Carbon Dioxide Sensing with 2D Conductive Metal-Organic Frameworks

by

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ABSTRACT

The research focuses on chemiresistive sensing of carbon dioxide (CO₂) using a series of two-dimensional (2D) conductive metal–organic frameworks (MOFs) with amine-based linkers. The 2D MOFs studied here show carbon dioxide sensitivity at concentrations as low as 1000 ppm. The identity of both the metal and ligand affects sensing performance in terms of sensitivity, reversibility, selectivity, and response to moisture. Experimental and computational data indicate that the amine groups of the ligands play a key role in the CO₂ sensing mechanism. This work represents the first use of electrically conductive MOFs for CO₂ sensing, and demonstrates a combination of sensitivity and selectivity that is promising for practical applications.

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Title: Associate Professor of Chemistry
INTRODUCTION

Carbon dioxide (CO₂) detection is crucial for applications such as indoor and outdoor air quality monitoring and process control in the food industry. For example, most indoor workplaces have an exposure limit of 5000 ppm over eight hours. However, the detection of carbon dioxide has proven to be challenging in that it is non-polar and relatively unreactive. Commercial detectors based on non-dispersive infrared (NDIR) spectroscopy are widely used, but they are usually expensive and non-portable.

Chemiresistive carbon dioxide sensors typically use metal oxides under heating (>200°C), which is energy-consuming and complicates the device structure in miniaturization. As a result, it is necessary to develop new materials that can sense carbon dioxide efficiently at room temperature.

Metal–organic frameworks (MOFs) have been targeted for use in gas sensors, due to their high surface area and robust chemical tunability via a “bottom-up” synthetic approach. To the best of our knowledge, there are only two cases where MOFs were tested for CO₂ sensing. First, based on changes in work function, Mg-MOF-74 was used for detecting CO₂, however, with guest ethylenediamine molecules for performance enhancement. The second example is CDMOF-2, a γ-cyclodextrin-derived material which changes proton conductivity upon exposures to high concentrations of CO₂ (≥10%). We hoped to develop independent CO₂ sensors with improved sensitivity using two-dimensional (2D) conductive MOFs. 2D MOFs have emerged as a class of chemiresistive sensors, with their high electrical conductivity providing efficient signal transduction. These materials have been shown to be promising sensors for analytes such as ammonia, water, nitric oxide, hydrogen sulfide, and a variety of volatile organic compounds (VOCs) at concentrations less than 1000 ppm without the need for guest molecules.

Industrially, carbon dioxide is adsorbed with aqueous amine-based absorbents. Similarly, in CO₂ adsorption literature, guest diamine molecules and amino groups appended on the frameworks have been found to significantly enhance CO₂ adsorption. In a mechanistic study by Long and coworkers,
cooperative insertion of CO$_2$ in diamine-appended Mn$_2$(dobpdc) ($\text{dobpdc} = 4,4'$-dioxidobiphenyl-3,3'$-\text{dicarboxylate}$) was experimentally observed. These results suggest that amino functionality is crucial in enhancing the interaction between the MOF and CO$_2$. We hypothesized that 2D conductive MOFs with amine-based ligands should be promising candidates for CO$_2$ sensing. Therefore, we chose two amine-based ligands: 2,3,6,7,10,11-hexaaminotriphenylene (HATP) and hexaaminobenzene (HAB) to construct the MOFs. The two ligands would also afford MOFs with different pore apertures and distinct packing patterns allowing for systematic examination of how these factors affect reversibility and selectivity in sensing. We also varied the metal center with Ni and Cu, because it may also affect the sensing behaviors, according to previous work from our lab. Herein, we report the discovery of three amine-based 2D conductive MOFs as carbon dioxide sensors: Ni$_3$(hexaiminotriphenylene)$_2$ (Ni$_3$(HITP)$_2$), Cu$_3$(hexaiminotriphenylene)$_2$ (Cu$_3$(HITP)$_2$) and Cu$_3$(hexaaminobenzene)$_2$ (Cu$_3$(HIB)$_2$). We examined their sensitivity under different humidity conditions, selectivity against other similar analytes, and used computational method supported by experimental data to discuss the mechanism of sensing. To the best of our knowledge, these are the first reported 2D-MOF-based chemiresistive carbon dioxide sensors.

