Rational Design of Semiconductor-Based Chemiresistors and their Libraries for Next-Generation Artificial Olfaction

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1. Introduction

A sense of smell is essential for the survival, life, and enjoyment of human beings. The realization of robust artificial olfaction (or electronic nose: e-nose) that can substitute for or surpass human olfaction has thus gained increasing attention. Wilkens and Hartman suggested an early version of the e-nose in 1964. Persaud and Dodd proposed an e-nose for odor classification in 1982. To date, numerous e-nose systems using sensor arrays have been explored to find new functionalities. These systems demonstrate promising potential in a wide range of applications, including medical diagnosis, environmental monitoring, food quality assessment, smart farming, identifying explosives, searching and rescuing, diagnosing disease, and discriminating among different harmful chemicals.

Artificial olfaction based on gas sensor arrays aims to substitute for, support, and surpass human olfaction. Like mammalian olfaction, a larger number of sensors and more signal processing are crucial for strengthening artificial olfaction. Due to rapid progress in computing capabilities and machine-learning algorithms, on-demand high-performance artificial olfaction that can eclipse human olfaction becomes inevitable once diverse and versatile gas sensing materials are provided. Here, rational strategies to design a myriad of different semiconductor-based chemiresistors and to grow gas sensing libraries enough to identify a wide range of odors and gases are reviewed.

Key approaches include the use of p-type oxide semiconductors, multinary perovskite and spinel oxides, carbon-based materials, metal chalcogenides, their heterostructures, as well as heterocomposites as distinctive sensing materials, the utilization of bilayer sensor design, the design of robust sensing materials, and the high-throughput screening of sensing materials. In addition, the state-of-the-art and key issues in the implementation of electronic noses are discussed. Finally, a perspective on chemiresistive sensing materials for next-generation artificial olfaction is provided.

In the mammalian olfactory system, odorants are initially detected by olfactory receptors (ORs) covering the surface of the cilia projected from olfactory sensory neurons (OSNs), which are located in the olfactory epithelium lining the nasal cavity. These signals are transmitted to the glomeruli in the olfactory bulb, where a high degree of signal integration happens. Finally, the signals are sent through mitral cells to a higher brain region (olfactory cortex), and the signals are subsequently combined or modified in a variety of ways by parallel processing for analysis and interpretation.

Each OR can detect various kinds of odorants, and similarly, each odorant can also be recognized by a number of ORs. That is, the olfactory system determines multiple odorants from various combinations of ORs. For better olfaction, both OSNs and ORs should be abundant. A larger number of OSNs is advantageous for detecting trace concentrations of analytes and ligands. For instance, dogs with more OSNs are better at detecting explosives, searching and rescuing, diagnosing disease, and assessing agricultural products. If a mammal can detect larger numbers of faint gas components within odors, he can perceive and identify the odors more accurately. From this perspective, gas sensors with lower detection limits would be assembled to the stronger artificial olfaction. Kinds of ORs are also important. Mammals are known to have ~1000 different kinds of ORs, and combinations of dissimilar ORs enable the discrimination of a myriad of odorants. To mimic this, sensor arrays consisting of small number (5–20) of sensors that show
incomplete but partial specificity toward different individual or complex airborne chemicals were proposed for odor identification via pattern recognition in the 1980s. These were called an "electronic nose" or "artificial olfaction."[2,3] Multivariate analysis has generally been used to extract smell patterns for recognition. However, a small number of sensors often limited the identification of complex chemicals, indicating the importance of sensor diversity for achieving high-performance artificial olfaction. Signal processing is another key parameter for determining the performance of artificial olfaction. The human has a smaller number of functional OR genes than other mammals but has a larger number of glomeruli in olfactory bulb, suggesting that humans have abundant information processed by glomeruli. Furthermore, humans possess an elaborate olfactory cortex for interpreting olfactory inputs.[35] Thus, the signal processing capability of human olfaction is excellent. This demonstrates that artificial olfaction can become stronger and more versatile through progress in signal processing assisted by computational capabilities.

There are many reasons we need to implement various new applications using well-defined artificial olfaction. First, artificial olfaction can substitute for human olfaction. The human nose suffers from olfactory fatigue, whereas artificial olfaction can be used for the automated, unmanned, uninterrupted, and fatigue-free monitoring of chemicals. Second, artificial olfaction can complement human olfaction. Note that different mammals have dissimilar olfactory capabilities due to different species-specific repertoires of OR genes. For instance, humans are more sensitive to floral, spicy, dairy, and sweaty/pungent smells, while mice show more sensitivity toward nutty, minty/camphor/menthol, and sulfurous/meaty odors (Figure 1d).[32] This suggests that human olfaction as it stands is the consequence of natural selection. That is, humans have evolved to detect ecologically important odors for survival. Therefore, artificial olfaction can be utilized to detect or discriminate among odors that humans are incapable of smelling. Third, artificial olfaction can detect various new synthetic odors and chemicals that are produced mostly through industrial development. Because the evolution of human olfaction is unable to catch up with the rapid appearance of uncountable numbers of new odors and chemicals, various and sophisticated on-demand electronic noses with new functionalities should be designed, fabricated and implemented in the near future.

The number of sensors in a sensor array is analogous to the number of kinds of ORs in mammals, which determines odor discrimination capabilities. The high sensitivity of sensors is similar to a large number of OSNs. Signal processing in artificial olfaction can be compared with glomeruli processing and analysis activity in the olfactory cortex. This hints that a larger number of sensors with different sensing patterns and high sensitivity are needed to discriminate among the more complex odors for applications such as smart farming, food quality control, and breath analysis (Figure 2).[36,37] Many different techniques are being used to analyze data, which have both benefits and limitations.[4,38] Data-driven analyses like principal component analysis (PCA), hierarchical cluster analysis (HCA), principal component regression (PCR), partial least squares (PLS) regression, and so on are generally simple to use but exhibit a relatively low tolerance to data, which is an impediment to making general classifications and/or prediction models. In contrast, when more abundant gas sensing data are available from more sensors, it is better to use event-driven artificial intelligence (AI) techniques such as the k-nearest neighbor algorithm (KNN), artificial neural networks (ANN), fuzzy logic based algorithms, genetic algorithms (GA), and so on, or combinations of AI algorithms for creating general models. With larger amounts of training data, the performance of deep
learning algorithms with more hidden layers is much better than that of classical learning algorithms,\cite{37} which will lead to stronger artificial olfaction. Triggered by rapid progress in computation capability, wireless data communication, and artificial intelligence, machine learning using big gas sensing data that are wirelessly collected from numerous sensors will become...
possible and popular, and it will lead to the next-generation of artificial olfaction in which highly complex chemical quantities can be discriminated in a precise manner. To accomplish this, huge numbers of highly integrated gas sensors with simple structures and low power consumption are necessary to collect big gas sensing data. Oxide semiconductor chemiresistors with many irreplaceable advantages—such as high and distinctive responses to a wide range of different gases, reversibility, simple structures, Si compatibility, facile miniaturization, and cost effectiveness—are excellent platforms for realizing sophisticated and integrated artificial olfaction. In addition, carbon nanotubes (CNTs), graphene-based materials, transition metal dichalcogenides (TMDs), and 2D early-transition metal carbides and nitrides (MXenes) are also considered as emerging chemiresistors for artificial olfaction that can be operated at low temperatures.

There are several key requirements for realizing high performance artificial olfaction. To identify or discriminate complex chemicals using highly integrated artificial olfaction, the use of many sensors with partial or high selectivity toward different chemicals is essential. High gas responses are often underestimated but essential in enhancing the performance of artificial olfaction because odors generally consist of hundreds to thousands of chemicals in extremely low concentrations. To recognize odors and to achieve steady-state signals within a short time, rapidly responding chemiresistors are needed. To decrease power consumption, sensing materials that can be operated at room temperature or mildly heated temperature are advantageous. A moderate sensing temperature is also important in protecting less thermally stable circuitry in monolithic sensor array systems. The gas sensing characteristics and baseline resistances of most chemiresistive sensors are
usually dependent on ambient moisture and temperature. If many sensors with significantly different operation temperatures are integrated within a small volume of a one-chip artificial olfaction, the heat transfer between sensors may induce additional interference due to temperature fluctuation. Accordingly, an array of sensors with the same operational temperature is better at simplifying artificial olfaction. Finally, sensor stability under operating conditions, chemical poisoning, and heat exposure is indispensable. Therefore, high-performance, integrated, cost-effective, accurate, and reliable artificial olfaction requires an array of many chemiresistive sensors with high gas responses, simple structures, rapid response speeds, distinctive partial gas selectivity, negligible interferences from ambient humidity/temperature, and low operation temperatures, and long-term stability. Most chemiresistors cannot satisfy all the above requirements simultaneously. However, sensor diversity and artificial olfaction diversity will enable the implementation of high performance next-generation artificial olfacton; both stem from diversity in sensing materials.

There have been many attempts to develop artificial olfaction using various chemiresistive sensing materials. Recent developments in artificial olfaction using different sensing materials have been previously reviewed. Nevertheless, the diversity of sensing materials still remains insufficient in implementing artificial olfaction with new and on-demand functionality; thus, new strategies should be established to design sensing materials that cover a wide range of odors and gases. Accordingly, in this contribution, rational and promising strategies to realize ultimate diversity in semiconductor-based sensing materials for next-generation artificial olfaction are reviewed, suggested, and discussed. In general, a variety of oxide semiconductor chemiresistors can lead to more combinations of different oxides and exhibit recognizable responses to a wide range of gases, suggesting the promising potential for use in various electronic noses in the near future. Therefore, in this review, the primary focus is directed toward the design of diverse oxide-based sensing materials using p-type oxide semiconductors, multinary perovskite and spinel oxides, and heterostructures/heterocomposites between different oxides. In addition, bilayer-design sensors with various filtering/catalytic overlayers and combinatorial sensor design were discussed as the powerful tools for tailoring of gas selectivity and high-throughput screening of optimal sensing materials for artificial olfaction, respectively. Emerging chemiresistors such as CNTs, graphene-based materials, TMDs, and MXenes are also discussed in relation to their distinctive gas sensing characteristics at low temperatures and their future potential. Finally, key challenges in the fabrication and optimization of electronic noses are discussed, and future perspectives on artificial olfaction are provided.

2. p-Type Oxide Semiconductor Chemiresistors

Oxide semiconductor chemiresistors are divided into n-type or p-type according to the majority charge carrier. In pure oxide semiconductors, the majority charge carrier is primarily determined by nonstoichiometry (cation deficiency, cation excess, oxygen deficiency, and oxygen excess), which can be altered by varying ambient oxygen partial pressure (\(P_{O_2}\)). However, most oxide semiconductor gas sensors are operated in air atmospheres with a constant of \(P_{O_2} = 0.21\), so the majority charge carrier is generally fixed during sensor operation.

Since the discovery of oxide sensors in 1960s, n-type oxide semiconductors, such as SnO\(_2\), ZnO, TiO\(_2\), WO\(_3\), In\(_2\)O\(_3\), Fe\(_2\)O\(_3\), MoO\(_3\), and V\(_2\)O\(_5\), have been widely investigated as practical gas sensing materials (87.94% of total publications on oxide semiconductor gas sensors) (Figure 3a), whereas p-type oxide semiconductors such as CuO, NiO, Co\(_3\)O\(_4\), Cr\(_2\)O\(_3\), MnO\(_2\), and Mn\(_3\)O\(_4\), have been relatively less studied (12.06% of total publications) (Figure 3b).

One of the key reasons for the decreased attention on p-type oxide chemiresistors is their low gas response. Distinctively different conduction paths in n-type and p-type oxide semiconductor chemiresistors account for dissimilar gas responses. In n-type oxide semiconductors, the adsorption of oxygen and its ionization to \(O_2^-\), \(O^-\), and \(O^{2-}\) at 100–450 °C establishes the electronic core(semiconducting)-shell(resistive electron depletion layer: EDL) configuration (Figure 3c, left). When the particles are larger than twice the thickness of the EDL, for conduction to occur, the electron must overcome the back-to-back Schottky barrier at the inter-particle contact (grain boundary), and the conduction is thus explained by the serial connection between semiconducting cores and resistive shells. In contrast, in p-type oxide semiconductors, the ionized oxygen \(O_2^-\), \(O^-\), and \(O^{2-}\) on the surface attracts the counter charge of majority charge carriers (holes), which establishes different electronic core(less conducting)–shell(accumulation hole accumulation layer: HAL) structures (Figure 3d, left). Under this configuration, when the particle diameter is larger than twice the HAL, conduction is determined by the parallel competition between two contributions: one along the semiconducting HAL with the narrower cross-sectional area and the other along the less-conducting core with the wider cross-sectional area. When the electrons are injected into the sensing materials by the reaction between ionized oxygen and the reducing gas, the electron concentration in the EDL increases in n-type chemiresistors (Figure 3c, right), whereas the hole concentration in the HAL decreases in p-type chemiresistors (Figure 3d, right), leading to the opposite chemiresistive variations. It should be noted that n-type oxide semiconductors with serial conduction paths are more advantageous for achieving higher variation of overall sensor resistance than the p-type semiconductors with parallel conduction paths. Indeed, Hübner et al. reported that the gas response in p-type oxide semiconductors is calculated to be the square root of that in n-type oxide semiconductors with identical morphology

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S_p = \sqrt{S_n}
\]

where \(S_p\) and \(S_n\) are the gas responses of p-type and n-type oxide chemiresistors. This suggests that the design of highly sensitive gas sensors using coarse particles of pure p-type oxide semiconductors is challenging.
Nevertheless, there are many reasons we need to further investigate p-type oxide semiconductors as new sensing materials for artificial olfaction. First, p-type oxide semiconductors show distinctive catalytic activity and thus can be used for detecting specific chemicals. [65] Most p-type oxide semiconductors (CuO, NiO, Co₃O₄, MnO₂, or Mn₃O₄) generally show one to two orders of magnitude higher oxygen adsorption than their n-type counterparts (Figure 3e). [66] In addition, they usually show multivalency and facile redox reactions. Accordingly, most p-type oxide semiconductors are excellent catalysts for oxidizing various reducing gases with low reactivity. It should be noted that n-type oxide semiconductors are usually used to detect highly reactive gases such as C₂H₅OH,[67,68] acetone,[69] HCHO,[70] CO,[71–73] H₂,[74] and NO₂,[75–78] but generally...
did not exhibit high responses to less reactive aromatic gases, stable gases, and gases with relatively high molecular weights. Note that p-type oxide semiconductors with excellent catalytic activity are more suitable for detecting less reactive gases. Accordingly, the use of both n-type and p-type oxide semiconductors with substantially different gas sensing characteristics is beneficial for extending detectable gas species and for widening the gas sensing library, which will strengthen artificial olfaction significantly.

Second, the problem of low gas responses can be solved by electronic sensitization via aliovalent doping, a powerful and promising approach to enhance the gas response of p-type oxide semiconductors (Figure 3f). When the same number of electrons is injected into p-type oxide semiconductors, a p-type gas sensor with lower background hole concentration would show higher chemiresistive variation. In this respect, doping higher valence cations is effective. For instance, the gas responses and sensor resistance of pure and Fe-, Cr-, Sn-, Ti-, and Nb-doped NiO sensors are shown in Figure 4.\textsuperscript{[79–83]} In all these studies, the pure NiO sensor showed negligibly low gas responses. However, the doping of higher valence cations dramatically increased the gas responses. For instance, the doping of 3.04 at% Fe, 2.56 at% Cr, 16.7 at% Sn, 10 at% Ti, and 9.09 at% Nb to various NiO nanostructures enhanced the gas responses 2179, 121, 50.3, 259.8, and 1460 fold, respectively. All the doped specimens showed no second phase in X-ray diffraction, and the sensor resistance in air \((R_a)\) markedly increased with aliovalent doping, indicating that the background hole concentration is decreased to a great extent by the incorporation of higher valence cations into the NiO lattice. Thus, the dramatic increase in gas response could be explained primarily by the decrease in background hole concentrations because the changes in surface area, mesopores, and catalytic activity due to aliovalent doping were relatively less significant. This is supported by the prominent increase in gas responses due to aliovalent doping in five different NiO sensors regardless of their morphology and doping cations, which is consistent with the literature reports that the doping of Al,\textsuperscript{[84]} W,\textsuperscript{[85]} and Sn\textsuperscript{[86,87]} also enhances the gas response of NiO-based sensors via controlling the charge carrier concentration. Note that the background hole concentration can be also controlled by contact with different oxide materials with dissimilar work function values. This effect will be discussed later in the heterostructure section.

