HKUST-1 coated piezoresistive microcantilever array for volatile organic compound sensing

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The HKUST-1 metal-organic framework (MOF) was selected because of the large internal surface area, excellent stability and known properties. Mechanical strain is generated upon the adsorption of analytes into the MOF; it is proportional to concentration and is a function of adsorbed species. Piezoresistive microcantilevers serve as a transduction mechanism to convert surface strain into electrical signals. N-doped piezoresistive cantilever arrays were fabricated with ten structures per die. Thin films of HKUST-1 were grown at room temperature using layer-by-layer techniques. Dry nitrogen was used as a carrier gas to expose devices to varying concentrations of 12 different volatile organic compounds (VOCs). Results show that stress-induced piezoresistive microcantilever array sensors with MOF coatings can provide a highly sensitive and reversible sensing mechanism for water vapour and methanol. Characteristic response features allow discrimination based on shape, response time constants and magnitude of response for other VOCs. Devices provided reliable data and proved durable over 18 months of testing. The key advantages of this type of sensor are higher sensitivity with a microporous MOFs, reversible response, α single chip sensing system and low power operation.

1. Introduction: We would like to emulate the exquisite sensitivity and selectivity observed in nature for olfaction [1] using low-cost sensing arrays with selective nanoporous coatings [2, 3]. Research on the artificial nose, using arrays of orthogonal sensors is widespread [4] along with finding increasingly diverse applications [5]. Metal-organic frameworks (MOFs) represent a class of materials that possess many desirable properties expected in a molecular sieve such as tailorable permanent microporosity, complete desorption, a high degree of chemical and thermal stability and analyte specific adsorption. Ideally, a sensor should be highly selective, compact and completely reversible, allowing for the long-term reliable detection of analytes. Recent advances in micro/nanofabrication techniques have allowed low-cost production of microelectromechanical systems of increased complexity, and the commercial success of microcantilevers in atomic force microscopy has allowed their acceptance as transducers for sensing [6]. We demonstrated the use of embedded piezoresistive elements as a transduction mechanism for detection of analyte concentrations by coupling the microcantilever with a MOF selective layer [7]. MOFs are a new class of nanoporous materials with tailorable pore size consisting of metal cations and organic linkers (anions or neutral molecules) arranged in a highly ordered fashion. MOFs exhibit high surface area, chemical and thermal stability and reversible analyte specific adsorption, making them perfect for small molecule sensing and separation applications [8–10]. Other sensors based on MOFs have been demonstrated, including quartz crystal microbalance [11, 12] and surface acoustic wave devices [13]. These devices are responsive to the mass changes in the film. However, other mechanisms could control the adsorption of analytes in MOFs. For example, gas uptake in rigid MOFs is a result of adsorbate–pore surface interaction and steric effects. Unlike conventional recognition layers, MOFs are unique in that they exhibit structural flexibility allowing their use in strain-based detection applications. An excellent review is provided by Kreno *et al.* [14].
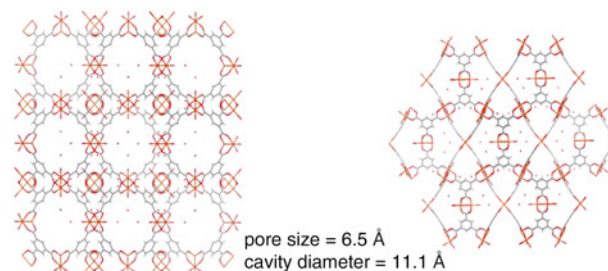