INSTRUMENTATION AND METHODS

Commercially available reagents and solvents were used as received without further purification. All reactions were performed under ambient atmosphere. The two-dimensional (2D) MOF materials Ni$_3$(HITP)$_2$, Cu$_3$(HITP)$_2$, Cu$_3$(HIB)$_2$, and Cu$_3$(HHTP)$_2$ were synthesized according to literature procedures. The fabrication of the MOF sensor devices was achieved by drop-casting suspensions of freshly prepared MOFs in acetone (about 1 mg/mL) onto interdigitated gold electrodes on a corundum substrate (CC1.W1, BVT Technologies). The resulting polycrystalline MOF films were dried under a flow of dry air (ultra zero grade, Airgas). All the prepared MOF sensors had resistances between 10 and 100 k$\Omega$. 
Powder X-ray diffraction (PXRD) patterns were obtained with a Bruker D8 Advance diffractometer equipped with a Göbel mirror, rotating sample stage, LynxEye detector and Cu Kα (λ = 1.5405 Å) X-ray source in a 0/2θ Bragg-Brentano geometry. An anti-scattering incident source slit (1 mm) and an exchangeable steckblende detector slit (8 mm) were used. During measurement tube voltage and current of 40 kV and 40 mA were used, respectively. Scattering at low angles was removed by knife-edge attachments. Samples for PXRD were prepared by placing a thin layer of the designated materials on a zero-background silicon (510) crystal plate. Scanning electron microscopy (SEM) images were recorded using a Zeiss Super55 SEM with an InLens detector, with an operating voltage of 4.00 kV.

Two probe pressed-pellet conductivity was measured using a home-built press which was previously described in the literature. The MOF powder was placed inside a glass capillary and pressed between two steel rods of 2 mm diameter. Typical thickness of the powder pellets was between 0.1 mm and 0.5 mm.

Gas detection measurements were performed by placing the sensor devices into a PTFE enclosure with a gas inlet and outlet and connecting the sensor electrodes to a PalmSens EmStat® potentiostat with a MUX16 multiplexer. The potentiostat applied a constant potential of 0.100 V across the electrodes, and the current was recorded using PSTrace® (version 4.8) software, as the devices were exposed to carbon dioxide and other gaseous analytes. The relative humidity of the carrier air was adjusted by Alicat® mass flow controllers and reconfirmed by a Traceable® humidity sensor. Data for MOFs were typically obtained with a 60s exposure of a given analyte at each concentration with a recovery time of 180s. Representative sets of sensing traces are shown in Appendix 1. The raw data in Appendix 1 were used to construct the plot of average sensing responses shown in Figure 3 in the Results and Discussion section.

Cu$_3$(HITP)$_2$ was geometrically optimized using DFT as implemented in VASP. A Γ-centered 2 x 2 x 4 k-grid and 500 eV plane-wave cutoff were paired with the PBEsol exchange-correlation functional (Perdew-Burke-Ernzerhof revised for solids) and a 1x10$^{-6}$ eV convergence criterion. Convergence testing showed that a Γ-only k-grid was sufficient to describe the electronic structure and was invoked for the
following CO₂-containing models. A two-monolayer surface model (19 Å of vacuum) was constructed from the bulk-optimized structure. CO₂ was introduced at positions of high electrostatic potential both within the pore of the bulk model, and on the surface of the surface model. Their positions of the CO₂ were geometrically optimized using the same aforementioned method. Grimme’s D3 dispersion correction was included to appropriately account for the diffuse π-interactions between CO₂ and the linkers. Adsorption energies were then calculated from the self-consistent energies.

