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Surface functionalized sensors for humidity-independent gas detection

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Abstract: Semiconducting metal oxides (SMOXs) are used widely for gas sensors. However, the effect of ambient humidity on the baseline and sensitivity of chemiresistors is still a largely-unsolved problem, reducing sensor accuracy and causing complications for sensor calibrations. Here we present a general strategy to overcome water-sensitivity issues by coating SMOXs with a hydrophobic polymer separated by a metal-organic frameworks (MOF) layer that preserves the SMOXs surface and acts as gas selective function. Sensor devices using these nanoparticles display near constant response even when humidity is varied across a wide range (0 to 90% relative humidity-RH). Furthermore, the sensor delivers notable performance below 20% RH where other water-resistance strategies typically fail. Selectivity enhancement and humidity-independent sensitivity are concomitantly achieved using this approach. The reported tandem coating strategy is expected to be relevant for a wide range of SMOXs, leading to a new generation of gas sensors with excellent humidity-resistant performance.

Introduction

Gas detection and monitoring is an important technology in many fields such as toxic gas detection and environmental air quality monitoring.[1] Among the various developed gas detection technologies, chemical sensors, such as semiconducting metal oxides (SMOXs)-based chemiresistive gas sensors, have been one of the most attractive platforms due to their low cost, easy intergration, and real-time detection.[2] However, there remain some notable drawbacks, such as high operating temperatures,[3] high limits of detection (LoD),[4] and humidity dependent sensitivity that hinder their further potential application. The latter is truly problematic because water vapor concentration can change greatly during operating conditions; e.g. from 6280 ppm at 20% relative humidity (RH) to 25740 ppm at 80 %RH in ambient air (1 atm, 25 ℃).[5] Water molecules (physisorbed water or stronger bound associatively adsorbed water) typically interacts by H bonding with surface oxygen or surface hydroxyl groups on the SMOXs surface, in which the adsorbed water molecule either acts as proton donor or acceptor, respectively, causing the deterioration of active sites (adsorbed surface oxygen species).[6]

In order to guarantee minimal affects by humidity for reliable sensing performance, various efforts have been devoted recently (*Supplementary Table S1*). Although these strategies were effective in suppressing the humidity-dependent gas-sensing characteristics, their use was usually accompanied by unintended side effects, such as response deterioration, selectivity alteration and resistance variation. For example, species such as NiO,[7] CuO,[8] and Al[9] can be used to capture hydroxyls and supply oxygen adsorption sites, and surface modification using noble metal (Pd[10] or Pr[11]) particles to catalyse the removal of hydroxyls can improve robustness to humidity. However, these methods suffer from limitations including poor performance in the low humidity range (0-20 RH%). Another approach is to add hydrophobic coatings for example coating of SMOXs with superhydrophobic polydimethylsiloxane (PDMS) can largely enhance the humidity-resistant performance.[12] Nevertheless, the hydrophobic layer was found to impede the efficient permeation of target molecules to the sensing materials, which hampered the SMOX surface activity leading to loss of detector sensitivity.

Nanoporous materials, such as zeolites,[13] porous polymers,[14] or metal-organic frameworks (MOFs),[15] can act as “breathable” supporting/filteration layers and so offer a solution to the above issues. Gas molecules can diffuse through the pores of these materials, thus showing negligible influence on the activity of the SMOXs sensing materials. Besides, selective permation of specific molecules can be achieved by tuning their pore size or surface chemistry functionalization. Among nanoporous materials, MOFs possess huge potential due to their excellent selective gas seperation as well as storage.[16] Surface modification methodologies (for example surface wettability) of MOFs materials are already used to improve the moisture/water-resistant performance of MOF-based catalysts.[17] We have thus hypothesised that PDMS/MOF tandem coating layers on SMOXs

