Dimethyl methylphosphonate Detection Using Zirconium Metal-Organic Framework Functionalized Quartz Crystal Microbalance

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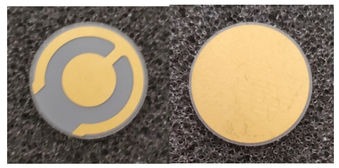
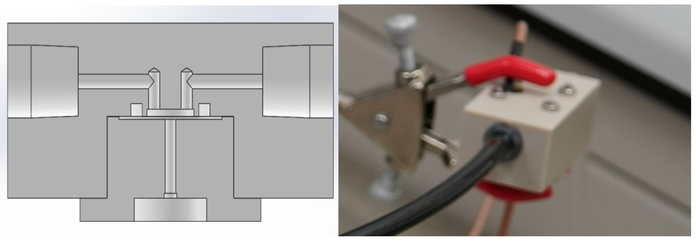
Introduction

- We face numerous challenges in detecting chemical threats both for civilians and our warfighters.
- A simple and rapid microwave synthesis method was developed to grow a thin film of metal organic frameworks (MOFs).
- UiO-66 or UiO-66-NH_2 were grown on unfunctionalized gold and silicon substrates.
- We have expanded this to the functionalization of quartz crystal microbalances (QCMs).
- We exposed our functionalized MOF-QCM to humid N_2 and dimethyl methylphosphonate (DMMP).
- DMMP is both a simulant and a precursor in CWA production and is used in other chemical processes.

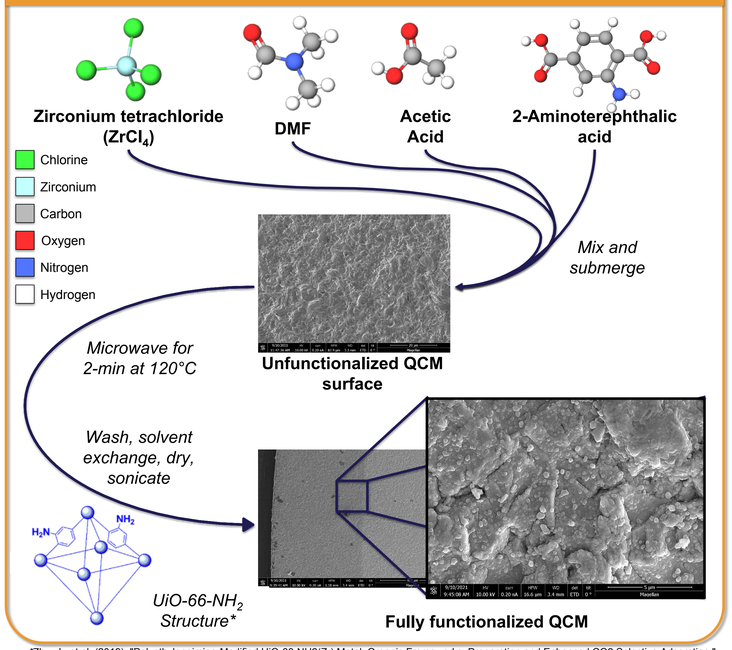


Quartz Crystal Microbalance



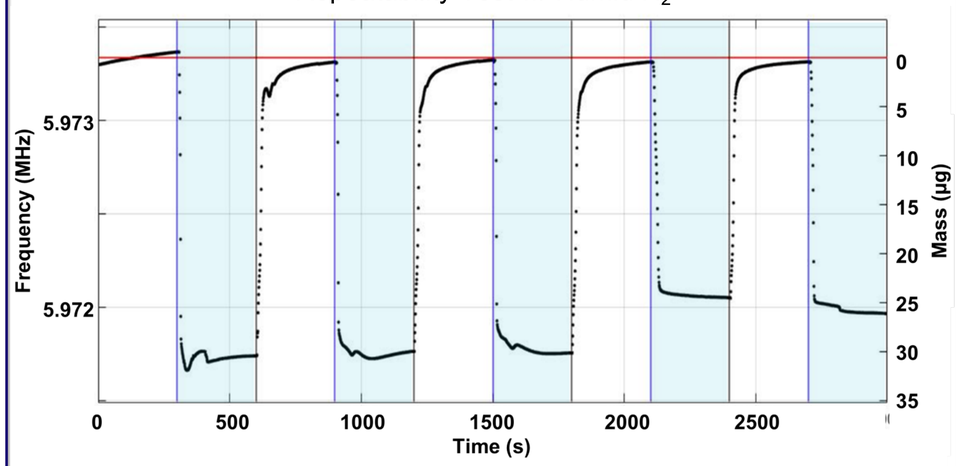
In house designed and manufactured flow cell with detachable QCM holder.

