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Transistor-Based Work-Function Measurement of Metal—Organic Frameworks for Ultra-Low-Power, Rationally Designed Chemical Sensors

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# Leveraging Work-Function Changes in Metal-Organic Frameworks Towards Selective Ultra-Low-Power Gas Sensing

David W. Gardner[b], Xiang Gao[c], Hossain M. Fahad[d], An-Ting Yang[e], Sam He[c], Ali Javey[d], Carlo Carraro[b], Roya Maboudian*[a]

**Communications** **Abstract:** A classic challenge in chemical sensing is selectivity. Metal-organic frameworks are an exciting class of material because their structures can be designed and tuned towards selective chemical adsorption. Adsorption events trigger changes in the material's electronic structure, which manifests as a work-function shift. In this work, the work-function shifts are detected with an ultra-low-power chemical-sensitive field-effect transistor. The work function modulation mechanism is studied with two metal-organic frameworks. First, HKUST-1 is used as a proof-of-principle sensor for humidity. The humidity sensing response is invariant with HKUST-1 thickness, suggesting that the response is surface-localized. Next, ZIF-8 is investigated as a practical $NO_2$ sensing material. The work function modulation is dominated by adsorption at zinc sites. This paper sets the groundwork for using the tunability of metal-organic frameworks for chemical sensing with distributed scalable devices.

Metal-organic frameworks (MOFs) are porous crystalline materials made up of metal nodes connected by organic linkers, with thousands of known structures. The tunability of MOFs makes them attractive for chemical sensing where selectivity is a figure of merit. One of the most promising avenues for chemical sensing with MOFs is by work-function measurement because work-function changes are highly MOF – analyte specific and available to all MOFs, unlike other modes such as luminescence[1] or conductivity[2–6]. The mechanisms for work-function modulation in MOFs remain poorly understood. The most reasonable guiding principles for work function modulation so far are molecules with a high heat of adsorption[7,8] and molecules that adsorb at open metal sites[9,10]. Unfortunately, the direct measurement of work function is not scalable because of the size of the sensors (e.g., a Kelvin probe). However, indirect measurements of work function with a bulk silicon chemical-sensitive field-effect transistor (CS-FET) can leverage the same sensing characteristics but with a smaller size, low cost, and low power[11]. These devices are advantageous over other work-function based sensors (e.g., silicon nanowires or metallic nanostructures[12,13]) because the bulk silicon is practically inert unless functionalized, whereas other structures tend to have very poor selectivity. In addition, bulk silicon provides a more manufacturable platform. The CS-FET sensing mechanism is facilitated by the modulation of the ultrathin charge inversion layer in silicon by work function change in the sensing layer. The inversion layer is as thin as a few Ångstroms with proper doping and substrate biasing conditions, thus providing a very sensitive response[14]. An optical image, a cartoon schematic, and the sensing mechanism for the device are given in Figure 1. In this work, we show how MOFs can be integrated with the CS-FET to yield high-performance gas sensors, and investigate the sensing mechanism of work-function modulation in MOFs.

Sensors are fabricated according to standard microfabrication methodologies[14]. For a proof-of-principle, the first MOF presented for integration with the CS-FET is HKUST-1 (Figure 2a) because it can be used to resolve two questions about the sensing material:

1. What is the impact of sensing layer thickness on the measured work-function change? i.e., is the response a bulk phenomenon or surface-localized?

2. How does the HKUST-1 CS-FET sensing response correlate with measured values on a Kelvin probe for the same exposure?

The first question was addressed by growing HKUST-1 in a cyclical or "layer-by-layer"[15–17] manner directly on the CS-FET with 10- and 60-cycles; the second by

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       the end of the document.

comparing the calculated work function change with values measured for HKUST-1 on a Kelvin probe[8].

