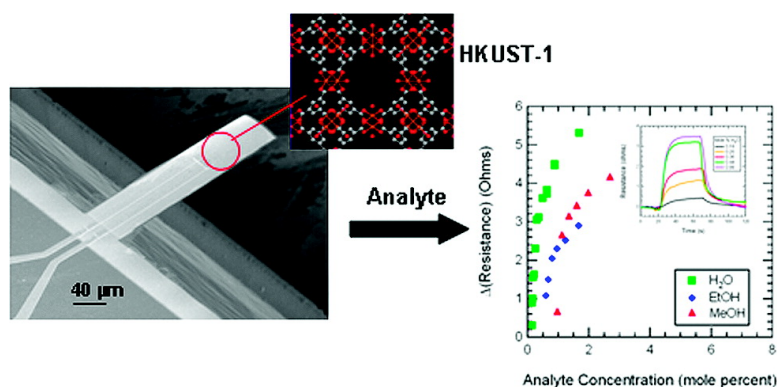


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J. Am. Chem. Soc., **2008**, 130 (44), 14404-14405 • DOI: 10.1021/ja805235k • Publication Date (Web): 09 October 2008

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Stress-Induced Chemical Detection Using Flexible Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) are currently attracting considerable attention because their tailorable nanoporosity and ultrahigh surface areas make them ideal candidates for a variety of sensing applications. Although this potential is often noted, to date there are no reports of MOFs serving as a component of a functioning device. An intriguing aspect of these materials is that they exhibit adsorbate-induced structural flexibility.^{1,2} The unit cell dimensions of some MOFs can vary by as much as 10% when molecules are adsorbed within their pores.³ This suggests a novel transduction mechanism in which distortions in a MOF thin film create stress at the interface with a second material. Such stresses can be measured by depositing a MOF film on the surface of a static microcantilever. In a device of this type, stress at the cantilever surface results in bending that can be detected optically or by means of a built-in piezoresistive sensor.⁴ Clearly, the sensitivity of such a device depends upon strong chemical bonding between the MOF and the surface, so that the stress is effectively transmitted to the cantilever. It also depends on the stiffness of the MOF. We recently reported the elastic properties of IRMOF-1 and find that, although the solvated and desolvated unit cell dimensions differ by only 0.8%, the Young's modulus of this material⁵ is sufficiently high to create easily measurable stresses. Here, we demonstrate the concept of stress-induced chemical detection by integrating a thin film of the MOF HKUST-1⁶ with a microcantilever surface. The results show that the energy of molecular adsorption within a porous MOF can be efficiently converted to mechanical energy to create a highly responsive, reversible, and selective sensor.

The choice of HKUST-1, a MOF composed of Cu(II) ions linked by benzenetricarboxylate (BTC) ligands [Cu₃BTC₂(H₂O)₃]_n, is a logical one for several reasons. First, methods of growing HKUST-1 on surfaces have recently been reported.^{7,8} The resulting coatings are dense and reproducible, in contrast with IRMOF-1, whose thickness, uniformity, and microstructure we find difficult to control with reported methods.⁹ Second, 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.¹⁰ Finally, the availability of open coordination sites in the dehydrated version of HKUST-1 suggests that analyte-specific adsorption may be possible. Indeed, adsorption isotherms for a variety of gases have been reported.¹¹

The platform for our investigation is a 10-microcantilever array, in which each cantilever incorporates a built-in piezoresistive sensor for stress-based detection.¹² HKUST-1 layers for gas testing were deposited on gold-coated microcantilevers using the step-by-step method of Shekha et al.⁸ We find this can be accomplished using the single-step method of Biemmi et al. as well.⁷ Both methods use an intervening thiol-based self-assembled monolayer (SAM)

