Metal Organic Frameworks enable sensitive, selective, and inexpensive chemical detection

Metal Organic Frameworks, with tailorable nanoporosity, ultrahigh surface areas, and many known structures, can serve as effective recognition chemistries for a variety of gases and, as such, enable a sensitive, selective, portable, and low cost chemical detection system.

The need for real-time, compact, and inexpensive chemical detectors has become more pressing in recent years. Homeland security and defense applications such as portal monitoring, chemical weapon detection, and water quality continue to be high priorities. Chemical detectors are also being developed as personal exposure monitors, sensors to provide advance warning of food spoilage, and breath analyzers that provide presymptomatic indication of infection. These existing and emerging applications pose a technical challenge as they require higher levels of sensitivity and specificity in small, economical packages.

Available technologies, such as mass spectrometry, flame ionization, fluorescence, and chemiluminescence, often lack the combination of sensitivity, selectivity, portability, and low cost essential for these applications. New sensing concepts based on micro electrical-mechanical systems offer a potential solution that can be mass produced. Microcantilever sensors have many of the desired characteristics and can be exquisitely sensitive platforms for chemical and biosensing.[1] An advantage of these devices is the simple instrumentation required, and the fact that arrays of cantilevers on a single chip can provide sensitivity to multiple analytes. As with many sensor technologies, however, recognition chemistries are needed to provide the specificity to identify a broad range of analytes.

We aim to leverage the tailorable nanoporosity and ultrahigh surface areas of MOFs, characteristics that make them ideal candidates for a variety of sensing applications. A typical MOF consists of metal cations such as Zn(II) linked by anionic organic linkers groups such as carboxylates, yielding a rigid but open framework that can accommodate guest molecules. An intriguing aspect of MOFs is that they exhibit adsorbate-induced structural flexibility.[2] The unit cell dimensions of some MOFs can vary by as much as 10% when molecules are absorbed within their pores.[3]

In this work we demonstrate for the first time that MOFs can be an integral part of a sensing device, providing both sensitivity and selectivity.[4] Furthermore, we show that the concept of stress-induced chemical detection using MOFs is feasible by integrating a thin film of the MOF HKUST-1[5] (Fig. 1) on a microcantilever surface. The cubic unit cell of this MOF undergoes a small (0.12 Å) but significant contraction upon removal of the two axially coordinated water molecules. In its dehydrated form HKUST-1 incorporates exchangeable coordination sites, suggesting that analyte-specific adsorption may be possible. Our results show that the energy of molecular adsorption within a porous MOF can be converted to mechanical energy, creating a highly responsive, reversible, and selective sensor.

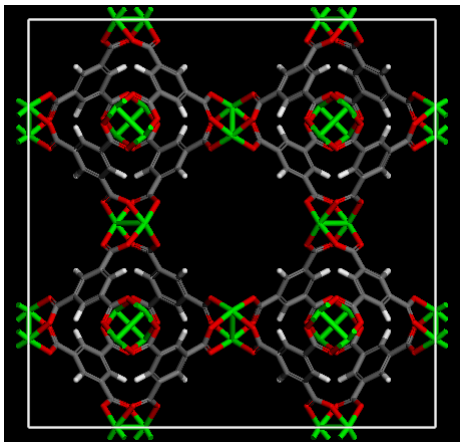

Figure 1. The structure of the MOF HKUST-1 (green: Cu; Red: oxygen; black: carbon; white: hydrogen), which enables stress-induced chemical detection when a thin layer is integrated on a microcantilever surface. In this view the exchangeable axial coordination sites on the Cu(II) ions are unoccupied.

We used a 10-microcantilever array, in which each cantilever incorporates a piezoresistive sensor for stress-based detection.[6] HKUST-1 layers for gas testing were deposited on gold-coated microcantilevers using the step-by-step method of Shekha et al.[7] An intervening thiol-based self-assembled monolayer (SAM) on gold attaches the MOF to the substrate. Certain cantilevers were physically masked to prevent gold deposition and thus MOF growth, allowing them to serve as a reference.

Exposing the MOF-coated cantilevers to gases shows that two adsorption mechanisms are operative. In its hydrated state, the MOF-coated microcantilever responds rapidly and reversibly to gas-phase H_2O (Fig. 2), CH_3OH, and EtOH. No response to N_2, O_2, or CO_2 is observed. Replacing the analyte gas with dry N_2 causes the signal to decay exponentially with a time constant of ~10 s. The magnitude of the response scales with concentration (Fig. 3) and can be fit by a Langmuir isotherm. Since the exchangeable sites are occupied by H_2O molecules, these signals must be largely due to adsorption on the MOF pore surfaces.

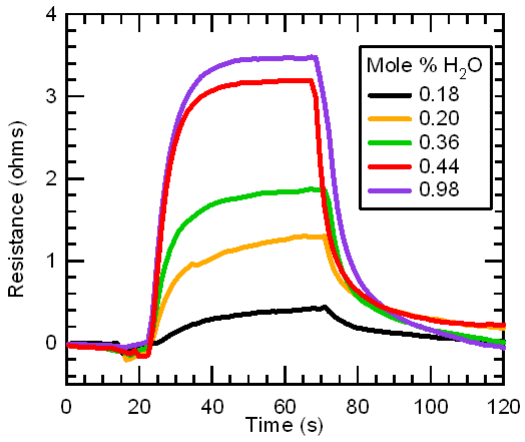

Figure 2. An microcantilever coated with HKUST-1 responds rapidly to H_2O vapor, but has no response to N_2, O_2, or CO_2.

In contrast, sensitivity to CO_2 is found only when the MOF is dehydrated (Fig. 3), which is consistent with the appearance of infrared bands assigned to CO_2 molecules coordinated to the exchangeable Cu(II) sites.[8] These results show that detection selectivity can be achieved by controlling the occupancy of coordination sites in a MOF. Moreover, in HKUST-1 it appears that molecules adsorbed by hydrogen bonding generate sufficient interfacial stresses to be detected, even though this interaction energy is expected to be much weaker than bonding directly to the exchangeable Cu(II) coordination sites.

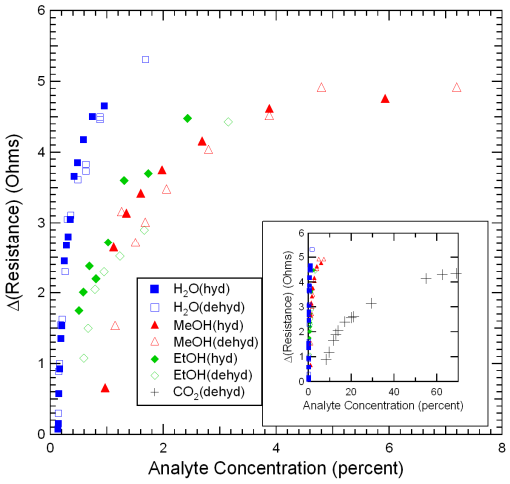

Figure 3. Measured resistance change as a function of analyte concentration (percentage of the total gas flow; balance N_2) at 298 K and 1 atm.

Our results demonstrate that MOFs, which exhibit a huge variety of structures, can serve as effective recognition chemistries for a variety of gases. Our current device is far

from optimized at this point; nevertheless, sensitivity to alcohols and insensitivity to N_2, O_2, and CO_2 in the hydrated state have been demonstrated. We are now evaluating different MOF chemistries with greater adsorption-induced distortions, to determine their ability to detect explosives, CW surrogates, and molecules such as PAH, which are of interest for environmental monitoring.

References

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