RESULTS AND DISCUSSION

The hexagonal structures of the three MOFs are shown in Figure 1. The pore diameters of Ni₃(HITP)₂ and Cu₃(HITP)₂ are estimated to be 1.5 nm, while that of Cu₃(HIB)₂ is 0.7 nm. Their 2-probe bulk pellet conductivities were measured to be 2 S/cm for Ni₃(HITP)₂, 0.2 S/cm for Cu₃(HITP)₂, and 0.01 S/cm for Cu₃(HIB)₂ (Figure 1).

<table>
<thead>
<tr>
<th>MOF</th>
<th>σ (S/cm)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃(HITP)₂</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Cu₃(HITP)₂</td>
<td>0.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Cu₃(HIB)₂</td>
<td>0.01</td>
<td>0.70</td>
</tr>
</tbody>
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*Figure 1.* Schematic representations of M₃(HITP)₂ (M=Ni, Cu) and Cu₃(HIB)₂ with their pressed pellet conductivity (σ) values (2-probe, room temperature) and estimated pore sizes.

All three MOFs were able to sense CO₂ at a concentration as low as 1000 ppm within three minutes (Figure 2), which is below the required health limit of 5000 ppm for indoor air at typical workplaces. At concentrations of 2000 ppm or higher, significantly shorter exposure times (≤60 sec) could be used.
Figure 2. Sensitivity at 1000 ppm of CO₂ in dry air for (a) Ni₃(HITP)₂, (b) Cu₃(HITP)₂ and (c) Cu₃(HIB)₂. The exposure time of the sensors to CO₂ was three minutes (indicated by the grey bars), followed by a recovery time of at least ten minutes. ΔG/G₀ indicates percentage conductance change.

Figure 3 shows the relative responses (ΔG/G₀) of the three materials upon exposure to 60 seconds of CO₂ (2000-6000 ppm) in air with various relative humidity (RH) levels. For all three materials, the
magnitude of the response increases as the concentration of CO$_2$ increases from 2000 to 6000 ppm at each RH. For Ni$_3$(HITP)$_2$, the response magnitude is largest under dry air, and decreases as the humidity level increases. Surprisingly for Cu$_3$(HITP)$_2$ and Cu$_3$(HIB)$_2$, the response is more pronounced under modest humidity levels (20% and 40% RH) than the dry and highly humid (80% RH) cases. We attribute this interesting feature to how water might facilitate the interaction between the Cu$_3$(HITP)$_2$/Cu$_3$(HIB)$_2$ framework and CO$_2$. Under modest RH levels (20% and 40%), water molecules bind to Cu centers and introduce extra electric field that interacts with the quadrupole moment of CO$_2$.$^{26}$ Effectively, water molecules act as additional interaction sites for CO$_2$, thus enhancing CO$_2$ adsorption and inducing larger responses. Under the highest humidity level (80% RH), the enhancement of the response is reduced in Cu$_3$(HITP)$_2$ and diminished in Cu$_3$(HIB)$_2$. This is probably because water molecules begin to fill the pores of the frameworks at high moisture levels and hinder the interaction between the MOFs and CO$_2$. In contrast to Cu$_3$(HIB)$_2$, the response enhancement is still present at 80% RH vs dry for Cu$_3$(HITP)$_2$ at most concentrations (except 2000 ppm), because Cu$_3$(HITP)$_2$ has a larger pore size than Cu$_3$(HIB)$_2$ (Figure 1). In the case of Ni$_3$(HITP)$_2$, the Ni(II) center has d$^{8}$ electronic configuration which prefers square planar geometry, and therefore it is less likely to bind axial water, which explains the absence of water-enhanced response in Ni$_3$(HITP)$_2$ experimentally. Instead, with increased humidity levels, the water molecules block the pores of Ni$_3$(HITP)$_2$ and render it less sensitive to CO$_2$.

