Ultra-effective room temperature gas discrimination based on monolithic Pd@MOF-derived porous nanocomposites: an exclusive scheme with photoexcitation†

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Chemiresistive sensing materials capable of efficiently identifying specific flammable gases are imperative. Although plenty of high-performance chemiresistive sensors have been developed in related fields, the high selectivity response to a single flammable gas at room temperature is still a great challenge. Conventional single chemiresistive metal oxide semiconductor materials exhibit similar response characteristics to flammable gases at high temperatures, while arrays are limited by high cost and miniaturization. Herein, the unique gas discrimination based on a monolithic MOF-derived chemiresistive sensor is achieved with photoexcitation at room temperature. 5.0Pd@ZnO exhibits a typical p-type semiconductor response (200 ppm, 52.89) to H2, while it displays a typical n-type semiconductor response to other flammable gases (CO, MeOH, EtOH, and H2S response of −25.15, −13.63, −49.92, and −40.36, respectively), which indicates that H2 can be fully identified merely from the original electrical signal. Meanwhile, the as-prepared sensors combined the advantages of MOF and MOS materials, and exhibited high linearity response, favorable repeatability, and long-term stability. The special response characteristics of the sensor to each flammable gas have been explored in detail, and the distinct effects of two different Pd surface states on gas molecules are discovered by DFT calculations. The mechanism of the high-selectivity response behavior at room temperature is systematically analyzed. This work provides a solid reference and feasible solution for the development of high-selectivity room temperature sensors.

Introduction

Metal oxide semiconductor (MOS) chemiresistive sensors have become one of the most promising sensing technologies in the fields of environmental monitoring, exhaled breath analysis, and flammable gas detection due to the significant advantages of high stability, repeatability, simple structure, and miniaturization. 1−4 Nevertheless, the MOS chemiresistive sensors are limited by the sensing mechanism of adsorbed oxygen species on the surface of MOS materials and usually work at elevated temperatures of 300−500 °C, which not only brings potential ignition risks but also greatly increases the power consumption of the system.5−14 Moreover, state-of-the-art MOS-based sensors typically exhibit high cross-sensitivity, which means similar response characteristics to gases of the same type, such as flammable gases. 15−17 Although higher-ordered sensing arrays may be a feasible solution for gas discrimination, the high cost and device size make it hard to meet the demands of miniaturization and large-scale manufacturing in practical applications. 18 With the development of nanotechnology, sensitivity is no longer a major concern for sensors, which can be achieved by either modified nanostructures or surface functionalization. 19−21 Selectivity, especially the unique selectivity gas sensing of a monolithic sensor at room temperature, is still a great challenge but imperative for chemiresistive sensors.

Metal−organic frameworks (MOFs), as a multi-functional porous coordination polymer with ultra-high surface area, have been regarded as potential candidates with great application prospects in the field of gas sensing in recent years. 22−24 MOF-based materials are mainly used as an outer filter material in related fields to improve the gas selectivity. 25−27 For example, a ZIF-8 (>0.34 nm pore size) nanofiltration layer is assembled on Pd nanowires to exclude the influence of O2 on the detection of H2 (0.289 nm diameter), 28 or coat the ZIF-8 shell on the metal oxide to improve the interference response of H2 over CO. 29 Unfortunately, due to the poor thermostability, electrical conductivity and long-term stability, conventional MOF-based...
sensors exhibit complex fabrication processes and unfavourable practicality. Specially treated MOF-derived corresponding metal oxide composite catalysts may be a feasible solution for practical applications, which can not only retain the rich porous properties of MOF-based materials, but also exhibit the high stability of MOS materials. However, the high operating temperature and poor selectivity of MOF-derived MOS-based sensors have become a major obstacle to the manufacture of advanced miniaturized sensors with high discrimination capabilities.

Optical excitation, especially the excitation of short-wavelength light (such as 365 nm UV light), is an important way to realize room temperature gas detection of MOS-based materials, which is also a hotspot in the research field. Significantly, ZnO is a wide bandgap semiconductor metal oxide material that can be well excited by 365 nm ultraviolet light, and it is also easy to obtain the corresponding controllable porous ZnO-based nanocomposites from ZIF-8 after an optimized process. Therefore, it may be a reliable solution for high-selectivity gas detection at room temperature by combining UV photoexcitation with ZIF-8/ZnO porous nanocomposites. So far, most research on UV enhanced room temperature gas detection has focused on the response characteristics of NO2, and studies on UV-enhanced high-selectivity flammable gas sensing are still in their infancy. The flammable gas response characteristics of the sensor under UV activation at room temperature exhibit great similarity in the resistance change, and it is still impossible to accurately identify a single gas at room temperature. In this regard, Pd particles in contact with hydrogen molecules generate PdHx to induce an increase in resistance, resulting in an opposite response characteristic to that of the n-type ZnO-based nanocomposites. Thus, MOF-derived Pd@ZnO porous nanocomposites excited by UV may be an effective strategy to achieve the unique selectivity response to hydrogen at room temperature.

Herein, we report a photoexcited room-temperature (25 °C) gas discrimination technology realized by monolithic MOF-derived MOS-based nanocomposites, which can completely distinguish H2 from other typical combustible gases based on the existing state-of-the-art theoretical basis and has not been reported in previous research work, as shown in Fig. 1. This work helped us to completely distinguish H2 from other typical flammable gases in terms of the original electrical signal. The elimination of the need for the identification of sensor arrays and complex algorithms greatly optimizes the power consumption, selectivity, and fabrication cost of existing sensors. Meanwhile, according to the verification of the principal component analysis (PCA) pattern recognition, it is found that 5.0Pd@ZnO porous nanocomposites could even achieve completely independent identification of each flammable gas (except CO) due to the unique room temperature response characteristics of various flammable gases, which further broadens the potential application of this work. Density functional theory (DFT) calculations elaborated the mechanism of the different combinations of Pd and ZnO in the adsorption of small molecular gases in detail, and confirmed the microscopic reaction process that produces the unique reverse response. This work achieved the specific selectivity of a single flammable gas at room temperature by facile experimental design, and provided a crucial and feasible path for room temperature gas detection of MOS-based materials. In combination with the future MEMS semiconductor device light-emitting layer technology, it is possible to realize the next generation of light-excited monolithic high-selectivity room temperature sensors.

