Metal organic frameworks for chemical recognition

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Frameworks with adjustable nanoporosity, high surface area, and many known structures may pave the way for portable, low-cost chemical sensors.

The need for real-time, compact, and inexpensive chemical detectors has become more pressing in recent years. Homeland security and defense applications need effective portal monitoring, chemical weapons sensing, and water quality testing. Devices that can serve as personal exposure monitors, provide advance warning of food spoilage, and enable breath analyzers to uncover pre-symptomatic infection are also in demand. These applications pose many challenges because they require high levels of sensitivity and specificity in small, economical packages.

Many existing technologies, such as mass spectrometry and chemiluminescence, lack the combination of sensitivity, selectivity, portability, and low cost needed for these applications. Micro electrical-mechanical systems (MEMS) offer a potential solution that can be cheaply mass produced. Microcantilever sensors have many of the desired characteristics and can be exquisitely sensitive platforms for chemical and biosensing. These devices require simple instrumentation, and arrays of cantilevers on a single chip can provide sensitivity to multiple analytes. Yet, such systems still need better recognition chemistries that can identify a broad range of analytes.

The tailorable nanoporosity and ultrahigh surface area of metal organic frameworks (MOFs) make them ideal candidates for recognizing analytes in sensing applications. A typical MOF consists of metal cations, such as Zn(II), linked by anionic organic linker groups, such as carboxylates, yielding a rigid but open framework that accommodates guest molecules. An intriguing aspect of these frameworks is their adsorbate-induced structural flexibility. The unit cell dimensions of some MOFs can vary by as much as 10% when molecules are absorbed within their pores. This behavior suggests a signal transduction mechanism, in which an adsorbate induces stress at an interface between an MOF thin film and a second material.

We demonstrated that MOFs can be an integral part of a chemical detector, providing both sensitivity and selectivity. We also showed their feasibility for stress-induced chemical sensing by integrating a thin film onto a microcantilever surface. The cubic unit cell of this MOF—called the Hong Kong University of Science and Technology (HKUST)-1—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, which enable 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.

Figure 1. The structure of the MOF HKUST-1 (green: copper; red: oxygen; black: carbon; white: hydrogen) 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.

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The device coated with HKUST-1 responds rapidly to water vapor, but has no response to N\textsubscript{2} or O\textsubscript{2}, 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.

We used an array of 10 microcantilevers, with each one incorporating a piezoresistive sensor for stress-based detection. We deposited HKUST-1 layers for gas testing onto gold-coated microcantilevers using the step-by-step method of Shekhah et al. An intervening thiol-based self-assembled monolayer on gold attached the MOF to the substrate. We physically masked certain cantilevers 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 at work. In its hydrated state, the microcantilever responded rapidly and reversibly to gas-phase water (see Figure 2), methanol, and ethanol. We did not observe a response to N\textsubscript{2}, O\textsubscript{2}, or CO\textsubscript{2}. Replacing the analyte gas with dry N\textsubscript{2} caused the signal to decay exponentially with a time constant of \(\sim\)10\textsuperscript{s}. The magnitude of the response scaled with concentration (see Figure 3) and can be fit by a Langmuir isotherm. Since water molecules occupy the exchangeable sites, these signals must be largely due to adsorption on the MOF pore surfaces.

In contrast, the MOF exhibited sensitivity to carbon dioxide only when dehydrated (see Figure 3), which is consistent with the appearance of infrared bands assigned to CO\textsubscript{2} molecules coordinated to the exchangeable Cu(II) sites. These results show that controlling the occupancy of coordination sites in an MOF can achieve detection selectivity. Moreover, in HKUST-1, the molecules adsorbed by hydrogen bonding seem to generate sufficient interfacial stresses to be detected, even though we expect this interaction energy to be much weaker than bonding directly to the exchangeable Cu(II) coordination sites.

Our results demonstrate that MOFs can serve as effective recognition chemistries for a variety of gases. Our current device is far from optimized, yet we showed sensitivity to alcohols and insensitivity to N\textsubscript{2}, O\textsubscript{2}, and CO\textsubscript{2} in the hydrated state. We are now evaluating different MOF chemistries with greater adsorption-induced distortions to determine their ability to detect explosives, chemical weapon surrogates, and molecules such as polyaromatic hydrocarbon, which are of interest for environmental monitoring.
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Mark Allendorf is a distinguished member of the technical staff at Sandia National Laboratories, where he directs a team focused on both fundamental and applied aspects of metal-organic frameworks. Themes of this research include chemical detection, radiation detection, hydrogen storage, and MOF templating. He is a past president and fellow of The Electrochemical Society and is currently a visiting scholar at the University of California, Berkeley.

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References