2022
9(2), 79-90

Journal of
MATERIALS NANOSCIENCE

Electronic Nose based on chemiresistive sensors for toxic gas detection

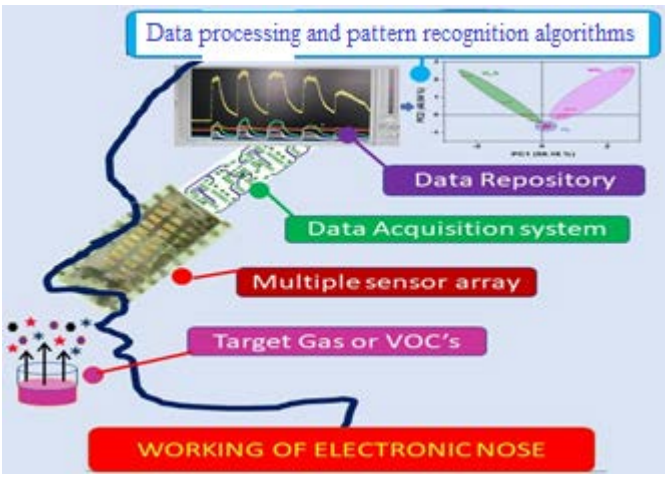
Niranjan S. Ramgir[1,2]*, K. R. Sinju[1,2], Bhagyashri. B. Bhangare[1], A. K. Debnath[1,2]

[1]*Technical Physics Division, Bhabha Atomic Research Center, Mumbai 400 085, India.* [2]*Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India*

Submitted on: 16-Nov-2021, Accepted and Published on: 15-Feb-2022

Review Article

ABSTRACT Development of gas sensors satisfying the '4-S sensor selection criterion' is a daunting challenge. This criterion demands the accomplishment of performance satisfying the parameters namely sensitivity (sensor response), selectivity, stability and suitability. For chemiresistive sensors to achieve an optimum sensor configuration, optimization of parameters namely, sensing material, its thickness, amount and distribution, deposition method, pre and post deposition treatment, operating temperature and involved sensing mechanism is pre-requisite and a humongous task. Use of multiple sensors each having partial specificity towards a target gas is looked upon as a means to achieve a configuration satisfying the 4-S criterion. Besides, it offers advantages of cross verification and/or validation, removal of false or faulty sensor, overall reliability and simultaneous detection of multiple gases. These systems are often classified as an electronic nose or e-nose. Their important function is to mimic the mammalian olfactory system. However, its usage involves the complexity of data acquisition and analysis employing advanced date analytics such as machine learning and artificial neural networks. The present article reviews and summarizes the activity on electronic nose especially for toxic gas detection. Care has been taken to include some of the recent findings crucial for realizing a complete working and portable e-nose.



Keywords: Electronic Nose, Nanowires, Metal Oxide Semiconductors, Chemiresistive Sensors, Toxic gases

INTRODUCTION

Wealth of novel nano-morphologies and associated enhanced surface area to volume ratio has enabled the utilization of numerous nanomaterials for the gas sensing applications. The tunable surface reactivity i.e., band gap engineering has led to the design of novel sensing materials for desired gases. To achieve the ultimate commercially deployable sensor however demands the satisfaction of "4-S sensor selection criterion". Herein, each S stands for sensitivity, selectivity, stability and suitability. In other words, the developed sensor should exhibit a high sensitivity towards the desired/target gas with high specificity i.e., showing no or minimal response towards other interfering gases. Importantly, it should demonstrate sufficient stability over the long-term period (~3-6 months), typically the time frame after which a sensor calibration is required. Usually, sensors deployed at actual sites demands recalibration of the sensors intermittently after every 3-6 months period. This is required and inevitable to avoid sensors going into the sleep mode and/or take care of drift related to aging and exposure to humid environment. For example, H_2S sensors based on SnO_2: CuO heterostructures usually requires re-calibration at regular interval of 3 months.[1] During the course the base line of the sensor drifts to a different value owing to the formation of $Cu(OH)_2$ with time. Formation of hydroxide results in the sluggish response due to slower rate of conversion from $Cu(OH)_2$ to CuS and this may cause delay in measurements and hence needs a continuous check.[2, 3] At every calibration the sensor is exposed to higher dose of H_2S typically > 50 ppm which leads to the conversion of all the available oxides and/or hydroxides namely CuO, Cu_2O and $Cu(OH)_2$ on the surface to CuS, which eventually recovers back to CuO thereby rejuvenating the surface completely.[4] Another important factor is suitability, which arises mainly from the economic point of view. Herein, the cost of sensor fabrication, testing and the working device and other related costs, all should be low or economically viable so as to sustain the batch production as required for industry level fabrication. Besides, suitably also takes into

*Corresponding Author: Dr. Niranjan S. Ramgir
Technical Physics Division, Bhabha Atomic Research Centre Mumbai 400 085. India
Tel: +91-022-25597084
Email: niranjanpr@yahoo.com

URN:NBN:sciencein.jmns.2022.v9.301 ISSN: 2394-0867

http://pubs.thesciencein.org/jmns

account whether a specific sensor can be used for the desired application or not especially application involving in a process stream. The 4-S sensor selection criteria is discussed in view of commercial viability of the developed sensor. A choice of sensor for a particular set of analytes or in a process stream is judged on its sensing performance and the parameters like sensor response, selectivity, detection range and response and recovery times are crucial. However, the major concern for the suitability for possible deployment arises from the commercial point of view. If the sensor exhibiting all the above-mentioned properties is expensive to fabricate it may not be suitable or find a place in the market.

All these factors put a constrain on the developed sensor and demands a humongous task of qualifying the criterion. It is noteworthy to mention that overall, nearly 90% of the developed sensor fails this important quality check process. Most of the work dies at the publication level, which is usually referred to as the valley of death.[5,6,7] Out of the 10% of the total developed sensors only 1% sees the sensor prototype development stage. Of which again many fails before the commercial deployment stage. This is mainly because of the complex or tedious process of getting the right sensor configuration truly satisfying the 4-S sensor selection criterion. The cumbersome task usually fails due to poor sensor performance and mainly because of lack of strong commitment. Of these also majority dies immediately within the first year of the deployment and thus very few of the developed sensor effectively reach the market and sustain. Thus, in spite of initial good sensor performance many sensors usually see very little or no commercial life at all. These were the main reason for the failure of thin films-based sensors.

The above discussion clearly demonstrated the humongous efforts and mindset required for the development of the commercial sensor product. Hence, there is a need to develop a process or system which can help to expedite the process of quality check and simultaneously provide data to overcome the valley of death. This is required so as to realize a faster approach for commercially deployable sensors. Nanomaterials with their associated chemical and physical properties are looked upon as a strong candidate which can assure the satisfaction of 4-S criterion. The inherent high surface area to volume ratio enables a faster reaction kinetics on the sensor surface which looks promising for the high sensitivity and selectivity. Besides the ease with which the surface and interface properties can be tailored provides an additional hand to play with the third parameter of stability. Also, the ease of synthesis using both physical as well as chemical approaches compatible to the complementary metal oxide semiconductor or CMOS processes is envisaged as a factor that can satisfy the last Suitability parameter.

Accordingly, in the present work efforts directed towards the development of nanomaterials-based chemiresistive sensors in particular electronic nose or e-nose has been discussed and elaborated citing some of our recent results and findings. Our results clearly demonstrate that the nanomaterials based on SnO_2 WO_3, ZnO and their heterostructures with organic and inorganic counterparts results in sensors with enhanced sensing performance towards target gases and are an ideal candidate for the realization of e-nose for toxic gas detection.

ELECTRONIC NOSE OR E-NOSE

With the advent in nanoscience and nanotechnology novel applications have emerged that are being employed for improving the comfort of humans. Besides, advances in the internet of things (IoT) and the capacity to handle large data sets has led to the fast technological advances in particular incorporation of artificial intelligence. Figure 1 shows the schematic of robot with novel features enabled due to scientific and technological advances. This includes replacement of the five of the human senses with the artificial one which are rightly called as e-eye, e-skin, e-tongue, e-ear and e-nose (EN). Of these, major work is carried out in the field of e-nose and has been attributed mainly to the requirement from the industry.

On an average, human nose contains approximately 400 scent receptors with which it can detect ~1 trillion odors.[8] However, there are several drawbacks associated with the human nose. Natural nose poses the risk of false human sensory evaluations and poor decision-making as they are dependent on the physiological and psychological status. Additionally, olfactory organs get paralyzed after prolonged exposure and un-ability to determine the concentration of the gas are other drawbacks of the olfactory system. On the contrary, an electronic or e-nose (EN) besides circumventing all the above-mentioned drawbacks can give a precise information both qualitatively and quantitatively about the gases under investigation. Accordingly, it is defined as intelligent system comprising sensing elements with a potential to mimic the mammalian system.[9, 10, 11] Gardner and Bartlett first used the term wherein they defined it as an instrument containing an array of chemical sensors along with the pattern recognition system that can give information about the target gas even in mixture form.[12, 13] Unlike human nose that works as an ideal or universal nose for several odor determination, an EN finds its application for a particular or desired application thereby making it application specific. However, as the response generated by the sensor is similar for applications such as toxic gas detection, environmental monitoring and/or food quality, the same combination of sensor array can be used for multiple applications. Similar to human nose, an EN also needs a training period which is required for improving the accuracy and precision of the measurements importantly algorithm to achieve

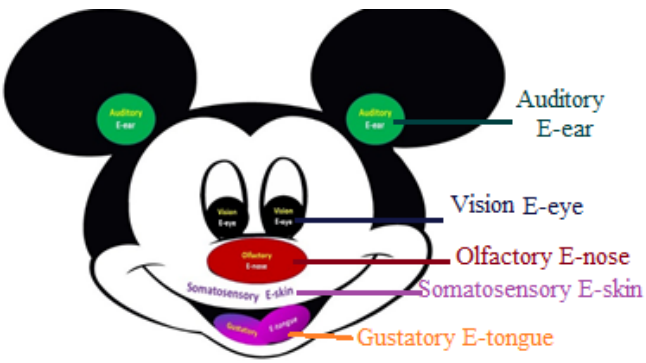


Figure 1. Schematic representation of the artificial human senses.

good classification, identification or quantification as desired for the target gases. A comparison between natural and artificial olfactory system clearly indicates that still natural systems are the best and surpasses the advantages offered by the artificial systems.[14] However, when specific application is considered the artificial system advantageously surpasses the natural olfactory systems. Besides, the data is interpreted without any bias.

