pt-electrodes and a micro-heater backside. The KSGAS6S commercial gas testing apparatus (KENOSISTEC Model, Italy) was used to investigate the sensing performance of TiO$_2$ nanostructures. The BTEX vapours were supplied by National Metrology Institute of South Africa, while the synthetic air was supplied by Air Liquid, South Africa. The sensing layers were properly heated by using precise voltage and current to the backside of the heaters employing DC-power supply and fine-tuning the exact values based on the sensor’s temperature.
calibration. The calibrated temperatures ranged from 25 to 150 °C. The sensing resistances of the sensors to various concentrations (5-100 ppm) of BTEX gases (i.e. benzene (C₆H₆), toluene (C₇H₈), ethylbenzene (C₆H₅CH₂CH₃), and m-xylene (C₈H₁₀) were measured by switching between the mixture of gases and synthetic dry air. The humidity influence was tested using the programmable temperature & humidity test chamber. The gases will be referred to as E- C₆H₆ for ethylbenzene, C₆H₅-benzene, C₇H₈-toluene, and C₈H₁₀ m-xylene throughout this work.

6.3 Results and discussion

6.3.1 Structural Characteristics

Fig. 6.1a displays the X-ray diffraction patterns of the as-synthesized and thermally treated TiO₂ hierarchical spheres. The as-prepared sample (T0) indicated an amorphous crystalline state due to the formation of Ti-O-Na and Ti-OH bonds during reduction of P25 in NaOH solution hence after washing, H₂Ti₆O₁₇ was formed (observed broad peak). However, when the material was subjected to thermal treatment, crystallinity improved and diffraction peaks were observed and assigned to anatase phase based on JCPDS. #00-021-1272. The facets of lower angle peaks of anatase TiO₂ possess high surface energy, however the commonly exposed (101) peak has {101} facet with surface energy of 0.44 J.m⁻², which is less than 0.90 J.m⁻² of {001} facet [21, 22]. Therefore, the increased (004) peak intensity as the annealing temperature increased to 700 °C was indicative of the exposed {001} facet, which is highly favourable to gas sensing performance. Furthermore, the samples exhibited a complete phase transition from anatase to rutile (JCPDS. #00-086-0147) TiO₂ at higher annealing temperature (T9).
It was clearly observed that the width of the diffraction peaks narrowed as annealing temperature increased due to the growth in crystallite size. This was supported by the crystallite size (\(L_{W-H}\) and \(L_{D-S}\)), lattice strain (\(\varepsilon\)) and full width at half maximum (FWHM (\(\beta\))) measurements presented in Table 6.1, obtained from the Williamson-Hall and Debye Scherrer. Lattice contraction and expansion was indicated by the positive/negative lattice strain and shift to higher angles of the (101) and (110) peaks. Additionally, the lattice parameters (\(a\) and \(c\)) and volume were calculated from the (200), (004) and (101), (110) peaks for anatase and rutile TiO\(_2\), respectively. As presented in Table 6.1 and Fig. 6.1c-e, parameters \(a\), \(c\) and volume (\(V=a^2c\) for tetragonal structure) were in agreement with contraction and expansion of T5 and T7. Even though the lattice volume decreased with an increase in crystallite size, the lattice symmetry (\(c/a\)) remained unchanged at about 2.51 for anatase and 0.65 for rutile TiO\(_2\). Similar behaviour was reported by Santara et al. [23] in rutile TiO\(_2\) nanostructures obtained by varying reaction temperatures and times. Moreover, quantitative phase analysis in Fig. 6.1d presented a direct relation between lattice volume and anatase content, i.e., as anatase percentage decreased as the volume decreased.

### 6.3.2 Morphology and Surface Characterization

The SEM images of the as-synthesized and thermally treated TiO\(_2\) nanostructures are presented in Fig. 6.2. Hierarchically arranged architecture of radial nanowires forming sea-urchin like microsphere were observed with non-uniform diameters. The T0 nanostructures displayed smaller microspheres with diameters 2-4 \(\mu\)m with thin nanowires of about 8.9 nm average diameters where else, when the samples were subjected to thermal annealing (T3, T5 and T7) they grew in diameter to above 5 \(\mu\)m.
Fig. 6 1: (a) X-Ray diffraction pattern of the annealed TiO$_2$ nanostructure. (b) Crystallite sizes calculated using Williamson–Hall and Scherrer equation. (c) Lattice parameters a, c and correlation of lattice volume with (d) anatase and (e) Rutile content as temperature increased.
**Table 6.1:** Summary of crystallite size and lattice parameters of the as prepared and thermally treated TiO$_2$ nanostructures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Lattice parameters</th>
<th>Crystallite size</th>
<th>FWHM $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$a$ (nm)</td>
<td>$c$ (nm)</td>
<td>$c/a$</td>
</tr>
<tr>
<td>T0</td>
<td>Amorphous</td>
<td>0.3736</td>
<td>0.9395</td>
<td>2.51</td>
</tr>
<tr>
<td>T3</td>
<td>semi crystalline</td>
<td>0.3756</td>
<td>0.9397</td>
<td>2.51</td>
</tr>
<tr>
<td>T5</td>
<td>Anatase</td>
<td>0.3751</td>
<td>0.9417</td>
<td>2.51</td>
</tr>
<tr>
<td>T7</td>
<td>Anatase</td>
<td>0.3751</td>
<td>0.9397</td>
<td>2.51</td>
</tr>
<tr>
<td>T9</td>
<td>Rutile</td>
<td>0.4575</td>
<td>0.2952</td>
<td>0.65</td>
</tr>
</tbody>
</table>
More remarkably, at annealing temperatures greater than 700 °C, the nanowires became rod-like in shape and increased in thickness and diameters of about 6 μm and 26.5 nm for the microspheres and nanowires were measured for T9. Moreover, the nanostructures displayed a porous surface of loose nanowires with voids/paths forming an interconnected pore structure which is favourable for gas adsorption and diffusion.

To further study the morphology and structure of the TiO$_2$ nanostructures, TEM analyses were carried out as displayed in Fig. 6.3. The TEM images are in agreement with the SEM observations of the hierarchical architecture of the nanostructures. The selected area electron diffraction (SAED) patterns confirmed the crystalline state of the nanostructures. The amorphous phase of T0 was confirmed by the diffused rings observed on the SAED patterns, while for the annealed samples (T3-T9) bright rings were observed due to diffraction of polycrystalline nanostructures and were assigned to (101) and (110) crystal planes of TiO$_2$.

Fig. 6.4a-c presents the nitrogen adsorption-desorption isotherms, their corresponding pore size distribution curves and the relation between surface area and porosity possessed by the as-prepared and thermally treated TiO$_2$ hierarchical spheres. The samples displayed type IV isotherms indicating the dominance of mesopores (2-50 nm) and a hysteresis loops at high relative pressures (>0.8 P/Po). For T0, T3 and T5 H2 hysteresis loop occurred at 0.8 P/Po and was governed by mesopores that leads to multilayer formation. Whereas, an H4 loop was observed for T7 and T9 and condensation occurred at higher pressures 0.9 and 0.95 P/Po respectively, giving sharp capillary condensation governed by mesopores in the higher
range (diameters closer to 50 nm). Similar behaviour was observed by Tan et al. [24] for nonporous gold plates subjected to thermal annealing.

**Fig. 6 2:** SEM micrographs of the as-prepared and thermally treated TiO$_2$ hierarchical spheres.
Fig. 6 3: TEM and HR-TEM micrographs and SAED patterns of the as-prepared and thermally treated TiO$_2$ hierarchical spheres.
The pore distribution curves in Fig. 6.4b revealed that the materials involved of funnel-like (open ends) pores with wide mouths and narrow bodies with volumes of 0.678, 0.929 and 0.585 cm$^3$/g for T0, T3 and T5. Consequently, as the annealing temperature increased the pores in T7 and T9 become wider in diameter and shallower in volume (0.299 and 0.0120 cm$^3$/g respectively). More interestingly the physisorbed quantity displayed in the isotherms decreased as the annealing temperature increased similarly on Fig. 6.4c, the surface area decreased. This behaviour was attributed to agglomeration of the nanowires closing the voids provided by the morphology and decreasing the surface area when annealed under high temperatures.

