

fabrication processes.^{18–20} SMONs have large specific surface areas with numerous active sites, which facilitate fast adsorption and reaction of target gases, thus enhancing their sensing performance. They have been used to detect various hazardous gases for different applications as shown in Fig. 1. These SMON sensing materials mainly include ZnO,^{31,32} CuO,^{33–36} SnO₂,^{37–39} TiO₂,^{40,41} Fe₂O₃,^{42,43} In₂O₃,^{44–47} Co₃O₄^{48–50} and WO₃.^{18,51} For further improvement of sensing performance, they have been modified using noble metals,^{52–55} metal ions,^{56–60} and carbon materials.^{61–64} Composites of multi-phase SMONs^{65–67} have also been frequently reported.

SMON-based sensors are usually heated to a higher temperature (between 100 °C to 400 °C) for performance enhancement at the expense of structural complications.^{42–47} Operation at elevated temperature levels significantly increases the energy consumption, overall device size and cost of gas sensors. Heating up to a high temperature could lead to changes in the microstructure of the sensing nanomaterials, which can result in degradation of sensing performance. In addition, high-temperature sensing has its practical limitations. Particularly, heating is very dangerous for the detection of flammable and explosive gases, with a risk of explosion. Therefore, sensors operated at room temperature (RT) are desirable for minimizing energy consumption and cost, increasing security and stability, realizing device miniaturization and suitability for handheld operations.^{68,69} For these reasons, RT gas sensors based on the SMONs have received extensive attention in recent years. Different configurations of SMONs employing nanostructures have been demonstrated with desirable performance enhancements,⁷⁰ regarding sensitivity, response/recovery time, selectivity, reversibility, reproducibility and long-term stability. Various SMONs have been designed and synthesized, such as nanorods,^{71–75} nanoparticles,^{76–81} nanowires,^{82–89} nanospheres,⁹⁰ nanosheets,^{91–94} nanotubes,^{95–98} and mesoporous nanostructures.^{99–103}

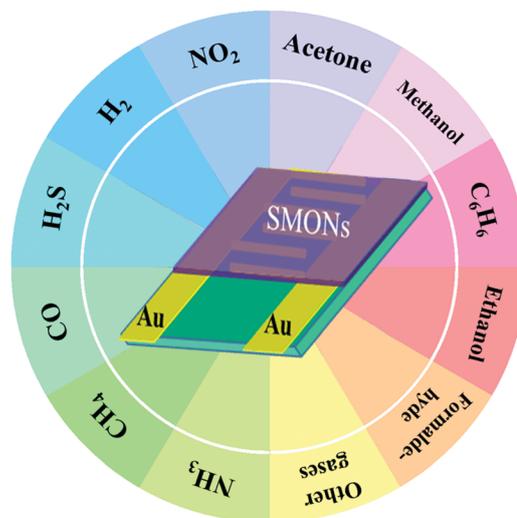


Fig. 1 Schematic diagram of resistance-type gas sensors based on semiconducting metal oxide nanostructures for detection of various hazardous gases.

The literature on SMON-based RT gas sensing is rich and the application area is very critical. New devices have been regularly introduced. Although the merits of the SMON based RT gas sensors have already been demonstrated, currently there are still some key challenges:

- (1) The sensing performance of these SMON based gas sensors is limited, when operated at RT. For example, many of these sensors exhibit insufficient sensitivities.^{104–108}
- (2) The response/recovery times of many RT gas sensors, which are crucial for rapid detection of target dangerous gases to timely trigger an alarm, are generally quite long, sometimes, up to tens of minutes.^{109–111}
- (3) Poor reversibility has been reported for some of these sensors operated at RT.¹⁰¹



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(4) Poor selectivity is another key limitation for the RT gas sensors. Selectivity of many SMON based RT gas sensors needs to be improved to avoid interference and cross-talks.¹¹²

The aim of this topical review is to critically evaluate the design and structure of SMON-based gas sensors that may help guide the design of new devices. The performance of these SMON based gas sensors operated at RT could be improved significantly by modifying the SMONs using noble metal nanoparticles,^{113–116} metal ions,^{117–119} composites of multiple SMONs^{120–123} and carbon nanomaterials.^{124–126} In addition, not only the quantity of chemisorbed oxygen species,¹²⁷ defects¹²⁸ and element compositions^{129,130} on the surface of SMONs, but also the structural properties, *i.e.*, porosity,¹³¹ heterojunction properties^{132–134} and conductivity^{135,136} can affect the RT gas sensing performance. Therefore, understanding the relationship between the sensing properties and structures of SMONs is crucial to design gas sensing materials with good sensing performance operated at RT.

Several review papers have been published on gas sensors based on different SMON sensing materials, including n-type oxide semiconductors such as ZnO,^{20,137} Fe₂O₃,¹³⁸ SnO₂,^{39,139,140} p-type oxide semiconductors,¹⁴¹ metal oxide-based heterojunctions,¹⁴² noble metal/metal oxide semiconductors^{143,144} and graphene–metal oxide nanohybrids.¹⁴⁵ However, these review papers discuss the sensing properties of the sensors which are generally operated at higher working temperatures above RT.^{146–150} Others about the RT gas sensors are focused more on certain types of SMONs based on RT sensors, such as nanostructured ZnO based RT gas sensors.¹⁵¹ However, there is no comprehensive review which is focused on the recent progress in various SMONs for high-precision gas sensors operated at RT. Therefore, this review will comprehensively summarize and discuss the recent developments of the RT gas sensors based on single phase SMONs, noble metal and metal ion modified SMONs, composites of SMONs with other metal oxides, and composites of SMONs with carbon nanomaterials, as shown in Fig. 2. In addition, we will discuss the effect of UV light stimulation on enhancing the performance of SMON based RT gas sensors, and mechanically flexible RT gas sensors based on SMONs.

2. Room temperature gas sensors based on single phase semiconducting metal oxide nanostructures

2.1 N-type semiconducting metal oxide nanostructures and gas sensors

N-type SMONs are the most reported sensing materials for RT resistive gas sensors, and they include ZnO,^{152–156} SnO₂,^{157–160} In₂O₃,¹⁶¹ WO₃,¹⁶² TiO₂,^{163–166} Fe₂O₃,^{167–169} MoO₃,¹⁷⁰ VO₂¹⁷¹ and CeO₂.¹⁷² Various forms of nanostructures including nanoparticles, nanorods, nanowires, nanoflowers, nanosheets, nanofilms, nanotubes, porous structures and hierarchical nanostructures have been employed to detect various types of gases including H₂S,^{99,101} NO₂,¹⁵⁷ H₂,¹⁷³ NH₃,¹⁷⁴ acetone,¹⁷⁵ alcohol,¹⁰⁶ HCHO,¹⁷⁶

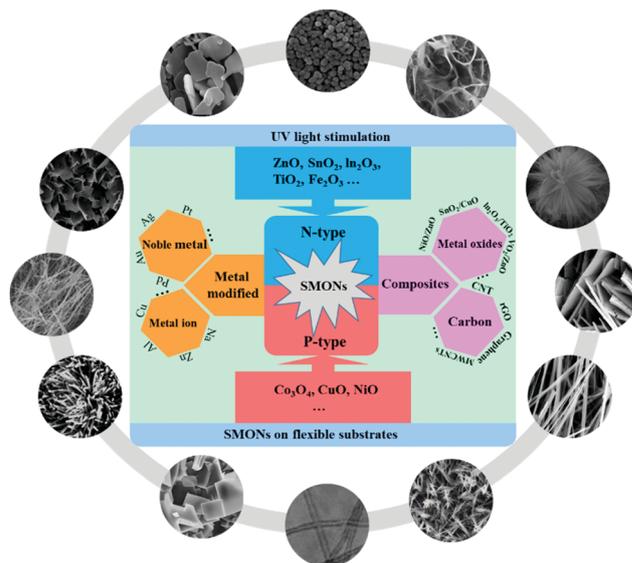
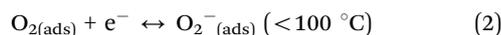


Fig. 2 Schematic diagram of various semiconducting metal oxide nanostructures used for RT gas sensors presented in this review.

liquefied petroleum gas (LPG), *etc.* Table 1 summarizes some of the reported RT sensors using the n-type SMONs.

2.1.1 Gas sensing mechanisms. The gas sensing mechanism of semiconductor oxide based resistive sensors is mostly based on the changes of resistance after they are exposed to the target gases due to the chemical interactions between target gas molecules and the adsorbed oxygen ions on the surface of SMONs.^{153,154} Conductance of n-type SMONs relies on electron carriers. When the n-type SMONs are surrounded by air, the oxygen molecules are adsorbed on their surfaces. The adsorbed oxygen molecules extract electrons from the conduction band of the surface layer, which results in the formation of negatively charged chemisorbed oxygen ions including O₂⁻, O⁻ and O²⁻ at different operating temperatures. Due to the decrease in the electron density, an electron depletion layer is formed on the surface of SMONs and a potential barrier is generated.^{42,43} Therefore, the conductivity of the SMONs decreases, thus resulting in an increased resistance.

The operation temperature of gas sensors determines the types of chemisorbed oxygen ions. For example, they are mainly O₂⁻ when the temperature is below 100 °C. When the working temperature is increased between 100 °C and 300 °C, the O₂⁻ ions will capture electrons and then transform into O⁻ ions. The O⁻ can be converted into O²⁻ ions at a higher working temperature above 300 °C. The formation process of oxygen ions can be summarized using the following equations:^{42,43}



Therefore, at RT, the oxygen ions on the surface of n-type SMONs are mainly O₂⁻ ions. When the sensor is exposed to



Table 1 (continued)

Material	Structure	Synthesis method	Target gas	C (ppm)	Response	t_{res}/t_{rec}	LOD	Ref.
VO ₂	Nanorods	Thermal evaporation	CH ₄	500	35 ^a	75/158 s	~100 ppm	75
V ₂ O ₅	Nanoneedles	Vapor deposition	Acetone	1.7	1.025	73/— s	941 ppb	175
CeO ₂	Nanowires	Hydrothermal	H ₂ S	0.05	1.11	24/15 s	50 ppb	86

C = concentration; t_{res}/t_{rec} = response time/recovery time; LOD = limit of detection; response is defined as R_a/R_g (for reducing gases) or R_g/R_a (for oxidizing gases), R_a : resistance of the sensor exposed to the reference, R_g : resistance of the sensor exposed to the target.^a Here the response is defined as $\Delta R/R_g$ (for reducing gases) or $\Delta R/R_a$ (for oxidizing gases), ΔR : the change in resistance. ^b Here the response is defined as $(\Delta R/R_g) \times 100\%$ (for reducing gases) or $(\Delta R/R_a) \times 100\%$ (for oxidizing gases).

the target gases, the gas molecules are absorbed on the surface of SMONs, and then react with these chemisorbed oxygen ions.

If the target gases are reducing gases, such as H₂S, H₂, NH₃, HCHO, or C₂H₅OH, the chemical reaction releases electrons, which are reinjected back to the electron depletion layer (see Fig. 3, the schematic diagram for H₂S gas sensing mechanism). This results in the reduction of the electron depletion layer and reduces the potential barrier energy ($\Delta\phi$). As a result, the surface resistance of SMONs is decreased. In contrast, if the target gases are oxidizing gases, such as NO, NO₂, Cl₂ and O₃, the reaction with the chemisorbed oxygen ions will capture the electrons, which will widen the electron depletion layer, resulting in an increase of the potential barrier energy ($\Delta\phi$). Accordingly, the surface resistance of the SMONs is increased.

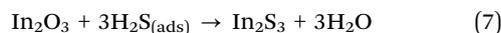
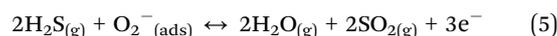
There are generally three definitions for the response values of n-type SMON based gas sensors, which are R_a/R_g , $(R_a - R_g)/R_g$ and $((R_a - R_g)/R_g) \times 100\%$ for the target reducing gases, respectively (where R_g and R_a are the resistance of sensors in the target gas and air, respectively). However, for the oxidizing gases, R_a and R_g need to be inter-changed in the above three definitions.¹⁹⁶ The time from the injection of the target gas to the time of reaching 90% of the final response is defined as the response time, and the time from the extraction of the gas to the time of reaching 10% of the final response is defined as the recovery time.

Generally, formation of chemisorbed oxygen ions determines the sensing performance. However, the gas sensing mechanism is sometimes attributed to the formation of new compounds as a result of reactions between the target gas and the surface of the SMONs. For example, H₂S gas molecules can react with ZnO

to form ZnS at RT.^{71,109} Formation of such type of conductive metal sulfide significantly decreases the resistance of the SMON-based sensors, which accounts for high sensitivities of n-type SMON-based sensors for H₂S.

Chemical and electronic sensitization of the SMONs can be realized by adding noble metals on their surface and thus can remarkably enhance their sensing properties. Surface modifications and introduction of defects on the surfaces and interfaces such as introduction of heterojunctions¹³⁴ and vacancies¹¹⁷ influence the sensing performance of SMON sensing materials. Addition of carbon nanomaterials on the surface of SMONs can also significantly improve their conductivity and enhance their sensitivities at RT.¹³⁵ In addition, an alkaline center¹²⁹ and hydroxide radicals¹⁹⁸ on the surfaces of SMONs have also been reported to affect the sensing properties, which will be discussed further.

