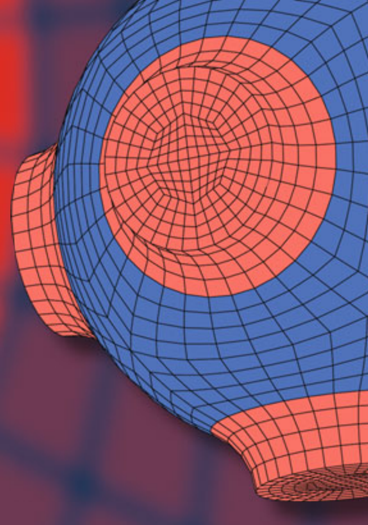
Advanced Structured Materials



Nirav J. Joshi
Sachin Navale *Editors*

Nanostructured Materials for Electronic Nose

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Advanced Structured Materials

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Common engineering materials are reaching their limits in many applications, and new developments are required to meet the increasing demands on engineering materials. The performance of materials can be improved by combining different materials to achieve better properties than with a single constituent, or by shaping the material or constituents into a specific structure. The interaction between material and structure can occur at different length scales, such as the micro, meso, or macro scale, and offers potential applications in very different fields.

This book series addresses the fundamental relationships between materials and their structure on overall properties (e.g., mechanical, thermal, chemical, electrical, or magnetic properties, etc.). Experimental data and procedures are presented, as well as methods for modeling structures and materials using numerical and analytical approaches. In addition, the series shows how these materials engineering and design processes are implemented and how new technologies can be used to optimize materials and processes.

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Nirav J. Joshi · Sachin Navale
Editors

Nanostructured Materials for Electronic Nose

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Editors
Nirav J. Joshi
Department of Electronics and Biomedical Engineering
University of Barcelona
Barcelona, Spain

Sachin Navale
Department of Electronics and Biomedical Engineering
University of Barcelona
Barcelona, Spain

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Preface

In “Electronic Noses-Recent Advances and Challenges,” the intricacies of electronic nose (e-nose) technology take center stage, delving into cutting-edge developments and intriguing features enabled by advanced nanostructured materials compatible with contemporary semiconductor fabrication techniques. The book highlights the emerging trend in utilizing materials such as metal oxide nanostructures, two-dimensional (2D) materials, graphene, and other carbon-based nanostructures, showcasing their versatile properties in electronics, mechanics, electricity, and thermal conductivity. Special emphasis is placed on addressing issues related to the stability, selectivity, and functionalization of e-nose devices and deposited materials, reflecting the rapid and consistent growth within the sensor field. Offering a comprehensive overview, the book meticulously examines each aspect of these novel materials, encompassing their gas-sensing mechanisms, engineering applications, and e-nose devices. Notably, the text incorporates an extensive array of up-to-date literature citations, market insights, and patent analyses. Furthermore, it underscores the significant strides made in both experimental and theoretical studies on various material properties in recent years. Ultimately, this book serves as a valuable resource for materials scientists and researchers in universities and national laboratories, offering an in-depth exploration of recent advances and addressing current challenges pertaining to the selectivity and stability of sensor devices.

This book comprises a total of 10 chapters. In the first chapter, **Niranjan Ramgir** explores the use of metal oxide nanostructures in e-noses for gas-sensing applications. It highlights the advantages of metal oxides, such as non-stoichiometry and tunable electronic properties, making them suitable for multiple sensors in a confined space. The discussion covers detection methods, nanomorphologies, surface modifications, and doping techniques to enhance e-noses performance. This chapter also reviews recent advancements, commercial prospects, and challenges in transitioning from laboratory research to practical applications in the market. In the second chapter, **Muhammad Abdul Basit** explores the role of 2D materials, such as graphene oxide (GO), MoS_2, WS_2, WSe_2, $MoSe_2$, in e-nose applications. It emphasizes their unique structural and chemical properties, high reaction sites, and significant surface-to-volume ratios, making them promising for sensing ions and molecules. The focus is on enhancing e-nose performance through innovation in portable devices, emphasizing sensitivity, selectivity, and stability. The chapter also delves into the critical aspect of accumulating diverse data from 2D materials for effective pattern recognition analysis, contributing to the advancement of e-nose technology. In the third chapter, similarly, **K. V. Patil** focuses on the applications of e-noses in diverse fields and the challenges in their development. It highlights the potential of nanostructured materials in addressing these challenges and discusses the use of metal oxides for creating sensitive and cost-effective e-noses. The integration of multivariate statistical methods for signal analysis is explored, emphasizing the design possibilities based on nanostructured materials. Additionally, the chapter anticipates future trends in e-noses, incorporating concepts like the Internet of Things, machine learning (ML), and wearable and mobile systems. In the fourth chapter, **Sanskruti H. Gondaliya** discusses the application of e-noses in diverse sectors such as the industrial sector (including environmental and food and beverages domains). It delves into the challenges of analyzing heterogeneous and homogeneous data using a single method and discusses the classification of this data using various machine learning algorithms. The chapter covers both advanced models like XGBoost and GBDT, as well as basic models such as SVM, RF, and ANN, demonstrating their utility in optimizing output across different fields. In the fifth chapter, **Abdul Shaban** outlines a comprehensive overview of nanostructured materials and their use in e-nose systems and discussed the usage in industrial and medical fields. The outlook and future directions of e-nose developments are also considered. In the sixth chapter, **Shulin Yang** discusses the impressive capabilities of nanostructured metal oxide-based e-noses in gas detection. It highlights their rapid response, selectivity, and potential applications such as monitoring air quality, identifying volatile liquids, assessing food freshness, and diagnosing diseases. This chapter also emphasizes the promising performance of metal oxide e-noses, coupled with machine learning algorithms, and addresses challenges and prospects for their future development. In the seventh chapter, **Naval Koralkar** explores the advancements in e-nose technology, covering sensor design, material improvements, software developments, and system integration. Despite the concept existing for two decades, a functional e-nose has recently entered the market. The chapter discusses how e-noses, with sensor arrays and pattern recognition systems, have significantly benefited various industries, including agriculture, biomedical, cosmetics, environment, food, manufacturing, military, pharmaceutical, and scientific research. Specifically, it provides an overview of the significant applications in the food and beverage industry and highlights the essential uses of e-nose technology. In the eighth chapter, **Vishnu G. Nath** provides a comprehensive review of ML algorithms and their pivotal role in developing e-nose systems. It begins by exploring ML algorithms such as supervised, unsupervised, and neural network algorithms relevant to e-nose development. The subsequent sections highlight the diverse applications of ML-driven e-nose systems, including environmental monitoring, food processing, and disease diagnosis. The chapter concludes by discussing challenges in implementing ML algorithms in e-nose systems and providing an outlook on their current progress. In the ninth chapter, **Rajeev Gupta** covers the advancements and applications of GO in e-noses over the past decade. It focuses on the fabrication, operational principles, selectivity, stability, and prospects of GO-based e-nose devices. The unique 2D structure of functionalized and partially reduced GO, with its extensive surface area and tailored conductivity, positions it as a revolutionary material for chemical sensors. This chapter highlights GO's adaptability, enabling selective and rapid detection of various vapor types, making it a promising contender in the field of gas-sensing technology. Finally, in tenth chapter, **R. S. Redekar** covers the growing significance of carbon nanotubes (CNTs) in e-noses, particularly in applications across diverse sectors such as food, medicine, military, cosmetics, and environmental monitoring. The focus is on summarizing recent studies showcasing CNTs' enhanced conductivity, mechanical strength, and thermal stability, contributing to improved electronic nose functionality. Additionally, the chapter reviews the development of CNT-based composite materials for e-noses and discusses challenges and future perspectives for the operational use of CNT-based materials.