**Fig. 6 4:** (a) N$_2$ adsorption-desorption isotherms (inset: hysteresis loop), (b) pore distribution and (c) the relation between surface area and pore diameter of the as-prepared and thermally treated TiO$_2$ hierarchical spheres.
6.3.3 Optical and Elemental Composition State

In order to study the type of defects (donor or acceptor) and impurities present in the energy band and also understand the effect of thermal treatment on the TiO$_2$ hierarchical spheres, PL measurements were conducted. Fig. 6.5 displays the room temperature PL spectra for the as-prepared (T0) and annealed (T3, T5, T7 and T9) TiO$_2$ nanostructures.

The nanostructures exhibited strong emission peaks in the visible region (3.5-1.9 eV) with a slight blue shift. It is noticeable from Fig. 6.5b that PL intensity increased with annealing temperature up to 500 °C (T0-T5). This behaviour was attributed to removal of moieties from the amorphous H$_2$Ti$_8$O$_{17}$ as crystallinity improved from amorphous structure to tetragonal TiO$_2$ structure. At temperatures above 500 °C, a thermal quench was observed for the T7 and T9 materials, owing to the transformation in crystallite phase and surface, as witnessed in XRD and BET analyses. The emission peak at 2.9 eV is more intense than 3.1 eV, which is an indication that the TiO$_2$ nanostructure is dominated by surface state emissions over excitonic emissions. Additionally, as annealing temperature increased to 500 °C, the emission peaks at 2.8, 2.7, and 2.3 eV sharpened and became more prominent.

The near band edge emission at 3.1 eV was observed for all the samples. The series of dominating emissions falling within the violet-blue region were centred between 2.9 and 2.7 eV, and attributed to the de-excitation from lower levels in Ti$^{3+}$ 3d states of TiO$_2$ lattice to the deep levels (acceptor) created by (OH$^-$) [23, 25, 26]. The green emission peaks at 2.34, 2.29 eV and yellow emission at 2.06 eV were assigned to the de-excitation from lower levels in the oxygen vacancies of TiO$_2$ lattice to the ground state [23, 25, 26]. At higher annealing temperature (T9) the defects intensity
decreased, due to interaction of the metal oxide with oxygen since the annealing was done under oxygen rich environment. The Commission International de l’Eclairage (CIE) chromaticity diagrams analyses were performed and the results confirmed blue emission, validating the formation of structural defects (see Fig. S1 in Appendix B).

**Fig. 6 5:** (a) Room temperature PL spectra of the as-prepared and thermally treated TiO$_2$ hierarchical nanostructures. (b) and (c) are high magnification regions extracted from Fig. 6.5a.
X-ray Photoelectron spectroscopy studies were conducted to affirm the chemical composition and surface state of the as-prepared and thermally treated TiO$_2$ hierarchical nanostructures. The wide scan survey spectra confirmed the presence of Ti, O and C and no other impurities were observed (see Fig. S2, appendix B). The carbon peak was noticed at an energy range of 290-280 eV and was used to baseline-correct the high resolution scans of Ti and O.

The Ti2p core level spectra for T0, T3, T5, T7 and T9 in Fig. 6.6a-e showed distinct peaks around 459 and 465 eV, due to the spin orbital splitting of the state into 2p$_{3/2}$ and 2p$_{1/2}$ duplets. The deconvoluted duplets of sample T0 showed peaks at 457.4, 459.1 eV for 2p$_{3/2}$ and 463.5, and 464.8 eV 2p$_{1/2}$. While the T3 sample showed peaks at 455.5, 457.1 and 458.9 eV for 2p$_{3/2}$ and 463.2 and 464.7 eV 2p$_{1/2}$. For T5, peaks were at 455.2, 456.9 and 458.8 eV corresponding to 2p$_{3/2}$ and 463.3 and 464.7 eV corresponding to 2p$_{1/2}$. Where sample T7 showed peaks at 457.4, 459.1 eV corresponding to 2p$_{3/2}$ and 463.5 and 464.8 eV linked to 2p$_{1/2}$. Sample T9 revealed at 456.5 and 458.5 eV associated to 2p$_{3/2}$ and 462.3 and 464.2 eV corresponding to 2p$_{1/2}$. The peaks at higher energies of the duplets (i.e. 459.1, 464.8 for T0, 458.9, 464.7 eV for T3, 458.8, 464.7 eV for T5, 459.1, 464.8 for T7 and 458.5 and 464.2 eV for T9) were attributed to Ti$^{4+}$ energy state. Whereas peaks at lower energy (i.e. 457.4, 463.5 for T0, 457.1, 463.2 eV for T3, 456.9, 463.3 eV for T5, 457.4, 463.5 for T7 and 465.5, 462.3 eV for T9) were attributed to Ti$^{3+}$ energy state. The appearance of the peaks at 455.5 and 455.2 eV in sample T3 and T5 indicated the presence of Ti ions at lower energy state (Ti$^{2+}$), indicating the non-stoichiometry of the materials, which is favourable for MOX gas sensors [23, 26-29].
The O1s core level spectra for the TiO$_2$ hierarchical nanostructures are shown in Fig. 6.6 f-j, and a characteristic curve centred at 530 eV with a broadening extending to higher energies was observed. The deconvoluted peaks centred at 530.3, 530.3, 530.1, 530.2 and 529.7 eV are attributed to $O_L$ ions within the TiO$_2$ lattice in T0, T3, T5, T7 and T9, respectively. The peaks at 531.3, 531.4, 531.0, 530.8 and 531.5 eV for T0, T3, T5, T7 and T9, respectively were assigned to hydroxyl groups (O$_{OH}$) on the surface. Additionally, peaks at 532.6, 532.3, 532.1 and 532.2 eV for T0, T3, T5 and T7 are due to the chemisorbed oxygen (O$_C$) species on the surface [23, 25]. As the annealing temperature increased, the OH peak decreased (disappeared in T9). The quantitative analysis of relative concentration of Ti$^{4+}$ and Ti$^{3+}$ related defects are displayed in Table 6.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti$^{4+}$ (%)</th>
<th>Ti$^{3+}$ (%)</th>
<th>Ti$^{4+}$/Ti$^{3+}$</th>
<th>$O_L$ (%)</th>
<th>O$_{OH}$+C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>64.12</td>
<td>35.88</td>
<td>1.79</td>
<td>59.85</td>
<td>40.16</td>
</tr>
<tr>
<td>T3</td>
<td>74.80</td>
<td>19.15</td>
<td>3.91</td>
<td>89.44</td>
<td>16.53</td>
</tr>
<tr>
<td>T5</td>
<td>74.05</td>
<td>21.32</td>
<td>3.47</td>
<td>76.50</td>
<td>23.53</td>
</tr>
<tr>
<td>T7</td>
<td>70.53</td>
<td>29.46</td>
<td>2.39</td>
<td>64.08</td>
<td>45.92</td>
</tr>
<tr>
<td>T9</td>
<td>74.36</td>
<td>25.62</td>
<td>2.30</td>
<td>93.09</td>
<td>6.91</td>
</tr>
</tbody>
</table>

Table 6.2: Relative percentage of Ti$^{4+}$ and Ti$^{3+}$ related defects of thermally treated TiO$_2$ hierarchical structures.
Fig. 6: X-ray Photoelectron (a-e) Ti2p and (f-j) O1s core level spectra of the as-prepared and thermally treated TiO$_2$ hierarchical nanostructures.
6.3.4 Gas Sensing Characteristics

Gas sensing performance based on the as-prepared and thermally annealed TiO$_2$ hierarchical nanostructures were investigated to study the influence of the phase, defects and surface structure presented by these sensing materials. Gas sensing in MOX is a surface phenomenon and is highly influenced by the change in charge concentration as the material interacts with a gas in the environment. Oxygen from the ambient air gets chemisorbed on the sensor surface and create acceptor levels for the analyte gas, however, the type of oxygen species (i.e. $O^-$, $O_2^-$, $O^{2-}$) formed are highly reliant on the operating temperature. Therefore, the optimum operating temperature for the TiO$_2$ hierarchical nanostructures was explored within 25-150 °C range at constant concentration of 100 ppm E- C$_6$H$_6$, C$_6$H$_8$, C$_7$H$_8$, and C$_8$H$_{10}$ vapours.