Fig. 1 Schematic illustrations of the synthesis process and sensing mechanism. (a) The preparation of MOF-derived xPd@ZnO porous nanocomposites. (b) UV-activated high-selectivity hydrogen sensing mechanism at room temperature (RT).
Experimental

Synthesis of MOF-derived Pd@ZnO porous nanocomposites

xPd@ZIF-8 were first prepared as precursor materials by a facile solvothermal method. Briefly, 5 mmol of [(NO$_3$)$_2$]·6H$_2$O and 20 mmol of 2-methylimidazole (2-MeIM) were dissolved in 50 mL of methanol, respectively. n (n = 0, 0.05, 0.125, 0.25, and 0.50) mmol of Pdc$_2$ and appropriate amounts of polyvinylpyrrolidone (PVP) were mixed in 50 mL of methanol to form a homogeneous solution, in which the addition of PVP was vinylpyrrolidone (PVP) were mixed in 50 mL of methanol to form a homogeneous solution, in which the addition of PVP was vinylpyrrolidone (PVP) were mixed in 50 mL of methanol to form a homogeneous solution, in which the addition of PVP was vinylpyrrolidone (PVP) were mixed in 50 mL of methanol to form a homogeneous solution, in which the addition of PVP was vinylpyrrolidone (PVP) were mixed in 50 mL of methanol to form a homogeneous solution, in which the addition of PVP was.

The PVP-stabilized Pd$^{2+}$ solution was transferred to a 2-MeIM methanol solution and stirred for 20 min. Subsequently, the mixed solution and stirred for 2 h, and then the self-assembly reaction process was allowed to complete without extra operation for 20 h at room temperature. Methanol acted as the reducing agent to promote the emergence of Pd nanoparticles during the formation of xPd@ZIF-8, while PVP acted as the stabilizer for the nanoparticles during the reaction process. The pure products of xPd@ZIF-8 were obtained by centrifugation and washing with methanol several times. The obtained products were dried in a vacuum oven at 60 °C for 24 h, and then put into a tube furnace for carbonization at 650 °C under an Ar atmosphere at a heating rate of 2 °C min$^{-1}$ for 2 h. The carbonized products were annealed in air at 380 °C for 3 h at a heating rate of 2 °C min$^{-1}$ to obtain the final gas-sensing nanocomposites. The final products are denoted as xPd@ZnO according to the atomic ratio of Pd/Zn, e.g. 5.0Pd@ZnO for the 5.0% atom ratio of Pd/Zn.

Fabrication of monolithic xPd@ZnO-based gas sensors.

In order to ensure the repeatability of the sensors, 50 mg of the xPd@ZnO nanocomposites and 1 mL terpineol were uniformly mixed by ultrasonication, and 20 μL of the mixed suspension was coated on the Au interdigitated electrodes (Au-IDEs) by the screen printing process. The as-prepared sheets were first dried in a vacuum oven at 80 °C for 12 h, and then sintered in a muffle furnace at 350 °C for 4 h. The sintered sheets were aged at 300 °C for 7 days to obtain the final stable sensors.

Gas-sensing measurements of the sensors.

The electrical signals were measured with 5 V bias voltage. The accurate temperature control was realized with the close-fitting heater at the bottom of Au-IDE. Dynamic tests with the total gas flow rates of 200 mL min$^{-1}$ (scm) were adopted for the sensing performance tests of the sensors. All the gases used in experiments were specially customized standard gases, for example, a calibrated 1000 ppm H$_2$/air mixture gas would be customized from Air Liquide Co., Ltd. The test instrument was equipped with multiple MFC-controlled air inlets. When a specific concentration of H$_2$ is required, the target concentration of the gas can be obtained by simply feeding the customized 1000 ppm H$_2$/air mixture gas with pure compressed air in the corresponding flow ratio. A special small-volume cylindrical gas chamber (diameter: 70 mm, height: 20 mm) with a top quartz cover was used to ensure the accuracy of light excitation tests and gas sensing performance tests. Different intensities of UV irradiation were realized using a xenon light source (Beijing Perfectlight Technology Co., Ltd, PLS-SXE 300) with a 365 nm filter. The response values are defined as $S = \Delta R/R_a \times 100\% = (R_g − R_a)/R_a \times 100\%$, in which $R_a$ represents the resistance value in the target gases, and $R_g$ represents the resistance value in air. The UV irradiation intensities on the surface of the as-prepared sensors could be accurately measured using an ultraviolet ray meter (Beijing Shida Photoelectric Technology Co., Ltd, UV-A).