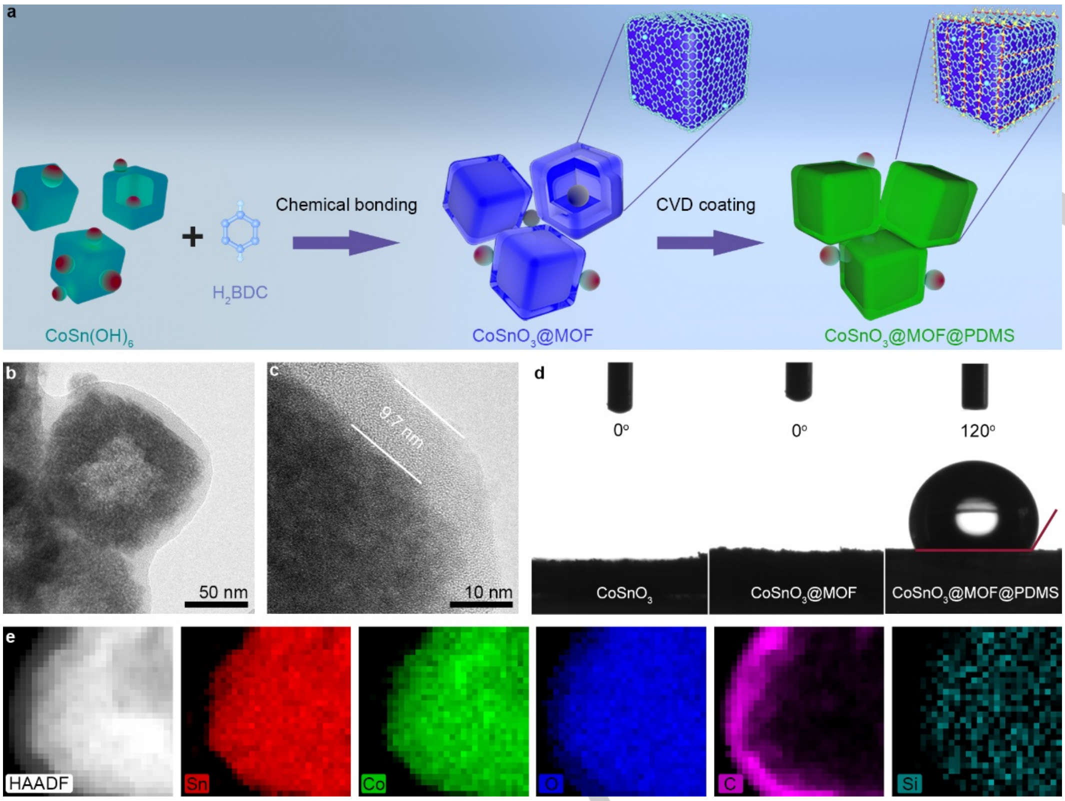

Figure 1. a) Schematic illustration of the preparation of MOF/PDMS-tandem coating on the surface of $CoSnO_3$ nanocubes. b-c) TEM image of $CoSnO_3$@MOF@PDMS NCs. d) The contact angles of a water droplet on $CoSnO_3$, $CoSnO_3$@MOF and $CoSnO_3$@MOF@PDMS. e) High-angle annular dark-field scanning TEM and corresponding electron energy-loss spectroscopy (EELS) elemental mapping of Sn, Co, O, C and Si of $CoSnO_3$@MOF@PDMS.

could improve humidity-resistant performance through reducing or avoiding the contact between water molecules and SMOXs sensing materials. Herein, we report that this is a highly effective and potentially general strategy to resolve humidity-sensitivity problems in SMOX sensors. Hybrid gas sensors based on SMOXs ($CoSnO_3$, SnO_2 and ZnO) tandem-coated by the MOF (Co-based MOF, CoBDC) and PDMS show a constant response to H_2S, ethanol or acetone under various humidity from 0 to 90 RH%. Also, compared to pristine SMOX sensors, our hybrid sensor improves baseline stability, and significantly reduces or even eliminates some interferring gases effects.

