# Fluorinated Nanomaterials for Energy and Sensing Applications

A Thesis submitted by Gaurav Bahuguna

in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** 



Indian Institute of Technology Jodhpur Department of Chemistry May 2021

ii

### Declaration

I hereby declare that the work presented in this Thesis titled *Fluorinated Nanomaterials for Energy and Sensing Applications* submitted to the Indian Institute of Technology Jodhpur in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy, is a bonafide record of the research work carried out under the supervision of Dr. Ritu Gupta. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.

yourar

Gaurav Bahuguna P16CY001

iv

### Certificate

This is to certify that the thesis titled *Fluorinated Nanomaterials for Energy and Sensing Applications*, submitted by *Gaurav Bahuguna* (P16CY001) to the Indian Institute of Technology Jodhpur for the award of the degree of *Doctor of Philosophy*, is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

v

fith

*Ritu Gupta* Ph.D. Thesis Supervisor

vi

### Acknowledgements

I thank my Ph.D. Thesis Supervisor, *Professor Ritu Gupta* for her constant support during my journey at IIT Jodhpur. The amount of time and efforts that she has given in my Ph.D journey is thankless. It has been my pleasure learning under her guidance. She has been a constant source of inspiration which gave me enough strength to learn new things with each passing day in my Ph.D. There has been tremendous learning in the past few years under her guidance which will also carry forward in the future. Apart from my academic excellence, she has also taken care of my physical and mental well being by providing a homely environment at IIT Jodhpur.

I would like to thank Professor Rakesh K. Sharma for providing valuable guidance and support during Ph.D from time to time. His presence around has been a source of positivity and cheerfulness.

I thank Professor G. U. Kulkarni for giving me a chance to work under his esteemed guidance. It has been a great experience working in his lab. The enthusiasm and energy that he carries has been a constant source of motivation.

I extend my thanks to all my lab mates Ajay, Mohit, Anandita, Vinay, Vinod, Vipin, Akshay, Chesta, Savi, Hamid and Parijat for active collaborations, being helpful and exhibiting work ethics of highest level.

I thank Dr. Vikas Janu (Defence Lab Jodhpur, Jodhpur), Dr. Pura Ram (IIT Jodhpur), Dr. Saswata Bhatacharya and Manish Kumar (IIT Delhi) and Dr. Ashutosh, Dr. S. Angappane Dr. N. Kambhala and Indrajit (CeNS, Bangalore) for the collaborative work and helpful discussions.

I thank Dr. Pragati, Dr. Kiran, Dr. Poonam and Devika for providing a cordial and learning environment during the initial years of my Ph.D.

I thank all the faculty members, technical staff (Mr Ganpat and Mr Shubham), office staff of the Department of Chemistry (Miss Swati, Mr. Sandip), IIT Jodhpur for being supportive throughout this time.

I would like to thank all my friends who has always been with me through my ups and downs. I failed in some of my experiments but they never failed to bring back the smile on my face. The precious time spent with some of them in the campus of IIT Jodhpur and outside will always be missed and cherished. I will have to write another thesis to acknowledge each one of them with thousands of stories.

At the end I acknowledge my parents and family who has always been with me. That one minute phone call each day gave me hope for working next day with same enthusiasm. They have sacrificed a lot for me and has always been supportive in all the circumstances. I pay my highest level of respect to my family for their love, sacrifice and blessings.

I Wholeheartedly Dedicate the Thesis to My Family...

