## Contents

Certificate	i
Acknowledgments	
Preface	
Abstract	
List of Figures	
List of Tables	
Abbreviations	
Chapter 1	1-34
Introduction	
1. 1 Solid-state gas sensors	2
1. 2 Nanostructured metal oxides	5
1. 3 Nanostructured metal oxides-based sensors	9
1. 3. 1 Resistive sensing	10
1. 3. 2 Capacitive sensing	12
1. 4 TiO <sub>2</sub> nanostructures for sensing application	
1. 5 Selectivity issue in nanostructured metal oxides-based sensors	15
1. 6 Objectives	19
References	0.0
Chapter 2	35-52
Equivalent electrical circuit of 1-D TiO <sub>2</sub> nanostructures-based sensor u	
analysis	
2. 1 Introduction	35
2. 2 Fabrication of 1-D TiO <sub>2</sub> nanostructure-based sensor	36
2. 3 Experimental setup for measuring impedance of the sensor	38
2. 4 Equivalent electrical circuit of the sensor	39
2.5. Impedance analysis of TiO, panetubes-based sensor	4.4

2. 5. 1 Effect of temperature	45
2. 5. 2 Effect of vacuum	47
2. 5. 3 Effect of reducing ambient	48
2. 6 Conclusions	
References	
Chapter 3	53-70
Selective detection of organic vapors using TiO <sub>2</sub> nanotubes-based single sensor	
3. 1 Introduction	53
3. 2 Experimental setup for VOC sensing	53
3. 3 Characterizations of TiO <sub>2</sub> nanotubes	54
3. 4 Technique for selective detection of VOCs	59
3. 5 Blind test: Unknown VOC detection	63
3. 6 Sensing mechanism of TiO <sub>2</sub> nanotubes-based sensor	64
3. 7 Conclusions	68
References	69
Chapter 4	71-88
Multi-layer TiO <sub>2</sub> nanotubes-based VOC sensors for high sensitivity and selectivity	,
4. 1 Introduction	71
4. 2 Synthesis of multi-layered TiO <sub>2</sub> nanotubes	71
4. 3 Experimental setup for VOC sensing	73
4. 4 Characterizations of single and multi-layered TiO <sub>2</sub> nanotubes	73
4. 5 Growth mechanism of multi-layered TiO <sub>2</sub> nanotubes	77
4. 6 Comparative sensing study of single and multi-layered TiO <sub>2</sub> nanotubes-based ser	nsors 78
4. 6. 1 Resistive sensing performance	78
4. 6. 2 Capacitive sensing performance	80
4. 7 Sensing mechanism of multi-layered TiO <sub>2</sub> nanotubes-based sensors	83
4. 8 Conclusions	86
References	87

Chapter 5	89-106
1-D TiO <sub>2</sub> nanorods array-based sensor for selective and stable detection of VO	Cs
5. 1 Introduction	89
5. 2 Synthesis of TiO <sub>2</sub> nanorods by hydrothermal method	90
5. 3 Fabrication of ${\rm TiO_2}$ nanorods-based sensor and experimental setup for VOC	sensing 9
5. 4 Characterizations of TiO <sub>2</sub> nanorods	9
5. 5 VOC sensing characteristics of TiO <sub>2</sub> nanorods-based sensors	94
5. 6 Sensing mechanism of TiO <sub>2</sub> nanorods-based sensors	102
5. 7 Conclusions	10:
References	104
Chapter 6	107-123
Design and implementation of a capacitive sensor system based on TiO <sub>2</sub> nanotu	
time detection of methanol contamination in alcoholic beverages	
6. 1 Introduction	107
6. 2 Experimental setup for VOC sensing	109
6. 3 Design of the sensor system	11:
6. 4 Detection of methanol contamination using TiO <sub>2</sub> nanotubes based-sensor	113
6. 5 Conclusions	12
References	122
Chapter 7	124-130
Summary, conclusions and scope of future work	
7. 1 Summary	124
7. 2 Conclusions	128
7. 3 Scope of future work	130
List of Publications	132
Brief Biography of the Candidate	
Brief Biography of the Supervisor	