2.1.2 Room temperature hydrogen sulfide sensors. N-type SMONs based on ZnO,¹⁵² In₂O₃,¹⁹⁹ CeO₂⁸⁶ and Fe₂O₃⁸⁰ have frequently been reported for H₂S gas sensing at RT. Among these, ZnO and In₂O₃ are wide band-gap semiconductors, with band gaps of 3.3 eV and 3.6 eV, respectively. They are very effective for H₂S sensing because H₂S molecules can be easily decomposed and can react with the chemisorbed oxygen species on the surface of these sensing materials due to the small bond energy of H–S–H. On the surface of ZnO or In₂O₃, the H₂S molecules not only react with the oxide ions of O₂[−] to form SO₂ and H₂O, but also react with ZnO or In₂O₃ to form ZnS or In₂S₃, based on the following reactions:^{71,101,109}



The reactions with the oxide ions increase electron concentrations on the surface of ZnO or In₂O₃, which leads to a significant decrease in resistance. Because ZnS and In₂S₃ are metallic conductors, the formation of ZnS or In₂S₃ also decreases the resistance of sensors, thus the responses to the gases are enhanced significantly at RT. Formation of ZnS or In₂S₃ is an exothermic process and spontaneously occurs at RT, so the sensors based on ZnO or In₂O₃ nanostructures are very suitable to detect H₂S at RT. Due to the formation of these metal sulfides, which are not reactive to most of the other gases, the selectivity of RT sensors made of the nanostructured ZnO or

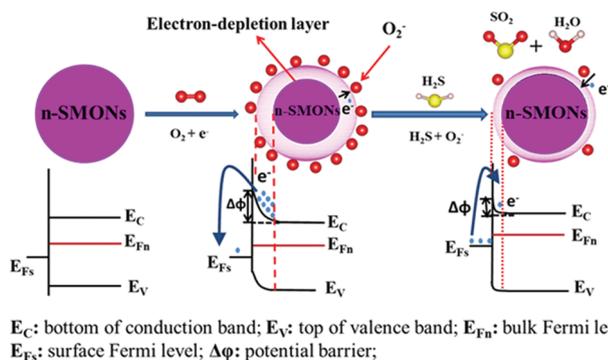


Fig. 3 Schematic diagram of the sensing mechanism of n-type semi-conducting metal oxide nanostructures for reducing gas of H₂S.



value of 2500 and good reproducibility with response and recovery times less than 20 s, both of which are better than those of the sensors made of In_2O_3 nanowires or nanoparticles. The performance enhancement is attributed to the porous structure and ultra-high surface-to-volume ratio of the porous In_2O_3 nanotubes, which can adsorb more oxygen molecules. Another gas sensor made of TiO_2 films prepared using a reactive magnetron sputter method also exhibits an excellent response with a value of 7857 to 100 ppm of NH_3 , fast response/recovery times of 34/90 s and a low LOD of ~ 5 ppm.¹⁷⁴ Kumar *et al.*⁸³ used an anodic aluminum oxide template route to prepare highly ordered ZnO nanowire arrays as the sensing layer for detection of NH_3 . The diameters of these nanowires are in the range of 60 to 70 nm and their length is about 11 μm as shown in Fig. 6a. At RT, the sensor exhibits 68% of response value (defined as $(\Delta R/R_g) \times 100\%$) to 50 ppm NH_3 and fast response/recovery times (28/29 s) (see Fig. 6b).⁸³ Another NH_3 sensor made of nanostructured ZnO thin films¹¹² synthesized using a magnetron sputtering technique shows a high response with a value of 304 to 100 ppm NH_3 with response/recovery times of 92/113 s.

Mani *et al.*¹⁸² reported a sensor made of a nanostructured ZnO thin film (shown in Fig. 6c) using a spray pyrolysis technique. As shown in Fig. 6d, the sensor using this thin film exhibits a high response with a value of 233 to 25 ppm of NH_3 at RT, and fast response and recovery times of 20/25 s. It has good selectivity to ammonia gas against other VOC gases (*i.e.* ethanol, methanol, benzyl alcohol, 2-propanol and acetone). Moreover, the sensor is insensitive to relative humidity. However, the sensor becomes saturated when the concentration of NH_3 is above 20 ppm, indicating that the LOD is about from 5 ppm to 25 ppm. In brief, high responses, fast response/recovery, and superior LOD have been achieved for the n-type SMON-based RT NH_3 gas sensors.

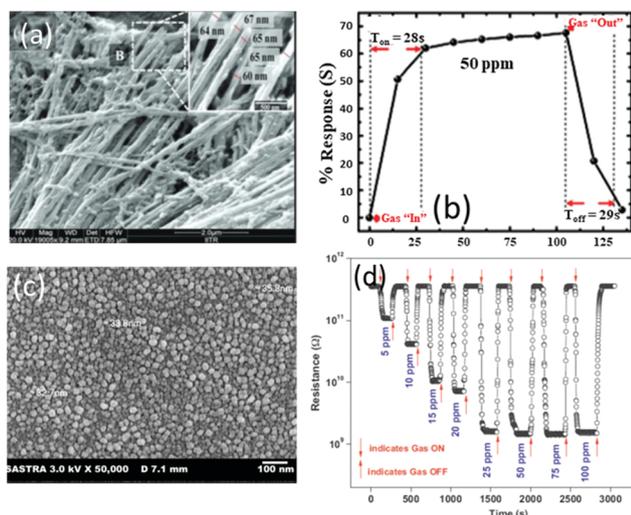


Fig. 6 (a) SEM images of the ZnO nanowire array; (b) response/recovery curves of the ZnO nanowire array for 50 ppm NH_3 .⁸³ Copyright 2014, Royal Society of Chemistry. (c) SEM image of nanostructured ZnO thin films on glass substrates; (d) response/recovery curves of the nanostructured ZnO thin film-based sensor for NH_3 .¹⁸² Copyright 2013, Elsevier.

2.1.5 Room temperature ethanol sensors. Most n-type SMONs made of ZnO ,^{218–220} Fe_2O_3 ,²²¹ SnO_2 ,²²² In_2O_3 ,¹⁰⁵ TeO_2 ⁸⁵ and WO_3 ¹⁰⁶ can be used for ethanol sensing. The sensing mechanism of n-type SMON-based ethanol gas sensors is based on the interaction of ethanol gas molecules with chemisorbed O_2^- ions on the surfaces of the SMONs. The ethanol molecules react with the adsorbed oxygen ions to form CO_2 and H_2O . Subsequently, electrons are released thus resulting in an increase in electron density and a decrease in potential barrier energy. These can be expressed using the following reactions:¹⁸⁰



The RT ethanol gas sensors based on the n-type SMONs usually exhibit rapid response and recovery. For example, a sensor based on In_2O_3 cubic crystals¹⁰⁵ prepared using a hydrothermal method exhibits very fast response/recovery (3/5 s). However, the response is poor with a value of only 1.4 to 100 ppm ethanol vapors. Fast response/recovery times together with high responses have been reported for a sensor made of ZnO nanowires.^{82,180} Shankar *et al.*⁸² reported an ethanol sensor made of ZnO nanowires (see Fig. 7a) prepared using electrospinning. Self-assembled ZnO nanowires with two different molecular weights of poly(vinyl alcohol) (PVA), *e.g.*, 14 000 and 140 000 g mol^{-1} , were prepared using an electrospinning technique, and then heat-treated to transform them into ZnO nanospheres and nanowires at a temperature of 600 $^\circ\text{C}$. These nanostructures have good selectivity to ethanol compared to other VOCs including ethanol, methanol, acetaldehyde, and acetone when operated at RT. The nanowire based sensors have a higher ethanol response (78 to 100 ppm) than those based on the nanoparticles (about 48 to 100 ppm).⁷⁶ The nanowire-based ones also show fast response/recovery times of 9/12 s. Furthermore, the nanowire-based sensor has excellent repeatability.

Fig. 7b shows a schematic diagram of the ethanol sensing mechanism for the ZnO-based sensor.⁸² The chemisorption of oxygen molecules on the sensor surface results in the formation of a space charge region on the surface of ZnO, which can act as a barrier for electron transport in the ZnO sensing layer.⁸² Due to the formation of double-spaced charge layers from the intergranular contacts of nanoparticles, the potential barrier energy is increased, which results in the broadening of the percolation path and hinders the electron transport. This further influences the adsorption-desorption rate and the sensing properties towards ethanol. However, the intergranular contact resistance will be reduced in the ZnO nanowires, which decreases the potential barrier energy, thus enhancing the sensing performance.

Similarly, TiO_2 nanotubes⁹⁶ prepared using an electrochemical anodization method and TeO_2 nanowires⁸⁵ prepared using thermal evaporation also show good responses to ethanol.^{85,96} However, the selectivity is poor as they are also sensitive to methanol and propanol.

2.1.6 Room temperature hydrogen sensors. Hydrogen gas is one of the extremely flammable and explosive gases. Therefore, detection of traces of hydrogen gas using RT gas sensors is



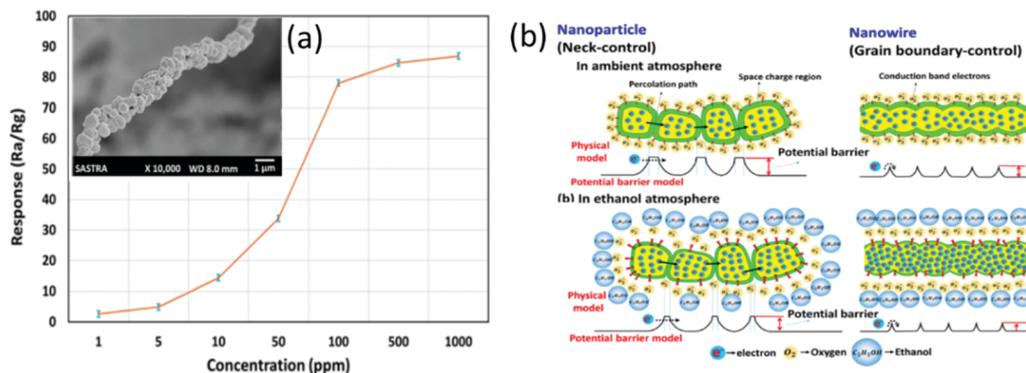
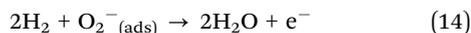


Fig. 7 (a) Responses of the ZnO nanowire sensor to different concentrations of ethanol at room temperature; the inset shows the SEM image of ZnO nanowires; (b) the schematic diagram of the ethanol sensing mechanism.⁸² Copyright 2017, American Chemical Society.

critical to avoid the dangers of explosion. For this application, the sensors must be fast, highly sensitive and selective. In particular, the fast response is paramount for a timely detection of a possible hydrogen leakage. As summarized in Table 1, the SMONs made of ZnO,^{188,189} MoO₃¹⁹² and SnO₂¹⁹³ have been demonstrated for hydrogen sensing at RT using various nanostructures including nanofilms,¹⁸⁹ nanowires,¹⁰⁸ nanotubes¹⁸⁸ and nanorods.^{190,191} The sensing mechanism is based on the reaction of H₂ molecules with chemisorbed O₂⁻ ions on the surface of the SMONs, as shown in the following chemical equation:¹⁸⁹



From the literature, sensors made from ZnO films¹⁸⁹ and ZnO nanorods¹⁹¹ show high responses to H₂, but long response/recovery times (see Fig. 8).

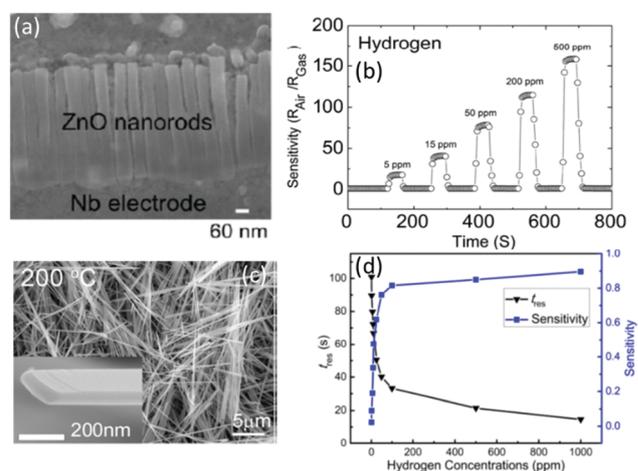


Fig. 9 (a) TEM image of vertical ZnO nanorods; (b) response/recovery curves of a vertical ZnO nanorod-based gas sensor versus different concentrations of H₂.¹⁹⁰ Copyright 2012, Elsevier. (c) SEM images of α-MoO₃ nanoribbons; (d) response values and times of an α-MoO₃ nanoribbon-based gas sensor versus different concentrations of H₂.¹⁹² Copyright 2015, American Chemical Society.

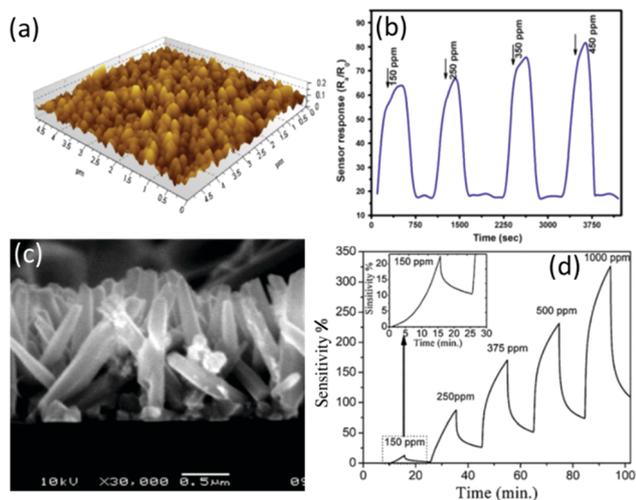


Fig. 8 (a) AFM image of the ZnO films and (b) response/recovery curves of a ZnO film-based gas sensor to different concentrations of H₂.¹⁸⁹ Copyright 2014, Springer Nature. (c) Cross section SEM image of the ZnO nanorods and (d) response/recovery curves of a ZnO nanorod-based gas sensor to different concentrations of H₂.¹⁹¹ Copyright 2013, Elsevier.

Using anodized aluminum oxides as nano-templates, Lim *et al.*¹⁹⁰ synthesized vertical ZnO nanorods (see Fig. 9a) using atomic layer deposition, and a highly sensitive and fast response/recovery H₂ gas sensor was fabricated using these vertical ZnO nanorods. A response value of 162 for 500 ppm H₂ and a response time of 30 s were demonstrated (see Fig. 9b).¹⁹⁰ A faster response H₂ gas sensor was also reported using [001]-oriented α-MoO₃ nanoribbons (see Fig. 9c)¹⁹² with a response time of 14.1 s for 1000 ppm of H₂ and a low LOD of 500 ppb (see Fig. 9d).¹⁹² It has good reproducibility and high selectivity against ethanol, CO and acetone.

In brief, RT gas sensors based on n-type SMONs can detect most of the hazardous gases, with advantages such as easy preparation, low cost, simple post-treatment and good stability of structure. Various morphologies of nanostructures for n-type SMONs have been synthesized and used in gas sensors operated at the RT. These sensors have been widely used to detect various gases and some good sensing properties have been achieved.



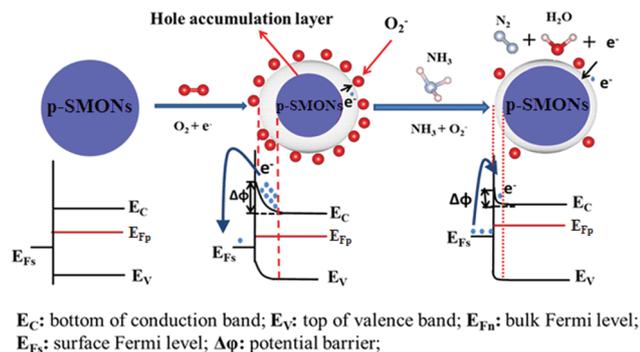


Fig. 10 Schematic diagram of the sensing mechanism for p-type semi-conducting metal oxide nanostructures to reducing gas of NH_3 .

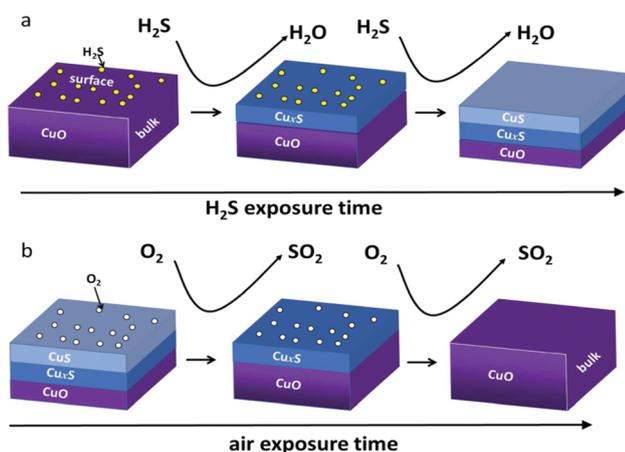


Fig. 11 Schematic diagrams of the sensing mechanism of CuO: (a) response process in H_2S and (b) recovery process in air.⁹³ Copyright 2016, American Chemical Society.

oxygen ions, the formation of CuS is highly responsible for the sensing response to H_2S at RT.