*Gaurav Bahuguna* Ph.D. Student

iv

# List of Figures

Figures	Title	page
1.1	Application of nanomaterials in various energy applications.	1
1.2	Important parameters of nanomaterials for VOC/gas sensors.	2
1.3	Overview of doped nanomaterials for different applications.	3
1.4	Advantages of Fluorination for different applications.	5
1.5	Properties and functionalization of carbon materials.	7
1.6	Different C-F bonds and their bond lengths. Figure adapted from reference [Feng et al., 2016].	7
1.7	Synthetic methods and precursors used for fluorination. Figure adapted from reference [Feng et al., 2016]	8
1.8	Physiochemical properties of the quaternary ammonium salts. (b-d) comparative CV plots of heteroatom substituted and un-substituted quaternary ammonium salts shown in (a). Figure adapted from reference [Han et al., 2016].	10
1.9	(a) Galvanostatic charge discharge at 1 A/g and (b) Cyclic voltammogram at 10 mV/s of the mesopore rich carbon. Schematic representation of (c) the mixture electrolyte used in the study and (d) the ionic interaction induced selective charging behavior of ionic mixture electrolyte. Figure adapted from reference [Wang et al., 2017d].	11
1.10	Humidity sensing characteristics of (a) Supramolecular nanofibre, (b) graphene polymer composite, (c) black phosphorous and (d) VS <sub>2</sub> nanosheets based humidity sensors. Figures in a-d are adapted from [Mogera et al., 2014], [He et al., 2018a], [Yasaei et al., 2015b] and {Feng et al., 2012a] respectively.	12
1.11	Application of new generation humidity sensors for (a) breath monitoring (b) skin-moisture sensing and (c) physiological monitoring. Figures in a-c are adapted from [Choi et al., 2018], [Li et al., 2017b] and [He et al., 2018a] respectively.	14
1.12	Synthesis methods for fluorination of metal oxides nanostructures using (a) HF, (b) TiF <sub>4</sub> , (c) NaF, and (d) fluorine gas as fluorine sources. Figures in a-d are adapted from [Lv et al., 2010], [Yang et al., 2008], [Lv et al., 2011] and [Zhou et al., 2015a] respectively.	15
1.13	Brief literature for enhancing the performance of $SnO_2$ based VOC sensor. (a) Au doped $SnO_2$ , (b) $SnO_2/TiO_2$ heterojunction (c) $SnO_2$ Nanostructuring and (d) $SnO_2@GaN$ . Figures in a-d are adapted from [Moon et al., 2019], [Chen et al., 2015], [Haddad et al., 2018] and [Bajpai et al., 2012] respectively.	19
2.1	Characterizations performed for analysis in the thesis.	23
2.2	Schematic demonstrating the working principle of (a) Vibrating Sample Magnetometer (VSM), (b,c) Superconducting Quantum Interference Device (SQUID) and its corresponding photograph.	25
2.3	Cyclic voltammogram of (a) redox couple (b) EDLC supercapacitor.	26
2.4	Galavanostatic charge/discharge cycles of supercapacitor.	26
2.5	Nyquist plot of supercapacitor. Figure adapted from[Mei et al., 2018].	27
2.6	Steps involved in fabrication of electrode pattern using photolithography technique.	28
2.7	Schematic diagram of the gold electrodes. Inset shows optical image of the interdigitated gold electrodes.	28
3.1	(a) TEM and (b) HRTEM images of VC. Insets in b show the magnified view. (c) Electron diffraction pattern of VC.	31
3.2	(a) Schematic demonstrating the steps involved in the fluorination of Vulcan Carbon (VC) using F-TEDA as a precursor. (b) $N_2$ adsorption-desorption BET isotherm of VC and F-VC. (c)Pore size distribution of VC and F-VC carbon material.	32
3.3	(a) Survey scan of F-VC and VC. (b) High resolution F1s spectrum of F-VC.	32
3.4	High resolution C1s spectrum of F-VC and VC.	33
3.5	High resolution N1s spectrum of F-VC and F-TEDA crystals.	33
3.6	Raman spectra of pristine and fluorinated VC.	36
3.7	(a) Schematic showing the preparation of F-VC/CC electrodes and corresponding surface contact angle measurement on F-VC/CC and VC/CC modified carbon cloth surface. (b) Swagelok cell assembly of supercapacitor device with the electrode and separator shown at the bottom.	37
3.8	Cyclic voltammetry curves at different scan rates for (a) VC/CC and (b) F-VC/CC electrode based devices.	37