Third, various gas-accessible nanostructures can be used to maximize gas response. Note that the gas response of n-type oxide semiconductors increases significantly when the particle size is decreased to twice or comparable to EDL thickness (so-called nano effect).\textsuperscript{[40,88–91]} Similarly, when the portion of chemiresistive HAL in a p-type oxide semiconductor is large, the gas response can become high enough to detect
trace concentrations of gases even after taking the square roots. Moreover, the design of highly gas accessible structures with minimal aggregation between nanostructures is also very important in achieving high gas response. Indeed, there have been many reports on enhancing the gas responses of p-type oxide semiconductors using highly gas accessible hierarchical,[92–96] mesoporous,[97–100] monolayer inverse opal,[101] macroporous,[102] hollow,[103,104] fibrous,[105] and well-dispersed[106,107] nanostructures.

Fourth, the gas response and selectivity of p-type oxide semiconductor gas sensors can be enhanced or tuned by loading noble metal catalysts. For instance, the loading of Pt, Au, and Pd is known to increase the gas response or to change the gas selectivity of NiO.[108–113] Co$_3$O$_4$,[114–118] Cr$_2$O$_3$,[119,120] and CuO-based based sensors.[121] This can be explained by the catalytic promotion of sensing reactions (chemical sensitization) and/or by a decrease in background hole concentration due to contact with noble metals with different work function values (electronic sensitization).

Finally, volatile sulfur compounds (VSCs) such as H$_2$S and CH$_3$SH can be detected in a highly selective manner using p-type CuO with a high chemical affinity to the sulfur molecule. Thus, p-type CuO[122–124] can be used for the selective detection of VSCs. The reaction between ionized surface oxygen ($O^-$) and H$_2$S is probable at low H$_2$S concentration, while the conversion of the near-surface region of CuO into metallic CuS can be considered as the sensing mechanism at high H$_2$S concentration.[126] It should be noted that VSCs are very important in our daily lives because they are associated with smells such as general malodor,[125] oral malodor,[126] and wastes or landfill gases,[127] as well as those found in the fermentation of food[128] and wine quality control.[129] From this perspective, p-type CuO can increase diversity in gas sensing and artificial olfaction.

3. Multinary Oxides (Perovskite and Spinel)

Gas sensing materials can be expanded further by considering multinary oxides with the structures of perovskite and spinel consisting of two or more different cations. A large number of combinations between different cations enables the design of the diverse sensing materials needed to explore new gas sensing properties and to implement stronger artificial olfaction.

3.1. Perovskite Oxides

In the perovskite structure ($ABO_3$), the eight larger A cations occupy the corner positions, the one smaller B cation occupies the body-centered position, and the six oxygen anions occupy the face-centered positions of a cubic unit cell.[130] There are abundant perovskite-structured oxides; most of them are semiconductors, although some perovskite materials show metallic conductivity and dielectric behaviors. When the sensing materials are highly insulating, it becomes difficult to measure sensor resistance using conventional and cost-effective electric circuits. In contrast, if the conductivity of an oxide is too high, the chemiresistive variation by the injection of charge carriers due to sensing reaction becomes low. Thus, the conductivity of chemiresistors should be moderate. Not all perovskite materials are used for gas sensing. However, it should be noted that ≈90% of metallic elements can be accommodated within perovskite-structured oxides in a stable manner. Moreover, in perovskite structures ($ABO_3$), each site can be occupied with multiple cations (A and A’, B and B’) with different sizes or charges (Figure 5) if the tolerance factor ($t = (r_A + r_O)/\sqrt{2}$ ($r_B + r_O$)): $r_A$, $r_B$, and $r_O$: ionic radii of cation A, cation B, and anion oxygen) to maintain the perovskite structure ranges from 0.8 to 1.0. Thus, even excluding small portions of perovskite oxides with metallic and dielectric behaviors, there still remains a huge number of perovskite oxides for gas sensing materials. The chemiresistive perovskite oxides reported in the literature are summarized in Table 1.[131–168] All the listed perovskite oxides are p-type oxide semiconductors. Note that the perovskite oxides show distinctive gas sensing behaviors toward many different analyte gases, which can provide a new gas sensing library.

Peña and Fierro reported a comprehensive review on perovskite oxides[169] and explained that cationic/anionic non-stoichiometry, gas and oxygen adsorption, stability, acid–base characteristics, redox properties, and catalytic activities can be designed or tailored by the compositional control of perovskite materials. Accordingly, perovskite oxides have been used as promising catalysts for NO oxidation/reduction, oxidation/ reforming of hydrocarbons, CO$_2$ reduction, oxygen evolution reaction in electrolytic water splitting devices, metal–air batteries, and regenerative fuel cells.[130,170–174] Most of these catalytic properties in perovskite oxides are also closely related to the gas sensing reaction in chemiresistors, suggesting the promising potential for perovskite-based gas sensing materials.

Figure 5. The structure of ABO$_3$ perovskite-type oxide and various possible doping strategies. Reproduced with permission.[130] Copyright 2015, American Chemical Society.
There are two different types of gas sensors using perovskite oxides as sensing materials. The first one is the oxygen sensor used to measure the oxygen concentration of engine exhaust gas, which assists in controlling the air-to-fuel ratio in internal combustion engines. The oxygen partial pressure dependence of point defect concentration and electrical conductivity is responsible for monitoring oxygen concentration in a relatively reducing atmosphere and at high temperatures (>500 °C); the sensor usually cannot detect other gases. Thus, it is difficult to use this type of sensor in composing sensor arrays for artificial olfaction in an ambient air atmosphere. The second one is the typical oxide semiconductor gas sensor to show chemiresistive variation through the charge transfer from the reaction between oxide semiconductor gas sensor to show chemiresistive variation and the use of multications in A or B sites.

Oxygen sensors can be tailored using synthetic methods and multiple cations at the A and B sites. The smaller cation A and larger cation B usually occupy tetrahedral and octahedral sites, respectively. In the normal spinel, oxygen forms a cubic close packing, cation A occupies 1/8 of tetrahedral sites, and cation B occupies 1/2 of octahedral sites. MgAl$_2$O$_4$ is a representative normal spinel, A cations replace half of the B sites. This type of material is also used to enhance gas response and selectivity (Table 1). Li et al. reported the CO response of the LaFe$_{1-x}$M$_x$O$_3$ (M = Cr, Mn, Co, and Ni) sensors increased with increasing catalytic activity to oxidized CO. The above results suggest that the response and selectivity of perovskite-based sensing materials can be tailored by the combination of A and B sites, the control of oxygen adsorption, and the use of multication in A or B sites.

### 3.2. Spinel Oxides

Oxides with spinel structure are another emerging sensing material. Spinels with the general formula of AB$_2$O$_4$ can also form a number of different materials by combining various A cations (Li, Mn, Zn, Cd, Co, Cu, Ni, Mg, Fe, Ca, Ge, Ba, and so on) and B cations (B = Al, Cr, Mn, Fe, Co, Ni, Ga, In, Mo, and so on). The smaller cation A and larger cation B usually occupy tetrahedral and octahedral sites, respectively. In the normal spinel, oxygen forms a cubic close packing, cation A occupies 1/8 of tetrahedral sites, and cation B occupies 1/2 of octahedral sites. MgAl$_2$O$_4$ is a representative normal spinel (Figure 6a). A unit cell consists of 8 A, 16 B, and 32 O. In the normal spinel, A cations replace half of the B sites. This is referred to as B(AB)O$_4$ (Figure 6b). NiFe$_2$O$_4$ is a typical inverse spinel. That is, half of the Fe$^{3+}$ occupies tetrahedral sites, and Ni$^{2+}$ and the remaining half of Fe$^{3+}$ occupy octahedral sites (Fe$^{3+}$Ni$^{2+}$Fe$^{3+}$)O$_4$ (Figure 6b). The complex spinel $A_xB_y(A_{1-x}B_{2-y})O_4$: 0 < y < 1 is the intermediate between normal and inverse spinels. CuAl$_2$O$_4$ is a representative complex spinel.
(Cu$_{1-y}$Al$_y$(Cu$_y$Al$_2$)$_{1-y}$)O$_4$) (Figure 6c). To date, various spinel oxides have been explored to design new gas sensors,[178,179] and the results in the literature are summarized in Table 2.[180–222] Note that a number of different gases can be detected using spinel oxides. Furthermore, considering that research on spinel-based gas sensing materials is still in the nascent stage, more gas sensing materials with different or new performance due to compositional variation are expected to be found. Both n-type and p-type semiconductors are balanced in spinel oxides, whereas most perovskite materials show p-type conductivity. Accordingly, spinel oxides show a promising potential for gas sensing materials to cover a wide range of different gases. These can be utilized in strengthening artificial olfaction. It is also worth noting that both A and B sites may be occupied by the same element with a different valence. For instance, Co$_3$O$_4$, Mn$_3$O$_4$, and Fe$_3$O$_4$ are spinel oxides. However, in this section, the gas sensing characteristics of multinary spinel oxides will be mainly discussed.

In spinel oxides, there are oxygen tetrahedra (AO$_4$) and oxygen octahedra (BO$_6$) with different metal-oxygen binding energies. Thus, even the same composition of materials can show different gas sensing characteristics depending on the spinel structures. Wu et al.[194] prepared partially inverse and normal Zn-ferrites (Zn$_{0.5}$Fe$_{0.5}$O$_4$ and Zn(Fe$_2$)O$_4$) and compared their gas sensing characteristics. The response ($R_a/R_g$; $R_a$: resistance in air, $R_g$: resistance in gas) of partially inverse Zn-ferrite sensors to 100 ppm H$_2$S at 260 °C was 64, which was approximately 9 times higher than that of a normal Zn-ferrite sensor. This clearly shows that the cation distribution in spinel oxides is a key parameter for determining gas sensing characteristics.

**Table 2.** Spinel-based oxide semiconductor chemiresistors reported in the literature.[180–222]

| Arial | Sensing material | Target gas$^a$ | Ref. | Type | Sensing material | Target gas$^a$ | Ref. |
|------|------------------|----------------|------|------|------------------|----------------|------|
| p    | CaFe$_2$O$_4$    | E              | [180] | p    | NiCo$_2$O$_4$    | O$_3$, NO$_x$  | [202,203] |
| p    | NiFe$_2$O$_4$    | C, A           | [181–184] | p    | CuCo$_2$O$_4$    |  | [204] |
| p    | CuFe$_2$O$_4$    | LPG, H$_2$     | [185,186] | p    | ZnCo$_2$O$_4$    | LPG            | [205–207] |
| n    | MgFe$_2$O$_4$    | P              | [187] | n    | CdIn$_2$O$_4$    | Cl$_2$         | [208] |
| n    | MnFe$_2$O$_4$    | NO$_x$, NH$_3$ | [188,189] | n    | MgIn$_2$O$_4$    | E              | [209] |
| n    | CoFe$_2$O$_4$    | NO$_x$         | [190] | p    | CoAl$_2$O$_4$    | CO, CO$_2$     | [210,211] |
| n    | ZnFe$_2$O$_4$    | E, A, I, T, H$_2$S | [191–195] | n    | NiAl$_2$O$_4$    | M              | [212] |
| n    | γ-Fe$_2$O$_3$    | E, A           | [196,197] | n    | CuAl$_2$O$_4$    | O$_3$          | [213] |
| p    | Co$_3$Ga$_2$O$_4$| B, A, AD, F    | [198] | p    | CoCr$_2$O$_4$    | X              | [214,215] |
| p    | Ni$_2$Ga$_2$O$_4$| B, A, AD, F    | [198] | p    | ZnCr$_2$O$_4$    | X              | [216] |
| n    | NiGa$_2$O$_4$    | TMA, E         | [199] | n    | Zn$_2$Sn$_2$O$_4$| A, E, T        | [217–219] |
| n    | Cu$_2$Ga$_2$O$_4$| A, AD          | [198] | n    | Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$| H$_2$S | [220] |
| n    | Zn$_2$Ga$_2$O$_4$| LPG            | [200] | n    | Mg$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$| H$_2$ | [221] |
| n    | Cd$_2$Ga$_2$O$_4$| F              | [201] | n    | Cd$_{0.5}$Mg$_{0.5}$Ga$_2$O$_4$| E | [222] |

$^a$A, acetone; AD, acetaldehyde; B, benzene; C, chlorine; E, ethanol; F, formaldehyde; I, isopropanol; M, methanol; P, petrol; T, toluene; TMA, trimethylamine; X, xylene.

**Figure 6.** a–c) Representative structures of: a normal spinel (MgAl$_2$O$_4$), b) an inverse spinel (NiFe$_2$O$_4$), and c) a complex spinel (CuAl$_2$O$_4$) in different styles and views. The green and purple polyhedra correspond to octahedral and tetrahedral metal occupation sites, respectively. Reproduced with permission.[177] Copyright 2017, American Chemical Society.
There are many multivalence cations (Mn, Fe, Co, Ni, and Cu) in the spinel oxides in Table 2, so the redox pair (M$^{n+}$/M$^{(n+1)+}$) can facilitate oxygen adsorption and promote the gas sensing reaction, as explained in the section about p-type oxide semiconductor chemiresistors. The correlation between oxygen adsorption and the gas sensing reaction in spinel oxide has been investigated by Šutka et al.\cite{182} They prepared two different p-type Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ ($x = 0, 0.01, 0.05$, and $0.1$) samples by slow cooling or rapid quenching next to thermal annealing at 800 °C and observed that the sensors prepared by slow cooling show higher gas response and sensor resistance than those prepared by rapid quenching. A slow-cooled sensor with high [Ni$^{2+}$]/[Ni$^{3+}$] value could make more ionized surface oxygen (O$^-$) by taking electrons from Ni$^{2+}$ (by the oxidation of Ni$^{2+}$ into Ni$^{3+}$) and thus enhance the gas response.

Chen et al. also reported the possibility to tune the gas sensing characteristics of spinel oxides by controlling oxygen adsorption (Figure 7).\cite{201} They prepared four different sensors by electrospinning: Ga-rich CdGa$_2$O$_4$ nanofibers containing CdO nanoparticles (CdO/Ga-rich CGO NFs), Ga-rich CGO NFs, stoichiometric CGO NFs, and CdO NFs. The work function of an n-type CGO is relatively smaller than those of SnO$_2$, In$_2$O$_3$, and ZnO, which can be used to have different oxygen adsorption amounts. The amount of oxygen adsorption can be also modulated by cation off-stoichiometry. From the temperature-programmed desorption results (Figure 7e,f), they revealed that the normalized oxygen adsorption amounts of CdO/Ga-rich CGO NFs and Ga-rich CGO NFs are significantly higher than that of stoichiometric CGO and explained that the aliovalent doping of Ga$^{3+}$ to Cd$^{2+}$ is responsible for the increase in oxygen adsorption and HCHO response. The nonstoichiometry is another key parameter that can control the gas sensing characteristics in spinel oxides. Finally, the gas-sensing materials and libraries will be more abundant and diverse through the use of multiple cations, both in the A and B sites of spinels (AB$_2$O$_4$).

