Smart gas sensor arrays powered by artificial intelligence

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Abstract: Mobile robots behaving as humans should possess multifunctional flexible sensing systems including vision, hearing, touch, smell, and taste. A gas sensor array (GSA), also known as electronic nose, is a possible solution for a robotic olfactory system that can detect and discriminate a wide variety of gas molecules. Artificial intelligence (AI) applied to an electronic nose involves a diverse set of machine learning algorithms which can generate a smell print by analyzing the signal pattern from the GSA. A combination of GSA and AI algorithms can empower intelligent robots with great capabilities in many areas such as environmental monitoring, gas leakage detection, food and beverage production and storage, and especially disease diagnosis through detection of different types and concentrations of target gases with the advantages of portability, low-power-consumption and ease-of-operation. It is exciting to envisage robots equipped with a "nose" acting as family doctor who will guard every family member's health and keep their home safe. In this review, we give a summary of the state-of the-art research progress in the fabrication techniques for GSAs and typical algorithms employed in artificial olfactory systems, exploring their potential applications in disease diagnosis, environmental monitoring, and explosive detection. We also discuss the key limitations of gas sensor units and their possible solutions. Finally, we present the outlook of GSAs over the horizon of smart homes and cities.

Key words: mobile robots; gas sensor array; electronic nose; artificial intelligence; environmental monitoring; disease diagnosis

1. Introduction

The human body is a remarkable integrated system with many attractive design features. A variety of functional devices inspired by humans have already been invented and applied into flexible intelligent robots, such as optoelectronics for computer vision[1–3], electronic skin for machine touch[4–7], and versatile algorithms for speech recognition[8]. Vision and hearing systems for robots are already mature after development of more than one hundred years. The tactile sense has also been successfully demonstrated to learn signatures of the human grasp by piezoelectric sensors[6]. With this background, a flexible and smart electronic nose remains undeveloped but in high demand.

Ever since the first electronic nose based on a gas sensor array (GSA) was introduced by Persaud and Dodd in 1981 to mimic the function of the mammalian olfactory system[9], researchers have put many efforts into fabricating different kinds of GSA[10–13] with both high sensitivity and selectivity for a diverse set of applications such as food quality control[14], environmental monitoring[15], disease diagnosis[16–18] and explosive detection[11]. GSA technology, also known as an "electronic nose", records a smell print by capturing responses to target chemical compounds. In the last forty years of development, GSA based on different technologies, including metal oxide thin films, nanowires and nanotubes has shown considerable potential in the detection of a wide vari-

ety of chemical compounds[19–22]. Flexible GSA with advantages such as outstanding electrical conductivity, excellent mechanical flexibility and light weight is also an essential component for both wearable devices and intelligent robots[23]. Fig. 1 gives an overview of GSAs from typical fabrication methods to main application scenarios.

The two most important components of an electronic nose system are the GSA as the sensing material to chemical compounds and automated pattern recognition algorithms which are one of the most powerful tools in the AI era. Firstly, gas molecules can activate a signature or pattern on GSA containing a set of different gas sensing units[24]. AI growing vigorously in recent years is capable of extracting the main characteristics of the gas samples for further application[12, 25, 26]. Typical machine learning models, including deep learning[27], long-term recurrent convolutional networks[28], deep reinforcement learning[29], deep convolutional generative adversarial networks[30], and deep residual learning[31] have high potential to be implemented into gas sensing systems to enhance both gas discrimination accuracy and efficiency. GSA in combination with AI, packaged as a chip-scale electronic nose, is in the early stage of commercialization.

2. Fabrication

Mammals can distinguish an immense range of inhaled odorants with the olfactory sensory organ made of a specialized olfactory neuroepithelium[32]. Important features, such as shape, size and functional group, from the inhaled odorants will be encoded by neuronal system in the next step to form the sense of smell. Each type of olfactory receptor cell will be activated by one corresponding gas molecule species, fol-
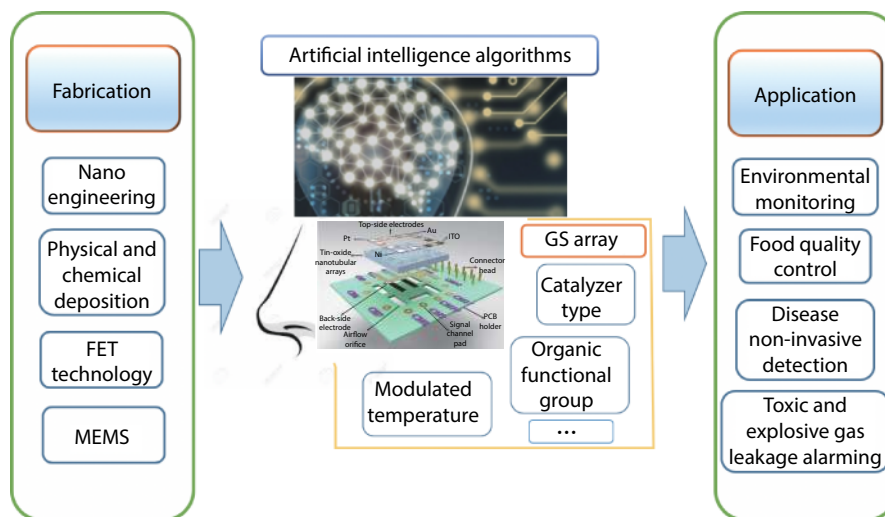
Fig. 1. (Color online) Smart gas sensor array fabricated by different techniques assisted by artificial intelligence algorithms can find many real-life applications, exhibiting great potential as a mammalian olfactory system in the areas of air and water quality monitoring, non-invasive disease detection, and dangerous gases leakage alarming.

Table 1.   Summary of different types of gas sensor[33–37].

Sensor type	Principle	Advantage	Disadvantage
Thermal (catalytic)	Catalytic combustion or reaction of target gases providing reaction heat which acts as the output signal	Low cost, fast response, simple	Detection of flammable gas only, possibly be poisoned by catalyst.
Mass	Monitoring gases using mass-sensitivity transducer	High sensitivity, good reliability, fast response	The piezoelectric substrate being influenced by temperature
Electrochemical	Reacting with target gases at electrodes and producing electrical signals that are proportional to the gas concentration	Low concentration detection, wide range of detectable gases, good selectivity	Relatively shorter lifetime, difficulty in revealing failure mode
Optical	Measuring optical absorption/emission scattering of target gases	High sensitivity, good stability, good selectivity	High cost, influenced by ambient light
Semiconductor	Gas adsorption and desorption at the surface of materials leading to electrical resistance change of the materials	Low cost, long lifetime, ease of miniaturization, wide range of detectable gases	Poor selectivity, humidity and temperature dependent, drift along time, normally working at high temperature
Surface acoustic wave	Measuring the velocity or amplitude of acoustic wave propagating through or on the surface of materials which is sensitive to target gases	Battery-less, ease of miniaturization, selectivity depending on receptor	Complex fabrication process

lowed by transmission of the activated pattern containing information about the odour to the brain by olfactory sensory neurons. Although olfactory systems with such a remarkable capacity can discriminate a wide variety of odour molecules, human receptor cells only have a life-time of about two weeks, corresponding to high cost by its nature[33].