Results and Discussion

Samples preparation and characterization

PDMS, a hydrophobic polymer, has been widely used to change the surface wettability of MOFs to enhance their moisture or water resistance.[17] In order to void the reacting sites being occupied by PDMS coverage, we chose the MOFs (CoBDC) as the first coating layer (supporting layer) due to its porous structure, which supplies molecular sieving function as well as catalytic oxidation characteristics.[18] $CoSnO_3$, a typical high gas sensing performance SMOX, has been chosen to demonstrate the feasibility of this general approach.[19] The $CoSnO_3$@MOF@PDMS hybrid nanoparticle sensor is fabricated through a simple three-step approach as described in Methods (see Methods Section for details and Figure 1a). Fristly, cubic shape $CoSn(OH)_6$ with a diameter of about 100-150 nm was prepared through a hrdrothermal reaction (*Supplementary Figure S1*). After annealing in Ar, $CoSnO_3$ nanoboxes (*Supplementary Figure S2*), with a homogenously amorphous texture and high porosity, are obtained by thermal-induced dehydration of $CoSn(OH)_6$. The reaction between Co ions and organic ligands in 1, 4-benzenedicarboxylic acid (H_2BDC) leads to the formation of a CoBDC layer on $CoSnO_3$ nanocubes (*Supplementary Figure S3*). Finally, after chemical vapor deposition (CVD) treatment to add the PDMS coating, the PDMS layer was succefully coated on the $CoSnO_3$@MOF, as shown in Figure 1b-c. SMOXs, $CoSnO_3$ included, are water sensitive to some degree with water contact angles near to 0^o (Figure 1d). After being coated by the MOF (CoBDC), the water contact is also about 0^o, indicating hydrophilic property. However, PDMS-coated samples ($CoSnO_3$@MOF@PDMS) have water contact angles up to 120 ± 3^o, revealing a change from hydrophilic to hydrophobic character. The contact angle of a water droplet increases as the coating time increases from 0 to 10 h and reaches a value approaching that of pure PDMS after 10 h coating (*Supplementary Figure S4*). The high-angle annular dark field scanning TEM (HAADF-STEM) image and the corresponding electron energy-loss spectroscopy (EELS) elemental