4. Oxide–Oxide Heterostructures and Heterocomposites

The formation of heterostructures or heterocomposites between two different oxides is an alternative strategy to achieve diverse gas sensing characteristics by modulating chemiresistive EDL/HAL, tuning the catalytic activity, modifying acid-base properties, and controlling chemical affinity toward a specific gas. The results in the literature to enhance/modify the gas response and/or selectivity using oxide–oxide heterostructures or heterocomposites are summarized in Table 3.\cite{214,216,223–327} The tailoring of gas sensing characteristics by the loading/doping of
Table 3. Gas sensors based on oxide–oxide heterostructures and heterocomposites.[214,216,223–327]

| Dimension | Junction | Sensing material | Catalyst Material | Target gas | Ref. | Dimension | Junction | Sensing material | Catalyst Material | Target gas | Ref. |
|-----------|----------|------------------|-------------------|-------------|------|-----------|----------|------------------|-------------------|-------------|------|
| 1–0       | n–p      | In$_2$O$_3$      | Bi$_2$O$_3$       | E           | [223] | 3–0       | n–p      | $\alpha$-Fe$_2$O$_3$ | Co$_2$O$_3$       | E           | [276] |
|           |          | Cu$_2$O$_3$      | E                 |             | [224] |           |          | Sn$_2$O$_3$       | NiO               | E, TEA       | [277,278] |
|           |          | SnO$_2$          | TMA, H$_2$        |             | [225,226]|           |          | Ti$_2$O$_3$       | NiO               | N           | [279] |
|           |          | CuO              | H$_2$S            |             | [227,228]|           |          | ZnFe$_2$O$_4$     | CuO               | X           | [280] |
|           |          | LSCM             | F                 |             | [229]  |           |          | ZnO              | NiO               | A            | [281,282] |
|           |          | TiO$_2$          | CuO               |             | [230]  | p–n       |          | Co$_2$O$_3$       | ZnO               | E            | [283] |
|           |          | NiO              | A                 |             | [231]  |           |          | NiO              | $\alpha$-Fe$_2$O$_3$ | T          | [284] |
|           |          | WO$_4$           | Cr$_2$O$_3$       | E, BE       | [232,233]| Sphere    |          | In$_2$O$_3$       | E                 | [285] |
|           |          | CuO              | H$_2$S            |             | [234]  | n–n       |          | $\alpha$-Fe$_2$O$_3$ | ZnO               | A            | [286] |
|           |          | NiO              | H$_2$S            |             | [235]  |           |          | SnO$_2$          | $\alpha$-Fe$_2$O$_3$ | E          | [287] |
|           |          | Ru$_2$O$_5$      | A, NO$_2$         |             | [236,237]|           |          | In$_2$O$_3$       | F                 |             | [288] |
|           |          | V$_2$O$_5$       | CuO               |             | [238]  |           |          | ZnO              | E                 |             | [289] |
|           |          | ZnO              | CO$_2$O$_3$       | NO$_2$, E   | [239]  |           |          | ZnO              | CdO               | E            | [290] |
|           |          | Cr$_2$O$_3$      | TMA, E            |             | [240,241]| Flower    |          | ZnSnO$_2$        | ZnO               | TEA          | [291] |
|           |          | CuO              | TMA               |             | [242]  |           |          | Mn$_2$O$_4$       | E                 |             | [243] |
|           |          | NiO              | E                 |             | [244]  |           |          | ZnCo$_2$O$_4$     | A                 |             | [245] |
|           |          | ZnSn$_2$O$_3$   | NiO               |             | [246]  |           |          | $\alpha$-Fe$_2$O$_3$ | H$_2$S          |             | [247] |
| p–n       |          | CuO              | $\alpha$-Fe$_2$O$_3$ | H$_2$S      | [248]  | NiO       | $\alpha$-Fe$_2$O$_3$ | E                 |             | [249] |
| n–n       | $\alpha$-Fe$_2$O$_3$ | ZnFe$_2$O$_4$    | TEA              |             | [250]  |           |          | TiO$_2$          | BL                |             | [251] |
|           |          | TiO$_2$          | Sn$_2$O$_3$       | H$_2$       | [254]  |           |          | ZnO              | E                 |             | [253] |
|           |          | ZnO              | E                 |             | [255]  |           |          | SnO$_2$          | E                 |             | [256] |
|           |          | MoO$_3$          | $\alpha$-Fe$_2$O$_3$ | X           | [258]  | Flower    |          | SnO$_2$          | E                 |             | [259] |
| p–p       |          | Co$_2$O$_3$      | NiO               |             | [260]  |           |          | SnO$_2$          | L$_2$O$_3$        |             | [261] |
| n–i       |          | SnO$_2$          | E                 |             | [262]  |           |          | SnO$_2$          | ZnO               | E            | [263] |
| 1–1       | p–n      | SnO$_2$          | Bi$_2$O$_3$       | NO$_2$      | [264]  |           |          | ZnO              | In$_2$O$_3$       | TMA          | [265,266] |
|           |          | NiO              | $\alpha$-Fe$_2$O$_3$ | T           | [266]  |           |          | ZnO              | In$_2$O$_3$       | TMA          | [267] |
|           |          | TiO$_2$          | $\alpha$-Fe$_2$O$_3$ | TMA         | [268]  |           |          | ZnO              | NiO               | E            | [269] |
|           |          | ZnO              | Sn$_2$O$_2$       | A           | [269]  |           |          | Ni$_2$O$_3$       | SnO$_2$          | E            | [270] |
|           |          | $\alpha$-Fe$_2$O$_3$ | A$_{0.35}$V$_2$O$_5$ | E           | [264]  |           |          | $\alpha$-Fe$_2$O$_3$ | E                 |             | [271] |
|           |          | ZnO              | Sn$_2$O$_2$       | NO$_2$, A   | [265,266]|           |          | In$_2$O$_3$       | F                 |             | [272] |
|           |          | NB(MoO$_4$)$_2$  | Ru$_2$O$_3$       | H$_2$S      | [267]  | Urchin    |          | Ni$_2$O$_3$       | SnO$_2$          | E            | [273] |
| 2–0       | n–p      | ZnO              | NiO               |             | [268]  |           |          | Ni$_2$O$_3$       | SnO$_2$          | E            | [269] |
|           |          | CuO              | TiO$_2$           | TEA         | [269]  |           |          | Ni$_2$O$_3$       | SnO$_2$          | E            | [270] |
|           |          | NiO              | WO$_3$            | NO$_2$      | [271]  |           |          | Co$_3$O$_4$       | G$_2$O$_3$        | X            | [272] |
|           |          | $\alpha$-Fe$_2$O$_3$ | E                 |             | [273]  | n–i       |          | In$_2$O$_3$       | Co$_2$O$_3$       | H$_2$         | [274] |
|           |          | SnO$_2$          | TiO$_2$           | TEA         | [274]  |           |          | SnO$_2$          | E                 |             | [275] |
|           |          | WO$_3$           | In$_2$O$_3$       | H$_2$S      | [275]  | Cube      |          | ZnO              | Y$_2$O$_3$        | M            | [276] |
|           |          | SnO$_2$          | A                 |             | [275]  |           |          | SnO$_2$          | E                 |             | [277] |

$^a$A, acetone; e, ethanol; F, formaldehyde; BE, 2-butanone; BL, butanol; X, xylene; T, toluene; TMA, trimethylamine; TEA, triethylamine; N, ammonia; M, 2-methoxyethanol; Abbreviation of materials: LSCM, La$_{0.75}$Sr$_{0.25}$Cr$_0.5$Mn$_0.5$O$_{3-\delta}$; NB(MoO$_4$)$_2$, NaBi(MoO$_4$)$_2$. 
noble metal catalysts such as Pt, Pd, Au, Ag, and Rh on oxide semiconductors was not investigated in this review because it has been intensively studied before.\textsuperscript{[128–138]}

In general, n-type and p-type binary oxides have been used as both sensing and catalytic materials. Accordingly, the wide range of combinations between different oxides offers diverse sensing materials. Moreover, the sensing materials can be further diversified through the combination between binary and multinary oxides or between different multinary oxides. In Table 3, the heterostructures or heterocomposites were classified according to the dimensions of two different oxide materials. Note that the heterostructures in this review generally refer a continuous configuration of structures decorated with a discrete configuration of other materials. For instance, a continuous configuration of 1D oxide nanowires/nanofibers decorated with a discrete configuration of 0D nanoparticles (NPs) is referred to as a 1–0 heterostructure. Similarly, 2D dense, macroporous, or monolayer inverse opal films decorated with 0D oxide NPs are referred to as 2–0 heterostructures. 3D structures decorated with 0D oxide NPs are 3–0 heterostructures. 1–1 heterostructures refer to 1D nanowires with many 1D branches of different oxides. The mixtures between two different 0D NPs are classified separately as 0–0 heterocomposites because both oxides in heterocomposites can play the role of the connecting (and thus conducting) phase, unlike the heterostructures. In this section, the main focus is directed at the tailoring of gas sensing patterns by the formation of various heterostructures and heterocomposites because there have been good reviews on the gas sensing mechanism of heterojunctions by Miller et al.\textsuperscript{[339]} the gas sensors using hybrid materials by Jian et al.\textsuperscript{[340]} and the sensitization mechanism of additively-loaded/doped oxide chemiresistors by Degler et al.\textsuperscript{[341]}

4.1. Oxide–Oxide Heterostructures

As shown in Table 3, various oxide catalytic have been decorated to detect a number of different analyte gases and/or to acquire distinctive gas detecting patterns. Although only the primary target gases for each sensor were given in Table 3, the majority of the sensors exhibited substantial responses to a wide range of different gases, and gas responses and/or selectivity were significantly altered by the formation of oxide heterostructures or heterocomposites. For instance, CoO$_2$(I)–NiO(0), NiO(1)–Fe$_2$O$_3$(0), ZnO(1)–Cr$_2$O$_3$(0), NiO(1)–Fe$_2$O$_3$(1), NiO(2)–WO$_3$(0), and ZnO(3)–NiO(0) heterostructures clearly demonstrated the potential to change gas sensing patterns toward 6–12 different gases by decorating a discrete configuration of oxide catalysts on a continuous configuration of gas sensors (Figure 8).\textsuperscript{[240,249,259,262,270,281]} The results suggest that the formation of heterostructures can be used to expand the coverage of analyte gases for detection as well as the gas sensing library for artificial olfaction.

In 1–0 sensors, the conduction occurs not along the discrete 0D nanoparticles (NPs), but along the continuous 1D nanowires, nanorods, nanobelts, or nanofibers. Accordingly, the 1°–0° sensor (1D n-type oxide semiconductors decorated with 0D p-type oxide NPs) follows the chemiresistive variation of n-type oxide semiconductors (e.g., Figure 8c), whereas the 1°–0° sensor does the chemiresistive variation of p-type oxide semiconductors (e.g., Figure 8a,b). Nevertheless, decorated 0D oxide catalysts also influence the gas sensing characteristics of 1D oxide gas sensors to a great extent. If one considers the n-type oxide semiconductors nanowires that have diameters that are significantly larger than twice the EDL, the contribution of chemiresistive variation in EDL is too low to achieve a high gas response.\textsuperscript{[39]} When n-type oxide nanowires are decorated with p-type oxide NPs, the EDL of n-type oxide semiconductors beneath the p-NPs becomes thicker because of the electron–hole recombination. Under this 1°–0° configuration, because the conducting n-channel shows larger configurational change upon exposure to reducing gas, chemiresistive variation becomes higher. Similarly, the hole concentration in the HAL of p-type oxide nanowires is decreased by decorating the n-NPs, which also enhances the gas response. Finally, the establishment of n–n’ or p–p’ heterocontacts with dissimilar work function values can also enhance the gas response when the majority charge carrier is transferred from 1D oxide nanostructures to contacting 0D NPs. In the 1°–0° sensor, the higher hole concentration of 0D p-NPs would lead to a wider EDL in 1D n-semiconductors because the extension of EDL involves electron–hole recombination procedures. Accordingly, the size and number density of 0D oxide NPs as well as charge carrier concentration and work function of 0D oxide materials play key roles in modulating the EDL and HAL of 1D oxide structures. The design of new and highly sensitive sensing materials using 2–0, 3–0, and 1–1 heterostructures by controlling the EDL and HAL can be understood from the same perspective.

4.2. Oxide–Oxide Heterocomposites

The formation of 0–0 heterocomposites provides another method to achieve diverse and demand-based gas sensing patterns (Table 3). For instance, Co$_2$O$_3$(0)–SnO$_2$(0), Cr$_2$O$_3$(0)–ZnCr$_2$O$_4$(0), SnO$_2$(0)–WO$_3$(0), and SnO$_2$(0)–CeO$_2$(0) composites demonstrate the promising potential to design various gas sensing patterns by controlling selectivity via compositional modulation (Figure 9).\textsuperscript{[216,298,300,324]} In 1–0, 2–0, 3–0, and 1–1 heterostructures, 0D or 1D oxide catalysts are generally decorated on sensing surfaces by various synthetic routes such as e-beam evaporation, vapor phase growth, sputtering, hydrothermal reaction, and impregnation after the fabrication of continuous configurations of 1D, 2D, or 3D sensing materials. Thus, sensing and catalytic materials are well-separated, and sensing materials show generally dispersed configurations. The former facilitates the control of gas sensing properties and the latter is advantageous to enhancing gas accessibility. In 0–0 heterocomposites, the conduction occurs along one oxide and/or the other oxide depending on their connecting configuration, which can be explained by the well-known percolation problem.\textsuperscript{[342]} Because the conduction path is one of the most important factors determining gas sensing characteristics, various parameters to influence percolation should be taken into account: the shape, size, size distribution, and agglomeration of oxide particles; the porosity and pore size of agglomerates; the majority charge carrier type, carrier concentration, and work function of the two oxide materials; heterococontact configuration; and the
degree of mixing. The complexity of these parameters may hamper the reproducible design of sensing materials. In contrast, however, these complexities can provide other opportunities to diversify the sensing materials once the key parameters are under good control.

To design diverse 0–0 heterocomposite sensing materials using a solid-state mixing method in a reproducible and reliable manner, it is necessary to simplify the parameters that influence the sensing characteristics. In principal, smaller nanoparticles exhibit a higher gas response because the chemiresistive parts near the surface can be maximized. However, the smaller nanoparticles tend to agglomerate into large secondary particles because the van der Waals interaction is inversely proportional to the particle size. The agglomeration hampers not only the dispersion, but also the mixing of the two different oxides. Moreover, the nanoscale particles are thermally less stable, which may deteriorate the long-term stability of sensors operated at elevated temperatures. Accordingly, it would be better to use highly standardized, reproducible, and thermally stable oxide particles that can be dispersed and mixed in a uniform way.

Figure 8. a) Schematic diagram of Co$_3$O$_4$ nanorods (NRs) decorated with NiO nanoclusters fabricated by multistep glancing angle deposition (GLAD) and gas responses ($R_\text{g}/R_\text{a} - 1$, $R_\text{a}$: resistance in air, $R_\text{g}$: resistance in gas) of pure and NiO-decorated Co$_3$O$_4$ NRs to 6 different gases (conc.: 50 ppm) at 350 °C. Reproduced with permission. Copyright 2018, American Chemical Society. b) Pristine NiO NRs and α-Fe$_2$O$_3$-decorated NiO nanocorals fabricated by multistep GLAD and their gas responses ($R_\text{g}/R_\text{a} - 1$) to 8 different gases (conc.: 5 ppm for NO$_2$ and 50 ppm for other gases) at 350 °C. Adapted with permission. Copyright 2017, Wiley-VCH. c) Pristine and Cr$_2$O$_3$-decorated ZnO nanowires (NWs) and their gas responses ($R_\text{g}/R_\text{a}$) to 12 different gases (conc.: 5 ppm) at 275 °C. Adapted under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0). Copyright 2016, Springer Nature. d) Pristine and α-Fe$_2$O$_3$-functionalized NiO nanotubes and their gas responses ($R_\text{g}/R_\text{a}$) to 12 different gases (conc.: 5 ppm) at 300 °C. Adapted with permission. Copyright 2019, American Chemical Society. e) Pristine and W-decorated NiO nanoigloos and their gas responses ($R_\text{g}/R_\text{a}$ or $R_\text{a}/R_\text{g}$) to 7 different gases (conc.: 5 ppm) at 300 °C. Adapted with permission. Copyright 2019, American Chemical Society. f) Pristine and NiO-decorated ZnO nanoflowers and their gas responses ($R_\text{a}$/$R_\text{g}$) to 6 different gases (conc.: 100 ppm) at 300 °C. Adapted with permission.
Because the uniform mixing of two different dry oxide NPs is challenging, the intimate mixing of two different oxide NPs in a slurry state and subsequent deposition of slurry onto microelectrodes via microdispensing, ink-jet printing, and direct electrohydrodynamic (EHD) patterning can be considered for fabricating sensing film in a reproducible manner. Instead of solid-state mixing, solution-based chemical routes can be considered for preparing well-defined 0–0 nanocomposites. For instance, spray pyrolysis and electrospinning enable the preparation of the intended morphology of secondary oxide particles (nanospheres or nanofibers) consisting of different oxide nanoparticles. The composition is not only uniform within secondary particles but also highly controllable. The porosity of spheres and nanofibers can be controlled using organic sacrificial precursors or by controlling the processing parameters, which facilitates the design of well-defined 0–0 heterocomposites for sensing applications. Galvanic replacement is another promising route for preparing 0–0 heterocomposites by replacing the cations in the host nanostructures with other cations with different ionization tendencies. Uniform mixing between two different cations can be achieved by atomic scale substitution, and there have been few reports that demonstrate the potential of this method in preparing composite gas sensing materials.

