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Improved Hydrogen Sensitivity and Selectivity in PdO with Metal-Organic Framework Membrane

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Metal-organic frameworks (MOFs) are highly designable porous materials and are recognized for their exceptional selectivity as chemical sensors. However, they are not always suitable for incorporation with existing sensing platforms, especially sensing modes that rely on electronic changes in the sensing material (e.g., work-function response or conductometric response). One way that MOFs can be utilized is by growing them as a porous membrane on a sensing layer and using the MOF to affect the electronic structure of the sensing layer. In this paper, a proof-of-concept for electronic modulation with MOFs is demonstrated. A PdO nanoparticle sensing layer on a chemical-sensitive field-effect-transistor is made more sensitive to a reducing gas, hydrogen, and less sensitive to oxidizing molecules, like H₂S and NO₂, by growing a layer of the MOF “ZIF-8” over the nanoparticles. The proposed mechanism is supported by X-ray photoelectron spectroscopy showing that the ZIF-8 membrane partially reduces the PdO sensing layer.

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Metal oxides as chemical sensors are ubiquitous with a number of favorable properties. These sensors also work as catalysts, inducing a reaction with the target molecule.

Metal-support interactions have long been known in the field of catalysis.¹ With metal-support interactions, the physical support that a metal or metal oxide catalyst is dispersed on induces changes in the catalyst's performance for a particular reaction. This metal-support interaction is usually engineered into the catalyst; however, this interaction is rarely considered in chemical sensing. MOF-metal interactions have been leveraged for a number of other applications.^{2–6} Studying this phenomenon in chemical sensing could lead to improvements in sensing performance, especially selectivity. Selectivity is a key metric in the growing market for small, distributed chemical sensors, which lack the power and form factor to hold a number of sensors needed to build a “chemical nose” utilizing machine learning techniques to discriminate between atmospheric conditions.

One promising platform for distributed chemical sensing is the chemical-sensitive field-effect transistor⁷ (CS-FET, Fig. 1). The CS-FET operates like a normal transistor, except that instead of a gate electrode voltage modulating the source-drain current, a sensing material's surface potential (or work function) modulates the source-drain current. The CS-FET is compatible with many metal and metal-oxide sensing materials; for example, Pd and PdO are quite sensitive to hydrogen.⁸

The mechanism of hydrogen sensing with Pd and PdO is the conversion of the material to its hydride. In the case of Pd, whose adsorption of hydrogen has been widely studied,^{9,10} the hydrogen integrates with the metal forming PdH_x.⁸ We observe a response on the CS-FET because the hydride has a different band gap from the metal and metal oxide. The change in band gap of the sensing material is analogous to a change in gate voltage for the transistor, leading to band bending in the silicon channel and modulated source/drain current.

To study a metal-support interaction on the CS-FET, we have used a metal-organic framework as a membrane over the PdO sensing layers. MOFs are porous, crystalline materials made up of metal ions connected by organic linkers and have been shown to have unique sensing properties on the CS-FET without a metal or metal oxide,¹¹ and as electrochemical sensors in their own regard.¹² There have been many examples showing how MOFs can be grown solvothermally on metal oxides.^{13–15} The identity of the metal and the linker affect the chemical adsorption properties of the MOF and affect the electronic properties of the MOF, and thus, they are good candidates for exploring the support interactions. The MOF ZIF-8 (Fig. 2) has been shown to improve the hydrogenation selectivity over some catalysts,¹⁶ so it can be expected to improve the performance of hydrogen sensing for PdO or Pd.

Here, we report a proof-of-concept with a PdO sensing layer on CS-FET becoming more sensitive to H₂ with ZIF-8 while Pd does not. The performance of the PdO/ZIF-8 composite is explained by measuring the oxidation state of the sensing material with X-ray photoelectron spectroscopy (XPS).¹⁷ We find that the ZIF-8 membrane partially oxidizes PdO, leading to more the changes in sensitivity observed here.