Fig. 6.7a-d presents the sensor response against operation temperature for the TiO$_2$ hierarchical sensors. The sensor response for the reducing gases was calculated using the following formula: $(R_a/R_g)-1$, where $R_a$ represents the sensor resistance in dry air, while $R_g$ represents the resistance towards a target gas. Upon exposure to E- C$_6$H$_6$ (Fig. 6.7a), which is a benzene derivative, the T5 sensor displayed optimum response at 75 °C in comparison to other sensors and gases. For instance, when the operating temperature increased its response decreased. While the responses of other sensors to other gases increased with operating temperature, showing optimum response at 150 °C towards all gases. This behaviour is in agreement with the observation displayed in Fig. 6.7e, where the sensor resistance in air decreased as temperature increased. This is due to the fact that conduction of extrinsic semiconductors is dependent to elevated temperatures (> 25 °C), thermal vibrational energy increases, so does the charge mobility. As the charges migrate to the conduction band the concentration increases, consequently conduction increased,
which was observed as a decrease in a sensor resistance [30]. Fig. 6.7c and Fig. S3 in appendix B clearly show an n-type behaviour of TiO$_2$ based sensor when exposed towards a reducing gas. A change in sensor resistance upon exposure to a target gas and when the gas has been flushed out clearly shows a good recovery, indicating no sensing poisoning.

Selectivity is one of the important properties of a sensor, therefore the ability of the as-prepared and thermally annealed TiO$_2$ hierarchical nanostructures to selectively respond towards 100 ppm of the BTEX was shown in Fig. 6.8a and b. As mentioned above, the sensors response drastically increased with temperature from 25 °C to 75 °C. It was observed from Fig. 6.8a that most of the sensors were responsive towards C$_7$H$_8$ vapour, where T9 displayed optimum response value of 10.14. T7 was more prone to C$_6$H$_6$ with a response value of 5.56. The T5 sensor was responsive to E-C$_6$H$_6$ and C$_8$H$_{10}$, which have the same chemical composition/molecular formula and gave maximum response of 9.07 towards E-C$_6$H$_6$ (Fig. 6.8a). No response was observed from the T3 sensor when exposed to E- C$_6$H$_6$ and C$_6$H$_6$. However, upon exposure to C$_7$H$_8$ and C$_8$H$_{10}$ a response was observed even at low operating temperatures and concentration. Such a poor response was attributed to the low defect concentration, as observed from the PL and XPS analyses.
Fig. 6 7: Response against operating temperature towards (a) E- C6H6, (b) C6H6, (c) C7H8, and (d) C8H10. (e) Resistance in air against operating temperature and (f) n-type resistance transition towards reducing gas.
As the temperature increased up to 150 °C, the sensitivity of the T7 sensor changed, since it displayed optimum response to all the gases compared to that observed at 75 °C, excluding E-C₆H₆. Even though the response value of T5 sensor decreased from 9.07 to 4.65 towards E-C₆H₆ at 150 °C and that of T7 sensor increased from 5.56 to 6.04, the response value at 75 °C was still the highest. Fig. 6.8c-f shows the response against gas concentration curve at 150 °C for the as-prepared and thermally treated TiO₂ hierarchical spheres. The sensor performance increased linearly with gas concentration from 5 ppm to 100 ppm. Likewise, the effect of annealing temperature was clearly observed from Fig. 6.8c-f, where the sensor response increased with temperature from 300 °C to 700 °C (T7 sensor) and decreased to lower values at 900 °C (T9 sensor). This behaviour is in agreement with the XRD observation, where the crystallinity improved for the mixture of anatase and rutile phase for T7 sample (see Fig. 6.1d-e). As a result, the {001} facets were more exposed for gas adsorption. The {001} crystal facets possess the highest surface energy, which contributes to decomposition of gas as it interacts with the sensor surface contributing to the enhanced response [21, 22]. Wang et al. [31] attributed the excellent sensing behaviour of hydrogenated TiO₂ nanosheets towards 100 ppm ethanol to the increased in density of the unsaturated Ti₅c atoms presented by the {001} facets, which acted as active sites for gas adsorption.

It was clearly observed from Fig. 6.8c-f that the T7 sensor has the highest response than that of other sensors at 150 °C, displaying response values of 13.59, 12.09, 7.11 and 6.04 towards C₇H₈, C₈H₁₀ and E-C₆H₆ and C₆H₆, respectively. This behaviour was associated with the bond dissociation energy, which is the energy needed to break chemical bond A-B into its constituents A and B at 24.9 °C. Among the BTEX, toluene (CH₃-C₆H₅) has the lowest binding energy (356 kJ/mol) followed by
xylene ((CH$_3$)$_2$-C$_6$H$_4$) at 375 kJ/mol, benzene (C$_6$H$_6$) at 431 kJ/mol and ethylbenzene (CH$_3$-CH$_2$-C$_6$H$_5$) at 435 kJ/mol[32-35]. It has been reported that the –CH$_3$ functional group present in the structure makes it effortless for bond cleavage and easier to adsorb on TiO$_2$ surface compared to C$_6$H$_6$ [32, 33]. Dutta et al. [2] reported on a similar behaviour, where electrochemically derived connected TiO$_2$ nanotubes were highly responsive towards 400 ppm of BTX at 150 ºC. Furthermore, Tang et al. [33] reported a good selectivity of ZnO flower-like nanostructures sensor towards 100 ppm toluene in comparison to C$_6$H$_6$, ammonia and acetone analytes.

A gas sensing device that is operational at low temperatures is advantageous for low power consumption and is cost effective, however the shift in working temperature to 150 ºC gives optimum response with improved sensitivity, reliable and stable recovery. Additionally, it is worthy to note that the T7 sensor was sensitive even within the limit expected by the occupational safety and health administration standards (OSHA) specifications of permissible exposure limit (PEL) in a working environment. A 100 ppm PEL set by the OSHA and the American Conference of Governmental Industrial Hygienists (ACGIH) for an 8-hour total weight average (TWA) towards C$_6$H$_{10}$ and E-C$_6$H$_6$ was satisfied by T7 sensor [6]. In addition, the sensor was able to respond to low concentration (i.e. 10 ppm) at 150 ºC, displaying response values of 1.22 and 1.02 for C$_6$H$_{10}$ and E-C$_6$H$_6$, respectively. The National Institute for Occupational Safety and Health (NIOSH) recommended a 100 ppm 10 hour TWA towards C$_7$H$_8$ and was later reviewed by the ACGIH to 20 ppm 8 hour TWA, due to its detrimental health effect [8]. The sensors in this work met both the 100 and 20 ppm PEL with response values of 13.59 and 4.33. Since, C$_6$H$_6$ is one of the lethal VOCs; hence, a 1 ppm airborne concentration of 8 hour TWA limit and a 5 ppm short term
limit over 15 min period were set by the OSHA [7]. As a result, the sensor showed a repeatable response of about 0.4 towards 5 ppm C₆H₆ (see Fig. 6.9b and d).

**Fig. 6 8:** Selectivity polar plots at (a) 75 °C and (b) 150 °C. Response against concentration curve of (c) E- C₆H₆, (d) C₆H₆, (e) C₇H₈, and (f) C₈H₁₀ for the as-prepare and thermally treated TiO₂ hierarchical spheres.
Sensitivity and prompt response are important qualities of a good sensor, thus the quantitative analysis for T7 sensor towards 100 ppm at 150 °C are displayed in Table 3. The sensitivity (change in response with change in gas concentration) was given by the slope of the linear fit fitted on the T7 sensor response versus concentration curves displayed in Fig. 6.8c-f. Table 6.3 shows the limit of detection (LOD) which was given by the expression \( \text{LoD} = 3 \left( \frac{\text{RMS noise}}{\text{Slope}} \right) \) where RMS noise is the root mean square deviation extracted from the sensor response before any analyte gas was injected. A steep increase in response was observed for C\textsubscript{7}H\textsubscript{8} as the concentration increased to 100 ppm with a slope of 0.1574 and LOD of 0.3908 was obtained. Furthermore, the response (\( \text{\Omega}_{\text{res}} \)) and recovery (\( \text{\Omega}_{\text{rec}} \)) times corresponding to T7 sensor towards the BTEX at 150 °C were measured from the time it takes to reach 90% of the total response change after introducing and flushing out the target gas, as recorded in Table 6.3. The sensor exhibited rapid response time that is less than 60 s towards 100 ppm BTEX and the recovery time of not more than 70 s. Such behaviour was ascribed to the combination (balance) of the \{001\} facet (discussed above) and large pores possessed by T7 sensor (see BET results in Fig. 6.4c).