X-ray diffraction spectra of the synthesized films are given in Figure S1. The diffraction peaks are in good agreement with previous characterization of these films[15]. Representative sensor responses to humidity are given in Figure S2. The recovery to humidity is slow because of the inherent hysteresis for water absorption in HKUST-1[18] and possibly interference from the gate SiO$_2$ dielectric. The work function change was calculated, as detailed in SI, by measuring the change in source-drain current, I$_D$, before and after exposure for a range of substrate voltages, V$_{SUB}$, and using the transistor design equation and device parameters, where the only fit parameter is the work-function change[14]. A representative I$_D$-V$_{SUB}$ plot is given in Figure S3. The calculated work function change for three 10-layer devices and three 60-layer devices is given in Figure 2b compared with the results obtained for HKUST-1 on a Kelvin probe[8]. The calculated change in work function is in excellent agreement with the measured result for the 10- and 60-layer devices, confirming that the change in work function of the MOF is modulating the current. The response is invariant with MOF thickness, demonstrating the thickness of the film has little impact on the magnitude of the response. Therefore, the response is a near-surface-localized phenomenon. This conclusion is supported by the electrically insulating nature of MOFs, so a potential difference should not be felt many unit cells away.
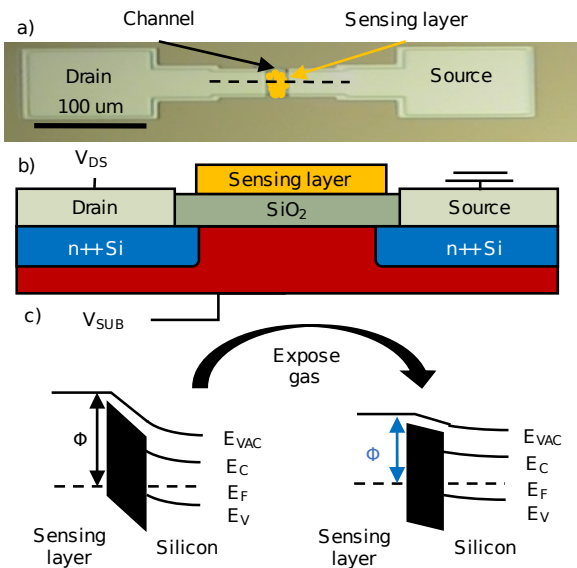


**Figure 1.** Chemical-sensitive field-effect transistor and its operation. (a) A top-down optical image of the device, showing the source and drain electrodes separated by a channel. An arbitrary sensing layer is sketched over the channel. (b) A cartoon cross-section of the dashed line in (a). The drain-source voltage V$_{DS}$, and the substrate voltage V$_{SUB}$ (with respect to ground) are marked. Substrate bias is used to increase sensitivity. (c) Sensing mechanism[19]: When a gas adsorbs to the sensing material, its work function (Φ) shifts, inducing band bending in the underlying silicon.

HKUST-1 is not an ideal sensing material because of its inherent instability in humidity[20]. A MOF based on Zn-N linkages rather than Cu-O linkages is expected to be more robust per hard-soft acid base theory[21]. One such MOF is ZIF-8 (Figure 3a), which we present next. This MOF is deposited with a solvothermal method[22]. X-ray diffraction spectrum of the thin film is provided in Figure S1, and compares well with previous characterization of these films.