EN comprises three main components namely an array of chemical sensors, electronic circuitry or data acquisition system and the data analysis software. Additionally, it may also consist of a sampling, filtering and conditioning system (for a reproducible collection of the analytes or target gases under investigation). It is clearly evident that the EN comprises technical equivalent of mammalian nose. More specifically, for the toxic gas detection, the EN is characterized by three main components namely multiple sensor array (MSA), data acquisition and the suitable pattern recognition algorithm (PRA).[15] The role of multiple sensors is to interact with the test gas under investigation and produce an electrical signal that can be carried away by the data acquisition system to the control unit. The control unit is the brain of the e-nose which is usually equipped with the software that performs the pattern recognition algorithm on the collected date and interpret it in terms of quality or nature of gas (reducing, oxidizing or volatile organic compound) and its quantity (concentration). Similar to human brain, an e-nose also requires a prior training. During training the response of the sensors towards the known gas and concentration is measured as a function of various parameters and stored as a data repository. The brain ultimately applies the suitable PRA to determine the meaningful information about the test gas.

EN have found applications in the determination of food quality,[16 - 21] medical diagnostics,[22-27] beauty and health care,[28-31] waste water management,[32] environment: air pollution,[33] water pollution,[34, 35] flammable liquids,[36] and warfare.[37-39] EN for gas sensors have been demonstrated for methane,[40] ethanol, toluene, o-xylene,[41] CO, CH4.[42] As per the recent studies the global sensors market is expected to account for USD 351.48 million by 2027.[43] This clearly highlights the importance of the sensor work and its requirement. For example; new variants of the car and its cost is directly proportional to the number of sensors that are installed in it. The user requirement is to have an automatic control of the indoor climate when driving with simultaneous monitoring of oxygen, humidity and CO_x inside the car cabin.

MULTIPLE SENSORS OR MULTIPLE SENSOR ARRAY

This is considered to be the heart of the e-nose. As the name implies the sensors array comprises of large number of sensors which are partially specific towards the target gases. The interaction with the gaseous environment causes an increase or decrease in the electrical response usually in terms of resistance. The relative change in the resistance of the sensing element before and after the test gas is monitored as a function of time and ambient conditions and stored as a data repository. Using nanomaterials, the multiple sensors can be realised either employing individual sensors or by using an array of the sensing element.

INDIVIDUAL SENSING ELEMENT USED AS AN ELEMENT IN MULTIPLE SENSORS (MS)

In this case the individual sensing element is connected to the measurement unit and the response curves is recorded as a function of gas, concentration, operating temperature and relative humidity. A multiple sensor network is formed by using number of such individual sensors. The individual sensors can be of similar or different type depending upon the target gas that needs to be detected. In order to save the measurement time or to maintain the similar conditions a test chamber can be designed in such a way that number of such individual elements can be tested simultaneously. Else, care has to be taken while comparing the response characteristics.

MULTIPLE SENSING ARRAY (MSA)

This approach rightfully exploits the advantage offered by nanomaterials i.e., high integration density. For example; the sensor film deposited on to the substrate can easily be masked using conventional masking techniques and modified with suitable sensitizers to achieve similar or different sensing elements. The whole array is then electrically connected using Ag paste and connecting wire to achieve the MSA.[44-45] Figure 2 shows the photograph of the multiple sensors realized using WO_3 films onto the alumina substrates. Herein, the WO_3 film was selectively masked using mask made up of stainless steel to expose the desired portion. The suitable sensitizer with desired thickness is then deposited on to the exposed area. Numerous masking and demasking steps are performed to achieve an array with network of sensing elements with desired sensitizers. As shown in figure 1, the WO_3 film is modified with sensitizers namely Au, Cu, Ni, Ti, Al, Pd and Pt using physical deposition methods i.e., thermal evaporation and sputtering techniques to achieve desired thickness of the sensitizers onto the sensor surface.[46] The whole array is then subjected to annealing. Final electrode deposition (Au with ~ 120 nm thickness) is then performed and the individual sensing element is isolated from the array using diamond cutter. The important task herein is to realize an electrical contact to all the sensing elements as it may give rise to large number of wires cluttering around. Using photolithography and smaller diameter Ag or Pt wire the cluttering can be reduced to a greater extent**.**

For toxic gas detection, metal oxide semiconductors are the obvious choice for the sensor material. This has been attributed mainly to the oxygen non-stoichiometry enabling the tuning of surface interactions crucial for optimizing the sensor properties. Further, the growth in the field of functional oxide nanomaterials has resulted in the novel nanomorphologies with tunable surface reactivity which is of added advantage for sensor application. Table 1 summarizes the different MOS which have been looked upon as a promising material to achieve multiple sensor configuration for EN application. Efforts are also being made to realize nanoheterostuctures or nanohybrids between MOS and other organic or inorganic counterparts. Formation of nanohybrids is considered to be advantageous as besides preserving the inherent advantages of the individual constituent, various novel functionalities are formed which are contributing towards the observed improved sensing performances.

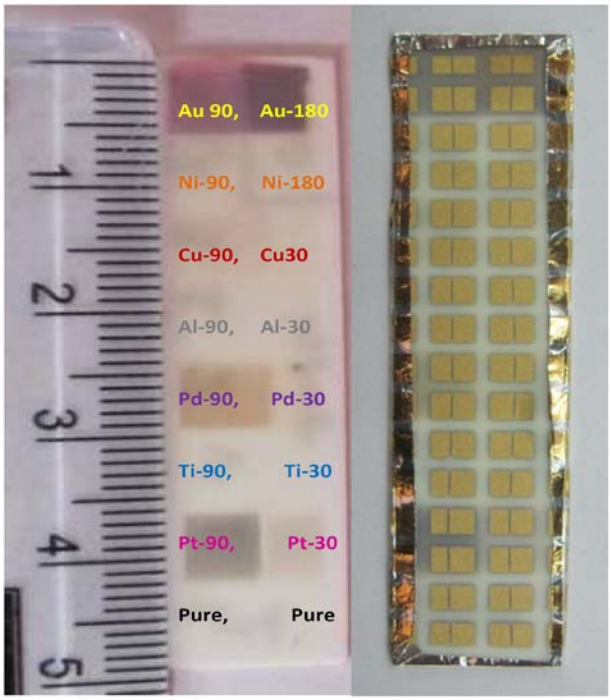


Figure 2. The photograph of the multiple sensor array indicating the sensitizers and the time used for the sputtering before and after electrode deposition.

DATA ACQUISITION UNIT

This is one of the important units of the e-nose. This is where actual changes affected due to interaction with the test gas is measured and passed on for processing using suitable PRA. One of the important challenges here is to address individual sensing elements without much of cluttering. The large number of wires or connection involved sometimes pose the threat of cross connection. Addressing the single sensors in an array and the network over the sensor film may act as an obstacle for the gas diffusion to the sensor surface. To avoid this, the wires connecting the sensors have to be taken from the backside of the film. Besides, most of the times the connection is provided from the periphery of the substrate with majority times a simple solder with the testing unit is often used. The complexity of the connection network increases with the increase in the number of sensors. Use of prefabricated electrodes on the substrates is preferred to avoid the cluttering. For chemiresistive sensors involving metal oxide semiconductors (MOS) the resistance is usually measured using two probe method. For low resistive sensing elements sometimes a four-probe method is employed which helps to overcome the contribution arising from using the two probes i.e., mainly the contact resistance which is usually few tens of ohms.

Recording response curves from multiple sensing elements requires use of many measurement units. Most commonly adopted method involves use of multiplexing wherein the resistance is measured by periodically swapping across the multiple sensor network. We have recently reported development of one such custom-made unit.[47] The unit is referred to as table top static gas sensing unit. As the name suggest it is a portable table top unit that comprises of two test chambers for recording the response curves in the static environment. One of the test chambers has the provision to mount seven individual sensing elements along with a temperature control circuit. The temperature of each of the element can easily be tuned to the desired value using the temperature control unit. Besides, the response curves can be recorded in the single test chambers with single exposure the response from the seven sensing elements can be measured, simultaneously. Importantly, the arrangement can be extended further if the number of individual sensing element required increases. The unit is also provided with another test chamber wherein the sensor array can be mounted directly. The DAQ has the provision to record response curves from the 16 sensing elements simultaneously. The same can be increased in number with further increase in the sensing array configuration. The DAQ has the provision to record six order change in the resistance i.e., kΩ to GΩ or Ω to MΩ.

Thus, the developed table top gas sensing unit is versatile in nature as it can be employed for both individual sensors as well as sensor array.[48] Although the developed unit is equipped to record response curves from 16 sensing element simultaneously, but the number of sensing elements that can be measured can be increased easily to the desired value as per the requirement. Importantly, the product is unique in itself as it has both measurement and testing provision into a single unit. The ability to tune the operating temperature further adds an advantage to the system. The system is more useful in case for the determination of optimized parameters for realizing a single sensor towards a specific gas. The ability to record response curves simultaneously can be used to tune the parameters namely sensing material, thickness, sensitizer, operating temperature, gas concentration range etc., at a faster rate. Employing unit with 16 DAQ channels thereby assures saving the optimization time to $1/16^{th}$ of the total time. This in a way helps for the fast and easy way of parameter optimization.

