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Major Goals: Briefly, our goals were to grow ultrathin films of ZIF-8 and also attempt to grow HKUST-1 films under ultrahigh vacuum (UHV) conditions. Very little research utilizing surface science tools toward the study of MOFs has been performed previously and such studies could advance the field significantly.

ZIF-8: ZIF-8 is a prototypical zeolitic MOF, in which zinc atoms are coordinated by organic imidazolate linkers, featuring large cavities which are interconnected by narrow windows that allow, in principle, molecular sieving. ZIF-8 has been examined extensively in the literature for separation through molecular sieving and adsorptive removal of specific molecules. In ZIF-8, zinc cations are coordinated to four 2-methylimidazolate ligands, resulting in a hybrid material with sodalite topology (SOD) which is chemically and thermally stable (up to 500 ° C). The sodalite cages possess a pore diameter of 11.6 Å and the aperture between two cages is 3.4 Å. The positions of the metal centers in ZIF structures are quite rigid, but the imidazolate ligands can rotate (flip) around the M-M axis, thereby modifying the size of the pore aperture. This flexibility of the ligands has led to gate opening effects in the adsorption of light hydrocarbons. This gate opening could be induced by gas adsorption or high pressure. Study of MOFs beyond ZIF-8: As stated earlier we will begin our investigations employing the ZIF-8 MOF since this framework has been heavily studied and we believe that we can gain valuable experience with this material. Together with our work on ZIF-8 we will also study the vacuum synthesis of other relevant MOFs, most particularly HKUST-1.

(HKUST-1): The HKUST-1 [M₃(BTC)₂] series of MOFs, where M = Zn(II), Fe(II), Mo(II), Cr(II), Ru(II) and BTC = 1,3,5-benzenetricarboxylic acid, have been widely studied because of their environmental friendliness, relatively low cost, high synthesis yields, and coordinately unsaturated open metal sites as indicated in Figure 1. In particular, the open metal sites in HKUST-1 function as the chemically active centers, and thus, the HKUST-1 series have shown various interesting applications such as selective gas adsorption and separation, hydrogen & methane storage, Lewis acid catalysis, and proton transfer channels. Moreover, it is reported that the HKUST-1 MOF, once damaged, can be easily reconstructed with a simple treatment using ethanol.

(MOF-74): MOF-74 [M₂(dobdc), dihydroxybenzenedicarboxylic acid] (shown in Figure 2) has unsaturated metal centers ideal for the adsorption and catalytic conversion of various gas molecules.

Vacuum Synthesis of UltraThin MOF ZIF-8 Films: Stassen et al. recently employed a chemical vapor deposition technique to deposit ~50 nm thick films of ZIF-8 on ZnO overlayers. Their synthesis was not fully in vacuum [the linker was deposited in air] and there was little mention of the role of water in their growth mechanism (but water very likely plays a critical role). Additionally, their films were thicker than those that we propose to grow and we are hopeful that we can be successful here and advance the field. We believe that we can grow very thin conformal films of desired thickness of ZIF-8 by careful control of substrate temperature and alternating exposure of a ZnO thin film (grown via evaporation) to water vapor and HmIM in high vacuum [see figure above]. We may even be

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able to grow single crystalline films of ZIF-8 using these methods and we will endeavor to accomplish this by employing single crystalline substrates (such as titania) as the template. We believe that careful control of the morphology and structure of these films will allow for more authoritative conclusions in our scientific measurements. The discovery of a viable synthetic method for a MOF may allow integration with microelectronic devices and advanced sensors for soldiers. After gaining experience with ZIF-8 we will move to other relevant MOFs (i.e., the HKUST-1 series).

Accomplishments: We have successfully grown very thin (~15nm) films of HKUST-1 under vacuum employing a combined Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) technique. We believe that these films are amongst the thinnest MOF thin films ever grown under vacuum. We think that we can grow the films even thinner in the future since we use a layer-by-layer (LBL) growth approach, which allows for the possibility of direct control of the thickness of the HKUST-1 thin films. Additionally, we have also experimented with LBL epitaxial wet-synthesis of HKUST-1 grown on a self-assembled monolayer (SAM) which was present on a gold-coated quartz crystal microbalance (QCM). By monitoring the change in frequency of the QCM, we observed that the wet growth technique was able to produce a near perfect coverage of HKUST-1 over the SAM layer. Studies were then performed with the HKUST-1 film covered QCM in vacuum, to show that analyte (ethanol) adsorption was detectable and quantifiable in sub-unit cell thick films of HKUST-1.