By imitating the special olfactory system of animals, researchers have developed plenty of approaches to achieve an electronic nose. An optical sensor system has been applied to the detection of carbon dioxide by measuring the absorbance in a special frequency range and a colorimetric sensor array has been demonstrated for the real-time indicators of analyte gases[34]. More recently, Ferry et al.[35] reported sub-second hydrogen detection with a plasmonic metal-polymer hybrid nanomaterial by measuring the optical hydrogen absorption and desorption isotherms. Gas chromatography-mass spectrometry (GC-MS) has been regarded as a "golden standard" to analyse gas samples. Gas chromatography, widely used in analytical chemistry[36], can separate gas mixtures by utilizing the difference in the chemical properties and relative affinity for the stationary phase, while mass spectrometry detects and discriminates gas molecules eluted from GC column by ionizing these molecules and measuring

mass-to-charge ratio. Another technology named ion mobility spectrometry (IMS) can also detect target gas molecules as GC-MS. A comparison of different types of gas sensors are summarized in Table 1[36–39]. Despite the thousands of techniques that can be employed in electronic nose systems, the simplest and most common method nowadays is still a gas sensor array consisting of a set of transducers as illustrated in Section 3: smart gas sensor array. Hereby, we mainly discuss gas sensors that convert chemical signals into electrical signals that can be recorded and analysed further.

The sensing materials of the electronic nose above are usually fabricated by nanoengineering which can offer high surface-area-to-volume ratio for enhanced sensitivity[24, 25]. In order to accomplish scalable manufacture, physical (such as evaporation[40] and sputtering[41]) and chemical (such as chemical vapor deposition[42] and hydrothermal methods) deposition technologies are utilized. Then the signals from sensing materials can be greatly amplified by field-effect transistor (FET) technology[16]. In general, current devices based on metal oxide semiconductors require a high working temperature for reasonable sensitivity and response/recover time. In order to reduce the power consumption, a micro-electro-mechanical-system (MEMS) process is adopted by integrating micro-

heaters into a thermally isolated thin Si_3N_4 membrane suspended within a silicon wafer[43, 44], followed by sensing material deposition on the interdigitated electrodes above the heating source.

3. Smart gas sensor arrays

The implementation of a chemosensory array to detect and discriminate chemical compounds including volatile organic compounds (VOCs) and other air pollutants, from the surroundings and convert them to electrical signals has attracted tremendous interest in recent years. This type of gas sensor array possesses special advantages of chip-scale miniaturization and ease-of-operation[16]. In general, the interaction between the target chemical compounds and gas sensing materials is captured and recorded as a change of resistance, current, or frequency, corresponding to different measurement metrics. Sensitivity is one of the key parameters of gas sensor units which describes the response of devices towards target gas molecules at certain concentration. It can be improved by reducing the grain size[45], synthesis of thin film structure[46], doping with additives[47], operating at high-temperature or light-activated mode. Normally, the sensitivity (S) of gas sensors can be defined as:

$$S = \frac{\Delta M}{M_0},$$

where M denotes the specific measurement metric used.

Recent efforts have been focused on developing nanostructured sensors with low-power consumption (operating at room temperature). Here we summarize representative achievements about fabrication methods and applications of GSA.

3.1. MOX gas sensor array

A variety of metal oxides (MOX) can be employed as gas sensing materials by simply measuring the change of resistance. Normally, ambient oxygen molecules will attract free electrons in MOX materials, forming oxygen ions. In this process free electrons inside the materials are consumed, resulting in band bending and an electron depletion region at the materials surfaces. The target gas molecules are either acting as reducing gas or oxidizing gas, corresponding to donor or acceptor of charge carriers. When the materials are placed in the environment of these gases, the resistance of the semiconductor metal oxide will increase or decrease depending upon the type of majority carriers in the sensing materials and types of target gases[48]. Taking an example of N-type sensing materials, the reducing gas will react with the pre-absorbed oxygen ions on the surface and release free electrons back to materials, leading to decreased thickness of the depletion region. As the conductance of MOX materials is proportional to the amount of free electrons, the more reductive the gas is, the more free electrons there will be available and thus the more conductive the materials will become.

Gao[49] divides MOX into two categories according to their electronic structure: transition-metal oxide such as Fe_2O_3 and NiO, and non-transition-metal oxides such as ZnO and SnO_2. SnO_2 is the most popular and stable material for thermal energy activated gas sensors[50], while ZnO and TiO_2 have attracted great interest for light-activated gas sensors[51, 52] due to their narrow bandgap. However, in practice, MOX materials themselves are not active enough to capture gas molecules within a short time[53], and MOX gas sensing materials are well-known for their cross-sensitivity problem, thus easily producing false signals when there are interfering gases[54]. These problems can be solved by introducing dopants into the MOX materials and gas sensing performance will be improved at the same time. The most common additives can be noble metals, such as Au[55], Pd[56], Co[57], Pt[58] and Ag[59]. The mechanism of noble metals here can be understood as "spill-over effect" around the noble metal particles and their high effective dissociation catalytic ability to specific gas molecules[60]. Combinations of different metal oxide films also exhibited better performance[61, 62]. De Lacy Costello and co-workers[61] demonstrated largely improved responses of ZnO–SnO_2 to 1-butanol and DMDS than individual component alone because of the synergistic effects between the two materials for the accelerated breakdown of butanol. Therefore, enhancement of selectivity MOX gas sensor devices can be achieved by functionalizing the surface with certain molecules.

The bottleneck factors impeding further development of MOX-based electronic nose attribute to: 1) normally in order to achieve decent sensitivity, fast response and recover time, and provide enough energy for the desorption of gases, gas sensors usually operate at high temperature (around 500 °C). Therefore, a power source is needed to provide enough power for the large scale of GSAs which consumes a great amount of electric power for real-life application. This leads to the research interests of developing devices working at room temperature. 2) Cross sensitivity problems produce interfering signals, because MOX films are sensitive to a wide variety of molecules and background interference in real-life application is always complex. To solve this problem, carefully picking up the sensor units will provide data without redundancy and pre-treatment of samples or a standard testing process may also be required. 3) The humidity level and temperature level affect sensors' signals significantly and furthermore the humidity and temperature of environmental air fluctuate unpredictably. Reaction between surface oxygen and water molecules will cause a shift in the baseline resistance and deteriorate the sensitivity of MOX sensors[63]. The humidity and temperature need to be controlled carefully when performing gas sensor tests. Nanostructure can also be employed to mitigate the humidity effect[64]. Temperature, on the other hand, can also be utilized for VOC detection[65].