ZIF-8 is a MOF that is reactive in highly acidic environments[23] because the linker becomes protonated and the metal is available for bonding with a Lewis base. This change should influence the electronic structure, and therefore the work function of the sensing layer. We hypothesize that in low concentrations of acidic gasses, when damage to the framework is minimal, the response might even be reversible, especially given the ease of linker exchange for Zn-based MOFs. Further, there are many safety-related applications where sensors are just needed one time, e.g., a safety badge that alerts a user about a toxic gas in the environment, so this hypothesized design heuristic is useful.
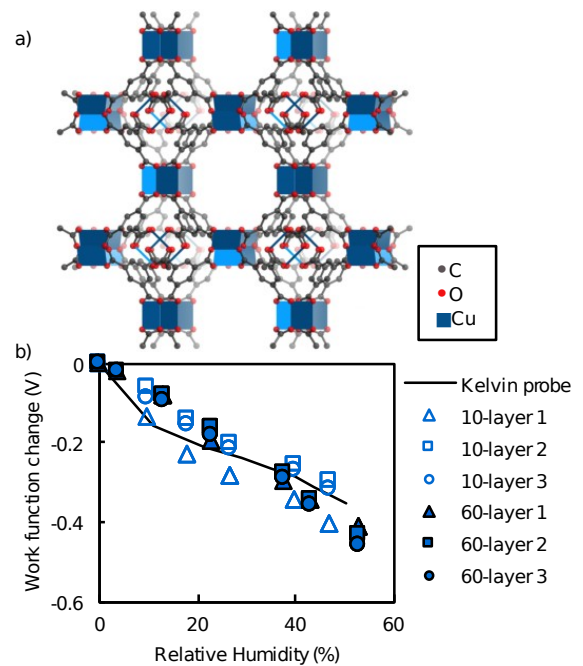


**Figure 2.** (a) Crystal structure of HKUST-1. (b) Calculated work-function change for the HKUST-1 sensing material compared to the value measured by a Kelvin probe[8], showing excellent agreement for all six sensors studied.

Figures 3b-d shows the response of a CS-FET sensor coated with ZIF-8 to NO$_2$ in three different humidity environments. The magnitude of the response increases with increasing concentration in NO$_2$ and increasing humidity. An on-stream humidity sensor verified that humidity remained within 0.2% of the target value during the exposure. When the change in work function is plotted against the NO$_2$ concentration, a first-order relationship with NO$_2$ is observed (Figure S4). The

positive $NO_2$ dependence is consistent with a disproportionation reaction for $NO_2$ in humid air, where it forms $HNO_3$ and $HNO_2$ that would attack the framework, analogous to the reaction of $SO_2$ with ZIF-8 in humid air[23].

The ligand exchange from imidazole to nitrate or nitrite provides a change in electronic structure manifesting as a change in work function. We also observe a faster recovery for the sensors in higher humidity environments, showing that humidity helps the framework recover from whatever defects have been introduced. Zn-based MOFs have ionic-type interactions with ligands, so the adsorption of a $NO_x^-$ species should be easily reversible. X-ray diffraction spectrum of the film exposed to $NO_2$ is given in Figure S1 and is nearly identical to the original material with only a slight decrease in diffraction intensity. These experiments demonstrate another mechanism for work-function modulation of MOFs: analytes that attack the structure and introduce defects affect the electronic structure of the MOF, leading to changes in work function. This heuristic is supported by a separate test, where the carboxylate-containing MOF "MFM-300(In)" was found unstable to $NH_3$ – a base – while there was no response to $NO_2$ (Figure S5).
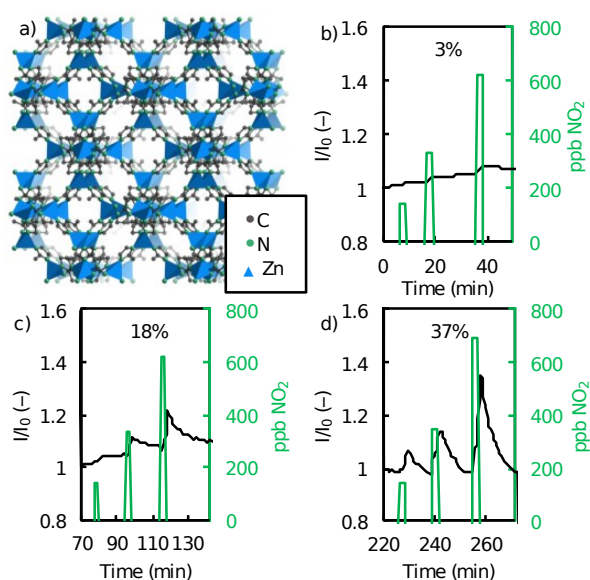


**Figure 3.** (a) Crystal structure of ZIF-8. (b-d) Normalized response for a CS-FET functinalized with ZIF-8 to $NO_2$ at 3%, 18%, and 37% relative humidity, respectively, indicated by the number at the top of each figure. Current was re-normalized as the beginning of each time window.