Figure 1 *Structure of CuBTC indicating cubic structure and pore diameter*

pore size = 6.5 Å
cavity diameter = 11.1 Å

In this Letter, we primarily focus on the response of microcantilevers coated with the well-characterised HKUST-1 MOF (also known as CuBTC) for the detection of volatile organic compounds (VOCs). The HKUST-1's ability to adsorb a number of species was previously demonstrated [15]. This study was consequently expanded to 12 analytes, all tested on the same device in over 100 experiments spanning 17 months. Through such a study, we aim to demonstrate the robustness of microcantilever-based sensors and the reliability of MOF coatings for sensing applications. HKUST-1 is a general formula $Cu_3(BTC)_2(H_2O)_x$, (BTC = benzene-1,3,5-tricarboxylate), and consists of a binuclear Cu_2 paddlewheel unit connected into a three-dimensional (3D) structure [16, 17]. The framework consists of two distinctive 'cages' (13.2 and 11.1 Å in diameter) separated by 9 Å 'windows' of square cross-section and connected to secondary tetrahedral pockets of 6 by 4.6 Å triangular shaped windows. Fig. 1 shows a schematic diagram of the structure of the CuBTC and the location of the large and small pores.

2. Methods: The cantilever measures 230 μm in length and 80 μm in width and was fabricated using traditional microfabrication techniques [18, 19]. Fig. 2 shows the schematic diagram and
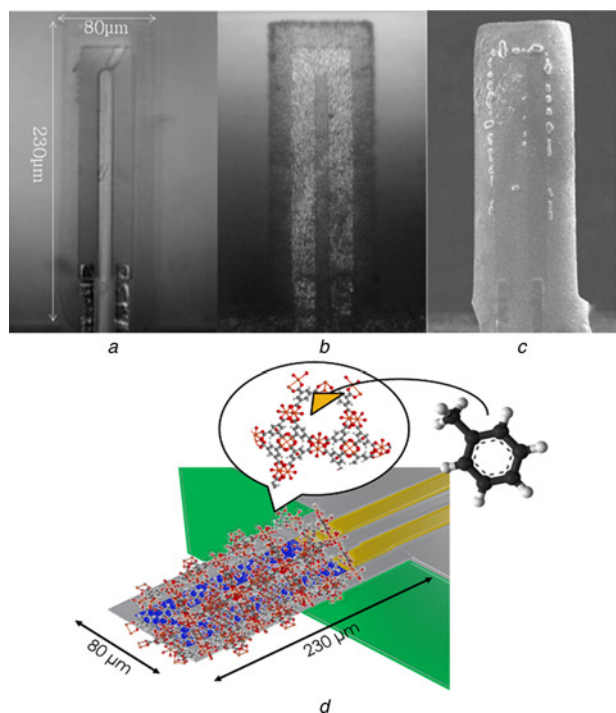
Figure 2 *Microcantilever sensor with dimensions and no coating (Fig. 2a); optical image of coated device (Fig. 2b); SEM image of coated device (Fig. 2c); schematic diagram indicating mechanism of response for toluene molecule entering HKUST-1 (Fig. 2d)*

scanning electron microscopy (SEM) images of these cantilever sensors with an estimated 100 nm-thick coating of HKUST-1 MOF as well as the overall detection arrangement. Use of silicon-on-insulator wafers provides a single crystal silicon strain gauge, which is doped n-type to improve the gauge factor over p-type for stress sensing [20]. Each microchip consists of a ten microcantilever array. Modelling results as well as detailed discussion are in provided in [18] and the details of the fabrication process have been published in previous papers [19].