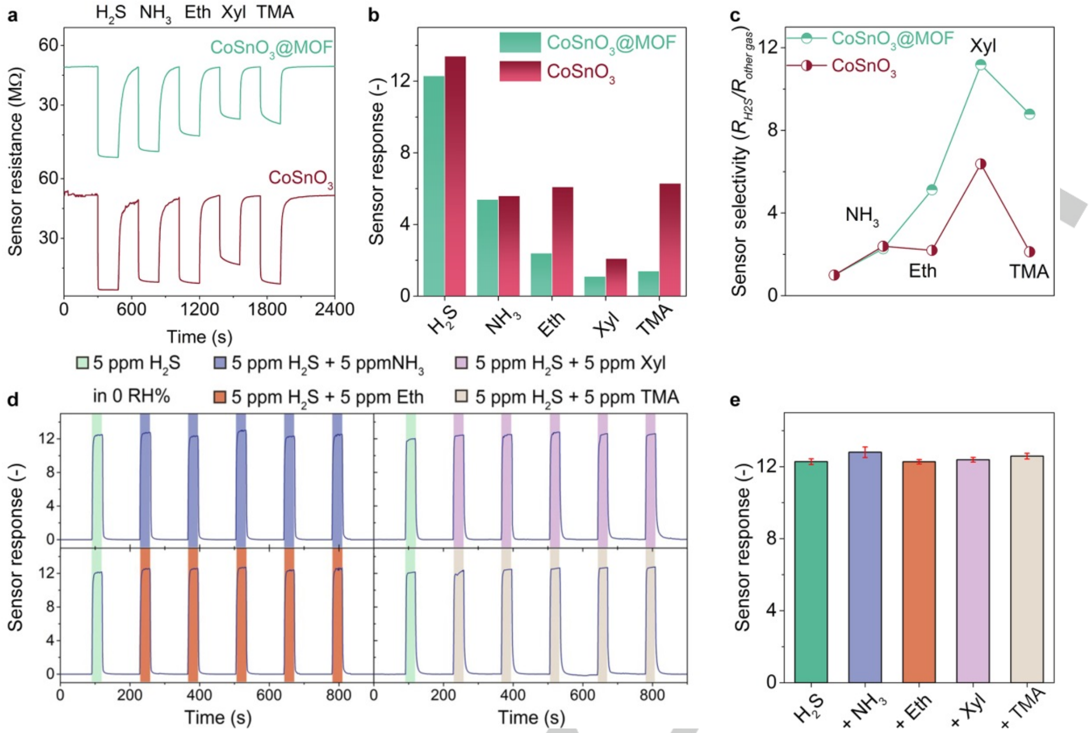

Figure 2. a-b) Dynamic sensing resistance curve and response of $CoSnO_3$ and $CoSnO_3$@MOF to different gases with a concentration of 5 ppm for H_2S and 100 ppm for other gases at 160℃ under 0 RH%. c) Selectivity improvements for $CoSnO_3$@MOF. d) Sensor response of $CoSnO_3$@MOF@PDMS to a pulse of 5 ppm H_2S followed by five pulses of 5 ppm H_2S and 5 ppm NH_3, 5 ppm H_2S and 5 ppm ethanol (Eth), 5 ppm H_2S and 5 ppm xylene (Xyl), 5 ppm H_2S and 5 ppm trimethylamine (TMA), respectively, in 0 RH%. e) The sensor responses are retained throughout exposure to the different mixture gases under 0 RH%. Error bars denotes SD (standard deviation) from 5 cycles.

maps of $CoSnO_3$@MOF@PDMS NCs (Figure 1e) reveal a larger area of C and Si distribution indicating that PDMS/Co-MOF has successfully formed the outer layer.

To investigate the porosity of the samples, the specific surface area and pore distribution of $CoSnO_3$@MOF and $CoSnO_3$@MOF@PDMS were analysed through nitrogen adsorption/desorption isotherms at 77 K. $CoSnO_3$@MOF and $CoSnO_3$@MOF@PDMS exhibited a specific surface area of 181 and 174 m^2/g, respectively (*Supplementary Figure S5* and *Table S2*). This reveals that the inherent porous structures are not blocked/collapsed after being covered with PDMS on the surface of $CoSnO_3$@MOF. The results demonstrate that the porous structure is retained even after the PDMS coating process is completed. This will obviously allow gas molecules to arrive at the surface of core-sensing materials ($CoSnO_3$).

Selective and humidity-resistant gas sensing performance

Prior to checking the selectivity performance, the optimum operating temperature was determined (*Supplementary Figure S6*). The $CoSnO_3$ exhibited the maximum response of 20.7 towards 10 ppm H_2S (a highly toxic gas present in sour natural gas) at 160 ^oC. Thus, 160 ^oC was selected as the optimum operating temperature and the following tests were all operated under 160 ^oC. Four kinds of typical gases/vapors, NH_3, ethanol, xylene and trimethylamine (TMA), are selected as the interfering gases/vapors. Figure 2a,b shows the dynamic sensing resistance curve and response of $CoSnO_3$ and $CoSnO_3$@MOF to the above gases with a concentration of 5 ppm for H_2S and 100 ppm for other gases at 160 ℃ under 0 RH%. The response of $CoSnO_3$@MOF to 5 ppm H_2S under 0% RH was about 12.1. This is much larger than that of other interfering gases, including NH_3, ethanol, xylene and trimethylamine. However, the $CoSnO_3$ showed similar response to NH_3, ethanol and TMA. It should be noted that the responses of $CoSnO_3$@MOF to VOCs (ethanol, xylene and TMA) are smaller than those of $CoSnO_3$. This could be due to Co^{2+} from Co-MOF, which has good catalytic property over the temperature range 100-300 ℃; this can result in dissociation of oxygen molecules yielding active oxygen species which in turn results in catalytic oxidation of VOCs.[20] Therefore, a fraction of the VOCs would likely degrade when passing through the MOF layer, prior to arriving at the surface of $CoSnO_3$. This is the likely reason for the decrease of response of $CoSnO_3$@MOF to VOCs. Figure 2c reveals that $CoSnO_3$@MOF sensor exhibits improved selectivity ($S = R_{H_2S}/R_{other\ gases}$) toward H_2S when compared with that of $CoSnO_3$ sensor.