Experimental

Device preparation.—The CS-FET devices are fabricated using a standard method on bulk silicon wafers.⁸ The source/drain contacts are W on Ni and the effective thickness of the SiO₂ dielectric between the sensing layer and the bulk silicon is approximately 5 nm. Palladium was evaporated at 0.1 Å/second to achieve 10 Å Pd, similar to Ref. 3. This condition favors the growth of a small PdO layer. A metallic Pd layer was achieved with a forming gas anneal at 150 °C with 5% H₂ in N₂ for 1 h. Devices were cleaned with acetone, isopropyl alcohol, water, and a UV/ozone atmosphere for 10 min prior to gas sensing or ZIF-8 film growth.

ZIF-8 was deposited in a solvothermal manner. The device was submerged in a methanol solution containing 20 mM zinc nitrate and 100 mM 2-methylimidazole for 30 min at room temperature. The device was then submerged three more times in baths of the same composition for the same time for a total of four baths and two total

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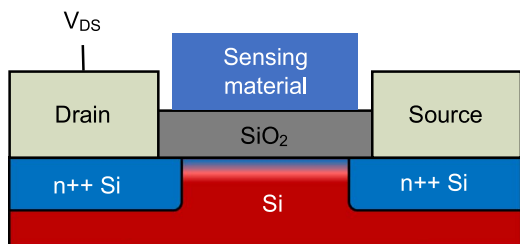


Figure 1. Schematic cross-section of chemical-sensitive field-effect transistor (CS-FET).

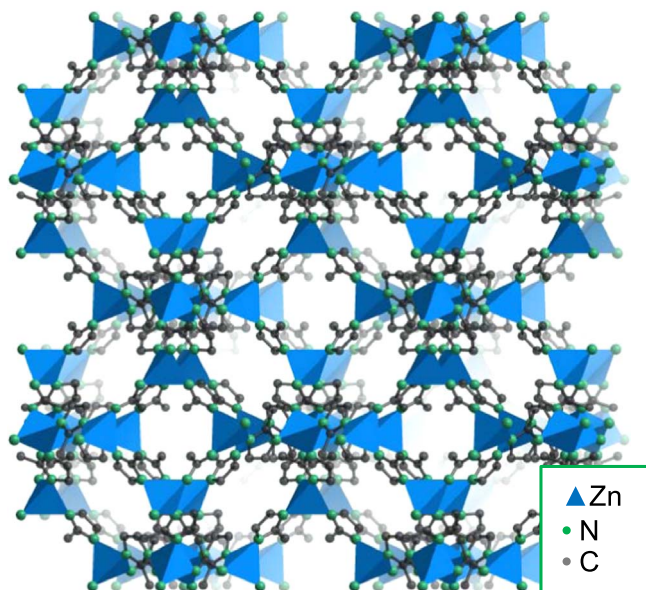


Figure 2. Crystal structure of the metal-organic framework ZIF-8.

hours.¹⁸ The synthesized ZIF-8 was activated in a bath of dimethylformamide overnight and stored in vacuum. The ZIF-8 membrane was also prepared on a clean silicon wafer following the same process for electrical and structural analyses of the MOF as in Ref. 11. The thickness is roughly 50 nm.

Material characterization.—X-ray diffraction (XRD) spectra were taken using a Bruker AXS D8 Discover GADDS XRD diffractometer system with a grazing angle of 0.3° and a Cu $K\alpha$ source. Scanning electron microscopy was done one a Phenom Pro benchtop SEM at 15 kV beam energy. X-ray photoelectron spectra (XPS) were collected with an Omicron Dar400 system with an achromatic Al $K\alpha$ source. XPS binding energies were normalized to the C 1s peak. The peaks were fit with a Shirley background, using the minimum number of peaks, using the CasaXPS fitting software. The R^2 values of the fit to XPS data were greater than 99% in all cases. Scanning electron microscopy was done one a Phenom Pro benchtop SEM at 15 kV beam energy.