In recent years, the MOX gas sensor array has been extensively studied in selective detection of volatile organic compounds (VOCs) as biomarkers of human diseases. In earlier years, Wang et al.[66] reported the fabrication of Cr-doped WO_3 by means of flame spray pyrolysis (FSP) for low concentration (0.2–1 ppm) acetone (a candidate for diabetes diagnosis) detection. Zhang and co-workers also proved that multiple VOCs can be detected by a single type of gas-sensing material simultaneously[67]. Up to now, a lot of scalable integrable fabrication methods of gas sensor array have been successfully demonstrated. For instance, Guntner et al.[13] demonstrated a compact SnO_2 based sensor array doped with different materials (Pt, Si, Pd, Ti) by FSP to test simulated breath. The formaldehyde (FA) in simulated breath as one of lung cancer biomarkers can be detected with an average error lower than 9 ppb without selectivity issues by multivariate linear regression model. Fig. 2(a) illustrates the set-up of FSP
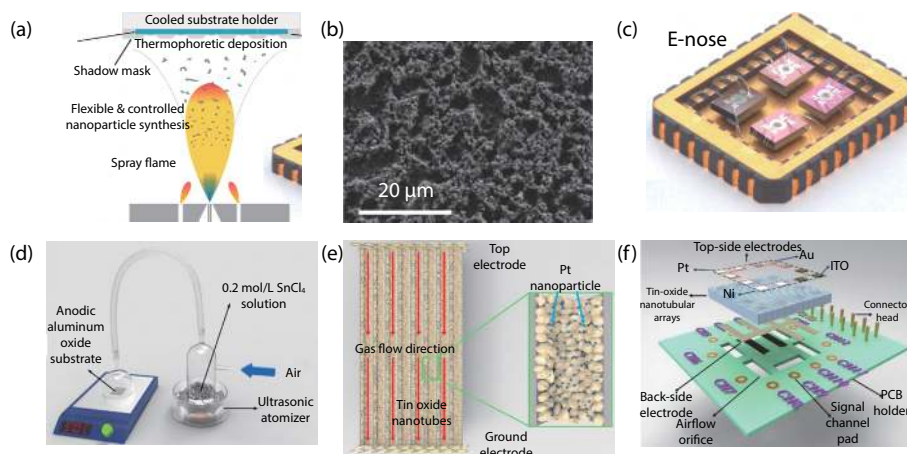
Fig. 2. (Color online) MOX sensor array fabrication method and morphology[10, 11]: (a) FSP set-up, (b) SEM image of porous doped SnO$_2$ film, (d) USP setup, (e) Cross-section of SnO$_2$ nanotube decorated with Pt nanoparticles, gas sensor array of (c) doped SnO$_2$ microsensors and (f) 3-D SnO$_2$ nanotube.

where produced nanoparticles are directly deposited on a water-cooled substrate above the FSP nozzle by thermophoresis. The morphology of the doped porous SnO$_2$ film is compact and uniform as shown in Fig. 2(b). The substrate is then diced into packages of 5 by 4 sensor arrays after sensor film deposition as shown in Fig. 2(c). A single sensor is able to detect FA level down to 3 ppb at breath-realistic 90% RH at 400 °C with 140 s response time, while a sensor array combined by four differently doped sensors can detect FA with averaged error less than 9 ppb among up to four-analyte interfering gases[13].

In addition to FSP methods discussed above, Fan's group proposed another method called ultrasonic spray pyrolysis (USP) as shown in Fig. 2(d) for fabricating ultra-low-power-consumption 3-dimensional SnO$_2$ nanotube arrays[14]. The as-fabricated devices can work at room temperature and a single heater-free sensor device only consumes power of 12.5 μW. The greatly increased surface-to-volume ratio is the key for such good performance at room temperature and Fig. 2(e) depicts the 3-dimensional device's 40 μm-thickness cross-sectional profile which consists of 70 nm thick polycrystalline SnO$_2$ decorated with 5 nm diameter Pt nanoparticles. Then different electrode materials including gold, platinum, nickel and indium tin oxide are deposited at different locations as top electrode array to form a gas sensor array for gas detection as illustrated by Fig. 2(f). They also demonstrate a real-life application case by integrating a read-out circuit, a wireless data transmission unit and mobile phone receiver, thus enabling real-time target gas monitoring in the phone App[14]. The packaged devices show a good discrimination to nitrogen dioxide, benzene and hydrogen by learning vector quantization algorithms.

For the above GSA devices, the largely increased sensitivity and decent room-temperature performance are attributed to high surface-to-volume ratio provided by porous film or nanostructure. Therefore, further research efforts can help to uncover the physicochemical process behind the phenomenon and create more versatile nanostructures with large surface area[68].

3.2. Nanoparticles and nanowires gas sensor array

It is worth mentioning that other materials such as metal or metal nanoparticles can also be employed as a unit of gas sensor array for many applications[69]. In 2009, Peng et al.[15] reported a gas sensor array based on functionalized 5-nm gold nanoparticles combined with pattern recognition methods to differentiate lung cancer patients. In their works, gold nanoparticles functionalized by nine organic groups were dispersed in chloroform and then drop-cast onto two adjacent electrodes as shown in Fig. 3(a). The sensor array in Fig. 3(c) showed larger than 86% accuracy towards breath samples of people without lung cancer. Following this work, various types of gas sensor were demonstrated to distinguish between the breath of healthy people and lung cancer patients, which attracted tremendous interest to explore a variety of materials. Toshio Itoh et al.[70] employed different types of sensors including doped MOX gas sensors to accomplish selective detection of target VOCs for lung cancer and diabetes detection.

GSA urgently needs versatile and robust fabrication methods for chemical and biological sensing. Field-effect transistor (FET) technology is a candidate with great potential in the sensor array manufacturing area[71, 72]. Chip-scale gas sensors with their remarkable scalability and compatibility to existing technology showed significant advantages with the increasing market scale of internet of things (IoT). In 2004, Fan et al.[73] demonstrated single-crystal ZnO nanowire FETs synthesized using the chemical vapor deposition (CVD) method for nanoscale electronics and chemical sensing devices. Recently, Javey and co-workers used industry-compatible processing techniques to integrate gas sensing materials into FETs overcoming miniaturization and low-power operation problems faced by other gas sensor arrays[16]. In this work, the ultra-thin silicon-on-insulator transistors were fabricated as substrate, then different kinds of metal alloy including Ni–Pd and Pd–Au were deposited sequentially by electron beam evaporation. The sensor array functionalized with sub-5-nm metallic sensing layers showed good selectivity to three target gases, H$_2$S, H$_2$ and NO$_2$. A possible reason for the selectivity is that Ni covering Pd surface will block any H$_2$S interaction and Pd–Au alloys interact weakly with H$_2$ compared to pure Pd.
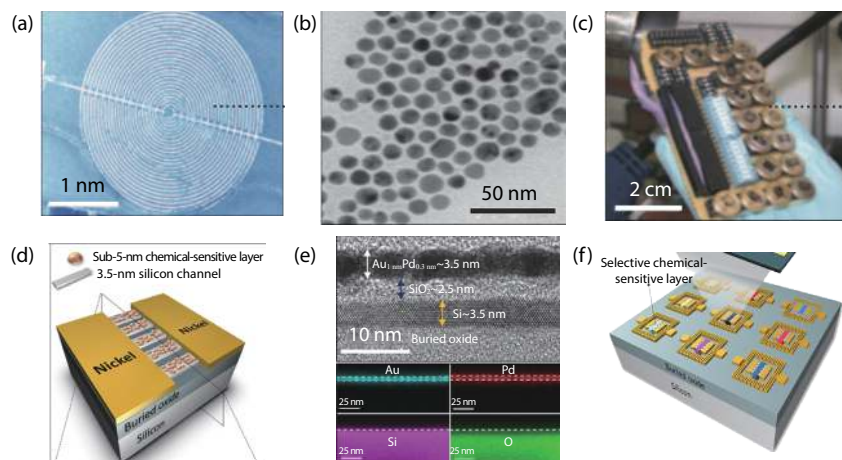
Combinations of different technologies can act favour-

Fig. 3. (Color online) (a) Sensor array fabrication methods and morphology[12, 13]: (a) an SEM image of organic functionalized gold nanoparticle film deposited between adjacent electrodes, (b) a TEM image of monolayer capped gold nanoparticles, (d) a TEM image of ultrathin silicon channel, (e) EDS indicating the elemental composition of a single Pd-Au CS-FET, gas sensor array of (c) gold nanoparticles, (f) CS-FET.

ably on gas sensing performance. The selectivity of a gas sensor can be accomplished by specificity of organic materials while the robustness can be achieved by inorganic materials. The signals are captured and amplified by FET for further processing. In summary, gas sensor arrays show great potential for real-world application with versatile fabrication methods, low-power consumption, and high sensitivity and selectivity.

