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Metal-Organic-Frameworks as an aldehyde sensing layer in work-function based gas sensing devices

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Abstract

Metal-Organic Frameworks (MOFs) are porous crystalline materials with a characteristic large surface area. These materials were mainly investigated for applications as gas storage and separation and catalysis. The approach for using MOFs for sensing application was already done. MOFs show high potential for applications involving work function based gas sensing devices. In this work the Cu-BTC MOF was investigated as an aldehyde sensing material for work function readout based gas sensors at ambient conditions. The cross-sensitivity to humidity was proved. It is shown that Cu-BTC MOF sensing layers allow the distinguishing of molecules with similar chemical properties but different lengths.

Key words: Gas sensor, Work function, Metal Organic Frameworks (MOFs), Cu-BTC MOF, aldehyde sensing.

Introduction

Metal-Organic Frameworks (= MOFs) are porous crystalline materials which feature a characteristic large surface area and were investigated mainly for gas storage and separation and catalysis [1,2,3]. Even though MOFs are promising candidates for gas sensing applications, only few investigations have been performed. In these experiments, analyses were based on impedance spectroscopy, sensing different concentration of O_2, CO_2, C_3H_8, NO, H_2, ethanol and methanol in a temperature range of 120°C – 240°C [4], gravimetric readout with quartz resonator sensing volatile organic gases, acetone, tetrahydrofuran and isopropyl alcohol [8], or the work-function-based, low cost, and low energy gas sensing FETs (GasFETs) [5,6]. The advantage of the work function readout based gas sensing devices is the possibility to use various sensing materials because this technique is not limited to conductors or semiconductors, also isolators can be utilized as gas sensing layers. Many different materials have already been successfully proved for trace gas sensing with GasFETs [7].

In this work commercial available Cu-BTC MOF was proved as a gas sensing layer for low concentrations (lower ppm) of two different aldehydes, acetaldehyde (=ethanal) and pentanal, at ambient conditions. The cross-sensitivity to humidity was proved.

Materials and Methods

For the preparation of sensing layers, an Al_2O_3 ceramic substrate "Rubalit 710" (CeramTec, Germany) was used. TiN layer (~2 µm) was sputtered on the top side of the substrate to serve as a back electrode. A platinum resistive heating element was screen-printed on the bottom side of the substrate (Figure 1b). Copper 1,3,5-benzene-tricarboxylate (Basolite™ C300 or Cu-BTC, chemical formula $C_{18}H_6Cu_3O_{12}$), was purchased from Sigma Aldrich, Germany.

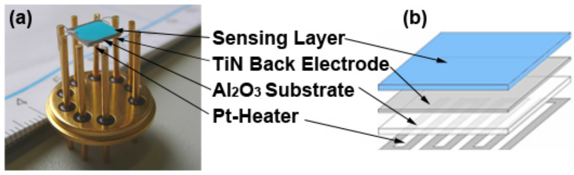

Fig. 1: Schematic view (b) and photo (a) of the Kelvin Probe sample. The alumina substrate with heating element, back electrode and sensing layer is represented.

Cu-BTC MOF has a cubic crystal system structure with large square-shaped pores of ~9 Å x 9 Å, tetrahedral pockets of 6 Å and triangular windows of 4.6 Å x 4.6 Å. The pores can absorb up to 10 water molecules per formula unit [10,11].

Cu-BTC sensing layers were drop coated on the TiN electrode from a freshly prepared aqueous dispersion and subsequent dried. 2 µl of Cu-BTC dispersion were used for the preparation of one Kelvin-sample with (5x5) mm^2 area (Fig. 2).

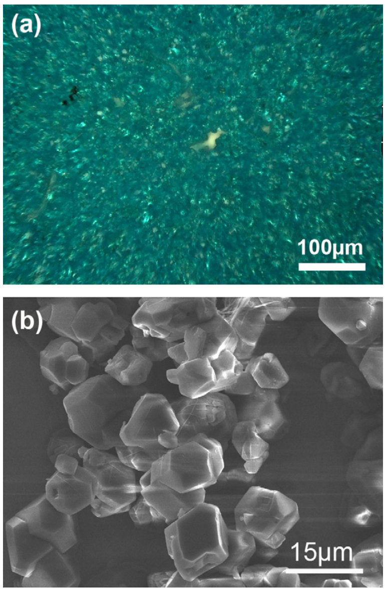

Fig. 2: Optical microscope image (a) and scanning electron microscope image (b) of the Cu-BTC sensing layer. Single crystals with typical shape can be observed.

