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Gas sensors using ordered macroporous oxide nanostructures

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Detection and monitoring of harmful and toxic gases have gained increased interest in relation to worldwide environmental issues. Semiconducting metal oxide gas sensors have been considered promising for the facile remote detection of gases and vapors over the past decades. However, their sensing performance is still a challenge to meet the demands for practical applications where excellent sensitivity, selectivity, stability, and response/recovery rate are imperative. Therefore, sensing materials with novel architectures and fabrication processes have been pursued with a flurry of research activity. In particular, the preparation of ordered macroporous metal oxide nanostructures is regarded as an intriguing candidate wherein ordered aperture sizes in the range from 50 nm to 1.5 μm can increase the chemical diffusion rate and considerably strengthen the performance stability and repeatability. This review highlights the recent advances in the fabrication of ordered macroporous nanostructures with different dimensions and compositions, discusses the sensing behavior evolution governed by structural layouts, hierarchy, doping, and heterojunctions, as well as considering their general principles and future prospects. This would provide a clear scale for others to tune the sensing performance of porous materials in terms of specific components and structural designs.

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1. Introduction

Reliable monitoring of air quality is currently a concern of the extensive worldwide scientific and technological communities, stimulated by the ever-worsening environmental pollution issues.¹ To wean us off this crisis, these communities have developed a range of gas sensors and achieved innovations in sensor technology over the past few decades.^{2,3} Nowadays, the

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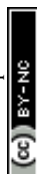
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Tingting Liang received her B.S. and M.S. degrees from the School of Materials Science and Engineering, Henan University of Science and Technology, in 2014 and 2018, respectively. Now, she is a doctoral candidate of Xi'an Jiaotong University, and she is conducting research on the fabrication and performance of gas sensor devices using nanostructured materials.



To further enhance the sensing performance, considerable effort has been devoted toward the synthesis of sensing materials with various nanostructures and the analysis of the sensing mechanism. For instance, Güntner *et al.* demonstrated that sensors preceded by activated alumina particle filters could dramatically enhance isoprene gas selectivity,¹⁷ and microporous zeolite membranes placed ahead of metal oxide sensors could decisively contribute toward superior formaldehyde selectivity even under high humidity conditions.¹⁸ It is indicated that structural parameters such as the crystallographic structure and morphology can considerably influence the gas-

sensing characteristics, particularly the response property, of SMO gas sensors.^{19–21} As compared to bulk counterparts, nanoarchitectures, such as nanosheets, nanowires, nanoparticles, *etc.*, can facilitate the enhancement of sensing performance due to the increased specific surface area to volume ratio, active surface sites and species (*e.g.*, O^{2−} and O[−]), and gas adsorption affinity.^{22–24} For practical gas-sensing utilization, these nanostructures (nanosheets, nanowires, and nanoparticles) need to be fabricated into a macroscopic film on the sensor electrode, usually *via* drop-casting or brush-coating, making the stability and reliability of gas-sensing properties difficult to be guaranteed.^{25,26} With this perspective, ordered macroporous nanostructures have been recently considered as worthwhile candidates to resolve the above problems and also attract considerable interest in a range of fields such as photonic crystals, catalysts, and energy storage and conversion technologies.^{27,28} In principle, the preparation of macroporous materials with aperture sizes in the range from 50 nm to 1.5 μm can increase the gas accessibility and chemical diffusion rate, while the fabrication of a macroscale aperture in an ordered manner can formidably strengthen the sensing stabilities and repeatabilities.²⁹ Moreover, these ordered macroporous nanostructures, usually prepared by polymeric microsphere sacrificial template method, can be a promising platform to perform heteroatom doping, interfacial and surficial tuning, as well as defect engineering to extract the maximum potential out of the oxide material's properties.³⁰ With respect to the influencing factors and enhanced sensing mechanism, many detailed investigations have been carried out on these ordered macroporous nanostructures.

In this review, we provide an overview on the designed syntheses of ordered macroporous metal oxides and summarize the existing protocols for colloidal crystals (CCs), as well as two-dimensional (2D) and three-dimensional (3D) ordered macroporous nanostructures. Furthermore, the key parameters to determine the gas-sensing characteristics of ordered macroporous nanostructures are discussed in relation to the sensing mechanism, which include macro/mesoporosity, heterojunctions, heteroatom dopants, surface adsorption, and their synergistic combinations. Some modification strategies are also demonstrated with a summary of the reported examples. With a better understanding of these topics, the rationales behind their enhanced sensing properties are revealed. Last, but not the least, imminent challenges and future prospects are discussed to provide new insights into the possible development of macroporous materials to be used in gas sensors. It is believed that this review can offer a clear guideline for the design and preparation of macroporous metal oxides with improved sensing performances.



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2. Synthesis methods for ordered macroporous nanostructures

2.1 Assembly of CC templates

It is well known that ordered macroporous metal oxide nanostructures can be prepared by means of several approaches,

such as CC hard template, anodized aluminum oxide template,^{31,32} and e-beam lithography.³³ Among them, studies have popularly focused upon hard spherical template methods due to their facile, controllable, and cost-effective characteristics.^{34,35} Herein, the main focus of this review is on the CC template method for ordered macroporous oxide nanostructures. The quality of the self-assembled colloidal spherical template plays an important role in fabricating uniform and ordered macroporous arrays. Fig. 1a shows the phase diagrams of monodisperse colloids at different volume fractions (ϕ). When ϕ is 74%, monodisperse colloids exhibit a hexagonal close-packed (*hcp*) structure due to energy minimization, thereby forming CCs.³⁶ Nowadays, 2D or 3D CCs have attracted increasing attention for their wide usage in far-ranging research areas such as photonics, sensors, catalysis, lithography, and bionics.^{37,38} Till now, a plethora of assembly methods have been developed by the research community, which are being continuously optimized and refined.^{39,40}