4. AI algorithms

Algorithms applied to GSAs resemble the human neural system connected to the human nose, being the indispensable part of the whole electronic nose system. Algorithms for mature electronic nose systems typically consist of three parts: 1) drift calibration algorithms, 2) signal pre-processing and feature extraction part, 3) pattern recognition system that can recognize the odours of chemical compounds.

Most gas sensors including MOX suffered a lot from drift issues consisting of small and non-deterministic temporal variations of the sensor response when they are exposed to the same analytes under identical conditions. Drift is caused by different reasons for different kinds of gas sensing materials, for example, the drift of MOX gas sensors is attributed to chemical diffusion of oxygen vacancies (as the simultaneous transport of oxygen vacancies and conduction electrons, the conductivity changes in the bulky or space charge layer of MOX grains). To deal with the drift issues of a sensor and ensure signal repeatability over time, after a period of time (several weeks) the artificial electronic nose system must be completely re-calibrated to ensure valid results. Cho et al.[74] developed a software platform based on multiplicative drift correction method to solve drift issues.

Following drift calibration, the next step of data analysis is pre-processing of the data collected from GSA which can form patterns of target gases, similar to the mammalian olfactory system. In this step, important features, such as sensitivity, response and recovery time, the slope at t_{10}, t_{50}, t_{90} of response and recovery curve can be extracted from the raw data. Next, redundancy of the data is removed by data analysis methods in which principal component analysis (PCA)[75] is the most frequently adopted technique. This technique converts the whole set of recorded n-dimensional data into smaller dimensions and reduces the complexity and computation power of the whole dataset.

The following step after the pre-processing of data is applying pattern recognition and classification algorithms, thus providing more insights into the pattern generated by GSA. The simplest method to process the data is to compare the testing data to those of known sources in the knowledge base through graphical evaluation including bar charts, profiles polar and offset polar plots[15].

Pattern recognition algorithms can be divided into several categories according to certain standards as summarized in Fig. 4. Basically, classification algorithms of gas sensors can be classified into linear/non-linear algorithms or supervised/unsupervised algorithms. PCA can reduce high dimensionality of multivariate data into smaller dimensions and then k-nearest neighbours (KNN) will sort out different data. KNN takes into account the Euclidean distance from the test sample to each of its k nearest neighbours among all stored training samples, and then form a clustering of similar samples[76]. This peculiarity makes it particularly suitable for applications of distinguishing breath of healthy people and early lung cancer patients with eventual clustering of the data visualized[76].

Artificial neural networks (ANNs) inspired by animal brains is a type of algorithm quite popular in recent years due to the benefits of greatly improved computation power and big data. It is a data driven self-adaptive method in that they can adjust themselves to the data without any explicit definition of the mathematical form for the underlying model and have potential to work as universal functional approximations with arbitrary accuracy. Up to now, ANN has found particular success in information processing areas such as computer vision, speech recognition, and natural language processing. Artificial olfactory system, equivalent to the human organ for smelling, will certainly prevail when powered by ANN. Pai Peng et al.[27] proposed a six-convolution-blocks DCNN coupled with seven MOX gas sensors to classify a single gas with an accuracy of 95.2%. Likewise a gas identification CNN based on LeNet-5 reached a 98.7% final accuracy[77]. All the works showed the great potential of ANN in the gases classification area. Training an ANN model normally requires
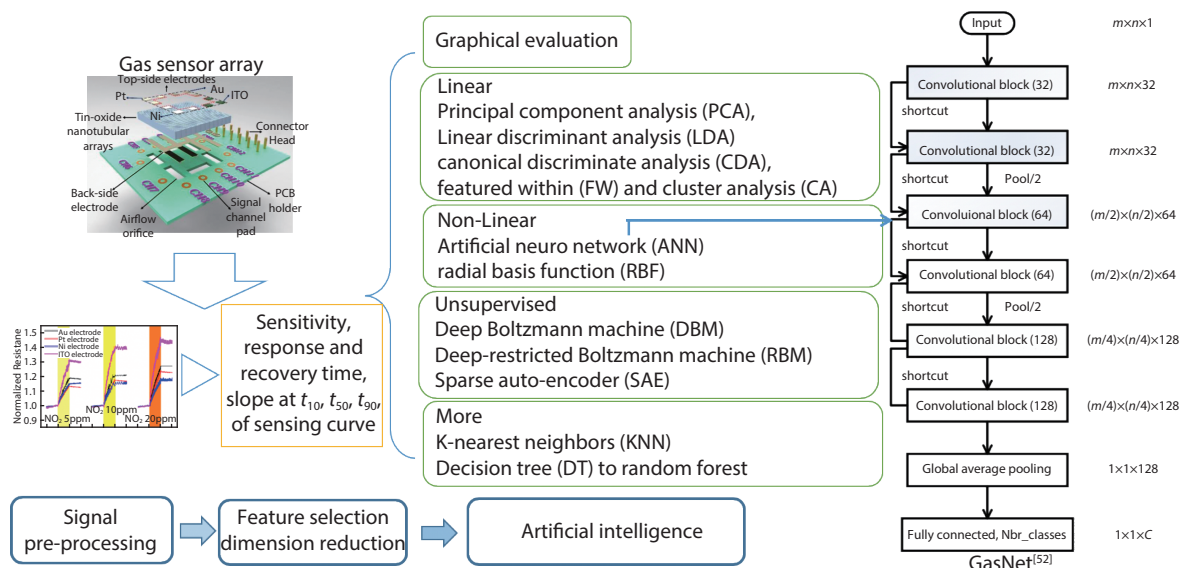
Fig. 4. (Color online) Artificial intelligence algorithms adopted in a gas sensor array.

a large dataset which exerts great pressure on collecting valid and large amount of data from a gas sensor array, pushing the need for a carefully design of gas sensor network.

5. Applications

In the past four decades since Persaud and Dodd's work in 1981[12], applications of gas sensor arrays as electronic noses have been involved in a variety of areas. In real-life, the ideal case is to treat the gas sensor array as a black box, which means input testing gases are analysed for species and concentrations automatically without considering what is going on inside the box. To test the feasibility of the proposed gas sensor array model, GC-MS with expert operation is employed to work as a benchmark to validate the accuracy and to what level the gas sensor array can achieve. Apparently, the prepared testing samples play a key role in the whole process, thus different parties need to set their own standards for gas sample collection. Nonetheless, there are not enough available products in the market, mainly due to high price and complex operation procedures. Here, we introduce the current application situation and prospect of GSAs in disease diagnosis and environmental monitoring as well as their great opportunity in the era of IoT.