Work function measurements were performed using a Kelvin Probe setup (Fig. 3) as described by Stegmeier [8]. The measured signal represents the difference in the work function between the oscillating gold paddle and the sensing layer. The gold paddle should be not reactive to the used gas, so it can be concluded that the signal is represented by the changes of the electronic structure of the Kelvin-sample.

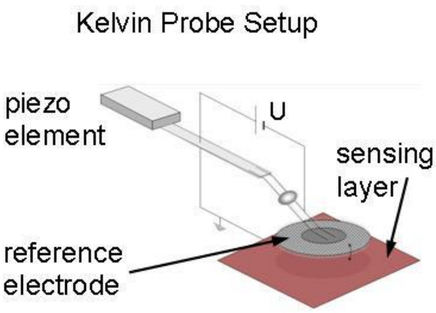

Fig. 3: Schematic depiction of the Kelvin Probe Setup. Sensing layer, the reference electrode and piezo driver for oscillation is represented.

Measurements were performed at ambient conditions in synthetic air (20% O_2, 80% N_2) at a total flow of 1 l/min at room temperature (25°C) with controlled relative humidity.

Results

To study the influence of the humidity on the Cu-BTC layer, the measurement with varying relative humidity levels from 0 to 50% in 5% steps were performed. Figure 4 displays changes in the work function (ΔΦ) of a Cu-BTC and a TiN layer to humidity variation. The measurement of the blank back electrode is required to assure that the sensor signal is originated from the sensing layer itself and is not influenced by the back electrode. The TiN back electrode was chosen because it is inert to the target gases used in this study. A stepwise and reversible response to the variation of the humidity level can be observed in the work function change of Cu-BTC. Only a small influence of the humidity variation can be seen on the work function response of the TiN sample.

Figure 5 represents the response of a Cu-BTC MOF sensing layer on TiN back electrode and a blank TiN back electrode during exposure to low concentrations of two different aldehydes, ethanal and pentanal in wet synthetic air at room temperature. No changes in the work function of the Cu-BTC MOF layer can be observed during exposure to 4 and 10 ppm ethanal. In contrast a strong, fast and reversible signal can be seen during exposure to 4 and 10 ppm pentanal. A minor influence of humidity on the pentanal sensing behavior at 0%, 40% and 70% r.h. can be observed.

Figure 6 shows the response of the Cu-BTC layer to different concentrations of pentanal at 40% r.h. The signal of the Cu-BTC layer clearly increases with increasing pentanal concentration, while only minor signal changes can be observed on the TiN sample.

Discussion

Cu-BTC MOF structure can include up to 10 H_2O molecules per unit cell [12]. Biemmi et al. coated QBC with dense Cu-BTC layer and performed thermogravimetric analysis measuring the weight loss in the temperature range between 0°C and 400°C and recorded water sorption isotherm at different temperatures [10].

Our Kelvin Probe measurements show reversible stepwise response to the changes of the humidity. We suppose that this effect is induced by the adsorption of the water molecules in the MOF structure.

The measurements with different aldehydes show promising results perspective possibility of MOFs application for selective gas sensing. Cu-BTC MOF layers allow the detection of low ppm concentrations of pentanal. The signal increases with increasing pentanal concentration. The response time t_{90} is between 3.6 and 11.6 minutes depending of pentanal concentration. The concentration of 1 ppm of pentanal can clearly be detected.

Both aldehydes investigated are very similar. They have the same functional group that is responsible for chemical properties of aldehydes, but their organic chains differ in length. We assume that the different sensing behavior of the Cu-BTC MOF samples towards ethanal and pentanal is influenced by the relationship of their length to the pore size of the Cu-BTC MOFs.

Summary and Outlook

We have shown here that Cu-BTC MOF layers can be used in work function based gas sensing devices for the differentiation of chemically similar but geometrical different aldehyde molecules. In the future, further investigation of adsorption and reaction mechanism will be performed.