Fig. 1b shows different colloidal crystallization methods for the self-assembly of 2D and 3D CCs, namely, horizontal deposition (for 2D CCs), vertical deposition (for 2D and 3D CCs), controlled evaporation (2D CCs), spin-coating (2D CCs), electrostatic deposition (2D CCs), natural sedimentation (3D CCs), and centrifugation (3D CCs).⁴¹ Apart from these methods, some liquid interface-mediated methods, such as Langmuir–Blodgett transfer, floating assembly, and air/water interfacial self-assembly, have also been employed to fabricate large-scale monodisperse colloidal spherical crystals and binary colloidal crystals (bCCs).⁴² For instance, Kotov *et al.* reported an ethylene-glycol-associated floating self-assembly technique for the first time to prepare 3D CCs with the *hcp* lattice structure from polystyrene (PS) particles of various diameters (10–240 μm).⁴³ More recently, Dai *et al.* determined the phase diagram of

monolayer bCCs for the rational design and accurately controlled fabrication of bCCs with tuned structures, and they fabricated large-area ($>10\text{ cm}^2$) monolayer bCCs based on the ethanol-assisted air/water interfacial self-assembly route.⁴⁴ Besides these close-packed CCs, a range of 2D and 3D non-close-packed CCs have also been developed by means of plasma treatment, heat treatment, and elastomeric substrate stretching on their close-packed parent crystals.^{45–47} The flexibility and diversity of CCs can offer us considerable freedom in the fabrication of ordered macroporous nanostructures and their structural engineering for sensing performance tuning.

2.2. Ordered macroporous nanostructures

Ordered porous metal oxides can be universally prepared by impregnation or deposition with guest precursors, followed by heat treatment to remove the template matrix, thereby forming crystalline metal oxide replicas.^{48,49} Silica spheres, poly(methyl methacrylate) (PMMA) spheres, and PS spheres are used as the representative hard templates for 2D macroporous networks like inverse opals (IOs). After the deposition/coating of the metal oxide materials, the nanospherical template can be removed *via* annealing in air or etching in some solvents (*e.g.*, CH_2Cl_2 for PS spheres and NaOH for SiO_2 spheres). Using a PMMA template, Kim *et al.* prepared 2D ordered macroporous (2DOM) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ thin films by pulsed laser deposition onto PMMA-templated substrates, exhibiting higher surface area, porosity, and permeability toward gases than those exhibited by untemplated films.⁵⁰ Sputtering methods have also been widely used for fabricating 2DOM nanostructures, for instance, a p-type NiO ordered porous film was prepared by RF sputtering.⁵¹ These “top-down” sputtering and deposition techniques provide high controllability over film thickness, channel connectivity, and precise elemental/layer regulation. However, the limited variety of sputtering targets may be a drawback in the broader achievement of different metal oxide compositions on demand; meantime, in certain sputtering methods, polymeric hard spheres cannot survive in a high-temperature environment. Hence, increasing attention has been focused on fabricating 2DOM nanostructures by means of other routes.

One technique that holds this promise is the solution dipping/permeation strategy that allows for the wide applicability to almost all the soluble metal salts for ordered macroporous metal oxides, and therefore, offers considerable freedom for controlling the composition and hierarchy of metal oxides and compounds.^{29,52,53} As shown in Fig. 2a, the pre-assembled close-packed PS spheres as the hard template matrix are immersed in a metal salt solution, followed by heat treatment for oxide formation and template removal.^{48,54} It is found that the PS colloidal monolayer can be peeled off from the substrate and then floated on the water or solution surface, eliminating the dependency on flat substrates.⁴⁹ For instance, based on the solution-dipping template transfer method, Cai *et al.* fabricated a series of metal oxides (*e.g.*, In_2O_3 , SnO_2 , and $\alpha\text{-Fe}_2\text{O}_3$) ordered macroporous hollow hemispherical arrays on curved substrates.^{30,55,56} By impregnation with mixed metal precursors, multicomponent metal oxides can be obtained.⁵⁷ Based on



Fig. 1 (a) Phase diagrams of monodisperse colloids at different volume fractions. Modified with permission.³⁶ Copyright 2016, Macmillan Publishers Limited. (b) 2D and 3D crystallization methods for close-packed CCs.





Fig. 2 (a) Schematic illustration of the formation process of ordered metal oxide macroporous hollow spherical arrays. (b–e) Fabricated Fe_2O_3 hollow spherical arrays with different aperture sizes by using 500, 1000, 2000, and 5000 nm PS spherical templates. Reproduced with permission.⁴⁸ Copyright 2017, Elsevier Ltd.

a stepwise floating–immersing approach (Fig. 2), Su *et al.* demonstrated the substrate-independent fabrication of hollow spherical arrays with tunable spherical diameters, material systems (Fe_2O_3 , In_2O_3 , NiO , Co_3O_4 , MgO , CuO , ZnO , SnO_2 , and polyaniline), and shell thickness on the desired substrates including flexible substrates.⁴⁸ Along with the bCC template, one can also achieve the fabrication of hetero-aperture ordered macroporous arrays.^{29,30,44} When adding certain colloids (*e.g.*, graphene oxide nanosheets and gold nanoparticles) into the metal salt solution, elegant oxide-based 2D macroporous composites can be obtained, such as SnO_2 –graphene ordered macroporous thin films.⁵⁸ Recently, Güntner *et al.* and Pratsinis *et al.* developed the flame spray pyrolysis (FSP) method to directly deposit highly porous films with controllable compositions (*e.g.*, $\text{Ti}:\text{ZnO}$ ⁵⁹ and $\text{Si}:\text{MoO}_3$ ⁶⁰) on sensor substrates to build a single sensor^{61–65} and sensors arrays^{66–68} for the selective detection of human breath biomarkers. If combined with *in situ* resistance measurements during deposition, the formation of highly porous networks can be monitored with morphology-dependent resistance patterns to systematically design metal-oxide-based gas sensors with high performances.⁶⁹