Conduction and chemiresistive variation are primarily dependent upon the continuous configuration of oxide semiconductors, while the discrete configurations of oxide NPs influence gas sensing characteristics by modulating the

**Figure 9.** a) Co$_3$O$_4$ and Co$_3$O$_4$–SnO$_2$ composite hollow spheres and their gas responses ($R_1/R_0$, $R_0$: resistance in gas, $R_0$: resistance in air) to 7 different gases (conc.: 5 ppm) at 275 and 300 °C. Reproduced with permission.[298] Copyright 2018, American Chemical Society. b) ZnO hollow spheres and Cr$_2$O$_3$–ZnCr$_2$O$_4$ nanocomposite powders and their gas responses ($R_1/R_0$ or $R_0/R_1$) to 9 different gases (conc.: 5 ppm) at 325 °C (for ZnO) and 275 °C (for Cr$_2$O$_3$–ZnCr$_2$O$_4$). Adapted with permission.[310] Copyright 2016, Elsevier. c) SnO$_2$ nanotubes and SnO$_2$–WO$_3$ composite nanofibers and their gas responses ($R_1/R_0$) to 6 different gases (conc.: 100 ppm) at 300 °C. Adapted with permission.[100] Copyright 2019, Elsevier. d) CeO$_2$, SnO$_2$, and CeO$_2$–SnO$_2$ nanoparticles (NPs) and their gas responses ($R_1/R_0$) to 6 different gases (conc.: 60 ppm) at 300 °C. Adapted with permission.[324] Copyright 2018, Elsevier.
EDL/HAL and promoting gas sensing reactions. Unlike 1–0, 2–0, and 3–0 heterostructures, in 0–0 heterocomposites, both oxides can form continuous conduction paths independently. For instance, in 0–0 heterocomposites, if both n-type and p-type oxide semiconductors are connected between electrodes, the resistance decrease in n-type oxide semiconductors upon exposure to reducing gas is counteracted by the resistance increase in p-type oxide semiconductors. Although the opposite chemiresistive variation tends to decrease the overall gas response, combining n- and p-type oxide semiconductors with significantly different gas sensing patterns can lead to a new and different gas sensing library. This can be tailored by controlling the cross-sectional area of each conducting path. The design of oxide semiconductor gas sensors using heterocomposites has been reviewed by Korotchenkov and Cho.\[361\]

4.3. Gas Selectivity in Oxide–Oxide Heterostructures and Heterocomposites

The control of conducting channels/paths in 1–0, 2–0, 3–0, and 1–1 heterostructures as well as 0–0 heterocomposites explains the enhancement of gas response effectively. However, it does not account for the variation in gas selectivity. The changes in gas selectivity and gas sensing patterns in heterostructures and heterocomposites are more closely associated with the acid-base property, catalytic activity, and chemical affinity toward a gas of decorating oxides.

Figure 10a shows the relative acidity scale ($N_M - 2\delta_M$, $N_M$: formal oxidation state of the metal in a compound, $\delta_M$: Sanderson's partial charges of the metal ion) of representative oxide chemiresistors and additives calculated by Jeong et al.\[362\] Note that the acid-base property of sensing/additive materials is known to influence the decomposition reaction of analyte gases. Jinkawa et al.\[363\] reported that the addition of 5 wt% basic oxides such as La$_2$O$_3$, Cs$_2$O, Sm$_2$O$_3$, CaO, Gd$_2$O$_3$, and NiO significantly enhances the C$_2$H$_5$OH response of the SnO$_2$ sensor. They explained the results in relation to the following two different C$_2$H$_5$OH decomposition reactions: 1) C$_2$H$_5$OH is dissociated into more reactive CH$_3$CHO (g) + H$_2$ (g) on basic oxide and 2) C$_2$H$_5$OH is dissociated into less reactive C$_2$H$_4$ (g) + H$_2$O (g) on acidic oxide. This is in line with other reports on the enhancement of the C$_2$H$_5$OH response of gas sensors from the loading of basic additives.\[360,364\] suggesting that gas selectivity can be modified by the acid-base property of sensing materials. Moreover, acidic oxides interact strongly with basic gases, and basic oxides interact strongly with acidic gases. For instance, acidic oxides such as MoO$_3$ and WO$_3$ exhibit high responses and selectivity to basic gases such as NH$_3$, dimethylamine, and trimethylamine.\[365–372\] Thus, the combining acidic and basic oxides can provide other opportunities to tune the gas selectivity.

The catalytic activities of materials in heterostructures and heterocomposites also play a key role in gas selectivity. As shown in Figure 10b,c, the catalytic activities of metal oxides differ significantly.\[373,374\] In general, the catalytic activities of noble metal oxides are the highest, and those of p-type oxide semiconductors are higher than those of n-type oxide semiconductors, although those depend upon the gases to be oxidized. It should be noted that the catalytic activity of a sensing material determines the oxidation as well as reforming of analyte gas during gas transport through the sensing film and influences the reaction between analyte gas and negatively charged oxygen in the gas sensing reaction. Accordingly, if catalytically dissimilar oxides were combined in the forms of heterostructures and heterocomposites, gas selectivity can be varied significantly.

The chemical affinity of decorated 0D NPs toward a specific gas can also significantly alter the gas selectivity. Shao et al.\[227\]

\[
\text{(a) Relative acidity}
\]

\[
\text{(b) T (°C) (activity) = 31.6 \mu mol/m^2s of Formic Acid oxidation)}
\]

\[
\text{(c) T1/2 (°C) (activity) = 50% combustion of hydrogen)}
\]

Figure 10. a) Relative acid scale ($N_M - 2\delta_M$, $N_M$: formal oxidation state of the metal in a compound, $\delta_M$: Sanderson's partial charges of the metal ion) of representative oxide catalysts. Adapted with permission.\[362\] Copyright 2008, Wiley-VCH. b) Temperature required to reach constant activity for HCOOH oxidation for various oxide catalysts. Adapted with permission.\[373\] Copyright 2002, Elsevier. c) Temperature for 50% combustion of hydrogen ($T_{1/2}$) for various oxide catalysts. Adapted with permission.\[374\] Copyright 1981, Elsevier.
reported that the H$_2$S response and selectivity of n-SnO$_2$ NWs increased significantly with decoration with p-CuO NPs (Figure 11). In air atmospheres, the extension of EDL in n-SnO$_2$ NWs beneath p-CuO NPs leads to high sensor resistance. Decorated p-type CuO NPs with a high chemical affinity to sulfur are converted into the metallic nature of CuS by reaction with H$_2$S, removing the nanoscale p–n junction and leading to a dramatic decrease in sensor resistance. Indeed, various heterostructures/composites between CuO and n-type oxide semiconductors (e.g., CuO–SnO$_2$,$^{[375–377]}$ CuO–ZnO,$^{[303,378]}$ and CuO–In$_2$O$_3$)$^{[295,379]}$ have been widely used for the selective detection of VSCs. Mo and Ag additives are also known to show high chemical affinity to H$_2$S.$^{[380,381]}$ In addition, the response and selectivity of ZnO and SnO$_2$ NW sensors to trimethylamine are enhanced by decoration with Cr$_2$O$_3$ O$_x$ NPs, which are also attributed to the high chemical affinity between decorating oxide NPs and gas.$^{[225,240]}$ In this perspective, the formation of heterostructures or heterocomposites using materials with a high chemical affinity toward specific gases can increase controllability in gas sensing and artificial olfaction.

5. Bilayer Oxide Semiconductor Gas Sensors

To tune gas selectivity, bilayer gas sensors consisting of lower oxide semiconductor sensing films and upper filtering/catalytic layers can be considered. When sensing electrodes are located beneath the sensing film, it is possible to modify the gas sensing characteristics by coating the film with various overlayers.

5.1. Bilayer Sensors with Molecular Sieve Overlayer

First, when filtering gas molecules with different kinetic diameters in a physical manner, molecular sieves using zeolite, metal organic frameworks, SiO$_2$-based layers, and graphene oxide can be utilized.$^{[186]}$ In Table 4,$^{[186–199]}$ the kinetic diameters of various gases and the pore sizes of candidate zeolites and metal–organic frameworks (MOFs) for molecular sieving are summarized. Table 4 clearly shows that analyze gases with...
Different sizes can be separated by molecular sieving. This has been proven as a promising strategy to achieve the selective detection of gases with relatively small kinetic diameters, such as H$_2$,[420–424] NH$_3$,[424] HCHO,[425] and H$_2$S.[426]

Güntner et al.[427] reported that a Pd–SnO$_2$ sensor located within a small cavity that is closed by a membrane (a dense support) shows excellent HCHO selectivity with negligible cross-responses to larger interference gases. The sensor structure can be simplified and miniaturized further by coating the sensing materials with the molecular sieve layer directly.

Furthermore, Zhou et al.[424] coated two different zeolitic imidozolate frameworks (ZIFs) with different pore sizes (≈ 3.4 Å for ZIF-8 and ≈ 4.8 Å for ZIF-71) on ZnO nanorods and demonstrated the control of gas sensing patterns toward five different gases (NH$_3$, H$_2$, C$_2$H$_5$OH, acetone, and benzene) by tailoring the molecular sieving effect (Figure 12a,b). Tian et al.[425] also reported that the coating of ZIF-8 significantly enhances HCHO selectivity in ZnO nanorods by suppressing interference from gases with larger kinetic diameters (C$_2$H$_5$OH, CH$_3$OH, acetone, and toluene) (Figure 12c,d). When the majority of constituting gases in an odor are small in kinetic diameter, the possible interferences from the gases with large kinetic diameters can be removed effectively using a molecular sieve. In this case, odor discrimination using artificial olfaction becomes simpler and more precise with the use of proper molecular sieves.

A bilayer sensor with a molecular sieve, in particular, shows the promising potential to discriminate among gases with similar chemistry. Note that oxide semiconductor gas sensors often show similar selectivity to gases with analogous chemistry, such as alcohols (methanol, ethanol, propanol, and butanol),[428,429] amine-based gases (NH$_3$, methylamine, dimethylamine, and propane),[429] and volatile sulfuric compounds (H$_2$S and methyl mercaptan).[430–432] Molecular sieving provides an effective solution when designing artificial olfaction for identifying gases with similar chemistry but dissimilar kinetic diameters.

The physical filtering of gas can be combined with the catalytic promotion of gas sensing reactions to further tune gas sensing characteristics. Both lower sensing and upper molecular sieving layers can be used for catalytic promotion. Weber et al.[423] decorated ZnO nanowires with Pd nanoparticles to enhance the overall gas responses (triangles and circles in Figure 12e) and then coated the nanowires with a ZIF-8 layer to achieve highly selective and sensitive detection of target H$_2$ with negligible cross-responses to interference gases with larger kinetic diameters (benzene, ethanol, toluene, and acetone) (circles and cubes in Figure 12e). The catalyst-loaded zeolite overlayer has been utilized to combine the physical and chemical tuning of gas selectivity.

Table 4. Various zeolites and metal organic frameworks (MOFs) for molecular sieving of analyte gas.[383–419]

| Size [Å] | Zeolites [pore size, Å] | MOFs[a] [pore size, Å] | Gases [kinetic diameter, Å] |
|----------|------------------------|------------------------|---------------------------|
| ≈3       | Cu(f-pymo)$_2$ [2.9], ZIF-7 [2.9] | M(NDV) [4.0], Zn(dtp) [4.1], MIL-102 [4.4], ZIF-69 [4.4], PCN-14 [4.5], Zn(btp) [4.5] NOTT-100 [4.8] | Water vapor [2.64], hydrogen [2.9], ammonia [2.9] |
| 3–4      | ZIF-100 [3.35], ZIF-8 [3.4], Er$_2$(pda) [3.4], MIL-96 [2.5–3.5], PCN-17 [3.5], PCN-13 [3.5 × 3.5], Mg$_3$(ndc) [3.5–3.6], ZIF-93 [3.65], Zn$_2$(cnc)$_2$(dpt) [3.7] | | Nitrogen monoxide [3.2], carbon dioxide [3.3], acetylene [3.3], oxygen [3.5] |
| 4–5      | Zeolite A [4.1 × 4.1] | Mn(NDV) [4.0], Zn(dip) [4.1], MIL-102 [4.4], ZIF-69 [4.4], PCN-14 [4.5], Zn(btp) [4.5] NOTT-100 [4.8] | Ethylene [4.16], sulfur dioxide [4.1], carbon monoxide [4.44], ethanol [4.5], n-butane [4.5], acetone [4.6], 1-propanol [4.7], dimethylamine [4.9], propane [4.9] |
| 5–6      | Canocrinite [5.9 × 5.9] | NOTT-103 [5.0], Cu(gla) [4.4′bipy)$_2$ [3.3 × 5.1], Zn$_2$(btp) [3.9 × 5.2], ZIF-71 [4.8–5.4], NOTT-101 [5.5] | 1-Butanol [5.0], i-butane [5.0], 1-3 butadiene [5.2], butanone [5.3], isoprene [5.5], ethylbenzene [5.8], benzene [5.85], p-xylene [5.9], toluene [5.9] |
| >6       | Ferrierite [4.2 × 5.5; 3.5 × 4.8], silicate_I [5.1 × 5.5], ZSM-5 [5.3 × 5.6], mordenite [6.5 × 7.0; 2.6 × 5.7], zeolite β [6.6 × 6.7; 5.6 × 5.6], zeolite Y [7.1 × 7.1], zeolite X [7.4 × 7.4] | Cu$_2$(pzdc)$_2$(py)$_2$ [4 × 6] NOTT-116 [6.3], PMOF-2 [6.4], HKUST-1 [6.6], Cu(hfipbb)(H$_2$hfpbb)$_2$ [3.2, 7.3], ZIF-68 [7.5] | Cyclohexane [6.0], trimethylamine [6.1], m-xylene [6.8], o-xylene [6.8], triethylamine [7.8] |

[a] bptc, 4,4′-bipyridine-2,6,2′,6′-tetracarboxylate; cnc, 4-carboxycinnamic; dpt, 3,6-di-pyridyl-1,2,4,5-tetrazine; dtp, 2,3-pyrazinediicarboxylate; f-pymo, 5-fluoropyrimidin-2-olate; gla, glutarate; 4,4′-bipy, 4,4′-bipyridine; H$_2$hfipbb, 4,4′-(hexafluoroisopropylidene)bis(benzoic acid); ndc, 2,6-aphthalenedicarboxylate; pda, 1,4-phenylendiacetate; tbip, 5-tert-butylisophthalicate.
H₂. Mann et al.⁴³⁷ demonstrated the control of gas selectivity in Cr₁.₉₅To₀.₀₅O₃ sensors using filter layers of Cr-zeolite Y and Cr-zeolite β. Binions et al.⁴³⁸,⁴³⁹ also revealed that the gas selectivity and gas sensing patterns of WO₃ and Cr₁.₉₅To₀.₀₅O₃ sensors can be tailored by coating with various zeolite overlayers (H-ZSM-5, Cr-ZSM-5, H-LTA (Linde Type A), Cr-LTA, H-A, and H-Y) with different catalytic activities, acidities, and pore sizes. All these data suggest that sophisticated artificial olfaction can be designed either by catalyst loading on lower sensing films or using pure and catalyst-loaded molecular-sieving overlayers. It should be noted that when filtering small molecules in a physical manner, the uniform coating of a molecular sieve overlayer is essential, but an excessively thick coating may lead to a decrease in gas response and sensing response speed due to limited gas transport. Thus, the coating of a thin and uniform overlayer is advantageous.