Results and discussion

Fabrication and micromorphology

The microstructures of the ZIF-8 derived nanocomposites and their associated sensors are shown in Fig. 2. As a high-energy particle that is easy to agglomerate and deactivate, Pd can be uniformly dispersed in the abundant channels of ZIF-8, which can effectively improve the utilization of the catalyst. As shown in Fig. 2a and e, the particle size expanded with the loading of Pd, which is mainly due to that the affinity of Pd nanoparticles to ZIF-8 can be improved by the coordination interaction between the zinc atom in ZIF-8 and the pyrrolidone rings (C=O) in PVP. Compared with the structural collapse failure (Fig. S1†) of direct sintering in air, the dodecahedral porous structure of ZIF-8-based nanocomposites can be well maintained after the initial carbonization in Ar (Fig. 2b and f) followed by oxidation in air (Fig. 2c and g). The particle size of the MOF-derived pure ZnO was slightly smaller than that of the original pure ZIF-8 materials after optimized heat treatment, while the corresponding particle size of the xPd@ZnO nanocomposite remains almost unchanged. The particle size variations of the xPd@ZnO nanocomposite under low-magnification SEM are shown in Fig. S2.† Compared with MOF-derived pure ZnO, the presence of Pd affected the size uniformity patterns of xPd@ZnO nanoparticles. The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) characterization and the corresponding EDS elemental mapping of MOF-derived 5.0Pd@ZnO are shown in Fig. S2e,† in which both states of lattice Pd and Pd nanoparticles are observed. In order to further explore the growth behaviour of high ratio Pd on the material surface, the growth model of MOF-derived 10.0Pd@ZnO is established in Fig. S2f,† in which 2 types of Pd atoms that existed in the form of lattice Pd and Pd$_{10}$ cluster grew on the surface without restraint. The Pd$_{10}$ cluster formed a tight connection with the lattice Pd and the surrounding lattice oxygen atoms. The optimized structure demonstrated the fact that as the Pd ratio increased, Pd clusters would preferentially grow on the surface of lattice Pd sites (Fig. S2g†), which occupied the active reaction sites of the lattice Pd. The specific surface area of the nanocomposite was reduced from 1294.81 m$^2$ g$^{-1}$ to 463.68 m$^2$ g$^{-1}$ after optimized heat treatment, which was reduced by ~2.8 times (Fig. S3†). Though the specific surface area of the ZIF-8 derived 5.0Pd@ZnO was reduced by 2.8 times after optimal heat treatment, it was still about 18 times that of the 26.27 m$^2$ g$^{-1}$ materials obtained by the direct oxidation treatment method (Fig. S4†). The abundant pore structure of the materials can also be evidenced by the TEM image of the 5.0Pd@ZnO nanocomposites (Fig. S5g†).
Thus, the ZIF-8 derived xPd@ZnO porous nanocomposites obtained by the optimized heat treatment method not only maintained a considerable specific surface area, but also retained the uniform abundant porous structure, which is a highly preferred property in the field of gas detection. The HRTEM lattice fringes of 5.0Pd@ZnO are shown in Fig. 2h, where interplanar spacings of 0.225, 0.248, and 0.282 nm corresponded to the planes of Pd (111), ZnO (101), and ZnO (100), respectively. The polycrystalline structure of 5.0Pd@ZnO was revealed by the diffuse Debye-ring in SAED patterns, as shown in Fig. 2i.

In order to investigate the existence state of Pd on the surface, the detailed HAADF-STEM images and high-magnitude EDS mapping of MOF-derived xPd@ZnO are shown in Fig. 2. The atomic images and high magnitude EDS mapping of MOF-derived pure ZnO are shown in Fig. 2j, in which the entire nanoparticle exhibited a single-crystal structure without any other impurities. As shown in Fig. 2k, a Zn/Pd transition region could be observed at the (101) crystal plane of ZnO, and the (111) plane of Pd nanoparticles could be found at the edge of the crystal. The high-magnitude EDS mapping of MOF-derived 5.0Pd@ZnO confirmed the presence of Pd clusters/nanoparticles, in which the combination form of Pd NPs and ZnO crystal surface was consistent with the growth pattern in the DFT calculation. In the HAADF-STEM image of 10.0Pd@ZnO, the simultaneous existence of two Pd states could be observed clearly, which also further confirmed the location and growth mode of Pd nanoparticles on the surface. The lattice dislocation between the Pd lattice and the ZnO lattice can be clearly observed from Pd clusters that grew at the edge transition region in Fig. 2k and l, which is also consistent with the growth mode of Pd and confirms that Pd atoms can be doped into the crystal lattice. The absence of observable lattice expansion caused by the substitution of Zn$^2+$ (0.74 Å) by Pd$^2+$ (0.86 Å) may be mainly due to the relatively low content of Pd, and the doping of Pd was not to replace a large amount of Zn in a relatively large area.$^{44,45}$ Thus, the surface-exposed lattice Pd sites may be the dominant factor in promoting the sensing properties at low Pd ratios, while the Pd NPs on the surface were still distributed at a lower level. As the Pd content continued to increase, Pd atoms that cannot be doped into the crystal may occupy lattice Pd sites on the surface, or directly contact the surface in the form of Pd NPs during the preparation process, resulting in the response characteristics with Pd NPs as the
dominant factor. Fig. 2m shows the HAADF-STEM and EDS mapping characterization results for a single cubic structure of MOF-derived 5.0Pd@ZnO nanocomposites, which clearly demonstrated the well-maintained morphological structure and uniform distribution of Pd elements after optimized thermal treatment at the monomer level. The elemental mapping of 5.0Pd@ZnO demonstrated the successful formation of porous cage-like nanocomposites, which greatly increased the active sites. The microstructure of the fabricated sensors based on the nanocomposites are shown in Fig. 2d. A uniform porous film of as-prepared nanocomposites was formed on the surface of the gold interdigital electrodes (Au-IDEs) by the screen printing technology. Further elemental mapping characterization of the sensors (Fig. S5†) indicated that the elemental distribution was still relatively uniform after the sensor fabrication process, which was more conducive to the consistency of the sensors.

**Unique H2 sensing characteristics**

The response performance tests of the ZIF-8 derived xPd@ZnO porous nanocomposites to H2 under different working conditions are systematically explored in Fig. 3. The response transients of the as-prepared sensors to 200 ppm H2 under dark conditions are shown in Fig. 3a. In the dark condition, the pure ZnO showed almost no response to 200 ppm H2 at room temperature, and the electrical signal of the xPd@ZnO nanocomposites exhibits huge noise interference, which makes the H2 response characteristics of the sensors unable to be effectively identified. Interestingly, when a 365 nm UV irradiation with an intensity of 7.5 mW cm⁻² was added to the surface of the sensors (Fig. S6†), the photoexcited rectification effect not only greatly reduced the baseline resistance (Rb) of the nanocomposites, but also eliminated the electrical signal noises of the as-prepared sensors (except for the pure ZnO). Furthermore, the nanocomposites displayed an activated gas-sensitive state at room temperature with the excitation of UV irradiation, which is a rare property for MOS-based materials.