Barcelona, Spain

Nirav J. Joshi
Sachin Navale

Contents

Metal Oxide Nanostructures in Electronic Nose: Recent Advances

Niranjan S. Ramgir, Deepak Goyal, Atharva U. Sapre, K. R. Sinju, B. K. Bhangare, and S. J. Patil

Abstract The inherent non-stoichiometry and ability to tailor or tune the electronic properties of the metal oxides makes them an ideal candidate for gas sensing applications. Additionally, the ease with which they can be synthesised into different nanoforms, controllable aspect ratio and position on the substrates pave the way to achieve multiple sensors in a smaller area. This is particularly important to design multiple sensors for e-nose (EN) application. For EN, use of multiple sensors with partial specificity to different analytes is required so as to improve the capability of discrimination between target gases. Both qualitative and quantitative information of the target analytes can be successfully achieved by employing numerous sensors and suitable pattern recognition algorithm. Unlike human nose, an EN cannot be used for all the applications. They are designed for a particular or at the most two applications. Herein, the detection methods like chemiresistive, electrochemical, and optical methods play an important role. The present chapter discusses and critically reviews the recent advances in the field of EN realised using different metal oxide nanostructures. Different advantages and limitations arising owing to use of metal oxide nanostructures are elaborated taking help of literature and some of our recent findings. Besides, the role of different nano-morphologies, and surface modification and doping techniques in improving the specificity and sensitivity thereby the performance of EN has been extensively reviewed. Also, recent findings with potential for commercial deployment and those already in the market are also discussed in terms of overcoming the valley-of-death syndrome. Finally, some of the daunting challenges that need to be addressed to realise the commercial product from the laboratory investigations are discussed extensively.

Keywords Metal oxides · Nanostructures · E-nose · Chemiresistive gas sensors · Pattern recognition algorithms · Machine learning

N. S. Ramgir (✉) · D. Goyal · A. U. Sapre · K. R. Sinju · B. K. Bhangare
Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India
e-mail: niranjanpr@yahoo.com

S. J. Patil
Department of Electrical Engineering, Indian Institute of Technology—Bombay, Mumbai 400076, India

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1 Introduction

The inherent characteristics of oxygen non-stoichiometry playing a crucial role in determining the extend of interaction with the target analyte, has been responsible for the widespread use of metal oxide semiconductor (MOS) for gas sensing application and EN in particular. This is further enhanced by employing bandgap engineering that is enabled by the choice of sensitizers, thereby imparting high sensitivity and selectivity towards specific gases. In particular for gas sensing, MOS offers the advantages of high sensitivity, stability, low cost fabrication, flexibility of synthesis, low power consumption, high temperature stability, and importantly that are governed by the simple gas sensing mechanism. Depending on the majority charge carriers, they are often classified as n-type (electrons) and/or p-type (holes). SnO_2, ZnO, WO_3, MoO_3, In_2O_3, and TiO_2 are among the widely studied n-type materials, while NiO, Ag_2O, CoO, and CuO are the widely studied p-type materials. Of these, n-type MOS forms the class of most investigated metal oxide materials for gas sensing application. The high mobility of the charge carriers along with the non-stoichiometry has been the main reason towards their widespread use. The recent advancement in the nanoscience and nanotechnology wherein it has been demonstrated to grow nanostructures with tuneable surface properties further paved the way for the numerous application.

The recent advances in the capability of handling large data sets coupled with IoT (Internet of Things) have facilitated the incorporation of artificial intelligence in the device forms. Accordingly, the five sense organs of the human being have found an electronic counterparts or replacements, namely e-skin, e-eye, e-tongue, e-ear, and EN. Each one of these has found to supersede the human performance, when being compared for a single application. However, in totality human sensory system is far more superior than the electronic ones. Incorporation of these (electronic) sensory system has brought technological revolutions especially into the field of health care, i.e. early disease diagnosis and therapeutics. More specifically, these systems are proving advantageous for the development of point-of-care devices which are miniaturised, smart, and superior. Of these, EN, i.e. EN is being studied for its wide applicability to nearly all the technological applications ranging from agriculture to manufacturing. Owing to its usage and corresponding performance enhancement, the fields are often referred to as smart agriculture and smart manufacturing. EN has found applications in the determination of food quality, medical diagnostics, beauty and health care, wastewater management, environment: air pollution, water pollution, flammable liquids, and warfare. EN for gas sensors has been demonstrated for methane, ethanol, toluene, o-xylene, CO, and CH_4.

EN is defined as the device that mimics the human olfaction system and has all the analogous counterparts to the ones existing in human system. In general, EN comprises three main parts, namely multiple sensor array, data acquisition system, and pattern recognition algorithm. All the three main components have seen a tremendous growth in their development. With availability of smarter alternatives that are both powerful and miniaturised, the data acquisition is made possible from multiple sensors, simultaneously. This is of particular significance in the light of recent advancement in the development of miniaturised sensor devices especially those involving use of novel nano-morphologies like nanowires, and nanobelts and exotic ones like nano-urchins, nanopencils, and nanoflowers. The role of data acquisition system is to record the signal owing to changes in the environment and carry the same to the control unit or brain of the EN. It is equipped with the suitable software that executes pattern recognition algorithms or models on the collected data and interprets the outcome in terms of nature of gas and its quantity.

Multiple sensor array forms the important part of the EN. It plays a similar role as to that of receptors in human olfactory system. There are over 400 receptors present in human nose which accounts for the measurement of over 1 trillion smells. At the present stage, it is difficult to achieve the similar performance using the EN, but for particular application, EN supersedes the performance of human nose. For example, mammalian olfactory system is known to depend on the mental and physical state. They become less responsive under fatigue and sleepy conditions, which is however not the case for EN. Also, for some gases like H_2S, the human nose gets paralysed after exposure, and it cannot identify the subsequent changes in the concentration even for higher and dangerous levels. This is not the case in terms of EN and hence becomes more reliable and trustworthy even for identification of gases that do not have any smell like CO. However, to achieve this identification, use of suitable multiple sensor configuration is required. For this, MOS has been looked upon as a promising candidate for realising the next-generation sensing devices or EN. Accordingly, the present chapter discusses the different metal oxides that have been found to be promising for achieving superior performance in the light of EN applications. Different MOSs, their nanoforms, and the achieved performance have been critically reviewed so as to check the feasibility for EN application. Different advantages and limitations arising owing to use of MOS are elaborated taking help of literature and some of our recent findings. Besides, the role of different nano-morphologies, surface modification and doping techniques towards satisfying the Ramgir Criteria, i.e. 4-S sensor selection criteria enabling improved specificity and sensitivity thereby the performance of EN has been extensively reviewed. Also, recent findings with potential for commercial deployment and those already in the market are also discussed in terms of overcoming the valley-of-death syndrome.