Fig. 11 shows schematic diagrams of the sensing mechanism for CuO-based H_2S sensors. H_2S molecules can react with CuO to form CuS on the surface at RT, based on the following reactions:^{93,225}

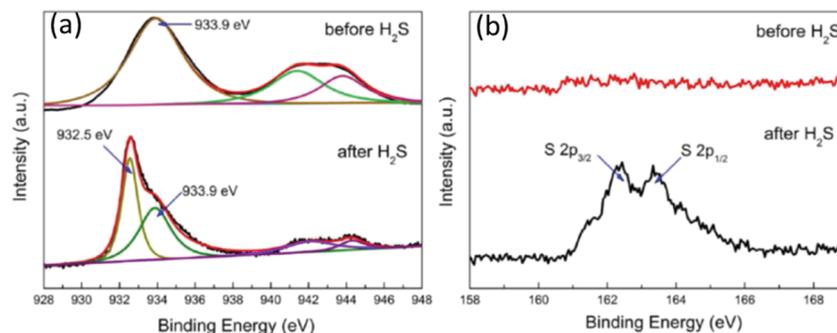
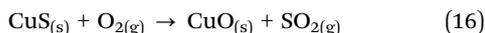


Fig. 12 (a) Cu $2p_{3/2}$ and (b) S $2p$ XPS spectra of porous CuO nanosheets before and after exposure to H_2S .⁹³ Copyright 2016, American Chemical Society.

CuS is a metallic-like conductor. Formation of CuS on the SMON's surface will dramatically decrease the resistance of the sensor. Consequently, although H_2S is a reducing gas, the response of the sensors exhibits a decrease in resistance. The RT H_2S gas sensors are highly selective owing to this unique interaction between H_2S and CuO. However, their recovery times are relatively long at RT due to the requirement for the transformation from CuS to CuO.

This H_2S sensing mechanism has been proved from different studies. For example, Li *et al.*⁹³ reported a H_2S sensor based on porous CuO nanosheets with a thickness of about 60 nm on alumina tubes, prepared using a hydrothermal method. The sensor based on these porous CuO nanosheets has excellent selectivity to H_2S . It exhibits high response values to H_2S , but no apparent responses to NH_3 , CO, NO, NO_2 , H_2 , and $\text{C}_2\text{H}_5\text{OH}$.⁹³ The sensor has a superior LOD as low as 10 ppb and good reproducibility at RT. The sensing mechanism based on the transformation from CuO into CuS on the surface of nanosheets has been verified using XPS analysis. As seen from the XPS spectra in Fig. 12, after the CuO is exposed to H_2S gas, a new peak of the Cu $2p_{3/2}$ state at 930.8 eV appears which is attributed to CuS, and the S $2p_{3/2}$ and S $2p_{1/2}$ states at 162.3 and 163.4 eV can be identified. Similarly, nanostructures of hierarchical flower-like CuO nanostructures²²⁵ have been prepared, and the sensors made of these nanostructured CuO exhibit high sensitivity, good reproducibility and high sensing selectivity to H_2S at RT. Zhang *et al.*⁹⁸ prepared tube-like CuO nanostructures using pomelo flesh as a bio-template. The unique tube-like CuO nanostructures enhance the diffusion of H_2S molecules and promote the rapid formation of CuS. The H_2S sensor based on the tube-like CuO nanostructures has good selectivity to H_2S , compared to gases such as gasoline, formaldehyde, CH_4 , H_2 , acetone, CO, toluene, and ethanol. The response/recovery times are lower than 60 s for the H_2S in a wide range of 10 ppb–10 ppm. In addition, the sensor demonstrates a stable detection performance at RT over 3 months.

2.2.3 Room temperature ammonia sensors. The CuO nanostructures are also suitable for NH_3 sensing at RT. Sakthivel *et al.*²²³ fabricated a flexible NH_3 sensor on a polyethylene terephthalate substrate using CuO nano-rectangles, which were synthesized using a surfactant-free hydrothermal method. The flexible RT sensor made of the CuO nano-rectangles is effective



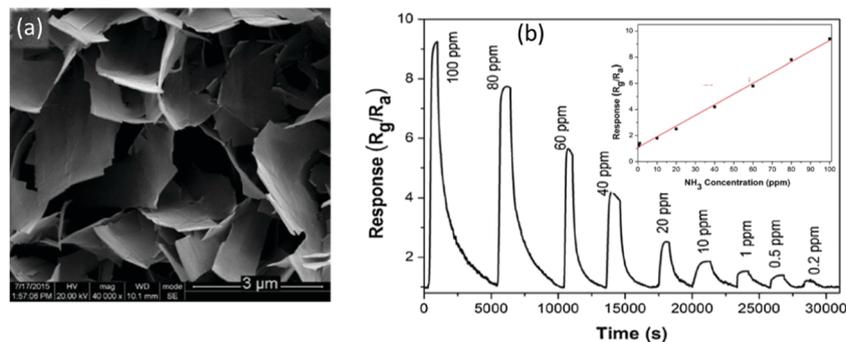


Fig. 13 (a) SEM image of network Co_3O_4 nano-sheet arrays; (b) response/recovery curves of the network Co_3O_4 nano-sheet array based sensor to different concentrations of H_2S at room temperature (the inset shows the response value).⁹² Copyright 2016, Elsevier.

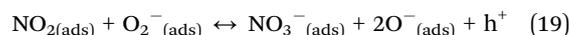
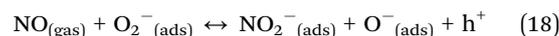
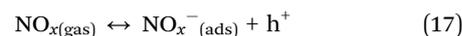
for sensing ammonia even under different bending conditions as it exhibits identical response and response/recovery times. Furthermore, this flexible NH_3 sensor exhibits both good stability and reproducibility in a three-month testing period.²²³

Co_3O_4 nanostructures⁹² have also been found to be effective for NH_3 detection with fast response speeds at RT. Fig. 13a shows an image of a Co_3O_4 nano-sheet array network deposited on an alumina tube prepared using a hydrothermal method. The average sheet thickness of the Co_3O_4 nano-sheet is 39.5 nm. NH_3 molecules react with the surface chemisorbed O_2^- ions and form N_2 and H_2O . As shown in Fig. 13b, the response time for the gas sensor is as short as 9 s for 0.2 ppm NH_3 at RT. The sensor responds linearly to the concentrations of NH_3 within a range between 1–100 ppm. It also exhibits good performance in terms of reproducibility, stability and selectivity to NH_3 (compared to H_2 , CO , H_2S and $\text{C}_2\text{H}_5\text{OH}$). 3D hierarchical porous Co_3O_4 nanostructures¹⁰³ were synthesized by Wu *et al.* using polystyrene spheres as the template. The average particle size is 20 nm and the specific surface area is $58.75 \text{ m}^2 \text{ g}^{-1}$. The structures have macro-size pores, mesopores and plenty of irregular structural defects. The sensor made of these porous Co_3O_4 nanostructures exhibits a sensitivity of 146% (defined as $(\Delta R/R_g) \times 100\%$) to 100 ppm NH_3 , and has a fast response time of 2 s. However, the recovery time is very long, *e.g.*, longer than 1000 s.¹⁰³

Apart from CuO and Co_3O_4 nanostructures, NiO ^{233,238} and MnO_2 ²³⁹ were also used to make RT NH_3 gas sensors, although the response was found to be very slow. Applying special nanostructures can improve the responses of the sensors. For example, the hierarchical hollow nanospheres of $\alpha\text{-MnO}_2$ composed of densely aligned nanowires were reported to exhibit an improved NH_3 gas sensing sensitivity, and faster response and recovery compared with the standard $\alpha\text{-MnO}_2$ nanowires.²³⁸ Doping with metal ions such as Al doped NiO was also reported as an effective route for improving the sensitivity and responses of the sensor operated at RT.²³³

2.2.4 Room temperature nitrogen dioxide sensors. P-type nanostructures have also been reported as good RT NO_2 sensing materials. When they are exposed to the oxidizing gases, such as NO_x , the NO_x molecules are absorbed on the surface and form NO_x^- and holes, and the reactions of NO_x with the chemisorbed oxygen ions also increase the concentration of holes on the surface,

which can be revealed from the reaction eqn (17)–(19).²³⁵ These reactions will widen the width of the accumulated hole layer on the surface of p-type SMONs, and cause the increase in conductivity of the sensors.



Self-assembled mesoporous Cu_xO virus-like microspheres²²⁹ exhibited a high response of 28.4 and response/recovery times of 22/42 s to 4 ppm NO_2 gas measured at RT. The good sensing performance of this special microstructure is attributed to the formation of hierarchical 3D nanostructures, micropores and large surface area for effective gas diffusion, the abundant surface oxygen vacancies and the heterojunctions at the interfaces between CuO and Cu_2O . The RT NO_2 gas sensors were also made using unique chain Co_3O_4 structures²³⁵ and self-assembled polycrystalline hexagonal NiO nanosheets.²²⁶ Because of the reduced grain boundaries, which minimizes the carriers' scattering at the interfaces during the chemisorption of NO_2 , these special Co_3O_4 nanostructures showed much better responses to NO_2 than those made of the Co_3O_4 and NiO nanoparticles.

Apart from detecting H_2S , NH_3 and NO_2 , the RT sensors based on the p-type SMONs have also been used for detecting other types of gases. For example, a sensor made of MnO_2 shows good sensing performance for acetaldehyde vapor,²⁴⁰ and at ambient temperature, $\beta\text{-MnO}_2$ thin films were reported to have good sensing responses and fast response/recovery. The sensitivity was found to be 89% for sensing 10 ppm acetaldehyde vapor, and the response and recovery times were found to be of 60 s and 11 s, respectively. This sensor also showed good selectivity to acetaldehyde gas, compared with the other reducing gases such as acetone, benzene, diethylamine, ethanol, dimethylamine, 2-propanol, monomethylamine and ammonia.²⁴⁰ Sensors made of Co_3O_4 nanosheets were also reported to have very fast response and recovery of 15/20 s to 50 ppm CO and CH_4 .²³⁴

The p-type Cr_2O_3 based gas sensor is normally operated at higher temperatures above 100 °C, and there are few reports about the Cr_2O_3 based RT gas sensors. However, 3D cubic



mesoporous Cr₂O₃ nanostructures were recently prepared and the sensor made of this nanostructure exhibits an enhanced sensitivity for detecting ethanol vapor at room temperature, which is much better than those of the dense Cr₂O₃ film.²³⁷ The response of the 3D cubic mesoporous Cr₂O₃ sensor is 13.0 to 1000 ppm ethanol, whereas it is only 2.0 for the dense Cr₂O₃ film.

Although there are some reports on using the p-type SMONs in gas sensors operated at high temperature, these are much fewer compared to those on using n-type SMONs. The sensitivity of p-type SMON sensors is generally not as high as that of the n-type SMON sensors. Modification of the p-type SMONs using noble metal nanoparticles or metal ions is an effective route to further enhance the sensing performance, which will be discussed in Section 3.

3. Room temperature gas sensors based on modified and composite semiconducting metal oxide nanostructures

3.1 Metal modified semiconducting metal oxide and gas sensors

3.1.1 Gas sensors based on noble metal modified semiconducting metal oxide nanostructures. Due to their chemical sensitization and electronic sensitization, noble metals have been widely applied for surface modifications of SMONs, which has become one of the effective routes to improve their sensing performance, especially for the sensors operated at RT.²⁴¹ This can be seen from the comparison of room temperature sensing properties between the pristine and noble metal modified SMONs as listed in Table 3. So far, the noble metals used to modify the SMON based gas sensors are mainly Au,^{242–246} Ag,^{247,248} Pt^{249,250} and Pd.^{251–254} Nanoparticles of the noble metals are usually decorated onto surfaces of SMONs using the wet-chemical method,¹¹⁶ thermal vaporization,²⁵³ sputtering method²⁵⁵ and electrospinning technology.²⁵⁶ Many of these sensors have the commonly reported spill-over effect,²⁴¹ which means that the active centers on the surface of the solid catalyst produce oxygen active species by adsorbing oxygen molecules. Due to this effect, more oxygen ions are formed on the surface of the SMONs. Being excellent active catalysts, noble metal nanoparticles can facilitate the adsorption of oxygen molecules and enhance the formation of oxygen ions by chemical reduction, which then spill onto the surface of the SMONs, thus increasing the concentration of oxygen ions. The target molecules can also be directly adsorbed onto these noble metal nanoparticles, and then they migrate onto the surface of the SMONs to react with the oxygen ions. These spill-over effects significantly enhance the sensing performance. In addition, these noble metal nanoparticles can also accelerate the transfer of electrons onto the surfaces of the SMONs. Therefore, both the chemical sensitization and electronic sensitization enhance the sensitivity and speed of the SMON-based sensors.