A Wheatstone bridge measured the response to analytes, delivered through a custom designed flow cell [21]. Dry nitrogen was selected as the carrier gas and a mixing chamber was designed for mixing low concentrations of analytes. The mixing chamber consisted of a hydrator with liquid analyte and tubing to mix the high flow purge gas with low flow hydrator gas (Fig. 3). Mass flow controllers (MFCs) 2 and 3 (MKS Inc.) delivered high flow rate gases able to achieve a range of ratios with 1:100 minimum dilution ratio. MFC 1 delivered low flow rate gas to the hydrator to introduce analyte into the stream. The high flow gas line was used for further dilution to as low as 1:1000. The Wheatstone
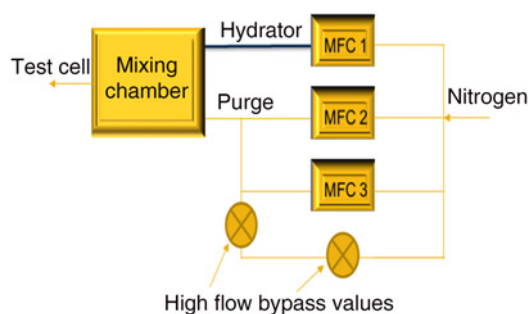
bridge consisted of two fixed resistors and two MOF coated microcantilevers arranged for additive response in the circuit. Voltage drop across the bridge was measured with a lock-in amplifier (Signal Recovery 7265). The lock-in amplifier was operated at 3 kHz with a bridge voltage of 200 mV, which produced minimal heating of the cantilever in the gas flow. Temperature was controlled to ±0.2°C with a temperature controller (Omega Inc.).

To ensure proper removal of water molecules from the MOF, high temperature and low vacuum bakes are necessary [21, 22]. This method can be used for oxide-based surfaces, however for the case of self-assembled monolayers (SAMs) with limited thermal stability an alternative method was developed. The MOF film was activated by flowing nitrogen at 40°C for 10 000 s (3.7 h). All experiments were conducted with constant nitrogen flow at room temperature (23°C) and at atmospheric pressure to ensure the film maintained its integrity. Bridge voltage was monitored to ensure a steady-state response was reached before introducing the first analyte concentration.

Previously we presented the response to water and five other analytes for the HKUST-1 coated microcantilevers [7, 22]. We discussed the reversibility of certain analytes and potential theories for this behaviour. Despite the importance of low noise, high selectivity and complete reversibility achieved with piezoresistive microcantilevers, reliability plays an important role in the adaptation of a given technology. The next Section discusses the promising reliability results achieved with an HKUST-1 MOF coated device with SAM on gold.

3. Results: Water vapour response exhibited reversible behaviour with rapid initial adsorption followed by slower response and desorption. The time responses are listed in Table 1 and compared with those for ethanol and methanol which also show a reversible response, but with lower induced strain response in the MOF. Fig. 4 shows a comparison of the response for each and fit to a Langmuir isotherm. Here, we can see strain induced is a function of the molecular size for the same concentration levels, that is, because of the difference is concentration in the MOF. We can calculate an effective Henry's constant for this, however without knowing the exact quantity of MOF on the cantilever it is

Table 1 Time response of HKUST-1 to different analytes

Analyte	Adsorption T, s	Concentration, ppm
water	128	1540
chloroform	162	1560
methanol	227	1210
ethanol	556	2110
isopropanol	562	1580
acetone	1242	2660

Figure 3 *MFCs allow for testing gasses, VOCs and mixtures of both*
MFC 1 is dedicated for delivery of VOCs, MFCs 2 and 3 are used to control dilution ratios
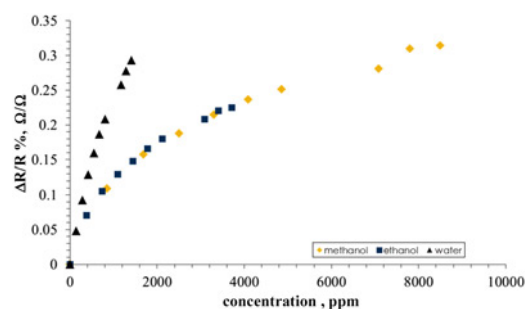