Besides such 2DOM nanostructures, 3D ordered macroporous (3DOM) metal oxides have also been similarly synthesized using 3D CC templates.^{70–72} When compared with a monolayer 2D counterpart, 3DOM thin films tend to be endowed with strengthened continuous connection channels, as well as improved avenues for conducting electrical signals.⁷³ The preparation of 3DOM metal oxides is often based on the metal precursor solution impregnation.^{74–76} Miyake *et al.* recently reported a novel epitaxial growth process of single-crystal 3DOM

ZnO through a 3D PS spherical template *via* a flow-reactor-assisted low-temperature hydrothermal route, exhibiting electrical properties superior to those of polycrystalline ZnO , as shown in Fig. 3a.⁵² In addition, by adding dopants into metal precursors, multicomponent or doped 3DOM metal oxides can be obtained, such as Pt-doped SnO_2 ,⁷⁷ Au-doped In_2O_3 ,⁷⁸ and Fe-doped TiO_2 .⁷⁹ Combined with some other physical/chemical deposition methods, the heterojunction can be constructed upon the 3DOM structure.⁸⁰ For example, Ling *et al.* fabricated a core-shell 3DOM TiO_2 – WO_3 thin film through the electrodeposition of 50 nm-thick WO_3 onto uniform 3DOM TiO_2 thin films, as shown in Fig. 3b, which can provide a tunable modification of the electrical and optical performances.⁵³

It is worth mentioning that the 3DOM structure can serve as an ideal framework to form a hierarchical porous system. By the combination with some surfactants, an ordered metal oxide hierarchical structure can be realized *via* CC templating.⁷⁴ As shown in Fig. 4, a hierarchically ordered mesoporous–macroporous (3DOM/M) TiO_2 structure was fabricated with the integration of the triblock copolymer P123 and PS CC.⁷⁴ This hierarchically porous TiO_2 structure exhibits a highly crystalline framework, huge pore volume ($\approx 1.2 \text{ cm}^3 \text{ g}^{-1}$), large surface area (up to $240 \text{ m}^2 \text{ g}^{-1}$), and periodic and highly interconnected pores. A similar example can be found on a 3DOM/M $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ perovskite prepared *via* the combination of meso-molding and colloidal sphere templating.⁸¹ It is believed that such a hierarchical porous framework can be a reliable candidate for many functional applications because of its large specific area and pore volume, high gas accessibility, and highly thermal stability.

3. Gas-sensing properties of ordered macroporous nanostructures

3.1 2D macroporous arrays for gas sensing

Owing to the above-discussed points, a number of ordered macroporous metal oxide nanostructures have been fabricated



Fig. 3 (a) Flow-reactor-assisted hydrothermal fabrication process and morphologies of 3DOM ZnO . Reproduced with permission.⁵² Copyright 2017, American Chemical Society. (b) Fabrication process and morphologies of core-shell 3DOM TiO_2 and TiO_2 – WO_3 . Modified with permission.⁵³ Copyright 2018, Royal Society of Chemistry.





Fig. 4 (a) Schematic illustration of the formation and (b) microstructure of a hierarchically 3D ordered mesoporous-macroporous TiO_2 structure. Reproduced with permission.⁷⁴ Copyright 2014, Wiley-VCH.

for gas sensing over the past years.^{55,56} Generally, a 2D inverse opal thin film shows distinctive advantages for gas sensing over its dense film counterpart. In a dense and agglomerated sensing film, gas transport to the lower sensing region close to the electrodes becomes difficult (Fig. 5a). For the untemplated dense metal oxide film, the upper layer of the particles with an electron depletion layer (EDL, n-type) or hole accumulation layer (HAL, p-type) is very thin and far away from the bottom electrodes; the conduction of the sensor could be explained by the parallel competition between the thin upper layer with EDL (or HAL) and relatively thick inner layer without EDL (or HAL).⁵⁴ Because only the particles near the surface participate in the gas-sensing reaction and the inner particles remain inactive, chemiresistive variations become low. In contrast, the 2D inverse opal structures provide high gas accessibility, activating most of the sensing materials and enabling rapid gas response. In particular, the chemiresistive variation at the thinnest region is the highest, which, in turn, significantly increases the overall gas response (Fig. 5b).

The configuration of the connection between adjacent hollow hemispheres is also an important parameter to modify the gas-sensing characteristics of 2DOM nanostructures.⁴⁸ Moon *et al.* prepared two different connecting configurations of TiO_2 hollow hemispherical arrays by controlling the plasma etching of 2D *hcp* PS ball array templates (Fig. 6a and b).⁸² The

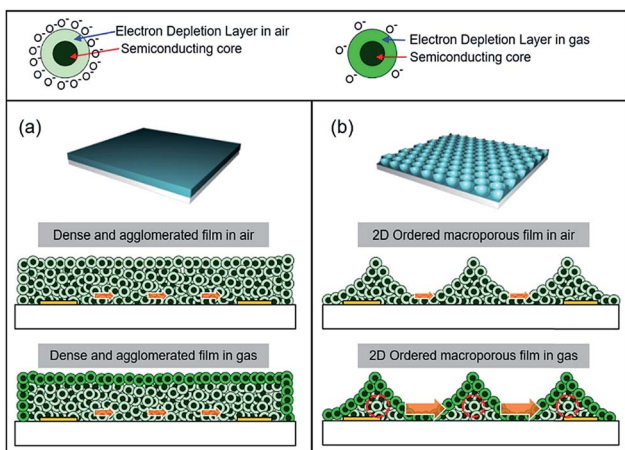


Fig. 5 Schematic gas-sensing mechanisms of (a) dense agglomerated films and (b) 2DOM films using n-type oxide chemiresistors.