Somewhat unexpectedly, the ZIF-8 sensors exhibit a large response to humidity (Figure 4). Computational studies suggest that liquid water pressures in excess of 20 MPa are needed to force water molecules inside the pores[24]. Therefore, we hypothesize that the large sensor response to humidity is due to the zinc terminations at the surface of the MOF that would be in contact with the CS-FET gate. Using X-ray photoelectron spectroscopy (XPS), we find that the surface of the ZIF-8

films are zinc-rich (Table 1, Figure S6), with the surface termination likely being oxygen as hydroxyl or water, in good agreement with previous characterization of ZIF-8[25]. In practice the humidity response would be compensated for with a parallel humidity sensor (e.g., HKUST-1 above).

To further test the metal-centric hypothesis, we prepared a sensor with a dilute zinc acetate sensing layer. These sensors also have a very strong response to humidity (Figure S7). Because the ZIF-8 surface is zinc-rich, the ZIF-8 surface is quite favorable for water molecule adsorption. Although ZIF-8 and the zinc salt sensing layers have responses of similar magnitude, the metal alone does not control the sensing response – the ZIF-8 sensing response recovers within seconds to the original baseline, while the sensor with the zinc salt recovers slowly and approaches a new baseline (Figure S8). We hypothesize that the ZIF-8 sensor is more reversible than the zinc salt sensor because in the salt, zinc hydrates form, whereas zinc hydrate formation is blocked by the imidazole ligands in ZIF-8. These results are consistent with the surface-localized mechanism we have proposed based on the HKUST-1 humidity sensing response.

The responses described here are clearly distinguished from the bare sensor (i.e., exposed oxide) sensing responses, provided in Figure S9.
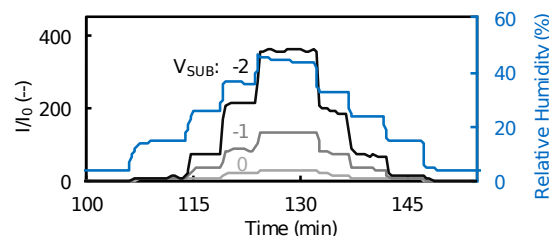


**Figure 4.** The normalized response for a CS-FET functionalized with ZIF-8 for varied $V_{SUB}$.

**Table 1.** Atomic ratios determined by X-ray photoelectron spectroscopy for ZIF-8 sensing films in this work on silicon.

| Element | Zn | N | C | O |
|---|---|---|---|---|
| This work | 1.0 | 1.7 | 4.1 | 0.4 |
| Stoichiometry | 1.0 | 4.0 | 8.0 | 0.0 |

Work-function responses in electrically insulating MOFs may seem surprising. Although adsorbate-induced work function changes are well understood for materials like metals[26,27], whose electronic structure can easily accommodate a change in electron concentration, the addition or removal of an electron in a MOF is not as straightforward. The mechanism(s) of adsorbate-induced work function changes in MOFs are not well understood.

Here we will present our understanding of the phenomenon based on the body of literature available and put our findings into context[9,10,28].

One heuristic is the correlation between adsorption energy and work function response. In HKUST-1, the marginal work function change per alcohol adsorbed correlates quite well with the adsorption energies for the alcohols in the framework[7,8]. The adsorption-energy heuristic is supported by an overlay of the work-function response with the isotherm for humidity adsorption in HKUST-1[8,18] (Figure S10). The response is strongest in the low-humidity regime when the most favorable sites, typically on metals, are being occupied.

