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Metal Organic Frameworks as Promising High Surface Area Material for Work Function Gas Sensors

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Abstract

Floating gate FET (FGFET) gas sensors based on work function readout allows usage of a wide range of materials to be included as sensing materials. Metal-organic frameworks (MOFs) are a new group of porous materials with extreme high inner surface area that have already shown high potential for applications in gas storage and separation, catalysis and sensing. In this work, MOFs are investigated for the first time with work function readout for gas sensing applications. The results demonstrate the high potential of MOFs for use as gas receptor materials in field-effect based gas sensors.

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Keywords: Metal Organic Framework, Work Function, Gas Sensor

1. Introduction

The readout of gas induced work function changes via suspended gate field effect devices is accepted as a promising technique for the realization of a versatile, low-cost sensor platform since several years [1]. Numerous sensing layers for a variety of gases have been developed which use different physical and chemical effects creating a signal in work function [2].

Metal-organic frameworks (MOFs) are a relatively new material group with a highly porous, modular structure, which can be modified regarding their chemical as well as morphological properties in order to obtain specific properties regarding gas adsorption [3]. The use of MOFs in gas sensing is already demonstrated using impedimetric readout [4].

In this work the work function readout of MOFs is investigated as a new approach to benefit from the exceptional properties of this material group for gas sensing applications. As an example, results obtained

from layers based on Cu-1,3,5-benzenetricarboxylate MOF (Cu-BTC MOF) using a Kelvin Probe setup for work function measurements are presented.

2. Experimental

The sensing layers are prepared on an Al_2O_3 -ceramic substrate with a platinum resistive heating element on the back side, while the top side is covered with an electrode layer made of sputtered gold or platinum (Fig. 1a). Commercial Cu-1,3,5-benzenetricarboxylate MOF powder is used as sensing material (BASF Basolite™ C300). The sensing layers are deposited by a screen printing process as described in [4] or drop coating from aqueous dispersion with subsequent drying at 200°C. The Kelvin Probe setup is characterized by an oscillating gold paddle as counter electrode to the sensing layer (fig. 1b) and outputs a signal, which is representing changes in work function ($\Delta\Phi$).

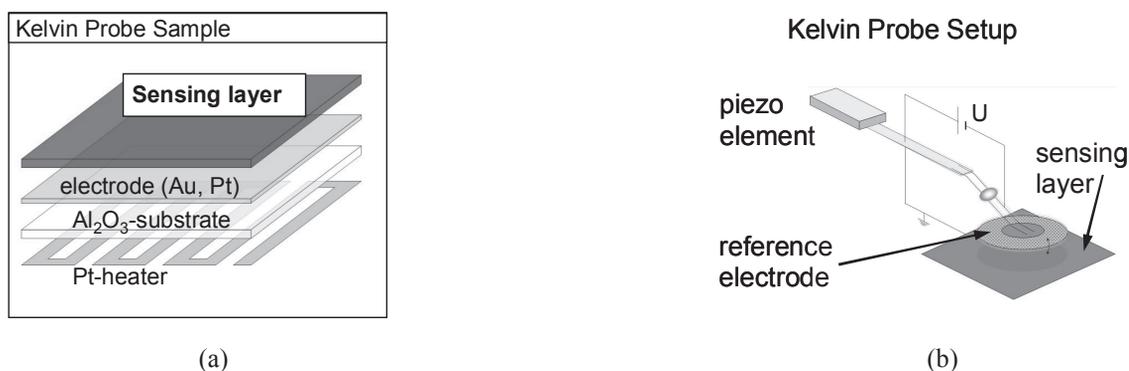


Fig. 1. Kelvin-Probe setup (a) schematic view on the sample structure including alumina substrate with Pt heater, Au or Pt back electrode and sensing layer, (b) schematic depiction including sensing layer, reference electrode and piezo driver for oscillation.

Measurements have been performed in the temperature range from room temperature to 200°C which is the limit of thermal stability of the MOF type used. Gas measurements have been carried out with synthetic air at a total air flow of 1 l/min at a humidity level of approx. 40% relative humidity. The test gas concentrations have been adjusted by a computer-controlled gas mixing station.

3. Results

Fig. 2 shows the Kelvin Probe response of a Cu-BTC MOF layer on Au back electrode to the application of 1ppm hexanal, 1ppm pentanal and 5ppm toluene at temperatures from 25°C to 100°C. While hexanal and toluene cause nearly no change in work function, a distinct and reversible response is observed during exposure to pentanal, which is increasing with temperature. It appears that some thermal activation is needed to facilitate the diffusion of the gas in the inner cavities. Due to the very similar chemical nature of the both aldehydes, hexanal and pentanal, it is obvious that the different response to these gases is not dominated by chemical properties but mainly influenced by the interaction of the pore size of the MOF and the size of the probe molecule.