CO response increased 4 times by decreasing the contact area between the hollow hemispheres (Fig. 6c) and 10 times in comparison to the plain film. This can also be explained by the high chemiresistive variations at the thin connecting portion.⁸³ The thinner neck width (D) leads to a lower D/λ_D ratio (λ_D , Debye length), and the sensor response increases as the D/λ_D ratio decreases, according to Yamazoe's studies.¹² Meanwhile, it is indicated that it becomes easier for gas molecules to access thin nanobridges in ordered nanostructures, which facilitates the sensing process.^{82–84} The results of both 2D IO structures and 2D hollow hemispheres clearly reveal that the 2DOM nanostructures are promising nanoarchitectures to simultaneously achieve high and rapid response. In addition, the ordered frame matrix would be robust in tolerating the compressive and tensile stresses experienced during the heating/cooling operations due to the more uniform force distribution in ordered porous films, which can yield higher sensing stability. For instance, Xu *et al.* demonstrated that a 2DOM ZnO sensor can retain the long-term sensing stability for 16 months.⁸⁵

Currently, a diversity of metal oxide 2DOM films have been *in situ* constructed on desired sensor substrates to fabricate SMO gas sensors *via* sputtering and solution-related templating methods.^{48,54,86} For instance, Xu *et al.* recently reported a new photochemistry-based solution-dipping method to prepare monolayer macroporous SnO_2 arrays with controlled surface pore sizes (varying the UV irradiation time) on ceramic tubes for ethanol sensors, showing rapid response-recovery rate (within 10 s) and high stability for temperatures lower than 300 °C.⁸⁷ However, the use of wide-spaced electrodes (in millimeters) on ceramic tubes can engender ultrahigh resistance (usually in hundreds of megaohms) in the metal oxide sensing film, which hampers the convenient measurement of sensor resistance using conventional electric circuits.⁸⁸ In this context, the creation of micro- or nanoscale electrode spacing is considered as an emerging trend to increase the electrical conductance and improve the signal-to-noise ratio of SMO gas sensors. Using a filament as the template, Duan *et al.* constructed a microgap electrode pair on the ceramic tube to load the 2DOM ZnO IO thin film.⁷⁹ A microgap ZnO IO sensor showed much lower device resistance and ultralow detection limit to acetone (60 ppb) as compared to normal sensors.

More precise micro/nanogaps and sensors could be achieved by microelectromechanical system (MEMS) processes, which has the potential to become the key sensor device for future practical applications.^{89,90} For instance, Rao *et al.* presented the localized on-chip synthesis of 2DOM SnO_2 on a MEMS-based microheater platform (Fig. 7a and b).⁸⁴ The fabricated SnO_2 integrated sensor exhibits high sensing performance toward formaldehyde gas at 300 °C (Fig. 7c and d), such as high response, high selectivity, fast response (1.6 s)/recovery (6.0 s) rate, and low detection limit (6.5 ppb).⁸⁴ Dai *et al.* also illustrated a similar sensor structure *via* the fusion of 2DOM SnO_2 film and MEMS-based sensing chip that contains micro-spaced interdigital electrodes and low-powered microheaters. The sensor exhibited high ethanol response (ppb level), fast response (<1 s), and low power consumption (32 mW at 350 °C).^{91,92} As compared to some non-ordered porous films,





Fig. 6 Top-view SEM images of (a) TiO_2 hollow hemispheres and (b) nanostructured TiO_2 hollow hemispheres (pointy contact between hemispheres); (c) sensing transients of plain TiO_2 film, hollow hemispheres, and nanostructured hollow hemispheres to 1–500 ppm CO at 250 °C. Reprinted with permission.⁸² Copyright 2010, Elsevier Ltd.

ordered porous SnO_2 sensors can exhibit enhanced response and sensing kinetics,⁶¹ but further efforts need to be made toward improving their gas selectivities, such as zeolite membrane filters¹⁸ and construction of even orthogonal sensor arrays (E-nose).⁶⁶

Although the 2D macroporous configuration and micro-spaced electrode are beneficial to the overall performance, it is still a challenge to realize high-performance gas sensing for pure metal oxides, particularly with regard to selectivity.^{83,93} Hence, certain modification strategies need be considered, such as heteroatom doping, surface modification, and interfacial engineering, to enhance the sensing of 2DOM metal oxides.⁹⁴ For instance, the ethanol response and selectivity of 2DOM NiO thin-film sensors are known to significantly increase by Mg doping.⁹⁵ It should be noted that ethanol sensing on different basic/acidic surfaces undergoes different interaction processes, as shown in reactions (1) and (2).^{96,97}



Fig. 7 (a) Schematic diagram and (b) morphology of the as-fabricated sensor with the integration of microheater platform and macroporous SnO_2 hollow spherical array. (c) Real-time sensor resistance transient to HCHO at 300 °C. (d) Sensor response versus HCHO concentration, and real-time sensor response and recovery behaviors to 0.5 ppm HCHO. Reproduced with permission.⁸⁴ Copyright 2017, American Chemical Society.



Fig. 8 (a) NO_2 response of 2DOM Fe_2O_3 at different temperatures (T) and concentrations (C). (b) T - C transition phase diagram. (c) Schematic illustration of different NO_2 sensing types at high and low C values, respectively. Reproduced with permission.⁹⁸ Copyright 2015, Royal Society of Chemistry.



Accordingly, the enhancement of the gas response by MgO doping can be understood in relation to the promotion of ethanol-sensing reaction *via* dehydrogenation on more basic surfaces.