5.2. Bilayer Sensors with a Porous Catalytic Overlayer

A catalytic overlayer without the molecular sieving effect has been suggested to modify analyte gases into less- or more-reactive species prior to the gas sensing reaction. The catalytic overlayer mainly aims to achieve highly selective sensing of a target gas by suppressing response to relatively reactive interference gases via oxidative filtering. Porous alumina films loaded with noble metal catalysts have been used as representative catalytic layers in order to maximize the reaction between gas and catalysts. Hubálek et al.⁴⁴⁰ reported the increase in benzene selectivity in WO₃ sensors by coating them with a Pt-loaded Al₂O₃ overlayer, and Sahm et al.⁴⁴¹ showed an increase in methane selectivity in Pd-doped SnO₂ sensors by coating them with a Pd-loaded Al₂O₃ overlayer. Jansat et al.⁴⁴² also reported that a RuO₂@SiO₂ overlayer is effective in selectively detecting propane with negligible interference from CO and NO₂ using a SnO₂ film. In order to enhance gas selectivity, porous catalytic overlayers of 3 wt% Pd-doped SnO₂ (thickness: ≈18 µm) have also been directly coated on Sb and Pt-doped SnO₂ sensing films (thickness: ≈17 µm) by flame spray pyrolysis.⁴⁴³ The gas response is generally decreased by the introduction of a porous and thick catalytic overlayer due to the consumption of analyte gas by partial/complete oxidation and/or the limitation of gas transport by the catalytic overlayer. However, the increase in the response to a specific gas after coating with a catalytic overlayer has ever been reported,⁴⁴⁰ which indicates the possibility for catalytic reforming of the gas into more active forms. This effect will be discussed in more detail in the next section. Note that the key concept of the catalytic overlayer is to increase selectivity toward stable or less reactive gases and to decrease cross-responses to more reactive interference gases. From the point of view of designing sensing materials for artificial olfaction, the gradual control of gas selectivity or gas sensing...
patterns by tuning catalytic materials and the loading amount of catalysts would also be of great interest for the feature extraction of complex chemicals with different reactivity.

5.3. Bilayer Sensors with a Nanoscale Catalytic Overlayer

A nanoscale catalytic overlayer can be also considered to control gas selectivity. The amount of analyte gases transported to the lower sensing region inevitably decreases when a thick catalytic overlayer configuration is employed. If the catalytic overlayer is ultrathin but sufficient to modify the analyte gases, the gas selectivity can be manipulated without limiting gas transport to the sensing region. This is not only convenient for sensor fabrication but also very effective in achieving a high and fast response. A key role of nanoscale catalytic overlayers is the catalytic oxidation of interference gases. The present authors\cite{36} reported that the response of thick sensor film (thickness: \(\approx 21\) \(\mu\)m) consisting of hollow SnO\(_2\) spheres to 2.5 ppm ethylene remained similar, but the responses to other gases such as trimethylamine, dimethylamine, NH\(_3\), C\(_2\)H\(_5\)OH, HCHO, and CO became negligibly low after coating with a relatively thin (\(\approx 300\) nm) Cr\(_2\)O\(_3\) overlayer. Because the overlayer is significantly thinner than the SnO\(_2\) sensing thick film and the ethylene responses with and without relatively thin Cr\(_2\)O\(_3\) overlayers are similar, the catalytic oxidation of more reactive interference gases into non- or less-reactive species (e.g., CO\(_2\), H\(_2\)O) has been suggested as the probable reason for the selective ethylene detection. This reveals that even a thin coating of a catalytic layer can be sufficient for the catalytic filtering of interference gases.

Another attractive feature of nanoscale catalytic overlayers is the tailoring of gas response by the catalytic reforming of gases. Figure 13 shows the schematic mechanisms for sensing the two gases with different reactivities using sensing films with and without nanoscale catalytic overlayers. When metal oxide (MO) chemiresistor films are coated on two sensing electrodes, the gas response is determined by the following serial reactions: 1) the gas transport from the ambient atmosphere to the top region of the sensing film, 2) gas transport through the sensing film, and 3) the sensing reaction between analyte gas and ionized oxygen on the surface of MO particles on the lower part of the sensing film near the sensing electrodes. If the reducing analyte gas is reactive (e.g., ethanol), the majority of gas transported to the lower sensing region will react with O\(^-\) on the MO particle surface, which will lead to a high gas response (Figure 13a1). The reaction products are CO\(_2\) and H\(_2\)O (gray arrow). In contrast, the less reactive analyte gas (e.g., aromatic hydrocarbon) barely reacts with O\(^-\), so the majority of analyte gas withdraws unreacted (Figure 13a2), which exhibits a low gas response. The four different catalytic overlayers in Figures 13b–d are assumed to be thin enough not to affect the gas transport. Under this configuration, the gas sensing characteristics will be primarily dependent upon the catalytic modification of gas. When a very thin catalytic overlayer is coated on sensing film, the majority of the reactive gas can be catalytically reformed into smaller and more active species (three amber arrows in Figure 13b1), which significantly enhances the gas response (Figure 13b1). In comparison, less reactive gas is partially reformed into more reactive species (one amber arrow in Figure 13b2), which slightly increases the gas response (Figure 13b2). Thus, the sensor

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Figure 13. Gas sensing mechanism of bilayer sensors consisting of thick sensing layer and nanoscale catalytic overlayer. a1–e1) Sensing mechanism for high reactivity gas; a2–e2) sensing mechanism for low reactivity gas; a3–e3) overall gas sensing mechanism.
response to both gases increased after coating them with a nanoscale catalytic overlayer (Figure 13b3). When the catalytic overlayer becomes thicker (Figure 13c), part of the reactive gas starts to oxidize into non- or less-reactive species (e.g., CO2 or H2O, gray arrow at the upper catalytic layer in Figure 13c1), while the remaining part of the gas is reformed into more reactive forms (two amber arrows in Figure 13c1). Accordingly, the response toward reactive gas decreases (Figure 13c1,c3). In contrast, in this configuration, the reforming of less reactive gas is significantly promoted by thicker catalytic layer (three amber arrows in Figure 13c2), which enhances the gas response up to the maximum value (Figure 13c2,c3). It is worth noting that the response to low reactivity gas becomes higher than that to high reactivity gas in this condition (Figure 13c3). Further thickening of catalytic layers (Figure 13d1,e1) diminishes the reforming but promotes the oxidation of reactive gas more, which gradually decreases the gas responses (Figure 13d3,e3). The response to low reactivity gas also tends to decrease with the thickening of the catalytic layer (Figure 13d2,e2,d3,e3).

Accordingly, the gas response and the thickness of the catalytic overlayer show a bell-shaped curve for each gas, and the location of the bell-shaped curve depends on the reactivity of the analyte gas. Gas reforming is predominant in the increasing part of a bell-shaped curve, whereas gas oxidation plays key role in the decrease in gas response. Gas reforming is similar to the amplification of intended signals, while gas oxidation is analogous to the removal of unnecessary noises in the electronic circuit. It should be mentioned that both reforming and oxidation can be tailored not only by changing catalytic overlayer thickness but also by controlling the sensing temperature or catalytic activity of overlayer materials because they are all associated with thermal activation as well as catalytic promotion. Thus, the choice of catalytic materials, control of catalytic overlayer thickness, and optimization of sensing temperature enable one to tune the gas selectivity via gas reforming and oxidation.

Figure 14 shows four different examples that demonstrate the selectivity control of bilayer design sensors with nanoscale catalytic overlayers. The thick films (thickness: \( \sim 30 \, \mu m \)) with SnO2 hollow spheres showed relatively low responses (\( R_d/R_b = 3.7-13.7 \)) to 5 ppm ethanol, xylene, toluene, and benzene at 350 °C (Figure 14a1). The decoration of SnO2 film with Au nanoclusters by an e-beam coating of 0.5 nm thick (nominal thickness) Au and subsequent thermal annealing substantially enhanced the gas responses toward xylene and toluene (Figure 14a2). The responses toward xylene and toluene became the highest (\( R_d/R_b = 61.4 \) and 56.2) when the thickness of the predeposited Au layer increased to 1.0 nm (Figure 14a3). The decoration of the film with more Au nanoclusters via e-beam coating of 3 nm thick Au decreased the responses to xylene and toluene (Figure 14a4). The increase and decrease in methylbenzene responses can be explained by the reforming of less reactive methylbenzenes into more reactive forms at a moderate amount of Au (Figure 14a2,3), and the oxidation of methylbenzene at excessive loading of Au (Figure 14a4), respectively. A schematic diagram displaying the variation in gas responses to less reactive xylene and highly reactive ethanol in relation to catalytic overlayer thickness is illustrated in Figure 14a5. Jeong et al.\(^ {445} \) also reported that the responses (\( R_d/R_b \)) of p-type Co3O4 hollow sphere thick film (thickness: \( \sim 5 \, \mu m \)) to 5 ppm xylene, toluene, and ethanol at 225 °C are enhanced significantly by coating it with a 2–5 nm thick TiO2 overlayer (Figure 14b2,3) and decreased by coating it with a 20 nm thick TiO2 overlayer (Figure 14b4). Similar increases and decreases in gas response due to gas reforming and oxidation reaction were also observed when 2, 5, and 20 nm thick SnO2 overlayers, respectively, were coated on Co3O4 sensing films (Figure 14c). The variation in responses to xylene and ethanol in both sensors could be also explained by the two bell-shaped curves on the right (Figure 14b5,c5), and the results reveal that not only catalytic noble metals but also catalytic oxides including TiO2 and SnO2 can be used to tune gas selectivity and gas responses.

Jeong et al.\(^ {446} \) reported that coating a 20 nm thick Co3O4 overlayer on Pd-loaded SnO2 yolk–shell sphere sensing film (thickness: 23 μm) increases its response to 5 ppm benzene (\( R_d/R_b = 879 \)) but decreases responses to xylene, toluene, and ethanol (\( R_d/R_b = 14.6-29.4 \)) (Figure 14d1,d2). Further thickening of the Co3O4 overlayer to 60 nm decreased the response to all the gases (Figure 14d3), although the benzene selectivity remained recognizable. This could also be explained by the bell-shaped gas responses to different gases depending on their reactivity (Figure 14d4). Among benzene, toluene, and xylene, benzene is the most stable gas. By attaching one or two methyl groups in the benzene ring, the reactivity increases.\(^ {443} \) Ethanol is more reactive to aromatic compounds. Thus, the reactivities of the gases are \( E > X > T > B \). Considering \( E, X \), and \( B \), the bell-shaped curve for \( E \) shows the highest gas response at the lowest catalytic promotion (thickness, activity, and thermal activation), while benzene requires the highest catalytic promotion to achieve the maximum gas response. All the results in Figure 14 clearly show that various materials with different catalytic activity can be used to control the selectivity of gases and to tune gas sensing patterns. More importantly, a large number of combinations among different sensing and catalytic materials will provide new opportunities to design diverse sensing materials for plentiful artificial olfaction.

Currently, catalytic materials are generally loaded on the entire sensing film. In this case, the catalytic promotion of gas sensing reactions at the lower part of the film as well as the counteracting catalytic oxidation of gas at the upper part of film can occur simultaneously. Thus, it is rather difficult to control gas reforming and oxidative filtering in a separate manner, which may hamper the tuning of gas sensing characteristics. In contrast, a bilayer sensor design enables separation between gas-modification and gas-sensing reactions in a more distinct manner, which enhances the controllability of gas sensing characteristics. Moreover, when the entire sensing film is loaded with catalytic materials with dissimilar work function values, the catalyst loading often increases sensor resistance up to an unmeasurable range using conventional electronic circuits, which impede the applications of artificial olfaction. In bilayer sensors, the catalytic overlayer is outlying and thus barely affects the conduction at the lower part of the sensing film close to the sensing electrodes.\(^ {16,444,446} \) Thus, the gas selectivity and response can be tailored without affecting the baseline sensor resistance. For artificial olfaction, diverse sensing materials are essential, and it is better to control the gas selectivity of sensors easily and precisely at a constant temperature.
Figure 14. a) Gas responses ($R_g/R_a$) of pure and Au-decorated SnO$_2$ thick films (thickness: $\approx 30 \, \mu m$) to 5 ppm ethanol (E), xylene (X), toluene (T), and benzene (B) at 350 $^\circ$C: a1) pure SnO$_2$, a2) Au(0.5 nm)-decorated SnO$_2$, a3) Au(1 nm)-decorated SnO$_2$, a4) Au(3 nm)-decorated SnO$_2$, and a5) sensing mechanism. a) Adapted with permission.[444] Copyright 2019, American Chemical Society. b) Gas responses ($R_g/R_a$) of pure and TiO$_2$-coated Co$_3$O$_4$ thick films (thickness: $\approx 5 \, \mu m$) to 5 ppm E, X, T, and B at 225 $^\circ$C: b1) pure Co$_3$O$_4$, b2) TiO$_2$(2 nm)-coated Co$_3$O$_4$, b3) TiO$_2$(5 nm)-coated Co$_3$O$_4$, b4) TiO$_2$(20 nm)-coated Co$_3$O$_4$, and b5) sensing mechanism. b) Adapted with permission.[445] Copyright 2017, American Ceramic Society. c) Gas responses ($R_g/R_a$) of pure and SnO$_2$-coated Co$_3$O$_4$ thick films (thickness: $\approx 5 \, \mu m$) to 5 ppm E, X, T, and B at 225 $^\circ$C: c1) pure Co$_3$O$_4$, c2) SnO$_2$(2 nm)-coated Co$_3$O$_4$, c3) SnO$_2$(5 nm)-coated Co$_3$O$_4$, c4) SnO$_2$(20 nm)-coated Co$_3$O$_4$, and c5) sensing mechanism. c) Adapted with permission.[445] Copyright 2017, American Ceramic Society. d) Gas responses ($R_g/R_a$) of pure and Co$_3$O$_4$-coated Pd-SnO$_2$ thick films (thickness: $\approx 23 \, \mu m$) to 5 ppm E, X, T, and B at 375 $^\circ$C: d1) pure Pd–SnO$_2$, d2) Co$_3$O$_4$(20 nm)-coated Pd–SnO$_2$, and d3) Co$_3$O$_4$(60 nm)-coated Pd–SnO$_2$, and d4) sensing mechanism. d) Adapted with permission.[446] Copyright 2017, Royal Chemical Society.
and with little variation in baseline resistance. In this respect, bilayer sensors with different compositions and configurations of catalytic overlayers are effective and facile platforms through which to realize strong and simple artificial olfaction.

6. Emerging Sensing Materials for Artificial Olfaction

CNTs, graphene or reduced graphene oxides (rGOs), transition metal dichalcogenides (TMDs), and 2D early-transition metal carbides and nitrides (MXenes) are emerging chemiresistors that can be used in artificial olfaction in the future. Because there have been many reviews on the sensing mechanisms and applications of gas sensors using CNTs,[448–451] graphene-based materials,[451–461] and TMDs,[452,458,460–463] the main focus of this section will be placed on the control of gas selectivity and the design of artificial olfaction. The target gases and the operation temperatures of pristine, noble-metal-loaded, and metal-oxide-loaded sensors using CNTs, graphene-based materials, and TMDs are analyzed based on recent publications in the literature (Figure 15) (sensors using graphene and rGO: publications since 2016, sensors using CNTs and TMDs: publications since 2010). Note that the studies on MXene-based gas sensors were not included in Figure 15 because the number of publications was not sufficient for statistical analysis. In the pristine and catalyst-loaded configuration, the sensors using CNTs, graphenes/rGOs, and TMDs showed responses to a relatively narrow range of gases such as NO2, NH3, H2, ethanol, and H2S. However, gas selectivity can be modified by functionalizing the surface or hybridizing other sensing materials. Moreover, they commonly offer flexible sensor design (Figure 16)[464–466] and enable the operation of sensors at room or mildly heated temperatures,[45,467] which can open pathways for wearable sensors and artificial olfaction.[453,455,468] The key features of these emerging chemiresistors for artificial olfaction are discussed in the following sections.

6.1. Carbon Nanotubes

During the past two decades, CNTs with high surface-to-volume ratios have been intensively investigated as gas sensors.[469,470] Schroeder et al.[448] provided comprehensive reviews on the chemical sensors using CNTs. In p-semiconducting CNTs, the chemiresistive variations are explained by: 1) the charge

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**Figure 15.** a–f) Gas sensors using: a,d) CNTs, b,e) graphenes and rGOs, and c,f) transition metal dichalcogenides (TMDs) and their target gases and operation temperatures. Because the numbers of relevant publications are too high, the analyses were carried on the literature published for the last 5 years (2016 onward, graphenes and rGOs) or 10 years (2010 onward, CNTs and TMDs).
transfer between analyte gas and CNTs, 2) the change in inter-CNT distance due to the swelling of the matrix phase in CNT-matrix composites, and 3) the gas induced modulation of the Schottky barrier between metal electrodes and CNTs. The first is an inherent gas sensing mechanism for pristine CNTs that has been well-demonstrated by the increase and decrease in CNT resistances upon exposure to electron-donating NH$_3$ and electron-accepting NO$_2$, respectively.