ix

3.9	(a) Cyclic voltammetry curves of VC/CC and F-VC/CC based devices at scan rates of 100 mV/s and (b) Current density as a function of scan rate and corresponding linear fitting for the	38
	data at 0.4V.	
3.10	Cyclic Voltammetry curves performed in 3-electrode geometry at different scan rates for (a) VC and (b) F-VC. (c) Specific capacitance at different scan rate and (d) Nyquist plot for VC and F-VC in 3-electrode geometry.	38
3.11	Galvanostatic charge-discharge (GCD) curves at current densities of (a) 0.05 A/g (b) 0.1 A/g.	39
3.12	Specific capacitance at different discharge current density of VC/CC and F-VC/CC devices.	40
3.13	Nyquist plots of the fabricated supercapacitors with fitted semicircle of (a) VC/CC (b) F- VC/CC.	40
3.14	Cyclic retention over 10,000 cycles of F-VC/CC based supercapacitor. The inset shows the GCD curve of 1 <sup>st</sup> and 10,000 <sup>th</sup> cycle.	41
3.15	Cyclic Voltammograms (a,b), Galvanostatic charge-discharge curves (c,d) of nanocarbon derived from polymer, and fluorinated nanocarbon, respectively. Comparative (e) Specific capacitance and (f) Nyquist plots for prinstine and fluorinated nanocarbon.	41
4.1	Role and effect of electrolytes on supercapacitor performance. Figure adapted from reference [Zhong et al., 2015].	43
4.2	Chemical structure of (a) F-TEDA with polar N-F bond and (b) TBABF <sub>4</sub> . Ionic conductivity of F-TEDA/TBABF4 mixture and TBABF4 in absence and presence of varying water content at 303 K. (d) Change in conductivity with increasing temperature of $0.5M$ F-TEDA/TBABF <sub>4</sub> mixture and TBABF <sub>4</sub> .	45
4.3	FESEM images of carbon cloth at (a) low and (b) high magnification. (c) Schematic of different components of supercapacitor. (d) Photograph of Swagelok-type supercapacitor assembly and (e) Carbon cloth electrodes and separator used in the study.	46
4.4	(a-e) Comparative cyclic voltammetry curves of supercapacitors assembled in ambient	47
	condition at scan rates of 50 mV/s, 500 mV/s, 5 V/s, 50 V/s and 200 V/s respectively. (f)	
	Current density at 0.4 V for varying scan rates of 0.02-1000 V/s. Inset shows the magnified	
	graph for the same. Note: The legends are same for (a-e) as in (a).	
4.5	Cyclic Voltammetry curves of (a) supercapacitor fabricated with TBABF <sub>4</sub> electrolyte (b)	47
	C:mixture (inert) and (c) D:control (inert) at increasing voltage window.	17
4.6	(a-d) Cyclic voltammetry curves of supercapacitors assembled inside glove box at scan rates of 50 mV/s, 500 mV/s, 50 V/s and 500 V/s respectively. (e) The electrochemical	48
	performance of device A and C compared with standard electrolyte (1M TBABF <sub>4</sub> in	
	acetonitrile). (f) Current density at 0.9 V for varying scan rates of 0.02-1000 V/s. Note that	
	the legends in (a-e) are same as in (a).	
4.7	Galvanostatic charge/discharge (GCD) curves at current density of 1 mA/cm <sup>2</sup> of (a) device A:mixture (ambient) and C:mixture (inert), (b) device B:control (ambient) and D:control (inert).	49
4.8	Specific capacitance at different discharge current of devices assembled in (a) ambient and (b) inert atmosphere. Bar graph representation of specific capacitance of (c) device A: mixture (ambient) and C:mixture (inert), (d) device B:control (ambient) and D:control (inert) at variable current density.	50
4.9	Normalized capacitance retention of (a A:mixture (ambient) and C:mixture (inert),	51
<b>т•</b> у	(b)B:control (ambient) and D:control (inert) at variable current density. Ragone plot of devices assembled in (a) ambient and in (b) inert condition.	).
4.10	Capacitance retention over 60,000 cycles for (a) A:mixture (ambient) and C:mixture (inert),	52
	(b) B:control (ambient) and D:control (inert) at applied current density of 1 mA/cm <sup>2</sup> . Inset	
	Figure 4.12 (a) and (b) show GCD curve of before and after 60,000 cycles for the	
	corresponding device.	
4.11	(a) Nyquist plot of fabricated devices (A-D) taken over 0.1-10 <sup>6</sup> Hz frequency range. Inset	53
1	shows the magnified Nyquist plot at higher frequency. (b) shows the fitting circuit with	"
	parameters. Experimental and fitted Nyquist plots of (c) A:mixture (ambient), (d) B:control	
	(ambient), (e) C:mixture (inert) and (f) D:control (inert).	
A 17		ГЛ
4.12	SEM image of pristine carbon cloth (CC) and graphene petals on carbon cloth (GP/CC)	54
4.13	Comparative cyclic voltammetry curves of supercapacitors assembled with graphene petals on carbon cloth (GP/CC) in (a,b) inert and (d,e) ambient condition at scan rates of 0.50 V/s, 50 V/s respectively. (c,f) Current density at 0.9 and 0.4 V for varying scan rates of 0.02-	54
	1000 V/s in (c) inert and (f) ambient conditions.	
1 14	Galvanostatic charge/discharge (GCD) curves of supercapacitors with GP/CC electrodes at	<b>FF</b>
4.14	current density of 1 mA/cm <sup>2</sup> in (a) inert (c) ambient conditions. Specific capacitance at	55
	content density of rinky continuation (c) and been conditions. Specific capacitance at	