Synthesis



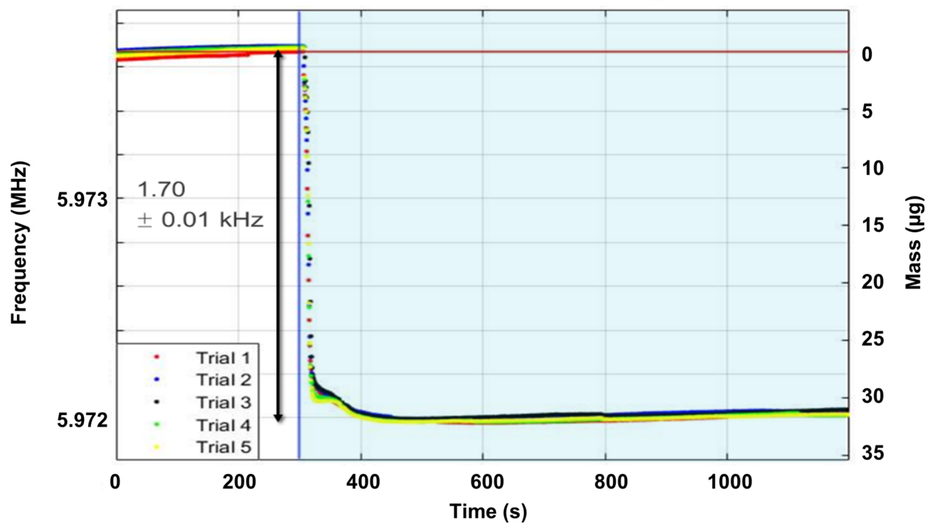
*Zhu, J., et al. (2019). "Polyethyleneimine-Modified UiO-66-NH2(Zr) Metal–Organic Frameworks: Preparation and Enhanced CO2 Selective Adsorption." ACS Omega 4(2): 3188-3197.

Results: Initial Humidity Testing



QCM output data following repeatability testing with water exposure.

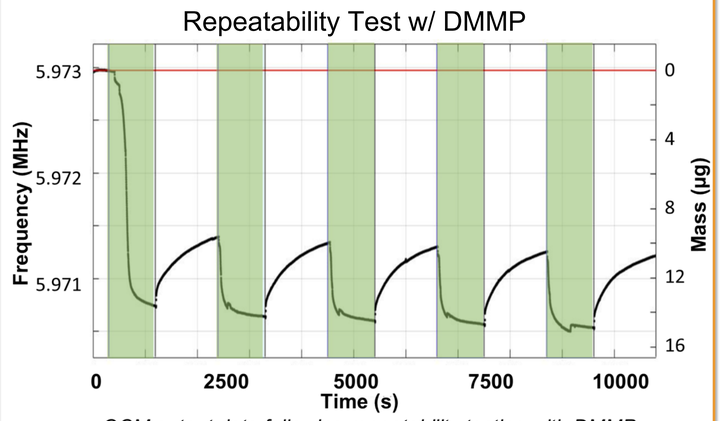
- Bubbler used to add humidity to N_2.
- MOF-QCM used in all trials.
- Baseline found by running pure N_2 for 5 minutes.
- Red line indicates baseline frequency.
- Humid N_2 for 5 minutes, pure N_2 for 5 minutes, 5 cycles.
- Blue highlights indicated humid air passing through the flow cell.
- Nonhighlighted areas indicate pure N_2 passing through the flow cell.
- In the repeatability test we see that prolonged exposure could be causing degradation which is likely the reason we have a lower adsorption on the 4th and 5th cycle.



QCM output data following reproducibility testing with water exposure.

- Baseline with pure N_2 for 5 minutes.
- Humid N_2 for 15 minutes.
- With sufficient time (over 30 minutes of drying) between trials we return to our initial baseline.
- We were able to get similar adsorption levels when starting at the initial baseline.

Results: DMMP Testing

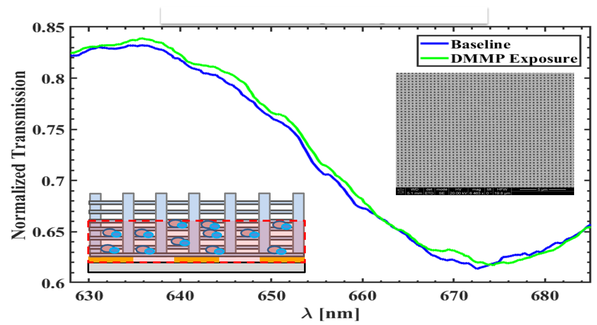


QCM output data following repeatability testing with DMMP exposure.

- DMMP trial run using a Kin-Tek.
- Baseline found by running pure N_2 for 5 minutes.
- DMMP for 15 minutes, pure N_2 for 20 minutes, 5 cycles.
- Green highlights indicated DMMP passing through the flow cell.
- Remarkably, the DMMP exposure shows a difference in desorption rate from the humid N_2 trials.
- This indicates the selectivity our MOF-QCM has to DMMP.
- If we are not able to find a simple and fast method of removing the DMMP we will likely have a precursor to design for a dosimeter instead of a sensor.

Conclusions & Future Work

We have shown successful detection of DMMP using a Zr-MOF functionalized QCM. Further development will investigate functionalizing a more robust sensor using nanohole arrays (NHA). By functionalizing an NHA with the Zr-MOF we hope to detect and quantify a shift in the extraordinary optical transmission (EOT) spectrum when in the presence of DMMP.



i) *spectral shift in EOT from DMMP exposure* ***ii)*** *NHA under SEM*

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