5.1. Disease diagnosis

In ancient China, smell, one of the four disease diagnostic methods (observation, olfaction, inquiry, palpation), has already been applied into disease diagnosis. With the fast development of modern measuring-instrument engineering and medical science, smell is fading from the stage of disease diagnosis because of the insufficient knowledge of the relationship between diseases and exhaled gases, and measurement inaccuracy of equipment. However, modern medical diagnosis methods such as chest X-ray, computerized tomography and biopsy may cause damage to the human body. Besides, the first two are expensive and emit radiation. Biopsy is usually painful with frequent complications. Benefiting from advanced technology, clinical trials demonstrated the possible relationship between diseases and corresponding gas species[78, 79]. As many illnesses have their own "smell print",

this made early detection and diagnosis possible. Thus, a non-invasive and portable electronic nose possesses great potential in disease diagnosis. Here the GSA distinguishes itself by its simplicity of operation and household usage features which can open up new fields of markets. Fig. 5(a) illustrates the complex multistep processes involved in breath testing. Researchers can undertake a comprehensive breath testing system according to these processes.

An ideal GSA for disease diagnosis of breath testing should be sensitive to low concentrations (tens of ppb) of VOC as thousands of VOCs in breath are mostly in ppb levels[19], and special care has to be taken when there are interfering gases in the background. Meanwhile, GSA units have to be carefully chosen for special needs and certain diseases. Diabetics have a sweet smell similar to fruity decomposing apples. Uremic patients have a fishy breath. People with kidney failure will have ammonia increase on breath. Examples of using breath VOCs for disease are described below:

(1) Exhaled acetone level is a sign of diabetes, especially type I diabetes. Reverse correlations between blood glucose and breath acetone concentration has been established[80]. This is a possible way to detect diabetes.

(2) Gang Peng et al.[21] employed GC-MS to identify 42 VOCs that can represent lung cancer biomarkers. Another work by Ji-Eun Chang et al.[81] in 2017 also demonstrated VOCs in exhaled breath from both early stage lung cancer patients and healthy volunteers can be discriminated with 75.0% total accuracy by MOX gas sensor array.

(3) Parkinson's has been identified to have a distinct volatile-associated signature, including altered levels of perillic aldehyde and eicosane, through a comprehensive analysis of sebum from Parkinson's disease patients[82].

More disease related breath VOCs can be looked up in Fig. 5(c), which is a concentration map for different diseases.

While important milestones have been established in the field of breath testing up to now, there is still much to accomplish in this field. Practical use of sensor arrays is impeded by individual difference which causes difficulties in obtaining a generalizable result. More systematic study or algorithms

need to be considered to deal with it. Further check-up of correlations between exhaled breath and diseases should be performed in the medical fields. The false negative rate of diagnosis results by electronic nose should be minimized. Critical parameters such as low-concentration-VOC sensitivity, selectivity, power-consumption should also be optimized. A combination of different technologies will increase the accuracy of VOC detection to a large scale and have the potential to solve the cross-sensitivity problems of compounding factors, enabling miniaturization and integration of medical devices. In the near future, the GSA will even be able to fit into smart phone for daily applications. In conclusion, disease diagnosis by GSA will require and in return boost the development of several areas including medicine, material science, and electronics.

5.2. Environmental monitoring

GSA nowadays is of great interest in environmental monitoring as a result of people's increasing concerns of health impact of air pollution. Meanwhile, a sensor array is capable of detecting and discriminating a wide variety of gases such as CO (resulting in smog formation), CO_2 (the leading greenhouse gases), NO_x (a toxic gas), SO_x (acid rain), and ammonia (caustic and hazardous). Traditional methods for air quality monitoring by analytical instruments such as GC-MS are not suitable due to not being on-site, real-time, and cost-effective. To tackle these issues, GSAs can work as an alternative to GS-MS in evaluating the existence of pollutants in air and water. The number and types of sensor units are selected generally based on different application cases.

By means of GSA, Abdullah et al.[83] performed continuous monitoring of air quality for malodour mapping in a chicken farm, which is based on an array of commercial MOX sensors. Likewise, Licinia et al.[84] reported both laboratory and field tests of two electronic nose systems equipped with six MOX gas sensors to discriminate environmental odours. Applications of gas sensor array can be used in but not restricted to the following aspects: (1) real-time environmental air quality monitoring, (2) water quality control, (3) locating the source of pollutant, (4) in-door air quality monitoring such as formaldehyde concentration detection after decoration, (5) supervising the emission of factory production[85].

As there are various sources of environmental problems including both anthropogenic sources and natural sources, GSAs can be employed to build a sensor network in smart city design. Recently, specific chemical molecules have been used as a sign of air quality. By analysing the response pattern of the whole sensor array, the pollutants emission sources can be located. However, despite sensor array responses showing appreciable correlation to chemical compound species and concentration, it is also heavily influenced by the humidity level of the ambient environment[75]. Thus, the humidity level must be taken into account when analysing air samples. Another critical factor should be taken into consideration is the cross-sensitivity of co-existence of other chemical compounds[86]. Besides, sensor drift over time caused much trouble when GSA meets reality. From a practical point of view, applications of the GSA in environmental monitoring are limited by the drift behaviour of sensors and humidity and temperature variation[83]. Thus the sensor units need to be calibrated from time to time and kept at constant-temperature and constant-humidity working mode.

GSA can be used not only in air quality monitoring, but also for the measurement of "biological oxygen demand" (BOD) concentration in water, a gauge of waste water treatment effectiveness, by analysing the headspace (air space over the water surface) of water[18]. BOD correlates with contents of organic biodegradable matter in waste water which builds the relationship between the quantity of consumed oxygen and aerobic biodegradation by microorganisms[44]. Several works have demonstrated the feasibility of water quality monitoring by BOD[87–89].

As discussed above, the application of GSA in real-life cases is still considerably problematic as the environmental condition including temperature and humidity are changing all the time accompanied with complex chemical compounds in ambient air. All in all, due to the unique superiority of GSA including on-site real-time continuous monitoring capability and low-cost, easy to operate features, it is certain to be preferable as a solution for environmental monitoring.

5.3. Smart home and smart city

The IoT industry is growing vigorously nowadays and foresees even greater opportunities in the future with 5G network enabling more equipment to connect into network. A typical application of GSA in this field is to cooperate with smart phone applications for building a smart home, and to form sensor networks for smart buildings and smart cities.

Typical scenarios of such field are gas leakage detection, indoor air quality control, explosive detection, and environmental safety monitoring[90–92]. Devices capable of spoilage detection of foodstuffs are suitable to be integrated into refrigerator or warehouse for food preservation and trigger appropriate operations such as pasteurization, refrigeration, and vacuum packages upon detecting abnormal signals. The whole process of food and beverage from production to storage can be fully monitored by GSA and ensure the best quality of food. Another usage for GSA in IoT is to enhance gas safety and security. The presence of unpleasant flavour and gas leakage inside a house can be notified to the owner at the earliest time. Illegal items such as drugs and explosives can be investigated timely at the customs instead of dogs which may suffer from behaviour variations[7].

Portable and scalable GSA devices are of special importance for the purposes outlined above. Fig. 5(c) shows a GPRS-based gas sensor network in smart city plan and Fig. 5(d) depicts real-time indoor gas monitoring by smart phone in smart building which consists of SnO_2 nanotube array as sensing materials, data transmission unit and data processing application in smart phone with user interface. This platform makes it possible to detect the chemical environments at home in a real-time and interactive manner.