	different discharge current of devices assembled in (b) inert and (d) ambient atmosphere.	
5.1	Schematic diagram showing the setup used for the characterization of a humidity sensor.	58
5.2	Optical photographs of crystals of F-TEDA prepared using different concentrations of	59
	solution (a) 5 mM, (b) 10 mM, (c) 25 mM, (d) 50 mM and (e) 100 mM.	
5.3	(a) Secondary electron image and the corresponding elemental maps of (b) C, (c) F, (d) N and (e) Cl and (f) Molecular Structure of F-TEDA.	59
5.4	(a) Optical photograph, (b) current response as RH is switched between 10% and 95% at different applied voltages (0.8, 1.0 and 1.2 V).	61
5.5	(a) Sensitivity of device 1, 2 and 3 at different humidity values fabricated using solutions of 25, 50 and 100 mM concentration on IDE-1. Inset shows the sensitivity of the <i>device-3</i> at lower humidity values (b) Sensitivity of <i>device-6</i> at different humidity values fabricated on	61
	IDE-2. Inset shows the optical photograph of the device. (Note: The error bars in a and b have been plotted with respect to mean of values over 50 s of continuous and stable data collection).	
5.6	Sensitivity of (a) device-4, (b) device-5, (c) device-7 and (d) device-8 at different relative humidity values.	62
5.7	Variations in the sensitivity of the device at 95% RH when monitored (a) for continuously 8	63
	hours (b) over different days. Optical photograph of crystals of F-TEDA drop-casted on Au- IDE (c) before measurement (d) 8 hour of continuous monitoring and (e) after 20 days	
	monitoring at 95% RH. (Scale bar in c, d and e is 100 $\mu$ m)	
5.8	Current response of sensor exposed to humidity pulses before and after exposure to various volatile organic compounds (polar and non-polar) and gaseous environment.	64
5.9	(a) I-V characteristics (Inset: semi-log plot of I-V characteristics), (b) C-V measurements at different relative humidity (RH%) values.	64
5.10	Cyclic voltammogram of the fabricated sensor at varying scan rates in RH conditions of (a)	65
F 11	35%, (b) 55%, (c) 75% and (d) 95%. (a) Impedance-frequency characteristics at different relative humidity (RH%) values. (b)	65
5.11	Nyquist plot of fabricated sensor at different RH%. (c) Charge Transport Resistance (R <sub>CT</sub> )	05
	with respect to RH%. Inset in (c) shows the corresponding equivalent circuit used for	
	modeling. Note that error bars in (c) have been plotted with reference to the error in $R_{CT}$	
	for the modeled circuit.	
5.12	(a,b) FTIR spectra of F-TEDA crystal in dry and wet state respectively.	66
5.13	(a) Signals corresponding to breathing response of F-TEDA based sensor upon inhalation	67
	and exhalation at six different breathing frequencies. (b) Bar-graph representation of	,
	breathing cycle time and breathing rate calculated from human breath experiment. Note	
	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.	
	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the	
5.14	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.	67
5.14 5.15	<ul> <li>that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.</li> <li>(c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor.</li> <li>Flexibility of the device for wrist band application.</li> <li>(a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different</li> </ul>	67 68
	<ul> <li>that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.</li> <li>(c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor.</li> <li>Flexibility of the device for wrist band application.</li> <li>(a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers.</li> </ul>	68
5.15	<ul> <li>that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.</li> <li>(c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor.</li> <li>Flexibility of the device for wrist band application.</li> <li>(a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different</li> </ul>	
5.15 6.1	<ul> <li>that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.</li> <li>(c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor.</li> <li>Flexibility of the device for wrist band application.</li> <li>(a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers.</li> <li>Various precursors and methods used for fluorination of metal oxides.</li> <li>Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other</li> </ul>	68 71
5.15 6.1	<ul> <li>that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.</li> <li>(c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor.</li> <li>Flexibility of the device for wrist band application.</li> <li>(a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers.</li> <li>Various precursors and methods used for fluorination of metal oxides.</li> <li>Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF<sub>4</sub> and (iv)</li> </ul>	68 71
5.15 6.1 6.2	<ul> <li>that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles.</li> <li>(c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor.</li> <li>Flexibility of the device for wrist band application.</li> <li>(a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers.</li> <li>Various precursors and methods used for fluorination of metal oxides.</li> <li>Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF<sub>4</sub> and (iv) NaF (v) NH<sub>4</sub>F are used as control in comparison to F-TEDA and HF, respectively. (b)</li> </ul>	68 71 72