2 Why Metal Oxides?

Use of metal oxides for achieving selective and sensitive response towards particular gases has been widely investigated. This has been predominantly attributed to the excellent charge carrier mobility for both n-type and p-type metal oxides. The inherent oxygen non-stoichiometry which enables processes like oxygen adsorption and desorption on the surface further helps to achieve the response towards most of the gases. Further, these responses could easily be modulated either increase or decrease employing strategies like surface modification, doping, and size reduction.

Use of different sensitizers with controlled amount and distribution further paves the way for improved selectivity. Herein, commonly adopted method is to increase the sensing response towards a particular gas keeping the response towards other interfering gases identical. For example, use of Pd and Cu is known to impart the selective response towards H_2 and H_2S attributed to close affinity of the respective molecules towards them. Thus, using them promotes a strong interaction with H_2 and H_2S while keeping the other interactions related to oxygen adsorption and desorption nearly unaltered. This eventually helps to improve the sensor response towards these gases, thereby making them highly selective.

The most widely investigated and accepted method to improve the response towards gases is the empirical or try and test method. In this method, different sensitizers are first introduced in the system, and later its effect is monitored by recording the response towards different gases as a function of operating temperature and gas concentration. The optimum condition for the improved response in terms of sensitivity, selectivity, response, and recovery time is monitored. This is, however, a time-consuming process that involves optimization of numerous parameters like film thickness, deposition parameters, structure, morphology, type of electrode, spacing between electrodes, sensitizer, its amount and distribution, operating temperature, nature of gas, its concentration, and range. This is seemingly a humongous task and often requires a huge amount of experimentation and consequently time. This results in the longer optimisation process. Often researchers use modern approaches like design of experiments to minimise the overall time. This method uses the statistical approach to determine the significant factors that need to be optimised first, thereby helping to reduce the overall time. Use of literature or already available references is also being used to shorten the optimization process. In all these methods, metal oxides which provide the advantage of complete understanding and available documentation related to growth methods, flexibility of synthesis, chemistry, crystal structure, morphology, oxygen non-stoichiometry, gas adsorption and desorption studies, and ease of tuning surface reactivity have become the obvious choice for sensor application. It is interesting to note here that the mobility of conduction electrons in SnO_2 and ZnO is quite high (160 and 200 cm^2/V.s respectively) compared to that of other semiconducting oxides like In_2O_3 (100) and WO_3 (10 cm^2/V.s). Further, hole mobility as low as 0.2 cm^2/V.s has been reported in p-type oxide such as NiO, which is one of the reasons for its less utility as a *p*-type oxide. The same is also true for some of the other *n*-type semiconducting oxides such as TiO_2, which has only 0.4 cm^2/V.s mobility of conduction electrons.

3 Different MOS-Based Sensor Configuration for EN Application

Different nanoforms have found several configurations to be used as a sensing material. For chemiresistive sensors, 1D nanoforms can be used as either single, multiple, or thin-film configuration. As the name suggests, for single configuration, nanomaterials like nanowires and nanobelts with their excellent aspect ratio are isolated and distributed over the pre-defined electrodes with care so as to result in only single structure being trapped between the electrodes. Often, high-end equipment like e-beam nanolithography are being used to identify and isolate the individual structure and deposit electrode material directly at the end tips so as to get a single nanostructure-based devices. Although remarkable sensitivities have been reported arising due to use of single nanostructures, but the complexity and time involved in the realisation of single device have restricted their widespread use. For use of multiple structures, techniques like dielectrophoresis are often being used to align the nanostructures between the pre-defined electrodes. The inherent randomness and non-reproducibility and repeatability have resulted in the limited growth in the use of multiple nanostructures. The most popular and widely accepted approach is the use of nanostructures in the thin-film configuration wherein they are either deposited directly on the pre-defined electrodes or electrodes are deposited later on the as-grown thin films. The important advantage offered by the present method is the averaging of electrical properties owing to use of several structures. This further helps to improve the repeatability and reproducibility by controlling the separation between electrodes which assures getting nearly identical number of nanostructures for sensing measurements.

Even in thin form, researchers have studied the different ways in which the contact can be realised. This can be either top contact, bottom contact, or sandwich contact. In all the cases, the gas sensing has been reported. The most popular and widely accepted method is the top contact with pre-defined separation which has found tremendous use.

4 Different Metal Oxides Used for EN Application

Metal oxides form the most widely investigated family that has exhibited interesting novel morphologies with completely understood growth mechanism. Both n- and p-type metal oxides have found application for EN. Some of the important and widely studied metal oxides are as below:

4.1 ZnO

ZnO exhibits itself into two main crystal forms, namely hexagonal wurtzite and cubic zinc blende structures. In wurtzite structure, Zn and O are bonded in a tetrahedrally coordinated manner, i.e. each zinc has four oxygen neighbours in a tetrahedral configuration and vice-versa. The bonding in ZnO is ionic (Zn^{2+} O^{2-}) with corresponding radii of Zn^{2+} and O^{2-} to be 0.074 and 0.140 nm, respectively. The Zn–O bond polarity is arising due to the very strong electronegativity of the oxygen on the Pauling scale (3.5). The polar Zn–O bonds in turn makes the Zn and O planes electrically charged. Besides the three basic nanoforms, namely nanoparticle (sphere), nanorod (1-d), and nanobelts (2-D), ZnO is characterised by the presence of wealth of interesting nano-morphologies. These include nanobelts [1], microspheres [2], hexagonal discs [3], ring, bows [4], flower [5], pencil [6], urchin [7], multipods [8], bipyramids [9], and sheets or walls [10]. The widespread growth in different nanoforms has been attributed to the morphological dependence of physical, chemical, photocatalytic, and magnetic properties of ZnO [11, 12] resulting in enhanced performance. Just second to Si, ZnO is one of the most widely studied materials. The widespread interest in the material is ascribed to the availability of the abundant literature that covers nearly all of its properties, synthesis methodologies, device, and technological applications. Additionally, as the era of research has shifted from pellets, thick films, and thin film to nanomaterials, the simple chemistry of ZnO has enabled its growth and utilisation in all the usable forms. In particular, to the latest growth in nanoscience and nanotechnology, ZnO belongs to the family that exhibits wealth of interesting nano-morphologies. By simple control over growth parameters, it has been synthesised in numerous nanoforms covering from the basic nanoforms like nanoparticles, nanowires, and nanobelts to the exotic and complex nanoforms like pencil, walls, urchin, flower, etc. One of the important reasons to grow material in its nanoforms is ascribed to the availability of high surface area-to-volume ratio that can be used effectively to realise and achieve various applications. For example, patterned array of nanowires with controllable tip diameters is promising candidate for field emission-based devices. The shape-selective synthesis of ZnO in different nanoforms enables the control over effective surface area-to-volume ratio which is very crucial to achieve tailor-made sensors for desired analytes. Further, the ability with which its bandgap, i.e. the electronic properties can be tuned by incorporation of suitable sensitizers has also paved a way for achieving the desired sensing properties.