To verify the selectivity under realistic conditions, we conducted the experiment for the $CoSnO_3$@MOF in 5 ppm H_2S or a mixture of 5 ppm H_2S and 5 ppm interfering gases under 0 RH% (Figure 2d, e). The sensor responses toward selected combination of gases is shown in Figure 3b. The response is within ±10 % of the standard deviation limit from the normalized response for 5 ppm

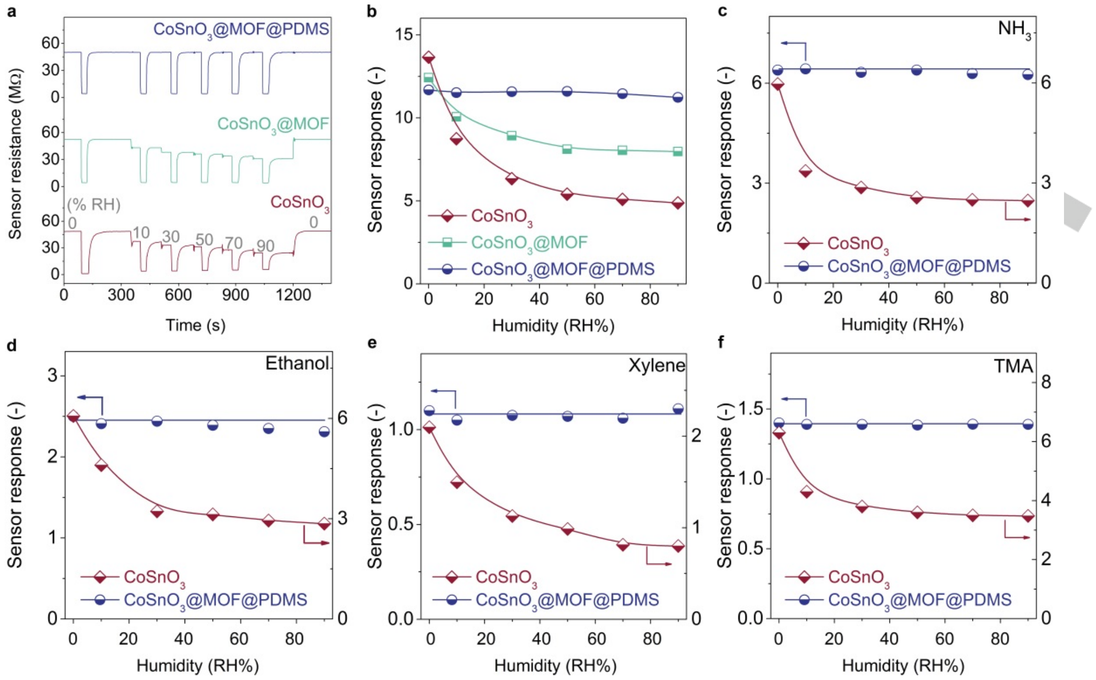

Figure 3. a) Dynamic gas sensing transients of $CoSnO_3$, $CoSnO_3$@MOF and $CoSnO_3$@MOF@PDMS to H_2S (5 ppm, 160 ℃) in dry and humid conditions (10, 30, 50, 70, 90 RH%). b) Humidity dependence of $CoSnO_3$, $CoSnO_3$@MOF and $CoSnO_3$@MOF@PDMS to 5 ppm H_2S at 160℃. Humidity dependence of $CoSnO_3$@MOF@PDMS and $CoSnO_3$ to other gases: c) NH_3, d) ethanol, e) xylene and f) TMA at 160 ℃. Concentration is 100 ppm.

H_2S. Clearly the $CoSnO_3$@MOF@PDMS based device has the desired selectivity.