## List of Figures

Fig. 1.1 Images of gas sensors: (a) SnO <sub>2</sub> nanoparticles-based gas sensor for detecting ethylene [30], (b) A micro hot plate sensor with interdigitated electrodes layered over heater leads [31], (c) Single-layer MoSe <sub>2</sub> based NH <sub>3</sub> sensor [32], and (d) Packed chip of the sensor based on nanocrystalline SnO <sub>2</sub> [33]
Fig. 1.2 A schematic showing the effect of dimensions on surface area, volume, and surface to volume ratio of the material [53]
Fig. 1.3 A schematic showing classification of nanomaterials based on their dimensionality [54]
Fig. 1.4 FESEM images of various reported metal oxide nanostructures: (a) ZnO nanorods [70], (b) SnO <sub>2</sub> /SnS <sub>2</sub> nanotubes [77], (c) SnO <sub>2</sub> nanoflowers [79], (d) SnO <sub>2</sub> nanofibers [83], (e) WO <sub>3</sub> nanorods [86], (f) WO <sub>3</sub> nanotubes [88], (g) WO <sub>3</sub> nanorods [89], and (h) In <sub>2</sub> O <sub>3</sub> nanoribbons [96]
Fig. 2.1 Electrochemical anodization setup for the synthesis of ${\rm TiO_2}$ nanotubes36
Fig. 2.2 A schematic showing sensing set-up via injection method
Fig. 2.3 (a) A schematic of $TiO_2$ nanotubes-based sandwich-type sensor device, (b) Top view of the sensor device, (c) Simplified device structure: $Au/TiO_2$ nanotubes/ $Ti$ , (d) Corresponding circuit model of the device, and (e) Simplified representation in Randle's circuit model. (Dimensions are not to scale)
Fig. 2.4 Device modeling of TiO <sub>2</sub> nanotubes for deriving the resistive and capacitive components; (a) FESEM (side view) of nanotubes array. Top view is fitted in hexagonal grid geometry in inset, (b) A schematic of single TiO <sub>2</sub> nanotube showing morphological parameters, (c) majority carrier distribution in nanotubes wall in different ambient i.e. vacuum, air and reducing vapor, and (d) A schematic of the cross-sectional view of TiO <sub>2</sub> nanotubes for showing free space (pore and void region)
Fig. 2.5 Equivalent electrical circuit of fabricated $\mathrm{Au/TiO_2}\mathrm{nanotubes/Ti}$ sensor44
Fig. 2.6 Impedance variation (or Nyquist plot) of $Au/TiO_2$ nanotubes/Ti device at variable temperature (45 °C to 105 °C) in air ambient45
Fig. 2.7 Effect of temperature on various device components like (a) contact resistance ( $R_C$ ), (b) device resistance ( $R_X$ ), and (c) device capacitance ( $R_X$ )
Fig. 2.8 Impedance variation of $Au/TiO_2$ nanotubes/Ti device in air ambient to vacuum condition reached after 20 min to 90 min at 30 °C47
Fig. 2.9 Effect of vacuum on various device components like (a) contact resistance ( $R_C$ ), (b) device resistance ( $R_X$ ), and (c) device capacitance ( $C_X$ )
Fig. 2.10 Cole-Cole plots of $Au/TiO_2$ nanotubes/Ti device in (a) methanol ambient, and (b) acetone ambient
Fig. 3.1 FESEM images of TiO <sub>2</sub> nanotubes/Ti sample showing (a) top view and (b) side view.