The complete understanding of the growth mechanism with associated control over both position and aspect ratio has been employed effectively to realise multiple ZnO NW-based sensors at a very small place and used to achieve multiple sensor array. For example, ZnO NWs grown using hydrothermal method were selectively modified with sensitizers, namely Au, CuO, NiO, and MgO, and demonstrated for their ability to discriminate H_2S and NO_2 gases using PCA. Importantly, the successful isolation of these two gases from their mixture was also successfully achieved. For this, the sequential application of three of the basic pattern recognition algorithms or the statistical evaluation techniques, namely principal component analysis (PCA), hierarchical cluster analysis (HCA), and linear discriminant analysis (LDA), were employed. Creation or data bank or the data repository is an important step prior to application of desired algorithm. Herein, the response curves of the individual sensing element were recorded as a function of pure gas, mixture in different proportions (concentration), and operating temperature. For this the resistance of the sensing material was measured using a two-probe method in a custom-made table-top static gas sensing unit (Model No.TPD-BARC-16CH). Using the system, seven different elements can be studied simultaneously with single exposure. The system has the provision of two inlets for simultaneous injection of gases so as to achieve the desired mixture (concentrations) of gases. Another important aspect is the data that is fed to the algorithm. From a typical response curve (Fig. 1), following data can be measured, namely sensor response, response time, recovery time, area under the response, and recovery curves which are strongly dependent of the type of gas and response of the sensor towards them [13]. Using these values, the feature matrix is generated which is then fed as an input to all the algorithm. The featured matrix is generally represented as:

$$M = \left[A_{hj}^{mi}\right]$$

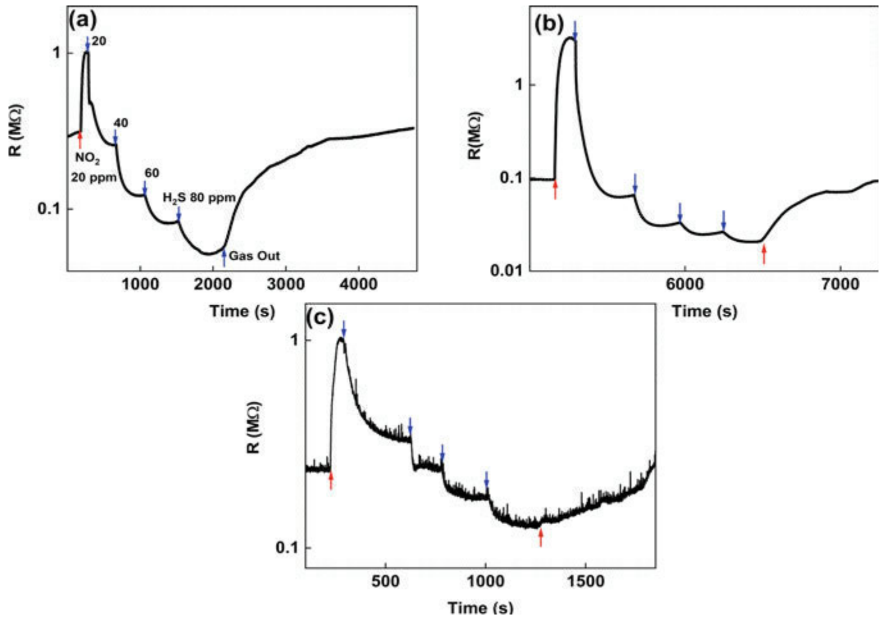

Fig. 1 Typical response curve for the binary mixture that contains 20 ppm NO_2 with H_2S varying as 20, 40, 60, and 80 ppm for **a** ZnO/Au, **b** ZnO/CuO, and **c** ZnO/NiO, respectively. Reprinted with permission from K. R. Sinju et al., J. Mater. Sci. Mater. Electron. 34 (2023) 1562. Copyright @ Springer

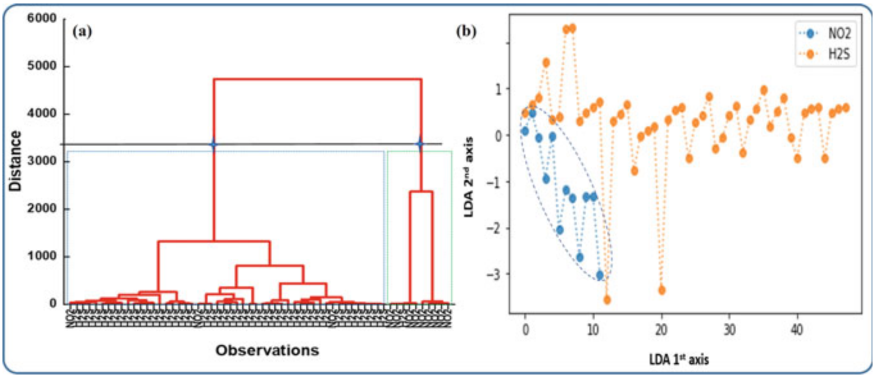

Fig. 2 **a** HCA, dendrogram shows two subgroups, and **b** LDA plot for the data repository created for the binary mixture comprising H_2S and NO_2. Reprinted with permission from K. R. Sinju et al., J. Mater. Sci. Mater. Electron. 34 (2023) 1562. Copyright @ Springer

where *A* is the feature, *m* is the number of samples, *i* represents the number of cycles, *h* represents the type of gas, and *j* represents the number of times the gas concentration has been changed.

Next step is the processing of the huge data using the algorithms so as to get qualitative and or qualitative information of the target gases. For this, following three algorithms are used as a first source of information:

Hierarchical Cluster Analysis

Herein the similarities among the observations are used to cluster the data by making a binary tree that used an agglomerative procedure (Fig. 2a). This involves first measuring of the distances between all pairs of observations. A cluster is generally formed by merging the two nearest clusters forming new centroid. The step is repeated till there is only one cluster left. The dendrogram obtained using HCA indicated a good clustering of the data into two subgroups representing good isolation among them.

Principal Component Analysis

This technique is often utilised to enable data, easy to explore, and visualise. It involves transformation of a group of correlated variables into uncorrelated one. This helps to bring out strong patterns present in the data through eigenvectors or principal components. Herein, the original data is first standardised followed by finding the covariance matrix with subsequent singular value decomposition to get the eigenvectors. (b) PCA results further improved the discrimination of the gases. More specifically, for PCA, the maximum explained variance of three principal components was found to be 95.89, 3.53, and 0.56%, respectively.

Linear Discriminant Analysis

This is also a dimensionality reduction technique that involves creation of a linear combination of data yielding the largest mean differences between the desired classes. This is achieved by maximising the variance of the data along with the separation of multiple classes. By estimating the probability of the classes, an accurate prediction of the gases with minimal misclassification was achieved (Fig. 2b).