Gas sensing measurements.—All gas sensing measurements were carried out in a walk-in fume hood. Devices were wire bonded to a 28-pin J-bend leaded chip carrier. A small-volume ($\sim 0.83 \text{ cm}^3$) 3D printed housing, made of polylactic acid, consisting of a $\frac{1}{4}$ -inch gas inlet was used to cover the chip carrier. Synthetic dry air was used as diluent gas and was procured from Praxair Technology Inc. Synthetic air–diluted gas cylinders were purchased from MESA International Technologies Inc. at a calibrated concentration. Typical gas flow rates were from 1 to 100 sccm, and diluent (synthetic air) flow rate was 100–1000 sccm. Humidity was controlled by diverting the diluent through a bubbler filled with $18 \text{ M}\Omega\text{-cm}$ deionized water.

Ambient temperature and humidity were monitored by commercial sensors purchased from Sensirion AG (models SHT2x and SHT3x). Gas delivery was controlled by mass flow controllers (Alicat Scientific Inc.). CS-FET sensors were biased using a Keithley 428 current preamplifier, and the current signals were acquired using a LabVIEW-controlled data acquisition unit (National Instruments, NI USB-6259). Unless otherwise mentioned, the sensing measurements in this manuscript were recorded with source-drain voltage, $V_{DS} = 3 \text{ V}$, and substrate bias, $V_{SUB} = 0 \text{ V}$. The current measured was unambiguously determined to be through the channel by measuring the resistance between two points on the silicon wafer that was coated in MOF, finding that the MOF thin films were unable to carry current. An on-stream sensor was used to monitor humidity and temperature of the gas sensing atmosphere. All results were confirmed with multiple devices.

Results

The sensors reported in this work are represented schematically in Figs. 3a and 3b. Optical images of the PdO CS-FET devices after coating with ZIF-8 show a uniform green-colored coating (Figs. 3c, 3d). Scanning electron microscopy of the channel shows that the ZIF-8 coats the entire channel but does tend to agglomerate into islands (Figs. 3e, 3f). The sensing results below suggest that there is conformal coating, although the SEM imaging shows that there are particles roughly 500 nm in size. Prior experiments have shown that the size of a MOF thin film does not affect the sensing response and has a small effect on sensing dynamics.¹¹

This coating of ZIF-8 on PdO is in good agreement with previous characterization of ZIF-8 thin films on SiO_2 .¹⁸ The crystal structure of ZIF-8, as measured by XRD, is as expected (Fig. 4). There is no difference between the spectra of ZIF-8 grown on SiO_2 and ZIF-8 grown on Pd. The relative intensities of the XRD peaks do not match the isotropic calculated spectra, indicating a preferred orientation. It is quite common to observe a preferred orientation in MOF thin films grown at room temperature.^{19,20} Using the Scherrer equation and assuming minimal instrumental broadening and negligible microstrain, we estimate that the ZIF film comprises crystals $\sim 400 \text{ nm}$ thick along their (200) axes, which is in good agreement with the SEM imaging. After many NO_2 exposure cycles (roughly 2 total hours of sensing at 100–2000 ppb, as in Ref. 11) the (200) and (220) peaks are unaffected, but the (112) reflection is weakened, suggesting that NO_2 reacts with the structure along that facet.

Figure 5a presents the sensor response to hydrogen, showing that the ZIF-8 coating on PdO leads to an improvement in hydrogen sensitivity (Fig. 5a). The results were repeated for two sets of sensors, indicating similar trends, and over a range of hydrogen exposures (Fig. 5b). The response time is improved and the recovery time is just as good with ZIF-8 as the PdO coating alone. Typically a microheater is used to re-set the sensing material and achieve a faster recovery to baseline, but doing so on this device actually led to charring of the ZIF-8 material and negatively affected the baseline stability.

The sensor with ZIF-8 is less selective against humidity (Fig. 5c). However, the ZIF-8 coating shows much better selectivity against NO_2 and H_2S (Fig. 5d). The response to NO_2 is especially improved with ZIF-8. The PdO sensing layer has a long recovery and the current responds erratically as the sensing material recovers from the exposure, yet there is no response in the ZIF-8 coated PdO. The PdO/ZIF-8 device is also less responsive to H_2S . The ZIF-8 thin film is very stable against NO_2 ^{11,22} and its XRD pattern is mostly unchanged, even after nearly an hour of elevated NO_2 exposure (Fig. 4). We have previously found that a ZIF-8 sensing film will recover back to baseline after many NO_2 exposures, and with minimal change in its diffraction pattern, so ZIF-8 should be considered chemically stable as a sensing film.⁸