The porosity played a vital role in sensor response as it provided paths for the gas diffusion into the depth of the sensing layer and the rate at which diffusion occurs is influenced by pore radius (r) and working temperature (T) and molar mass (M) of the target gas and gas constant (R= 8.3145 J.mol\(^{-1}\).K\(^{-1}\)) as described by Knudsen diffusion coefficient, \( D = \frac{4}{3} r \sqrt{ \frac{2RT}{\pi M} } \) [1]. The diffusion constant of about 9.8x10\(^{-4}\), 9.1x10\(^{-4}\), 9.1x10\(^{-4}\) and 10.7x10\(^{-4}\) cm\(^2\).s\(^{-1}\) were calculated for T7 sensor when exposed to C\textsubscript{7}H\textsubscript{8}, C\textsubscript{8}H\textsubscript{10}, E- C\textsubscript{6}H\textsubscript{6}, and C\textsubscript{6}H\textsubscript{6} at 150 °C with pore diameter of 30.495 nm. Even though C\textsubscript{6}H\textsubscript{6} shows a higher diffusion coefficient towards T7 sensor, the high working
temperature limited the diffusion and penetration of the gas inside the sensing layer, thus only the surface interactions contributed to sensing, hence the decreased sensor response towards C₆H₆. Shen et al. [36] reported on a similar behaviour where Au decorated hierarchical ZnO rose-like architectures were more prone to xylene followed by toluene and least towards C₆H₆. The measurements were carried at 40 ppm gas concentration and 206 ºC optimal temperature. Likewise, various morphologies of Zn₂SnO₄ prepared by Wang et al. [37] displayed a superior response towards C₇H₈, which was 4 folds higher than that of C₆H₆ at a constant gas concentration of 20 ppm, at the operating temperature of 280 ºC. Table 6.4 displays a comparative study based on TiO₂ gas sensors towards C₇H₈. From the table, our current sensor displays a competitive performance in comparison to that reported in the literature.

Table 6.3: Quantitative analysis of the T7 BTEX sensor at 150 ºC.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Response (ppm)</th>
<th>Slope (ppm⁻¹)</th>
<th>LOD (ppm)</th>
<th>T_res (s)</th>
<th>T_rec (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₇H₈</td>
<td>13.59</td>
<td>0.1574</td>
<td>0.3908</td>
<td>29</td>
<td>51</td>
</tr>
<tr>
<td>C₆H₁₀</td>
<td>12.09</td>
<td>0.1365</td>
<td>0.4586</td>
<td>56</td>
<td>68</td>
</tr>
<tr>
<td>E-C₆H₆</td>
<td>7.00</td>
<td>0.09721</td>
<td>0.1201</td>
<td>37</td>
<td>65</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>6.04</td>
<td>0.06164</td>
<td>0.4214</td>
<td>54</td>
<td>55</td>
</tr>
</tbody>
</table>

Cross sensitivity towards interfering gases and humidity is one of the limitations faced by chemiresistive sensors. The cross sensitivity analysis of T7 sensor towards C₇H₈ with the other gases in the BTEX group was displayed in Fig. 6.9a and the ratio was given by the response to 100 ppm C₇H₈ over the response of the interfering gas at 150 ºC. Fig. 6.9a illustrates major interference by C₆H₁₀ (1.12) compared to the other gases with C₆H₆ (2.24) showing minimal interference. Fig. 6.9b and c displays
the sensor transients in the presence of relative humidity (RH). Note that for the humidity study the measurements were carried out at 60 ppm constant toluene concentration while RH varies for 10, 30 and 40 %. The T7 sensor was stable to RH, since no major influence on the change in resistance was observed at 10% RH. A slight decrease in amplitude that further carried on was observed upon exposure to 30 and 40% RH. More remarkably, to demonstrate the sensitivity of T7 sensor towards benzene, RH measurements were carried out up to 90% RH at 5 ppm C\_6H\_6 at 150 °C and the resistance amplitude increased with RH% up to 90%. This was an indication of how the sensor is susceptible to water vapour in the presence of C\_6H\_6 and at 90% RH the sensor shows two responses. The first response (with dry air) was due to the interaction of the gas and the hierarchical nanostructure and the second response was due to the water vapour. Fig. 6.9e illustrates the repeatability of the sensor upon exposure to 5 ppm C\_6H\_6 and 100 ppm C\_7H\_8.

<table>
<thead>
<tr>
<th>Sensing layer</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>Response</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO_2 nanotubes</td>
<td>400</td>
<td>150</td>
<td>45%</td>
<td>[2]</td>
</tr>
<tr>
<td>TiO_2 nanotubes</td>
<td>50</td>
<td>500</td>
<td>25</td>
<td>[12]</td>
</tr>
<tr>
<td>3D TiO_2/G-CNT</td>
<td>500</td>
<td>25</td>
<td>42%</td>
<td>[14]</td>
</tr>
<tr>
<td>TiO_2 –ZnO Nanoflowers</td>
<td>100</td>
<td>290</td>
<td>17.1</td>
<td>[38]</td>
</tr>
<tr>
<td>Au-TiO_2 pecan-kernel</td>
<td>100</td>
<td>375</td>
<td>7.3</td>
<td>[39]</td>
</tr>
<tr>
<td>Pt@ZnO-TiO_2 nanotubes</td>
<td>5</td>
<td>300</td>
<td>11.1</td>
<td>[40]</td>
</tr>
<tr>
<td>TiO_2 nanotubes</td>
<td>150</td>
<td>25</td>
<td>17%</td>
<td>[41]</td>
</tr>
<tr>
<td>Co_3O_4/TiO_2 heterojunction</td>
<td>50</td>
<td>115</td>
<td>55</td>
<td>[42]</td>
</tr>
<tr>
<td>TiO_2 sea-urchin like Hierarchical nanoflowers</td>
<td>100</td>
<td>150</td>
<td>13.6</td>
<td>In this work</td>
</tr>
</tbody>
</table>

Note: for %, it means that the response was measured using this formula: \((R_a/R_0)\times100\)
Fig. 6 9: Cross selectivity plots in the presence of (a) interfering gases, relative humidity and (b) 60 ppm C7H8 and (c) 5 ppm C6H6. (d) The repeatability measurements of T7 sensor when exposed to 5 ppm C6H6 and 100ppm C7H8.
6.3.5 Sensing Mechanism

Gas sensing is a surface phenomenon and the adsorption-desorption of the gas molecules on the sensing layer results to a change in resistance. When the sensing surface interacts with ambient air, oxygen is chemisorbed forming oxygen species. As mentioned above, the type of oxygen ions present on the surface is influenced by the operating temperature at which analysis occurs, as illustrated by equations (6.1-6.3).

\[
O_{2,\text{ads}} + e^- \rightarrow O_{2,\text{ads}}^- \quad (T < 100 \, ^\circ\text{C}) \tag{6.1}
\]

\[
O_{2,\text{ads}}^- + e^- \rightarrow O_{\text{ads}}^- \quad (100 \, ^\circ\text{C} < T < 300 \, ^\circ\text{C}) \tag{6.2}
\]

\[
O_{\text{ads}}^- + e^- \rightarrow O_{\text{ads}}^{2-} \quad (T > 300 \, ^\circ\text{C}) \tag{6.3}
\]

For an n-type semiconductor, the chemisorbed oxygen accepts electrons from the TiO$_2$ surface creating a thick charge depleted region near the surface, consequently upward bending the potential barrier is observed as an increase in resistance (see Fig. 6.10a). At 150 °C operation temperature $O_{2,\text{ads}}^-$ and $O_{\text{ads}}^-$ are the dominating oxygen ion on the surface. Upon exposure to a reducing gas, such as the BTEX (see equations (6.4-6.7)),

\[
C_6H_6 + 15 \, O_{\text{ads}}^- \rightarrow 6\text{CO}_2 + 3\text{H}_2\text{O} \tag{6.4}
\]

\[
C_6H_5\text{CH}_3 + 18 \, O_{\text{ads}}^- \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} \tag{6.5}
\]

\[
C_6H_4(\text{CH}_3)_2 + 21 \, O_{\text{ads}}^- \rightarrow 8\text{CO}_2 + 5\text{H}_2\text{O} \tag{6.6}
\]

the gas gets oxidized by the chemisorbed oxygen and inject the electrons back into the surface of the material, subsequently a downward bending of the potential barrier is observed and the depleted region becomes narrow due charge accumulation as see
on the schematic in Fig. 610b, this accumulation of electrons is observed as a steep decrease in a resistance. The dissociation of C₆H₆, C₇H₈, and C₈H₁₀ (which is similar to E- C₆H₆) by TiO₂ hierarchical nanostructures is expressed equations (6.4) to (6.6) respectively [36, 39, 42].