The effect of morphology on the performance of the EN towards classification of toxic gases has also been studied. More specifically, different morphologies of ZnO, namely nanoflowers (NF), nanogranules (NG), and nanowires (NWs), exhibited partial specificity towards H_2S, NO, and their mixture. NWs and NFs were synthesised using the hydrothermal method, while incorporation of Pt during the growth has resulted in the growth of nanogranules (NGs). The bandgaps as calculated using the Tauc's plot were found to be 3.247, 3.257, and 3.264 eV for NFs, NGs, and NWs, respectively, indicating a strong effect of morphology. This is further anticipated to alter the sensor response characteristics. NWs exhibited moderate sensitivity towards both the gases, while NF and NG exhibited excellent response towards NO and H_2S, respectively. The partial sensitivity exhibited by these morphologies is thus anticipated to be useful for the discrimination of the gases. Exposure to mixture of reducing and oxidising gases has a strong influence on response and recovery times. Interestingly, the response and recovery times take a different curve as shown in Fig. 3, implying a strong influence on the area under the curve during response and recovery. This information can also act as one of the input parameters for the PRA analysis.

PCA studies were performed using the original data set which is first standardised. Next the covariance matrix is determined that helps to identify the variance between dimensions, and eigen decomposition finds the corresponding eigenvalues and eigenvectors (principal components). Herein, the values of first three components were found to be 1.3, 0.9, and 0.8, respectively. An excellent clustering of the three classes was observed which indicates that the individual observations from each class fit into the feature space of corresponding classes.

4.2 SnO_2

The characteristics of SnO_2 containing cations with mixed valency and the adjustable oxygen deficiency enable tuning of their structure and properties. SnO_2 is a wide bandgap semiconducting oxide (Eg = 3.57 eV at 300 K) crystallising in a tetragonal rutile structure. It belongs to the P^{42}/mnm space group and has a ditetragonal

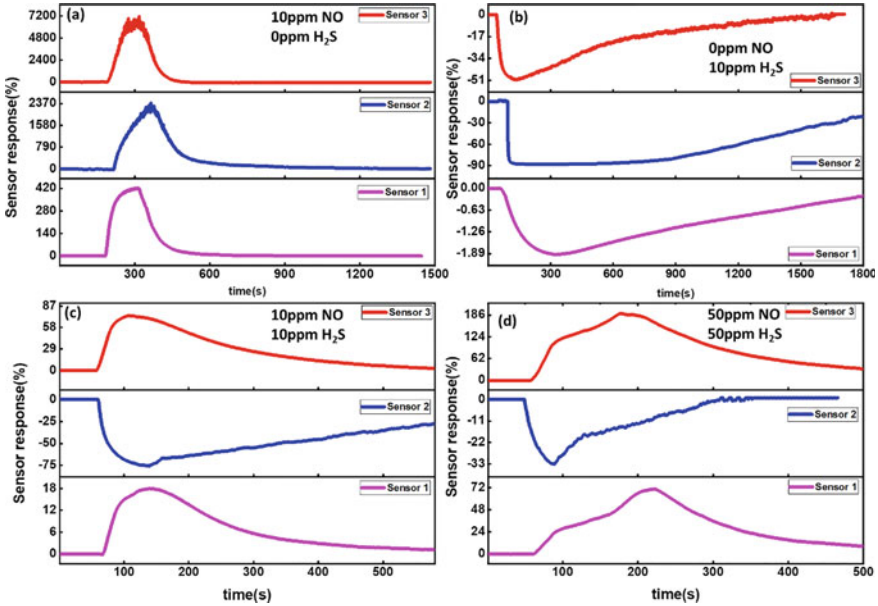

Fig. 3 Response curves obtained for multiples sensors towards different concentration of gas mixtures

bipyramid type of symmetry. The number of macrocrystal habits observed is approximately 10. Its unit cell consists of two Sn and four O atoms. Each Sn atom is surrounded by a distorted octahedron of six O atoms, while O atom has three nearest Sn neighbours at the corners of an almost equilateral triangle. Its composition is also represented as $SnO_{2-\delta}$, where $10^{-5} < \delta < 10^{-3}$ indicating deviation in stoichiometry [14, 15]. The wide bandgap of tin oxide offers possibilities of n-type or p-type conduction depending upon impurities. The type of doping leads to the formation of energy levels in the bandgap. In addition to these characteristic bulk energy levels, there are also surface states in which electrons are localised and cannot move into the bulk without exchanging energy with the outer medium. The changed structure at the surface can also give rise to electronic states with corresponding energy values in the forbidden gap. Since the electrical conductivity of SnO_2 is related to the DOS as well as the energy levels in the mid-gap region caused by doping, it is easy to tailor its conductivity by appropriate doping or controlling surface states (functionalization). In this n-type material, the conductivity is very sensitive to the surface states in a temperature range between 300 and 700 K. At this temperature range, the redox reaction takes place on the surface of oxides. Besides, SnO_2 surface exhibits good adsorption/desorption phenomenon and surface reactivity, mainly due to the availability of free electrons in its CB and the presence of surface and bulk oxygen vacancies and active chemisorbed oxygen species. Further, it can be more easily processed in the bulk, thin film, and dispersed state of crystallite sizes of 5–20 nm. Nanosized powder has shown promising properties in sensor applications especially at low operating temperatures with enhanced sensitivity [16]. Different forms of nanostructured SnO_2 have been prepared in thin film, belts/ribbons, wires, tubes, diskettes, and network forms with higher thermal stability [17, 18]. The availability of high surface area and stability of such structures demonstrates their usefulness to make improved and reliable gas sensors.

Nanohybrids of SnO_2

Nanohybrids (NHs) refer to the new generation of materials that are formed using two dissimilar materials with improved functionalities. Herein the advantages offered by the individual components are retained and new functionalities are introduced. In particular for sensing application, NHs demonstrated the possibility of overcoming numerous disadvantages vital for commercial acceptability [19, 20]. These include enhanced sensor response, improved selectivity, low operating temperature, and overall cost effectiveness [21]. Of the different NHs, SnO_2/rGO has exhibited remarkable improvement in sensing characteristics. Herein, SnO_2 offers the advantage of reversible chemisorption of gases on its surface corresponding with reversible changes in its electrical properties [22]. GO causes an increase in the oxygen adsorption capability assuring increased interaction with target gas [23, 24]. Work function of rGO is slightly higher than that of SnO_2, and hence, when they are in contact with each other result in a band bending [25]. The property of the interface could easily be altered upon exposure to test gases and hence can be used to tailor sensor response characteristics. In SnO_2/rGO nanohybrids, rGO provides the active sites for controlled and nanosized growth of semiconductor metal oxides nanoparticles (SnO_2). The decoration of nanoparticles helps to prevent the agglomeration of rGO nanosheets and preserve surface area, thereby providing large number of reactive sites for gas adsorption. SnO_2 is an n-type semiconductor having Debye length of ~5 nm and mainly responsible for change in electrical resistance of the nanohybrid. The synergistic behaviour owing to doping, co-doping, surface modification, and formation of heterostructures of two or more components in the hybrid accounts for ultrasensitive sensor response even at room temperature. It has been shown that modification of SnO_2-rGo nanohybrids by sensitizers like Pd and Pt imparts highly selective response towards gases like H_2S, NO_2, and H_2 [26]. In pure form, SnO_2 is n-type, while rGO is p-type in nature, and hence in NHs randomly distributed p-n junctions are formed. Pristine SnO_2/rGO NH exhibited maximum response towards H_2S, while incorporation of Pd and Pt has resulted in an improved response towards NO_2 and H_2, respectively, as shown in Fig. 4.