At RT, some gases such as CO and H₂ are very difficult to detect using the sensors made of pristine SMONs. However, this problem might be solved by modifying the surface of these SMONs using noble metal nanoparticles. For example, Arunkumar *et al.*¹¹³ prepared ZnO nanostar features using a hydrothermal route and then decorated these nanostars using Au nanoparticles with an average size of ~5–6 nm as shown in Fig. 14a. The ZnO nanostars decorated with 3 wt% gold nanoparticles can enhance the response (~15 for 50 ppm CO) and achieve very fast response/recovery times (~8/15 s) at 35 °C.¹¹³ The selectivity of the sensor for Co sensing is excellent against the other interfering gases including methanol, ethanol, acetone and hydrogen. Fig. 14b shows the energy band diagrams of ZnO and Au/ZnO nanostars before and after CO exposure. Due to the spillover effect, a nanoscale depletion region is formed at the interface between Au nanoparticles and ZnO as a result of strong electronic interactions, thus altering the height of the Schottky barrier. Therefore, the enhanced performance of the sensor operated at RT is attributed to the spillover effect.¹¹³

Choi *et al.*¹¹⁴ grew a network of ZnO nanowires using a vapor–liquid–solid method and then these nanowires were functionalized with Pd nanodots using a γ -ray radiolysis method, and the sensor made of these decorated nanowires shows an improvement of the sensing performance. This improvement is attributed to the electronic and chemical sensitizations from the Pd nanodots.¹¹⁴ Wang *et al.*¹¹⁵ reported a highly sensitive RT CO sensor based on Pt/SnO₂ porous nanostructures. The porous SnO₂ nanostructures were synthesized using a solvothermal method, and Pt nanoparticles were then decorated onto the SnO₂ using hexachloro-platinic acid. The sensor exhibits a good response with a value of 64.5 to 100 ppm CO at RT. It also shows good selectivity, compared to the other gases including CO, H₂, N(CH₃)₃, NH₃ and CH₄. Similarly, a RT CO gas sensor made of Au/In₂O₃ composite nano-rods was fabricated, and showed a high response and fast response/recovery times (30/30 s to 100 ppm CO).²⁴⁴

Modification of SMONs by noble metals can not only enhance the sensitivity, but also significantly improve the selectivity and response/recovery speed. For example, a ZnO nanowire-based sensor modified with Pd nanoparticles exhibits both ultra-high sensitivity and very fast response and recovery.^{252,265} A Pd-modified ZnO nanowire-based RT nanosensor was prepared using electrochemical deposition by Lupan *et al.*,²⁵² and it exhibits very fast response/recovery times of 6.4/7.4 s and a super-high response value of 13 100 to 100 ppm H₂ as shown in Fig. 15a and b. This H₂ sensor shows very good selectivity against the other gases such as CO, CH₄, ethanol and acetone. The sensor can be operated at very low current levels with ultra-low power consumption.²⁵²

Ultra-sensitive RT hydrogen gas sensors based on noble metal modified SnO₂ have also been reported. For example, the sensor based on Pt/SnO₂ nanoparticles exhibits a super-high response (*e.g.*, 10 500 to 1000 ppm H₂) at RT.²⁴⁹ Lee *et al.*²⁵³ reported a RT hydrogen sensor made of Pd/SnO₂ nanowires (as shown in Fig. 15c) prepared using a thermal evaporation method, and the sensor shows an ultra-high sensitivity of about 120 000% (defined as $(\Delta R/R_g) \times 100\%$) to 10 000 ppm H₂ and a



Table 3 Comparison of room temperature sensing properties of the noble metal modified semiconducting metal oxide nanostructures

Material	Structure	Synthesis method	Target gas	Concentration (ppm)	Response value	t_{res}/t_{rec}	LOD	Ref.
Pt/ZnO ZnO	Nanowires	Vapor-liquid-solid	CO	0.1	1.02 0	120/180 s	100 ppb	114
Au/ZnO ZnO	Nanostars	Hydrothermal	CO	50 1000	55.3 0	10/12 s	5 ppm	113
Au/ZnO ZnO	Nanowires	Hydrothermal	H ₂ S	5	79.4 5	—/170 s —/860 s	~1 ppm	242
Au/ZnO ZnO	Nanorods	Vapor phase transport	H ₂ S	3	~475 ~125	11/20 min 10/13 min	~0.5 ppm	257
Au/ZnO ZnO	Core-shells Shells	Sol-gel	HCOH	5	10.57 1.91	138/104 s 332/736 s	500 ppb	258
Pd/ZnO	Nanoparticles	Sol-gel	NO ₂	50	45.2 ^b	67/250 s	10 ppm	251
Pt/SnO ₂	Porous	Solvothermal	CO	100	64.5	144/882 s	~50 ppm	115
Au/SnO ₂ SnO ₂	Nanoparticles	Sputtering	NO ₂	50	90 ^b ~25 ^b	70/— s	600 ppb	243
Au/In ₂ O ₃ In ₂ O ₃	Nanorods	Aqueous solution	CO	100	9 0	30/30 s	~50 ppm	244
Au/TiO ₂ TiO ₂	Core-shells Shells	Sol-gel	O ₃	2.5	3.27 1.36	5/24 s 32/76 s	0.4 ppm	259
Ag/TiO ₂ TiO ₂	Nanoparticles	Sol-gel	Ethanol	5	4.35 1.54	52/61 s 112/136 s	0.15 ppm	247
Pd/TiO ₂ TiO ₂	Nanofiber array	Electrospinning	NH ₃	100	6.97 0	3/150 s	~0.1 ppm	260
Ag/TiO ₂ TiO ₂	Nanorods	Wet chemical	Ethanol	50	11.98 ^a 8.15 ^a	3/73 s 6/213 s	~5 ppm	116
Au/VO ₂ VO ₂	Nanowires	CVD/Ion sputtering CVD	NO ₂	5	3.22 ~1	~50/~600 s	~0.5 ppm	130
Pt/VO _x	Thin films	Magnetron sputtering	CH ₄	500	18.2 ^b	~1000/~2000 s	~500 ppm	261
Au/VO ₂ VO ₂	Nanosheets	CVD	CH ₄	500	~70 ^b ~35 ^b	~50/~100 s	~100 ppm	262
Pd/Ga ₂ O ₃ Ga ₂ O ₃	Nanowires	Thermal evaporation	NO ₂	100	41.44 ^b 0	200/70 s	~10 ppm	263
Pd/ZnO ZnO	Nanorods	Aqueous solution	H ₂	1000	91.2 ^b ~20 ^b	18.8/— s	0.2 ppm	264
Pd/ZnO	Nanowires	CVD	H ₂	4000	1017.9 ^b	36/50 s	20 ppm	265
Pd/ZnO	Nanowires	Electrochemical deposition	H ₂	100	13 100	6.4/7.4 s	—	252
Pd/SnO ₂ SnO ₂	Nanofibers	Electrospun	H ₂	1000	12.09 ~3	4/3 s 2/— s	0.02 ppm	266
Pt/SnO ₂ SnO ₂	Nanoparticles	Aqueous solution	H ₂	1000	10 500 0	20/— s	—	249
Pd/SnO ₂ Pd/TiO ₂	Nanoparticles Nanotubes	Thermal vaporization Sputtering	H ₂	10 000 8000	12 0000 ^b 92.05 ^b	2/— s 3.8/43.3 s	40 ppm	253 255
TiO ₂				5000	54.6 ^b	73.8/103.8 s	—	—
Pt/TiO ₂	Nanocomposites	Pressing and sintering	H ₂	1000	6000	10/20 s	—	267
Pd/WO ₃ WO ₃	Nanocomposites Nanoplates	Hydrothermal	H ₂	1000	34 ~0	24/— s	—	268
Pt/Nb ₂ O ₅ Nb ₂ O ₅	Porous ceramics	Pressing and sintering	H ₂	10 000	165 0	7/39 s	200 ppm	269
Au/In ₂ O ₃ In ₂ O ₃	Nanofibers	Electrospinning	Ethanol	100	11.12 5.4	47/351 s	20 ppm	270
Pt/In ₂ O ₃	Nanocubes	Hydrothermal	H ₂	15000	~20	33/66 s	—	241

C = concentration; t_{res}/t_{rec} = response time/recovery time; LOD = limit of detection; response is defined as R_a/R_g (for reducing gases) or R_g/R_a (for oxidizing gases), R_a : resistance of the sensor exposed to the reference, R_g : resistance of the sensor exposed to the target.^a Here the response is defined as $\Delta R/R_g$ (for reducing gases) or $\Delta R/R_a$ (for oxidizing gases), ΔR : the change in resistance.^b Here the response is defined as $(\Delta R/R_g) \times 100\%$ (for reducing gases) or $(\Delta R/R_a) \times 100\%$ (for oxidizing gases).

fast response time of 2 s as shown in Fig. 15d. The Pd/SnO₂ nanofibers²⁶⁶ were also synthesized using an electrospinning method, and the sensor made of these nanofibers exhibits super-fast response/recovery times to H₂ (4/3 s to 1000 ppm H₂) and an ultra-low LOD of 20 ppb. The response of a sensor made of Pt/TiO₂ nanocomposites to 1000 ppm H₂ in N₂ was also reported as high as 6000 at RT, with short response/recovery times of only 10/20 s.²⁶⁷

Apart from the chemical sensitization and electronic sensitization, there are other mechanisms to enhance the sensing performance of the SMONs: for example, the formation of

nano-scale Schottky type junctions between Au nanoparticles and ZnO nanorods and Au sulfidation with high concentrations of H₂S.²⁵⁷ Hosseini *et al.*²⁵⁷ prepared ZnO nanorods using a vapor phase transport method, and found that H₂S sensing performance has been significantly enhanced at RT after the modification of the surface of ZnO nanorods with Au nanoparticles (see Fig. 16a). As shown in Fig. 16b and c, both high response (1270 to 6 ppm of H₂S) and good H₂S selectivity of the Au/ZnO nanorods have been achieved, which are much better than those of the pristine ZnO nanorods.



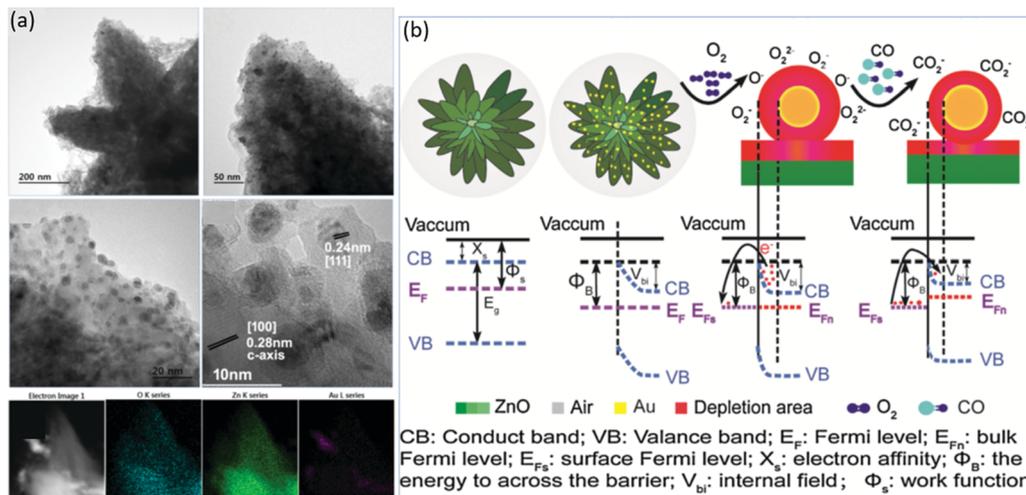


Fig. 14 (a) TEM images and element mapping of Au/ZnO nanostars; (b) energy band diagrams of ZnO and Au/ZnO nanostars before and after CO exposure.¹¹³ Copyright 2017, Elsevier.

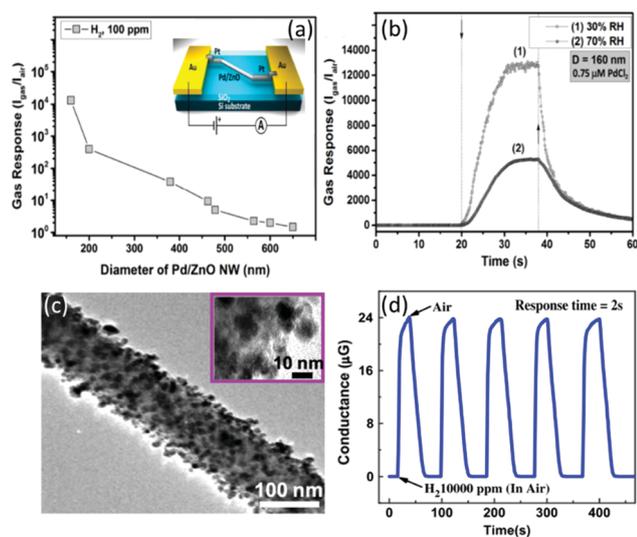


Fig. 15 (a) Responses of nanosensors based on single Pd/ZnO nanowires with different diameters to 100 ppm of H₂ at RT and 30% RH (the inset shows the schematic of the nanosensor device structure); (b) response of the Pd/ZnO nanowire based sensor to 100 ppm of H₂ at 30% and 70% RH at RT.²⁵² Copyright 2018, Elsevier. (c) TEM image of 30 at% Pd/SnO₂ nanofiber; (d) the response/recovery curves of the 30 at% Pd/SnO₂ nanofiber based sensor for H₂ gas.²⁵³ Copyright 2010, Elsevier.

In summary, due to the combined effects of chemical sensitization and electronic sensitization, noble metal nanoparticles and other nanostructures are suitable to be used to modify the SMONs in order to improve the sensing performance of the RT gas sensors. One significant improvement is the shortening of the response and recovery times, along with the enhanced response values and selectivity.

3.1.2 Gas sensors based on conventional metal ion doped semiconducting metal oxide nanostructures. Doping of metal ions in SMONs can increase the number of active sites and defects on the surface of SMON nanocrystals, and thus enhance

the amount of oxygen species and increase the adsorbed gas molecules on the sensor's surface. Therefore, the gas sensing performance of the SMONs can be effectively improved by doping of metal ions including Al³⁺,^{117,271} Cu²⁺,^{272,273} Zn²⁺,²⁷⁴ Ni²⁺,^{275,276} Co³⁺,^{277,278} Fe³⁺,²⁷⁹ Mg²⁺,²⁸⁰ and Sb⁵⁺.²⁸¹ The recent key sensing applications of RT gas sensors using this method are summarized in Table 4.

The amount of dopant Al³⁺ ions was found to significantly affect the gas sensing properties of NiO nanosheets.¹¹⁷ Al³⁺ doped NiO nanosheets have introduced many new oxygen vacancies due to aliovalent ion doping. Superoxide complexes such as Ni²⁺-O₂⁻ are easily formed on the surface of the NiO due to the existence of oxygen vacancies. As they are very active, they can significantly increase the sensitivity of the NiO nanosheets. Compared with those of the pure NiO nanosheets, the response of the Al doped NiO nanosheet based sensor to NO₂ was enhanced up to 35 times at RT. Doping with metal ions including Sb, Cd, and Ce has also been proved to enhance the sensing properties of the WO₃ nanoparticles to NO₂ gas at RT.²⁰⁹ Among these, Sb-doped WO₃ nanoparticles exhibit a 6.8 times higher response and much better selectivity than those of the undoped WO₃ (as shown in Fig. 17). The enhancement mechanisms have been identified to be the increase in the number of oxygen vacancies on the surface of metal doped WO₃ based on the analysis results from photoluminescence, Raman spectroscopy and XPS.²⁰⁹

The responses and recovery speeds of the sensor can be significantly improved by doping of metal ions into the SMONs, which is important for practical applications of the RT gas sensors. For example, a Zn-doped NiO dendritic nanostructure¹¹⁹ exhibits faster responses (5–8 times) and faster recovery (30–50 times) rates than those of the pure NiO dendritic crystals. A sensor based on Mg-doped ZnO thin films on glass substrates deposited through a spray pyrolysis process²⁸³ shows a much higher response (796 towards 100 ppm of NH₃) and faster response/recovery speeds (34/28 s) than those of the pure ZnO film measured at RT.



