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# MOF Thin Film-Coated Metal Oxide Nanowire Array: Significantly Improved Chemiresistor Sensor Performance

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As a critical family of chemiresistor materials, metal oxides (MOX), such as ZnO, $SnO_2$, and $In_2O_3$, have been developed for many industrial and domestic applications in volatile organic compound (VOC) detection due to their low cost, portability, real-time operability, and ease of use.[1] To pursue higher sensitivity, better selectivity, faster responsivity, and lower working temperature, nanostructured MOX materials have been extensively studied due to their increased surface-to-volume ratios and reactive surface areas compared with bulk.[1b,2] However, selectivity is still a major challenge for commercial MOX gas sensor devices, although several ways, such as cross-sensitivity adjustment, electronic noses and gas preseparation by other instrument, have been developed to address this issue.[3] For instance, water vapor is a typical interference of MOX gas sensor for VOC detecting, which commonly exists in the air with high concentration (40–70 RH%, ≈11 440–20 019 ppm) and will generate false responses to a major source for unreliable results.[4] Although many efforts like doping, p–n junctions, and noble metal decoration have been made to reduce the negative effects of humidity, an ideal solution is still in need.[4b,c]

Metal organic framework (MOF) is a class of crystalline framework-structured material constructed by connecting metal center with organic linker. Such materials feature regular pores, ultra large surface areas, tunable framework structures, and open-metal sites and demonstrate potential applications on catalysis, gas storage and separation, drug delivery, nanoscale reactors, proton conduction, etc.[5,6] Particularly, their selective gas adsorption behavior makes MOF very attractive for overcoming the selectivity problem in gas sensor.[7–9] For example, Zhang's group reported two hydrophobic MOFs, $[Co(im)_2]_n$ and $[Co(mim)_2]_n$, exhibiting selective response to VOC gases without the interference of humidity.[7a,b] In contrast, Achmann et al. first found that hydrophilic MOF, Fe-1,3,5-benzenetricarboxylate, selectively shows higher response to humidity than VOCs.[8] Even so, the reported MOF-based chemiresistor sensors suffer from low sensitivity to analytes.[8–10]

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Here, we propose a new material design strategy to improve the performance of chemiresistor gas sensor by combining the high sensitivity of nanostructured MOX with the high selectivity and catalytic activity of MOF into one material. First, MOX nanowire is used as core material for gas sensing reaction and subsequent electrical signal transport. Then, by coating a layer of MOF thin film on the surface of MOX nanowire, a MOX@MOF core–sheath nanowire material could be obtained. In such a core–sheath nanostructured material, the porous sheath material is used to selectively usher desired target species and reject interfering gases from passing through to reach MOX surface. By this manner, the selectivity of MOX gas sensor could be greatly improved. Moreover, catalytic properties of MOF may also be introduced into such materials to enhance their sensing performance.

For the first time, the above described strategy was successfully demonstrated by coating a layer of hydrophobic and catalytic Zeolitic Imidazolate Framework - CoZn (ZIF-CoZn, isostructural with ZIF-8(Zn) or ZIF-67(Co)) thin film on ZnO to form a core–sheath nanowire array for chemiresistor gas sensor, which can improve the performance on detecting acetone under humidity interference. The detection of ppb/ppm-level acetone is of great essence for environmental monitoring and clinic application.[11] On one hand, acetone is one of most used solvents and reagents in industry and laboratory. It can anaesthetize the central nervous system of human and cause damage to kidney, pancreas, and liver. On the other hand, acetone is an important breath biomarker for diagnosing diabetes, because its concentration would increase from 3 to 9 ppm in health human body to more than 18 ppm in diabetic patients. Breath acetone analysis was found to be more effective than urine sampling for monitoring ketosis for insulin-dependent diabetic patients.[12] However, the humidity in environment and human breath can vary within a broad range, and the cross-sensitivity of humidity may plague the precise detection of acetone by MOX sensors due to their intrinsically poor selectivity. We found that ZnO@ZIF-CoZn nanowire array-based sensor shows greatly enhanced selectivity of acetone to humidity, much better response, accelerated response and recovery behavior, and significantly decreased working temperature, compared with ZnO nanowire array-based sensor.

The ZnO@ZIF-CoZn gas sensor was prepared by coating a layer of ZIF-CoZn thin film on ZnO nanowire array via a simple solution method (for details see **Figure 1** and Table S1, Supporting Information). Notably the synthesis of MOF-coated metal oxide nanorod has been reported by others.[13] In their work, metal oxide nanorod works as sacrificial template to supply $Zn^{2+}$ for constructing MOF. Differently, besides $Zn^{2+}$ dissolved from ZnO nanorod, foreign $Co^{2+}$ source was also involved in the synthesis of ZnO@ZIF-CoZn. The competition

  