Fig. 6 10: Schematic diagram displaying sensing mechanism in the presence of (A) dry air and (B) and upon exposure to toluene (similar behaviour for the rest of the BTEX).
6.4 Conclusion

Sea-urchin like TiO$_2$ hierarchical nanostructures synthesized via hydrothermal method and further thermally treated from 300 to 900 °C demonstrated potential use as BTEX gas sensors. Anatase phase was achieved at 500 °C, a mixture of 80% anatase and 20% rutile at 700 °C was observed and a complete phase transformation was achieved at 900 °C. The (004) peak became more pronounced at 700 °C revealing the presence of the high surface energy {001} facets. The combination of relatively high specific surface area of 100.5 m$^2$/g and pore diameter of 21.9 nm achieved at 500 °C played a crucial role in the intense response 10.1 displayed by sensor T5 towards 100 ppm E- C$_6$H$_6$ at low operating temperature i.e. 75 °C. Consequently, the surface provided active sites for gas adsorption and pore networks allowed percolation into the material. At higher operating temperature (150 °C), T7 sensor displayed superior response of about 13.6 towards C$_7$H$_8$ and a response and recovery times of 29 s and 51 s, respectively. This behaviour was attributed to the surface properties of T7, such as the high surface energy provided {001}, which plays a vital role in dissociation of the gas as it interacts with sensing layer. The T7 sensor demonstrated a clear stability towards relative humidity, which is very vital for practical and real-time applications in ambient conditions.
6.5 References


CHAPTER 7: An Approach for Realization of Astonishing Surface Area and Porosity in Mn doped TiO$_2$ hierarchical nanostructures: Selective Detection in Ethanol Vapour

Abstract

The present discovery offers a simple synthesis strategy that permits the realization of a Mn doped TiO$_2$ hierarchical structure having, beyond a doubt, the uppermost surface area reported up to the present time. The said invention process utilized no template and is simple and has low synthesis costs. This process indicated that the improvement of the surface area with an increase in Mn doping concentration shows a clear dependency on the doping concentration. The texture and crystal quality of the material transformed with an increase in Mn doping, resulting into extraordinary surface area of approximately 4347 ±14 m$^2$/g and pore volume of 27.849744 cm$^3$/g. The optical bandgap narrowed with increased Mn content, while the phase transition was observed, an increase in rutile percentage promoted by cation substitution in the TiO$_2$ lattice. As a consequence, the gas sensor based on optimized Mn4 established a poor response when tested to reducing gases (CO and CH$_4$), volatile organic compounds (C$_7$H$_8$, C$_3$H$_7$OH, C$_6$H$_6$, E-C$_6$H$_5$ and C$_8$H$_8$) while tested to C$_2$H$_5$OH vapour, unprecedented and reproducible response, improved sensitivity and selectivity towards C$_2$H$_5$OH vapour at 100 °C was witnessed. This was due to a remarkable surface and abundant porosity allowing more gas adsorption. The Mn4 sensor displayed the same initial resistance after being stored for 20 days in ambient conditions. And it further showed a strong repeatability over 10 cycles at 100 ppm C$_2$H$_5$OH after 20 days, without showing any drift, confirming its robust stability, which
could be useful for detection of $\text{C}_2\text{H}_5\text{OH}$ in real applications. The influence of relative humidity on the sensor performance was also investigated.

### 7.1 Introduction

Exposure to Volatile organic compounds such as the alcohol group has long term detrimental impact on human health such as death. Depending on exposure level, ethanol present early symptoms such as headaches, ringing in ears, dizziness, nausea and vomiting, loss of coordination and respiratory and central nervous system depression [1-3]. Major exposure to ethanol occur in work places as it is widely used as an industrial solvent where its vapour get released during processes such as brewing (fermentation and distillation) alcoholic beverages, and is also found in fuel additives. However, indoor exposure has increased over the years as humans spend more time in enclosed spaces such as homes, offices and cars thus getting exposed from products such as cosmetics, cleaning, and pharmaceutical product, paints and adhesives [4-5]. Detection and monitoring of these toxins below and at their permissible safety concentration is imperative to maintain good indoor quality consequently assuring health and safety of occupants.

Semiconducting metal oxides have been widely used as gas detectors owing to their chemical, electrical and optical properties, facile synthesis. However, there is a great need for highly sensitive, selective and stable sensor with fast response. Among a great number of metal oxides titanium dioxide (TiO$_2$) is a promising material for gas sensing due to its well-known catalytic surface chemical stability [6], and ability to achieve various morphologies such as hierarchical architectures forming brushes, flowers, hedge-hogs and sea-urchin [7-10], with high surface area contributing to the sensitivity of the sensor surface. However due to poor selectivity in the presence of
interfering gases addition of dopants and heterostructures [10-14] have been explored to enhance sensitivity, improve selectivity and decrease power consumption. Metal doped TiO$_2$ nanostructures illustrate promising ability to degrade VOC [5, 6, 9, and 11] due to the ability to improve the conductivity of the sensor by improving charge mobility. Manganese (Mn) is one of the promising transitional metal with enhanced photocatalysis. Moreover, incorporation of Mn is known to improve adsorption properties of TiO$_2$ by narrowing the band gap [11, 15].

In this work we report on astonishing surface area and porosity and enhanced response and ultra-selectivity of Mn-doped TiO$_2$ sea-urchin hierarchical spheres synthesized via hydrothermal method. To best of our knowledge surface area of $\geq$ 4000 g/m$^2$ has never been reported for any semiconductor metal oxides, let alone TiO$_2$. Moreover, a response of 53 towards 100 ppm ethanol (C$_2$H$_5$OH) vapour at 100 $^\circ$C operating temperature has never been achieved utilizing TiO$_2$ based sensor. The findings showed that the sensing mechanism driven by band narrowing due to Mn doping and ultra-high surface area providing abundant adsorption sites and swift gas diffusion through mesoporous channels was proposed.

7.2 Experimental Procedure

We should strongly point out to the reviewers/examiners that this chapter is currently being filed for patent, as result we cannot disclose detailed experimental procedure used for preparation of these nanostructures. In summary, 0-1 wt% manganese was incorporated in the synthesis of TiO$_2$ sea-urchin like hierarchical nanostructures.

The current innovation disclosure granted is: Disclosure number: T18/19-00029.
7.2.1 Material Characterization

Surface morphology analyses were examined using an Auriga ZEISS scanning electron microscopy (SEM) at an accelerating voltage of 3 kV. The Brunauer-Emmett-Teller (BET) technique was used for surface area and the pore volume analysis of the samples using the Micrometrics TRISTAR 3000 surface area analyzer using nitrogen (N\textsubscript{2}) as the probe gas. The crystal structure of TiO\textsubscript{2} was examined using Panalytical X'pert PRO PW 3040/60 X-ray diffractometer (XRD) equipped with a Cu-K\textalpha\, (\(\lambda = 0.154\) nm) monochromatized radiation source. High-resolution transmission electron microscopy (HR-TEM) JEOL-TEM 2100 instrument was used to examine the crystalline structure of the samples and elemental composition was determined by EDS mapping. The optical properties were determined using Lambda 950 UV–VIS spectrometer and the PL spectra were measured using Cary Eclipse fluorescence spectrophotometer. PHI 5000 Versaprobe-Scanning ESCA Microprobe was used to carry out X-ray photo-electron spectroscopy (XPS) analysis.