This observation leads us to the second heuristic for MOF work function responses: adsorption at metal sites. This is consistent with a mechanism proposed by Stassen, et al.,[10] who studied phosphonate adsorption at defect sites in UiO-66. Open metal sites may be a promising motif to incorporate, given that work-function responses even to $CO_2$ have been observed in Mg-MOF-74[9]. This is physically consistent with the fact that electrons are highly localized at metal sites in MOFs, so adsorption at these sites should disturb the MOF's electronic structure and therefore the work function. Our results are consistent with this picture. We prepared acid and base sensors from ZIF-8 and MFM-300(In) based on their linkages and their chemical sensitivity using well known chemical resistance rules[29]. In an extreme case of metal-as-arbiter, the zinc-rich surface of ZIF-8 betrays the hydrophobic pores by responding quite strongly to humidity. The hydrophilic, surface terminating zinc is able to interact with water easily and strongly.

Several open questions remain about work-function responses. Examining Figure S10, the work-function response continues well past the point where open metal sites would be filled and nearly all adsorption is taking place inside the pores. It is not clear how these pore-filling guests are able to modulate the work function in the MOF if the open-metal sites and defect sites are the arbiters of work function change. Yet another open question is why the work-function response to a phosphonate in the MOF UiO-66 is increased when amines are appended inside the pores[10]. Further work is needed to understand more fully the origins of the response so that sensors can be prepared with greater predictive power for the performance.

In conclusion, the integration of two well-characterized MOFs with a chemical-sensitive field-effect transistor is demonstrated. The MOF HKUST-1 answered two questions: (i) the interface between MOF and the gate controls the response, and (ii) the sensing response on the device is predicted by experiments that directly measure the work function change. The second MOF, ZIF-8, is shown to be a more practical sensing material. Sensors with a ZIF-8 sensing layer respond to and recover from the acidic gas NO2 in realistic humidity environments. The response is greater in humid atmospheres, supporting the acid-attack hypothesis. The large ZIF-8 response to humidity is attributed to the surface-terminating zinc sites coordinating with water. These experiments provide guidelines for selection of MOF – analyte combinations for work-function based sensing on chemical-sensitive field-effect transistors.

## Experimental Section

The metal-organic framework HKUST-1 was deposited in a standard layer-by-layer method[1,15–17,22]. The device and the partner silicon coupon were given 10- or 60- cycles. ZIF-8 was prepared with a solvthermal approach in methanol[22]. The MOF "MFM-330-In" was prepared by a standard method. The crystals were dropcast over the surface of the device in acetone and activated in gentle heating[30]. The Zn-acetate sensor was prepared by immersing a cleaned device in a 50 mM methanolic solution of zinc acetate for one hour followed by a rinse in a methanol bath. The device was then transferred to a beaker of DMF for one hour and stored in vacuum.

In-depth details of device fabrication, MOF thin film growth, gas dosing, work function calculation, X-ray diffraction, and X-ray photoelectron spectroscopy characterization are given in the Supporting Information.

## Acknowledgements

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**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

# COMMUNICATION

Metal-organic frameworks are an attractive sensing material because their adsorptive properties can be tuned for selective adsorption. Strong adsorption events change the work-function of the sensing material. Here, we show how to integrate MOF sensing layers with devices capable of measuring their work function shift and outline strategies for rational design of MOF sensing
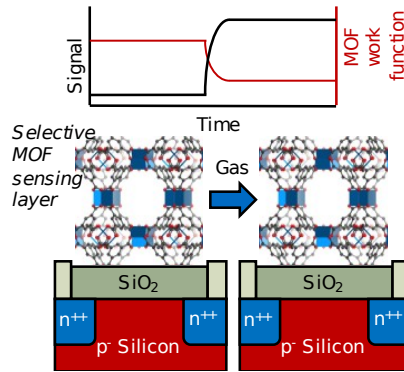
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**Leveraging Work-Function Changes in Metal-Organic Frameworks Towards Selective Ultra-Low-Power Gas Sensing**

Layout 2:

# COMMUNICATION

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