Figure 4 *Response to methanol, ethanol and water vapour compared for same sensor*
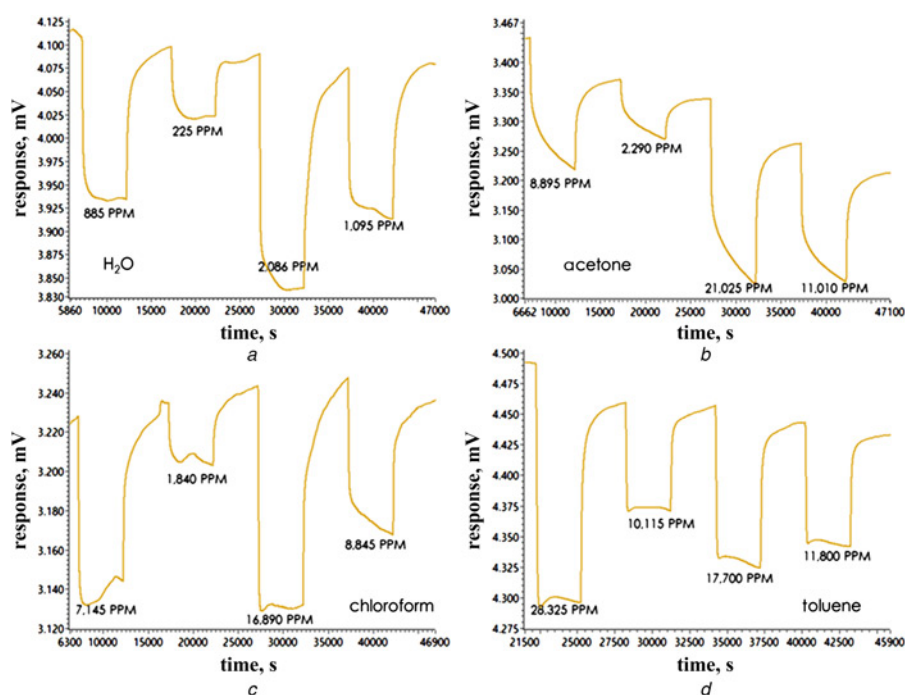
Figure 5 *Response of HKUST-1 to water (Fig. 5a); acetone (Fig. 5b); chloroform (Fig. 5c); toluene (Fig. 5d)*

not possible to express the uptake. Comparing reported values of adsorption for CuBTC, they show the same trend.

Fig. 5 shows sample response curves to mixed concentration exposure of water, acetone, chloroform and toluene. Piezoresistive elements are highly sensitive to temperature changes, as such data was affected by temperature variations of the test cell. The temperature coefficient of response was 4 Ω/°C, hence a temperature variation of 0.1°C corresponds to voltage shift of 20 µV.

No response was observed for hexamethyldisiloxane, 1,2-dichloroethane and carbon dioxide, whereas response to *n*-hexane and *n*-decane was reversible only after baking the cell at 40°C and in nitrogen flow. As such, *n*-hexane and *n*-decane were classified as irreversible. Toluene, isopropanol, ethanol, acetone and chloroform displayed reversibility, however after exposure to the first concentration devices did not return to the original baseline without a heating the cantilever. These analytes were classified as exhibiting poor reversibility. Methanol and water were classified as reversible because of the return of the devices to the original baseline with flow in dry nitrogen for 90 min.

4. Discussion and conclusion: The microcantilever sensor has a sensitive response to water vapour which is reversible at room temperature. The response is proportional to the concentration and can be fitted to a Lamgmuir type isotherm. In this case the saturation occurs at $C_H = 540$ with the affinity constant $\alpha = 0.006$ (Table 2). The response time is also a function of the water concentration, with a more rapid adsorption, but slower desorption. For methanol a reversible response is also observed, however the magnitude of the induced stress is lower for the same analyte concentration. The response time and recovery time

are much slower than for water vapour. Ethanol exhibits a similar magnitude of response to that of methanol, however it is classified as irreversible because of the shift of baseline after the first concentration exposure. Reversibility was interpreted by accounting for temperature shifts during the experiment and factoring any response because of the temperature effects.

Acetone, chloroform and toluene all show much longer time constants and some irreversible behaviour suggesting different adsorption sites within the framework. However, these measurements have not been performed with a completely dehydrated MOF coating, so there is water present within the framework during all tests. For toluene a rapid response is observed with a short overshoot which suggests some kind of mechanical hysteresis is taking place because of re-arrangement of the analyte within the framework. A similar hysteresis is observed in chloroform, however chloroform appears to exhibit a degree of saturation not seen in the toluene response.