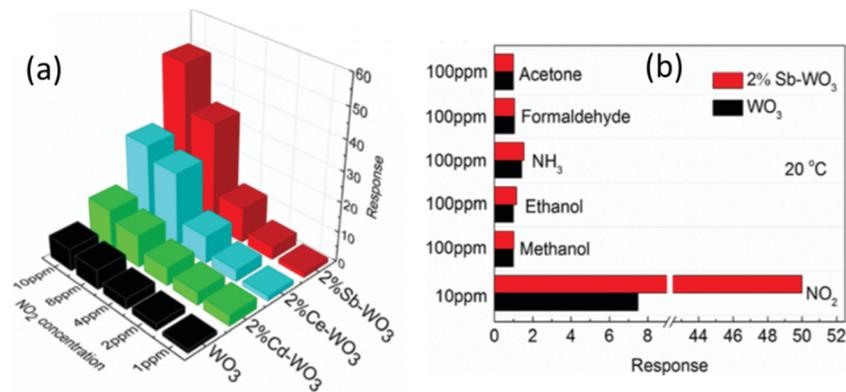


Fig. 17 (a) Responses of sensors made of 2%-Sb-WO₃, 2%-Ce-WO₃ and 2%-Cd-WO₃ to different concentrations of NO₂; (b) responses of sensors made of 2%-Sb-WO₃ to different gases.²⁰⁹ Copyright 2017, American Chemical Society.

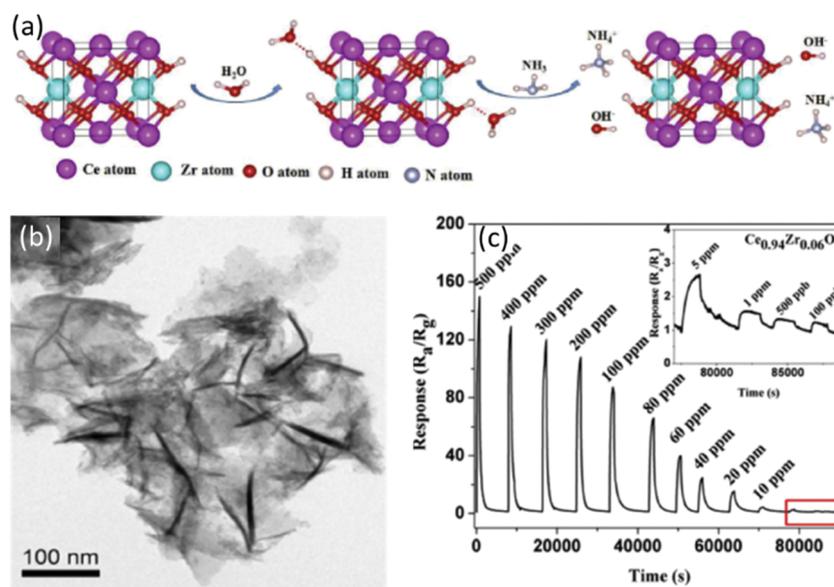


Fig. 18 (a) Schematic diagrams of the NH₃ reaction mechanism on the surface of Ce_{0.94}Zr_{0.06}O₂ nano-sheets; (b) TEM image of porous Ce_{0.94}Zr_{0.06}O₂ nano-sheets; (c) response/recovery curves of the porous Ce_{0.94}Zr_{0.06}O₂ nanosheet based sensor to NH₃.¹²⁷ Copyright 2018, Elsevier.

However, the SMONs can be modified simultaneously by both metal ions and noble metal nanoparticles, which will combine the advantages of both metal ions and noble metal nanoparticles.

3.2 Composites of semiconducting metal oxide nanostructures and gas sensors

3.2.1 Mechanism for enhanced sensing performance. The RT gas sensing performance of the SMONs operated at RT can be improved by integrating them with other metal oxides or carbon nanomaterials. For example, heterojunctions can be formed at the interfaces of different metal oxides or at the interfaces between SMONs and carbon nanomaterials, as schematically illustrated in Fig. 19. At the p-n heterojunctions between p-type and n-type SMONs, the electrons at the conduction band states of n-type SMONs will transfer to the lower energy valence band states of p-type SMONs across the interface. Thus, a depletion layer will form at the p-n heterojunction due to recombination of electrons and holes.

For the n-n heterojunction, the electrons will be transported at the interfaces between different materials due to the differences in their conduction band states. As a result, a depletion layer forms at the surface of n-type SMONs with higher-energy conduction band states due to the loss of electrons. At the same time, an accumulation layer forms at the surface of n-type SMONs with lower-energy conduction band states due to the accumulation of electrons.

For the p-p heterojunction, the major charge carriers are holes. Due to the differences of valence band energies of different SMONs, the charge carriers are transported from one p-type SMON (which has a higher energy valence band state) to the other p-type SMON (which has a lower-energy valence band state). Therefore, a hole depletion region is formed at the surface of the first SMONs (with higher energy valence band state) and a hole accumulation region is formed at the surface of the second SMONs (with a lower energy valence band state) as shown in Fig. 19.



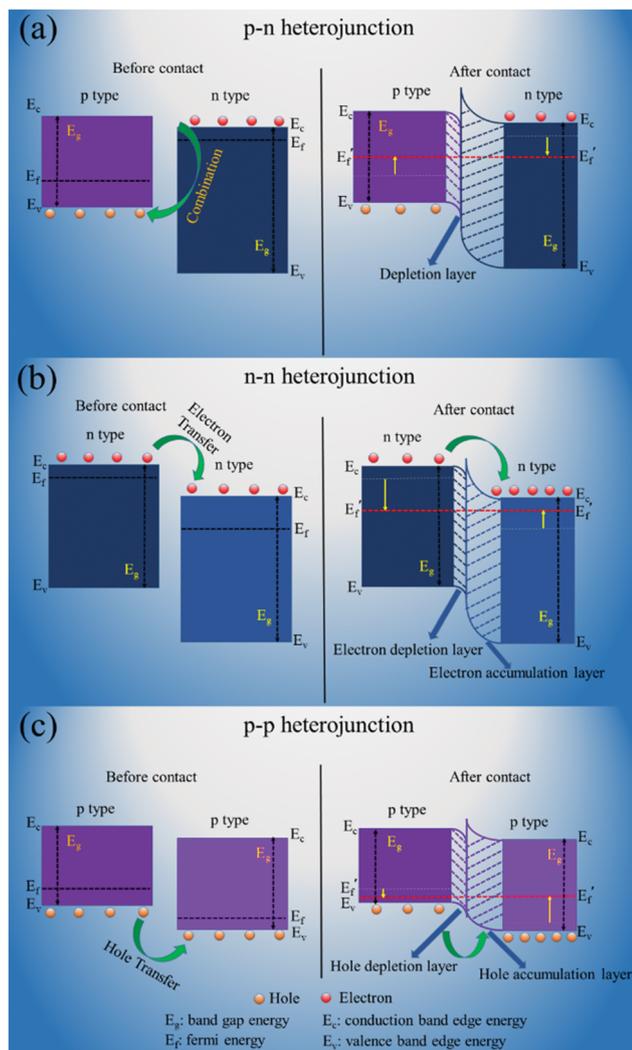


Fig. 19 Schematic illustrations of the energy band structures at heterojunction interfaces of different types of heterojunctions: (a) p–n junction, (b) n–n junction and (c) p–p junction.

These formed heterojunctions can effectively accelerate the transport of electrons. On the other hand, these heterojunctions can also enhance oxygen adsorption, therefore, abundant oxygen vacancies are formed on the surfaces of the SMON composites, which can provide new active sites for sensing reactions. In addition, the composites of SMONs often contain numerous mesopores, which are beneficial to the adsorption and desorption of gas molecules. All of these effects will improve the sensitivity and response rates of the RT gas sensors made of composites of the SMONs.

3.2.2 Gas sensors based on composites of semiconducting metal oxide nanostructures and other metal oxides. Composite oxides of the SMONs have been proposed to combine two or more semiconducting metal oxides together to enhance the gas sensing performance at RT. The examples of composites include n-type SMONs with n-type SMONs (e.g. $\text{Fe}_2\text{O}_3/\text{ZnO}$,²⁹² ZnO/SnO_2 ,²⁹³ $\text{In}_2\text{O}_3/\text{SnO}_2$ ^{134,294}), p-type SMONs with n-type SMONs (e.g. $\text{NiO}-\text{ZnO}$,¹²⁰ CuO/TiO_2 ,¹²¹ $\text{In}_2\text{O}_3/\text{CuO}$,¹²² NiO/WO_3 ²⁹⁵)

and p-type SMONs with p-type SMONs (e.g. $\text{Cu}_2\text{O}/\text{Co}_3\text{O}_4$ ²⁹⁶ and NiO/CuO ¹³¹). In addition, composites formed by integrating the SMONs with non-semiconductor metal oxide (e.g. $\text{K}_2\text{O}/\text{In}_2\text{O}_3$ ¹²⁹ and CaO/SnO_2 ²⁹⁷) have also been reported.

Table 5 summarizes the recently reported RT gas sensors made of composite oxides of the SMONs and/or other metal oxides. For these composite oxides, a number of oxygen vacancies are formed on both the surfaces and interfaces, which provides many active sites for the gas sensing reactions. Plenty of defects will also be formed at the interfaces of nanostructures in different metal oxide nanoparticles. In addition, the heterojunctions are usually formed at the interfaces of different metal oxides, which can effectively accelerate the electron transfer between different particles, thus accelerating the response speed of the sensor. Besides, the composite oxides often contain lots of mesoporous structures due to the accumulation of nanoparticles, which are beneficial to the adsorption and desorption of gas molecules. These factors can improve the sensing performance of the sensor made of these composite oxides, especially for the sensitivity and response speed. Most sensors made of the composite oxides exhibit very fast response times at RT. For example, the gas sensor based on the nanocomposite of CuO/TiO_2 ¹²¹ shows a very fast response time of 2 s at RT, and the sensor based on plate-like NiO/WO_3 nanocomposites²⁹⁵ exhibits excellent sensitivity and ultrafast response/recovery times (2.5/1.1 s) to NO_2 at RT.

The composite of mesoporous $\text{In}_2\text{O}_3/\text{CuO}$ multijunction nanofibers¹²² was prepared using an electrospinning method by Zhou *et al.* The composite is composed of the In_2O_3 nanoparticles and CuO nanoparticles (with a molar ratio of $\text{Cu}:\text{In}$ of 100 : 5). The TEM images shown in Fig. 20a and b indicate that the composite has many mesoporous structures with diameters from 1.9 to 22.9 nm and large specific surface areas ($48.7 \text{ m}^2 \text{ g}^{-1}$). The In_2O_3 nanoparticles are surrounded by the CuO nanoparticles to form numerous p–p homojunctions and p–n heterojunctions.¹²² XPS analysis indicates that the ratio of oxygen defect/vacancy on its surface is as high as 45.4%. Due to the existence of larger specific and mesoporous surface areas and the availability of chemisorbed oxygen and the formation of heterojunctions, the sensor has a much higher response to NH_3 than that of a CuO nanostructured sensor. The response time is also very short with a value lower than 8 s for NH_3 from 0.3 to 100 ppm (see Fig. 20c). The selectivity and LOD are also significantly improved due to the addition of In_2O_3 .

Xu *et al.*¹³⁴ prepared composites of $\text{In}_2\text{O}_3/\text{SnO}_2$ nanorod heterostructures (see Fig. 20d and e) using electrospinning to improve the oxygen deficiency and carrier density of SnO_2 . The SnO_2 nanoparticles are distributed along with the In_2O_3 to form numerous heterojunctions and defects at their interfaces. The availability of oxygen vacancies on the surface and at the interface has been verified using XPS.¹³⁴ Compared with pure SnO_2 nanorods, $\text{In}_2\text{O}_3/\text{SnO}_2$ nanorods (with the atom ratio of 25 : 0.3 of $\text{Sn}:\text{In}$) exhibit 11 times higher response to NO_x with a very faster response time of 4.67 s and a lower LOD with a value of 0.1 ppm (see Fig. 20f).

NiO/CuO nanocomposites with a $\text{NiO}:\text{CuO}$ molar ratio of 1 : 1 have been synthesized using a hydrothermal method,¹³¹



Table 5 Room temperature sensing properties of composites of semiconducting metal oxide nanostructures and other metal oxides

Material	Structure	Synthesis method	Target gas	C (ppm)	Response	t_{res}/t_{rec}	LOD	Ref.
ZnO/SnO ₂	Thin films	Hydrothermal	NH ₃	20	1.1	300/— s	5 ppm	293
In ₂ O ₃ /CuO	Nanofibers	Electrospinning	NH ₃	100	1.9 ^a	2/— s	0.3 ppm	122
Cr ₂ O ₃ /ZnO	Thick films	Screen-printing	NH ₃	300	13.7 ^a	25/75 s	—	298
NiO/ZnO	Nanocones	Hydrothermal	NH ₃	50	42 ^b	27/150 s	~15 ppm	120
CuO/TiO ₂	Nanoparticles	Sol-gel	NH ₃	50	97 ^b	2/55 s	~5 ppm	121
CuO/MnO ₂	Flowers/sheets	Hydrothermal	NH ₃	100	135 ^b	120/600 s	20 ppm	299
Silica/CeO ₂	Nanoparticles	Hydrothermal	NH ₃	80	3244 ^b	750/— s	0.5 ppm	198
Fe ₂ O ₃ /ZnO	Nanorods	Sol-gel	NH ₃	0.4	10 000	20/20 s	—	292
NiO/WO ₃	Plates	Annealing	NO ₂	30	4.8	2.5/1.1 s	5 ppm	295
NiO/SnO ₂	Nanosheets	Annealing	NO ₂	60	~7.5 ^a	—	~5 ppm	300
NiO/CuO	Flower-like	Hydrothermal	NO ₂	100	77.16 ^b	2 s/—	1 ppm	131
CaO/SnO ₂	Rod-like	Electrospinning	NO _x	97	6.63 ^a	—	10 ppb	297
In ₂ O ₃ /SnO ₂	Nanorods	Electrospinning	NO _x	100	8.98 ^a	4.67/— s	0.1 ppm	134
In ₂ O ₃ /TiO ₂	Nanofibers	Electrospinning	NO _x	97	41.1 ^b	3/— s	97 ppb	301
Al ₂ O ₃ /TiO ₂	Nanotubes	Induction	NO _x	97	88.04 ^b	~8/~8 s	0.97 ppm	302
K ₂ O/In ₂ O ₃	Nanowires	Template	NO _x	97	151.78 ^a	12/— s	48.5 ppb	129
NiO/In ₂ O ₃	Nanofibers	Electrospinning	H ₂ S	3	6	14/22 s	3 ppm	303
CuO/ZnO	Nanorods	Pulsed laser deposition	H ₂ S	0.5	25 ^b	180/15 s	~0.5 ppm	304
SnO ₂ /NiO	Thin films	RF sputtering	H ₂ S	10	440	—	100 ppb	123
In ₂ O ₃ /ZnO	Core-shells	Hydrothermal	H ₂ S	700	925 ^b	—	20 ppm	305
Cu ₂ O/Co ₃ O ₄	Heteroarrays	Electrodeposition	H ₂ S	20	~2600	~100/~100 s	~0.1 ppm	296
SnO ₂ /CuO	Heterojunctions	Screen printing	H ₂ S	1	3672 ^a	15/— s	10 ppm	306
NiO/Nb ₂ O ₅	Nanoparticles	Hydrothermal	H ₂	500	1.68	100.42/524.84 s	—	307
Cr ₂ O ₃ /Nb ₂ O ₅	Nanoparticles	Hydrothermal	H ₂	200	5.24	40/— s	—	308
ZnO/CuO	Nanoparticles	Hydrothermal	Alcohol	20	3.32	62/83 s	~150 ppm	309
VO ₂ /ZnO	Heteronanostuctures	Heteroepitaxial	Acetone	100	4.51	8/18 s	~10 ppm	310
ZnO/SnO ₂	Heterojunctions	Hydrothermal	Ozone	0.06	12	13/90 s	20 ppb	311
CuO/ZnO	Thick film	Screen-printing	Cl ₂	300	195 ^a	18/50 s	—	312
α-Fe ₂ O ₃ /ZnO	Nanowires	Piezo-surface coupling	Ethanol	700	706.8 ^b	—	~100 ppm	313

C = concentration; t_{res}/t_{rec} = response time/recovery time; LOD = limit of detection; response is defined as R_a/R_g (for reducing gases) or R_g/R_a (for oxidizing gases), R_a : resistance of the sensor exposed to reference, R_g : resistance of the sensor exposed to target.^a Here the response is defined as $\Delta R/R_g$ (for reducing gases) or $\Delta R/R_a$ (for oxidizing gases), ΔR : the change in resistance.^b Here the response is defined as $(\Delta R/R_g) \times 100\%$ (for reducing gases) or $(\Delta R/R_a) \times 100\%$ (for oxidizing gases).

and the nanocomposites are consisted of CuO nanoparticles and NiO nanoplates with lots of mesoporous structures. The p-p heterojunctions formed at the interfaces of NiO and CuO accelerate the electron transfers from NiO to CuO, thus resulting in a faster response. The mesoporous hierarchical nanostructures with much larger surface areas facilitate effective adsorption and desorption of gas molecules on the surface. Thus, the sensor exhibits an ultra-fast response speed (2 s to 100 ppm NO₂) to NO₂ at RT.