The response transients of the nanocomposites to different concentrations of 50–1000 ppm H2 under UV irradiation are shown in Fig. 3b. The pure ZnO and 1.0Pd@ZnO nanocomposites exhibited typical n-type semiconductor gas-sensing characteristics towards H2, and the response increased with the increase of H2 concentration. The presence of Pd makes the as-prepared materials exhibit faster response/recovery properties and more stable electrical signals under the excitation of UV irradiation, which means higher signal-to-noise ratio and lower theoretical detection limit (LOD). As the contents of Pd increased up to 2.5 at%, the n-type response value of the nanocomposite decreases with the increase of H2 concentration, and finally transitions to show the typical p-type...
Electrical conductivity and response characteristics to H₂. The response characteristics of 2.5Pd@ZnO exhibited an unstable transition state. Due to the competitive dominant reaction mechanism of n-type semiconductor response and p-type semiconductor response, the final response was greatly affected by the gas type and concentration, which brought uncontrollable factors to the actual sensing application process. Notably, when the contents of Pd were continuously increased to the molar ratio over 5.0%, the response behaviours of nanocomposites were completely transformed into the p-type semiconductor response characteristics to H₂, and the response value increased with the increase of H₂ concentration. The p-type semiconductor response characteristics of the nanocomposites were reduced due to the over-coverage of the excessive Pd content, as shown by 10.0Pd@ZnO nanocomposites in Fig. 3b. The reversibilities of the as-prepared sensors toward 200 ppm H₂ under UV irradiation are shown in Fig. 3b. All the as-prepared sensors showed favourable reversibility, which is a great advantage of MOS-based materials. The combination of the porous Pd-based ZnO nanocomposites and the excitation of UV irradiation not only achieved the rectification of the materials, but also realized the room-temperature H₂ detection of the MOS-based materials, which was a long-term difficulty in the field of gas detection. Furthermore, the transition of the sensor response characteristics to H₂ from the n-type to the p-type with the increase of Pd content provides a feasible method for high selectivity H₂ sensing. The response points and corresponding fitted-response curves of as-prepared sensors to different H₂ concentrations of 0.5–1000 ppm under UV irradiation are displayed in Fig. 3c. The excellent linearity exhibited in a wide concentration range indicates the great potential of the as-prepared sensors in the quantitative detection of H₂. The response of the xPd@ZnO porous nanocomposites in the continuous tests over 60 days (Fig. 3d) fluctuated around –17.33, –22.28, –29.76, 52.86, and 14.40, respectively. The promising long-term stability of the as-prepared sensors are benefited from the optimized heat treatment, which is a favourable characteristic in practical applications. The comparison in the response of the nanocomposites toward 200 ppm H₂ is shown in Fig. 3e. The 5.0Pd@ZnO porous nanocomposites exhibit a high p-type semiconductor response of 52.86 to 200 ppm H₂, which may be able to completely distinguish H₂ from other typical flammable gases in terms of the electrical signal. As another key property in the practical application, the results of relative humidity (RH = 0%, 11%, 33%, 54%, and 75%) interference experiments show that the as-prepared sensors exhibit better moisture resistance under low relative humidity (RH < 54%) [Fig. S7†]. With increase of relative humidity, the response of the as-prepared sensors to H₂ decreased significantly, which was due to the reaction of H₂O molecules with the adsorbed oxygen species and the occupation of the active sites. The response values of the 5.0Pd@ZnO nanocomposites to 200 ppm H₂ under different relative humidity conditions (0–75%) are 52.86, 51.36, 48.58, 42.69, and 35.53, respectively. The effects of different UV intensities on the resistance and response of 5.0Pd@ZnO nanocomposites were further examined, and are shown in ESI Fig. S8.† As the irradiation intensity increased, the resistance values of the nanocomposites were 16.31 MΩ, 14.58 MΩ, 12.07 MΩ, and 12.87 MΩ, respectively. The variation trend of the resistance under irradiation is due to the combined effect of the concentration of photoexcited carriers in the bulk phase of the material and the oxygen species adsorbed on the surface. Since the concentration of photoexcited carriers plays a major role in the change of resistance at relatively small irradiation intensities (≤7.5 mW cm⁻²), the resistance decreases with the increase of irradiation intensity. As the increase of irradiation intensity continues, the material is fully excited, and the oxygen species continue to abstract electrons from the surface, which increases the resistance. The response values of the as-prepared sensor under different UV intensities were 39.51, 45.04, 52.86, and 44.22, respectively, which exhibited an opposite trend to the change in resistance. The decrease in response at high UV intensity could be due to the reaction of adsorbed oxygen species with H₂, which produced an electrical signal opposite to that of the reaction between Pd nanoparticles and H₂ molecules, resulting in a decrease in the final response. It may also be an effective approach to achieve gas discrimination by adjusting the light wavelength and irradiation intensities in the future research.

Selectivity tests toward typical flammable gases

In order to verify the uniqueness of the p-type transition phenomenon discovered in previous H₂ sensing experiments, the response characteristics of the ZIF-8 derived xPd@ZnO porous nanocomposites to typical flammable gases are explored as shown in Fig. 4. The response transients of the as-prepared sensors to flammable gases such as CO, C₃H₂+2 (x ≤ 3), MeOH, ETOH, NH₃, H₂S, and H₂ are displayed in Fig. 4a–4u, and the corresponding impulse response curves are shown in Fig. 4b–4u, which are aimed to make a more intuitive comparison of the transient response values of the sensor to each gas. Materials with low Pd content (x ≤ 2.5) exhibit typical n-type semiconductor response characteristics to all the detected flammable gases. With the increase of Pd content, the transition of the p-type response characteristics of the sensors only partially occurs in the detection of H₂, NH₃, and C₃H₂+2, x ≥ 3. And due to the unique reaction of Pd nanoparticles with H₂ molecules, the sensors exhibited much higher response values to H₂, which can be clearly distinguished from the same concentration of other gases. For the in-depth study of the selectivity of each sensor to typical flammable gases, the relative response values of xPd@ZnO nanocomposites to different typical flammable gases are summarized in Table 1. The presence of 1.0% molar ratio of Pd produced a strong facilitation effect on the response to CO molecules, and the facilitation effect decreased with increasing Pd content. The n-type response of the sensors to C₃H₂+2, x ≥ 3, gradually decreased with the increase of Pd content, and finally turned into the p-type semiconductor response properties. The as-prepared sensors showed the normal n-type semiconductor pulse response to methanol (MeOH) molecules at lower Pd contents (x

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And the sensors exhibited a response behaviour in which the resistance increased first and then decreased at relatively high Pd contents ($x = 2.5$) to MeOH (Fig. S9cIII†), which may be attributed to the catalytic reaction of methanol molecules on the surface of Pd nanoparticles.