7.2.2 Sensing Films Preparation and Characterization

The KSGAS6S gas testing apparatus (KENOSISTEC Model, Italy) was used to investigate the sensing performance of pure and doped TiO\textsubscript{2} nanostructures. The sensing materials were homogenously coated on alumina substrates (size: 0.5 mm × 2 mm) with two Pt electrodes (on its top surface) and a micro-heater (on its bottom surface). The deposited sensing layers were heated in a furnace at 200 °C for 30 min in order to remove the unwanted organic solvent used and to obtain good adhesion. The resistances of the sensors to various gas concentrations (5-100 ppm) were measured by switching between the mixture gases and synthetic dry air and the
sensing measurements were carried out at temperatures between 25 to 150 °C. The tested target gases, include carbon monoxide (CO), methane (CH₄), ethanol (C₂H₅OH), propanol (C₃H₇OH) and BTEX gases, that is benzene (C₆H₆), ethylbenzene (which we will refer to as E- C₆H₆ since it has the same chemical formula as xylene), toluene (C₇H₈) and Xylene (C₈H₁₀).

7.3 Results and discussion

7.3.1 Structural and Morphological Characteristics

X-ray diffraction patterns for the pure and Mn doped TiO₂ hierarchical nanostructures are displayed in Fig. 7.1a. The pure TiO₂ nanostructures displayed mixed phase represented by the diffraction peaks centred at 25.65° and 27.78° corresponding to (101) and (110) planes of the anatase and rutile phase TiO₂ according to JCPDS. #00-021-1272 and JCPDS. #00-086-0147. Introduction of Mn²⁺ ions promoted the growth of rutile phase (up to 44%) as shown by the improved intensity of the (110) peak as doping concentration increases. Furthermore, using the Spurr-Meyrs equation the rutile content was quantified and presented in Table 7.1. An increase in particle size was observed as the tensile stress decreased signalling lattice expansion up to 0.5 mol% Mn (Mn2) and decrease there after (see Fig. 1b). Due to low metal content, no observations were made of diffraction peaks corresponding to MnO₂ however, a shift to lower Bragg’s angle induced by incorporation of Mn²⁺ ions into the TiO₂ lattice. Summarized in Table 1 are the lattice parameters a, c and volume of the pure and Mn-doped TiO₂ nanostructure given by Vegard’s law [16]. An increase in unit cell volume in agreement with crystallite size observations was confirmed and attributed to the large atomic radii of Mn²⁺ ions (0.08 nm) substituting those of Ti⁴⁺ (0.068 nm) in the lattice [11].
Fig. 7. 1: (a) X-ray diffraction patterns and (b) crystallite size of the pure and Mn-doped TiO$_2$ hierarchical nanostructures.

Table 7. 1: Lattice parameters of pure and Mn-doped TiO$_2$ nanostructures.
High resolution TEM (HRTEM) and selected area electron diffraction (SAED) analyses were carried out to investigate the structure of the pure and doped hierarchical nanostructures. HRTEM micrographs displayed in Fig. 7.2 show that the hierarchical nanospheres are made of rod-like particles building up a network of nanoribbons. The lattice fringes with d-spacing corresponding to (101) was observed and SAED confirmed the polycrystalline structure as shown by XRD. Additionally, elemental mapping (in Fig. 7.3) displayed a uniform distribution of Ti, O, and Mn in the hierarchical nanostructures.

Furthermore, the scanning electron microscopy analysis confirmed the formation of sea-urchin like spherical hierarchical spheres made of nanowires in a radial arrangement, as shown in Fig. 7.4. The morphology was maintained through incorporation of Mn ions till Mn$^{2+}$ (0.5 mol %). However, as dopant concentration is increased, poor formation of the hierarchical structure was observed. Consequently, a web-like structure/arrangement was observed for Mn4 sample, where the spherical arrangement was completely deformed.
Fig. 7.2: HRTEM images and SAED patterns for pure and Mn-doped TiO$_2$ hierarchical nanostructures.
**Fig. 7.3**: Elemental mapping images of the surface of Mn-doped TiO$_2$ hierarchical nanostructures.
Fig. 7. 4: SEM images of the Mn-doped TiO$_2$ hierarchical nanostructures.
The surface area and pore structure of the pure and Mn-doped TiO$_2$ hierarchical nanostructures are displayed in Fig. 7.5. The adsorption-desorption isotherms displayed type IV characteristics, which is mainly due to capillary condensation in mesopores at high relative pressure above 0.9. From the pore distribution, it was observed that mesopores in the upper range (> 20 nm) are dominating. Furthermore, the H2 hysteresis loop was observed as a result of interconnected pore structure. More interestingly, a steep increase in isotherms and an intense increase in BET specific surface area were observed from 100 m$^2$.g$^{-1}$ to 2452, 4111, 3414 and 4347 m$^2$.g$^{-1}$ for the Mn doped TiO$_2$ nanostructure, respectively. Consequently, a steady increase in pore volume was observed from 0.66 cm$^3$.g$^{-1}$ to 18.12, 27.81, 21.60 and 27.48 cm$^3$.g$^{-1}$. Such high surface area and pore diameter provide larger adsorption site for the target gas to interact through the material.
Fig. 7. 5: N$_2$ adsorption-desorption isotherms and the pore distribution of the pure and Mn doped TiO$_2$ hierarchical nanostructures.
7.3.2 Optical Characteristics

UV-Vis and Photoluminescence analysis were conducted to study the optical properties of the pure and Mn doped TiO₂ hierarchical nanostructures. A noticeable change in colour was observed after Mn doping from white to grey-brownish colour as shown in Fig 7.6a. The diffused reflectance spectra in Fig. 7.6b revealed a strong absorption edge in the UV region (< 400 nm) for all samples, which were assigned to indirect transition near band edge [17]. Mn1 displayed a blue shift however, increasing the dopant concentration induced a red shift which is indicative of band narrowing. The samples displayed a second adsorption edge at upper visible region (530-660 nm), which was attributed to the presence of oxygen vacancies and Ti⁴⁺ opposite oxygen vacancies in the lattice [18]. Moreover, an adsorption edge related to transitions involving oxygen vacancies associated to Ti³⁺ was detected on pure TiO₂ at 470 nm. Lower Mn concentrations (Mn1 and Mn2) promoted reflection of infrared (>700 nm) where else reflectance decreased to 48% with increased Mn concentration. Decrease in reflectance could be attributed to stronger optical absorption of Mn-TiO₂ with higher specific surface area.

The energy band gap (E₉) of pure and Mn-doped TiO₂ nanostructures was estimated by extrapolation from the linear part of the Tauc plot given by equation (7.1).

\[(\alpha hv)^{1/n} = A(hv - E_g)\]  

(7.1)

\(\alpha\) is the absorption coefficient, \(h\) is the Planck’s constant, \(\nu\) is the frequency of vibration, \(A\) is a proportionality constant, and \(n\) stands for the nature of material transition where \(n=1/2\) for direct and \(n=2\) for indirect transitions.
The Tauc plot for the pure and Mn doped TiO$_2$ hierarchical nanostructures are shown in Fig. 7.6 c. Anatase and rutile TiO$_2$ have indirect and direct bang gaps of 3.2 and 3.0 eV respectively [11, 17-19]. The band gaps of about 3.34, 3.4, 3.31, 3.18 and 3.03 eV were estimated for Mn0, Mn1, Mn2, Mn3 and Mn4 respectively. The bandgap narrowing was in agreement with the phase transition observations made from XRD analysis and the increase in rutile percentage promoted by cation substitution in the lattice. Binas et al. [11] and Tripathi et al. [19] reported similar band narrowing induced by Mn$^{2+}$ doped TiO$_2$ nanoparticles.