PATTERN RECOGNITION ALGORITHM

Identification of the suitable PRA that can be used to achieve the desired outcome from the data repository is a huge task and a daunting challenge. Numerous methods are employed to achieve the desired performances. The simplest of the PRA is the graphical analysis employing 3-D bar chart. Herein in the sensor response exhibited by the sensor array is plotted as a histogram with reference to the concentration of the test gas. The pattern generated by the array as a whole is a unique signature pattern with the intensity of the histogram varying with the type of gas and its concentration. The complexity in the analysis increases with increase in the number of gases that needs to be identified and also with the increase in the number of sensors. The choice of the sensors and the sensitizers employed is generally determined by the choice of the user, gases under investigations and the desired output or the requirement. For better isolation and exact determination, it would be necessary to incorporate large number of sensors. The large number of sensors further increases the complexity of connectivity and thereby data analysis.

Table 1. Different MOS based e-nose.

Sr. No.	E-nose Materials	Configuration	Analytes	OT (^{0}C)	Ref.
1.	SnO_2 nanotubes	Chemiresistive	H_2, NO_2, Benzene	RT.	49
2.	TGS-type sensors (Taguchi Gas Sensors)	Chemiresistive	VOC's (Wheat bread baking process)	60-250	50
3.			Chinese pecan quality	200	51
4.			Olive oil quality	200	52
5.	SnO_2 nanotubes	Amperometric	H_2, CO, and ethylene	240−285	53
6.	TiO_2 Nanostructures.	Chemiresistive	Ethanol, Acetone, Formaldehyde	23 ±2	54
7.	TiO_2 Nano helix array	Chemiresistive	NO_2, CO, H_2	150	55
8.	ZnO				56
9.	ZnO-CuO nanohybrids	Amperometric	NO_2, CO, H_2		57
10.	CuO heterojunctions	Chemiresistive	liquor		58
11.	MoO_3 micro sheets	Chemiresistive	VOCs	275	59
12.	MOS- thick film and thin film sensors and the AlphaSense dual sensors	Chemiresistive	VOCs- acetone, isopropanol and 1-propanol and isobutylene		60
13.			Chronic Obstructive Pulmonary Disease (COPD)		61
14.	Cr_2O_3 and SnO_2 (AlphaMOS, Toulouse, France)	Chemiresistive	Bacteria based individual colonies	-	62
15.	commercial EOS507C (Sacmi Imola scarl, Imola, IT) – SnO_2, MoO_3	Chemiresistive	Enterobacteriaceae in vegetable soups	400	63
16.	Sensor array - SnO_2, WO_3, ZnO, MoO_3	Chemiresistive	Food and Skin pathogen microbiota	245-500	64

SnO_2 BASED E-NOSE FOR TOXIC GAS DETECTION

SnO_2 is one of the widely investigated material for gas sensing applications that has been attributed mainly to the oxygen non-stoichiometry. This provides a tool to play with the adsorption and desorption kinetics on the sensor surface. Interestingly the nature of oxygen species and its concentration on the sensors surface is a strong function of the operating temperature and the defect density on the sensor surface.[65, 66] The high surface area to volume ration with tuneable surface reactivity has resulted in use of large number of nanomaterials for the gas sensing applications. These includes nanoparticles, nanowires, nanobelts and nanohybrids etc,. In particular for the nanohybrid configuration, SnO_2 is often combined with other organic and inorganic counterparts which enables preservation of independent properties and incorporation of novel functionalities due to nanohybrid formation. SnO_2 nanowires and nanoparticles have shown excellent sensing characteristics towards H_2S and NO_2. An improvement in the response characteristics has been observed upon incorporation of sensitizers namely CuO and Fe.[67-68] Very recently, formation of nanohybrids with other counterparts has been demonstrated to be an effective way to tune the response towards a specific gas.[69, 70] For example, figure 3 shows the NO_2 response curves recorded for SnO_2-reduced graphene oxide (RGO) nanobydrids at 180°C.[71] Using nanohybrids NO_2 concentration upto 400 ppb were repeatably measured.

Use of sensitizers along with the nanohybrid has also been demonstrated as an effective way of tuning the response characteristics.[72] For example, the selectivity of SnO_2-RGO has been systematically tailored from H_2S to NO_2 to H_2 by careful choice of sensitizers namely Pt and Pd.[73] An electronic nose was also attempted based on SnO_2 thin films modified with sensitizers namely Cu, Au, Fe and Ag. Multiple sensor array (MSA) was realized by selectively modifying and loading of sensitizers. The developed e-nose could qualitatively distinguish between H_2S, NO_2 and NO.[55] The unique bar chart obtained using the sensor response values from the MSA has been used for the qualitative discrimination of the gases.

WO_3 BASED E-NOSE

WO_3 is yet another interesting material widely investigated for sensors that requires higher operating temperatures. Using sputtering a well adherent films comprising of nanostructured particles could be obtained. We have demonstrated a MSA comprising of 32 sensing elements realized by selectively masking and deposition of different sensitizers as shown in figure 2. An XRD spectra recorded for the sensor films is shown in figure 4. The XRD profile is matching with the monoclinic structure of the WO_3 with no other peak corresponding to the presence of sensitizers and is mainly because of the small concentration being employed. Use of sensitizers and its amount could further be used effectively to generate the unique signature

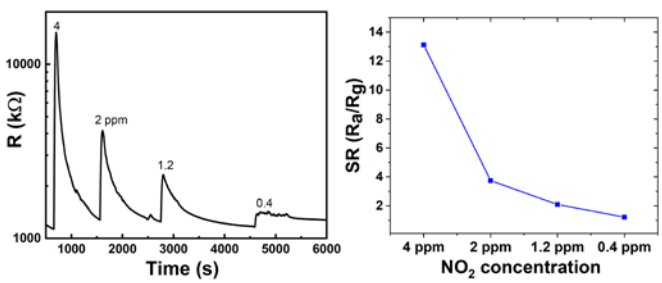


Figure 3. NO_2 response curves recorded for SnO_2-reduced graphene oxide (RGO) nanobydrids at 180°C.

pattern towards target gases. For example, figure 5 shows the bar chart generated for the WO_3 based MSA towards different gases as a function of the operating temperature. Herein, the unique pattern is considered to be the signature of the gas and the intensity of the bar could effectively be used to determine the concentration.

The MSA was also fabricated using SnO_2 and WO_3 thin films. 12 different sensing elements were realized by modifying the SnO_2 and WO_3 thin films. Of these, 8 sensors were realized using SnO_2 modified with different Pd (4) and Pt (4) layer thicknesses, respectively. For this, Another, 4 sensors were realized by depositing WO_3 with 4 different thickness. Figure 6 shows the histogram depicting the sensor response values recorded towards 3 ppm of H_2S upon subjecting the MSA based on SnO_2 modified with different Pd and Pt thicknesses and pure WO_3. Figure 6 (b) shows the effect of concentration on the SR which is found increasing with the concentration.

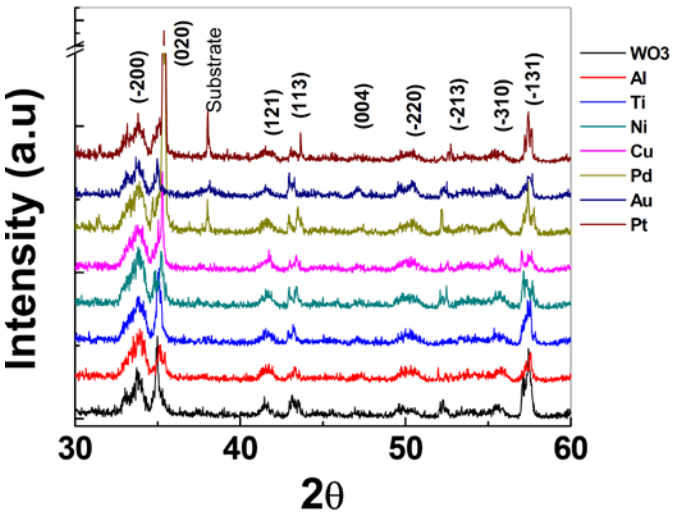


Figure 4. XRD spectra for the individual sensing elements modified with different sensitizers.

ZnO BASED E-NOSE

ZnO is one of the most widely studied material for various device applications and is next only to Si.[74] It exhibits one of the most versatile, exotic and interesting banks of nanomorphologies. Different nanomorphologies like nanowires, nanobelts, nanorings, nanopencils, nanowalls, nanoflowers, hexagonal discs etc., have been successfully and repeatedly synthesised.[75] With simple control over the process parameter's, it has been shown that not only the size but also the shape, in particular the aspect ratio of the resulting nanostructures could