All the as-prepared sensors (except for $x = 10.0$) showed a higher n-type response to ethanol (EtOH), and the high response of the sensors to EtOH was suppressed by the over-coverage effect of excessive Pd content. The MOF-derived pure ZnO exhibited almost no response to 200 ppm of NH$_3$ and H$_2$S, and the corresponding characteristic responses were produced with the existence of Pd. The as-prepared sensors also showed a transition in response characteristics to NH$_3$ and exhibited typical p-type semiconductor response characteristics at the relatively high Pd ratios ($x = 2.5$).

All the as-prepared sensors ($x \neq 0$) showed typical n-type semiconductor response to H$_2$S. The response of each sensor to different gases, as shown in Fig. 4c, indicates that the complete distinction of H$_2$ from other typical flammable gases was achieved by 5.0Pd@ZnO porous nanocomposites at room temperature.

For the detection of CO, 1.0Pd@ZnO exhibited the highest response value of $-40.71$. As for the detection of CH$_4$, the pure ZnO showed the best n-type semiconductor response of $-15.83$. The p-type semiconductor response characteristics of 5.0Pd@ZnO to CH$_4$ can be used in the detection process that may encounter interference such as CO and EtOH. Due to the catalytic reaction between methanol molecules and surface aggregated Pd nanoparticles, it is more appropriate to use 1.0Pd@ZnO in the detection of MeOH, which exhibits the ordinary response/recovery curve and a high response value of $-32.07$. It can be found from Fig. S9cV† that the change of Pd contents has almost no impact on the response value of the sensors to EtOH and the higher response can be used as a signal feature to selectively identify ethanol molecules.

Notably, the 5.0Pd@ZnO porous nanocomposite is an ideal candidate material for the hydrogen detection scenario, which
not only has a high response value of 52.89 but also exhibits unique response behaviour characteristics opposite to other typical flammable gases (Fig. S9f). Fig. 4d intuitively shows the changes in the response of each sensor to different flammable gases, which can provide a reference for the subsequent gas sensing research of ZIF-8 derived ZnO-based sensors. The performance comparison of the relevant ZnO-based sensors is shown in Table 2, in which the sensors exhibit typical n-type semiconductor response characteristics (resistance drop) to related reducing gases. The sensors exhibit reversed responses to H₂ (resistance rise) and related reducing gases (resistance drop).

Table 2 Performance comparison with related sensors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Concentration (ppm)</th>
<th>Responsea (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanotubes</td>
<td>RT</td>
<td>500</td>
<td>−29.6%</td>
<td>47</td>
</tr>
<tr>
<td>ZnO/In$_2$O$_3$-CS-NRs</td>
<td>RT</td>
<td>500</td>
<td>−20.5%</td>
<td>48</td>
</tr>
<tr>
<td>Pd/ZnO NFs</td>
<td>RT</td>
<td>50</td>
<td>−70.0%</td>
<td>49</td>
</tr>
<tr>
<td>ZnO NTs/graphene</td>
<td>RT</td>
<td>100</td>
<td>−28.8%</td>
<td>50</td>
</tr>
<tr>
<td>NiO/ZnO</td>
<td>RT</td>
<td>1200</td>
<td>−71.0%</td>
<td>51</td>
</tr>
<tr>
<td>Pd–NCs/ZnO NRs</td>
<td>100</td>
<td>10 000</td>
<td>−74.0%</td>
<td>52</td>
</tr>
<tr>
<td>rGO/Ni–ZnO</td>
<td>150</td>
<td>100</td>
<td>−63.8%</td>
<td>53</td>
</tr>
<tr>
<td>Pd–Zn$_3$SnO$_4$/ZnO HNs</td>
<td>255</td>
<td>1000</td>
<td>−75.0%</td>
<td>54</td>
</tr>
<tr>
<td>Pd/BN/ZnO NWs</td>
<td>200</td>
<td>50</td>
<td>−91.9%</td>
<td>55</td>
</tr>
<tr>
<td>Pd@ZnO–In$_2$O$_3$ CSNPs</td>
<td>300</td>
<td>100</td>
<td>−97.6%</td>
<td>56</td>
</tr>
<tr>
<td>Pd@ZnO core–shell</td>
<td>350</td>
<td>100</td>
<td>−95.5%</td>
<td>56</td>
</tr>
<tr>
<td>NPs</td>
<td>5.0Pd@ZnO</td>
<td>RT</td>
<td>200</td>
<td>52.89% This work</td>
</tr>
</tbody>
</table>

a All the response values have been normalized as $S = (R_g - R_r)/R_r × 100$. b The sensors exhibit similar response characteristics (resistance drop) to related reducing gases. The sensors exhibit reversed responses to H₂ (resistance rise) and related reducing gases (resistance drop).

Chemical characterization

The chemical composition characterization and electrical characteristics of the nanocomposites are further carried out, as shown in Fig. 5. The XRD diffraction pattern of ZIF-8 obtained in this work is the same as that reported previously, which confirms the successful preparation of ZIF-8 based materials (Fig. 5a). The amorphous XRD characteristic curves of the typical carbon-based materials can be obtained from Fig. S11 (ESI), and it is observed that the peak of Pd increases as the molar ratio increases, which further confirms the completion of the carbonization process and the successful loading of Pd nanoparticles. All the ZIF-8-based materials exhibit high intensity peaks around 31.78°, 34.52°, and 36.38° after optimized heat treatment, which are in good agreement with the (100), (002), (101) planes of hexagonal wurtzite ZnO (JCPDS card no. 89-0511). The peak around 40.36° corresponds to the (111) crystal plane of Pd (JCPDS card no. 87-0645), which is enhanced with the increase of Pd molar ratio. The actual content of Pd loaded in xPd@ZnO porous nanocomposites is further explored by EDX spectra (Fig. 5b), and the actual overall Pd molar ratios of 2.5Pd@ZnO and 5.0Pd@ZnO turn out to be 2.7% and 5.1%, respectively, which are in good agreement with the theoretical contents. And due to the inhomogeneity of local doping areas, more detailed clarification of the specific content of Pd doped into ZnO in the presence of two forms of Pd needs to be explored in the subsequent related work.

