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Zeolitic Imidazolate Framework as Formaldehyde Gas Sensor

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Supporting Information

ABSTRACT: Traditional semiconducting metal oxide-based gas sensors are always limited on low surface areas and high operating temperatures. Considering the high surface area and high stability of zeolitic imidazolate framework (ZIF), ZIF-67 (surface area of 1832.2 $m^2\ g^{-1}$) was first employed as a promising formaldehyde gas sensor at a low operating temperature (150 °C), and the gas sensor could detect formaldehyde as low as 5 ppm. This work develops a new promising application approach for porous metal–organic frameworks.

Detection of toxic and combustible gases plays a crucial role in health risk factors, industrial processes, and environmental protection. Especially formaldehyde, which widely exists in daily life and industrial manufacturing processes, is considered as one of the dominating pollutants in the indoor environment and one of the contributors to sick building syndrome.[1] In the past decades, a variety of gas sensors based on semiconducting metal oxides, such as SnO_2, ZnO, In_2O_3, and NiO film or their metal-doped phases, have been developed to monitor formaldehyde.[2] However, such inorganic sensors often require a high temperature (200–400 °C) to achieve optimum measurements. Furthermore, they are always limited on low surface areas, because a promising gas sensing process is strongly dependent on the large surface area that permits the sensing material to absorb more gas molecules and then improve the response.

As typical high surface area materials, metal–organic frameworks (MOFs) have attracted significant attention because of their structural diversity and potential applications in many fields, including gas separation and storage, drug delivery, catalysis, and sensors.[3−5] Since many MOFs show a high band gap (e.g., E_g of ZIF-8 is 4.9eV.), low thermal stability, and poor electrical conductivity, so far their sensing applications in the gas phase are rarely explored and remain great challenges.[6] An exceptional class in MOFs is those zeolitic imidazolate frameworks (ZIFs) with outstanding thermal and chemical stability. Although the applications of ZIFs related to energy use and environmental conservation have been developed, gas sensing exploration is still in the embryonic stage.[7]

In this work, we present for the first time that ZIF-67 ($Co(mim)_2$; mim = 2-methylimidazolate) is a promising formaldehyde gas sensor at a low operating temperature (150 °C). Good selectivity and high sensitivity to formaldehyde are successfully achieved. The ZIF-67 sensor could detect formaldehyde as low as 5 ppm, and the response reached 1.8 at 150 °C.

Porous ZIF-67 has three-dimensional zeolite-like structure with SOD topology and shows a high Langmuir surface area of 1832.2 $m^2\ g^{-1}$ (Figure 1).[8] Moreover, it has low band gap (E_g = 1.98eV) and high thermal stability in the air. Themogravimetric analyses in the air and further powder X-ray diffraction measurement demonstrate that the desolvated framework of ZIF-67 is stable at 250 °C in the air (Figures S1 and S2). The as-synthesized powder sample of ZIF-67 was coated on the Ag–Pd interdigitated electrodes for the gas sensing measurements (Figure S3).

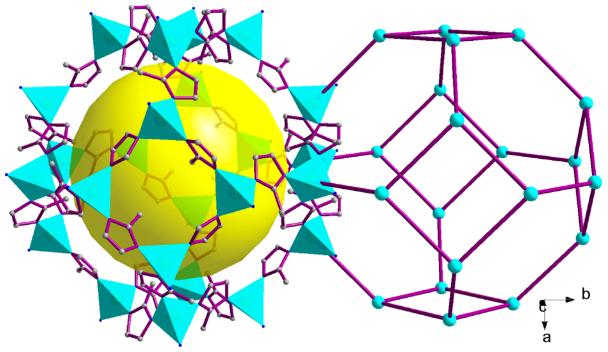

Figure 1. SOD-type structure of ZIF-67.

To find the optimum conditions, gas sensing measurements were performed by exposing the obtained sensor to 100 ppm diverse gases (formaldehyde, methanol, acetone, ammonia, and methane) at different operating temperatures (Figure 2). The sensor response was evaluated as a function of operating temperature. For the ZIF-67 sensor, maximum response was observed at 150 °C operating temperature. It is noticeable that the ZIF-67 sensor has the highest response (13.9) to formaldehyde at 150 °C. In contrast, the response to methanol (7.5) and acetone (7.3) at 150 °C is low. Remarkably, the response to ammonia and methane is very weak and neglectable. These results reveal that the ZIF-67 sensor possesses good selectivity to formaldehyde at 150 °C.

The sensitivity of the ZIF-67 sensor versus different formaldehyde concentrations at a 150 °C operating temperature has been further investigated. As shown in Figure 3, with an increasing of formaldehyde concentration from 5 to 500

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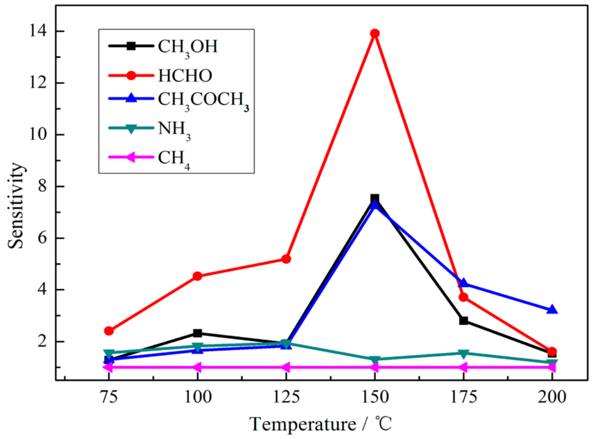

Figure 2. Sensitivity of the ZIF-67 sensor to different 100 ppm gases measured between 75 and 200 °C.