Based on 2DOM Fe₂O₃ with an amphoteric surface, Dai *et al.* discovered an abnormal NO₂ sensing behavior with reversible transitions from n- to p-type sensing, as shown in Fig. 8a.⁹⁸ This p-n sensing-type transition has been further revealed to be dependent on the operating temperature (*T*) and NO₂ concentration (*C*); accordingly, a *T*-*C* transition phase diagram was determined (Fig. 8b). Three zones can be observed in the *T*-*C* transition diagram, namely, p-type, n-type, and mixed p + n sensing zones, which facilitate the sensing and identification at different *T* and *C* levels. Such a *T*-*C* transition phase diagram can guide the design of SMO sensors that can be tuned accurately and as desired through an appropriate choice of *T* and *C* values. Furthermore, using classical Lennard-Jones (LJ) model, the mechanism for sensing-type transition was effectively explained, where the sensing reactions are different at high and low *C* conditions, as shown in Fig. 8c.⁹⁸ A sensing-type transition has also been observed on a MEMS-based n-type 2DOM SnO₂ sensor after aging the sensor in 100 ppm ethanol.⁹⁴ It was discovered that the modified SnO₂ sensor exhibited abnormal resistance increase to the reducing sarin gas only at 300 °C, providing a reliable route to distinguish the nerve agent sarin from other reducing interference gases (*e.g.*, dimethyl methylphosphonate, EtOH, and acetone). Such a sensing-type transition can offer us a novel and intriguing avenue for selective and discriminative gas detection.^{100–102}

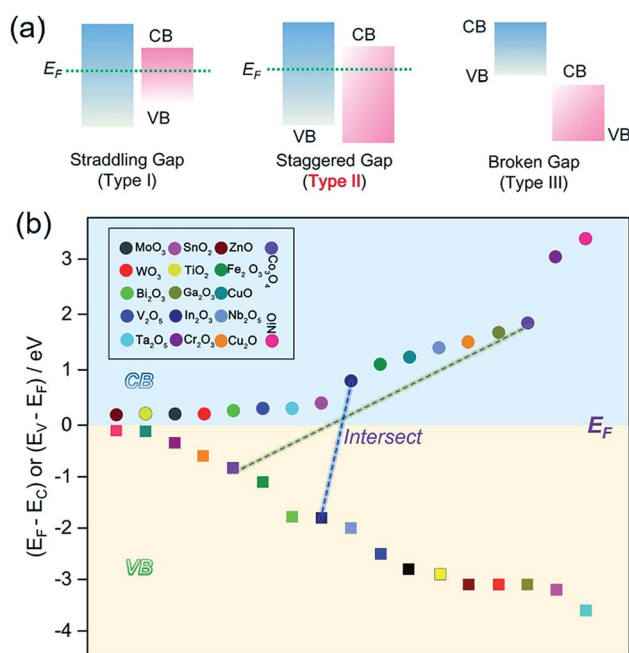


Fig. 9 (a) Three types of semiconductor heterojunctions organized by band alignment. (b) CB and VB band positions referred to the Fermi level ($E_C - E_F$ or $E_V - E_F$). In the upper portion, the CB position is arranged according to the distance to E_F for these oxides; in the bottom part, the VB position is also arranged according to the distance to E_F .

Interfacial engineering is also considered as an elegant alternative to modify the gas-sensing characteristics due to band alignment and altered electronic structures at the interfaces.^{103,104} For semiconducting oxide-oxide junctions, the interface can be classified into three types of heterojunctions, as shown in Fig. 9a. It is proven that a staggered-gap (type-II) heterojunction facilitates the separation of electron and holes at the interface, enhancing the gas-sensing performance.^{105,106} The junction diagram (band aligned by Fermi level), as shown in Fig. 9b, can be employed for determining which two oxides can form a type-II heterojunction. In Fig. 9b, only the conduction band-valence band (CB-VB) linking lines of two oxides (*e.g.*, In₂O₃-Co₃O₄ couple shown in Fig. 9b) shows an intersection, where a staggered-gap (type-II) heterojunction will be formed. For example, Zhang *et al.* fabricated 2DOM CuO/In₂O₃ bilayer 2DOM films *via* a solution-dipping and sputtering route. With regard to their sensing performance, it was revealed that the CuO/In₂O₃ p-n junction can obviously improve the gas response and lower the working temperature in comparison to the non-junction counterparts.⁹⁴ Metal decoration (*e.g.*, Au, Ag, and Pt) on the surface of hollow metal oxide nanostructures can enhance the gas-sensing properties because metal nanoparticles on the surface play the roles of chemical and/or electronic sensitizers.^{107,108} Recently, Lee *et al.* developed an ultrafine Au-loaded In₂O₃ 2DOM thin film (Fig. 10a and b) with the solution-dipping template route followed by Au evaporation and beam deposition, demonstrating ultrahigh responses (674.9–1012.9) to 5 ppm benzene, *p*-xylene, and toluene.¹⁰³ Further, the sensing responses and selectivities can be easily tuned by the size and spatial distribution of Au nanocatalysts. Based on a simple and reliable algorithm established from the signals of two sensors (Fig. 10c), harmful aromatic VOCs (benzene, xylene, and toluene) could be discriminated from the less toxic ethanol.¹⁰³ By a range of sputtering or physical vapor deposition (PVD) methods, metals can be uniformly decorated on the 2DOM outer surface,¹⁰⁹ but the inner shell could not be utilized for metal loading for further improving its sensing performance. To address this, Shim *et al.* firstly developed an elegant strategy to realize Au decoration on both sides of 2DOM SnO₂ shells, as shown in Fig. 10d; this is clearly verified by the transmission electron microscopy (TEM) images (Fig. 10e).¹⁰⁴ Excitingly, such both-side Au-decorated SnO₂ 2DOM films showed 18 times higher gas response than that by bare SnO₂ films, as shown in Fig. 10f and g. Because of the fact that extended EDLs can be formed on both outer and inner surfaces, the total EDL thickness can be maximized when compared with those of single-side-decorated samples, resulting in ultrahigh response to several gases. Apart from Au, Ag, Pt, and Pd can be the other choices of decorations as both chemical and electronic sensitizers.^{110,111}