X-ray photoelectron spectroscopy (XPS) analysis is employed to verify the surface chemical state of the nanocomposites, as shown in Fig. 5e–f. The two strong peaks at 1021.54 eV and 1044.62 eV in Fig. 5d correspond to the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$, respectively. The binding energy difference between the two strong peaks of Zn 2p is 23.08 eV, indicating the Zn$^{2+}$ oxidation state of Zn.$^{53}$ The high resolution spectra of Pd 3d are shown in Fig. 5e, in which the two peaks with binding energies of 336.47 eV and 341.80 eV could be assigned to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$, respectively. The existence of metallic state Pd is confirmed by the 5.33 eV binding energy gap between the two peaks of Pd 3d in 5.0Pd@ZnO.$^{54}$ The peak centers of Pd 3d shift slightly to higher binding energy with the increase of Pd molar ratio, which may be due to that the Pd$^{2+}$ produced by the interaction between ZnO and Pd atoms partially entered the ZnO lattice in the case of lower Pd content.$^{55}$ Meanwhile, the relative intensity of Pd 3d peaks increased with the increase of Pd content, which further proved the successful loading of Pd.
and the controllability of \(x\text{Pd@ZnO}\) porous nanocomposites. The O 1s spectrum in Fig. 5f is deconvoluted into two peaks around 530.24 eV and 531.49 eV, which are assigned to the lattice oxygen (O\(_{\text{lat}}\)) and adsorbed oxygen (O\(_{\text{ads}}\)), respectively.\(^{61}\) The ratio of O\(_{\text{ads}}\)/O\(_{\text{lat}}\) increases first and then decreases with the increase of Pd content, which is caused by the significant effect of different states of Pd on oxygen species. The higher relative intensity of O\(_{\text{ads}}\) at lower Pd molar ratios \((x \leq 2.5)\) may be attributed to the adsorption of oxygen species, which could be enhanced by the Pd in the lattice. And the n-type response to flammable gases could be improved by the increase of surface adsorbed oxygen species according to the traditional theory of the “ionosorption model.”\(^{62}\) With the continuous increase of Pd content \((x \geq 5.0)\), the relative strength of O\(_{\text{ads}}\) is greatly enhanced, which is favourable evidence for the dominant effect of Pd nanoparticles on the surface. A strong XPS characterization proof for the new experimental phenomenon is provided by the variation of surface oxygen species, and it is further explained in combination with DFT in the mechanism part. The baseline resistance of the as-prepared sensors reduced by 3 orders of magnitude under the photoexcitation of UV irradiation, which greatly increases the carrier concentration in the material (Fig. 5g). The increased resistance of the nanocomposites after the loading of Pd was caused by the sharply increased amounts of oxygen species on the surface of the materials. And the resistance of nanocomposites increased first and then decreased with the increase of Pd content, which may be caused by the different effects of the existent Pd states. In the case of lower Pd content, the surface “spillover” effect by lattice Pd dominates, which makes more adsorbed oxygen species abstract electrons from the material and increases the resistance of the sensors.\(^{63}\) With the further increase of Pd content,
the effect of metallic Pd nanoparticles on the surface gradually turns to be the dominant factor, which leads to a decrease in electrical resistance. In order to further study the structural changes of the nanocomposites induced by the potential elemental doping, the UV-vis absorption spectra of MOF-derived xPd@ZnO nanocomposites are shown in Fig. 5h. All the nanocomposites exhibited an absorption edge of $\lambda < 400$ nm owing to their wide band gap, which indicated the great potential of photoexcited gas sensing properties. The corresponding curves of $(a \nu h)^{2}$ versus $(h \nu)$ are displayed in Fig. 5i, which can be used to calculate the energy band gap. The band gap of the as-prepared nanocomposites can be calculated by UV-vis absorption spectra with the simplified formula $a \nu h = A (h \nu - E_g)^{2}$. The parameters $A$, $\alpha$, and $E_g$ represent the constant, absorption coefficient, and band gap, respectively. The band gaps of as-prepared MOF-derived xPd@ZnO ($x = 0.0$, $1.0$, $2.5$, $5.0$, and $10.0$) were calculated to be $3.17$ eV, $3.14$ eV, $3.11$ eV, and $3.09$ eV, respectively. The energy band decreases with the presence of doping elements, which may be due to the introduction of impurity energy levels in the band gap of the nanocomposite, resulting in a decrease in the electron transition energy.

Mechanism of xPd@ZnO to realize unique H$_2$ selectivity

As the Pd content increased, the sensors exhibited a transition from n-type to p-type semiconductor response characteristics for H$_2$ detection. The existence of two different Pd states (lattice Pd and metallic Pd nanoclusters) in the material could be the reason for this phenomenon. Based on this, the density functional theory (DFT) calculations and energy band analysis were carried out to reveal the adsorption behaviour of O$_2$/H$_2$ molecules on the surface, which could provide a theoretical basis for the high selectivity H$_2$ detection of xPd@ZnO porous nanocomposites. A supercell of the ZnO (10–10) surface was established with a vacuum layer of $15 \AA$. And according to the actual molar ratios of Pd, three typical cases of pure ZnO, 2.5Pd@ZnO, and 5.0Pd@ZnO were selected as representatives for modelling (Fig. S12†). In actual experiments, two states of Pd always exist in xPd@ZnO nanocomposites, and different effects are produced due to changes in Pd content. Nevertheless, considering its local inhomogeneity, it is difficult to simulate and reproduce every working condition exactly like the actual material surface. Therefore, the optimal solution is to select representative working conditions and the corresponding model constructions. In this work, a calculation system of 120 Zn atoms was selected for simulation, and three different surface states were used as representatives of this model precisely for the above considerations. Notably, in the case of 2.5Pd@ZnO porous nanocomposites, 3 Pd atoms replaced the Zn atoms in the surface lattice and existed in the form of lattice Pd. And in the model of 5.0Pd@ZnO, in addition to the existence form of lattice Pd, a Pd$_4$ cluster was added to the surface according to the actual experimental phenomenon. Through the optimized configuration, it is found that the Pd$_4$ cluster was preferentially anchored on the surface of lattice Pd, which covered the surface adsorption sites of lattice Pd. In the actual detection process, the sensor is usually in the air (O$_2$) atmosphere first, and then encounters the target gas (H$_2$) to generate a corresponding response. Therefore, O$_2$ molecule was first added in the model to explore the influence of different Pd existence states on the adsorption of oxygen species on the surface (Fig. S13†). The adsorbed O$_2$ molecule interacts with Zn atoms on the surface of pure ZnO and acquires $0.5108$ e of charges from the surface. The presence of lattice Pd in 2.5Pd@ZnO significantly improved the adsorption capacity for O$_2$ molecule, and the adsorption energy ($E_{ads}$) increased from $-0.06$ eV (pure ZnO) to $-1.15$ eV, which was consistent with the significant increase in the relative intensity of the O$_{ads}$ peak of the 2.5Pd@ZnO in Fig. 5f. The adsorbed O$_2$ molecule acquired more free charges of $0.5896$ e from the surface of lattice Pd, which provided a theoretical explanation for the experimental results of resistance increase in Fig. 5g. As for the case of 5.0Pd@ZnO, the O$_2$ molecule was more inclined to adsorb on the Pd$_4$ cluster, and the O=O bonds were further stretched. However, the O$_2$ molecule adsorbed on the Pd$_4$ cluster did not acquire more free electrons from the surface ($0.5833$ e) than that adsorbed on the lattice Pd surface. Meanwhile, the metallic Pd cluster could provide more free electrons to the surface of the material, which was consistent with the decreasing trend of resistance with high Pd content, as shown in Fig. 5g, and confirmed the rationality of the models.