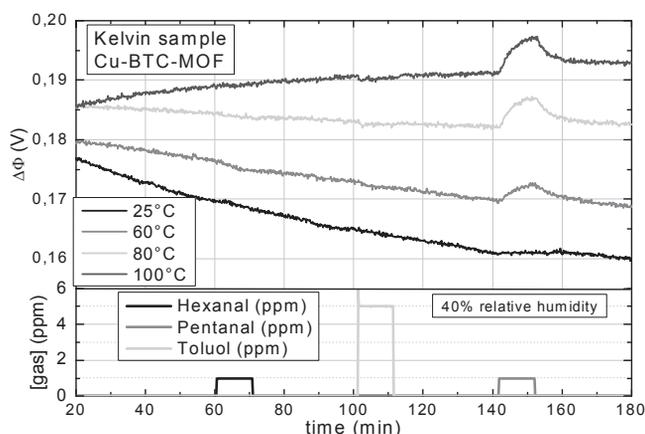


Fig. 2. Kelvin-Probe measurement of a Cu-BTC MOF at temperatures from 25°C to 100°C. The work function response to hexanal, pentanal and toluol is shown.

A further indication for the considerable role of the ratio of pore size to molecule size is given from fig. 3. The low response of Cu-BTC MOF on Au back electrode at 80°C to dimethylether displayed here is negligible, while the gases NH_3 and H_2S , which are distinctly smaller compared to dimethylether cause a strong change in work function.

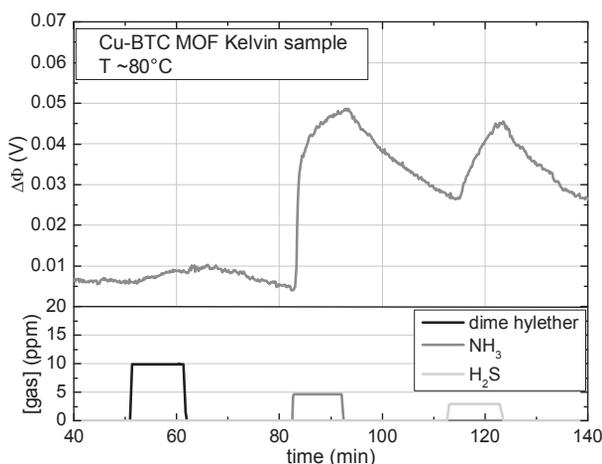


Fig. 3. Work function response of a Cu-BTC MOF sample to acetone, dimethylether, ammonia and H_2S at 80°C.

Fig. 4 compares the response of Cu-BTC MOF samples on Au and Pt back electrodes to ethanol and acetone as a function of temperature. Similar to the response to hexanal shown in fig. 2, the response to ethanol and acetone becomes large with increasing temperature for samples with Au back electrode, Au backed samples exhibit a strongly increased response to both gases at temperatures $> 100^\circ\text{C}$. The samples with Pt back electrode behave very different. During exposure to ethanol the response of samples on Pt is of opposite sign compared to the Au backed samples. In the case of acetone the response of both types of samples has the same sign, but a different temperature dependency. The acetone response of the Au based sample increases with temperature, while the Pt based sample shows a clear maximum of the response to acetone at 80°C.

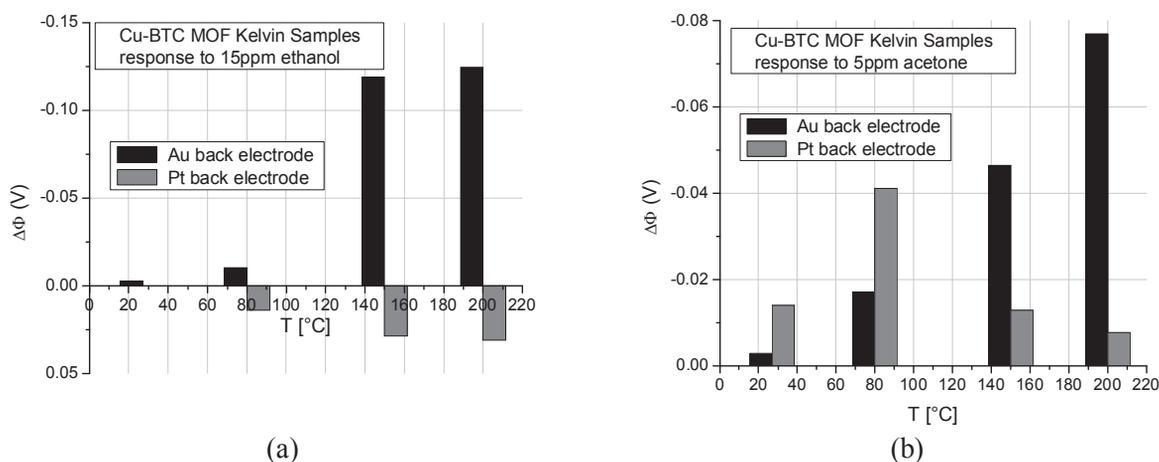


Fig. 4. Work function response of a Cu-BTC MOF sample to 15ppm ethanol (a) and 5ppm acetone (b) as function of temperature

4. Summary and Conclusions

These results on work function measurements of the gas response of Cu-BTC MOF presented in this work indicate the opportunity for a steric engineering of the base sensitivity. As a further extension, these properties can later be combined with additional chemical reactivity engineering to optimise the selectivity. The evident role of the electrode materials gold and platinum, on which the MOFs have been deposited, demonstrates that the catalytic activity of the back electrodes plays an important role in the gas sensing properties of these devices. It has to be investigated, whether this is due to the gas sensitivity of the electrodes itself or due to catalytically induced reactions of the analyte gas. Potentially this can be further used to enhance a desired sensitivity.

Further work will be presented on the influence of pore size and chemical structure of MOF on gas-induced work function changes. This will also include modifications of the MOF structure itself.

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