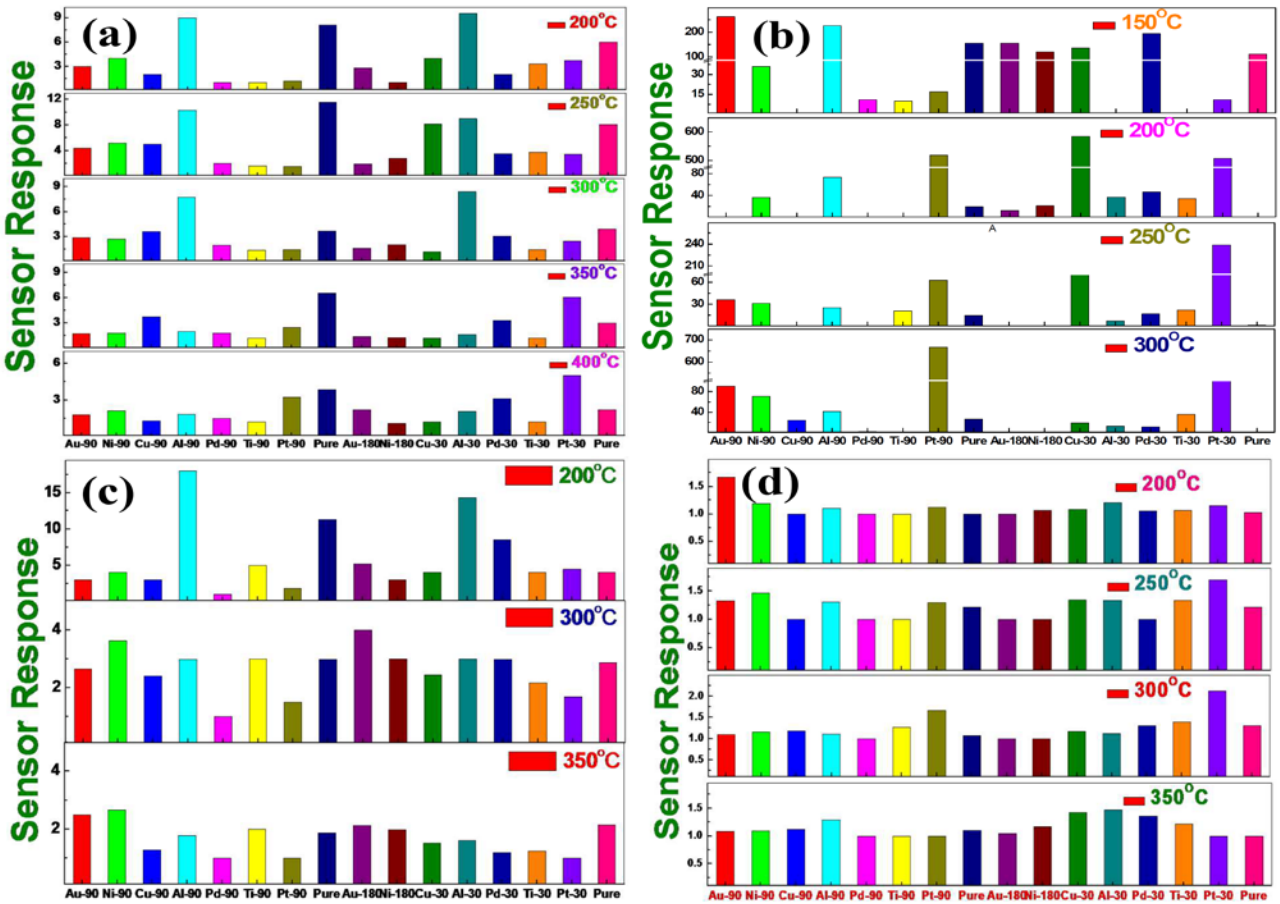


Figure 5. A simple bar graph representing the sensor response values as a function of operating temperature towards (a) NH_3, (b) H_2S, (c) NO and (d) C_2H_5OH, respectively.

easily be controlled.[76] Using simple photolithography process, it is easy to pattern the surface of the substrate with the seed layer, in the present case ZnO nanoparticles synthesised using chemical route. Later the substrate is subjected to hydrothermal growth wherein nanowires were grown selectively on the seed layer. Figure 7 the photograph and scanning electron microscope (SEM) image of ZnO grown on Si wafer using hydrothermal method. One of the advantages of the method is that the free suspended wires with highly dimensions as shown in figure 7 (c) and (d) were also found grown in the solution. Using physical vapor deposition, it is also possible to grow ZnO nanowire films well adherent to the substrate. For example; figure 8 (a) shows the schematics of the commonly used carbothermal reduction method. Herein the ZnO mixed with carbon is used as source material which is heated at an elevated temperature between 600 – 1100℃. The nanowires were found to grow on substrate kept downstream at lower temperature. The growth mechanism of such nanowires has been extensively studied and established. Figure 8 (b) shows the SEM images of ZnO nanowires grown using this method. Thus, the simple and controllable growth mechanism and its understanding are the seeds for such widespread utility.

Besides, tailoring of the adsorption kinetics owing to the engineerable surface and interface properties enabled realization of sensors towards different gases. For instance, ZnO nanowires grown using hydrothermal method has been made sensitive and selective towards different gases namely H_2S, NO_2, C_2H_5OH, by use of sensitizers namely Au/CuO, Al/Ti and Au, respectively.[77, 78] The formation and collapse of heterojunctions namely p-n and Schottky junctions formed between n-type ZnO and/or p-type sensitizers (CuO, NiO) and metal (Au) has been attributed to be the main contributors for the improvement in the gas sensing characteristics.[79] Heterostructure formation namely inorganic-organic (ZnO-rGO) and/or inorganic-inorganic (ZnO-TiO_2) with other materials has also been demonstrated to be an effective way of tailoring the sensors response.[80] The excellent compatibility with the CMOS technology and bio-compatibility has been the main reasons for the exhaustive investigations. Importantly, the precise control over the growth process enables high integration density on the substrate with selective modification enables generation of MSA onto a very small substrate size.

Using hydrothermal growth, it is possible grow ZnO nanowire films onto the substrate sizes of 2 inch in diameter. The actual sensing area contributing to the sensing measurements is very large and owing to the high surface area to volume ratio of the 1-D nanostructures an enhanced sensing response could easily be achieved. For example; modification of nanowire surface with Au and CuO has resulted in enhanced and specific response towards H_2S with the operating temperature systematically brought down to room temperature i.e., 25°C.[81-82] Additionally, modification with Ti, Al and Mg has also resulted in specific response towards NO2. Thus, it is possible to selectively modify the nanowire surface with different sensitizers so as to achieve a MSA with partial sensitivity towards different gases. This enables fabrication of MSA in very small dimensions.

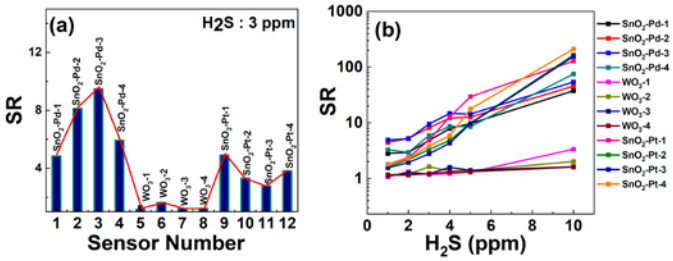


Figure 6. Histogram indicating the SR values for the 12 different sensors in an MSA. (b) Variation of SR with H_2S concentration for 12 different sensors.

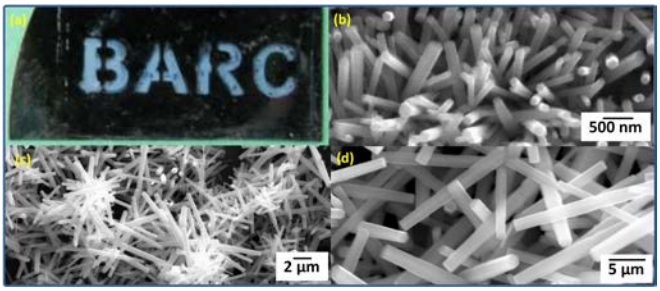


Figure 7. (a) Photograph of nanowires grown using seeded approach employing hydrothermal method. SEM image of the (b) nanowires on the substrate, (c) wires grown in the solution and (d) corresponding magnified image.

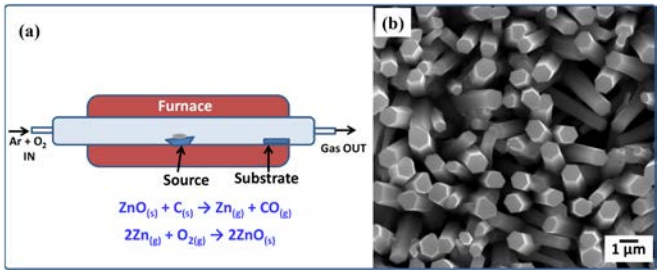


Figure 8. (a) Schematic representation of the carbothermal reduction method and (b) SEM image of ZnO nanowires.

An e-nose was attempted for the toxic gas detection in pure form using ZnO nanowires modified with Au, CuO, NiO and MgO.[83] Importantly, using the multivariate data analysis technique more specifically principal component analysis a correlation between measured parameters is investigated and established. For this the data repository was prepared by exposing the MSA towards incremental concentration of pure gases at a preselected operating temperature. Upon complete recovery the response curves were measured for another test gas. Herein the three principal components have demonstrated a strong correlation with sensor response and gas concentration, response time and response kinetics, respectively. The correlation thus achieved resulted in distinct separation between H_2S and NO_2 gases. The study is further extended to the possibility of achieving both the qualitative and quantitative discrimination of toxic gases in their mixture and currently is underway.

It is interesting to note that the choice of PRA is mostly dependent upon the desired output and the information that is required. Commonly adapted PRA involves machine learning (ML) modules. Such modules are considered to be one of the

types of artificial intelligence (AI) that allows computer applications to become more accurate and precise. Thereby enabling the algorithm to predict outcomes without being explicitly programmed to do so. Such ML models are generated using algorithms that generally cluster the output or the response generated based upon the responsible and contributing variables. Observations and relationships between the responsible variables are used to rightly predict the value of variables Numerous methods have been effectively employed for classification and identification of the pattern from the measured data repository. These includes cluster analysis (CA), supervised and non-supervised models. More specifically, the CA itself has many of its variation such as k-means,[84] k-medoid[85] and hierarchical CA (HCA).[86] Use of the unsupervised approaches is required when the trained data/input is already known. Commonly used approaches include principal component analysis (PCA), Representational Oriented Component Analysis (ROCA) and non-linear PCA (NLPCA).[87-89] In case of supervised learning, the data repository is used which assists as a teacher to enable the software to rightly predict the output. Some of the algorithms are linear DA (LDA),[90] quadratic DA (QDA), Mahalanobis DA (MDA), Canonical DA,[91] Symbolic data analysis (SDA),[92] Uncorrelated LDA,[93] Kernel- Partial Least Squares (K-PLS),[94] Nonlinear Iterative Partial Least square (NIPALS)[95] and statistically inspired modification of the partial least squares (SIMPLS).[96] It is apt to mention that the choice of the algorithm is governed by the output and the information sought. The most successful algorithm employed is the PCA, however when the desired output demands use of large sensor network involving multiple sensors use of artificial neural network is desired and advantageous. However, such algorithms are costly and may restrict the overall use as it may lead to non-fulfilment of the suitability factor.