In order to simulate the surface adsorption behaviour and electrical properties of the nanocomposites in real scenarios, the optimal configuration information of the above models with the addition of H$_2$ molecule is shown in Fig. 6. Pure ZnO exhibits a low adsorption energy of $0.25$ eV for the H$_2$ molecule, and the instability of the adsorption of H$_2$ and O$_2$ molecules may be the reason for the high electrical noise of the material at room temperature. While the adsorbed O$_2$ molecule acquired $0.5176$ e from the material, H$_2$ provided $0.0179$ e to the surface as an electron donor, which is consistent with the typical n-type semiconductor response of the material to H$_2$. In the ground state, none of the H$_2$ molecules interacted directly with the adsorbed O$_2$ molecules on the surface. Due to the presence of lattice Pd, the adsorption energy of H$_2$ molecule on the surface of 2.5Pd@ZnO was enhanced to $-0.24$ eV. Interestingly, H$_2$ molecule on the surface of 5.0Pd@ZnO was not adsorbed on the surface of lattice Pd as expected, but interacted with the lattice oxygen. The detailed adsorption states of H$_2$ and O$_2$ molecules on the material surface are shown in Fig. 6a and b. The presence of lattice Pd had a significant effect on the adsorption behaviour of O$_2$ molecules, while the effect on H$_2$ molecules was only reflected in the enhancement of adsorption energy. However, the Pd$_4$ cluster on the surface of 5.0Pd@ZnO in Fig. 6c exhibited a completely different behaviour towards the H$_2$ molecule. H$_2$ molecule was completely cleaved on the surface of the Pd$_4$ cluster, and the adsorption energy reached $-1.10$ eV, which indicated the formation of PdH$_x$. In this case, H$_2$ no longer acted as an electron donor, but obtained electrons of $0.2365$ e from the material (Fig. 6f), which provided a reasonable explanation for the increase in the resistance of 5.0Pd@ZnO in a H$_2$/air atmosphere.

Fig. 6g–j further explores the UV photoexcited response mechanism of nanocomposites to H$_2$ based on the energy band
structure. The most widely adopted gas sensing mechanism of MOS-based sensors is the change of the depletion layer caused by the reaction of adsorbed oxygen species (O, O^2-) and H2 molecules at high temperature (eqn (1) and (2)), which produced a detectable electrical signal as the response of the sensors.\textsuperscript{43} However, under dark conditions, the recognizable response signal to H2 molecules could not be produced at room temperature due to the low carrier concentration and the poor reactivity of adsorbed oxygen species. The introduction of UV irradiation not only stimulated the carrier concentration of the materials but also activated the oxygen species adsorbed on the surface,\textsuperscript{46} as shown in eqn (3) and (4).

\[ \text{O}_2 \leftrightarrow \text{O}_{2,\text{ads}} \leftrightarrow \text{O}_{2,\text{ads}}^2 \] \text{low temperature} \leftrightarrow \[ \text{O}_{\text{ads}} \leftrightarrow \text{O}_{\text{ads}}^2 \] \text{higher temperature} \quad (1)

\[ \text{H}_2 + \text{O}_{\text{ads}}^x \rightarrow \text{H}_2\text{O} + x\text{e}^- \] \quad (2)

\[ \text{UV}_{hv} \rightarrow h_{hv}^+ + e_{hv}^- \] \quad (3)

\[ e_{hv}^- + \text{O}_{2,\text{ads}}^- \rightarrow 2\text{O}_{hv}^- \] \quad (4)