Data in Figure 3 also indicate that the current changes are larger in the case of Cu$_3$(HIB)$_2$ than both Ni$_3$(HITP)$_2$ and Cu$_3$(HITP)$_2$ under each corresponding CO$_2$ concentration and humidity level. We attribute this feature to the different stacking modes of these materials: Cu$_3$(HIB)$_2$ has a staggered configuration between sheets, compared to the slipped-parallel stacking mode in M$_3$(HITP)$_2$ (M=Ni, Cu) (Figure 4). The copper atoms and amino groups in the staggered mode of Cu$_3$(HIB)$_2$ are more exposed, allowing the possibility to bind more CO$_2$ molecules, hence a more significant impact on the conductivity of the material.
Figure 3. Sensing responses of (a) Ni₃(HITP)₂, (b) Cu₃(HITP)₂ and (c) Cu₃(HIB)₂ to 2000, 3000, 4000, 5000 and 6000 ppm of CO₂ in dry air and air with 20%, 40% and 80% relative humidity (RH), where ΔG/G₀ is the percentage change in conductance upon a 60s exposure; each response is averaged from six separate devices for each MOF; error bars show one standard deviation.
Figure 4. Two neighboring layers viewed down the c-axis for (a) Ni₃(HITP)₂, (b) Cu₃(HITP)₂ and (c) Cu₃(HIB)₂ (Ni: green; Cu: yellow; N: blue; C: dark grey; H: white). Ni₃(HITP)₂ and Cu₃(HITP)₂ are stacked in the slipped-parallel fashion, and Cu₃(HIB)₂ is stacked in the staggered fashion.¹¹,²³,²⁴
We next examined the reversibility of the signals by exposing the sensors to repeated cycles of CO₂ (Figure 5). The reversibility of M₃(HITP)₂ (M=Ni, Cu) is better than that of Cu₃(HIB)₂, which can be explained by the smaller pore size of the latter that renders it more difficult for the CO₂ molecules to dissociate from the pores of the MOF.

**Figure 5.** Raw traces showing responses of (a) Ni₃(HITP)₂, (b) Cu₃(HITP)₂ and (c) Cu₃(HIB)₂ under repeated exposures to 5000 ppm of CO₂ in dry air with an exposure time of 30 seconds and a recovery time of 6 minutes for each cycle.
We also measured the selectivity of the MOFs against other gases that may be common interferents in practical and industrial applications (Figure 6). All the materials are more responsive towards molecules with multiple bonds (CO, C₂H₄ and CO₂) than those without (CH₄ and H₂), which suggests that the π orbitals may be responsible for the sensing responses. Figure 6 also shows that Ni₃(HITP)₂ and Cu₃(HITP)₂ are selective towards CO₂ over other tested gases (H₂, CH₄, CO, and C₂H₄), whereas Cu₃(HIB)₂ shows additional responses to CO and ethylene. We propose that the difference in selectivity is due to the dissimilar packing modes of the MOF materials (Figure 4). In the staggered configuration of Cu₃(HIB)₂, the more exposed copper atoms can bind analytes such as ethylene and carbon monoxide that may not otherwise interact significantly with the amino groups of the linkers.

Figure 6. Selectivity responses for Ni₃(HITP)₂ (red), Cu₃(HITP)₂ (blue) and Cu₃(HIB)₂ (green), each obtained from a 60s exposure to 2000 ppm of the analyte (CH₄, H₂, CO, C₂H₄ and CO₂) in dry air; each response was averaged from 12 measurements (four separate devices for each MOF with three exposures); error bars represent one standard deviation.