Both Pd and Pt can facilitate the adsorption, dissociation, and interaction of the target gases with oxygen as per chemical sensitisation or the spill-over effect [27]. Alternatively, they also form nano-Schottky barrier with SnO_2 and effectively modulate the surface properties. The underlying sensing mechanism is depicted schematically in Fig. 5. Both Pd and Pt cause catalytic dissociation of molecular oxygen, thereby increasing the adsorbed oxygen species on sensor surface. Catalytic activity towards NO_2 and H_2 further helps to improve both sensitivity and selectivity [28].

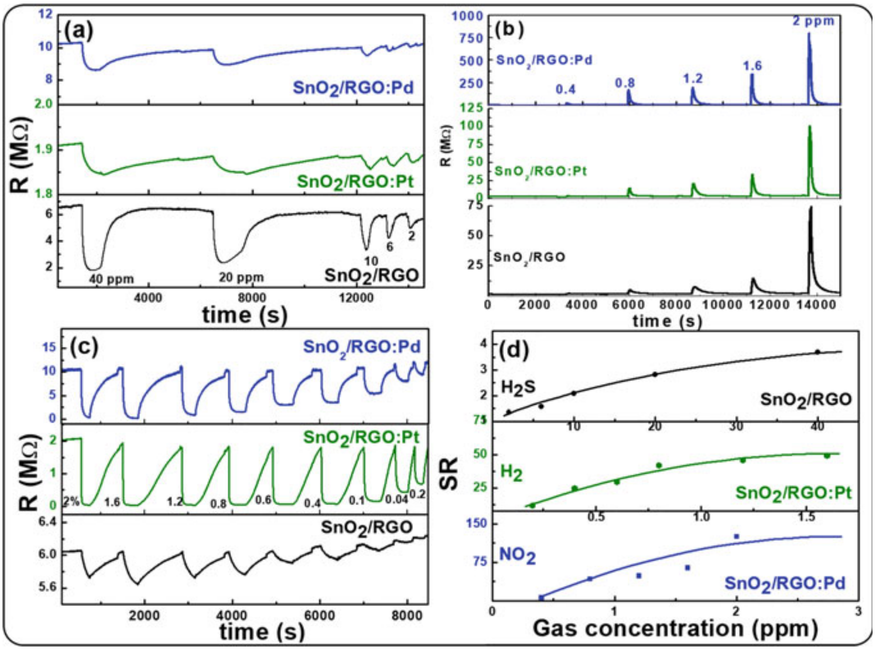

Fig. 4 Response curves towards different concentrations of **a** H_2S, **b** NO_2 and **c** H_2 recorded at an operating temperature of 200 °C for SnRG, PdSnRG, and PtSnRG samples. Reprinted with permission from B. K. Bhangare et al., Mater. Sci. Semicond. Processing, 105 (2020) 104,726. Copyright @ Elsevier

The noble metals play crucial role to improve the selectivity, sensitivity, and adsorption–desorption kinetics, thereby enabling the detection of the analytes below the safety limits concentrations. These nanohybrids can be used further as an EN for successful detection and determination of H_2S, NO_2, and H_2 gases. The obtained real-time sensor data was subjected for feature extraction to generate the data repositories. The resultant feature matrices were later analysed using multivariate statistical data analysis (MSDA) tools for the successful discrimination of gases. The featured matrix was studied by applying the PCA which is performed by using the correlation matrix form. Here the two-dimensional PCA helps to discriminate the real data into three subgroups of H_2, H_2S, and NO_2. In overall data, the two-dimensional PCA classifier accounts for the variance of about 59.16 and 40.54% for PC1 and PC2, respectively, as shown in Fig. 6.

HCA is a tool to group the similar observations into a characteristics cluster by means of the intra-relationship and inter-relationships in the groups. The dendrogram from HCA was plotted including the Wards cluster method which is known for minimum variance criterion, and Euclidian distance is used to represent the dissimilarity among the clusters and observations (Fig. 7). Here, the sensor response values of EN data are depicted into three different clusters which contain the group of data

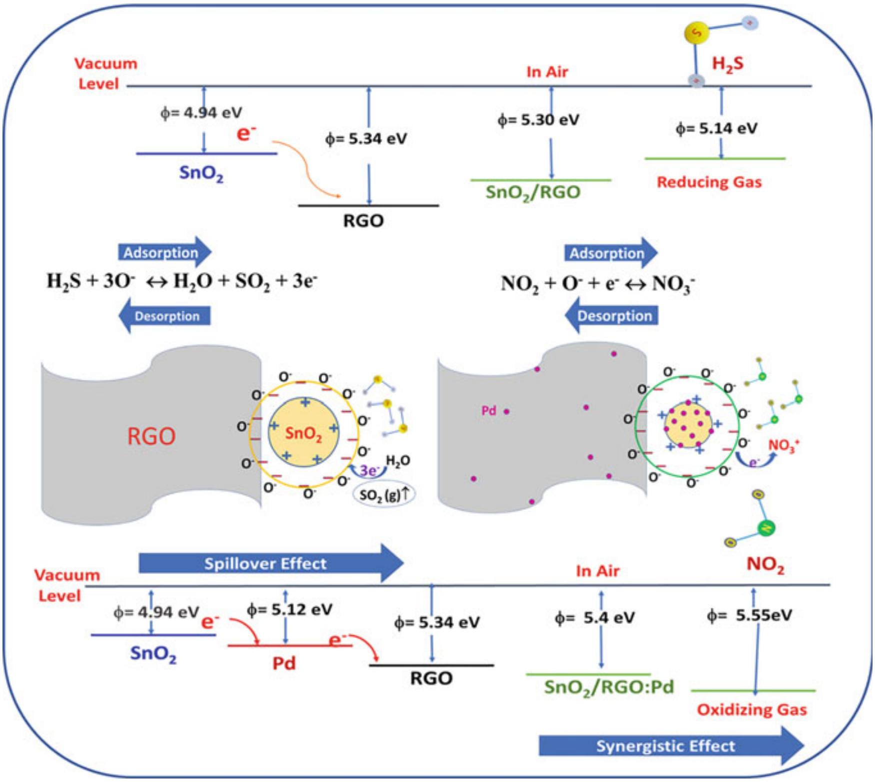

Fig. 5 Schematic representation of the underlying sensing mechanism. Reprinted with permission from B. K. Bhangare et al., Mater. Sci. Semicond. Processing, 105 (2020) 104,726. Copyright @ Elsevier

points representing H_2S, H_2, and NO_2. The principal branches of the dendrogram show the clusters of H_2S, H_2, and NO_2, respectively. The connectivity axis of the plot indicates the similarity of the observations and helps for qualitative or characteristic classification. In addition, the Euclidean space distance represents the magnitude of the dissimilarity.