The representative approach to endowing gas selectivity to CNTs is surface functionalization. To accomplish this, DNA and various functional groups have been decorated on the surfaces of CNT-based sensors. Staii et al.[472] reported that the gas selectivity of SW-CNT field-effect transistors (FETs) can be tailored by the decoration of single-stranded DNAs and sequence variations in the decorated DNA. The same research group[473] further demonstrated that the control of the DNA sequence enables the discrimination of homologous gases of aldehydes (octanal, nonanal, and decanal) and carboxylic acids (propionic acid, hexanoic acid, and octanoic acid). It has been reported that DNA-CNT gas sensors can be made using commercially available CNTs[474] and be integrated on complementary metal oxide semiconductor (CMOS) circuitry.[475] Moreover, the diverse sequences of DNA suggest the controllability of gas selectivity, and the constant responses that occurred over 50 repetitive sensing events indicate sensor stability. From this perspective, DNA-CNT gas sensors can be implemented in electronic noses, although the detailed mechanism for gas selectivity control needs further investigation. It is worth noting that sensor stability is primarily determined by the bonding nature (covalent or noncovalent) between the functional group and CNTs.

Peng et al.[476] fabricated 10 random networks of CNTs FET sensors coated with different nonpolymeric organic layers for exhaled breath analysis and reported the responses both to polar and nonpolar biomarker gases. The response to polar biomarker gas was attributed to the charge transfer from the polar adsorbates, whereas that to nonpolar biomarker gas was explained by carrier scattering due to the swelling of organic films. This reveals that not only the direct charge transfer...
between gas and CNTs but also the modulation in conduction path due to analyte-specific swelling behaviors can be utilized to control the gas selectivity in CNT-based gas sensors as well as to design electronic noses using composites of CNT and organic material. Finally, gas sensing behaviors of CNT-based sensors can also be modified by loading noble metal catalysts such as Pt,[477,478] Au,[477,479,480] and Pd[478] or by decorating with metal oxide semiconductors such as SnO2,[481] ZnO,[482] Fe2O3,[483] CuO,[484] and Co3O4.[485]

### 6.2. Graphene and Reduced Graphene Oxides

Graphene and rGOs are other promising gas sensing materials owing to their high surface area to volume ratios, distinctive electronic properties, flexibility, and low operation temperatures.[451–461,486–488] Pure graphene can be used as a gas sensing material to detect NO2 and NH3.[489,490] However, graphene oxide (GO), with its low production cost, is more applicable for gas sensors.[491] Because the resistance of GO is often too high to measure, for practical applications, partially reduced GO (rGO) with p-type semiconductivity is more frequently used in gas sensors. The rGO provides facile control of the charge carrier concentration as well as abundant chemically active defect sites for tailoring gas sensing characteristics.

Oxygen functional groups are active sites for gas sensing reactions that play a key role in selective gas detection. From the DFT calculation, Maity et al.[492] suggested that the carboxyl functional group is advantageous in enhancing NH3, CO, and H2O sensing, while the hydroxyl functional group can facilitate NO2 sensing. Wang et al.[493] prepared rGOS with various ratios of oxygen functional groups (–OOH, –OH, and C=O) using three dissimilar reduction methods, and they reported that the rGO with the highest number of hydroxyl groups exhibits high response and selectivity to NO2. Choi et al.[494] also reported that the fast and reversible NO2 sensing in rGO is associated with the surface hydroxyl group.

Similar to CNT-based sensors, the functionalization of graphene[495] and graphene nanomesh[496] with DNA also presents a valid means through which to control gas selectivity. However, control of gas selectivity done simply by tailoring the surface functionality of rGO is not sufficient to cover a wide range of analyte gases. Hybridization with noble metal catalysts and other oxide semiconductors[497,498] is a complementary approach to tuning gas selectivity. To date, various noble metals such as Pt,[499,500] Pd,[501] and Au[502] and metal oxide semiconductors including SnO2,[503] ZnO,[504] CuO,[505] In2O3,[506] and Co3O4.[507] are loaded or decorated on graphene-based sensors to control gas sensing characteristics.

### 6.3. Transition Metal Dichalcogenides

Transition metal dichalcogenides (TMDs) (MX2, M: transition metals, X: S, Se, and Te) have received considerable attention in various functional devices.[508] In particular, their 2D layered structures with high surface area and semiconducting characteristics with tunable bandgaps are advantageous for gas sensor applications. To date, various TMDs have been explored as chemiresistors, including MoS2,[509–511] WS2,[512] SnS2,[513,514] and SnSe2.[515] Similar to carbon-based CNTs, graphene, and rGOs, most TMD-based sensors offer flexible design and low operation temperatures. Combining different transition metals and chalcogen elements provides diverse sensing materials. From this perspective, sensors using TMDs can be considered as potential platforms for artificial olfaction. However, TMD-based sensors often show sluggish sensing/recovery kinetics as well as incomplete recovery after sensing events, probably due to the low operation temperature and irreversible adsorption of analyte gases. Accordingly, researchers have tried to improve the reversibility and sensing kinetics by applying light to the sensors,[516] increasing the operation temperature,[516] or decorating noble metal catalysts.[517] The control of gas selectivity and the establishment of gas sensing libraries in TMD-based sensors are in the nascent stage and need further investigation.

### 6.4. 2D Early-Transition Metal Carbides and Nitrides

Recently, MXenes are considered as new chemiresistive materials with 2D structures, which are generally prepared by the exfoliation from “MAX” phase (M: Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, or Mo, A: Al, Ga, In, Ti, Si, Ge, Sn, Pb, P, As, Bi, S, or Te; and X: C or N).[518–520] To date, Ti3C2Tx, V4C3Tx, V2CTx, and TiO2 have been explored to detect NH3,[521–526,530] C2H5OH, CH3OH, NO2, H2, and acetone.[529] Similar to other 2D chemiresistors such as graphenes, rGOS, and TMDs, the MXene-based sensor also offers operation at low temperature[521–530] and flexible design.[523] The termination of MXene surface with O, OH, and F functional group can lead to the metal-to-semiconductor conversion and the change of surface chemistry.[528] Although the more investigation is necessary, the compositional diversity in M and X will allow the design of various MXene-based gas sensors and the surface functionalization can be used to tailor the gas sensing characteristics.

### 7. Reliable Sensing Materials for Artificial Olfaction

Artificial olfaction discriminates among odors based on sensor signals for multiple analyte gases. However, gas response as well as baseline sensor resistance depend on ambient temperature and humidity.[531,532] For reliable electronic noses, the temperature and humidity dependence of gas sensing characteristics should be reduced to a negligible level.

In oxide semiconductors, thermal activation is an important origin for generating charge carriers. The ionization of adsorbed oxygen that establishes EDL and HAL near the surfaces of n-type and p-type oxide semiconductors is also dependent upon sensing temperature. Accordingly, the baseline resistance and gas response of oxide-based gas sensors are heavily dependent upon the sensing temperature. For reliable and reproducible operation of electronic noses, the operation temperature of a sensor in a sensor array should be kept constant by the careful control of heater power. If the sensors in a sensor array are operated at different sensing temperatures,
the heat transfer between neighboring sensors may induce fluctuations in the sensing temperatures. This issue becomes more important when the thermal insulation between sensors is not effective. From this perspective, the operation of multiple sensors at constant or similar temperatures is more advantageous. The sensing temperature can be also influenced by variations in ambient temperature (−20 to 40 °C) and the flow rate of analyte gases. In order to design robust sensors irrespective of ambient temperature and gas flow rate, the temperature dependence of gas sensing characteristics should be minimized. This can be accomplished in part by increasing the charge carrier concentration via aliovalent doping. However, if the same number of charge carriers is injected into the sensing materials by the gas sensing reaction, the sensing materials with extrinsically generated higher charge carrier concentrations would exhibit low gas response. Thus, there is a tradeoff between the gas response and sensor robustness against temperature fluctuation.

The gas sensing characteristics and baseline resistance of the sensors using CNTs, rGOs, TMDs, and MXenes also depend on temperature variation. The adsorption of analyte gas as well as the reaction among gases, surface functional groups, and the species of ionized oxygen will be influenced by sensing temperature. However, because sensing temperature is relatively low, the sensor temperature is less affected by the ambient temperature compared to oxide semiconductor gas sensors.

Humidity is another critical parameter to be controlled in order to achieve reliable artificial olfaction using semiconductor-based chemiresistors because both sensor resistance and gas response are dependent upon humidity. For medical diagnoses using exhaled breath, the amount of moisture in the sample can vary depending on the method used to collect the sample, so a dehumidification step is usually used to improve the discriminating capability of artificial olfaction. For instance, Peng et al. used sensor arrays consisting of 10 different single-wall carbon nanotubes (SWCNTs) coated with nonpolymeric organic materials to discriminate between the exhaled breaths of lung cancer patients and healthy controls (Figure 17). When the RH was 80%, the discrimination was impossible (Figure 17a). However, the cancerous and healthy patterns could be discerned by decreasing the humidity to 10% RH via a dehumidification step (Figure 17b). Finally, the diagnosis became more precise at 1% RH by further dehumidification (Figure 17c). If one used the exhaled gas sample with 80% RH, for successful discrimination, preconcentration of 50 times was necessary (Figure 17d). This clearly demonstrates that the humidity-dependent gas sensing characteristics of chemiresistors make discrimination using artificial olfaction difficult. It is worth noting that sampling and preconditioning take a long time and require additional components. Accordingly, the instantaneous discrimination of odors without preconditioning and sampling should be used in the future. This can be achieved using high performance and miniaturized gas sensors with negligible humidity dependence.

In oxide semiconductor gas sensors, ambient water vapor is known to react with ionized oxygen on the surface of oxide semiconductors, which forms hydroxyl group and generates electrons.

$$\text{H}_2\text{O}(g) + \text{O}^{\cdot\cdot\cdot}_\text{ads} \rightarrow \text{M} - 2\text{OH} + e^- (\text{or } 2e^-)$$

(2)
The generation of electrons due to interaction with water vapor changes the baseline resistance of sensors in air atmospheres, and the consumption of available ionized oxygen (O$^-$ or O$_2$)$^-$ for gas sensing reactions decreases the gas response (Figure 18a).[537] Considering that water vapor is not only ubiquitous but also dynamically changing depending on weather, climate, day/night, and location, the humidity dependence of gas sensing characteristics inevitably affects the reproducibility of gas sensors and the precision of electronic noses. In principle, the humidity interference can be compensated for or calibrated by developing algorithms based on humidity sensor signals.[532,538] However, the humidity dependence of sensing characteristics differs depending on the materials,[539] and signal compensation using a large number of sensors in an electronic nose is not simple.

Thus, various dopants/additives, including NiO (Figure 18a),[537] Sb (Figure 18b),[540] Pd (Figure 18c),[541] Co$_2$O$_4$,[542] Tb,[54] Pr (Figure 18d),[543] and CuO,[544] have been explored to suppress the humidity dependence of gas sensing characteristics. In addition, the nanoscale ZIF-CoZn layer has been coated on ZnO NW-based sensor to mitigate humidity interference.[50] The main mechanisms for suppressing the humidity dependence of gas sensing characteristics are stronger interactions between additives and moisture,[537] a decrease in –OH radicals due to a change in oxygen adsorption species,[540,541] regenerative oxygen adsorption assisted by multivalent redox pairs (Ce$^{3+}$/Ce$^{4+}$, Pr$^{3+}$/Pr$^{4+}$, and Tb$^{3+}$/Tb$^{4+}$)[542,543] and the blocking of water molecule using ZIF overlayer.[50]

Graphene is hydrophobic and can be fabricated as a gas sensor with low humidity interference.[465] In contrast, rGOs are hydrophilic and have thus been widely investigated as humidity sensors.[545] Protons are known to interact with –O–, –OH, and –COOH functional groups in rGO, which migrate through the hydrogen bonded networks within the adsorbed water film.[546] This indicates that gas and water vapor compete for the sensing sites. Accordingly, although rGOs are more cost-effective gas sensors than graphene, the humidity dependence of gas sensing characteristics should be suppressed for designing reliable rGO-based artificial olfaction devices. Most TMDs, including MoS$_2$,[547] WS$_2$,[548–551] SnS$_2$,[552] NbS$_2$,[553] are known for significant humidity dependence in their gas sensing characteristics. MoS$_2$[554,555] and WS$_2$[549,556] are also good humidity sensors. These indicate that the removal of humidity dependence in TMD-based sensors is challenging and needs further investigation.

Although there has been significant progress in decreasing the humidity dependence of all chemiresistors, gas sensing libraries with negligible humidity dependence are still insufficient for covering a wide range of different analyte gases. Moreover, the gas selectivity of sensors can be altered by additives to suppress the moisture effect, although some sensors (e.g., in Figure 18d) showed similar gas sensing patterns even after loading additives. Moreover, the concentration range of water vapor in an ambient atmosphere is wide and high. For instance, water vapor concentration is 1207 ppm at RH 20%
at 0 °C and 55026 ppm at RH 80% at 38 °C. Thus, the detection of sub-ppm or ppm levels of analyte gases with negligible interference from water vapor is still quite challenging. However, the interaction between oxide chemiresistors and moisture can be considered as another chemical sensing reaction in artificial olfaction. Thus, in principle, it will not be completely impossible to eliminate interference from humidity using machine learning for big gas sensing data that is assisted by a large number of sensors and high computing capability, if one can find a hidden layer irrespective of moisture in the sensor array.

8. High-Throughput Screening of Diverse Sensing Materials for Artificial Olfaction

To design high-performance artificial olfaction in the future, we will need a greater number of sensors and more diverse sensing materials to show distinctive gas sensing patterns for many different complex chemicals. To this end, various sensing materials with high compositional controllability should be prepared in a facile, reproducible, rapid, and automated manner, and gas sensors with different orthogonalities or partial selectivity should be screened using a high-throughput method.

The combinatorial approach provides a high-throughput solution for discovering new materials with the intended functionality\[561–563\] that can be applied to screen sensing materials\[561,563\] and to optimize the operating conditions of sensors. Siemons and Simon prepared the nanoparticles of 64 different oxide semiconductor chemiresistors using the polyol method, coated a multielectrode substrate with a suspension of sensing materials,\[561,563\] and analyzed the gas sensing characteristics using high-throughput impedance spectroscopy (Figure 19a). They also showed the Trellis plot of various doped LnFeO\(_3\) and LnCrO\(_3\) (Ln: lanthanides) materials visualizing the responses to six different analyte gases (H\(_2\), CO, NO, NO\(_2\), C\(_2\)H\(_5\)OH, and C\(_2\)H\(_4\)) at five different temperatures (225, 250, 275, 300, and 325 °C) (Figure 19b).\[561\] The results clearly show the validity and promising potential of the high-throughput screening of gas sensing materials for high performance artificial olfaction, as well as for gas sensors. The Simon group also applied this combinatorial method to 64 surface-doped In\(_2\)O\(_3\) and doped WO\(_3\) sensors\[564,565\] to rapidly screen gas sensing materials.

Schroeder et al.\[566\] made an array of 20 CNT gas sensors with different selectors for discriminating cheese, liquor, and edible oil. They analyzed the sensing transient data sets using two different models, then 67% of the collected data were used to train the model, and 33% of the data were used to test for machine learning. They analyzed all possible combinations of 4 out of 20 sensors (\(32C_4 = 4845\) combinations) and suggested the best combinations for accurately discriminating among cheeses or oils. This high-throughput screening of all possible combinations of sensors assisted by machine learning will be used more in the future and will significantly shorten the time needed to develop on-demand artificial olfaction with high functionality.

The combinatorial approach has been used to rapidly determine the optimal operating temperatures for multiple sensors. Zhang et al.\[567\] suggested a combinatorial temperature-programmed method for the high-throughput optimization of sensing temperatures using a 36-matrix material chip (Figure 19c). Considering that the response, selectivity, responding/recovering speed, and endurance of sensors against humidity are closely dependent upon operation temperature, this method is useful for the rapid optimization of gas sensing characteristics.