Kaur *et al.*¹²³ prepared a SnO₂/NiO thin film using a sputtering method and then fabricated a RT H₂S sensor. As shown in Fig. 21a, the sensor exhibits a high response with a value of 440 to 10 ppm H₂S, which is 9 and 415 times higher than those made of pure SnO₂ and NiO films, respectively. Selectivity has also been improved using the SnO₂/NiO thin film (see Fig. 21b). The formation of p-n heterojunctions using the p-type NiO and n-type SnO₂ semiconductors apparently changes the resistance of the composite film. The enhanced response of the SnO₂:NiO nanocomposite sensor is mainly due to the modifications of p-n junctions resulted from the conversion of NiO to metallic NiS. However, the recovery time is quite long (> 20 000 s, see Fig. 21c).

Wang *et al.*¹⁹⁸ reported a composite oxide sensor using 8% silica modified CeO₂ nanomaterials (see Fig. 21d) synthesized using a sol-hydrothermal route. The addition of silica increases the specific surface areas (83.75 m² g⁻¹) and decreases the crystal sizes. Due to the existence of silica, lots of OH⁻ species

are formed on the surface of the sensor, which facilitate the adsorption of water, and the water molecules react with NH₃ to generate NH⁴⁺ and OH⁻ and decrease the electrical resistance of the sensor. As shown in Fig. 21e and f, the NH₃ gas sensing performance of the sensor is significantly enhanced as compared to that of pure CeO₂ at RT. Its response value reaches 3244% (defined as $(\Delta R/R_g) \times 100\%$) for 80 ppm of NH₃ gas.

The composites of alkali metal oxide and SMONs have also been reported as an effective way to enhance the sensitivity for sensing acidic gases, such as NO_x.¹²⁹ As shown in the gas sensing mechanism of mesoporous K₂O-In₂O₃ nanowires in Fig. 22 the alkali metal oxides on the surfaces can serve as the alkaline center, which is beneficial to the adsorption and diffusion of acidic gases. Using mesoporous Santa Barbara Amorphous Material-16 (SBA-16) as a template, Rehman *et al.*¹²⁹ prepared highly crystalline mesoporous K₂O-In₂O₃ nanowires with diameters of 4–8 nm and pore sizes of 3–5 nm. The composite nanowires possess numerous chemisorbed oxygen and alkaline centers on their surfaces. The gas sensing performance of the mesoporous K₂O-In₂O₃ composite nanowires has been significantly improved with the addition of K₂O. Its response is 151.78 to 97 ppm of NO_x, the response time is decreased to 12 s, and the LOD is as low as 48.5 ppb at RT.¹²⁹

Most reported composite SMON sensors exhibit higher response values and faster response time than those of the single phase SMONs. Many active sites can be generated in the



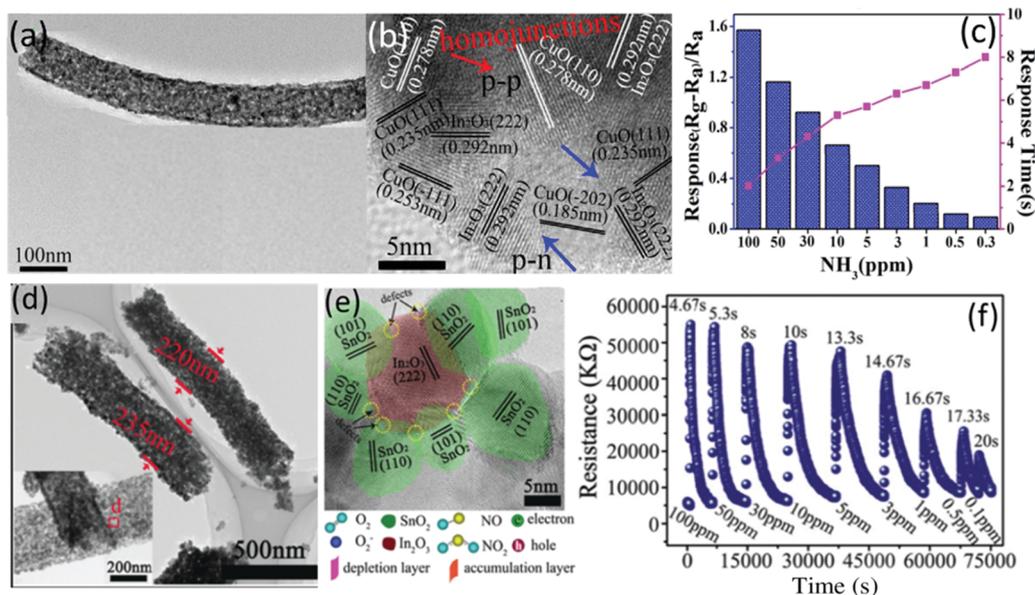


Fig. 20 (a) TEM and (b) HRTEM images of mesoporous $\text{In}_2\text{O}_3/\text{CuO}$ composite multifunctional nanofibers, (c) response values and times of the sensor to different concentrations of NH_3 .¹²² Copyright 2018, Elsevier. (d and e) TEM images of composite of $\text{In}_2\text{O}_3/\text{SnO}_2$ nanorod heterostructures; (f) response/recovery curves of the sensor to different concentrations of NO_x .¹³⁴ Copyright 2015, Royal Society of Chemistry.

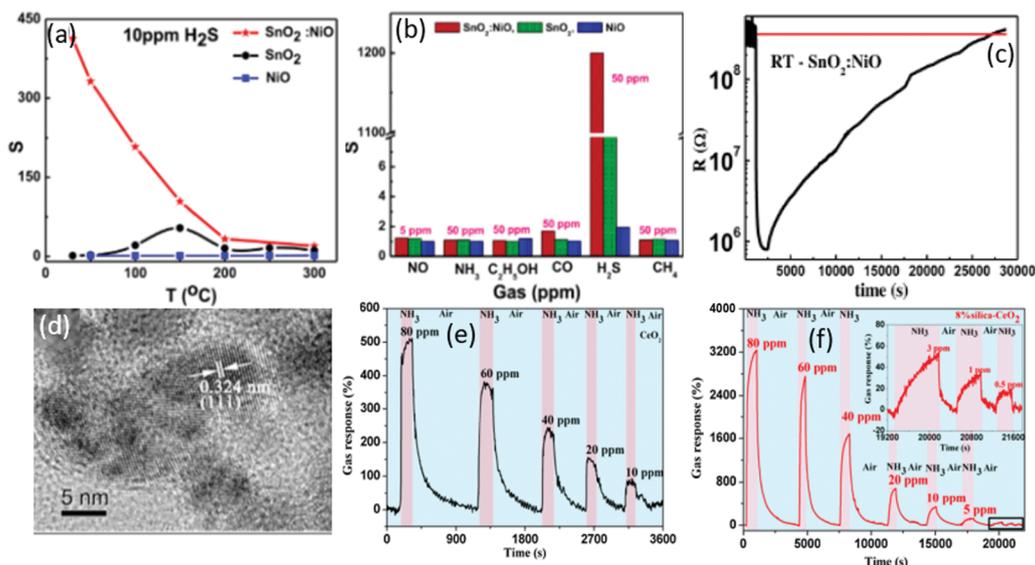


Fig. 21 (a) Response histogram of a SnO_2/NiO thin film-based room temperature gas sensor to different gases; (b) response values of the SnO_2/NiO thin film-based RT gas sensor to different concentrations of H_2S ; (c) response/recovery curve to 100 ppm H_2S .¹²⁵ Copyright 2017, Elsevier. (d) TEM image of 8% silica- CeO_2 ; (e) response/recovery curves of the pure CeO_2 -based sensor to NH_3 ; (f) response/recovery curves of the 8% silica- CeO_2 -based sensor to NH_3 .¹⁹⁸ Copyright 2017, Elsevier.

composite SMONs, such as oxygen vacancies, heterojunctions, defects and mesopores, which can effectively enhance the sensing performance. The composite SMON can be further modified by noble metal nanoparticles, which takes advantage of the chemical sensitization and electronic sensitization of noble metal nanoparticles on the composite SMONs.

3.2.3 Gas sensors based on composites of semiconducting metal oxide nanostructures and carbon nanomaterials. Carbon nanomaterials including carbon nanotubes and graphene

have been demonstrated as promising sensing materials.³¹⁴ However, the carbon nanomaterial-based gas sensors generally show low sensitivity and slow response/recovery speeds at RT. The synergistic effect by combining SMONs and carbon nanomaterials can improve the sensing performance because (1) conductivity is significantly improved; (2) many active sites (such as oxygen functional groups, vacancies and defects) are formed at the interfaces. Because of the fast carrier transport kinetics, the composites of the SMONs combined with carbon



Table 6 Room temperature sensing properties of composite nanostructures of semiconducting metal oxide nanostructures and carbon nanomaterials

Material	Structure of SMONs	Synthesis method of SMONs	Target gas	C (ppm)	Response	t_{res}/t_{rec}	LOD	Ref.
NiO/rGO	Nanosheets	Hydrothermal	NO ₂	0.25	0.04 ^a	576/121 s	~ 0.25 ppm	328
WO ₃ /MWCNTs	Nanoparticles	Metal organic decomposition	NO ₂	0.1	0.25 ^a	10.5/20 min	100 ppb	125
Ag/SnO ₂ /rGO	Nanoparticles	Hydrothermal	NO ₂	5	2.17	49/339 s	1 ppm	329
SnO ₂ /rGO	Nanoparticles	Hydrothermal	NO ₂	1	3.8	14/190 s	50 ppb	330
α-Fe ₂ O ₃ /rGO	Nanoparticles	Hydrothermal	NO ₂	5	3.86	76/946 s	0.1 ppm	126
Cu ₂ O/rGO	Nanoparticles	Chemical solution	NO ₂	1	5.2	29.2/76.8 s	100 ppb	331
ZnO/graphene	Spheres	Solvothermal	NO ₂	50	8 ^b	132/164 s	~ 10 ppm	332
Co ₃ O ₄ /rGO	Thin sheets	Hydrothermal	NO ₂	800	~ 8 ^b	1.5/1 min	60 ppm	333
In ₂ O ₃ /rGO	Nanosheets	Hydrothermal	NO ₂	30	8.25	4/24 min	~ 5 ppm	334
SnO ₂ /graphene	Nanoparticles	Sol-gel	NO ₂	20	~ 9.5	< 1/5 min	5 ppm	124
ZnO/rGO	Nanowalls	Solution	NO ₂	50	9.61	25/15 s	~ 5 ppm	135
CuO/rGO	Nanosheets	Chemical solution	NO ₂	1	14	66/34 s	60 ppb	335
SnO ₂ /S/rGO	Nanoparticles	Hydrothermal	NO ₂	5	20.31 ^b	40 s/357 s	1ppm	336
CeO ₂ /rGO	Bilayer	Spray	NO ₂	10	20.5 ^b	92/— s	~ 1 ppm	337
SnO ₂ /rGO	Nanoparticles	Hydrothermal	NO ₂	1000	22.87 ^b	100/— s	1 ppm	338
Fe ₃ O ₄ /graphene	Nanoparticles	Hydrothermal	NO ₂	400	24.2 ^b	275/738 s	~ 30 ppm	339
ZnO/rGO	Nanorods	Oriented growth	NO ₂	1	119 ^b	75/132 s	50 ppb	340
WO ₃ /S/rGO	Nanorods	Hydrothermal	NO ₂	20	149.5 ^b	6 s/56 s	0.25 ppm	341
α-Fe ₂ O ₃ /rGO	Nanospheres	Hydrothermal	NO ₂	90	150.63 ^b	-/1648 s	0.18 ppm	342
In ₂ O ₃ /rGO	Layers	Reflux	NO _x	97	1.45 ^a	25/— s	970 ppb	343
CeO ₂ /graphene	Nanosheets	Solvothermal	NO _x	300	12.76 ^b	1.3/— s	5 ppm	344
Cu _x O/graphene	Nanoflowers	Reflux	NO _x	97	95.1 ^b	9.6/— s	97 ppb	345
VO ₂ /CNT	Nanocomposites	Hydrothermal	NH ₃	45	0.04 ^a	290/1800 s	20 ppb	346
SnO ₂ /rGO	Nanorods	Hydrothermal	NH ₃	200	1.3	8/13 s	20 ppm	347
Cu ₂ O/rGO	Nanorods	Hydrothermal	NH ₃	200	2.04	28/206 s	~ 100 ppm	348
TiO ₂ /rGO	Microspheres	Hydrothermal	NH ₃	30	~ 3.5 ^b	~ 10/ ~ 10 min	5 ppm	349
Pd/SnO ₂ /rGO	Nanoparticles	Chemical solution	NH ₃	5	7.6 ^b	7 min/50 min	~ 5 ppm	350
Pd/TiO ₂ /rGO	Nanorods	One-pot polyol	NH ₃	50	14.9 ^b	184 s/81 s	2.4 ppm	351
ZnO/GrO	Nanosheets	Chemical solution	NH ₃	1	24 ^b	6/2-3 s	1 ppm	352
SnO ₂ /MWCNTs	Nanocomposites	Microelectronic	NH ₃	200	26	< 5/5 min	~ 40 ppm	136
SnO/graphene	Hybrid films	CVD	NH ₃	100	35 ^b	~ 10/— s	~ 5 ppm	353
ZnO/CNT	Networks	Flame	NH ₃	100	330	18.4/35 s	200 ppb	354
SnO ₂ /MWCNT	Nanofibers	Electrospinning	CO	50	1.29	—	47 ppm	355
CuO/rGO	Nanocomposites	Hydrothermal	CO	1	2.56 ^b	70/160 s	0.25 ppm	356
Pd/SnO ₂ /rGO	Nanoparticles	Hydrothermal	CO	1600	9.5 ^b	2 min/2 min	~ 50 ppm	357
Au/SnO ₂ /CNT	Nanotubes	Chemical solution	CO	2500	70	—	—	358
SnO ₂ /F-MWCNTs	Networks	Sputtering	H ₂	500	5.4 ^b	—/9 s	—	359
CuO/rGO/CuO	Sandwich	Hydrothermal	H ₂	1500	~ 12 ^b	80/60 s	10 ppm	360
ZnO/graphene	Nanotubes	Hydrothermal	H ₂	100	28.08 ^b	30/ ~ 150 s	10 ppm	361
Pd/SnO ₂ /rGO	Nanoparticles	Chemical solution	H ₂	10000	50 ^b	—	100 ppm	362
TiO ₂ /rGO	Nanosheets	Spray method	HCOH	0.5	0.4 ^b	70/126 s	~ 0.1 ppm	363
SnO ₂ /graphene	Nanohybrids	Electrochemical deposition	HCOH	5	4.6 ^b	46/95 s	0.02 ppm	364
Pd/TiO ₂ /RGO	Nanotubes	Electrochemical anodization	Methanol	700	~ 70 ^b	—	—	365
TiO ₂ /rGO	Nanotubes	Hydrothermal	Methanol	800	96.93 ^b	18/61 s	10 ppm	366
Pd/SnO ₂ /rGO	Nanoparticles	Hydrothermal	Methane	4000	2.07 ^b	10 min/—	—	367
SnO ₂ /rGO	Hybrid films	Hydrothermal	Acetone	10	2.1 ^b	107/95 s	~ 10 ppm	368
ZnO/MWNTs	Nanorods	Hydrothermal	Ethanol	50	4.5 ^b	7/11 s	~ 5 ppm	369
SnO ₂ /Ni-graphene	Nanoparticles	Chemical solution	NO	40	15	—	—	370
SnO ₂ /rGO	Quantum wires	Spin coating	H ₂ S	50	33	2/292 s	43 ppb	4