6. Conclusion

GSA coupled with AI greatly promotes the development of the electronic nose. Low-power-consumption and chip-scale devices can be manufactured by various scalable techniques including FSP, USP, and FET fabrication techniques. As a result, such a device has the potential to be placed at our home and operated by ourselves without the need of skilled specialists. In addition to the original purpose of imitating human odor sensing, GSA can also be utilized to detect odor-
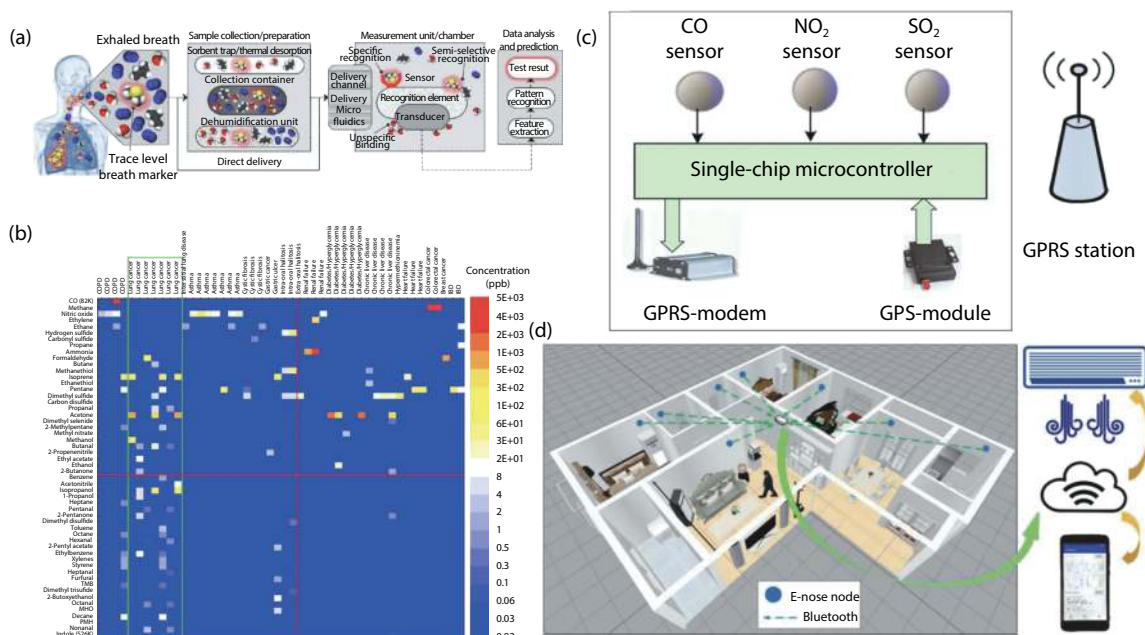
Fig. 5. (Color online) Application of gas sensor array [11, 17, 98]. (a) Processes involved in breath testing, (b) gases associated with different kinds of diseases including cancer, (c) GPRS based air pollution monitoring system, (d) real-time indoor gas monitoring by smart phone in smart buildings.

less gas including explosives and toxics. GSAs are application-oriented devices, thus, to arrange a GSA system with minimum redundancy, one needs to select each type of sensor unit based on the target gas molecules, requiring prior knowledge about the chemical compounds to be detected in the corresponding scenarios.

Research efforts around GSA in the future may fall into several parts. Devices working at room temperature are highly expected for package simplification and continuous working mode with ultra-low-power consumption[93, 94]. The influence of temperature and humidity on GSA need to be mitigated, and long recover time of MOX sensors are desired to be optimized[95]. The design and optimization of AI algorithms suitable for gas classification and gas mixture differentiation requires large datasets of sensor response as well as good repeatability. From the application perspectives, GSA finds large potential in disease diagnosis but at the same time faces the challenge of meeting strict medical regulations. Gas sensors in wearable and flexible smart electronics as newborn can meet with explosive growth of smart watch and sport bracelets in the market[96, 97]. Typical devices as a part of Internet of things integrated into smart home/city can greatly enhance life quality of people and promote performance and interactivity of infrastructure in modern life. Joint efforts from material science, chemistry, electronics, and computer science will surely bring a bright future for GSA.

Acknowledgements

References

[1] Ko H C, Stoykovich M P, Song J, et al. A hemispherical electronic eye camera based on compressible silicon optoelectronics. Nature, 2008, 454(7205), 748

[2] Song Y M, Xie Y, Malyarchuk V, et al. Digital cameras with designs inspired by the arthropod eye. Nature, 2013, 497(7447), 95

[3] Yang Y, da Costa R C, Fuchter M J, et al. Circularly polarized light detection by a chiral organic semiconductor transistor. Nat Photonics, 2013, 7(8), 634

[4] Lorenzo N, Wan T L, Harper R J, et al. Laboratory and field experiments used to identify Canis lupus var. familiaris active odor signature chemicals from drugs, explosives, and humans. Anal Bioanal Chem, 2003, 376, 1212

[5] Bartolozzi C, Natale L, Nori F, et al. Robots with a sense of touch. Nat Mater, 2016, 15, 921

[6] Sundaram S, Kellnhofer P, Li Y, et al. Learning the signatures of the human grasp using a scalable tactile glove. Nature, 2019, 569(7758), 698

[7] Romano J, Hsiao K, Niemeyer G, et al. Human-inspired robotic grasp control with tactile sensing. IEEE Trans Robot, 2011, 27, 1067

[8] Hochreiter S, Schmidhuber J. Long short-term memory. Neural Comput, 1997, 9(8), 1735

[9] Persaud K, Dodd G. Olfactory system using a model nose. Nature, 1982, 299, 352

[10] Güntner A T, Koren V, Chikkadi K, et al. E-nose sensing of low-ppb formaldehyde in gas mixtures at high relative humidity for breath screening of lung cancer. ACS Sens, 2016, 1(5), 528

[11] Chen J, Chen Z, Boussaid F, et al. Ultra-low-power smart electronic nose system based on three-dimensional tin oxide nanotube arrays. ACS Nano, 2018, 12(6), 6079

[12] Peng G, Tisch U, Adams O, et al. Diagnosing lung cancer in exhaled breath using gold nanoparticles. Nature Nanotechnol, 2009, 4(10), 669

[13] Fahad H M, Hiroshi H, Amani M, et al. Room temperature multiplexed gas sensing using chemical-sensitive 3.5-nm-thin silicon transistors. Sci Adv, 2017, 3, e1602557

[14] Penza M, Cassano G. Chemometric characterization of Italian wines by thin-film multisensors array and artificial neural networks. Food Chem, 2004, 86(2), 283

[15] Capelli L, Sironi S, Del Rosso R. Electronic noses for environmental monitoring applications. Sensors, 2014, 14(11), 19979

[16] Hakim M, Broza Y Y, Barash O, et al. Volatile organic compounds of lung cancer and possible biochemical pathways. Chem Rev, 2012, 112, 5949

[17] Konvalina G, Haick H. Sensors for breath testing: from nanomaterials to comprehensive disease detection. Accounts Chem Res, 2014, 47(1), 66

[18] Peng G, Hakim M, Broza Y Y, et al. Detection of lung, breast, colorectal, and prostate cancers from exhaled breath using a single array of nanosensors. British J Cancer, 2010, 103(4), 542-551