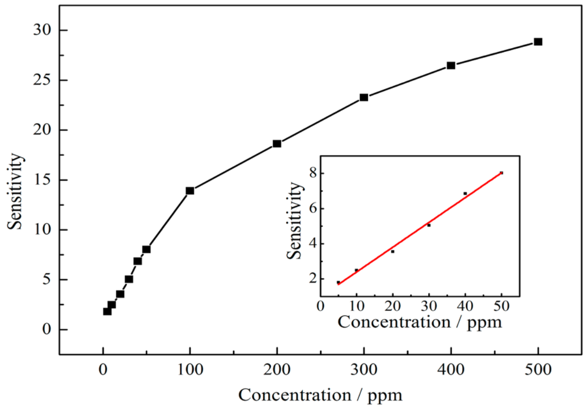

Figure 3. Sensitivity of the ZIF-67 sensor to different formaldehyde concentrations at 150 °C. The inset shows a linear dependence of the sensitivity on formaldehyde concentration in the range of 5−50 ppm.

ppm, the sensitivity promptly increases. ZIF-67 shows the highest response of 30 to 500 ppm of formaldehyde. Worthy of mention is that there is good linearity between concentration and sensitivity in the low concentration range (from 5 to 50 ppm; Figure 3 insert). These results indicate that ZIF-67 may serve as not only a sensitive material for formaldehyde detection but also a tool to determine the possible concentration of formaldehyde in the environment.

Figure 4 shows the response−recovery characteristics of the ZIF-67 sensor to formaldehyde at 150 °C, which further demonstrates the practice application of ZIF-67 as a formaldehyde gas sensor. It is obvious that this response−recovery curve of the ZIF-67 sensor is totally different from those of metal-oxide sensors. For common metal-oxide sensors, the highest resistance is often very fast to reach. However, for ZIF-67 with such a high surface area, the resistance under each concentration is very slow to reach the top, but the response time is still fast. That means the first-step diffusion of formaldehyde into the pore surfaces of ZIF-67 is fast, which dramatically changed the resistance of the ZIF-67 sensor. Since there are still enough empty spaces in ZIF-67 to accommodate formaldehyde molecules, the resistance keeps increasing slowly and finally gets a balance after the adsorption is saturated. Although such a step-by-step adsorption process makes the resistance of the ZIF-67 sensor change exceptionally, the gas desorption process and the recovery of the ZIF-67 sensor are not unusual. It can quickly release the formaldehyde molecules and get back to the original state. To the best of our knowledge, this is the first time a dynamic sorption process of porous MOFs via the resistance approach has been identified.

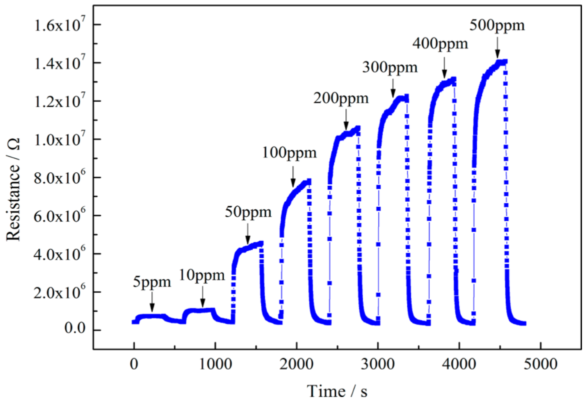

Figure 4. Response−recovery curve of the ZIF-67 sensor.

The effect of environmental humidity on the ZIF-67 sensor sensitivity is shown in Figure 5. It can be seen that the impact of relative humidity below 70% is less significant and could be negligible. Above 70%, relative humidity has a great influence on ZIF-67 sensor sensitivity.

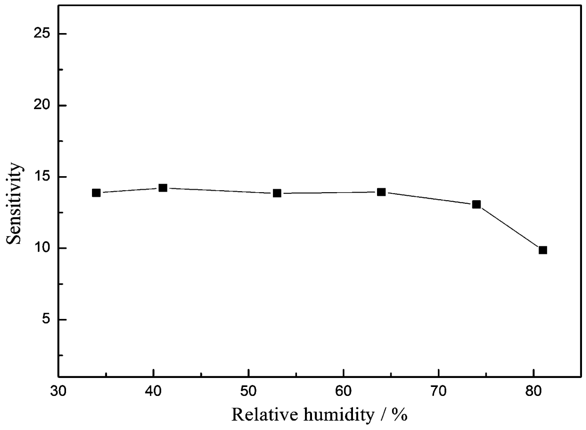

Figure 5. Effect of environmental humindity on ZIF-67 sensor sensitivity.

In summary, the ZIF-67 sensor has been demonstrated to possess good selectivity, high response, and low detection limit to formaldehyde at a low operating temperature (150 °C). It may be a promising candidate for formaldehyde detection in practice applications. Our future work will explore the possible mechanism of the high response of ZIF-67 as a gas sensing material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TGA curves in nitrogen and air atmosphere, Powder XRD patterns, pictures of ZIF-67 sensor. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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