For faster and more convenient screening, the high-throughput automated fabrication of sensing materials is also necessary. Mao et al.\[568\] fabricated 55 different sensing films using pure, Pt-, Rh-, Ru-, Pd-, Ir-, Au-, and Ag-loaded SnO\(_2\) NPs with an inkjet printing method and demonstrated unmanned testing platform. It should be noted that 400 different sensor compositions can be made by mixing the six kinds of jettable inks, and the times for solution mixing and film printing are two and three minutes, respectively. This suggests that inkjet printing is a potential approach for the high-throughput fabrication and screening of gas sensors for artificial olfaction.

9. Artificial Olfaction: State-of-the-Art and Strategies for Integration

9.1. Artificial Olfaction Using Oxide Semiconductor Gas Sensors

In the beginning stage of artificial olfaction design using oxide semiconductors, researchers attempted to discriminate among various odors using combinations of several commercial sensors that were typically fabricated by screen printing slurry.\[569–570\] Because commercial gas sensors have been developed for specific purposes, it may be difficult to develop high performance and demand-based artificial olfaction. Thus, researchers designed artificial olfaction using tailor-made oxide thick sensing films.\[572,573\] For highly miniaturized artificial olfaction, a single sensor should be small. Accordingly, various oxide nanostructures or films have been grown, deposited, or coated on microhotplates\[578–583\] by several different synthetic routes in order to fabricate integrated sensor arrays.

Güntner et al. fabricated an electronic nose to detect HCHO in highly humid conditions and in the presence of interference gases such as acetone, ammonia, and ethanol using Pt-, Si-, Pd-, and Ti-doped SnO\(_2\) sensing films by flame spray pyrolysis (Figure 20a).\[58\] Porous sensing films with different compositions were directly deposited onto a Si substrate with electrodes using a shadow mask. The flame spray pyrolysis method also provides high controllability of composition as well as particle size\[584,585\] for the sensing film and offers bilayer sensor design with a porous catalytic overlayer.\[441,443\] Kühne et al.\[586\] demonstrated that 69 Pt–SnO\(_2\) porous sensing films (thickness: 22 ± 3 µm) can be directly deposited on a wafer scale by flame spray pyrolysis (Figure 20b), suggesting the potential of CMOS-compatible large-scale fabrication of micro-gas-sensors. From this perspective, flame spray pyrolysis can be considered as a promising synthetic route to fabricating electronic noses with a large number of sensors.

Single-crystalline oxide nanowires (NWs) with high surface area to volume ratio, high crystallinity, and good thermal stability have received considerable attention as gas sensing materials.\[41,437–439\] Several studies have worked to design electronic noses using oxide NWs.\[590\] Sysoev et al.\[592\] coated SnO\(_2\) NW mats on a Karlsruhe Micro Nose (KAMINA) microarray chip.
Figure 19. a) Layout of the $8 \times 8$ multielectrode array. Reproduced with permission.\cite{562} Copyright 2005, American Chemical Society. b) Trellis plot of relative responses of one sample plate (containing p-type oxide semiconductors) to $H_2$, air, CO, air, NO, air, $NO_2$, air, $C_2H_5OH$, air, $C_3H_6$, and air ($S_\Delta$; gas response, $R_{test}$; resistance under test gas, $R_{ref}$; resistance in reference atmosphere). Reproduced with permission.\cite{561} Copyright 2007, Elsevier. c) Schematic illustrations of test chamber of high-throughput screening platform of gas-sensing materials and schematic layout of 36-matrices material chip. Reproduced with permission.\cite{567} Copyright 2014, American Chemical Society.
with 39 Pt coplanar electrodes and measured the gas sensing characteristics under a temperature gradient (520 (green)–600 K (red) along the electrode array) (Figure 20c). Although only SnO$_2$ NWs were used as sensing materials, the electronic nose could discriminate among several different gases because the gas sensing characteristics depended on the sensing temperature and the formation of a NW–NW junction. Vallejos et al.[333] deposited pristine, Au-, Pt-, and Au/Pt-loaded WO$_3$ nanoneedles on microhotplates via aerosol-assisted chemical vapor deposition and utilized this sensor array to discriminate among NO$_2$, CO, and humidity. Note that SnO$_2$ NW network sensors can be fabricated on a large scale by single-step and site-selective vapor growth on Au electrodes.[592] The decoration of noble metal[330,593-596] or metal oxide catalysts (Table 3) is known to significantly modify the response and selectivity of NW based gas sensors. Accordingly, the loading of different catalytic materials on several oxide nanowires can be considered as a possible strategy for designing NW-based electronic noses. However, the accurate compositional control of oxide NWs and the growth of multinary oxide NWs remain challenging, requiring further investigation.

Various pristine and catalyst-coated oxide thin films have been deposited by sputtering as a means to implement electronic noses. Horrillo and co-workers fabricated an electronic nose consisting of 16 different NWs (WO$_3$, Ge, and SnO$_2$ NWs) site-selectively grown on micromembranes and demonstrated the capability to discriminate among NO$_2$, CO, and humidity. Note that SnO$_2$ NW network sensors can be fabricated on a large scale by single-step and site-selective vapor growth on Au electrodes.[592] The decoration of noble metal[330,593-596] or metal oxide catalysts (Table 3) is known to significantly modify the response and selectivity of NW based gas sensors. Accordingly, the loading of different catalytic materials on several oxide nanowires can be considered as a possible strategy for designing NW-based electronic noses. However, the accurate compositional control of oxide NWs and the growth of multinary oxide NWs remain challenging, requiring further investigation.

Various pristine and catalyst-coated oxide thin films have been deposited by sputtering as a means to implement electronic noses. Horrillo and co-workers fabricated an electronic nose consisting of 16 different NWs (pure SnO$_2$ and SnO$_2$ doped with Cr and In) deposited by the sputtering method to discriminate ham[597] and wine[598] and to detect...
wine ageing. They also used sputtering to fabricate an electronic nose consisting of 15 different thin films (pure SnO$_2$, Pt-doped SnO$_2$, and TiO$_2$-coated SnO$_2$) in order to identify volatile organic compounds. It is worth noting that they changed the thickness of sensing and catalytic layers to control gas selectivity, suggesting that not only sensing materials, but also their thicknesses, can be tuned to modulate gas sensing patterns.

One of the key advantages of sputtering will be its compositional controllability and diversity. However, flat and dense oxide thin films prepared by sputtering are often less sensitive than the same composition of embossed 2D thin films or 2D inverse opal films. This is because of the low gas accessibility of dense thin films. To enhance the performance of artificial olfaction, high gas response as well as good gas selectivity are extremely necessary because, to discriminate among complex chemicals, the detection of trace concentration of gas components can be a critical step. Moreover, sluggish gas diffusion through dense film may affect the gas sensing speed. Therefore, it is advantageous to utilize sensing materials with highly gas-accessible nanostructures. Glancing angle deposition (GLAD) of thin films via sputtering or e-beam evaporation provides an excellent solution. When the angle between substrate normal and the vapor flux produced from sputtering (or e-beam evaporation) is $>70^\circ$, discrete nuclei grow along the vapor flux direction, whereas a shadow region of nuclei does not, leading to the formation of periodic arrays of slanting nanostructures (Figure 21a–d). Since the growth of nanostructures is determined by $\theta$ (the angle between the vapor flux and substrate normal), $\Phi$ (substrate rotation angle), and the deposition rate, various morphologies of nanostructures such as zigzags, helices, and vertical posts can be fabricated (Figure 21e–i). In addition, this synthetic route allows for the fabrication of heterostructures (Figure 21e6) that can be used for the bilayer design of sensors. Various nanorods of oxide semiconductors—such as SnO$_2$, In$_2$O$_3$, WO$_3$, V$_2$O$_5$, Cu$_2$O, ITO, Au–SnO$_2$, TiO$_2$, and Rh–WO$_3$—have been grown for gas sensor applications. Moon et al. prepared Pt-, Pd-, and Rh-loaded WO$_3$ nanofibers by electrospinning, and slurries containing nanofibers were drop-coated on the electrodes for the fabrication of electronic noses to discriminate among various gases (Figure 22a). Drop coating has been also used to coat various nanostructures such as oxide nanowires, porous nanowires, hollow spheres, and nanoparticles onto sensing electrodes. The dip pen nanolithographic technique has also been used for the controlled deposition of a tiny amount of slurry containing oxide nanowires or nanoparticles on the designated area of MEMS-based microhotplates (Figure 22b).

For the well-defined, reproducible, and economic coating of sensing materials, the slurry should be prepared and designed carefully considering the surface tension of the solvent, dispersion of particles, drying of droplets, and decomposition of organic components. Moreover, for precise and automated dispensing of slurry, it is better to utilize robot-assisted microdispensers. The sizes of the nanostructures should be smaller than the typical inner diameter of the dispenser nozzle (50–200 $\mu$m) to prevent clogging the nozzle. The typical sensing area formed by dispensing, drying, and thermal annealing ranges from 100 to 300 $\mu$m (Figure 22c). Thus, the electrode area in the microhotplates should be comparable to the sensing area (Figure 22d). It is worth noting that the successful commercialization of slurry coated MEMS-based sensors with ultralow power consumption confirms the reproducibility and mass productivity of sensors. Microdispensing of slurry solutions provides a universal method to coat nearly all morphologies of nanostructures, heterostructures, and heterocomposites to the sensing electrodes that is compatible with MEMS based microhotplates and thus advantageous in fabricating electronic noses on a large scale with a low cost.

Currently, microelectrodes with an area of 100 $\times$ 100 $\mu$m$^2$ can be used to fabricate sensors using microdispensing. However, for the further miniaturization of sensors, sensors with smaller sensing areas are required. EHD printing can decrease sensing areas because a very small amount of slurry is ejected when the intense pulse electric field is applied between the nozzle and substrate. For instance, Kang et al. formed a narrow sensing area (diameter: 40–70 $\mu$m) by EHD-coating slurries containing SnO$_2$, In$_2$O$_3$, WO$_3$, and NiO nanofibers on the sensor array (Figure 22e1).

To date, the number of sensors in most electronic noses is generally $<10$. In the future, more sensors are expected to be used (e.g., >30). To this end, there should be no limitations in choosing sensing materials, catalysts, and sensor design. In addition, the facile fabrication of highly integrated sensor arrays is required. In general, two different approaches may be used to fabricate electronic noses with a greater number of oxide semiconductor-based sensors: the slurry-based method...
Figure 21. GLAD of an array of nanorods by e-beam evaporation. a) The angle between the substrate normal and vapor flux is \( \theta \), and the substrate rotation along the substrate normal axis is \( \phi \). b) Islands of depositing materials (with the height of \( h \)) are formed on the substrate at the initial stage of GLAD. The magnified view shows self-shadowed regions (\( h \tan \theta \)) formed by highly oblique angle of vapor flux. c) Highly porous nanorod arrays fabricated by GLAD. d) Cross-sectional SEM image of SiO\(_2\) nanorod film with a deposition angle of 80°. e) Cross-sectional and top-view SEM images of various nanostructured films fabricated by GLAD (scale bar = 500 nm): e1) SnO\(_2\) zigzags, e2) TiO\(_2\) helixes, e3) Al vertical posts, e4) WO\(_3\) helixes grown on ZnO prepatterns by nanoimprint lithography, e5) top-view SEM image of WO\(_3\) helixes grown on prepatterned substrate (inset shows top-view SEM image of patterned ZnO by nanoimprint lithography), and e6) WO\(_3\)-SiO\(_2\)-WO\(_3\) hetero-nano-helixes. a–e) Adapted under the terms of the CC-BY Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/). Copyright 2015, The Authors, published by Springer Nature. f1) 3 × 3 sensors array using pristine thin films, Au-functionalized thin films, and nanorod structures of SnO\(_2\), WO\(_3\), and In\(_2\)O\(_3\); f2–f4) PCA plots showing: f2) thin films, f3) thin films + Au-functionalized thin films, and f4) thin films + Au-functionalized thin films + nanorod structures with PC1 and PC2 using responses of 7 gases (H\(_2\)S: 2 ppm, NO: 1 ppm, other 5 gases: 10 ppm) as input data in 80% RH. f) Adapted with permission. Copyright 2016, American Chemical Society.
and physical vapor depositions (Figure 23). For demonstration, the design concept will be explained using arrays of 8 × 8 sensors, which can be further expanded on demand. First, 64 different compositions of sensing materials can be deposited directly onto an 8 × 8 array of sensing areas by microdispensing (or inkjet printing) (Figure 23a). In order to use diverse sensing materials, it is advantageous to prepare the sensing materials through chemical routes with high compositional controllability, e.g., ultrasonic spray pyrolysis, flame spray pyrolysis, electrospinning, and the polyol method. Bilayer sensor design with a combination of sensing films and catalytic overlayers is also promising. After the deposition of eight different kinds of sensing materials in a row by microdispensing along the direction and following thermal annealing (Figure 23b, middle), the eight different catalytic overlayers can be coated by a second session of microdispensing along the x-direction (Figure 23b, upper), leading to 64 different configurations of bilayer sensors. Similarly, eight different kinds of sensing layers prepared by microdispensing can be combined with eight different kinds of catalytic nanoclusters by physical vapor deposition (i.e., e-beam evaporation and sputtering) (Figure 23b, lower). These 64 different configurations of bilayer
Figure 23. Schematic diagram for fabricating $8 \times 8$ sensor arrays for electronic nose by various synthetic routes; a) microdispensing of 64 different slurry solutions, b) 1st microdispensing of 8 kinds of sensing layers along the $y$ direction + subsequent 2nd microdispensing of 8 different continuous catalytic overlayers along $x$ direction (middle to upper), 1st microdispensing of 8 kinds of sensing layers along the $y$ direction + physical vapor deposition of 8 different kinds of discrete catalytic overlayers along $x$ direction (middle to lower), c) physical vapor deposition of 8 different kinds of dense sensing films + physical vapor deposition of 8 different kinds of discrete catalytic overlayers along $y$ direction, d) growth of 8 different kinds of oxide nanorods by glancing angle physical vapor deposition + decoration of 8 different kinds of discrete catalytic overlayers by physical vapor deposition.
sensors can be used to diversify gas sensing libraries. The deposition of sensing films along a direction by physical vapor deposition and the decoration of catalyst nanoclusters along the perpendicular direction by a second physical vapor deposition can be also used to make 64 different gas sensors with distinctive sensing patterns (Figure 23c). Moreover, GLAD enables the preparation of highly gas-accessible nanorods as sensing films for the further decoration of catalysts (Figure 23d). In addition, many different synthetic routes can be also combined to implement a wide range of electronic noses, including inkjet printing, slurry deposition, EHD coating, on-axis physical vapor deposition (sputtering and e-beam evaporation), and aerosol assisted CVD.

9.2. Artificial Olfaction Using rGO- and CNT-Based Sensors

Lipatov et al.[60] coated GO flakes (average thickness: 10 ± 2 nm) on a modified KAMINA multisensory chip (Figure 24a–f) and partially reduced the GO flakes in a vacuum at 150 °C. From the analysis of gas sensing patterns using a perception-type artificial neural network (ANN), they suggested that four different gases (methanol, ethanol, isopropanol, and water vapor) could be discriminated. With increasing cycles of ANN training, more precise discriminations could be achieved (Figure 24g–i). Similar to artificial olfaction using a kind of oxide nanowires mentioned in the previous section,[582] the different gas sensing patterns of a sensing material stem from wide distributions in size, shape, thickness, degree of reduction, and junction configuration of rGO flakes. Simplicity of materials is beneficial. However, it is necessary to train each electronic nose because of nose-to-nose variation. Shirsat et al.[631] made an electronic nose using CNT-based sensors functionalized with various porphyrins (octaethyl porphyrin (OEP), Ru–OEP, Fe–OEP, Mn–OEP, tetraphenyl porphyrin (TPP), Ru–TPP, and Fe–TPP). The eight sensors showed distinctively different sensing patterns toward water, methyl ethyl ketone (MEK), acetone, methanol, and ethanol (Figure 24j). The gases could be discriminated.