[19] Derek R M, Sheikh A A, Patricia A M. nanoscale metal oxide-based heterojunctions for gas sensing: a review. Sens Actuators B, 2014, 204, 250

[20] Chen X, Wong C K Y, Yuan C A, et al. Nanowire-based gas sensors. Sens Actuators B, 2013, 177, 178

[21] Yeow J T W, Wang Y. A review of carbon nanotubes-based gas sensors. J Sens, 2009, 2009, 493904

[22] Abdellah A, Abdelhalim A, Loghin F, et al. Flexible carbon nanotube based gas sensors fabricated by large-scale spray deposition. IEEE Sens J, 2013, 13(10), 4014

[23] Park H J, Kim W J, Lee H K, et al. Highly flexible, mechanically stable, and sensitive NO2 gas sensors based on reduced graphene oxide nanofibrous mesh fabric for flexible electronics. Sens Actuators B, 2018, 257, 846

[24] Peng P, Zhao X J, Pan X F, et al. Gas classification using deep convolutional neural networks. Sensors, 2018, 18, 157

[25] Yoon J W, Lee J H. Toward breath analysis on a chip for disease diagnosis using semiconductor-based chemiresistors: Recent progress and future perspectives. Lab on a Chip, 2017, 17(21), 3537

[26] Yang Z, Sassa F, Hayashi K. A robot equipped with a high-speed LSPR gas sensor module for collecting spatial odor information from on-ground invisible odor sources. ACS Sens, 2018, 3(6), 1174

[27] Lecun Y, Bengio Y, Hinton G. Deep learning. Nature, 2015, 521(7553), 436

[28] Donahue J, Hendricks L A, Rohrbach M, et al. Long-term recurrent convolutional networks for visual recognition and description. IEEE Trans Patt Anal Mach Intell, 2017, 39(4), 677

[29] Mnih V, Kavukcuoglu K, Silver D, et al. Human-level control through deep reinforcement learning. Nature, 2015, 518(7540), 529

[30] Radford A, Metz L, Chintala S. Unsupervised representation learning with deep convolutional generative adversarial networks, 1-16. Retrieved from http://arxiv.org/abs/1511.06434

[31] He K, Zhang X, Ren S, et al. Deep residual learning for image recognition. Proceedings of the IEEE Computer Society Conference on Computer Vision and Pattern Recognition, 2016, 770

[32] Lledo P M, Gheusi G, Vincent J D. Information processing in the mammalian olfactory system. Physiol Rev, 2005, 85, 281

[33] Korsching S I. Olfactory receptors. In: Encyclopedia of Biological Chemistry. 2nd ed. 2003, 61, 149

[34] Suslick K S, Rakow N A, Sen A. Colorimetric sensor arrays for molecular recognition. Tetrahedron, 2004, 60, 11133

[35] Nugroho F A A, Darmadi I, Cusinato L, et al. Metal-polymer hybrid nanomaterials for plasmonic ultrafast hydrogen detection. Nat Mater, 2019, 18(5), 489

[36] Gan T, Hu S. Electrochemical sensors based on graphene materials. Microchimica Acta, 2011, 175, 1

[37] Pavia L, Lampman G M, Kritz G S, et al. Introduction to organic laboratory techniques. 4th ed. Thomson Brooks/Cole, 2006, 797

[38] Liu H, Zhang L, Li K H H, et al. Microhotplates for metal oxide semiconductor gas sensor applications-towards the CMOS-MEMS monolithic approach. Micromachines, 2018, 9(11), 557

[39] Bodenhöfer K, Hierlemann A, Noetzel G, et al. Performances of mass-sensitive devices for gas sensing: Thickness shear mode and surface acoustic wave transducers. Analyt Chem, 1996, 68(13), 2210

[40] Punetha D, Pandey S K. CO gas sensor based on e-beam evaporated ZnO, MgZnO, and CdZnO thin films: a comparative study. IEEE Sens J, 2019, 19(7), 2450

[41] Di Giulio M, D'Amico A, Di Natale C, et al. SnO2 thin films for gas sensor prepared by RF reactive sputtering. Sens Actuators B, 1995, 25(1), 465

[42] Park J, Mun J, Shin J S, et al. Highly sensitive two dimensional MoS2 gas sensor decorated with Pt nanoparticles. Royal Soc Open Sci, 2018, 5(12), 1

[43] Kim I, Choi W Y. Hybrid gas sensor having TiO2 nanotube arrays and SnO2 nanoparticles. Int J Nanotechnol, 2017, 14, 155

[44] Guo B, Bermak A, Chan P C, et al. Characterization of integrated tin oxide gas sensors with metal additives and ion implantations. IEEE Sens J, 2008, 8, 1397

[45] Yamazoe N. Grain size effects on gas sensitivity of porous SnO2-based elements. Sens Actuat B, 1991, 3, 147

[46] Huang J, Wan Q. Gas sensors based on semiconducting metal oxide one-dimensional nanostructures. Sensors, 1991, 9(12), 9903

[47] Seiyama T, Futada H, Era F, et al. Gas detection by activated semiconductive sensor. Denki Kagaku, 1972, 40(3), 244

[48] Shankar P, Bosco J, Rayappan B. Gas sensing mechanism of metal oxides: The role of ambient atmosphere, type of semiconductor and gases - A review. Sci Lett J, 2015, 4, 126

[49] Wang C, Yin L, Zhang L, et al. Metal oxide gas sensors: Sensitivity and influencing factors. Sensors, 2010, 10(3), 2088

[50] Das S, Jayaraman V. SnO2: A comprehensive review on structures and gas sensors. Prog Mater Sci, 2014, 66, 112

[51] Xu F, Ho H. Light-activated metal oxide gas sensors- a review. Micromachine, 2017, 8, 333

[52] Fan S W, Srivastava A K, Dravid V P. UV-activated room-temperature gas sensing mechanism of polycrystalline ZnO. Appl Phys Lett, 2009, 95, 142106

[53] Korotcenkov G. Metal oxides for solid-state gas sensors: what determines our choice. Mater Sci Eng B, 2007, 139, 1

[54] Jin C G, Kurzawski P, Hierlemann A, et al. Evaluation of multitransducer arrays for the determination of organic vapor mixtures. Anal Chem, 2008, 80, 227

[55] Wang D, Ma Z, Dai S, et al. Low-temperature synthesis of tunable mesoporous crystalline transition metal oxides and applications as Au catalyst supports. J Phys Chem C, 2008, 112, 13499

[56] Korotcenkov G, Brinzari V, Boris Y, et al. Surface Pd doping influence on gas sensing characteristics of SnO2 thin films deposited by spray pyrolysis. Thin Solid Films, 2003, 436, 119

[57] Korotcenkov G, Gulina L, Cho B K, et al. The role of doping effect on the response of SnO2-based thin film gas sensors: analysis based on the results obtained for Co-doped SnO2 films deposited by spray pyrolysis. Sens Actuators B, 2013, 182, 11

[58] Khakani M A E, Dolbec R, Serventi A M, et al. Pulsed laser deposition of nanostructured tin oxide films for gas sensing applications. Sens Actuators B, 2001, 77, 383

[59] Natkaeo A, Phokharatkul D, Hodak J H, et al. Highly selective sub-10 ppm H2S gas sensors based on Ag-doped CaCu3Ti4O12 films. Sens Actuators B, 2018, 260, 571