Early identification and quantification of VOCs is regarded as the important parameter required for the timely diagnosis and related treatment of disease. Presence of different VOCs in particular concentrations has been assigned to the health conditions or diseases. For example, acetone is found to be <0.8 ppm in healthy persons, while its concentration increases to >1.76 ppm for patients with diabetes. NH_3 in concentration range of 0.82–14.7 ppm is associated to the kidney disorders and ulcers [29]. For intestinal diseases, the concentration of H_2 is >12 ppm; for halitosis, the concentration of H_2S is >2 ppm. Formaldehyde (HCHO) is a lung cancer biomarker found in the exhaled breath with threshold concentration of 83 ppb. Employing rGO-SnO_2-superstructures in EN configuration could discriminate the healthy subjects,

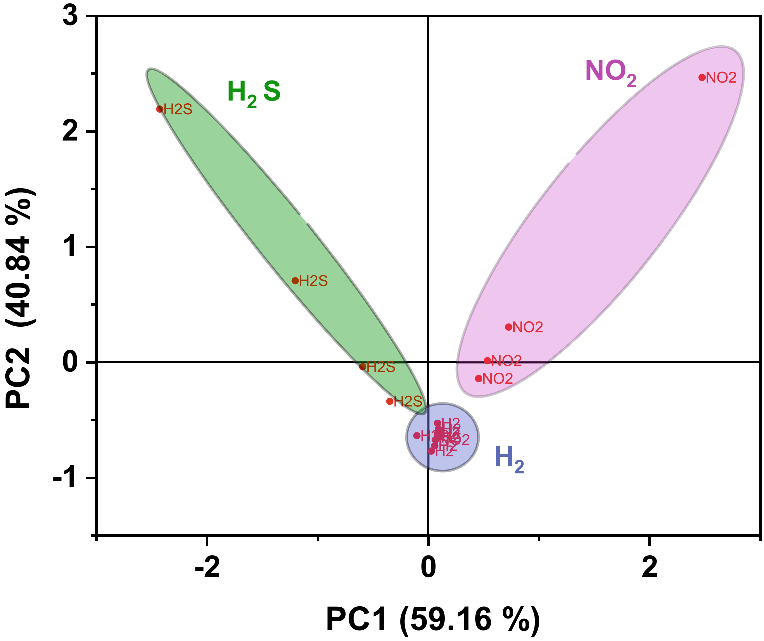

Fig. 6 Two-dimensional PCA showing discrimination of H_2, H_2S, and NO_2. Reprinted with permission from B. K. Bhangare et al., Mater. Sci. Semicond. Processing, 47 (2022) 106,706. Copyright @ Elsevier

and the developed sensor has been demonstrated for the successful detection of the HCHO as shown in Fig. 8.

4.3 Other Metal Oxide-Based EN

Different metal oxides have also found their use in the development of EN. Table 1 indicates the different metal oxides and their morphology that have found their use for the development of EN. WO_3 is yet another interesting material widely investigated for sensor application wherein higher operating temperatures are required. A multiple sensor array (MSA) comprising 32 sensing elements realised by selectively masking and deposition of different sensitizers was reported by Ramgir et al. [31]. Thus was accomplished using RF sputtering which resulted in a unique signature pattern (bar chart) towards target gases. Herein, the unique pattern generated using the sensor response values is considered to be the signature of the target gas, while the intensity of the signal is correlated to the concentration of measured gas. Some of the important metal oxide nanostructures with potential EN performances are listed in Table 1. As is evident from Table 1, heterostructures and the 1D nanostructures have found more application as sensing material for EN.

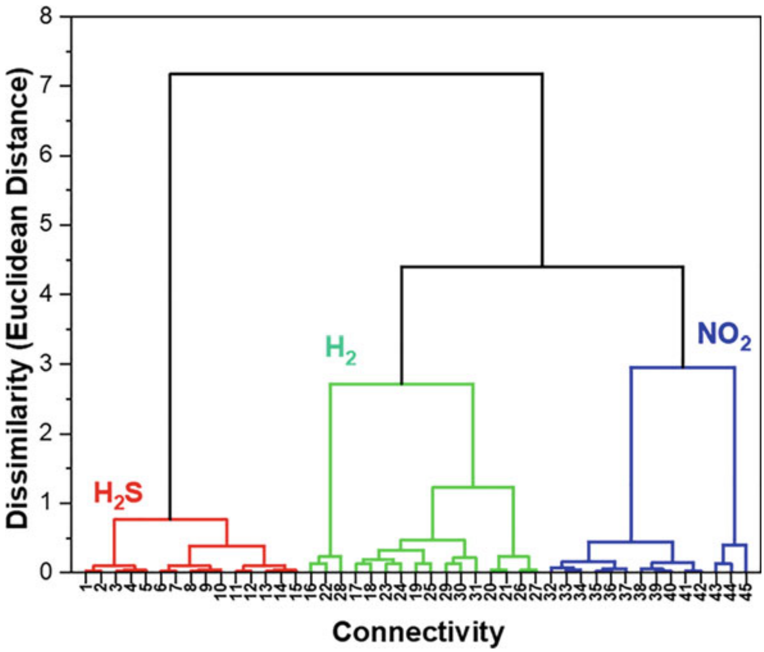

Fig. 7 HCA dendrograms showing discrimination of H_2, H_2S, and NO_2 for total number of observations $N = 45$. Reprinted with permission from B. K. Bhangare et al., Mater. Sci. Semicond. Processing, 47 (2022) 106,706. Copyright @ Elsevier

5 Present Status

The ability to precisely control the position, location, and resulting morphology is being used to achieve multiple sensors in a very narrow region of the substrate. For example, the growth mechanism of ZnO nanowires is well established for both physical as well as chemical methods. It is now possible to grow them in the desired location with pre-defined uniformity and aspect ratio crucial to realise repeatable and reproducible measurements. Efforts are now being directed towards incorporation of such MSA into wearable platform. For example, using the novel amalgamation of the approaches, efforts are directed towards achieving the commercially viable processes. For example, Kinkeldei et al. demonstrated a complete incorporation of EN into a smart textile [50]. For this, the sensors were first fabricated onto the flexible substrate, i.e. polymer, and later the substrate was cut into yarn like strips and finally integrated into the textile fabrication process. The performance of the fabricated deice was tested for its response towards four different solvents, namely methanol, acetone, isopropanol (IPA), and toluene. Principle component analysis (PCA) was successfully employed to easily differentiate the all the test gases.