The chemical selectivity of a material is a direct consequence of a material's electronic structure. The electronic structure of a material can be assessed with X-ray photoelectron spectroscopy. Figure 6

Discussion

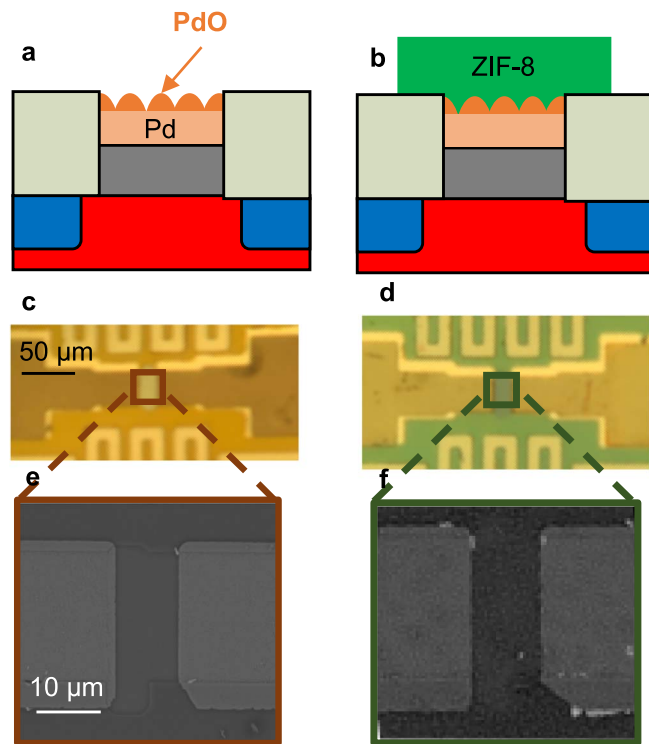


Figure 3. (a) Schematic side cross-section of chemical-sensitive field-effect transistor (CS-FET) with PdO and (b) PdO/ZIF-8 sensing layers. (c) Top-down optical image of CS-FET device with PdO and (d) PdO/ZIF-8 sensing layers. SEM image of sensor with (e) PdO and (f) PdO/ZIF-8 sensing layers.

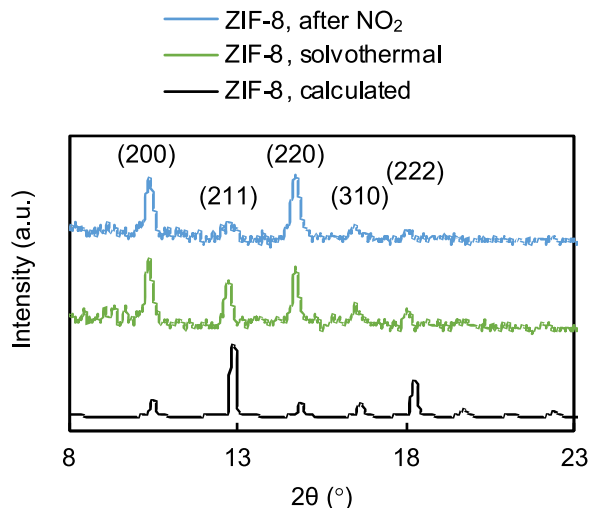


Figure 4. XRD spectra of ZIF-8 deposited on SiO₂ compared to the expected structure, and after many sensing experiments. Calculated spectrum from Ref. 21. Spectra after NO₂ is for ZIF-8 on SiO₂ from Ref. 11.

shows that the Pd binding states in PdO/ZIF-8 are shifted to higher energies by several hundreds of meV, indicating a more oxidized character, compared to the as-deposited PdO. In parallel, the Zn 2p^{3/2} peak obtained on ZIF-8 left-shifts from 1025.5 eV in ZIF-8 grown on SiO₂ to 1025.0 eV for ZIF-8 grown on PdO, indicating a more reduced character (Fig. 6).