5.15 6.1 6.2 6.3	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of $0\%$ , $10\%$ , $20\%$ , $30\%$ and $40\%$ by weight of HF and F-TEDA. (d) Intensity ratio of (110)/(104) peak intensities of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with	68 71 72 74
5.15 6.1 6.2 6.3 6.4	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesized with 20% by weight of different fluorinating agents. XRD patterns of $\alpha$ , 10%, 20%, 30% and 40% by weight of HF and F-TEDA. (d) Intensity ratio of (110)/(104) peak intensities of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with respect to (104) orientation. Note that star symbol (*) in (b) indicates impurity phase.	68 71 72 74 74
5.15 6.1 6.2 6.3 6.4	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesized with 20% by weight of different fluorinating agents. XRD patterns of $\alpha$ . Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with respect to (104) orientation. Note that star symbol (*) in (b) indicates impurity phase. SEM images of (a) pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesis.	68 71 72 74
5.15 6.1 6.2 6.3 6.4 6.5 6.6	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesized with 20% by weight of different fluorinating agents. XRD patterns of $\alpha$ , 10%, 20%, 30% and 40% by weight of HF and F-TEDA. (d) Intensity ratio of (110)/(104) peak intensities of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with respect to (104) orientation. Note that star symbol (*) in (b) indicates impurity phase. SEM images of (a) pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesis. Elemental composition of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> fluorinated with different fluorinating agents.	68 71 72 74 74 74 75 75
5.15 6.1 6.2 6.3 6.4	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of α-Fe <sub>2</sub> O <sub>3</sub> synthesized with 20% by weight of different fluorinating agents. XRD patterns of $\alpha$ , 10%, 20%, 30% and 40% by weight of HF and F-TEDA. (d) Intensity ratio of (110)/(104) peak intensities of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with respect to (104) orientation. Note that star symbol (*) in (b) indicates impurity phase. SEM images of (a) pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesis. Elemental composition of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> fluorinated with different fluorinating agents. (a-e) Field-Emission Scanning Electron Microscope images and corresponding (f-j) Transmission Electron Microscopy images of pristine and $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> with 10%, 20%, 30% and	68 71 72 74 74 74 75
5.15 6.1 6.2 6.3 6.4 6.5 6.6 6.7	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesized with 20% by weight of different fluorinating agents. XRD patterns of $\alpha$ , 10%, 20%, 30% and 40% by weight of HF and F-TEDA. (d) Intensity ratio of (110)/(104) peak intensities of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with respect to (104) orientation. Note that star symbol (*) in (b) indicates impurity phase. SEM images of (a) pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> fluorinated with different fluorinating agents. (a-e) Field-Emission Scanning Electron Microscope images and corresponding (f-j) Transmission Electron Microscopy images of pristine and $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> with 10%, 20%, 30% and 40% of F-TEDA respectively.	68 71 72 74 74 75 75 75 76
5.15 6.1 6.2 6.3 6.4 6.5 6.6	that error bars in (b) have been plotted with reference to the mean of 5 breathing cycles. (c) Normalized response curve of a typical breathing profile used for measuring the response and recovery time of the fabricated humidity sensor. Flexibility of the device for wrist band application. (a) Current response of the fabricated device at different humidity corresponding to varying finger height and (b) Skin-moisture response from human fingers of different volunteers. Various precursors and methods used for fluorination of metal oxides. Schematic showing (i) F-TEDA and (ii) HF used as fluorinating agents in the study. Other fluorinating species with common fluorine containing counter anions (iii) TBABF <sub>4</sub> and (iv) NaF (v) NH <sub>4</sub> F are used as control in comparison to F-TEDA and HF, respectively. (b) XRD patterns of α-Fe <sub>2</sub> O <sub>3</sub> synthesized with 20% by weight of different fluorinating agents. XRD patterns of 0%, 10%, 20%, 30% and 40% by weight of HF and F-TEDA. (d) Intensity ratio of (110)/(104) peak intensities of α-Fe <sub>2</sub> O <sub>3</sub> is prefered due to its anisotropic conductivity with respect to (104) orientation. Note that star symbol (*) in (b) indicates impurity phase. SEM images of (a) pristine α-Fe <sub>2</sub> O <sub>3</sub> synthesis. Elemental composition of α-Fe <sub>2</sub> O <sub>3</sub> synthesis. Elemental composition of α-Fe <sub>2</sub> O <sub>3</sub> fluorinated with different fluorinating agents. (a-e) Field-Emission Scanning Electron Microscope images and corresponding (f-j) Transmission Electron Microscopy images of pristine and α-Fe <sub>2</sub> O <sub>3</sub> with 10%, 20%, 30% and	68 71 72 74 74 74 75 75