The effect of ambient humidity on the baseline and sensitivity of chemiresistors is still a largely-unsolved problem, which will reduce sensor accuracy and cause complications for calibrations. The effects of water vapor from 0 to 90 RH% on the resistance and response to H_2S is shown in Figure 3. The electrical baseline resistance of both $CoSnO_3$ and $CoSnO_3$@ MOF (Figure 3a) decreases drastically with increase in humidity, which is in accordance with previous reported SMOXs.[21] Whereas, the coating of PDMS layer provided two significant improvements over these un-coated samples: (1) the electrical baseline was less influenced by humidity changes (Figure 3a), and (2) the sensor response exhibited hardly any noticeable difference (a coefficient of variation/CV value of 1.3%) when the humidity varied (Figure 3b). Using the tandem-coating based approach, we obtain similar improvements in humidity-resistant performance for sensing of other gases/vapors as well (Figure 3c-f). The response of $CoSnO_3$@MOF@PDMS to NH_3, ethanol, xylene and TMA (100 ppm, 160 ℃) under different humidity conditions (from 0 RH% to 90 RH%) is found to be nearly unchanged with a CV value of 1.35%, 1.87%, 2.79% and 1.07%, respectively, which is much smaller than those of un-coated $CoSnO_3$ (19.93%, 44.23%, 65.33% and 26.18%). The results demonstrate that $CoSnO_3$@MOF@PDMS shows superior humidity tolerance for the detection of the selected gases.

The chosen CVD time is optimal because, with a smaller time, the PDMS can not fully cover the surface of $CoSnO_3$@MOF, while with a longer time a too thick layer will form to cut off the permeation of gas molecules. To investigate the influence of PDMS CVD time on the humidity-tolerant performance, the responses of $CoSnO_3$@MOF coated with different PDMS CVD time samples (CMP-x donated as $CoSnO_3$@MOF with x hours coating PDMS) towards 100 ppm H_2S under 0 RH% and 90 RH% were tested and shown in *Supplementary Figure S7*. It can be observed that, with the increase of CVD time, the response exhibited slightly decrease from 0 to 6 h and dramatic decrease after 6 h under dry condition. This may be caused by the fully covered of PDMS, which blocked the permeability of H_2S molecules through PDMS layer to the core-sensing material ($CoSnO_3$). Nevertheless, when the humidity increased to 90 RH%, the response showed an 'increase-maximum-decrease' trend. When the CVD time is shorter than 6 h, the response under 90 RH% shows a decrease compared to that under dry air (0 RH%) as a consequence of partly coverage of PDMS. These results were in accordance with the surface wettability confirmed by water contact angles test (*Supplementary Figure S4*). In addition, an obvious deterioration of response could be observed by comparing the sensing performance between $CoSnO_3$@MOF@PDMS and $CoSnO_3$@PDMS (*Supplementary Figure S8*), which revealed that MOF layer can avoid the reacting sites being occupied by PDMS coverage, shown in *Supplementary Figure S9*.

The limit of detection (LoD) of pristine $CoSnO_3$ and $CoSnO_3$@MOF@PDMS was derived by exposing them to pulses of gradually increasing H_2S concentration and by measuring the resistance of the sensors. Firstly, the LoD was defined as $3\sigma/S$, where σ was the noise of the acquired resistance signal, and S was the sensitivity (the slope of liner calibration curve) of the sensors. To provide extended experimental determination of the noise, we carried out a prolonged measurement of the $CoSnO_3$ and $CoSnO_3$@MOF@PDMS sensor in 90 RH% atmospheres.

Supplementary Figure S10 showed the response of the pristine $CoSnO_3$ and $CoSnO_3$@MOF@PDMS sensor under 30 min of synthetic air followed by 30 min 5 ppm H_2S and synthetic air mixture in 90 RH% atmospheres. The noise of the pristine $CoSnO_3$ and $CoSnO_3$@MOF@PDMS sensor calculated from the curves were 0.004 and 0.001 in air, respectively. The theoretical H_2S LoD of $CoSnO_3$ and $CoSnO_3$@MOF@PDMS sensor were calculated to be 14.7 and 1.8 ppb, respectively, using response noise in air, σ_a.