One of the major limitations of the EN is the requirement of training period. And the main drawback of the chemiresistive sensors is the drift in the baseline resistance with time that is mainly arising due to the grain growth due to continuous operation at higher operating temperatures. Also, the ambient in particular the humidity plays a foul role in degrading the response of the sensors which thereby puts the constraint of base line correction i.e., periodic calibration.[97] Thus, the EN developed using chemiresistive sensors also needs to be periodically calibrated and the algorithm needs to re-trained, accordingly.[98] Such works are needed to achieve the reliable information from the EN and importantly for the longer period.

It is noteworthy to mention that the choice of sensors and their number is purely a user and/or application specific which every EN to be a unique device and hence demands a training period. Moreover, during the development stage often it is necessary to optimize the sensor configuration so as to achieve the desired performance.[111] It would be interesting to come up with a provision employing a similar type of sensors and numbers along with a suitable pattern recognition algorithm. This in a way will pave a way towards the realization of universal data bank for pattern recognition which otherwise is not available. The work related to the creation of universal library of sensors,

Table 2. Survey of applications of E-noses in India

E-Nose materials and application	Type	Analytes	T (ºC)	Ref.
TGS sensors developed by Figaro Engineering Inc. USA	Chemiresistive	COPD and Lung cancer discrimination		99
MoS_2 based sensor array	Chemiresistive	Acetone, 2-propanol, benzene, ethanol, methanol, toluene, and xylene,	50	100
Phosphonium Ionic Liquid Composites.	QCM	VOCs	-	101
Monitoring the fermentation process of black tea	QCM	Linalool, Linalool oxide, trans-2-hexenal, methyl salicylate and geraniol	-	102
Doped SnO_2 Nanomaterials	Electrochemical	Lung Cancer Biomarkers, 1-propanol and isopropyl alcohol	-	103
TGS sensors developed by Figaro Engineering Inc. USA. E-Nose for the determination of perishable quality and shelf-life of cultured Pacific white shrimp	Chemiresistive	Methane, CO, Ethanol, and H_2, NH_3, H_2S, Toluene, Amines,	-	104
TGS sensors developed by Figaro Engineering Inc. USA, TGS-832, TGS-823, TGS-2600, TGS-2610, and TGS-2611, Black tea classification,	Chemiresistive	Linalool oxide, Linalool, B-ionone, Terpeniol and Geraniol	-	105
Hybrid neuro-fuzzy-assisted electronic nose for Rhyzopertha dominica infestation in wheat				106
ZnO nanostructures sensor array	Chemiresistive	O_2, CO and CO_2	250 - 350	107
ZnO–CuO, ZnO–Au, ZnO–NiO and ZnO–MgO heterojunctions.	Chemiresistive	H_2S, NO_2	180	108
Suspended graphene arrays	Chemiresistive	NH_3, NO_2 , HCHO and CO	RT	109
Spray layer-by-layer assembly of POSS functionalized CNT quantum chemo-resistive sensors	Chemiresistive	Acetone, Butanone, Propanol, Toluene, Ethanol, Cyclohexane, Pentane, Methanol	RT.	110

performance, condition and appropriate algorithms is a humongous task and should be undertaken at the earliest so as to achieve a uniform and steady progress of realizing application specific EN bank.

APPLICATION OF EN

The detection and monitoring of toxic gases, PM, and hazardous chemicals in process plants, industries and biomedical field is a prime need in environmental safety and air quality monitoring.[112] Till date, in India, the different configurations such as quartz crystal microbalance (QCM),[113] optical, chemiresistive [114, 115] amperometric and biomimetic[116] EN have been studied for the environmental, food quality testing, agricultural monitoring systems and medical applications as also listed in Table 2.[117-118] The recent trends are mainly focused on the development of miniaturized EN in order to make them handy and portable by avoiding the bulky instrumentation. The miniaturized EN needs the optimized nanomaterials to improve the sensitivity. In India, the research is being carried out to develop the nanomaterials to be employed in E-noses for medical application and toxic gases monitoring, in particular.

SUMMARY AND FUTURE PROSPECTS

Thus, it is evident that the nanotechnological advances have caused tremendous upsurge in the utilization of nanomaterials in smart devices that includes Internet of things (IoT) enabled communication, multichannel data transmission, neural network-based data analysis and fusion among them. In view of the need to not only improve the comfort but also provide the point of care services, it is desired to understand the correlation and challenges involved in the fusion of various aspects of smart devices. For extracting the desired or meaning full information use of multi sensors is must and the role of e-noses is tremendous. With reduction in the dimensions of the material the overall density of the nanodevices can be increased. However, this causes an increase in the complexity of addressing the individual or array. The associated wiring, data transfer or communication greatly alters the performance of the device and needs to be checked continuously so as to assure repeatable and reproducible performance. Such systems have and are finding applications in various domains that include environmental and structural systems (e.g., lakes, rivers, dams, bridges, roads, tunnels, buildings), agricultural and food processing systems, and manufacturing systems. Herein along with the acquisition, it becomes important to analyse and apply suitable model or feature extraction techniques so as to enable control and related decision making using such smart devices.

ACKNOWLEDGMENTS

BB would like to acknowledge Council of Scientific and Industrial Research (CSIR) for the Research Associate (RA) fellowship. KRS acknowledges CSIR-University Grants Commission (UGC) for the junior research fellowship (JRF).

CONFLICT OF INTEREST

Authors declare no conflict of interest.

REFERENCES AND NOTES

1. V. R. Katti, A. K. Debnath, K.P. Muthe, M. Kaur, A.K. Dua, S.C. Gadkari, S.K. Gupta, V.C. Sahni, Mechanism of drifts in H2S sensing properties of SnO2: CuO composite thin film sensors prepared by thermal evaporation, *Sens. Actuators B* **2003**, 96, 245-252.
2. N. S. Ramgir, K. R. Patil, S. R. Sainkar, I. S. Mulla, High H2S-sensitive copper-doped tin oxide thin film, *Mater. Chem. Phys.*, **2003**, 80(1), 250-256.
3. N. S. Ramgir, C.P. Goyal, P.K. Sharma, U.K. Goutam, S. Bhattacharya, N. Datta, M. Kaur, A.K. Debnath, D.K. Aswal, S.K. Gupta, Selective H2S sensing characteristics of CuO modified WO3 thin films, *Sens. Actuators B* **2013**, 188, 525-532.
4. N. S. Ramgir, S. Kailasa Ganapathi, M. Kaur, N. Datta, K. P. Muthe, D. K. Aswal, S. K. Gupta, J. V. Yakhmi, Sub-ppm H2S sensing at room temperature using CuO thin films, *Sens. Actuators B*, **2010**, 151, 90-96.
5. Paul Ellwood, Ceri Williams, John Egan, Crossing the valley of death: Five underlying innovation processes, *Technovation*, **2022**, 109, 102162.
6. Stephen K. Markham, Moving Technology from Lab to Market, *Res. Tech. Management* **2002**, 45(6).
7. Bridging the valley of death: improving the commercialisation of research, Eighth Report of Session 2012–13, HC 348, [Incorporating HC 1936-i and ii, Session 2010–12], Published on 13 March **2013**, by authority of the House of Commons London: The Stationery Office Limited.
8. C. Bushdid, M. O. Magnasco, L. B. Vosshall, A. Keller Humans Can Discriminate More than 1 Trillion Olfactory Stimuli, *Science* **2014**, 343, 1370-1372.
9. F. Röck, N. Barsan, U. Weimar, Electronic Nose: Current Status and Future Trends, *Chem. Rev.* **2008,** 108, 705–725.
10. K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Vaid, D. R. Walt, Cross-Reactive Chemical Sensor Arrays, *Chem. Rev.* **2000**,100, 2595–2626.
11. R. Glatz, K. Bailey-Hill, Mimicking nature's noses: From receptor deorphaning to olfactory biosensing, *Prog. Neurobiology*, **2011**, 93, 270-296.
12. J. W. Gardner, P.N. Bartlett (eds.), Sensors and sensory systems for the electronic nose, Kluwer Academic Publishers, London, (1992).
13. K. Persaud, G. Dodd, Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose, *Nature*, **1982**, 299, 352- 355.
14. S. Sankaran, L. R. Khot, S. Panigrahi, Biology and applications of olfactory sensing system: A review, *Sens. Act. B* **2012**, 171–172, 1-17.
15. N. S. Ramgir, Electronic Nose Based on Nanomaterials: Issues, Challenges, and Prospects, *ISRN Nanomaterials*, **2013**, 941581.
16. Escuder-Gilabert, A 21st century technique for food control: Electronic noses, *Anal. Chimica Acta* **2009**, 638, 1-15.
17. J. S. Vestergaard, M. Martens, P. Turkki, Application of an electronic nose system for prediction of sensory quality changes of a meat product (pizza topping) during storage, *LWT - Food Sci. Tech*, **2007**, 40, 1095-1101.
18. H. L. Gan, Y. B. Che Man, C. P. Tan, I. NorAini, S.A.H. Nazimah, Characterisation of vegetable oils by surface acoustic wave sensing electronic nose, *Food Chemistry*, **2005**, 89, 507-518.
19. A. Eriksson, K.P. Waller, K.S. Sjaunja, J.E. Haugen, F. Lundby, O. Lind, Detection of mastitic milk using a gas-sensor array system (electronic nose), *Int. Dairy J.*, **2005**, 15, pp. 1193–1201.
20. Y. Huichun, W. Jun, X. Hong, L. Miao, Quality grade identification of green tea using the eigenvalues of PCA based on the E-nose signals, *Sens. Actuators B* **2009**, 140, 378–382.
21. V. Yu. Musatov, V. V. Sysoev, M. Sommer, I. Kiselev, Assessment of meat freshness with metal oxide sensor microarray electronic nose: A practical approach, *Sens. Actuators B* **2010**, 144, 99-103.
22. E. H. Oh, H. S. Song, T. H. Park, Recent advances in electronic and bioelectronic noses and their biomedical applications, *Enzyme Microbial Tech.* **2011,** 48, 427-437.
23. A. D'Amico, C. Di Natale, R. Paolesse, A. Macagnano, E. Martinelli, G. Pennazza, M. Santonico, M. Bernabei, C. Roscioni, G. Galluccio, R.