6.10	20%, HF-20%, NH <sub>4</sub> F-20%, TBABF <sub>4</sub> -20% and NaF-20% at (a) 20 K and (b)300 K respectively. Zero-field cooled and field-cooled magnetic measurements at 500 Oe applied field for (a) pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> and fluorinated Fe <sub>2</sub> O <sub>3</sub> synthesized with (b) F-TEDA-20%, (c) HF-20%, (d)	78
	$NH_4F-20\%$ (e) TBABF <sub>4</sub> -20% and (f) NaF-20%.	
6.11	(a) Room-temperature magnetization M–H curves of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> with different	79
	percentage of Selectfluor (F-TEDA): 0%, 10%, 20%, 30%, and 40% (b) Magnified view of low- field region of M-H curves at 300 K and (c) H <sub>C</sub> and (d) M <sub>S</sub> along with (e) Fluorine wt% for	
	different percentage of F-TEDA.	
6.12	Schematic showing the pristine $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> with canted spins, which upon fluorination with F-	79
	TEDA becomes ferromagnetic due to uncompensated spins on the surface of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> due to additional fluorine atoms. Note that spherical shape is used as a model system in place	
	of dendritic morphology, and the effect of surface fluorine shown as a shell around $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	
	is considered for the sake of clarity.	
6.13	Temperature dependent magnetization at 500 Oe of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesized at different Selectfluor (F-TEDA) %; (a) 0%, (b) 10%, (c) 20% and (d) 30%. Insets show corresponding	80
	differential ZFC curves indicating Morin Transition Temperatures.	
6.14	Comparative plot of (a) temperature-dependent magnetization at 500 Oe and (b) $M-H$	80
	curves of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> synthesized at different F-TEDA percentage i.e. 0%, 10%,	
6.15	20%, 30% and 40%. Experimental setup for photoelectrochemical measurements. (b) Chronoamperometric	81
0.1)	measurements performed at 1.6 V versus RHE. (c) The photocurrent response with respect	01
	to pristine Fe <sub>2</sub> O <sub>3</sub> film.	
7.1 7.2	Schematic showing the working of F-SnO₂ based transparent display as VOC sensor. Hypothetical data demonstrating (a) a typical response of a VOC sensor at low temperature	85 86
7.2	(150 °C) with no recovery for prolonged hours, (b) sensor recovery process on activation by	80
	UV-illumination for pristine $SnO_2$ and $F-SnO_2$ -based sensor at an operating temperature of	
	150 °C after exposure to VOCs.	0-
7•3 7•4	Schematic showing mechanism behind the working of F-SnO <sub>2</sub> based VOC sensor. (a) Schematic demonstration of the fabrication process of F-SnO <sub>2</sub> films. (b) SnO <sub>2</sub> film	87 87