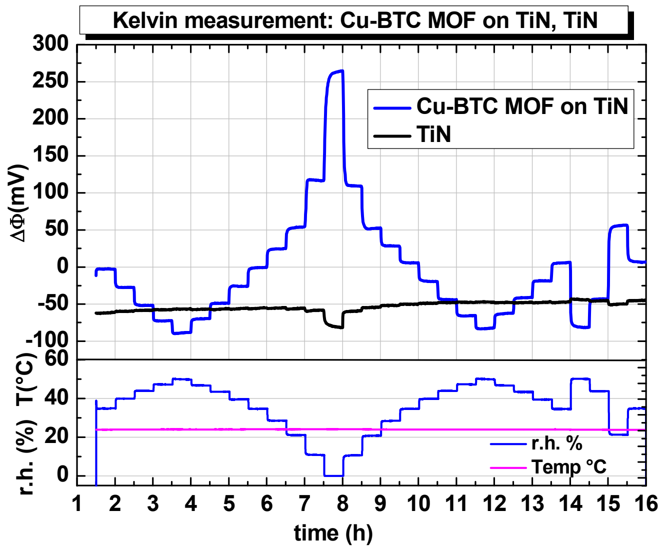

Fig. 4: Kelvin Probe measurement: Work function response ΔΦ of Cu-BTC MOF layer on the TiN back electrode (blue line) and the blank TiN back electrode (black line) to different levels of relative humidities. The measurements were performed in synthetic air (20% O_2, 80% N_2) at a total air flow of 1 l/min, at room temperature (25°C).

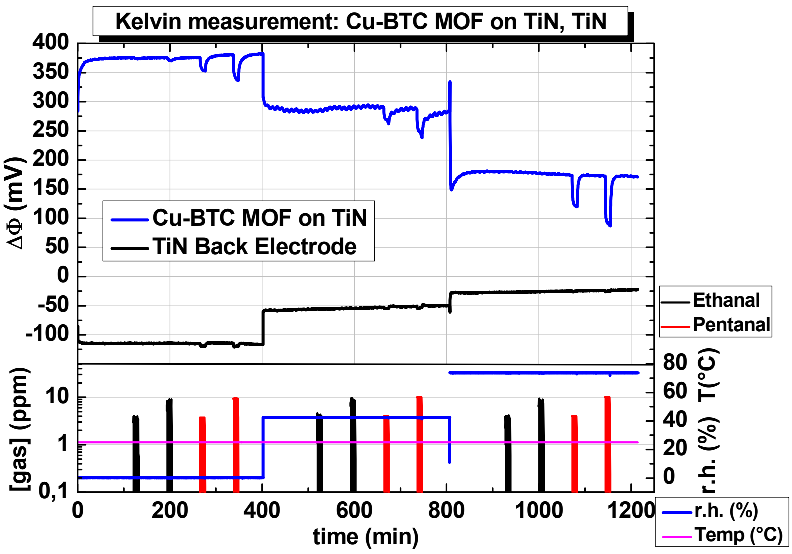

Fig. 5: Kelvin Probe measurement: Work function response ΔΦ of Cu-BTC MOF layer on the TiN back electrode (blue line) and the blank TiN back electrode (black line) to 4 ppm and 10 ppm ethanal and pentanal respectively. The measurements were performed in synthetic air (20% O_2, 80% N_2) at a total air flow of 1 l/min, at room temperature (25°C) and relative humidity of 0%, 40% and 70%.

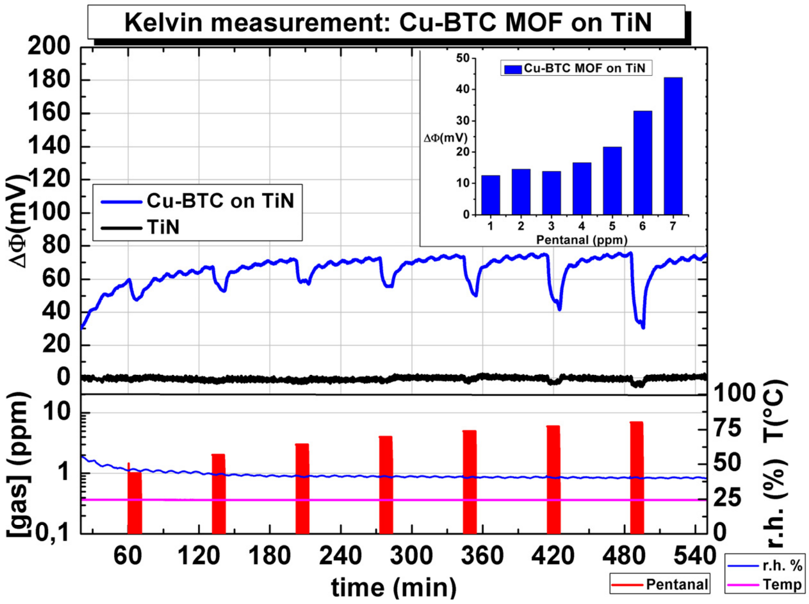

Fig. 6: Kelvin Probe measurement: Work function response ΔΦ (mV) of Cu-BTC MOF layer on the TiN back electrode (blue line) and the blank TiN back electrode (black line) to different concentration of pentanal. The measurements were performed in synthetic air (20% O_2, 80% N_2) at a total air flow of 1 l/min, at room temperature (25°C) and relative humidity of 40%.

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