Fig. 3.2 XRD spectra of ${\rm TiO_2nanotubes/Tisample}$
Fig. 3.3 TEM image of TiO <sub>2</sub> nanotubes
Fig. 3.4 PL spectra of ${\rm TiO_2}$ nanotubes/Ti sample
Fig. 3.5 (a) XPS survey spectra of TiO <sub>2</sub> nanotubes/Ti sample; High resolution XPS spectra with fitted peaks of (b) Ti(2p), and (c) O(1s)
Fig. 3.6 (a) Transient resistive change and, (b) transient capacitive change of the sensor upon exposure to methanol, ethanol, acetone, and 2-propanol; (c) Magnified version of Fig. 3.6 (a) for showing resistive response details and, (d) magnified version of Fig. 3.6 (b) for showing capacitive response details; (e) $\ln(R)$ of the sensor vs different VOCs concentration, and (f) $\ln(C)$ of the sensor vs different VOCs concentration when concentration of VOCs was increased from 100 ppm to 300 ppm with a step size of 50 ppm
Fig. 3.7 Identification of an unknown VOC; (a) resistive response and (b) capacitive response of the sensor upon exposure to an unknown VOC and concentration. (c) Graphical method to measure the concentration of target VOC after calculating "S" value
Fig. 3.8 (a) A schematic of ' $Au/TiO_2$ nanotubes/ $Ti$ ' sandwich-structured sensor; FESEM images of $TiO_2$ nanotubes: (b) top view, and (c) side view; (d) Cross-sectional view of the sensor (at $XX^{/}$ line) with structural dimensions; Device cross-section and R-C circuit model (e) in air ambient, and (f) in reducing vapour ambient.
Fig. 4.1 Anodization voltage and current density (J) profile for (a) single layer TiO <sub>2</sub> nanotubes, (b) double layer TiO <sub>2</sub> nanotubes, and (c) triple layer TiO <sub>2</sub> nanotubes
Fig. 4.2 FESEM images of single and multi-layered nanotubes. SL-NTs: (a) side view, and (b) top view. DL-NTs: (c) side view, (d) top view of first layer, and (e) top view of second layer. TL-NTs: (f) side view, (g) top view of first layer, (h) top view of second layer, and (i) top view of third layer
Fig. 4.3 XRD patterns of TiO <sub>2</sub> nanotubes having (a) single layer TiO <sub>2</sub> nanotubes, (b) double layer TiO <sub>2</sub> nanotubes, and (c) triple layer TiO <sub>2</sub> nanotubes
Fig. 4.4 A schematic of the steps involved in the growth of multi-layered ${\rm TiO_2}$ nanotubes77
Fig. 4.5 Resistive response magnitude as a function of ethanol concentration for three different sensors tested at room temperature $(27^{\circ}\text{C})$
Fig. 4.6 Transient behavior of (a) single, (b) double, and (c) triple layered nanotubes-based sensors in presence of 80 ppm of ethanol at 27 °C79
Fig. 4.7 Baseline resistance stability test of (a) single, (b) double, and (c) triple layered nanotubes-based sensors operating at $27~^{\circ}\mathrm{C}$ in air ambient over a span of seven days79
Fig. 4.8 Comparative resistive response magnitude (RRM) of SL, DL, TL-NTs based sensors towards 160 ppm of methanol, ethanol, acetone, 2-propanol, and benzene at 27 °C80
Fig 4.9 Capacitive response magnitude (CRM) as a function of ethanol concentration for three different sensors tested at room temperature (27 °C)
Fig. 4.10 Transient behavior of capacitive response for (a) single, (b) double, and (c) triple

layered nanotubes-based sensors in presence of 80 ppm of ethanol at 27 $^{\circ}\mathrm{C}82$
Fig. 4.11 Baseline capacitance stability test of (a) single, (b) double, and (c) triple layered nanotubes- based sensors operating at 27 °C in air ambient over a span of seven days82
Fig. 4.12 Comparative capacitive response magnitude (CRM) of SL, DL, TL-NTs based sensors towards 160 ppm of methanol, ethanol, acetone, 2-propanol, and benzene at $27$ °C82
Fig. 4.13 Schematics showing sensing mechanism. (a) SL-NTs, (b) DL-NTs with one interlayer junction, and (c) TL-NTs with two interlayer junctions. Energy band diagrams of Schottky barrier at inter layer junction (d) in air, and (e) in reducing ambient (ethanol)84
Fig. 5.1 Schematics showing sequence of the steps involved in fabricating $Au/TiO_2$ nanorods/ $Ti$ type sensor90
Fig. 5.2 (a) FESEM images of the annealed $TiO_2$ nanorods with top view, (b) side view; (c) TEM image of a single $TiO_2$ nanorods
Fig. 5.3 XRD pattern of hydrothermally grown ${\rm TiO_2}$ nanorods over ${\rm Ti}$ substrate94
Fig. 5.4 I-V characteristics of $Au/\ TiO_2$ nanorods/ $Ti$ based sensor operated at 50 °C in air and different methanol concentrations95
Fig. 5.5 Transient behavior of (a) the resistive change and (b) the capacitive change of the sensor when methanol concentration was increased from 50 ppm to 300 ppm96
Fig. 5.6 (a) Resistive response magnitude (RRM) and (b) Capacitive response magnitude (CRM) of the sensor operating at 50 °C for 100, 200 and 300 ppm concentration of methanol, ethanol, acetone, 2-propanol and benzene
Fig. 5.7 Resistive selectivity coefficient (RSC) of the sensor for (a) methanol, (b) ethanol (c) acetone, and (d) 2-propanol
Fig. 5.8 Capacitive selectivity coefficient (CSC) of the sensor for (a) methanol, (b) ethanol (c) acetone, and (d) 2-propanol
Fig. 5.9 Stability test of (a) resistance and (b) capacitance of TiO <sub>2</sub> nanorods sensor in air and 300 ppm methanol ambient
Fig. 5.10 A schematic of TiO <sub>2</sub> nanorods sensor with surface reactions related to the sensing mechanism (a) in air ambient and (b) in methanol ambient102
Fig. 6.1 Block diagram of the sensor system111
Fig. 6.2 Sensor system having sensor mounted inside a glass bottle and signal generator and processing circuit on bread board
Fig. 6.3 Resistive response of the sensor upon exposure to 200 ppm of (a) ethanol, (b) 10% methanol contaminated ethanol, (c) 25% methanol contaminated ethanol, and (d) pure methanol. Capacitive response of the sensor upon exposure to 200 ppm of (e) ethanol, (f) 10% methanol contaminated ethanol, (g) 25% methanol contaminated ethanol, and (h) pure methanol.
Fig. 6.4 Real environment capacitive response of the sensor placed in a 250 ml bottle having 10 ml of (a) ethanol, (b) 10% methanol in ethanol, (c) 25% methanol in ethanol, and (d) pure methanol