7.1	thickness measurement using surface profilometer. (c) XRD patterns of $SnO_2$ and $F-SnO_2$	- /
	and (d) FESEM image of $F-SnO_2$ film.	_
7.5	(a) High-resolution F1s XPS spectrum of $F-SnO_2$ (b) Comparative high-resolution Sn3d XPS spectra of $SnO_2$ and $F-SnO_2$ . (c,d) O1s XPS spectra of $SnO_2$ and $F-SnO_2$ , respectively.	89
7.6	(a) Optical transmittance of $SnO_2$ and $F-SnO_2$ films. (b) Photograph of the transparent F-	90
	$SnO_2$ sensor. (c) Low-temperature resistivity plot for $SnO_2$ and $F-SnO_2$ films. I-V	-
	characteristics of the films in the dark and under UV-illumination of 365 nm wavelength at $(d) 25^{\circ}$ and $(a) 45^{\circ}$ respectively. (f) contributions to the inherent conductivity of SpO	
	(d) 25°C and (e) 150°C, respectively. (f) Contributions to the inherent conductivity of $SnO_2$ and $F-SnO_2$ from thermal and photo-induced carriers (y-axis is not to the scale; it is a	
	conceptual depiction for clarity).	
7.7	(a) Schematic showing the crack network templating process involved in the fabrication of	91
	Al-mesh network as transparent heater. (b) Sensor setup with integrated transparent metal mesh heater and UV-LED for temperature-dependent photoconductivity	
	measurements. (c) Transmittance of SnO <sub>2</sub> film with integrated metal mesh heater. (d)	
	Heating profile and thermal image of the metal mesh-based transparent heater at a	
7.8	temperature of 150 °C (operated at 6 V). Photoresponse of SnO <sub>2</sub> and F-SnO <sub>2</sub> towards UV source of 365 nm wavelength at (a) 25 °C,	92
7.0	(b) 150 °C, and (c) 250 °C. (d) Temperature dependence of photoresponse decay time.	92
7.9	(a) High resolution deconvoluted F1s XPS spectra of heavily doped F-SnO <sub>2</sub> . Photoresponse	93
	of SnO <sub>2</sub> , lightly-doped F-SnO <sub>2</sub> (0.6 at%) and heavily-doped F-SnO <sub>2</sub> (5.7 at%) films towards UV- light at (b) 25 °C, (c) 150°C and (d) 250°C.	
7.10	Normalized experimental data (open circle) overlaid with fitted (solid line) photocurrent	94
	decay curves at different temperatures for (a) $SnO_2$ and (b) F-SnO <sub>2</sub> films. Temperature	21
	dependence of (c) lifetime of photo-induced charge carrier ( $\tau$ ) and (d) decay exponent ( $\beta$ )	
	for SnO <sub>2</sub> and F-SnO <sub>2</sub> films. Note: In Figure (c), data points are linearly fitted with the x-axis (bottom). The symbols are experimental data, and the connecting lines in (d) are only to	
	guide the eye.	
7.11	(a) The sensitivity of the pristine and $F-SnO_2$ films toward humidity at room temperature.	95
	(b) Change in resistances of the films under dry and moist air.	
7.12	(a) Normalized response of F-SnO₂ sensor towards ethanol at different operating	95