C = concentration; t_{res}/t_{rec} = response time/recovery time; LOD = limit of detection; response is defined as R_a/R_g (for reducing gases) or R_g/R_a (for oxidizing gases), R_a : resistance of the sensor exposed to the reference, R_g : resistance of the sensor exposed to the target.^a Here the response is defined as $\Delta R/R_g$ (for reducing gases) or $\Delta R/R_a$ (for oxidizing gases), ΔR : the change in resistance. ^b Here the response is defined as $(\Delta R/R_g) \times 100\%$ (for reducing gases) or $(\Delta R/R_a) \times 100\%$ (for oxidizing gases).

nanohybrids can detect a low-concentration of NO₂ with a highly sensitive response (14 to 1 ppm NO₂) and fast response/recovery times (66/34 s), mainly due to the formation of large surface areas and enhanced carrier transfers between the CuO and NO₂ molecules.³³⁵ Furthermore, Ding *et al.* reported that the integration of chemically functionalized three-dimensional graphene oxide hydro-gels with metal-organic framework derived Co₃O₄ nanostructures achieved ultra-high response, short response time and distinct cross-selectivity.³⁷²

The composite of SMONs with carbon nanotubes (CNT) such as SWCNTs/SnO₂³⁷³ and CNT/SnO₂³⁷⁴⁻³⁷⁷ can also improve the

sensing performance.³⁷⁸ The p-n junctions formed between the SMONs and p-type MWCNTs are responsible for their enhanced gas sensing responses. For example, Srivastava *et al.*¹²⁴ reported an RT NO₂ gas sensor based on multi-walled carbon nanotubes/SnO₂. The sensor exhibits a much higher response to NO₂ than the pure SnO₂ based sensor operated at RT. Due to the good conductivity of the CNTs and the high porosity of the ZnO networks,³⁵⁴ the response value of 2%CNTs/ZnO networks has been increased from 37 to 330 when the sensor was exposed to 100 ppm NH₃ at RT (see Fig. 24c). The response/recovery times are decreased from 58/61 s to 18/35 s, respectively. The sensor



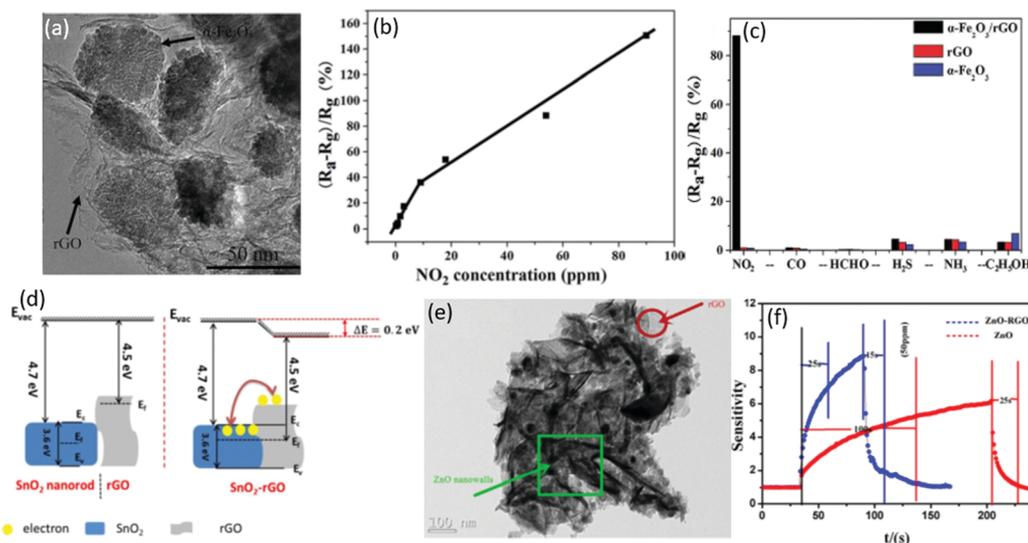


Fig. 23 (a) TEM image of the α -Fe₂O₃/rGO composite; (b) response values of the sensor based on α -Fe₂O₃/rGO at different NO₂ concentrations; (c) response histogram of the sensor to different gases.³⁴² Copyright 2014, Royal Society of Chemistry. (d) Band gap diagrams of SnO₂-nanorods/reduced graphene oxide nanostructures before and after combination.³⁴⁷ Copyright 2017, Elsevier. (e) TEM image of the ZnO/rGO composite; (f) response/recovery curves to 50 ppm NO₂ of the sensor based on a-ZnO/rGO or ZnO.¹³⁵ Copyright 2017, Elsevier.

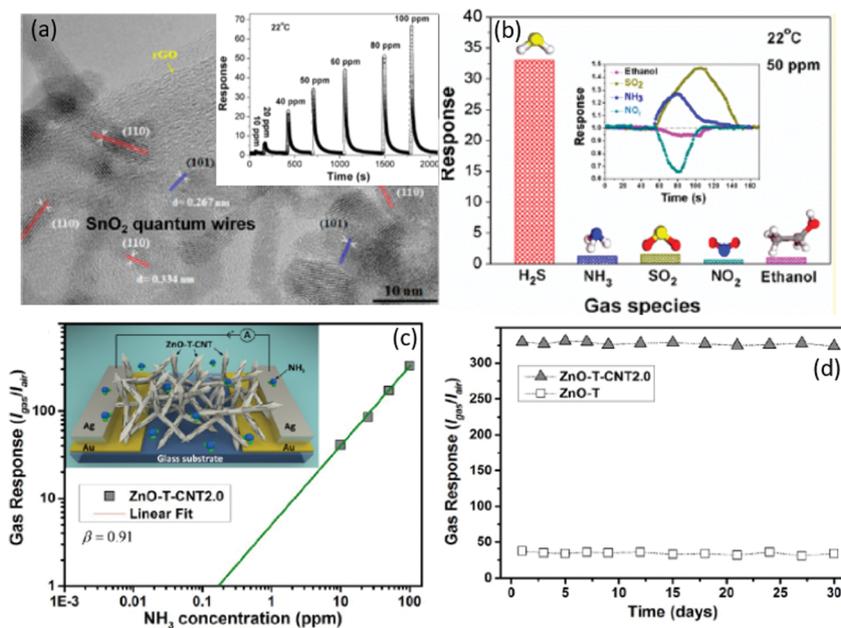


Fig. 24 (a) TEM image of the SnO₂ quantum wires/rGO nanosheets, the inset shows the response/recovery of the sensor based on SnO₂ quantum wires/rGO nanosheets for different H₂S concentrations; (b) response histogram of the SnO₂ quantum wires/rGO nanosheet based sensor to different gases.⁴ Copyright 2016, American Chemical Society. (c) Response values at different concentrations of NH₃ gas for 2%CNTs/ZnO networks (the inset presents the sensor structure); (d) long-time stability of the RT gas sensors to 100 ppm of NH₃ at 30% RH.³⁵⁴ Copyright 2017, American Chemical Society.

also displays good stability at RT over a duration of one month (see Fig. 24d). In addition, the CNTs can serve as acceptors for the released electrons, which are injected into the SMONs from the target gases. A H₂S gas sensor made of nanocomposites of SnO₂ quantum dots/MWCNTs reported by Liu *et al.*³⁷⁹ exhibited a high response value of 108 to 50 ppm H₂S with fast response/recovery times of 23/44 s.

Adding noble metal nanoparticles into the composite is another method to further improve the gas sensing performance of SMONs/rGO composites. Being good catalysts, these noble metal nanoparticles can enhance the catalytic efficiency by creating extra new sites to promote fast adsorption of gas molecules and decrease the reaction temperatures by lowering the activation energy of the gas sensing reactions. For example,



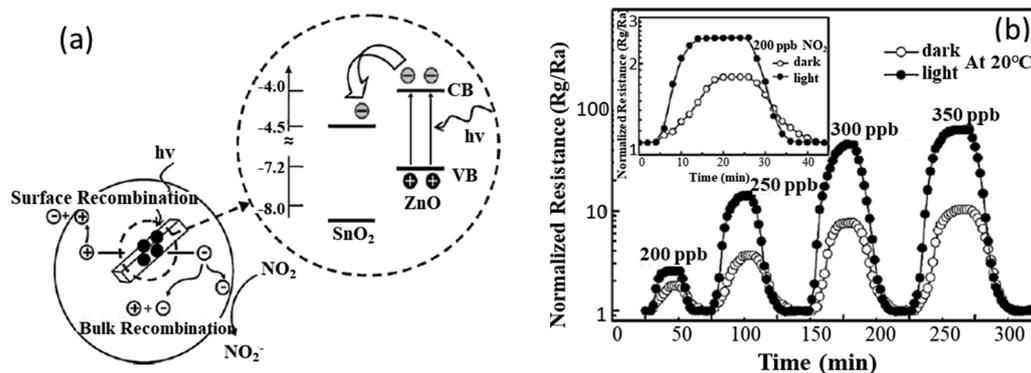


Fig. 25 (a) Schematic diagram of the carrier transport under UV light and the electron–hole pair separation on heterostructure of ZnO/SnO₂ composite; (b) response/recovery of ZnO/SnO₂ composites at different concentrations of NO₂ with and without UV light stimulation at room temperature.³⁹⁵ Copyright 2011, Elsevier.

sensing properties at RT with high response and good selectivity after being illuminated with white light. Similarly, infrared (IR) light should also be beneficial for the improvement in the sensing performance.

Although the photoactivated SMON gas sensors could achieve the improved gas sensing performance operated at RT, the light-emitting diodes, UV source, or infrared light, as well as optical power detection devices are necessary to be used, which will increase the size and production cost of the sensor device. The integration and shrinkage of the devices along with mass production capabilities are challenges. In addition, for the application of the gas sensors in a real environment, the gas sensor will be exposed to air for real-time monitoring. Sunlight will severely influence the gas sensing response.

4. Mechanically flexible gas sensors based on semiconducting metal oxide nanostructures

Mechanically flexible gas sensors are in great demand due to their promising applications in wearable electronic devices. SMONs with a potentially higher carrier mobility and mechanical robustness are good candidates for the realization of stretchable and flexible sensors.²²³ The mechanically flexible and wearable RT gas sensors based on SMONs have been an active research area recently as listed in Table 8. Compared with those on the rigid substrates, the wearable devices need substrates which are flexible, light weight, transparent, transportable, with a small volume, and low cost.⁴⁰¹ Due to their excellent dielectric

Table 8 Sensing performance of room temperature flexible gas sensors based on semiconducting metal oxide nanostructures

Material	Structure	Substrate	Synthesis method	Target gas	C (ppm)	Response	t_{res}/t_{rec}	LOD	Ref
ZnO	Nanowires	PET	Hydrothermal	H ₂	1000	5 ^b	~ 600/— s	—	402
Ga/ZnO	Nanorods	PI	Hydrothermal	H ₂	1000	91 ^b	~ 18.8/— s	0.2 ppm	264
Pd/ZnO	Nanorods	PI/PET	Hydrothermal	H ₂	1000	91.2 ^b	~ 18.8/— s	0.2 ppm	173
ZnO	Nanorods	Nylon	Hydrothermal	H ₂	500	109 ^b	149/122 s	—	409
CuO	Nanorectangles	PET	Hydrothermal	NH ₃	5	~ 0.25 ^a	90/120 s	5 ppm	223
SnO ₂ /SnS ₂	Nanotubes	PET	Hydrothermal	NH ₃	100	2.48	21/110 s	1 ppm	403
Polyaniline/WO ₃	Flowerlike	PET	Polymerization	NH ₃	10	7	13/49 s	500 ppb	410
ZnO	Nanoparticles	Cotton fabrics	Sol-gel	NH ₃	100	9	39/34 s	—	411
Au/In ₂ O ₃ /Polyaniline	Nanospheres	PI	Hydrothermal	NH ₃	100	46	118/144 s	—	412
CeO ₂ /CuBr	Nanoparticles	PI	Electron beam evaporation	NH ₃	5	68	112/74 s	20 ppb	413
Polyaniline/ α -Fe ₂ O ₃	Fiber network	PET	Sol-gel	NH ₃	100	72 ^b	50/1575 s	2.5 ppm	414
Polyaniline/CeO ₂	Thin films	PI	Self-assembly	NH ₃	50	262.7 ^b	14/6 min	16 ppb	415
In/Ga/Zn/Oxide	Thin-Films	PI	CVD	NO ₂	5	~ 1.3	—	2 ppm	407
ZnO _{1-x}	Sheet-like	PP	Suspension flame spraying	NO ₂	1	2.568 ^a	60/230 min	0.25 ppm	405
MWCNTs/WO ₃	Nanoparticles	PET	Hydrothermal	NO ₂	5	14 ^b	10/27 min	0.1 ppm	416
WO ₃ /MWCNT/rGO	Nanoparticles	PI/PET	Hydrothermal	NO ₂	5	17 ^b	7/15 min	1 ppm	417
SWNT/Fe ₂ O ₃	Composites	PP	CVD	NO ₂	100	18.3 ^b	—	~ 1 ppm	406
PdO/Co ₃ O ₄	Nanocubes	PI	Chemical precipitation	NO ₂	20	27.33 ^b	—	1 ppm	408
Cellulose/Fe ₂ O ₃	Nanoparticles	PET	Hydrothermal	NO ₂	200	~ 1100 ^b	50/30 s	1 ppm	418
WO _{3-δ}	Films	PI	Granule spray	NO ₂	10	18500 ^b	17/25 s	1.88 ppm	419
In ₂ O ₃	Cubic crystals	PVA	Hydrothermal	Ethanol	100	~ 1.4	5/3 s	10 ppm	105
rGO/WO ₃	Nanoneedles	PET	Hydrothermal	Isopropanol	200	~ 8.5	60/— s	1 ppm	404
Ag/ZnO	Nanorods	PI	Hydrothermal	C ₂ H ₂	1000	26.2	66/68 s	3 ppm	420

C = concentration; t_{res}/t_{rec} = response time/recovery time; LOD = limit of detection; response is defined as R_a/R_g (for reducing gases) or R_g/R_a (for oxidizing gases), R_a : resistance of the sensor exposed to the reference, R_g : resistance of the sensor exposed to the target.^a Here the response is defined as $\Delta R/R_g$ (for reducing gases) or $\Delta R/R_a$ (for oxidizing gases), ΔR : the change in resistance. ^b Here the response is defined as $(\Delta R/R_g) \times 100\%$ (for reducing gases) or $(\Delta R/R_a) \times 100\%$ (for oxidizing gases).