3.2 3D macroporous arrays for gas sensing

Because of the similar routes from colloidal templates to ordered macroporous nanostructures, some strategies of 2DOM can be effectively migrated to the 3DOM system. In general, the thickening of the sensing film can deteriorate the transport of



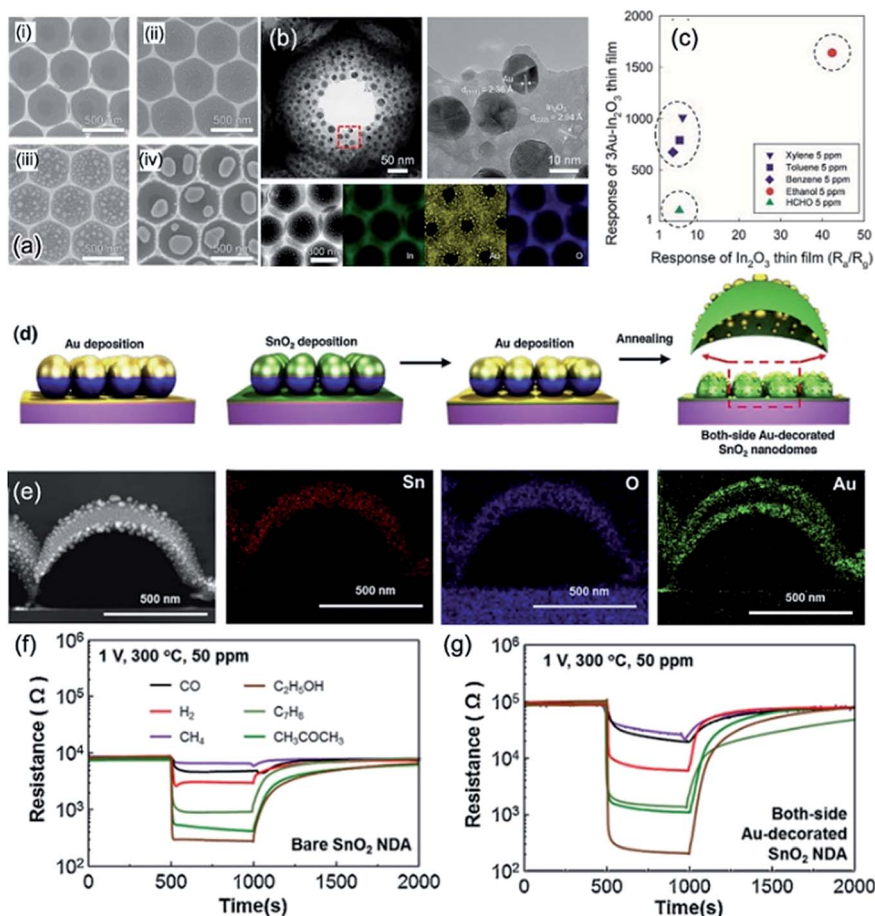


Fig. 10 (a) The morphologies of Au-decorated In_2O_3 2DOM thin films with different Au loading densities. (b) the TEM images and the corresponding elemental mapping. (c) Discriminatory behaviour between ethanol, HCHO and harmful aromatic VOCs (benzene, xylene, and toluene) using two selective sensor responses of Au- In_2O_3 2DOM sensor and pure dense In_2O_3 sensor. Reproduced with permission.¹⁰³ Copyright 2018, Elsevier Ltd. (d) Schematic illustration of the fabrication process for both-side Au-decorated In_2O_3 2DOM thin films. (e) TEM images and the corresponding elemental mapping of both-side Au-decorated In_2O_3 2DOM. (f and g) The sensing responses of the both-side Au doped In_2O_3 and bare In_2O_3 2DOM gas sensors operating at 300 °C. Reproduced with permission.¹⁰⁴ Copyright 2015, Elsevier Ltd.

the analyte gas to the inner sensing regions close to the electrodes. With this perspective, the gas response can be decreased by changing the structure from 2DOM to 3DOM. On the contrary, certain irreplaceable advantages could be engendered when using 3DOM nanostructures. For instance, a 3DOM film can exhibit higher conductance than that of a 2DOM film owing to the increased material thickness and connectivity. Moreover, the 3D frame matrix would be more robust toward tolerating compressive and tensile stresses during the heating/cooling operations as compared to the fragile 2D ones. Importantly, a 3D periodic array of macropores provides highly interconnected pores. It should be noted that the methanol (500 ppm) response of 3DOM SnO_2 with highly periodic macropores is 2.1 times higher than that of the SnO_2 porous structure containing the same size of random macropores, clearly confirming that the rapid and effective gas transport to all the sensing surfaces can be obtained with ordered macroporous structures.¹¹² Accordingly, 3DOM is also an attractive nano-architecture for fabricating high-performance gas sensors.

Due to the all-in-one formation of 3D CCs, it may be harder to control the pore hierarchy of 3DOM films than those of 2DOM ones. Herein, we will mainly introduce the recent efforts expended by researchers to enhance the sensing performance of metal oxide 3DOM films, such as surficial and interfacial effects.^{113,114} Metal decoration has also been indicated as a facile way to promote the sensing properties of 3DOM metal oxides. For example, Wang *et al.* prepared Pd-loaded 3DOM WO_3 samples with better sensing performance than pure 3DOM WO_3 , demonstrating the fact that Pd loading is an effective method to simultaneously improve the gas response (*ca.* 225 times higher), enhance the selectivity, and reduce the working temperature.¹¹⁵ The synergistic effect between Pd sensitization and structural defects of Pd-loaded 3DOM WO_3 nanomaterials leads to dramatically enhanced H_2 -sensing properties. Similarly, a Pd-loaded 3DOM In_2O_3 sensor showed enhanced NO_2 -sensing performance (resistance ratio of 980 to 500 ppb of NO_2 at room temperature) due to the Pd-induced surface modification of the EDL thickness.¹¹⁶ A Au-loaded 3DOM In_2O_3 gas sensor fabricated by Xing *et al.* was able to detect 5 ppm acetone