The magnitude of the hydrogen sensing response is not improved for metallic Pd, shown in Fig. 7a, and the recovery is somewhat longer. The humidity sensitivity of a metallic Pd sensor is slightly improved (Fig. 7b).

The ZIF-8 thin film grows quite well on PdO nanoparticles. The growth is fairly uniform with some larger crystals. The recipe is easily adaptable and suited for microfabrication processes. ZIF-type MOFs can also be easily manipulated to form new structures, changing the identity of the metal ion from Zn to Co²³ or 2-methyl-imidazole to other imidazole-type molecules.²⁴

There are a few possible explanations for the improved H₂ selectivity against NO₂ in the PdO/ZIF-8 sensing material. The most likely is that the material is acting as a sacrificial layer and reacts with the NO₂. Previous characterization of ZIF-8 exposed to ppm-levels of NO₂ shows that the crystallinity is decreased, indicating some damage to the ZIF-8 structure, although the material is remarkably stable.²² Both the hydrophobic nature and the sacrificial role contribute to the low sensitivity to NO₂. Regardless, the ZIF-8 membrane prevents any change in the underlying PdO sensing layer's band gap, so there is no response to NO₂.

Hydrogen sensing with Pd and PdO tends to have a long recovery at ambient temperatures. The mechanism—hydrogen diffusion into the Pd or PdO⁸—means that even in a thin layer, the time delay is quite long. The MOF sensing layer does not seem to affect the time constant of the recovery, as in Fig. 5a, when the Pd and PdO sensing layers are both 70% recovered 30 min after the first exposure. The sensor reliability is demonstrated by the sensitivity curve in Fig. 5b, whose points were collected over several days. This particular sensing setup is well suited to show the proof-of-principle that a metal oxide's sensing layer's electronic structure is affected, although these sensors in particular may not be the optimum sensing layer for hydrogen.

The mechanism for improved sensitivity to H₂ over H₂S in the PdO/ZIF-8 sensing material is most likely a result of the change in the PdO electronic structure caused by the ZIF-8 coating. The Zn 2p^{3/2} peak is left-shifted, indicating more reduced character, for ZIF-8 on PdO compared to ZIF-8 on SiO₂, so electron density pulled from PdO goes to the Zn of the ZIF-8 coating. A more oxidized PdO is more sensitive to hydrogen compared to a less oxidized PdO. The more oxidized PdO under the ZIF-8 coating does not accept the oxidizing sulfur of the H₂S as much as the as-deposited PdO, so the band gap of the sensing material is less affected by the H₂S interferant.

The increased response to water in the PdO/ZIF-8 is most likely a result of the hydrophilic ZIF-8 surface trapping humidity nearer the interface. While the pores of ZIF-8 are hydrophobic,²⁵ the exterior zinc-terminating surface is hydrophilic, adsorbing water. This result suggests that for NO₂ the ZIF-8 does not act so much as a membrane but as a protective layer that could eventually be eroded, because the dynamic response shows that water vapor can diffuse to the PdO surface.

The “electronic structure” argument is supported by the results obtained on the ZIF-8 coating on a more noble (i.e., unreactive) surface, namely metallic Pd. Noble metals—by definition—are not easily oxidized, which makes the effect of ZIF-8 less pronounced, if at all. Comparing the responses of metallic Pd and metallic Pd with ZIF-8 coating shows no difference between the two conditions, only longer recovery dynamics. The response to water appears to be a convolution of the intrinsic Pd response to water and the response of ZIF-8 (Figs. 5 and 7).

Other researchers have improved hydrogen selectivity using a size-selective membrane of ZIF-8²⁶ or of amorphous silica²⁷ to reduce sensitivity to small organic molecules while maintaining sensitivity. However, these membranes do not protect against other small molecules, and both sensing platforms use much higher power than the CS-FET platform.⁸ MOFs have also been used as part of a composite with carbon-based sensing materials,^{28–31} especially for adsorption of biologically relevant molecules, but these systems are still mostly leveraging the size and chemistry of the MOF and not the potential electronic effect the MOF can have on the support.