![Fig. 7.6](image)

**Fig. 7. 6:** images indicating physical colour variation due to doping. (b) UV-Vis Diffused reflectance spectra and (c) Tauc's plot of pure and Mn-doped TiO$_2$ hierarchical nanostructures.
The room temperature photoluminescence (PL) analysis was carried out to detect the presence of defect states and impurity bands induced by Mn dopant within the bandgap of the pure nanostructure. The emission spectra for pure and Mn doped TiO$_2$ hierarchical nanostructures shown in Fig. 7.7 displayed strong luminescence in the visible region of 3.0 - 2.2 eV consisting of three major emissions as violet- blue (3.1 - 2.9 eV), blue (2.8-26 eV), green (2.5 - 2.2 eV) and yellow (2.1).

The occurrence of the violet emission at 3.13 eV was attributed to near band edge emission since anatase TiO$_2$ nanostructures present an indirect band gap [17, 18, 20]. The most intense peak at 2.92 eV is indicative of the dominance of excitonic emissions. The violet-blue emission peaks observed at 2.9 eV was due to self-trapped excitons located at TiO$_6$ octahedra [17, 18]. While the blue emissions observed at 2.78, 2.69 and 2.55 eV were due to transitions from Ti$^{3+}$ state to OH$^-$ acceptor level above the valence band [18, 20, 21]. The green emissions at 2.33, 2.28 and 2.18 and yellow (2.07 eV) were associated with transition from oxygen vacancies just below the conduction band to the valence band [18, 20, 21]. More over a peak at 2.48 eV was presented by Mn1 indicating a Mn sub-lattice.

Photoluminescence is a surface dependent phenomenon. Thus a change in the surface environment significantly influences the emission spectra. An intensity quench of the exciton (2.9 eV) peak was observed and was attributed dominance of non-radiative recombination (Auger) and the interaction of excitons with dopant ions as Mn$^{2+}$ concentration increased. Besides, the peaks at 2.55 and 2.33 eV related to oxygen vacancies showed intense decrease at Mn1 and increased for Mn2, thereafter gradually decreased further with concentration. The intensity quench was attributed to Mn d-states formed within the energy gap which act as acceptors of electrons from the conduction band. An increase of these intermediate band state increase the chances
of interacting with defects resulting into non-radiative emission hence decreasing luminescence [17, 18].

![Room temperature photoluminescence spectra for pure and Mn-doped TiO$_2$ hierarchical nanostructures.](image)

Fig. 7. 7: Room temperature photoluminescence spectra for pure and Mn-doped TiO$_2$ hierarchical nanostructures.

### 7.3.3 Gas sensing Characteristics

Gas sensing properties of the pure and Mn doped TiO$_2$ hierarchical nanostructures were tested towards different environments, in order to extract the optimum sensing capabilities of the nanomaterials. Operating temperature is one of the most significant properties of a sensor as it influences sensor characteristic and efficiency. Therefore, the optimum operating temperature of the pure and Mn-doped...
TiO$_2$ nanostructures were investigated between 25 and 150 °C at constant gas concentration and the results are displayed in Fig. 7.8a-c. While such a lower operating temperatures offers best sensitivity, it also provides better lower power consumption. In this case 100 ppm of C$_2$H$_5$OH, C$_3$H$_7$OH and CO were used as target gases and are reducing gases therefore, sensor response was given by \(((R_a/R_g)-1)\) where $R_a$ is the resistance in dry synthetic air and $R_g$ is resistance in the presence of target gas. The TiO$_2$ nanostructures showed poor response at low temperature (25 °C) and a drastic increase in response as temperature increased attaining maximum response at 75 °C for C$_3$H$_7$OH and 100 °C for C$_2$H$_5$OH and CO.

Further increase in temperature resulted into a decrease in response. Similar behaviour was observed by Motsoeneng et al. [22] where hydrothermally synthesized SnO$_2$ hollow-spheres displayed high response of 20.1 towards 100 ppm C$_3$H$_7$OH at 75 °C. However, increasing the operation temperature to 150 °C resulted into decrease in response down to value $\sim$5. K. Chen et al. [13] tested SnO$_2$ nanoparticles loaded on TiO$_2$ nanofibers towards 100 ppm C$_2$H$_5$OH in a temperature range 240-290 °C. The sensors displayed maximum response at 240 °C and decreased thereafter. Tomer et al. [5] reported on C$_2$H$_5$OH selective Ag loaded mesoporous carbon nitrides with monotonic increase in response as temperature increased to 400 °C. The Ag(1)-meso-CN sensor displayed a significantly high response of 49.2 at 250 °C. This behaviour was attributed to insufficient energy to activate charge carriers for the reaction between target gas and sensor surface at low temperature. Whereas, at higher temperatures, the gas molecules have less interaction with the surface thus retarding response [5].

Moreover, response increased with doping concentration and maximum response value of 53 was exhibited by Mn4 sensor towards C$_2$H$_5$OH vapor at 100 °C.
Similar behavior was observed by G. Chen et al. [23] where Sn₃O₄/TiO₂ nanobelts heterostructure displayed a temperature-dependent C₂H₅OH sensing. However, their operating temperature (250 °C) was higher than the one used in this study (i.e. 100 °C). Moreover, the heterostructure displayed enhanced response as Sn₃O₄ loading ratio increased up to 4:1 and thereafter decreased (6:1). Typical, n-type sensor transient response was observed (Fig. 8d-f) when the sensors were exposed to reducing gas whereby, resistance decreased due to injection of electrons back into conduction band and increased in the presence of dry synthetic air.

Fig. 7.9a-c displays the response of the TiO₂ nanostructures upon exposure to C₂H₅OH, C₃H₇OH and CO to concentration range of 5-100 ppm at 100 °C. Upon exposure to C₂H₅OH and C₃H₇OH the sensors displayed an exponential increase in response with gas concentration. The response was also enhanced by dopant concentration. The Mn4 sensor displayed significantly high response towards C₂H₅OH, reaching maximum value of 53, which is four times higher than pure TiO₂. Consequently, sensitivity which is given by the change in response with concentration, was extrapolated from the linear region (40-80 ppm) and was found to be 0.695 ppm⁻¹. The presence of Mn²⁺ ions does not only increase conductivity, it enhanced sensitivity and catalytic activity of the sensor surface. It further lowers the energy bandgap, which is beneficial to the interband electron transfer (seen UV-Vis analysis). The Mn3 and Mn4 sensors exhibited (Fig 7.9c) a step ladder response behavior in the presence of CO as the concentration increased, which is opposite to the increase-maximum-decay pattern exhibited by pure TiO₂.
Fig. 7.8: (a-c) Response against operating temperature of pure and Mn-doped TiO$_2$ nanostructures and (d-f) their corresponding sensor transient when exposed to C$_2$H$_5$OH, C$_3$H$_7$OH and CO.
In the concentration range of 5-20 ppm, the response was 1.5, followed by an intense response increase to 5.2 in the range of 40-80 and further increases with concentration reaching maximum of 10.7 at 100 ppm. Such behavior can be attributed to the ultra-high surface area with interconnected pore structure of mid-upper mesopores and high surface to volume ratio that promotes rapid gas adsorption through the network and chemisorption on the surface with quick desorption before condensation occurs [24]. Fig. 7.9d-f displays the response-recovery times of Mn4 sensor towards 100 ppm C₂H₅OH, C₃H₇OH and CO at 100 °C. A rapid response of about 32 s and recovery of 90 s when exposed to C₂H₅OH, in the presence of C₃H₇OH, response-recovery times of 51 and 83 s were observed and 62 and 92 s for CO.