Density functional theory (DFT) calculations were used to assess the mechanism of CO₂ binding both within the pore and on the surface of Cu₃(HITP)₂. The most favorable interaction between Cu₃(HITP)₂ and CO₂ was found to be within the pore. The highest heat of adsorption (−
5.86 kcal/mol) was calculated for CO₂ positioned between two layers such that each oxygen has two hydrogen bonding interactions with the N-H moieties on either side of a metal site (Figure 7b). The value of −5.86 kcal/mol can be attributed to hydrogen bonds. Surface binding was found to be less favored than in-pore adsorption in almost all conformations. The most favored surface binding mode with a heat of adsorption value of −3.04 kcal/mol (Figure 7a) is less favorable than two out of the three in-pore binding modes (Appendix 2).

Figure 7. DFT calculational results for the interaction of CO₂ with Cu₃(HITP)₂, showing the most favored (a) surface and (b) in pore binding modes, each viewed from out-of-plane and in-plane angles (Cu: yellow; C: dark grey; N: blue; O: red; H: white). The heat of adsorption values were −3.04 kcal/mol for (a) and −5.86 kcal/mol for (b). The closest distances between CO₂ and the MOF framework were 3.25 Å for (a) and 2.38 Å for (b).

The computational result of the most favored binding mode (Figure 7b) is consistent with our experimental data, where we tested Cu₃(hexahydroxytriphenylene)₂ (Cu₃(HHTP)₂) for CO₂ sensing. Cu₃(HHTP)₂ and Cu₃(HITP)₂ are structurally analogous MOFs, where the most important difference is in the chelating atom: NH vs O (Figure 8a). However, unlike Cu₃(HITP)₂,
Cu$_3$(HHTP)$_2$ did not show any significant response towards various concentrations of CO$_2$ in dry air for the same exposure time of 60s (Figure 8c). Therefore, it is highly likely that the amino groups play a crucial role in sensing CO$_2$.

**Figure 8.** (a) Schematic and (b) PXRD pattern of Cu$_3$(HHTP)$_2$; (c) sensing responses of Cu$_3$(HHTP)$_2$ (black) towards 2000, 3000, 4000, 5000 and 6000 ppm of CO$_2$ in dry air (60s exposure) plotted along with responses from Cu$_3$(HITP)$_2$ (blue); responses were averaged from four sensor devices; error bars indicate one standard deviation.
CONCLUSION

We have developed the first examples of 2D conductive MOFs as chemiresistive carbon dioxide sensors. Through this study, we have illustrated that the nature of the metal and ligand can affect the sensing performance in aspects such as sensitivity, reversibility, selectivity, and response to moisture. While we are continuously studying the relationship between the chemiresistive behavior and the chemical and electronic structure of 2D MOFs, current results give a basis for future rational design of MOFs that may interact with a specific target.

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Appendix 1. Raw traces of the responses of (a) Ni$_3$(HITP)$_2$, (b) Cu$_3$(HITP)$_2$ and (c) Cu$_3$(HIB)$_2$ to 2000 to 6000 ppm of CO$_2$ at various (20% to 80%) relative humidity levels.
Appendix 2. Other computed interaction modes between CO$_2$ and Cu$_3$(HITP)$_2$ with their respective calculated heat of adsorption values. (a)-(c) show three modes on the surface of the MOF, and (d) and (e) show two modes in the pore. All modes shown here have lower calculated heat of adsorption values than the two modes presented in the main body of the thesis (Figure 7). Cu: yellow; N: blue; C: dark grey; O: red; H: white.
Appendix 3. Powder X-ray Diffraction (PXRD) patterns of (a) Ni$_3$(HITP)$_2$, (b) Cu$_3$(HITP)$_2$ and (c) Cu$_3$(HIB)$_2$.
Appendix 4. SEM images of the deposited MOF materials on the sensor electrodes: (a) Ni$_3$(HITP)$_2$, (b) Cu$_3$(HITP)$_2$, (c) Cu$_3$(HIB)$_2$ and (d) Cu$_3$(HHTP)$_2$. 
Appendix 5. A schematic showing the sensing setup (MFC = mass flow controller).