7.13	conditions. (b) Response of MQ3 sensor towards ethanol. Inset in (b) shows the thermal image of MQ3 sensor. The operating temperature of the sensor is ~260 °C. The F-SnO <sub>2</sub> sensing characteristics towards (a) 100 ppm of ethanol and (b) 100 ppm triethylamine (TEA) vapors. (c) Response of sensor towards different concentration of TEA (inset in c shows response at 10 and 5 ppm) and (d) same concentration (20 ppm) of TEA at 150 °C.	96
7.14	Sensing characteristics of (a) SnO <sub>2</sub> and (b) F-SnO <sub>2</sub> towards different concentrations of TEA vapors and (c,d) corresponding sensitivity profile with respect to concentration variation along with the $R^2$ values.	97
7.15	Histogram of F-SnO₂ sensor towards different target VOCs at 150 °C under UV-illumination. Note: The error bar is over three consecutive sensor measurements.	97
7.16	The sensor current response profile with the UV-on after saturated ethanol response is obtained at 150 °C. Note: Once the saturated photoresponse is obtained, UV is also turned-off for the complete recovery of the sensor.	98

### List of Tables

Title	page
Brief literature survey on various methods adopted for the fluorination of carbon materials.	8
A brief literature survey of humidity sensors.	12
Tabulation of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> magnetic parameters reported in the literature.	16
Literature summary of VOC sensor using different types of nanomaterials.	17
Literature survey of the fluorinated materials used for sensing applications.	19
X-ray photoelectron spectra (XPS) literature reference of C1s, F1s, N1s and O1s.	34
Comparison of BET surface area, conductivity and specific capacitance of common carbon materials.	39
Literature survey of carbon material based supercapacitors.	48
Comparative performance of fabricated supercapacitors.	52
Details of the humidity sensing devices fabricated in this study.	60
Specifications of IDE-1 and IDE-2.	60
Optimization of conditions for SnO <sub>2</sub> fluorination.	88
XPS analysis of O1s for SnO <sub>2</sub> and F-SnO <sub>2</sub> films.	89
Percentage of oxygen defects (%) in SnO <sub>2</sub> and F-SnO <sub>2</sub> .	89
Resistivity change in $SnO_2$ and F-SnO <sub>2</sub> films with temperature and UV illumination.	91
	Brief literature survey on various methods adopted for the fluorination of carbon materials. A brief literature survey of humidity sensors. Tabulation of α-Fe <sub>2</sub> O <sub>3</sub> magnetic parameters reported in the literature. Literature summary of VOC sensor using different types of nanomaterials. Literature survey of the fluorinated materials used for sensing applications. X-ray photoelectron spectra (XPS) literature reference of C1s, F1s, N1s and O1s. Comparison of BET surface area, conductivity and specific capacitance of common carbon materials. Literature survey of carbon material based supercapacitors. Comparative performance of fabricated supercapacitors. Details of the humidity sensing devices fabricated in this study. Specifications of IDE-1 and IDE-2. Optimization of conditions for SnO <sub>2</sub> fluorination. XPS analysis of O1s for SnO <sub>2</sub> and F-SnO <sub>2</sub> films. Percentage of oxygen defects (%) in SnO <sub>2</sub> and F-SnO <sub>2</sub> .

xvi

# List of Symbols

Symbol	Description
I	Current
V	Voltage
Ċ	Capacitance
t	Time
-	-
S	Second
T	Temperature
mL	Milliliter
$\mu L$	Microliter
Α	Ampere
nA	Nano Ampere
F	Farad
М	Molar
C	Capacitance
А	Area
ε <sub>r</sub>	Dielectric constant of electrolyte
0	Degree
I	Intensity
Ω	ohm
%	Percentage
θ	Theta
λ	Wavelength
ν	Frequency
Å	Angstrom
К	Kelvin
Oe	Oersted
H <sub>c</sub>	Coercivity
Ms	Saturation Magnetization
mV	Millivolt

## List of Abbreviations

Abbreviation	Full form
XRD	X-Ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
UV	Ultra Violet
FTIR	Fourier Transform Infrared spectroscopy
BET	Brunauer-Emmett-Teller
SAED	Selected Area Electron Diffraction
ТЕМ	Transmission Electronic Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
SEM	Scanning Electronic Microscopy
XRD	X-ray Diffraction
EDX	Energy Dispersive X-ray Spectroscopy
RHE	Reference Hydrogen Electrode
PEC	Photoelectrochemical
ppm	Parts Per Million
JCPDS	Joint Commission on Powder Diffraction sheet
ICSD	Inorganic Crystal Structure Database
FTO	Fluorine Doped Tin Oxide
F-TEDA	Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane
	bis(tetrafluoroborate)
СС	Carbon Cloth
VC	Vulcan Carbon
F-VC	Fluorinated Vulcan Carbon
DI	Deionized water
EIS	Electrochemical Impedance Spectroscopy
CV	Cyclic Voltametry
IV	Current-Voltage
I-t	Current-time
GCD	Galvanostatic Charge discharge
VOC	Volatile organic Compound
PPC	Persistent Photoconductivity
LOD	Limit of detection
DC	Direct Current
Ace	Acetone
EtOH	Ethanol
MeOH	Methanol
tBuOH	t-butyl alcohol
PrOH	Iso-Propanol
MEK	butanone
Chl	Chloroform
AcOEt	Ethylacetate
Tol	Toluene
DCM	di-chloro methane
DMF	dimethyl formamide
Pentanal	Pentanal Acotopitrilo
ACN	Acetonitrile
Hexane TEA	Hexane
DEA	Triethylamine diethylamine
	accityianine

Room Temperature Relative humidity