Bono, E. Finazzi Agròand, S. Rullo, Olfactory systems for medical applications, *Sens. Actuators B* **2008,** 130, 458–465.
24. A. Lamagna, S. Reich, D. Rodriguez, N.N. Scoccola, Performance of an e-nose in hops classification, *Sens. Actuators B* **2004**, 102, 278–283.
25. H. Knobloch, W. Schroedl, C. Turner, M. Chambers, P. Reinhold, Electronic nose responses and acute phase proteins correlate in blood using a bovine model of respiratory infection, *Sens. Actuators B* **2010**, 144, 81–87.
26. H.C. Chang, L.B. Kish, M.D. King, C. Kwan, Fluctuation-enhanced sensing of bacterium odors, *Sens. Actuators B* **2009**,142, 429–434.
27. Z. Zheng, X. Lin, Study on Application of Medical Diagnosis by Electronic Nose, *World Sci. Tech.*, **2012,** 14, 2115-2119.
28. E.Z. Panagou, N. Sahgal, N. Magan, G.J.E. Nychas, Table olives volatile fingerprints: potential of an electronic nose for quality discrimination, *Sens. Actuators B* **2008**, 134, 902–907.
29. R. Stella, J.N. Barisci, G. Serra, G.G. Wallace, D.D. Rossi, Characterization of olive oil by an electronic nose based on conducting polymer sensors, *Sens. Actuators B* **2000**, 63, 1–9.
30. H. Ulmer, J. Mitrovics, G. Noetzel, U. Weimar, W. Gopel, Odors and flavors identified with hybrid modular sensor systems, *Sens. Actuators B* **1997**, 43, 24–33.
31. T. Nakamoto, A. Fukuda, T. Moriizumi, Perfume and flavor identification by odor-sensing system using quartz-resonator sensor array and neural-network pattern recognition, *Sens. Actuators B* **1993**, 10, 85–90.
32. T. Dewettinck, K. Van Hege, W. Verstraete, The electronic nose as a rapid sensor for volatile compounds in treated domestic wastewater, *Water Research*, **2001**, 35, 2475-2483.
33. A. Szcuzurek, P.M. Szecowka, B.W. Licznerski, Application of sensor array and neural networks for quantification of organic solvent vapors in air, *Sens. Actuators B* **1999**, 58, 427–432.
34. A.C. Bastos, N. Magan, Potential of an electronic nose for the early detection and differentiation between Streptomyces in potable water, *Sens. Actuators B* **2006**, 116, 151–155.
35. C. Laura, S. Selena, C. Paolo, D.R. Renato, I.G. Massimiliano, Electronic noses for the continuous monitoring of odors from a wastewater treatment plant at specific receptors: focus on training methods, *Sens. Actuators B* **2008**, 131, 53–62.
36. S. Zhang, C. Xie, D. Zeng, Q. Zhang, H. Li, Z. Bi, A feature extraction method and a sampling system for fast recognition of flammable liquids with a portable E-nose, *Sens. Actuators B* **2007**, 124, 437-443.
37. T. Alizadeh, S. Zeynali, Electronic nose based on the polymer coated SAW sensors array for the warfare agent simulant classification, *Sens. Actuators B* **2008**, 129, 412–423.
38. D. Matatagui, J. Martí, M.J. Fernández, J.L. Fontecha, J. Gutiérrez, I. Gràcia, C. Cané, M.C. Horrillo, Chemical warfare agents simulants detection with an optimized SAW sensor array, *Sens. Actuators B* **2011**, 154, 199–205.
39. A. D. Wilson, Review of Electronic-nose Technologies and Algorithms to Detect Hazardous Chemicals in the Environment, *Procedia Tech.*, **2012**, 1, 453-463.
40. J. Orts, E. Llobet, X. Vilanova, J. Brezmes, X. Correig, Selective methane detection under varying moisture conditions using static and dynamic sensor singles, *Sens. Actuators B* **1999**, 60, 106–117.
41. E. Llobet, J. Brezmes, X. Vilanova, J.E. Suerias, X. Correig, Qualitative and quantitative analysis of volatile organic compounds using transient and steady-state responses of a thick-film tin oxide gas sensor array, *Sens. Actuators B* **1997**, 41, 13–21.
42. T. Sundic, S. Marco, A. Perera, A. Pardo, S. Hahn, N. Bârsan, U. Weimar, Fuzzy inference system for sensor array calibration: prediction of CO and CH4 levels in variable humidity conditions, *Chemometr. Intell. Lab. Syst.*, **2002,** 64 (2), 103–122.
43. https://www.databridgemarketresearch.com/reports/global-sensors-market
44. C. P. Goyal, N. S. Ramgir, P. K. Sharma, N. Datta, S. Kailasaganapathi, M. Kaur, A. K. Debnath, F. Z. Haque, D. K. Aswal and S. K. Gupta, Multiple sensor array based on pure and surface modified WO_3 thin films for e-nose application, *AIP Conf. Proc.* **2013**, 1536, 1215.
45. C. P. Goyal, N. S. Ramgir, P. K. Sharma, N. Datta, M. Kaur, A. K. Debnath, F. Z. Haque, D. K. Aswal, S. K. Gupta, Design and Development of e-nose Based on Pure and Modified WO_3 Thin Films, *Sixth ISSS National Conference 2012 (ISSS-NC6)*, 6-7 Sept, Pune (**2013**).
46. C. P. Goyal, N. S. Ramgir, P. K. Sharma, N. Datta, M. Kaur, V. Pare, A. K. Debnath, F. Z. Haque, D. K. Aswal, S. K. Gupta, NH_3 Sensing Characteristics of Pure and Al Modified WO_3 Thin Films, *Proc. "International Conference on Advanced Nanomaterials & Emerging Engineering Technologies*" 560-562, **2013**.
47. N. S. Ramgir, R. Datta, K. Avhad, R. Bhusari, M. M. Vedpathak, M. Meera, V. V. Katke, E. Ravisankar, A.K. Debnath, T.K. Saha, K.P. Muthe, S.C. Gadkari, A Table Top Static Gas Sensing Unit: Model No. TPD-BARC-16CH, *BARC News Letter*, **2017**, May-June, 14-18.
48. N. R. Linge, N. S. Ramgir, A. K. Debnath, K. P. Muthe, S. C. Gadkari, Ag-ZnO Nanowires: An efficient NO2 sensor, *Int. Res. J. of Science & Engineering*, **2017,** Special Issue A1: 183-185.
49. J. Chen, Z. Chen, F. Boussaid, D. Zhang, X. Pan, H. Zhao, A. Bermak, C.-Y. Tsui, X. Wang, Z. Fan, *ACS Nano* **2018,** 12, 6079−6088.
50. M. Gancarz, U. Malaga-Toboła, A. Oniszczuk, et.al. Detection and measurement of aroma compounds with the electronic nose and a novel method for MOS sensor signal analysis during the wheat bread making process, *Food and Bioprod. Proc.* **2021**, 127, 90–98.
51. K. Xu, J. Wang, Z. Wei, F. Deng, Y. Wang, S. Cheng, An optimization of the MOS electronic nose sensor array for the detection of Chinese pecan quality, *Food Engineer*. **2017**, 203, 25-31.
52. G. G. Teixeira, L. G. Dias, N. Rodrigues, Í. M. G. Marx, A. C. A. Veloso, J. A. Pereira, A. M. Peresa, Application of a lab-made electronic nose for extra virgin olive oils commercial classification according to the perceived fruitiness intensity, *Talanta*, **2021**, 226, 122122.
53. J. M. Baik, M. Zielke, M. H. Kim, K. L. Turner, A. M. Wodtke, M. Moskovits, Tin-Oxide-Nanowire-Based Electronic Nose Using Heterogeneous Catalysis as a Functionalization Strategy, *ACS Nano* **2010,** 4, 3117–3122.
54. P. P. Conti, R. S. Andre, L. A. Mercante, L. Fugikawa-Santos, D. S. Correa, Discriminative detection of volatile organic compounds using an electronic nose based on TiO2 hybrid nanostructures, *Sens. Actuators B*, **2021**, 344, 130124.
55. S. Hwang, H. Kwon, S. Chhajed, et.al. A near single crystalline TiO_2 nanohelix array: enhanced gas sensing performance and its application as a monolithically integrated electronic nose, *Analyst* **2013**, 138, 443–450.
56. S. Kanaparthi. S. G. Singh, Discrimination of gases with a single chemiresistive multi-gas sensor using temperature sweeping and machine learning, *Sens. Actuators B*, **2021**, 348, 130725.
57. W. J. Park, K. J. Choi, M. H. Kim, B. H. Koo, J.-L. Lee, J. M. Baik, Self-Assembled and Highly Selective Sensors Based on Air-Bridge-Structured Nanowire Junction Arrays. *ACS Appl. Mater. Inter.* **2013,** 5, 6802−6807.
58. Kang Liang, Yu Wang, Jia-Qi He, Hu Meng, Shu-Qin Chen, Jun-Yu Chang, Jian-Mei Gao, Ji-Hui Wang, Liang Feng, An Electronic Nose Based on Copper Oxide Heterojunctions for Rapid Assessment of Liquor, *Chinese J. Anal. Chem.*, **2019**, 47, 19073-19080.
59. W. Jiang, D. Wei, S. Zhang, X. Chuai, P. Sun, F. Liu, Y. Xu, Y. Gao, X. Liang, G. Lu, The facile synthesis of MoO3 microsheets and their excellent gas-sensing performance toward triethylamine: high selectivity, excellent stability and superior repeatability, *New J. Chem.*, **2018,** 42, 15111.
60. Akira Tiele, Alfian Wicaksono, Sai Kiran Ayyala, and James A. Covington, Development of a Compact, IoT-Enabled Electronic Nose for Breath Analysis, *Electronics* **2020**, 9(1), 84;
61. Cristhian Manuel Durán Acevedo, Carlos A. Cuastumal Vasquez, Jeniffer Katerine Carrillo Gómez, Electronic nose dataset for COPD detection from smokers and healthy people through exhaled breath analysis, *Data in Brief* **35** (2021) 106767.