Fig. 6.5 Scattered plot showing various repetitive capacitance values of the sensor when placed in 250 ml of bottle having air, 10 ml of ethanol, 10 ml of 10% methanol contaminated ethanol,
10 ml of $25%$ methanol contaminated ethanol, and $10$ ml of pure methanol117
Fig. 6.6 GC-HS spectra of (a) pure whiskey, (b) 10% methanol contaminated whiskey, and (c) 25% methanol contaminated whiskey
Fig. 6.7 Capacitive response of the sensor when placed in 250 ml of bottle containing 10 ml of (a) pure whiskey, (b) 10% methanol contaminated whiskey, and (c) 25% methanol contaminated whiskey.  119
Fig. 6.8 Schematics of the $Au/TiO_2$ nanotubes/Ti based sensor showing (a) equilibrium state in air ambient, (b) sensor response in alcohol ambient, and (c) sensor recovery in air ambient.

## List of Tables

Table 1.1 Various metal oxide nanostructures-based gas sensors working in resistive mode. 11
Table 1.2 Summary of various sensors reported for detecting VOCs with high selectivity17
Table 3.1 Details of de-convoluted XPS spectra of ${\rm TiO_2}$ nanotubes
$ \begin{tabular}{ll} Table 3.2 Sensor characteristics towards 200 ppm of methanol at different RH levels61 \end{tabular} $
Table 3.3 Values of resistive slope, capacitive slope, and selectivity constant for different VOCs
Table 4.1 Morphological parameters of ${\rm TiO_2}$ nanotubes from FESEM study75
Table 4.2 Resistance of the sensor upon exposure to 40-160 ppm of ethanol at room temperature
Table 4.3 Capacitance of the sensor upon exposure to 40-160 ppm of ethanol at room temperature
Table 6.1 Contents of the test samples
Table 6.2 Resistive and capacitive sensing performance of the sensor in static mode113

## Abbreviations

O-D Zero Dimension
1-D One Dimension
2-D Two Dimension
3-D Three Dimension

**AFM** Atomic Force Microscopy

CMOS Complementary Metal Oxide Semiconductor

**CRM** Capacitive Response Magnitude

**DI** Deionized

DL-NTs Double Layer NanotubesFET Field Effect Transistor

FESEM Field Emission Scanning Electron Microscopy

FTO Fluorine-doped Tin Oxide

GC-HS Gas Chromatography Headspace

ICIntegrated Circuit ITO Indium Tin Oxide LED Light Emission Diode **MFC** Mass Flow Controller PLPhoto Luminescence PPM Parts Per Million  $\mathbb{Q}$ - $\mathbb{V}$ Charge to Voltage RHRelative Humidity

**RRM** Resistive Response Magnitude

SL-NTs Single Layer Nanotubes
SVR Surface to Volume Ratio

**TBOT** Titanium Butoxide

**TEM** Transmission Electron Microscopy

TL-NTs Triple Layer Nanotubes
VLS Vapor Liquid Solid

VOC Volatile Organic Compound
WHO World Health Organization

XPS X-ray Photoelectron Spectroscopy

**XRD** X-ray Diffraction