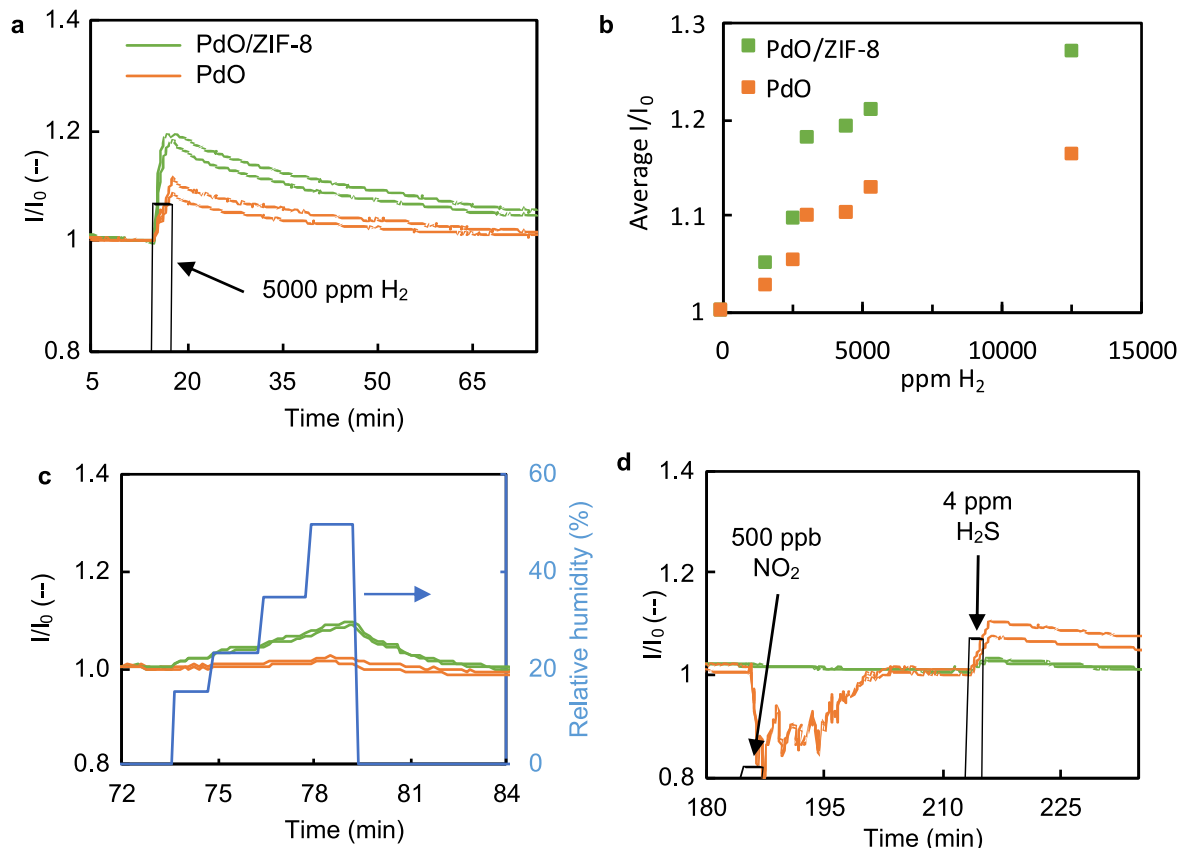


Figure 5. (a) Response curves of two sensors functionalized with PdO and PdO/ZIF-8 to 5000 ppm H₂. (b) Comparison of average response to a five-minute dose of H₂ at a given concentration. Response curves to (c) humidity and (d) 500 ppb NO₂ and 4 ppm H₂S.