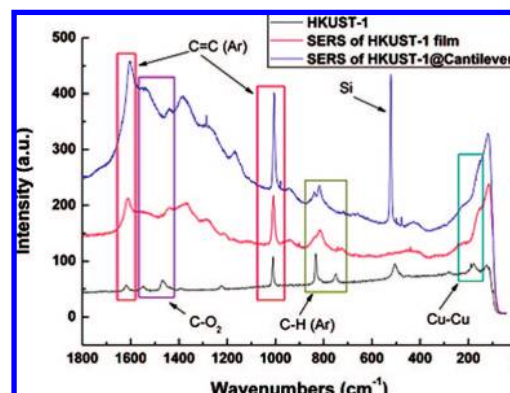


Figure 1. Verification of HKUST-1 on the microcantilever using SERS: (blue) SERS spectrum of HKUST-1 on a microcantilever; (red) SERS spectrum of an HKUST-1 film on a macroscopic substrate; (black) unenhanced Raman of a thick HKUST-1 layer used as a reference. Peaks labeled C–H(Ar) correspond to out-of-plane aromatic C–H bends.

on gold to attach 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. MOF growth was initiated by immersing the entire array sequentially in solutions of Cu(OAc)₂ and BTC in EtOH. A series of 20 immersion cycles yields an average film thickness of ~100 nm, based on comparison with a macroscopic substrate subjected to the same procedure.

The microcantilever is too small to characterize by standard methods, such as X-ray diffraction (XRD), which could verify that HKUST-1 is present on the surface. Energy dispersive X-ray spectroscopy established the presence of copper and carbon in the film,¹³ but the large penetration depth interferes with determination of the elemental composition. However, we find that microsurface-enhanced Raman spectroscopy (μ SERS) is a viable method for probing MOF films on microcantilevers. This method, previously unreported for MOF characterization, has a spatial resolution in our instrument of 2.0 μ m². Large enhancement factors were achieved by evaporating silver onto the microcantilever (~2.5 nm equivalent). The resulting spectrum (Figure 1, blue) is almost identical to that obtained from an HKUST-1 layer of similar thickness deposited on a macroscopic Au-coated silicon substrate (Figure 1, red).¹³ The unenhanced μ -Raman spectrum of a thick reference film (i.e., without the Ag layer; Figure 1, black), whose composition was validated by comparing with the reported Raman spectrum¹⁰ and XRD⁶ of bulk HKUST-1, displays the same characteristic vibrational modes. Importantly, we obtain essentially the same SERS spectrum regardless of the surface morphology of the MOF film. Highly crystalline microstructures with clearly identifiable cube-octahedral shapes were obtained in some cases, while in others the surface had an amorphous appearance, but is likely highly nanocrystalline. Although the reasons for this are

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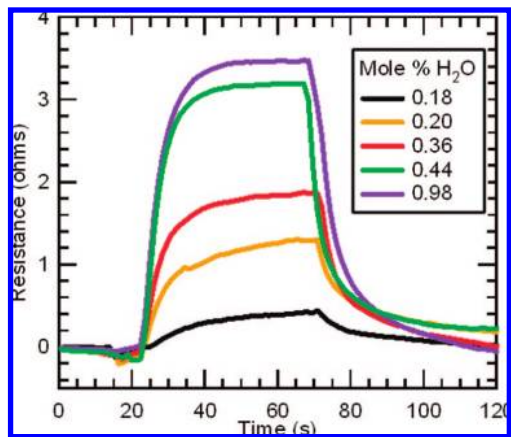


Figure 2. Temporal response of the cantilever piezoresistive sensor to water vapor diluted in N_2 (room temperature, 1 atm).

unclear, various morphologies are known to form as a result of minor changes in synthetic procedures, such as the degree of agitation during growth.¹¹

Since HKUST-1 has two exchangeable coordination sites, which are occupied by water molecules in the as-synthesized form, we measured the cantilever response in both the hydrated and dehydrated states of the MOF film. The latter was prepared by heating the cantilever using a DC voltage across the piezoresistor. A two-hour flow of dry N_2 at 50 °C is sufficient to remove the coordinated water, as shown by a color change from blue to purple in bulk samples subjected to this procedure.