[60] Kolmakov A, Klenov D.O, Lilach Y, et al Enhanced gas sensing by individual SnO2 nanowires and nanobelts functionalized with Pd catalyst particles. Nano Lett, 2005, 5, 667

[61] De Lacy Costello B P J, Ewen R J, Jones P R H, et al. A study of the catalytic and vapour-sensing properties of zinc oxide and tin dioxide in relation to 1-butanol and dimethyldisulphide. Sens Actu-

at B, 1999, 61, 199

[62] Zhu C L, Chen Y J, Wang R X, et al. Synthesis and enhanced ethanol sensing properties of α-Fe$_2$O$_3$/ZnO heteronanostructures. Sens Actuat B, 2009, 140, 185

[63] Jing Z, Zhan J. Fabrication and gas-sensing properties of porous ZnO nanoplates. Adv Mater, 2008, 20, 4547

[64] Pan X, Zhao X, Bermak A, et al. A humidity-insensitive NO$_2$ gas sensor with high selectivity. IEEE Electron Device Lett, 2016, 37(1), 92

[65] Fan Z, Chen J, McKinley A, et al. Breath level acetone discrimination through temperature modulation of a hierarchical ZnO gas sensor. IEEE Sens Lett, 2017, 1(5), 1

[66] Wang L, Teleki A, Pratsinis S E, et al. Ferroelectric WO$_3$ nanoparticles for acetone selective detection. Chem Mater, 2008, 20(15), 4794

[67] Zhang Y, Zhao J, Du T, et al. A gas sensor array for the simultaneous detection of multiple VOCs. Sci Rep, 2017, 7(1), 1

[68] Pan X, Liu X, Bermak A, et al. Self-gating effect induced large performance improvement of ZnO nanocomb gas sensors. ACS Nano, 2013, 7(10), 9318

[69] Li X, Lu Y, Hemminger J C, et al. Catalytically activated palladium@platinum nanowires for accelerated hydrogen gas detection. ACS Nano, 2015, 9, 3215

[70] Itoh T, Miwa T, Tsuruta A, et al. Development of an exhaled breath monitoring system with semiconductive gas sensors, a gas condenser unit, and gas chromatograph columns. Sensors, 2016, 16(11), 1891

[71] McAlpine M C, Ahmad H, Wang D, et al. Highly ordered nanowire arrays on plastic substrates for ultrasensitive flexible chemical sensors. Nat Mater, 2007, 6, 379

[72] Lu J G, Fan Z. Chemical sensing with ZnO nanowire field-effect transistor. IEEE Trans Nanotechnol, 2006, 5(4), 393

[73] Fan Z, Wang D, Chang P C, et al. ZnO nanowire field-effect transistor and oxygen sensing property. Appl Phys Lett, 2004, 85(24), 5923

[74] Cho J H, Kim Y W, Na K J, et al. Wireless electronic nose system for real-time quantitative analysis of gas mixtures using micro-gas sensor array and neuro-fuzzy network. Sens Actuators B, 2008, 134, 104

[75] Ozmen A, Dogan E. Design of a portable e-nose instrument for gas classifications. IEEE Trans Instrum Meas, 2009, 58, 3609

[76] Ha D, Ahmed U, Pyun H, et al. Multi-mode operation of principal component analysis with k-nearest neighbor algorithm to monitor compressors for liquefied natural gas mixed refrigerant processes. Comput Chem Eng, 2017, 106, 96

[77] Wei G, Li G, Zhao J, et al. Development of a LeNet-5 gas identification CNN structure for electronic noses. Sensors, 2019, 19(1), 217

[78] Buszewski B, Kesy M, Ligor T, et al. Human exhaled air analytics: Biomarkers of diseases. Biomed Chromatogr, 2007, 21, 553

[79] Boots A W, van Berkel J J, Dallinga J W, et al. The versatile use of exhaled volatile organic compounds in human health and disease. J Breath Res, 2012, 6, 027108

[80] Rydosz A. A negative correlation between blood glucose and acetone measured in healthy and type 1 diabetes mellitus patient breath. J Diabetes Sci Technol, 2015, 9(4), 881

[81] Chang J E, Lee D S, Ban S W, et al. Analysis of volatile organic compounds in exhaled breath for lung cancer diagnosis using a sensor system. Sens Actuators B, 2018, 255, 800

[82] Trivedi D K, Sinclair E, Xu Y, et al. Discovery of volatile biomarkers of parkinson's disease from sebum. ACS Cent Sci, 2019, 5(4), 599

[83] Abdullah A H, Shakaff A Y M, Adom A H, et al. Chicken farm malodour monitoring using portable electronic nose system. Chem Eng Trans, 2012, 30, 55

[84] Dentoni L, Capelli L, Sironi S, et al. Development of an electronic nose for environmental odour monitoring. Sensors, 2012, 12, 14363

[85] Di Francesco F, Lazzerini B, Marcelloni F, et al. An electronic nose and indicatorvolatiles for monitoring of the composting process. EnViron, 2001, 35, 1225

[86] Helli O, Siadat M, Lumbreras M. Qualitative and quantitative identification of H$_2$S/NO$_2$ gaseous components in different reference atmospheres using a metal oxide sensor array. Sens Actuators B, 2004, 103, 403

[87] Bastos A C, Magan N. Potential of an electronic nose for the early detection and differentiation between streptomyces in potable water. Sens Actuators B, 2006, 116, 151

[88] Stuetz R M, George S, Fenner R A, et al. Monitoring waste water BOD using a non-specific sensor array. J Chem Technol Biotechnol, 1999, 74, 1069

[89] Lamagna A, Reich S, Rodriguez D, et al. The use of an electronic nose to characterize emissions from a highly polluted river. Sens Actuators B, 2008, 131, 121

[90] Chen K, Gao W, Emaminejad S, et al. Printed carbon nanotube electronics and sensor systems. Adv Mater, 2016, 28, 4397

[91] Pan Z W, Dai Z R, Wang Z L. Nanobelts of semiconducting oxides. Science, 2001, 291, 1947

[92] Zampolli S, Elmi I, Ahmed F, et al. An electronic nose based on solid state sensor arrays for low-cost indoor air quality monitoring applications. Sens Actuators B, 2004, 101, 39

[93] Lin Y, Chen J, Tavakoli M M, et al. Printable fabrication of a fully integrated and self-powered sensor system on plastic substrates. Adv Mater, 2019, 31(5), 1

[94] Lin Y J, Gao Y, Fang F, et al. Recent progress on printable power supply devices and systems with nanomaterials. Nano Res, 2018, 11(6), 3065

[95] Pan X, Zhao X, Chen J, et al. A fast-response/recovery ZnO hierarchical nanostructure based gas sensor with ultra-high room-temperature output response. Sens Actuators B, 2014, 206, 764

[96] Huang L, Lin S, Xu Z, et al. Fiber-based energy conversion devices for human-body energy harvesting. Adv Mater, 2019, 1902034, 1

[97] Fan Z, Ho J C, Takahashi T, et al. Toward the development of printable nanowire electronics and sensors. Adv Mater, 2009, 21(37), 3730

[98] Al-Ali A R, Zualkernan I, Aloul F. A mobile GPRS-sensors array for air pollution monitoring. IEEE Sens J, 2010, 10(10), 1666