Fig. 6 The optimal adsorption configuration information based on ZnO (1010) and schematic diagrams of the sensing mechanism. The most stable structures of O2 and H2 molecules adsorbed on the MOF-derived (a) Pure ZnO, (b) 2.5Pd@ZnO, and (c) 5.0Pd@ZnO. (d–f) The corresponding charge density difference of O2 and H2 adsorbed on the monolayer. The yellow and blue isosurfaces with an isosurface level of 0.0015 eÅ\textsuperscript{-3} correspond to charge accumulation and depletion, respectively. (g and h) The gas sensing mechanism with enhanced response of low Pd ratio (x \approx 2.5) nanocomposites. (i and j) The gas sensing mechanism with high H2 selectivity of high Pd ratio (x \approx 5.0) nanocomposites.
The difference in work function between ZnO ($\Phi = 4.5$ eV) and Pd ($\Phi = 5.1$ eV) made electrons more inclined to transfer to the Pd. Combined with the enhanced adsorption of oxygen species on the Pd surface under UV excitation, a deeper depletion layer of the material was formed in the air atmosphere, as shown in Fig. 6g. When the sensors were placed in the H$_2$/air environment, the H$_2$ molecules reacted with the photoexcited oxygen species ($O_{hv}$) on the surface of the material, as shown in eqn (5). Fig. 6h displays the depletion layer changes of the materials in a H$_2$/air atmosphere, and the resistance of the nanocomposites was greatly reduced with the return of electrons, which produced the typical n-type semiconductor response characteristics to H$_2$. The band structure of the nanocomposites with a higher Pd content in air was similar to that with a low Pd content (Fig. 6i). However, when it was placed in a H$_2$/air atmosphere, an interesting electrical signal variation occurred due to the formation of PdH$_x$, as shown in eqn (6). In fact, in the actual gas detection process, the reactions of formulae (5) and (6) were simultaneously carried out on the surface of 5.0Pd@ZnO. The DFT calculation in Fig. 6f indicated that the cracking of H$_2$ on the surface of the Pd cluster not only abstracted more electrons from the material, but also enhanced the electron acquisition ability of adsorbed oxygen species (0.6382 e). Combined with the occupancy of the Pd clusters on the catalytic sites of the lattice Pd, and the disturbance of the electron flow in the material by the scattering source of PdH$_x$, the overall resistance of the material exhibited a tendency to increase in the H$_2$/air atmosphere. Thus, even though the work function of the formed PdH$_x$ ($\Phi = 3.2$ eV) was lower than that of ZnO ($\Phi = 4.5$ eV), the flow of surface electrons caused a deeper depletion layer of the material, which explained the reason for the typical p-type semiconductor response characteristics of the sensors to H$_2$ under the UV/air atmosphere. This work systematically expounds the adsorption behaviour, charge transfer and response characteristics of O$_2$/H$_2$ molecules on the surface of different states of Pd/ZnO, which provides a solid theoretical basis for the design of high selectivity gas sensors.

$$H_2 + O_{hv} \rightarrow H_2O + e^- \tag{5}$$

$$xH_2 + Pd_{\text{cluster}} \rightarrow PdH_x \tag{6}$$

In addition, the sensors with high Pd ratios exhibit partial p-type response characteristics to CH$_4$H$_{2x-2}$, which may be due to the cleavage of the C-H bond of the corresponding gas molecules on the surface of Pd$^0$ clusters to produce the transition state $\cdot$H. And PdH$_x$ was formed by the combination of transition state $\cdot$H and Pd. Taking the reaction of CH$_4$ on the Pd surface as an example, the different cleaved transition state groups simultaneously captured and released electrons on the surface, which produced a weaker p-type semiconductor response than H$_2$ molecules:$$CH_4 \xrightarrow{Pd} \cdot CH_3 + \cdot H \tag{7}$$

$$\cdot H + Pd \rightarrow PdH_x \tag{8}$$

Furthermore, Chen et al.$^{6b}$ investigated the reactions of Pd with CH$_4$, C$_2$H$_6$, and C$_2$H$_8$ (C$_2$H$_{2x-2}$, x = 3) by guided ion beam mass spectrometry, in which different ionic products are observed in the reaction process. The related reactions can be summarized as follows, which are also the potential reasons that may lead to the p-type semiconductor response characteristics of the sensors:

$$C_2H_{2x+2} + Pd \rightarrow C_xH_{2x+1} + PdH \tag{10}$$

$$C_2H_{2x+2} + Pd \rightarrow PdC_{x-1}H_{2x-2} + CH_4 \tag{11}$$

$$C_2H_{2x+2} + Pd \rightarrow PdC_xH_{2x} + H_2 \tag{12}$$

$$C_2H_{2x+2} + Pd \rightarrow C_{x-1}H_{2x-3} + CH_4 + PdH \tag{14}$$

Similar p-type semiconductor response characteristics for NH$_3$ were mainly due to the successive dehydrogenation reactions of adsorbed NH$_4$ species on the Pd surface under UV excitation, and the reactions are as follows:$$NH_3 \xrightarrow{Pd} \cdot NH_2 + \cdot H \tag{15}$$

$$2NH_3 \xrightarrow{Pd} N_2 + 3H_2 \tag{16}$$

$$2NH_3 + O_{ads} \rightarrow N_2 + 3H_2O + xe^- \tag{17}$$

The related gases that produce the reversed response of typical p-type semiconductor characteristics all produced transition state $\cdot$H or generated H$_2$ molecules, which is also consistent with the theoretical analysis and DFT calculations in the mechanism of this work. Utilizing unique electrical signal changes generated by special materials and gas molecules to achieve direct discrimination of flammable gases at room temperature can provide meaningful reference for subsequent design of high selectivity sensors.

**Conclusions**

In summary, an efficient gas discrimination scheme that synergistically combined the advantages of MOF-derived MOS nanocomposites, noble metal nanoparticles, and photoexcitation is demonstrated. The MOF-derived porous nanocomposites are fabricated by an optimized heat treatment process and used as sensing materials directly. The nanocomposites not only retained the porous structures of MOF-based materials but also displayed the advantages of typical metal oxide semiconductor materials, which endowed the as-prepared sensor with a favourable linearity response, repeatability, and long-term stability. A novel room-temperature reversed response phenomenon (+52.89) of 5.0Pd@ZnO to H$_2$ under UV photoexcitation was discovered, which is distinguished from the typical n-type response characteristics of other flammable gases. Furthermore, the ultra-effective gas
discrimination of the monolithic MOF-derived sensor is achieved by the differentiated response (CO: $-25.15$, CH$_4$: 9.64, C$_2$H$_6$: 16.33, C$_3$H$_8$: $-1.65$, MeOH: $-13.63$, EtOH: $-49.92$, NH$_3$: 7.15, H$_2$S: $-40.36$, H$_2$: 52.89). The special adsorption behaviours of O$_2$ and H$_2$ molecules on the surface with different Pd states were systematically demonstrated by chemical characterization and DFT calculations. The results of theoretical calculations corroborated well with the transition of n-type to p-type semiconductor response characteristics produced in practical experiments, which provided an advanced theoretical basis for the application of Pd in high-selectivity materials. This work may provide a solid experimental reference and theoretical basis for the development of the next generation of photoexcited high-selectivity room temperature sensors.

**Author contributions**


**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**