In its hydrated state the MOF-coated microcantilever responds rapidly and reversibly to gas-phase H_2O , MeOH, and EtOH. For example, the time-dependent responses to H_2O are shown in Figure 2. Easily measurable resistance changes relative to the reference sensor are generated within 500 ms (our shortest measurement interval), in contrast with uncoated cantilevers, which respond only minimally due to imperfect matching with the reference cantilever. No response to N_2 , O_2 , or CO_2 is observed. Upon replacement of the analyte gas with dry N_2 , the signal decays exponentially with a time constant of ~ 10 s. A fit of the H_2O resistance to a Langmuir isotherm agrees reasonably well with a reported 0–3 mbar isotherm¹¹ and yields a saturated resistance of 7.0 ohms, which we predict¹³ corresponds to a change in the HKUST-1 lattice parameter of $0.016 \pm 0.002\%$. XRD indicates a lattice expansion of 0.45% upon rehydration,¹⁰ indicating that the MOF-cantilever interface is not completely rigid. This is reasonable and is most likely due to the SAM interface, film polycrystallinity, and incomplete coverage of the cantilever surface by the MOF layer.

A significant finding is that the sensor responds to CO_2 only when the MOF layer is dehydrated (Figure 3 inset). New infrared bands assigned to CO_2 coordinated at axial Cu(II) sites suggest this is the cause of the sensor response.¹⁴ The response is weaker than that induced by H_2O , consistent with the isotherms for these gases.¹¹ In contrast, the H_2O , MeOH, and EtOH responses are little affected by baking the sensor, suggesting that these signals are primarily due to adsorption on MOF pore surfaces and consistent with experiments indicating that fully hydrated HKUST-1 contains as much as 40 wt % water.^{6,11} Thus, it appears that physisorbed molecules capable of hydrogen bonding generate sufficient interfacial stress to be detected, while weakly interacting gases such as CO_2 must coordinate to the Cu(II) ions to be detected. Therefore, detection selectivity can be achieved by controlling the hydration state of the axial Cu(II) sites.

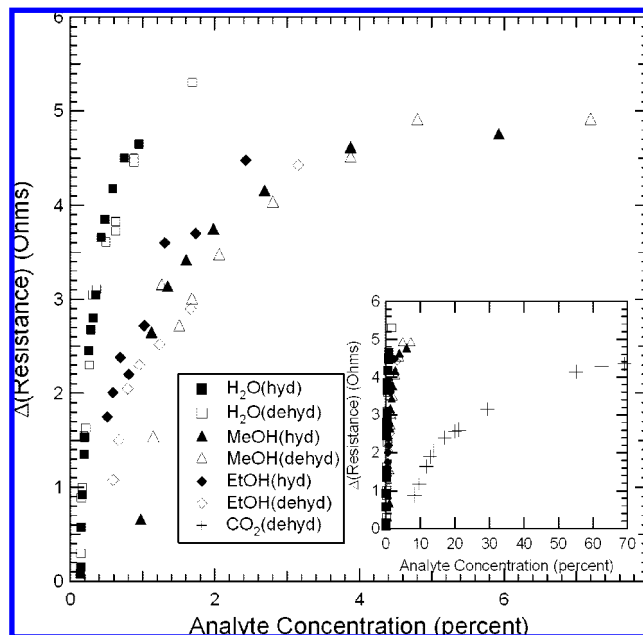


Figure 3. Resistance change versus analyte concentration expressed as a percentage of the total gas flow (balance N_2) at 298 K and 1 atm.

Our results indicate that MOFs can be effective recognition chemistries for a variety of gases. Since the adsorption-induced distortions in HKUST-1 are likely quite small, we expect that higher sensitivities can be achieved using MOFs exhibiting greater structural flexibility. Although the current device is far from optimized, sensitivity to alcohols and CO_2 and insensitivity to N_2 and O_2 suggest that this MOF might be useful in breath analysis if H_2O is removed prior to testing.

Acknowledgment. This work was supported by the Sandia Laboratory Directed Research and Development Program.

Supporting Information Available: Synthetic methods, characterization data, gas-testing procedures, stress/strain modeling, and H_2O Langmuir isotherm fit. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA805235K