HKUST is characterised by a limiting pore diameter of 9 Å [16] which we can compare with the kinetic diameter of different gas molecules and volatile organic compounds, see Table 3. Hence, selectivity arises for the steric hindrance for molecules diffusing into the MOF film. Large molecules, such as cyclohexane are not adsorbed because of the steric effects.

Adsorption of water onto the copper sites within the MOF has been proposed by Wang *et al.* [23] because of the polar nature of the bond between copper and the carboxylic group attached to the di-carboxyl-benzene organic linker in the framework. The flexibility of the MOF allows the bond angle to change when the water is adsorbed at this site, producing a deformation in the cubic lattice [24]. The sensitivity can be estimated based

Table 2 Langmuir isotherm coefficient for water, ethanol and methanol

Analyte	a	C_H	Henry's constant
water	0.006	542	2.50
methanol	0.004	223	0.89
ethanol	0.003	99	0.79

Table 3 Kinetic diameters of selected analytes

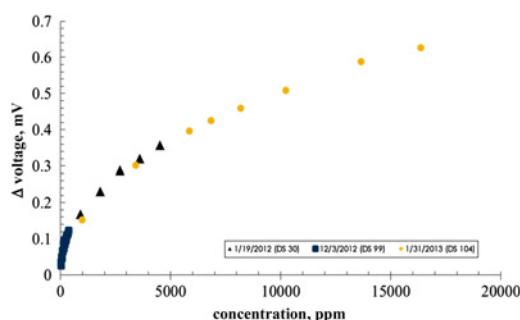| Analyte	Kinetic diameter, Å
water	2.65
methanol	3.76
ethanol	4.46

Figure 6 *Response of HKUST-1 to water for different experiments spanning 12 months*
Illustrates reproducibility of data and reliability of device

upon the signal-to-noise ratio. In our measurements, the noise was the order of 10 μV so that a limit of detection in the sub-100 ppm was achieved with water vapour.

Effectively, the response to different analytes can be distinguished by a number of characteristics. First, discrimination can be achieved by observation of reversible characteristics of the response. Secondly, response time constants for adsorption can be measured and compared. In addition, desorption characteristics can be compared with adsorption characteristics along with the magnitude to identify the particular analyte being tested. The detection limits obtained with these MOF coated cantilevers was not as low as those associated with metal oxide and surface acoustic wave sensors used in electronic noses, which are typically in the ppm or lower range, depending upon the analyte. Combined with additional MOF coatings, the unique response characteristics of each analyte could provide a fingerprint for the detection. Our results indicate that selective features of HKUST-1 film can be used to identify a single analyte effectively and accurately.

A successful sensor should not only identify analytes of interest, but should also perform reliably over its lifetime. All data presented in this Letter was collected on the same microchip over a period of 18 months. During this span, the device was exposed to 12 different analytes in over 180 separate experiments. Fig. 6 shows the response of the same device to water in three separate experiments conducted over 12 months. The data sets match very well, forming a continuous isotherm despite data points being collected at different ranges of concentration on different dates. This suggests neither MOF coatings nor microcantilevers have degraded over time, and the device can be used to accurately and consistently detect different water concentrations.

This work has demonstrated chemically induced strain-based detection utilising MOF-coated microfabricated cantilever sensors. An HKUST-1 coated device has proven to be a reliable detection mechanism for water vapour over a wide range of concentrations. The reliability and chemical stability of the MOF coating are encouraging and hold promise for the further development of microcantilever-based sensors. For those analytes which are not reversible, the application of mild heating in dry nitrogen recovers the film to the base line response. Through the selection of MOFs with smaller pore limiting diameters, the molecular selectivity based upon size could be achieved. In addition, MOFs with different chemical functional groups within the framework, including more acidic or basic sites, could influence the selective nature of the chemical adsorption and hence provide selectivity during sensing.

6   References

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