Fig. 11 (a) Dynamic response curves of typical 3DOM samples to different concentrations of ethanol at 250 °C. (b) Schematic diagram of ethanol sensing on the surface of pure and In-doped 3DOM ZnO. Reproduced with permission.¹¹³ Copyright 2016, American Chemical Society. (c) Morphologies and microstructure of 3DOM ZnO–CuO arrays. (d) Acetone responses of S1–S5 ZnO–CuO 3DOM sensors as a function of the working temperature; here, Zn/Cu atomic ratios are 1 : 0, 3 : 1, 1 : 1, 1 : 3, and 0 : 1 and marked as samples S1–S5, respectively. (e) Schematic illustration of p–n-junction-enhanced sensing mechanism. (f) Response of S3 ZnO–CuO 3DOM sensor to very low acetone concentration under ~93.5% RH. Reproduced with permission.¹¹⁴ Copyright 2015, Elsevier Ltd.

with response of 42.4 within 11 s at 340 °C in addition to good selectivity, showing promising potential in exhaled breath analysis for diabetes diagnosis. The excellent gas-sensing properties of the Au/In₂O₃ material could be attributed to the spillover effect between Au and In₂O₃ and the special 3D IO structure.¹¹⁷

In addition to doping noble metallic nanoparticles, oxide additives can be employed for tuning the gas-sensing characteristics. Rare-earth-(Tm, Er, La, Yb, and Ce)-doped 3DOM In₂O₃ nanostructures were prepared by a CC templating method by Han *et al.*¹¹⁸ In particular, Tm-doped 3DOM In₂O₃ exhibited the best gas-sensing performance, and the gas response for 100 ppm ethanol (122 at 175 °C) was 7 times higher than that of pure 3DOM In₂O₃. Meantime, Gu and his co-workers prepared In-doped ZnO 3DOM with an aperture size of 150 nm and fabricated a gas sensor with higher response (~88) to 100 ppm ethanol at 250 °C than that of the nondoped one, as shown in Fig. 11a.¹¹³ The enhanced gas response could be attributed to the increase in oxygen adsorption (Fig. 11b). Moreover, the low-temperature active nature of indium could lead to a decrease in the working temperature in addition to improving the ethanol response. A sensor based on Sn-doped 3DOM NiO also showed

enhanced formaldehyde-sensing performance, where the substitution of high-valence Sn⁴⁺ into Ni²⁺ enriched the surface-adsorbed oxygen to facilitate the sensing process.¹¹⁹ Alkali-metal (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺)-doped 3DOM WO₃ materials were also prepared using a simple CC template method by Gu *et al.*¹²⁰ Among these samples, Li-doped 3DOM WO₃ exhibited the highest sensing response of 55 to 500 ppb NO₂ at 25 °C along with fast response and excellent selectivity; this could be attributed to the optimized structure defects and carrier mobility of 3DOM WO₃/Li. Besides these n-type 3DOM materials, p-type 3DOM metal oxides have been also fabricated, as illustrated by the example of 3DOM La_{1-x}Mg_xFeO₃ fabricated by Qin *et al.*, among which 3DOM La_{0.95}Mg_{0.05}FeO₃ shows the optimum methanol response of 146.5 to 100 ppm at 190 °C, as well as good selectivity toward methanol due to the basic surface nature of LaFeO₃ material.¹²¹

In addition, the gas-sensing characteristics of 3DOM nanostructures can also be enhanced or tuned by appropriate heterojunctions of two different kinds of SMOs.^{122–124} Among them, ZnO–CuO nanocomposites have attracted considerable interest for their capacity toward detecting low-concentration gases.^{105,125–127} A series of 3DOM ZnO–CuO films with different Zn/Cu atom ratios were synthesized using a simple PMMA template method described by Xie *et al.*, as shown in Fig. 11c.¹¹⁴ By mixing of n-type ZnO and p-type CuO materials, numerous p–n heterojunctions and EDLs are formed at the interface, resulting in a new Fermi level and higher response to acetone gas at 20 ppm (Fig. 11d and e). The excellent sensing performance of 3DOM ZnO–CuO composites shows the promising potential in monitoring and detecting diabetes in a noninvasive and accurate manner (Fig. 11f).¹¹⁴ According to Pratsinis' studies, it should be mentioned that acetone, as a byproduct of fat metabolism, can be altered by exercise⁶³ or ketogenic diet.⁶⁴



Fig. 12 (a) Morphology of 3D inter-connected macro-mesoporous ZnO (3D-IMM-ZnO) nanostructure. (b) Schematic illustration of 3D-IMM-ZnO for gas sensing. Response and recovery time curves of 3D-IMM-ZnO nanostructures to (c) 100 ppm acetone at 260 °C and (d) 100 ppm methanol at 240 °C. Reproduced with permission.¹³⁰ Copyright 2016, American Chemical Society.



Table 1 Gas-sensing properties of representative ordered macroporous metal oxide materials. Here, the selectivity value is defined with the sensing response ratio of the target gas to the reference gas, and the stability is evaluated with the declining proportion (%) of sensing response within a specified period (month)

