

Sub-ppm Gas Detection with Metal Organic Frameworks Functionalized Quartz Microbalances

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Summary:

MOF coated Quartz microbalance show an enhanced sensitivity to gases with sub-ppm limits of detection. The sensitivity pattern of three investigated materials is sufficient for a complete identification, independent from concentration, of gases and vapors of different chemical structure such as methane, CO₂, ammonia, and NO.

Keywords: Gas sensor, MOF, Quartz Microbalance, Sensor Array

Introduction

Quartz microbalances (QMBs) are often associated with limited concentration resolution. This limitation typically arises in sensors functionalized with compact sensitive layers, whereas highly porous materials—with their large effective surface area—are expected to improve detection limits. In this context, metal-organic frameworks (MOFs) represent a promising class of materials for QMB functionalization. Owing to their high porosity and large internal surface area, MOFs provide an abundance of accessible adsorption sites and have therefore attracted significant interest in gas sensing applications.

Despite their inherent sensitivity, the low electrical conductivity of many MOFs can hinder their use in electronic sensing platforms. Thus, mass-sensitive devices offer an opportunity to fully exploit MOF sensitivity. Previous work has demonstrated the detection of carbon dioxide and methane using MOF-functionalized surface acoustic wave sensors and QMBs [1]. In this study, we investigate the response of QMBs functionalized with three different MOFs—Cu-BTC, Ni-doped ZIF-67, and Fe-BDC—to ammonia, nitric oxide, carbon dioxide, and methane.

Methods

The octahedral Cu-BTC MOF was synthesized hydrothermally using copper ions and 1,3,5-

benzenetricarboxylic acid (BTC) as the organic linker. The hexagonal micro-spindle-shaped Fe-BDC MOF was prepared hydrothermally using terephthalic acid (BDC). The bimetallic rhombic dodecahedral Ni-doped ZIF-67 was synthesized sonochemically using nickel and cobalt salts with 2-methylimidazole. Structural and morphological characterization was performed using XRD, FTIR, Raman spectroscopy, and SEM (see figure 1). Each MOF was deposited onto 20 MHz QMBs (KVG GmbH, Germany) by drop-casting. Certified gas mixtures were diluted in nitrogen using mass flow controllers (CMA 10B, MKS Instruments, Inc.) and delivered to a Teflon-sealed sensor cell at 100 sccm.



Fig. 1: appearance and SEM figure of MOF films.

Results

Figure 2 shows the response curves of the sensors to the four investigated gases. The adsorption isotherms exhibit an approximately linear trend across the tested concentration ranges. Sensitivities, calculated as the slopes of the linear fits, are compared in Figure 3. All

sensors exhibit the highest sensitivity to nitric oxide and ammonia, whereas the less interactive methane and carbon dioxide produce lower responses.

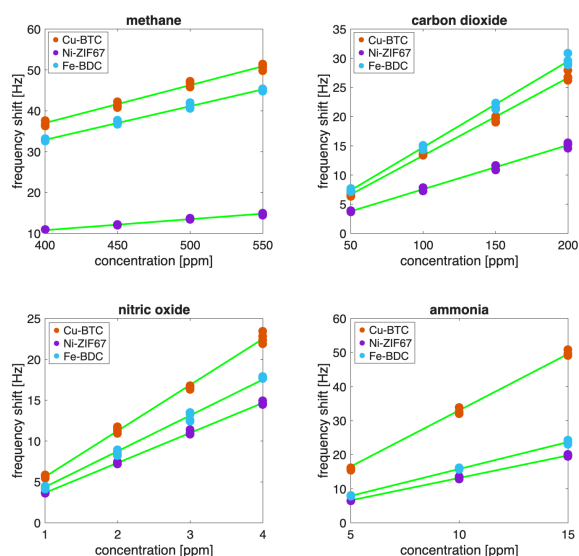


Fig. 2. Response curves of sensors to the four tested gases.

Limits of detection (LOD) were calculated as the ratio between the noise level and the sensitivity [2]. Signal fluctuation varied among sensors, ranging from 0.5 Hz to 3 Hz. These differences likely originate from non-uniform MOF films and interfacial defects between the gold electrode and the MOF layers. The resulting LODs are shown in Figure 3. For nitric oxide, the LOD ranges from 190 to 280 ppb; for ammonia, from 320 to 650 ppb. The LODs for carbon dioxide and methane are substantially higher, between 7–14 ppm for CO₂ and 11–38 ppm for CH₄.

Although the sensitivity patterns (Figure 3) are broadly similar, the remaining differences are sufficient for gas discrimination. This is demonstrated by principal component analysis of the sensor responses. Figure 4 shows the scores of the second and third principal components; the first component, dominated by overall signal magnitude, does not distinguish among gases. In this representation, each gas exhibits a concentration-dependent trajectory, and the divergence between gases increases with concentration. Interestingly, methane does not show a clear concentration trend within these

components, although such behaviour appears in the first principal component. This behaviour further supports the presence of distinct sensor–analyte interactions.

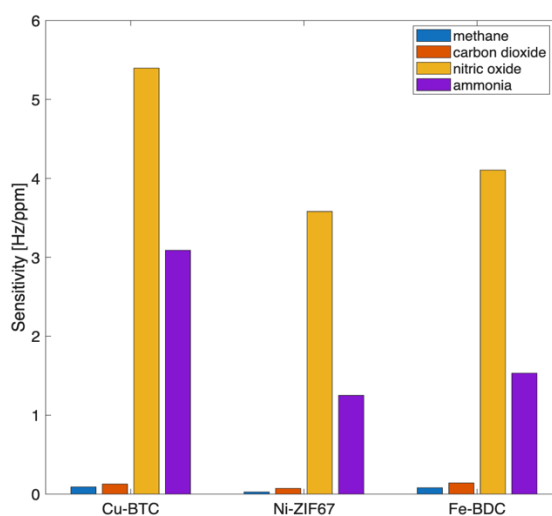


Fig. 3. Sensitivity patterns of the tested sensors

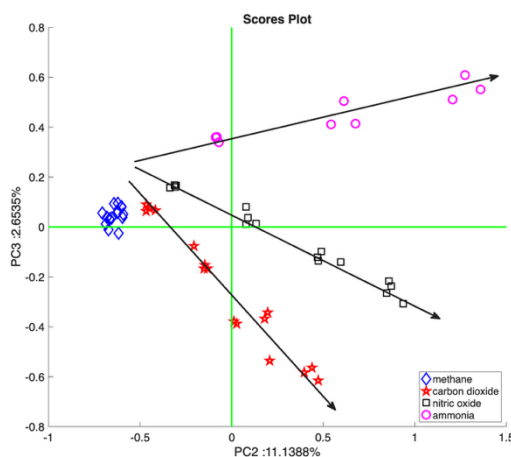


Fig. 4: scores plot of second and third principal components

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