Figure 24. a) Optical photograph of a multielectrode KAMINA chip. The following images (b)–(e) show sequential magnifications of the chip. b) Optical photograph of the active part of the KAMINA chip. The white arrows show a dark vertical strip that corresponds to an rGO film. c) SEM image of rGO sensors. Bright horizontal lines correspond to Pt electrodes; darker vertical strip corresponds to rGO. d) SEM image of a fragment of one of the devices shown in (c). e) AFM image of an rGO film on a Si/SiO2 substrate. f) An average height profile for the area shown by the square in (e). g–h) Analyte recognition by an rGO-based multisensor array. The results of recognition of water (1), methanol (2), ethanol (3), and isopropanol (4) by the ANN at training goals (weight factors to minimize the mean squared error) equal to: g) 10⁻³, h) 10⁻⁶, and i) 10⁻⁹. a–i) Reproduced with permission.[60] Copyright 2013, Royal Society of Chemistry. j) Histogram showing comparison of responses of bare and free-base and metal-substituted porphyrin-functionalized CNT gas sensors toward acetone, methanol, ethanol, MEK, and water (@100% saturated vapors). k) PCA plot (PC2 vs PC3) of seven sensors showing well-separated clusters for four VOCs tested (MeOH, EtOH, MEK, and acetone). j,k) Reproduced with permission.[631] Copyright 2012, American Chemical Society.
well by multivariate analysis (Figure 24k). The Haick group used an array of SWCNT sensors coated with nonpolymeric organic materials for detecting biomarker gases from exhaled breath. They succeeded in the diagnosis of lung cancer in human beings\textsuperscript{[536]} and chronic renal failure in rats\textsuperscript{[533]} using CNT-sensor-based electronic noses. They also demonstrated diagnoses of Alzheimer's and Parkinson's diseases using a combination of sensors based on CNTs and Au NPs\textsuperscript{[632]}. The reports on the flexible gas sensors using CNTs, graphene, rGOS, TMDs, and MXenes strongly suggest the implementation of wearable artificial olfaction in the future. For this, it is necessary to design more diverse sensing materials and the wider gas sensing libraries that can be fabricated on flexible substrates on a large scale.

10. Key Issues for Designing New Sensing Materials for Next-Generation Artificial Olfaction

Although there has been considerable progress in the field of artificial olfaction, the precise discrimination of numerous complex airborne chemicals in nature and industry using sensor arrays still remains a challenging issue and thus needs further investigation. The difficulties in odor recognition primarily originate from the complexity of mixed chemicals. This should be solved by a diversity of sensing materials in sensor arrays along with more computation of sensing signals. In order to enhance the performance of artificial olfaction to accomplish demand-based chemical recognition in real applications, many aspects should be taken into account:

1) sensing materials that show different responses to a single gas;
2) sensing materials that show different partial selectivity to a wide range of odors consisting of multiple gases;
3) sensing materials with different acid-based properties, catalytic activity, surface adsorption, and chemical affinities toward a specific gas;
4) high response to trace concentrations of gases;
5) rapidly responding kinetics;
6) reversible sensing characteristics;
7) diverse physical/chemical filtering materials with different kinetic diameters of pores and dissimilar catalytic activity;
8) reliable sensing materials that are less dependent upon ambient moisture or temperature;
9) high compositional tunability of sensing materials;
10) facile fabrication of heterostructures and heterocomposites;
11) high controllability of loading/doping catalytic materials;
12) reproducibility of sensing materials and sensors (particle size, contact configuration between particles, degree of mixing, and porosity);
13) reproducibility of sensor arrays (reproducibility of all the sensors);
14) mass producibility for widespread applications;
15) high-throughput screening of optimal sensing materials and operating conditions;
16) facile integration and miniaturization;
17) low operation temperatures;
18) connectivity to wireless communication and the Internet of Things.

In the beginning stages of artificial olfaction, several key analyte gases out of hundreds to thousands of chemicals have been primarily analyzed to extract important features. To enhance discrimination capability and to suppress possible interference from minor gases, more sensors should be used along with higher computation power. For this to happen, an integrated configuration of sensor arrays using various chemiresistors is necessary. It is also essential to minimize the sensor-to-sensor variation of baseline resistance, gas response, humidity dependence, and temperature dependence. This change would lead to the implementation of robust electronic noses with negligible array-to-array variations.

Diverse sensors that cover a wide range of gases or complex odors can be designed using new sensing materials, designing new sensor structures, and the combination of different sensing and/or catalytic materials (Figure 25):

1) use of both n-type and p-type oxide semiconductors with distinctively different gas sensing patterns and characteristics;
2) use of multinary oxides such as perovskite and spinel oxides;
3) combination between A and B cations as well as the use of multinations in A and B sites in perovskite oxides (ABO\textsubscript{3});
4) combination between A and B cations as well as the use of multinations in A and B sites in spinel oxides (AB\textsubscript{2}O\textsubscript{4});
5) heterostructures designed by combinations among all sensing oxide materials and catalytic metal/oxide materials;
6) heterocomposites designed by combinations among all the sensing and catalytic materials;
7) use of bilayer sensors with physical filtering of large gases;
8) use of bilayer sensors with catalytic overlayers to reform or oxidize analyte gases;
9) use of emerging sensing materials such as CNTs, graphene, rGOS, TMDs, and MXenes with low operation temperatures and flexible structures;
10) functionalization and surface modification of CNTs, graphene, and rGOS;
11) combination between lower sensing layers and upper physical filtering layers;
12) combination between lower sensing layers and upper catalytic layers.

There will be many new challenges with the use of diverse and different sensing materials and new sensor structures. First, more attention should be paid to the reproducibility of sensing materials. When preparing phase-pure multinary oxides through the reaction between two different oxides, incomplete reactions may lead to the formation of residual minor phases in addition to the intended multinary oxides. Increasing the thermal annealing temperature to obtain a complete reaction can affect gas sensing characteristics by excessive particle coarsening. In addition, the precise control of cation-to-cation ratios is also necessary. Thus, it is necessary to prepare nanocrystalline and phase-pure multinary oxides at relatively low processing.
temperatures. Second, the interfaces in heterostructures and heterocomposites should be controlled carefully. For instance, the growth of decorative oxides on sensing materials at high temperatures can form unintended second phases at the interface, which can influence the p–n, n–n’, and p–p’ junctions, as well as the gas sensing characteristics. Even if we used the same composition of heterocomposites, the conduction path, interface interaction, and gas sensing reaction could vary based on the sizes and connecting configurations of the two different phases and the porosity of secondary particles. Accordingly, attention should be paid to designing robust heterocomposites. Third, the sensing performance of bilayer sensors depends on the interfaces between lower sensing and upper catalytic layers. A physical filtering layer should be coated uniformly to exclude possible gas leaks. The bonding between the thick and porous catalytic filtering overlayer and lower sensing layer should be strong. Thermal expansion coefficients of two layers should be similar in order to decrease thermal shock. When implementing high performance artificial olfaction, diverse sensing materials with high endurance against moisture are required. More progress is necessary to diversify gas sensing performance in sensors using CNTs, graphene, rGOs, TMDs, and MXenes in order to open new pathways in wearable artificial olfaction.

Most of the challenges in forthcoming artificial olfaction can be solved by diversity in sensing materials. That is, a myriad of gas sensors with distinctive gas sensing patterns and consequent huge gas sensing libraries can be designed by uncountable combinations of semiconductor-based sensing materials and sensor structures. High-throughput design of artificial olfaction will be accelerated by the combinatorial preparation, screening, and optimization of sensing materials as well as by machine learning with big gas sensing data. Diverse sensing materials pave a new road to high-performance, robust, and on-demand electronic noses.

11. Conclusion

Artificial olfaction can sniff various odors without fatigue and discriminate among different smells, and it can monitor hazardous chemicals that are inodorous to humans, which will substitute for, complement, and surpass human olfaction. Like the olfactory system of human beings, highly complex odors consisting of thousands of different chemicals can be better recognized by a larger number of sensors and more computation of sensing signals. The collection and signal processing of gas
sensing data is becoming easier owing to rapid progress in computing capabilities and data communication. Thus, a diversity of sensing materials will be a key to designing new functional, on-demand, and highly integrated artificial olfaction. To date, several n-type oxide semiconductors have typically been used as sensing materials when designing electronic noses. Sensing materials can expand to p-type oxide semiconductors with distinctive catalytic properties, a variety of multinary oxides such as perovskites and spinels with dissimilar catalytic activities and acid-properties, the numerous heterostructures and heterocomposites made from a combination of different sensing and modifying materials, and new materials based on CNTs, graphene, reduced graphene oxides, transition metal dichalcogenides, and 2D early-transition metal carbides and nitrides. In addition, the utilization of various physical filtering layers and catalytic over-layers offers unique and tailored sensor design with new functionalities, and combining two different layers provides another set of abundant sensors. The ultimate diversity of semiconductor-based sensing materials achieved through uncountable combinations among these new materials can overcome the challenges associated with complexity in artificial olfaction and will provide high sniffing capability through the support of high-throughput combinatorial methods and computing technology.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

artificial olfaction, chemiresistors, electronic noses, gas sensors, oxide semiconductors

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[1] W. F. Wilkens, J. D. Hartman, Ann. N. Y. Acad. Sci. 1964, 116, 608.
[2] K. Persaud, G. Dodd, Nature 1982, 299, 352.
[3] F. Röck, N. Barsan, U. Weimar, Chem. Rev. 2008, 108, 705.
[4] W. Hu, L. Wan, Y. Jian, C. Ren, K. Jin, X. Su, X. Bai, H. Haick, M. Yao, W. Wu, Adv. Mater. Technol. 2019, 4, 1800488.
[5] A. Loufis, S. Coradeschi, G. K. Mani, P. Shankar, J. B. N. Rayappan, J. Food Eng. 2015, 144, 103.
[6] A. D. Wilson, Metabolites 2015, 5, 140.
[7] A. P. Turner, N. Magan, Nat. Rev. Microbiol. 2004, 2, 161.
[8] G. Peng, U. Tisch, O. Adams, M. Hakim, N. Shehada, Y. Y. Broza, S. Billan, R. Abdah-Bortnyak, A. Kuten, H. Haick, Nat. Nanotechnol. 2009, 4, 669.
[9] Y. Y. Broza, X. Zhou, M. Yuan, D. Qu, Y. Zheng, R. Vishkin, M. Khatib, W. Wu, H. Haick, Chem. Rev. 2019, 119, 11761.
[10] J. W. Gardner, M. Craven, C. Dow, E. Hines, Meas. Sci. Technol. 1998, 9, 120.
[11] A. T. Günther, S. Abegg, K. Königstein, P. A. Gerber, A. Schmidt-Trucksäss, S. E. Pratsinis, ACS Sens. 2019, 4, 268.
[12] M. Righettoni, A. Amann, S. E. Pratsinis, Mater. Today 2015, 18, 163.
[13] W. Bourgeois, A.-C. Romain, J. Nicolas, R. M. Stuetz, J. Environ. Monit. 2003, 5, 852.
[14] L. Capelli, S. Sironi, R. D. Rosso, Sensors 2014, 14, 19979.
[15] M. Sliwirská, P. Wińiewska, T. Dymerski, J. Namieśnik, W. Wardencki, J. Agric. Food Chem. 2014, 62, 1423.
[16] M. Peris, L. Escuder-Gilabert, Trends Food Sci. Technol. 2016, 58, 40.
[17] Z. Li, R. Paul, T. B. Tis, A. C. Saville, J. C. Hansel, T. Yu, J. B. Ristaino, Q. Wei, Nat. Plants 2019, 5, 856.
[18] J. Laathawornkitkul, J. P. Moore, J. E. Taylor, M. Possell, T. D. Gibson, C. N. Hewitt, N. D. Paul, Environ. Sci. Technol. 2008, 42, 4833.
[19] A. Lichtenstein, E. Havivi, R. Shacham, E. Hahamy, R. Leibovich, A. Pevzner, V. Krivitsky, G. Davivi, I. Presman, R. Elnathan, Y. Engel, E. Flaxer, F. Patolsky, Nat. Commun. 2014, 5, 4195.
[20] C. Zhou, Z. Wu, Y. Guo, Y. Li, H. Cao, X. Zheng, X. Dou, Sci. Rep. 2016, 6, 25588.
[21] C. J. Bright, E. C. Nallon, M. P. Polcha, V. P. Schnee, Anal. Chem. 2015, 87, 12270.
[22] K. Brudzewski, S. Osowski, P. Pawlowski, Sens. Actuators, B 2012, 161, 528.
[23] J. M. Schnorr, D. van der Zwaag, J. J. Walish, Y. Weizmann, T. M. Swager, Adv. Funct. Mater. 2013, 23, 5285.
[24] S. F. Liu, L. C. H. Moh, T. M. Swager, Chem. Mater. 2015, 27, 3560.
[25] J. Gebicki, B. Szulczynski, M. Kaminski, Meas. Sci. Technol. 2015, 26, 125103.
[26] M. Nitta, M. Haradome, IEEE Trans. Electron Devices 1979, 26, 247.
[27] J. Watson, D. Tanner, Radio Electron. Eng. 1974, 44, 85.
[28] D. G. Laing, W. S. Cain, R. L. McBride, B. W. Ache, Perception of Complex Smells and Tastes, Academic Press, New York 1989.
[29] S. Firestein, Nature 2001, 413, 211.
[30] L. B. Buck, Angew. Chem., Int. Ed. 2005, 44, 6128.
[31] B. Malnic, J. Hirono, T. Sato, L. B. Buck, Cell 1999, 96, 713.
[32] L. R. Saraiva, F. Riveros-McKay, M. Mezzavilla, E. H. Abou-Moussa, C. J. Arayata, M. Makhlof, C. Trimmer, X. Ibara-Soria, M. Khan, L. V. Gerven, M. Jorissen, M. Gibbs, C. O’Flynn, S. McGrane, P. Mombaerts, J. C. Marioni, J. D. Mainland, D. W. Scott, Sci. Adv. 2019, 5, eaax0396.
[33] E. K. Jenkins, M. T. DeChant, E. B. Perry, Front. Vet. Sci. 2018, 5, 56.
[34] J. W. Gardner, P. N. Bartlett, Sens. Actuators, B 1994, 18, 211.
[35] J. P. McGann, Science 2017, 356, eaam7263.
[36] S.-Y. Jeong, Y. K. Moon, T.-H. Kim, S.-W. Park, K. B. Kim, Y. C. Kang, J.-H. Lee, Adv. Sci. 2020, 7, 1903093.
[37] M. Z. Alom, T. M. Taha, C. Yakopic, S. Westberg, P. Sidike, M. S. Nasrin, M. Hasan, B. C. V. Essen, A. A. A. Awwal, V. K. Asari, Electronics 2019, 8, 292.
[38] S. M. Scott, D. James, Z. Ali, Microchim. Acta 2006, 156, 183.
[39] N. Yamazoe, Sens. Actuators B 1991, 5, 7.
[40] M. E. Franke, T. J. Koplin, U. Simon, Small 2006, 2, 36.
[41] A. Kolmakov, M. Moskovits, Annu. Rev. Mater. Res. 2004, 34, 151.
[42] N. Barsan, U. Weimar, J. Electrochem. 2001, 7, 143.
[43] X. Hu, J. C. Yu, J. Gong, Q. Li, G. Li, Adv. Mater. 2007, 19, 2324.
[44] J.-H. Lee, Sens. Actuators, B 2009, 140, 319.
[45] J. Zhang, X. Liu, C. Neri, N. Pinna, Adv. Mater. 2016, 28, 795.
[46] N. Du, H. Zhang, B. Chen, X. Ma, Z. Liu, J. Wu, D. Yang, Adv. Mater. 2007, 19, 1641.
[47] M. Graf, D. Barretino, S. Taschini, C. Hagleitner, A. Hierlemann, H. Baltes, Anal. Chem. 2004, 76, 4437.
[48] D. Koziej, N. Barsan, K. Shimanoe, N. Yamazoe, J. Szuber, U. Weimar, Sens. Actuators B 2006, 118, 98.
[257] J.-S. Jang, S.-E. Lee, S.-J. Yoon, D.-H. Kim, H. Shin, H. J.-H. Lee, Mater. Sci. Eng. C 2019, 93, 3092.
[258] J. Kim, S.-J. Yoon, D.-H. Kim, H. Shin, H. J.-H. Lee, Adv. Eng. Mater. 2019, 21, 1719.
[259] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2019, 295, 8743.
[260] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2019, 282, 11
[261] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2018, 261, 505.
[262] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
[263] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
[264] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
[265] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
[266] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
[267] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
[268] J. Liu, T. Wang, B. Wang, P. Sun, Q. Yang, L. Liu, Y. Gao, Sens. Actuators, B 2017, 245, 551.