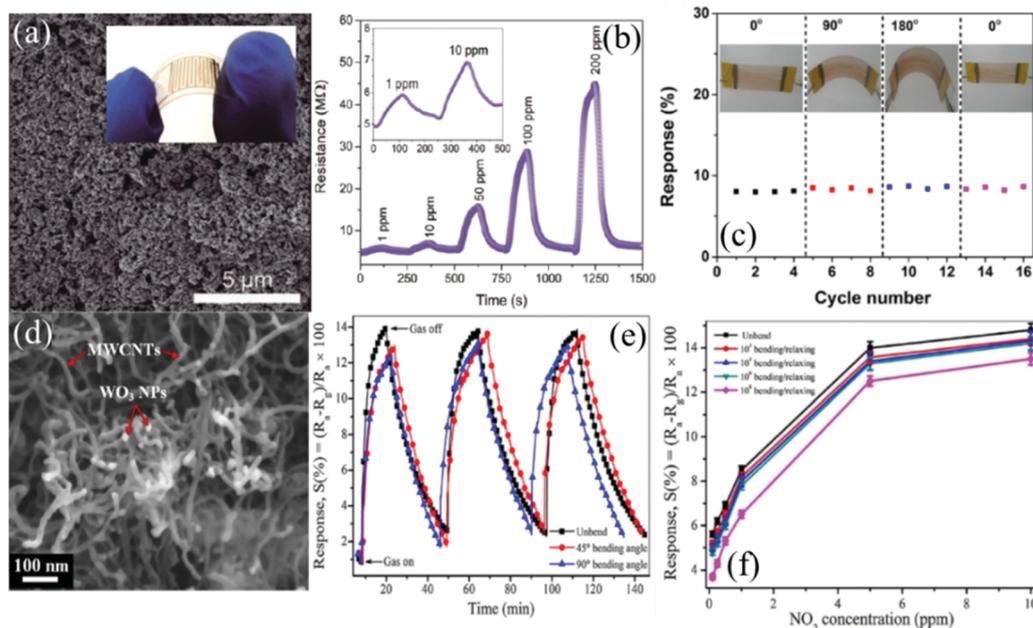


Fig. 27 (a) SEM images of 5%rGO/WO₃-0.33H₂O deposited on polyethylene terephthalate; the inset is the photograph of the flexible gas sensor, (b) response/recovery curves to isopropanol with different concentrations.⁴⁰⁴ Copyright 2018, Royal Society of Chemistry. (c) Responses of the SWNT/Fe₂O₃ gas sensor to 20 ppm H₂S under different bending angles from 0° to 180° and back to 0°.⁴⁰⁶ Copyright 2017, Elsevier. (d) SEM images of the MWCNTs/WO₃ composite. (e) response curves to 5 ppm NO₂ at RT under different bending angles, (f) responses to different NO₂ concentrations at RT after bending/relaxing several times (90° angle).⁴¹⁶ Copyright 2015, Elsevier.

an improved response to H₂S at RT. Under repeated bending to large angles (such as 90° and 180°) for 16 times as shown in Fig. 27c, the flexible sensor exhibited stable sensing response values to H₂S. As another example, hydrothermally synthesized WO₃ nanoparticles were mixed with MWCNTs (see Fig. 27d), and then cast onto a PET substrate to fabricate a flexible NO₂ gas sensor.⁴¹⁶ This sensor not only shows good sensing performance, but also has excellent mechanical flexibility (see Fig. 27e). There was no significant degradation of response values after bending/relaxing for 10⁶ cycles, demonstrating the excellent mechanical robustness of the MWCNTs/WO₃ composite layers on the flexible gas sensors (see Fig. 27f).

Cotton fabrics are also reported to be used as a good substrate for flexible RT gas sensors, for example, a flexible NH₃ gas sensor was made by growing nanostructured ZnO onto cotton fabrics.⁴¹¹ Flexible nanowires of the SMONs can also be isostatically pressed into a thin paper, and then the nanowire paper is cut into small pieces to directly fabricate a flexible gas sensor. Based on this idea, a-MoO₃ nanowire paper⁴²¹ has been fabricated and a flexible gas sensor was made to detect hydrogen gas. The sensor shows fast response and recovery speeds (3.0 and 2.7 s toward 1.5% H₂), good selectivity, and high sensitivity at RT. Wei *et al.*⁴²² also reported a flexible gas sensor based on cellulose/TiO₂/PANI composite nanofibers, which showed excellent ammonia gas sensing performance at RT. Similarly, a stretchable ZnO nano-accordion structure has also shown good applications in flexible RT gas sensors.⁴²³

In summary, flexible RT gas sensors can be fabricated using SMONs as the sensing materials on a mechanically flexible platform,

and the sensors have demonstrated excellent mechanical robustness and can maintain good sensing performance at RT after bending/recovering many times. Furthermore, the composite of SMONs with graphene or CNT can achieve better mechanical robustness for the flexible gas sensor. However, so far, excellent sensing performance and reliability and stability have not been achieved in the case of flexible RT gas sensors compared with their rigid counterparts.

5. Conclusions and outlook

In this paper, we have summarized the recent progress in designs and mechanisms of RT gas sensors based on different SMONs. Our emphasis has been on the critical review of different structures of SMON-based gas sensors that may help the design of new devices. The key topics covered in this paper include single phase n-type SMONs, single phase p-type SMONs, noble metal nanoparticle modified SMONs, metal ion modified SMONs, SMON composites with multiple metal oxides, and SMON composites with carbon nanomaterials. The different nanostructures of these SMONs include nanoparticles, nanowires, nanofibers, nanorods, nanosheets, nanotubes *etc.* The sensing performance of these SMON based RT sensors has been reviewed for detecting various toxic or flammable gases, such as hydrogen disulfide, nitrogen dioxide, ammonia, carbon monoxide and hydrogen, as well as organic gases of formaldehyde, acetone, methanol and ethanol, *etc.* In addition, photoactivated RT gas sensors and flexible RT gas sensors based on SMONs are also summarized.



Availability of numerous surface chemisorbed oxygen species of O_2^- at RT was identified to be the key reason for the high sensitivity of these RT gas sensors. These oxygen species react with the target molecules to change the electronic resistance of the sensor. However, many RT H_2S sensors are exceptional as the sensing mechanism is dominated by the formation of metallic conducting metal sulfide.

Noble metal nanoparticles on the surface of SMONs can stimulate the adsorption of oxygen molecules to form oxygen ions by reduction processes. These oxygen ions spill onto the surface of SMONs to improve the concentration of oxygen ions on the surface of SMONs for sensing reactions. In addition, noble metal nanoparticles can accelerate the transfer of electrons to SMONs. Therefore, both the chemical sensitization and electronic sensitization enhance the sensitivity and speed of the SMON-based sensors. Doping of metal ions in the SMONs can increase the number of active sites and defects on the surface of SMON nanocrystals, and thus enhance the amount of oxygen species and increase the adsorbed gas molecules on the sensor surface. Heterojunctions can form at the interfaces of different metal oxides or at the interfaces between the SMONs and carbon nanomaterials. These can effectively accelerate the transformation of electrons and enhance oxygen adsorption, and are beneficial to improve the sensitivity and response rates in application of RT gas sensors. The sensing performance also depends significantly on the nanostructures of the SMONs. Large specific surfaces are beneficial to the formation of more oxygen species, and porous nanostructures facilitate the adsorption and desorption of target gases, thus achieving fast response and recovery.

Generally, the RT SMON based gas sensors show high response values and low LODs; however, their response and recovery times could be too long. Modifications of the SMON sensors using various methods can improve their sensing performance, which include using noble metal modified SMONs; metal ion doped SMONs, composite SMONs, and composites with carbon nanomaterials. The key conclusions are summarized below:

(1) Surface modifications of the SMONs using noble metal nanoparticles can effectively enhance their sensitivity, response/recovery speeds, selectivity and LODs through both chemical sensitization and electronic sensitization.

(2) Metal ion doped SMONs have increased number of active sites and more defects on their surfaces, which can enhance the oxygen species for sensing reactions and improve the adsorption of gas molecules.

(3) SMON composites can form abundant oxygen vacancies on their surfaces, thus providing many active sites. Heterojunctions can be formed at the interfaces of different metal oxides, which can effectively accelerate the transformation of electrons between different particles, thus improving the response rates. The composite SMONs often contain numerous mesopores which are beneficial to the adsorption and desorption of gas molecules. Hence, sensors based on the majority of reported composite oxides exhibit a high response value and very fast response.

(4) Because of the high conductivity of carbon nanomaterials, the composites of SMONs combined with carbon nanomaterials can achieve fast response/recovery.

(5) The photo-generated electrons on the surfaces of SMON sensing materials can enhance the chemisorption of oxygen molecules to form more O_2^- , which can enhance the sensitivity and response/recovery speed of the SMONs.

(6) RT flexible gas sensors based on the sensing layer of the SMON sensing materials have excellent mechanical robustness and can maintain good sensing performance after repeated bending/recovering.

Although there has been significant progress in developing novel SMONs for gas sensing at RT, there are still many challenges and problems towards achieving high response, fast response/recovery speed, good selectivity and long-term stability:

(1) One of the key challenges is the durability and long-term stability of the sensors for application under varying environmental conditions, such as different humidity levels and different temperatures, which could have significant influences on the sensing properties of many RT gas sensors. This is especially important for RT NH_3 sensing, as high humidity seriously affects the sensitivity and the response time. Light exposure, especially ultraviolet and infrared light, and even visible light, all influence the response of the RT SMON sensors. In the literature, the performance of sensors has been normally characterized based on experiments conducted in a well-controlled laboratory environment. However, in a practical setting with variable environmental conditions, the sensing performance may be altered with light exposure. Therefore, the sensing properties under different environmental conditions should be systematically investigated in order to establish the relationship between environmental conditions and sensing properties, which are then used to correct the sensing results.

(2) Interfering gases often affect the sensing performance, resulting in a drastically reduced response. Lack of good selectivity is still the most serious problem hindering the wide applications of these RT gas sensors. There are few reports on specific gas sensors which only respond to a target gas but not all the other gases. Because the resistive gas sensors rely on their changes in resistance upon adsorption of gas molecules, it can distinguish between the reducing gases and oxidizing gases based on the increase or decrease of resistance; however, it is difficult to discriminate a group of gases which can produce similar changing trends of resistance values.

Therefore, selectivity is particularly important for multiple-agent gas sensors. To solve this problem, arrays of different sensing materials can be fabricated such that forming an array of gas sensors, which could obtain good selectivity by analyzing and comparing data from the different single sensors.⁴²⁴ For example, Zhang *et al.*⁴²⁵ reported a method to detect multiple VOCs using an array of gas sensors based on Ag doped $LaFeO_3$ (ALFO). The device was optimized for the detection of acetone, benzene, methanol and formaldehyde to monitor air quality. The selectivity of ALFO can be altered using a molecular imprinting technique towards specific targets. Responsivity values of individual sensing elements vary between 14 and 21 while the values to other VOCs are lower than 4. The response and recovery times are on the order of 10 s and 100 s levels. Flitti *et al.*⁴²⁶ reported a micromachined 4×4 array of sensors



for multiple target detection. The sensing film for individual elements is based on SnO₂ and the elements are post-treated using metal catalysts of Pt, Pd, and Au and ions implanted using B, P, and H. The basic post-treatment methods are effective in selectively detecting gases of CO, CH₄, ethanol, CH₄-CO, ethanol-CO, and ethanol-CH₄ using an algorithm based on vector angle similarity. Recognition accuracy higher than 95% is reported in this study.⁴²⁷

This method has been demonstrated being capable of forming 12 000 virtual sensors using dedicated temperature modulations. Sensing networks will be the future trends.

(3) The sensing mechanism of the SMONs is mainly based on the interaction between the target gas molecules and chemisorbed oxygen species, such as O₂⁻, O⁻ and O²⁻ ions. However, other oxygen groups such as OH⁻ can also react with the target gas molecules. More effective analysis and theory development of the surface groups is urgently needed to assess their effect on the sensing properties, and the surface modification methods should be developed to minimize this influence.

(4) Many gas sensing mechanisms of SMON based materials with various sizes and morphologies have been presented to explain their sensing properties. However, it is not clearly elucidated why the same SMON based materials with similar sizes and morphologies show markedly different sensing properties. Therefore, *in situ* characterization techniques and theory development for the sensing mechanisms are necessary.

(5) Response times of many RT gas sensors are very long, which cannot meet the need for timely triggering of the alarm. Exploring novel SMON based sensing materials for rapid response at RT is still necessary. 3-D nano-arrays of SMONs facilitate gas diffusion, which might be promising to shorten the response time.

(6) Flexible wearable RT gas sensors are in great demand due to their promising applications. SMONs with the potential of higher carrier mobility and mechanical robustness are among the good candidates for making stretchable and flexible gas sensors. For RT gas sensors, there are still challenges regarding their manufacturing technologies, and cracking and spalling problems of SMON layers on the flexible substrates usually happen, which need to be solved to achieve reliable RT flexible gas sensors. Therefore, finding new low-cost SMON based sensing materials with excellent sensing performance and mechanical robustness is still the major challenge.

Conflicts of interest

There are no conflicts to declare.

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