One of the challenges that needs to be addressed for the EN devices is the requirement of the training period and the inherent drift in the base line resistance of the

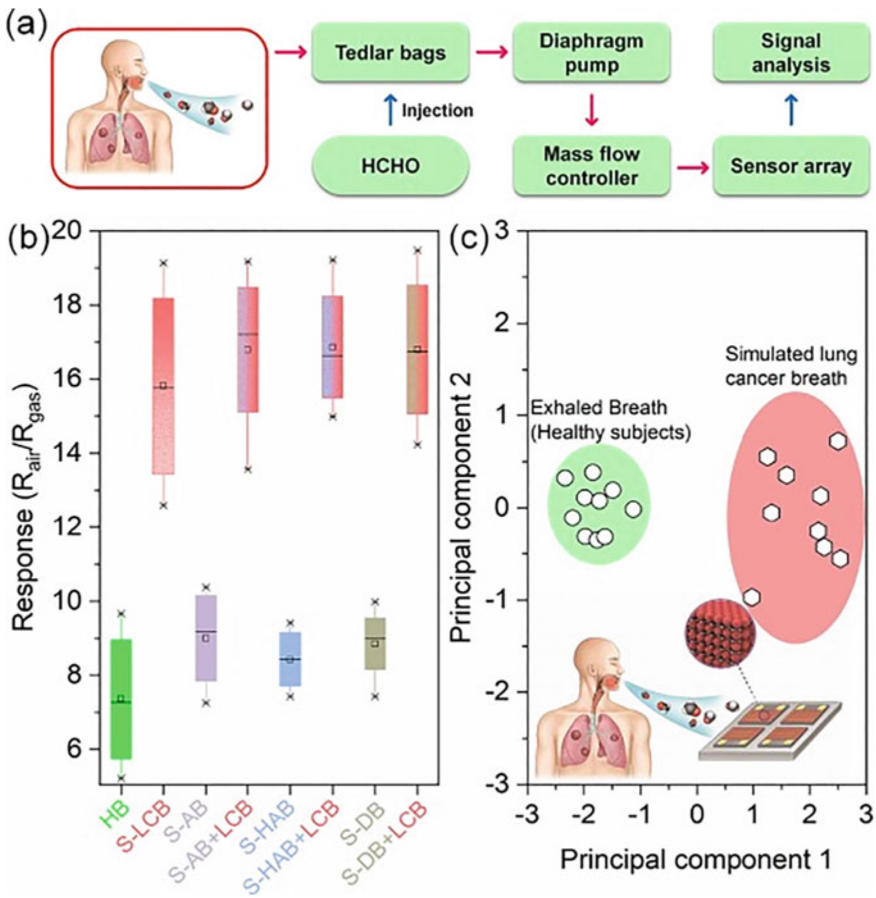

Fig. 8 rGO-SnO_2-superstructures (SS) EN being used for health monitoring [30]. Reprinted with permission from A. Shanmugasundaram et al. (2022) Chem. Eng. J. 448:137,736. Copyright @ Elsevier

sensor films. A complete automation of the training period and corrective measures like exposure to heavy concentration of gases are the possible solution to overcome these limitations. With advancement in the automation and the faster response kinetics observed for metal oxide nanostructures, a quicker training period is envisaged. Humidity also foul plays the response characteristics, so it is often required to use the filter or mention the range of use for the developed EN devices.

Other important challenge is the creation of data repository. With wealth of interesting nanostructures and bank of different metal oxides, it would be a humongous task to create a universal data repository. Often the choice of sensor films and the array combination is driven by the user which advertently is governed by the target application or the analyte of the interest. At present, the reported sensors and the available EN device ask to generate a data repository first and run the algorithm

Table 1 Different metal oxide nanostructures used for nano-EN application

Sr. No.	EN materials	Configuration	Analytes	OT (°C)	Ref.
1	SnO_2 nanotubes	Chemiresistive	H_2, NO_2, benzene	RT	[32]
2	SnO_2 nanotubes	Amperometric	H_2, CO, and ethylene	240–285	[33]
3	ZnO-CuO nanohybrids	Amperometric	NO_2, CO, H_2		[34]
4	TiO_2 Nanostructures	Chemiresistive	Ethanol, acetone, formaldehyde	23 ± 2	[35]
5	TiO_2 nano-helix array	Chemiresistive	NO_2, CO, H_2	150	[36]
6	MoO_3 microsheets	Chemiresistive	VOCs	275	[37]
7	SnO_2 nanotubes	Chemiresistive	H_2, NO_2, benzene	RT	[32]
8	TGS-type sensors (taguchi gas sensors)	Chemiresistive	VOC's (wheat bread baking process)	60–250	[38]
			Chinese pecan quality	200	[39]
			Olive oil quality	200	[40]
9	SnO_2 nanotubes	Amperometric	H_2, CO, and ethylene	240−285	[33]
10	TiO_2 nanostructures	Chemiresistive	Ethanol, acetone, formaldehyde	23 ± 2	[35]
11	TiO_2 nano-helix array	Chemiresistive	NO_2, CO, H_2	150	[36]
12	ZnO				[41]
13	ZnO-CuO nanohybrids	Amperometric	NO_2, CO, H_2		[34]
14	CuO heterojunctions	Chemiresistive	Liquor		[42]
15	MoO_3 microsheets	Chemiresistive	VOCs	275	[37]
16	MOS thick-film and thin-film sensors and the AlphaSense dual sensors	Chemiresistive	VOCs-acetone, isopropanol and 1-propanol, and isobutylene		[43]
			Chronic obstructive pulmonary disease (COPD)		[44]
17	Cr_2O_3 and SnO_2 (AlphaMOS, Toulouse, France)	Chemiresistive	Bacteria-based individual colonies	–	[45]
18	Commercial EOS507C (Sacmi Imola scarl, Imola, IT) – SnO_2, MoO_3	Chemiresistive	Enterobacteriaceae in vegetable soups	400	[46]
19	ZnO nanostructures sensor array	Chemiresistive	O_2, CO and CO_2	250–350	[47]

(continued)

Table 1 (continued)

Sr. No.	EN materials	Configuration	Analytes	OT (°C)	Ref.
20	ZnO–CuO, ZnO–Au, ZnO–NiO and ZnO–MgO heterojunctions	Chemiresistive	H_2S, NO_2	180	[48]
21	Doped SnO_2 nanomaterials	Electrochemical	Lung cancer biomarkers, 1-propanol, and isopropyl alcohol	–	[49]

of user choice, and if the expected outcome is satisfactory, it is advised to use the combination for all future requirement. As of now, a complete package with known and replaceable sensors, pre-defined algorithm for a particular application is still being pursued.

6 Conclusion and Future Scope

Thus, it is clear from the above discussion that the inherent advantages offered by metal oxide nanostructures make them the ideal material for realising EN devices with commercial prospects. Additionally, recent advances in the field of Internet of Things (IoT)-enabled communication, 5G services, wireless communication, ChatGPT, multichannel data transmission, and artificial neural network analysis further fuelled the growth in the field. This is particular significance so as to realise smart devices that not only helps to identify the analytes of interest but also suggest immediate actions based on the target purpose. For example, using the output from the EN for healthcare application, it is possible to send the simultaneous communication in respect to diagnosis and suggest therapeutics in consultant with doctors. In some urgent cases, one can envisage a situation wherein the AI first interprets the results and depending on the severity could inform ambulance, doctor, medical shop, hospital, and relatives for the possible course of action. This prompt futuristic service when achieved would help to save life and, importantly, time required for such arrangements. The future is not far when one carries the EN devices in the smartphones that already has the strong communication network, and the novel services will be offered by the insurance companies wherein they will provide all the inclusive service so as to maintain the good health of an individual.

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