Improvement in humidity-independent performances for other SMOXs

Encouraged by the improved gas sensing performance of $CoSnO_3$@MOF@PDMS, Co-MOF/PDMS coating was attempted to boost the characteristics of other SMOXs. Representative examples, include SnO_2 and ZnO, two typical gas sensing materials, are selected to evaluate the tandem coating strategy to improve humidity-resistant performance (Figure 4). The SnO_2 and ZnO were coated with CoBDC and PDMS layers using a similar method. The commerical SnO_2-based sensor exhibits a degradation of 50.3 %, while SnO_2@MOF@PDMS sensor shows only a degradation smaller than 1.8 %. Similar to SnO_2, the additional stabilization of ZnO achieved by MOF/PDMS coating endowed ZnO@MOF@PDMS sensor with enhanced humidity-independent properties when compared with pristine ZnO. This implies that the approach is likely to be generic.

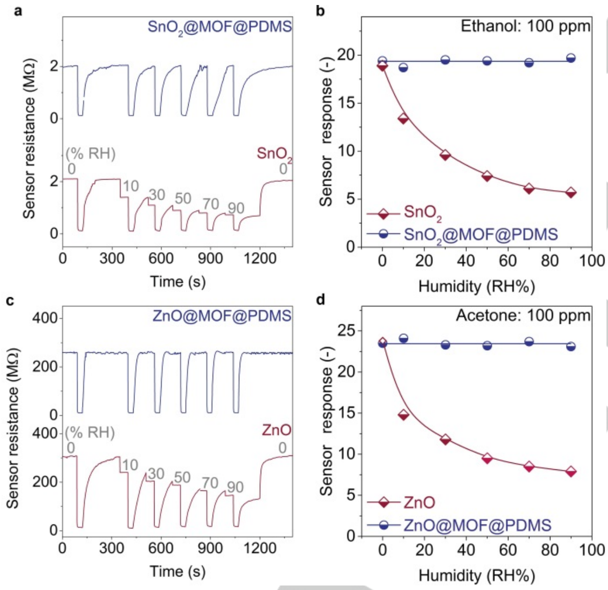

Figure 4. a,b) Dynamic gas sensing transients and sensor response of SnO_2 and SnO_2@MOF@PDMS to ethanol (100 ppm, 180 ℃) in dry and humid conditions. c,d) Dynamic gas sensing transients and sensor response of ZnO and ZnO@MOF@PDMS to acetone (100 ppm, 180 ℃) in dry and humid conditions.

Conclusion

We have demonstrated a simple and potentially generic approach for ensuring humidity-resistance for SMOXs gas sensors. The approach offers a combination of robust humidity resistance and selectivity enhancement by introducing hydrophobic polymer and MOF coatings on the surface of metal oxide sensing materials. The dual-shell demonstration product, $CoSnO_3$@MOF@PDMS responds in a robust, humidity-invariant manner to H_2S and other gases, such as ethanol, xylene and NH_3. Importantly, this has a coefficient of variation that is near constant regardless of the relative humidity (even for RH < 20%). Similar performance is observed for SnO_2 and ZnO based analogues. This coating strategy is thus expected to be generally applicable to metal oxide semiconductor-based gas sensors and offers a versatile approach to render such gas sensors humidity resistant for practical applications.

Acknowledgements

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Keywords: PDMS • humidity-resistance • metal-organic frameworks • hydrophobization • gas sensors

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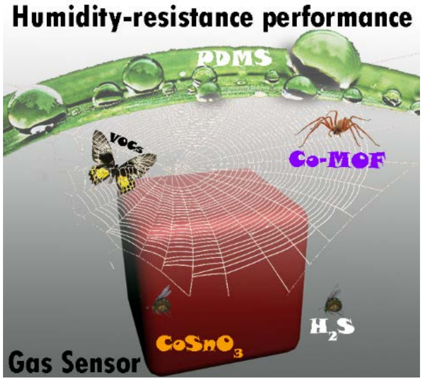

A surface functionalized strategy, utilizing Co-MOF/PDMS as tandem coating layer, was proposed to overcome humidity-sensitive problem of semiconducting metal oxides-based gas sensor. This approach can be extendable to various humidity-independent gas sensing materials.