62. Geoffrey C. Green, Adrian D.C. Chan, Hanhong Dan, Min Lin, Using a metal oxide sensor (MOS)-based electronic nose for discrimination of bacteria based on individual colonies in suspension, *Sens. Actuators B* **152** (2011) 21–28.
63. Emanuela Gobbi, Matteo Falasconi, Giulia Zambotti, Veronica Sberveglieri, Andrea Pulvirenti, Giorgio Sberveglieri, Rapid diagnosis of Enterobacteriaceae in vegetable soups, by a metal oxide sensor based electronic nose, *Sens. Actuators B* **2015**, 207, 1104–1113.
64. Estefanía Núnez Carmona, Veronica Sberveglieri, Andrea Ponzoni, Vardan Galstyan, Dario Zappa, Andrea Pulvirenti, Elisabetta Comini, Detection of food and skin pathogen microbiota by means of an electronic nose based on metal oxide chemiresistors, *Sens. Actuators B* **238** (2017) 1224–1230.
65. P. K. Sharma, C. P. Goyal, N. Ramgir, N. Datta, M. Kaur, S. Kailasaganapathi, A. K. Debnath, D. K. Aswal, S. K. Gupta, Design and development of multiple sensor array based on SnO2 thin Films for e-nose application**—** International Conference on Recent Trends in Applied Physics and Materials Science (RAM-2013), Feb. **2013**, Govt. College of Engineering and Technology, Bikaner, India.
66. M.N. Padvi, A.V. Moholkar, S.R. Prasad and N.R. Prasad, A Critical Review on Design and Development of Gas Sensing Materials, *Eng. Sci.*, **2021**, 15, 20–37.
67. S. Kumar, N. Ramgir, N. Datta, M. Kaur, S. Kailasaganpathi, A.K. Debnath, D.K. Aswal, S.K. Gupta, E-nose based on metal oxide thin films for qualitative and quantitative determination of H_2S, *National Seminar on Physics and Technology of Sensors (NSPTS-18)*, T. C. College, Baramati, March 6-8, **2014**.
68. P. K. Sharma, N. S. Ramgir, C. P. Goyal, N. Datta, S. Kailasaganapathi, M. Kaur, A. K. Debnath, D. K. Aswal and S. K. Gupta, Design and development of multiple sensor array based on SnO_2 thin films for e-nose application, *AIP Conf. Proc.* **2013**, 1536, 1229.
69. B. Bhangare, Niranjan S. Ramgir, K.R. Sinju, A. Pathak, S. Jagtap, A.K. Debnath, K. P. Muthe, S. W. Gosavi, Reduced Graphene Oxide (rGO) based Nanohybrids as Gas Sensors: State of the Art, in Functional Nanomaterials: Advances in Gas Sensing Technologies, Ed. S. Thomas, N. Joshi, V.K. Tomer, Springer Nature Singapore Pte Ltd. (**2020**).
70. A. Kumar, M.M. Krishnan, V. Singh, S. Samanta, N. S. Ramgir, Room Temperature Chemiresistive Gas Sensing Characteristics of Pristine Polyaniline and Polyaniline/TiO2 Nanocomposites, 383-397, **2020**, in: Thomas S., Joshi N., Tomer V. (eds) Functional Nanomaterials. Materials Horizons: From Nature to Nanomaterials. Springer, Singapore.
71. B. Bhangare, N. S. Ramgir, S. Jagtap, A. K. Debnath, K. P. Muthe, C. Terashima, D. K. Aswal, S. W. Gosavi, A. Fujishima, XPS and Kelvin probe studies of SnO_2/RGO nanohybrids based NO_2 sensors, *Appl. Surf. Sci.* **2019,** 487, 918-929.
72. N. S Ramgir, V Patnaik, A Patel, A K. Debnath, D K Aswal, S K Gupta, SnO_2 thin film based electronic nose: A case study, *Asian J. Physics*, **2015**, 24, 11, 1541-1548.
73. B. Bhangare, N. S. Ramgir, A. Pathak, K. R. Sinju, A. K. Debnath, S. Jagtap, N. Suzuki, K. P. Muthe, C. Terashima, D. K. Aswal, S. W. Gosavi, A. Fujishima, Role of sensitizers in imparting the selective response of SnO2/RGO based nanohybrids towards H_2S, NO_2 and H_2, *Mater. Sci. Semicond. Processing*, **2020,** 105, 104726.
74. N. S. Ramgir, S. J. Patil, ZnO Nanowires: An Excellent Nanomaterial for Nanotechnology, *Encyclopedia of Semiconductor Nanotechnology*, January **2017**, ca. 4210 pages, ISBN: 1-58883-199-X.
75. N. S. Ramgir, S. Kumar, N. Datta, M. Kaur, A. K. Debnath, D. K. Aswal, S. K. Gupta, Chapter 15: ZnO Nanowires: An excellent nanomaterial for next generation sensing devices, Innovations in Nanomaterials, Nova Science Publishers, NY 11788, USA, Ed. Abu Bin Imran, (**2015**).
76. N. S. Ramgir, Gas Sensing and Field Emission Properties of SnO_2 and ZnO Nanomaterials, LAP LAMBERT Academic Publishing,
77. K. R. Sinju, N. S. Ramgir, Ankita Pathak, A. K. Debnath, K. P. Muthe, Multiple Sensor Array Based On ZnO Nanowires for Electronic Nose Applications Towards Toxic Gases, *AIP Conf. Proc.* **2020,** 2265, 030282.
78. N. S. Ramgir, R. Bhusari, N. S. Rawat, S. J. Patil, A. K. Debnath, S. C. Gadkari, K. P. Muthe, TiO_2/ZnO Heterostructure Nanowire based NO_2 Sensor, *Mater. Sci. Semicond. Processing*, **2020,** 106, 104770.
79. N. S. Ramgir, N. Datta, M. Kaur, A. K. Debnath, D. K. Aswal, S. K. Gupta, Semiconductor nanowires and heterostructures based gas sensors, (**2011**) Nova Science Publishers, NY 11788, USA
80. Niranjan S. Ramgir, C. P. Goyal, Deepak Goyal, S. J. Patil, H. Ikeda, S. Ponnusamy, K. P. Muthe, A. K. Debnath, NO_2 Sensor based on Al modified ZnO Nanowires, *Mater. Sci. Semicond. Processing*, **2021,** 134, 106027.
81. N. S. Ramgir, P. K. Sharma, N. Datta, M. Kaur, A.K. Debnath, D.K. Aswal, S.K. Gupta, Room temperature H_2S sensor based on Au modified ZnO nanowires, *Sens. Actuators B* **2013**, 186, 718-726.
82. N. S. Ramgir, N. Datta, M. Kaur, S. Kailasaganapathi, A.K. Debnath, D.K. Aswal, S.K. Gupta, Zinc oxide nanowires for gas sensing applications, *BARC Newsletter*, **2012**, 325, 28-33.
83. K. R. Sinju, B. Bhangare, A. Pathak, S. J. Patil, N. S. Ramgir, A. K. Debnath, D. K. Aswal, ZnO nanowires-based e-Nose for the detection of H_2S and NO_2 toxic gases, *Mater. Sci. Semicond. Processing*, **2022**, 137, 106235.
84. M. H. Rezazadeh Mehrizi, A cluster analysis of the KM field, *Manag. Decis.*, **2009**, 47, 5, 792-805.
85. H.-S. Park, C.-H. Jun, A simple and fast algorithm for K-medoids clustering, *Expert Syst. Appl.*, **2009,** 36, 3336–3341.
86. C. Temperini, A. Scozzafava, D. Vullo, C. T. Supuran, Carbonic Anhydrase Activators. Activation of Isozymes I, II, IV, VA, VII, and XIV with L- and D-Histidine and Crystallographic Analysis of Their Adducts with Isoform II: Engineering Proton-Transfer Processes within the Active Site of an Enzyme, *Chem. Eur. J.* **2006**, 12, 7057 – 7066.
87. M. Hubert, P.J. Rousseeuw, K. Vanden Branden, ROBPCA: A New Approach to Robust Principal Component Analysis, *Technometrics* **2005**, 47, 64–79.
88. M. Hubert, S. Engelen, Fast cross-validation of high-breakdown resampling methods for PCA. *Comput. Stat. Data Anal.* **2007,** 51, 5013–5024.
89. M. A. Kramer, Nonlinear Principal Component Analysis Using Autoassociative Neural Networks, *AIChE Journal*, **1991,** 37, 2.
90. M. Ghasemi-Varnamkhasti, M. Tohidi, P. Mishra and Z. Izadi, Temperature modulation of electronic nose combined with multi-class support vector machine classification for identifying export caraway cultivars, *Postharvest Biol. Technol.*, **2018**, 138, 134–139.
91. A. Trujillo-Ortiz, R. Hernandez-Walks, S. Perez-Osuna, R. A. Fisher2cda: Canonical Discriminant Analysis, A MATLAB file, [WWW document], (2004)
92. W. Wang, H. Li, Partial Least Squares Regression for Predicting the Speed of Electromagnetic Fuze Plate, *J. Phys.: Conf. Ser.* **2020**, 1549, 032084.
93. D. Yuan, Y. Liang, L. Yi, Q. Xu, O. Kvalheim, Uncorrelated linear discriminant analysis (ULDA): A powerful tool for exploration of metabolomics data, *Chemom. Intell. Lab. Syst.* **2008,** 93 ,70–79.
94. M. Wang, G. Yan, Z. Fei, Kernel PLS based prediction model construction and simulation on theoretical cases, *Neurocomputing*, **2015,** 165, 389–394.
95. P. Geladi, B.R. Kowalski, Partial least-squares regression: a tutorial, *Analytica Chimica Acta* **1986,** 185, 1–17.
96. S. de Jong, SIMPLS: an alternative approach to partial least squares regression, *Chemom. Intell. Lab. Syst.* **1993,** 18, 251–263.
97. Tao Liu, Dongqi Li, Jianjun Chen, An active method of online drift-calibration- sample formation for an electronic nose, *Measurement*, **2021,** 171, 108748.
98. A. C. Romain, J. Nicolas Long term stability of metal oxide-based gas sensors for e-nose environmental applications: An overview, *Sens. Actuators B* **146**, 2010, 502-506.
99. V. A. Binson, M. Subramoniam, Luke Mathew, Discrimination of COPD and lung cancer from controls through breath analysis using a self-developed e-nose, *J. Breath Res.* **2021**, 15, 046003.