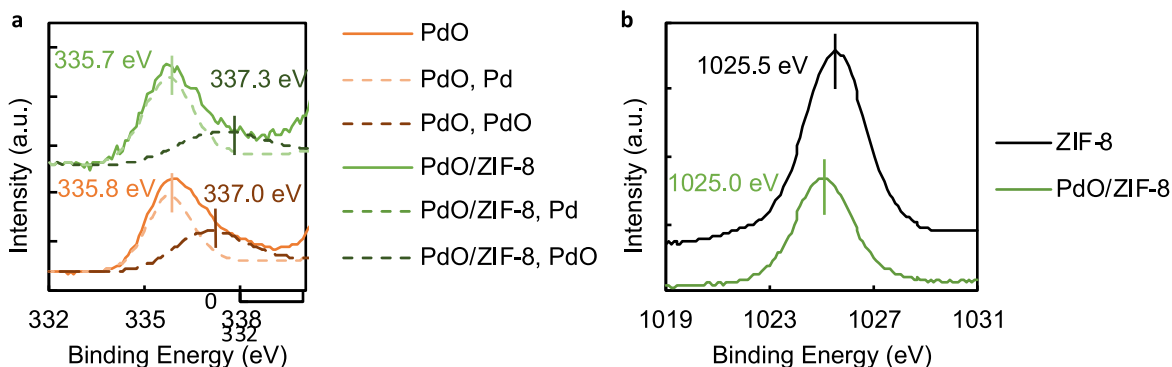


Figure 6. (a) X-ray photoelectron spectra of PdO and PdO/ZIF-8 samples in the Pd 5d^{3/2} region. Dashed lines show the deconvolution of the spectra into the metallic phase and the oxidized phase. (b) XPS results of ZIF-8 membrane grown on SiO₂ and on PdO in the Zn 2p^{3/2} region.

Using a support to affect the electronic structure of the sensing layer, as we show here, is another tool to improve selectivity.

Conclusions

MOF membranes can affect the sensitivity and selectivity of metal oxide sensing layers by affecting the electronic structure of the metal oxide sensing layer. This paper used a proof-of-concept material in PdO with a ZIF-8 membrane. XPS of the PdO and PdO/ZIF-8 sensing layers show that the ZIF-8 partially oxidizes the PdO sensing layer by ~ 0.3 eV, leading to increased sensitivity to H₂ and decreased sensitivity to H₂S. One drawback to this approach is a slight increase in sensitivity to humidity. The approach did not affect the sensitivity of Pd to hydrogen; we expect this is because as a noble metal, Pd is not as readily oxidized. This work shows that MOFs can be used to affect the adsorption properties of metal oxides

at an electronic-structure level, and could be used to enhance selectivity towards a desired small molecule³², especially ZIFs, which have been shown to be quite tunable³³.

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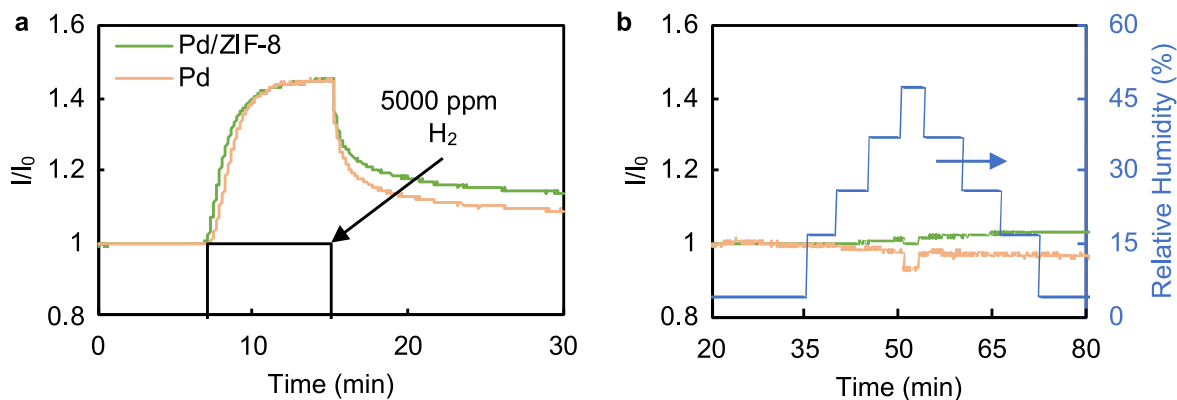


Figure 7. Comparison of metallic Pd and metallic Pd/ZIF-8 sensor response to (a) hydrogen and (b) humidity.

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