The radar plot in Fig. 7.10a displays the selectivity test conducted at 100 °C operating temperature and constant gas concentration of 100 ppm. The sensors were more inclined towards the VOCs, mainly the hydroxyl group, due to the fact that the –CH₂- molecules can be decomposed effortlessly and oxidized giving an electron back to the material, thus increasing the response [5, 13, 22]. The Mn4 sensor displayed ultra-selectivity to C₂H₅OH followed by C₃H₇OH at 100 °C. It is worthy to note that even though C₃H₇OH displayed optimum response of 33 at 75 °C, however, such behavior was also noticed towards C₂H₅OH, showing a response of 34, which led to high cross-sensitivity. Fig. 7.10b illustrates the cross selectivity plot, which is the response ratio of Mn4 sensor towards C₂H₅OH as target gas in the presence of other interfering gases. Major interference can be expected from C₃H₇OH, whereas CH₄ displays no impact.
Fig. 7. (a-c) Response against gas concentration. (d-f) Real time response and recovery times of pure and Mn-doped TiO$_2$ nanostructures when exposed to 100 ppm C$_2$H$_5$OH, C$_3$H$_7$OH and CO.
Moreover, cross sensitivity of the Mn4 sensor towards 100 ppm C$_2$H$_5$OH vapor in the presence of 10, 30, and 60 % relative humidity (RH) is shown in Fig. 10c. The sensor displayed major increase in resistance with respect to initial resistance in the presence of RH compared to dry synthetic air. When comparing the change in resistance in the presence of 10% RH, with 40 and 60% RH, it is very clear that the sensor is stable and only minor variation in resistance was observed as RH increased to 60%, as shown in the inset. To further study the robust behavior of the sensor, we performed repeatability analyses after storing the sensor for 20 days in ambient conditions. It is clear in Fig. 7.10d that the sensor displays almost the same initial resistance compared to that in Fig. 7.10c in dry air. Furthermore, the sensor shows a strong repeatability over 10 cycles of constant gas concentration (100 ppm) after 20 days, with showing any drift, confirming its robust stability, which could be useful for detection of C$_2$H$_5$OH in real applications.

7.3.4 Sensing mechanism

In this study, the proposed sensing mechanism is driven by the oxygen ions (O$^{−}$) that are due to oxygen chemisorption on the sensor surface at operating temperature between 100 and 300 °C. Ionization of oxygen results into the formation of charge depleted region on the sensor surface and thus increase sensor resistance. When the Mn doped TiO$_2$ nanostructure (Mn4) were exposed to C$_2$H$_5$OH, an electronic mechanism displayed due to the content of Mn$^{2+}$ ions in the TiO$_2$ lattice which accelerates the redox reaction (given by equation 7.2) [5].

$$\text{CH}_3\text{CHO} + 5\text{O}_{\text{ads}}^{−} \rightarrow 2\text{CO}_2 + 5\text{e}^{−}$$

(7.2)

The gas molecules get oxidized on the surface and inject an electron back to the conduction band consequently decreasing sensor resistance.
**Fig. 7.10:** (a) Selectivity polar plots, Cross sensitivity in the presence of (b) interfering gases and (c) Relative humidity. (d) Real time repeatability Mn4 sensor resistance exposed to 100 ppm C₂H₅OH.
7.4 Conclusion

We successfully designed and synthesized Mn doped TiO$_2$ hierarchical structure with astonishing and record surface area and pore volume using a simple synthesis strategy that permits a clear control and reproducible morphology. Such surface area improved with an increase in Mn doping concentration shows a clear dependence on the doping concentration. When tested to eight various gases, the gas sensor based on optimized Mn4 revealed improved sensitivity and selectivity towards C$_2$H$_5$OH vapour at 100 °C. This was due to a remarkable surface and abundant pores allowing more gas adsorption. The Mn4 sensor showed a strong repeatability over 10 cycles at 100 ppm C$_2$H$_5$OH after 20 days, without showing any drift, validating its robust stability, making it a suitable candidate for detection of C$_2$H$_5$OH in real applications. The findings showed that the sensing mechanism driven by band narrowing due to Mn doping and ultra-high surface area providing abundant adsorption sites and swift gas diffusion through mesoporous channels was proposed. Finally, this work has been adopted for intellectual property and an innovation disclosure has been granted (Disclosure number: T18/19-00029), while the US patent is currently being filed.
7.5 References


CHAPTER 8: Summary

In summary, we have fruitfully designed a simple synthesis strategy that permits easy and reproducible results, by preparing Mn doped TiO$_2$ hierarchical structure having record surface area and pore volume. Through this process, we have shown that our synthesis results are reproducible. We further proved that the improvement of the surface area is dependent on the doping concentration. By optimized Mn doping we established that our sensor is sensitive to C$_2$H$_5$OH vapor and displayed an excellent response, improved sensitivity and selectivity at 100 °C. The Mn4 sensor showed a strong repeatability over 10 cycles at 100 ppm C$_2$H$_5$OH after 20 days without showing any drift. The study will further probe the long term-stability over 6 months for detection of C$_2$H$_5$OH in real applications. Finally, through this work an intellectual property and an innovation disclosure has been granted (Disclosure number: T18/19-00029), while the US patent is currently being filed.

We further managed to design for the first time the dual-functionality sensor for detection of toluene (C$_7$H$_8$) and p-xylene (C$_8$H$_{10}$) from TiO$_2$ nanowires operating at room and low temperatures, for low power consumption. To best of our knowledge, a temperature-dependent selectivity dual sensor operating a room temperature and 125 °C has never been reported. By testing the sensor in various relative humidity as to mimic the real environment, the findings validated that the current sensor can be used for detection of C$_7$H$_8$ and C$_8$H$_{10}$ in a vastly sensitive and selective way with insignificant interference from ambient humidity.

Besides, through annealing, we further showed that the selectivity of the nanostructures can be tuned, due to exposed facets containing plentiful active oxygen species, which are more active for adsorption. The T5 sensor displayed temperature-
dependent selectivity towards ethylbenzene at 75 °C. The T7 sensor revealed the highest response towards toluene at 150 °C, which could be justified by exposed high surface energy \{001\} facets. The sensor illustrated a robust stability towards relative humidity (10-90%), which is very vital for practical and real-time applications in ambient conditions.

For future work, we intend to improve the long-term stability of the sensors for a period of over six months, by carrying the analyses in different relative humidity conditions. Such stability will provide an opportunity to penetrate the sensor markets. We further intend to reduce the operating temperature of all our sensors to room temperature, except the dual sensors, which require two different operating temperatures.
APPENDIX A

Chapter 5: Designing of Vastly Sensitive and Selective Dual-Functionality of Toluene and Xylene Gas Sensors Based on TiO₂ Nanowires

Fig. A 1: Low resolution SEM micrographs of (a) HHC and the insets show particle size distribution.
Fig. A 2: Low resolution TEM micrographs of (a) HHC, (b) TNP (c) TNW.
Fig. A 3: Photoluminescence spectra of TiO$_2$ nanostructures with different morphology (a) HHC, (b) TNP (c) TNW measured at 30 to 150°C.
**Fig. A 4:** XPS survey spectrum of TiO2 nanostructures.

**Table A 1:** Quantitative analysis defect 0.83, 1.49, 6.57 % from PL and concentration of Ti$^{3+}$ and V$_0$ from XPS Ti 2p and O 1s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PL</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Ti$^{3+}$]%</td>
<td>[Ti$^{3+}$]%</td>
</tr>
<tr>
<td>HHC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 °C</td>
<td>68.1</td>
<td></td>
</tr>
<tr>
<td>150 °C</td>
<td>79.6</td>
<td></td>
</tr>
<tr>
<td>TNP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 °C</td>
<td>74.7</td>
<td></td>
</tr>
<tr>
<td>150 °C</td>
<td>68.7</td>
<td></td>
</tr>
<tr>
<td>TNW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 °C</td>
<td>72.8</td>
<td></td>
</tr>
<tr>
<td>150 °C</td>
<td>70.2</td>
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</table>
Fig. A 5: Resistance transient of sensors (a) HHC to CO at 25 °C , and TNW (b) to C7H8 and (c) C8H10 at 25 and 125 °C, respectively.
Fig. A 6: Dynamic resistance of sensors (a) HHC to 40 ppm CO at 25 °C, (b-c) TNW to 100 ppm C\textsubscript{3}H\textsubscript{6} and C\textsubscript{8}H\textsubscript{10} at 25 and 125 °C, respectively at various relative humidity.
Chapter 6: Improved BTEX Gas Sensing Characteristics of Thermally Treated TiO$_2$ Hierarchical Spheres Manifested by High-Energy {001} Crystal Facets

Fig. B 1: CIE chromaticity diagram of the thermally treated TiO$_2$ nanospheres.

Fig. B 2: The survey spectra of the thermally treated TiO$_2$ nanospheres.
Fig. B 3: n-type resistance transition towards (a) Ethylbenzene, (b) Benzene, (c) m- Xylene and (d) Toluene.
Fig. B 4: Cross selectivity towards Ethylbenzene at 75 °C.