100. U. N. Thakur, R. Bhardwaj, A. Hazra, Statistical Analysis for Selective Identifications of VOCs by Using Surface Functionalized MoS_2 Based Sensor Array, *Chem. Proc.* **2021,** 5, 35.
101. S. R. Vaughan, R. L. Pérez, P. Chhotaray, I. M. Warner, Quartz Crystal Microbalance Based Sensor Arrays for Detection and Discrimination of VOCs Using Phosphonium Ionic Liquid Composites, *Sensors* **2020**, 20, 615.
102. P. Sharma, A. Ghosh, B. Tudu, S. Sabhapondit, B. D. Baruah, P. Tamuly, N. Bhattacharyya, R. Bandyopadhyay, Monitoring the fermentation process of black tea using QCM sensor based electronic nose, *Sens. Actuators B* **2015**, 219, 146-157.
103. Z. Khatoon, H. Fouad, O. Y. Alothman, M. Hashem, Z. A. Ansari, S. A. Ansari, Doped SnO2 Nanomaterials for E-Nose Based Electrochemical Sensing of Biomarkers of Lung Cancer, *ACS Omega* **2020**, 5, 27645–27654.
104. P. Srinivasan, J. Robinson, J. Geevaretnam, J. B. B. Rayappan, Development of electronic nose (Shrimp-Nose) for the determination of perishable quality and shelf-life of cultured Pacific white shrimp (Litopenaeus Vannamei), *Sens. Actuators B* **2020**, 317, 128192.
105. Mahuya Bhattacharyya Banerjee, Runu Banerjee Roy, Bipan Tudu, Rajib Bandyopadhyay, Nabarun Bhattacharyya, Black tea classification employing feature fusion of E-Nose and E-Tongue responses, *Food Engineer.* **2019**, 244, 55-63.
106. G, Mishra, S, Srivastava, B. K. Panda, H. N. Mishra, Sensor array optimization and determination of Rhyzopertha dominica infestation in wheat using hybrid neuro-fuzzy-assisted electronic nose analysis, *Anal. Methods* **2018**, 10, 5687-5695.
107. J. K. Radhakrishnan, M. Kumara, Geetika, Effect of temperature modulation, on the gas sensing characteristics of ZnO nanostructures, for gases O_2, CO and CO_2, *Sensors Inter.* **2021**, 2, 100059.
108. K. R. Sinju, B. Bhangare, A. Pathak, S. J. Patil, N. S. Ramgir, A. K. Debnath, D. K. Aswal, ZnO nanowires-based e-Nose for the detection of H_2S and NO_2 toxic gases, *Mater. Sci. Semicond. Processing*, **2022**, 137, 106235.
109. R. K Gupta, F. H Alqahtani, O. M. Dawood, M. Carini, A. Criado, M. Prato, S. K Garlapati, G. Jones, J. Sexton, K. C. Persaud, Suspended graphene arrays for gas sensing applications, *2D materials* **2021**, 8, 025006.
110. S. Nag, A. Sachan, M. Castro, V. Choudhary, J.F. Feller,Spray layer-by-layer assembly of POSS functionalized CNT quantum chemo-resistive sensors with tuneable selectivity and ppm resolution to VOC biomarkers, *Sens. Actuators B* **2016**, 222, 362-373.
111. Anil Kumar Bag, B, Tudu, J. Roy, N. Bhattacharyya, R. Bandyopadhyay, Optimisation of sensor array in electronic nose: A rough set-based approach, *IEEE Sensors Journal*, **2011**, 11, 3001-3008.
112. S. Deshmukh, R. Bandyopadhyay, N. Bhattacharyya, R. A. Pandey, A. Jana, Application of electronic nose for industrial odors and gaseous emissions measurement and monitoring – An overview, *Talanta*, **2015**, 144, 329-340.
113. M. Bhattacharyya S. Banerjee, R. B. Pradhan, B. Tudu, Roy, D. K. Das, R. Bandyopadhyay, P. Pramanik, Detection of Benzene and Volatile Aromatic Compounds by Molecularly Imprinted Polymer Coated Quartz Crystal Microbalance Sensor, *IEEE Sensors J.*, **2019**, 19(3), 885-892.
114. R. Ghosh, J. W. Gardner, P. K. Guha, Air Pollution Monitoring Using Near Room Temperature Resistive Gas Sensors: A Review, *IEEE Transactions on Electron Devices* 66 (2019) 3254 – 3264.
115. B. K. S. Reddy, Pramod H. Borse. Review—Recent Material Advances and Their Mechanistic Approaches for Room Temperature Chemiresistive Gas Sensors. *J. Electrochem. Soc.*, **2021,** 168, 057521.
116. N. Pandey, D. Pal, D. Saha, S. Ganguly, Vibration-based biomimetic odor classification, *Sci. Rep.* **2021**, 11, 11389.
117. S. H. Nile, V. Baskar, D. Selvaraj, A. Nile, J. Xiao, G Kai, Nanotechnologies in Food Science: Applications, Recent Trends, and Future Perspectives. *Nano-Micro Lett.* **2020**, 12, 45.
118. A. K. Sundramoorthy, S. Gunasekaran, Applications of graphene in quality assurance and safety of food, *Trends in Anal. Chem.* **2014**, 60, 36-53.

AUTHORS BIOGRAPHIES

Dr. Niranjan Ramgir completed his Ph.D. (Physics) in 2006 from National Chemical Laboratory, Pune, India. After completing his Alexander Von Humboldt fellowship at Nanotechnology Group, University of Freiburg, Germany, he joined Technical Physics Division, Bhabha Atomic Research Centre (BARC) as Scientific Officer. His current research work is focused on applications of organic (e.g., polypyrrole, polyaniline, 2-D graphene) and inorganic semiconducting materials (like ZnO, WO_3, CuO and SnO_2 based thin films and nanostructures) and their heterostructures or nanohybrids for gas sensing, e-nose and photovoltaic devices. He has more than 110 journal publications, 17 book chapters, 3 patents, 3 successfully commercialised sensor technologies to his credit.

Ms. Sinjumol K Rajan is a CSIR-UGC senior research fellow at Homi Bhabha National Institute (HBNI), Mumbai. She is pursuing her PhD at Technical Physics Division (TPD), Bhabha Atomic Research Centre, Mumbai. Her research work is focused on the development of electronic nose based on ZnO nanowire thin films for toxic gas detection. Her research interest includes hydrothermal synthesis of ZnO nanowires, fabrication of thin films using physical vapor deposition (PVD) namely thermal evaporation and electron beam evaporation techniques, development and analysis of pattern recognition algorithm for supervised and unsupervised machine learning models using python programme for the development of electronic nose application.

Dr. Bhagyashri Bhangare completed her Ph.D. (Physics) in 2019 from Savitribai Phule Pune University (SPPU), Pune, India. (Formerly University of Pune). She is presently working as a CSIR-Research Associate at Bhabha Atomic Research Centre (BARC), Mumbai, India. Her current research interest includes development of functionalized reduced graphene oxide (rGO) nanohybrids based e-nose for the detection of toxic gases namely NO_2, H_2S, H_2 and VOCs.

Dr. A. K. Debnath joined Bhabha Atomic Research Centre (BARC) in 1988 as a Ph.D. student to work in high-Tc superconducting thin films after completing M.Sc. (Physics) from North Bengal University, (W.B.) India. Later, he joined as a permanent employee in 1993 at Technical Physics Division of BARC. Presently he is Scientific Officer (H) and Head, Gas Sensing Devices Section. His 2 years (2001-2002) post-doctoral research work was in CMR materials at Centre for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan. He has extensively worked on oxide materials-based gas sensor, particularly for H_2S detection. He has also developed catalytic type H_2 gas sensors for (LEL 0-4%). His major achievements in basic research on MBE grown metal phthalocyanine (MPc) thin films were highest mobility ~150 cm^2/Vs in CoPc films, metallic type conduction in organic heterojunctions, growth of nanoweb and nanobrush structures and demonstration of ppb level Cl_2 gas sensing using MPc films. He is a recipient of DAE Science and Technical excellence award-2011. His current research interest is to study the toxic gas mixture analysis, charge transport and gas sensing properties of organic-inorganic composite films, chemical state of analysis of both organic and inorganic materials using X-ray photoelectron spectroscopy technique and work function measurement by Kelvin probe technique.