Samples	Template	Pore size (nm)	Temp. (°C)	Target gas	Conc. (ppm)	Gas response	Selectivity value	Stability (%/month)	Res./Rec. time (s)	Ref.
Close-network ZnO	PS spheres	400	25	NO ₂	50	27.5	213.75 to ethanol	—	35/65	48
Bowl-like ZnO	PS spheres	280	25	NO ₂	50	4.5	2.25 to ethanol	—	125/210	
Ordered SnO ₂	PS spheres	200	350	Ethanol	3	3.9	1.625 to acetone	−11.8/6	0.73/—	91
Porous LaFeO ₃	PS spheres	500	450	Ethanol	5	15	3.21 to HCHO	—	6/5	97
2D hollow SnO ₂	PS spheres	~1000	300	HCHO	0.5	23	3.67 to CH ₄	—	1.8/5.4	84
2D porous ZnO	PS spheres	420	300	Acetone	10	17	1.7 to ethanol	−5/6	—/—	85
Ordered SnO ₂	PS spheres	~500	350	Ethanol	0.1	1.24	—	—	1/1	92
Bowl-like SnO ₂	PS spheres	500	300	Ethanol	1	4.3	—	−48/2	2/2	90
α-Fe ₂ O ₃ IO film	PS spheres	500	400	NO ₂	5	—	—	−4.2/1	12/—	98
Embossed TiO ₂	PS beads	1000	250	Ethanol	500	219	4.38 to CO	—	10/—	83
Monolayer Mg–NiO	PS spheres	700	325	Ethanol	100	10.4	6.5 to benzene	−10.6/1	13/19	95
Au–SnO ₂ : 5% In	PMMA spheres	250	275	Ethanol	100	292	41.71 to MeOH	—	7/12	108
Hollow Pt–SnO ₂	PMMA spheres	800	250	H ₂	250	4.08	—	—	31/—	86
Ethanol-aged SnO ₂	PS spheres	500	400	Sarin	0.006	40	1.2 to DMMP	—	—/—	99
Porous In ₂ O ₃ /CuO	PS spheres	450	250	Ethanol	1000	9.6	5.33 to CO	—	48	94
2D Au/In ₂ O ₃	PS spheres	500	350	Ethanol	5	1640.2	282.79 to HCHO	—	—/—	103
3D IO SnO ₂	PMMA spheres	400	215	HCHO	100	629	104.83 to ethanol	−6/2	12/58	71
3D IO WO ₃	PMMA spheres	422.2	370	Acetone	5	7	3.89 to MeOH	—	10/34	76
3DOM Tm–In ₂ O ₃	PMMA spheres	200	175	Ethanol	100	122	7.63 to acetone	−2.4/1	9/13	118
3DOM Sn–NiO	PMMA spheres	200	225	HCHO	100	145	96.7 to NO ₂	−2.1/1	30/160	119
3DOM In–ZnO	PMMA spheres	150	250	Ethanol	100	88	1.83 to acetone	—	25/10	113
3DOM Li–WO ₃	PMMA spheres	~330	25	NO ₂	0.5	55	42.31 to NH ₃	−9.1/1	100/100	120
3DOM Li/K–WO ₃	PMMA spheres	200	25	NO ₂	0.5	4.5	4.09 to NH ₃	—	15/10	138
3DOM Pd/In ₂ O ₃	PMMA spheres	210	25	NO ₂	0.5	980	196 to NH ₃	0/1	270/286	123
3D IO Au/In ₂ O ₃	PMMA spheres	420	340	Acetone	5	42.4	10.6 to ethanol	—	—/—	117
3DOM Au/In ₂ O ₃	PMMA spheres	140	230	Ethanol	100	205	6.83 to MeOH	—	15/21	78
3DOM Pd/WO ₃	PMMA spheres	~330	130	H ₂	50	382	191 to HCHO	−1/1	10/50	115
3D IO ZnO–In ₂ O ₃	PS spheres	170	300	Acetone	100	35.2	25.14 to benzene	−9.1/1	1/—	129
3D IO In ₂ O ₃ –CuO	PMMA spheres	410	370	Acetone	50	39.1	9.5 to ethanol	−2.8/1.3	8/20	124
3DOM ZnO–CuO	PMMA spheres	282	310	Acetone	1	1.8	1.53 to toluene	−11/1	—/—	114
3D IO PdO@In ₂ O ₃	PS spheres	636.6	250	Acetone	100	50.9	11.31 to C ₆ H ₆	−11.6/1	—/26	139
3DOM/M LaFeO ₃	PMMA spheres	191/8–20	190	Methanol	100	96	2.44 to ethanol	—	25/23	140
3DOM/M–SnO ₂	PS spheres	100/20/3	400	Ethanol	5	316.5	3.50 to ethanol	—	1/416	141
3DOM/M–ZnO	PMMA spheres	600/25	260	Acetone	100	137	—	—	13/50	130
3DOM/M In ₂ O ₃ –ZnO	PS spheres	80/4	25	NO ₂	5	54.3	6.9 to MeOH	—	586/188	128
3DOM/M Pt–SnO ₂	Electrosprayed spheres	300/17	250	H ₂ S	1	10.8	—	—	192.4/76.5	142
3DOM/M ZnO–Fe ₃ O ₄	PMMA spheres	350/30	485	Acetone	50	47	8.44 to C ₅ H ₁₂	—	—/—	137

More recently, a series of 3D IO In₂O₃–ZnO 3DOM heterostructures have been fabricated as n–n junctions.¹²⁸ Unlike an EDL formed by the p–n junction, the electron at the n–n or p–p interface can migrate into the low-energy CB, changing the charge carrier concentration at the EDL and sequent oxygen adsorption. As a result, a 3DOM ZnO–In₂O₃ multilayer film with a pore size of 170 nm developed by Wang *et al.* exhibited improved acetone-sensing properties, such as 2-fold higher response, faster recovery, better selectivity, lower detection limit (332 ppb), and long-term stability.¹²⁹

3.3 Multimodal porosity control for gas sensing

Ordered mesoporous metal oxides are regarded as a type of promising sensing materials for gas sensors because of their high specific surface areas and excellent gas accessibility.^{130–132} The combination of macro–mesoporous (M/M) structures can not only provide highly connected diffusion channels but also engender surface accessibility, facilitating rapid sensing kinetics and high gas response.^{133,134} For instance, Liu *et al.* successfully prepared aperture-controllable 3D interconnected M/M ZnO (3D-IMM-ZnO) nanostructures by template-based



Conflicts of interest

There are no conflicts to declare.

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