Layer-by-Layer Growth of HKUST-1 Thin Films in Vacuum

Layer-by-layer (LBL) growth is a bottom-up approach for growing thin films of MOFs, which can be advantageous for controlling the thickness of the film. This method has been applied to solution-based growth of thin films for various MOFs including HKUST-1 and ZIF-8 based on separated metal precursor and ligand solutions. Recently, solvent-free ZIF-8 films (the thinnest being ~150 nm) have been grown via the conversion of ZnO to ZIF-8 via chemical vapor deposition (CVD) of the ligand of ZIF-8, 2-methyl imidazole (2-MIM), onto the ZnO surface. However, in this case, the growth of ZIF-8 begins at the top layer of the ZnO surface and continues to the inner portions of the ZnO film, a so-called top-down approach. Thus, the diffusion of 2-MIM is a rate limiting step in the conversion of ZnO to ZIF-8. To overcome these type of limitations, we have developed a new MOF thin film growing method under vacuum which is based on the concept of LBL, and it has been successfully employed here for the growth of HKUST-1 thin films.

For the controlled growth of our HKUST-1 films, we used physical vapor deposition (PVD) of Cu using an e-beam evaporator and CVD of trimesic acid, H3BTC, in the vacuum chamber (base pressure of 1.0×10^{-8} torr). Here we follow the fundamental concept of a neutralization reaction of CuO to HKUST-1 ($\text{CuO} + \text{H3BTC} \diamond \text{HKUST-1} + \text{H}_2\text{O}$). To perform this operation, we first filled the chamber with O₂ (2.5×10^{-5} Torr) and H₂O (2.5×10^{-5} Torr). O₂ is an oxidant for Cu, which converts Cu⁰ to Cu²⁺, and H₂O is expected to accelerate the overall reaction by forming hydroxyls (-OH) on top of the Cu_xO_y layer and also stabilize the structure of HKUST-1. SiO₂ (300 nm)/ Si (100) wafers were used as growth substrates. We kept the surface at room temperature (RT) during the growth of the HKUST-1 films, since it is known that Cu surfaces under UHV can dissociatively adsorb O₂ at RT, and also form hydroxyl groups from H₂O on the atomic oxygen covered Cu surfaces near room temperature.

The unit cell of HKUST-1 along the <110> direction can be described as a stack of unit clusters composed of Cu and H3BTC. These unit clusters are aligned with a 1 – 2 – 1 sequence along the <110> direction, and the distance between the center Cu ion to the edge Cu ion in each unit cluster is about 8 Å, which is close to the distance between Cu atoms at 0.25 ML coverage (~7.5 Å when the Cu atom has a 2.56 Å diameter); thus, on the basis of this analysis, we first deposited 0.25 ML of Cu to form the first layer of HKUST-1 and then 0.25 ML of a Cu covered surface was exposed to H3BTC vapor for 5 minutes to react with the deposited Cu atoms. After this, we subsequently deposited 0.5 ML of Cu to form the second layer of HKUST-1 and then exposed the surface to H3BTC for 10 minutes. These two LBL steps were continuously repeated (0.25 ML of Cu \diamond 5 mins of H3BTC \diamond 0.5 ML of Cu \diamond 10 mins of H3BTC \diamond 0.25 ML of Cu \diamond 5 mins of H3BTC \diamond and then repeat), and we were able to preferentially grow the HKUST-1 thin film along the <110> direction. A sample grown by 12 LBL steps which has a thickness of ~15 nm and shows a strong XRD peak at 9.2° of 2θ for the (220) plane of HKUST-1 and a small peak at 18.5° of 2θ for the (440) plane of HKUST-1. Moreover, a sample grown with 20 LBL steps which we expect to be about 25 nm in thickness, shows stronger XRD peaks for the (220) and (440) planes than the sample grown with 12 LBL steps, and it also begins to show a small peak for the (200) plane at 6.7°. The difference in the (220) plane peak intensity between these two cases indicates that thickness control is possible with this growth method.

Compared to the typical XRD patterns for the powder samples of HKUST-1 (shown in the inset of Figure 1b),⁵ which have three strong peaks for (200) at 6.7°, (220) at 9.5°, and (222) at 11.7°, our thin films selectively show a strong peak for the (220) plane, which suggests directional growth of our thin films.

Here we have grown relatively thick films of HKUST-1 (the thinnest being about 15 nm thick) so that we could quickly and easily verify the growths via x-ray diffraction. In the future we will be growing films as thin as possible to explore the limits and characterizing these growths with other techniques including adsorption of target

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molecules.

Wet layer-by-layer epitaxial growth has shown exceptional ability to grown films of MOFs ranging from the nanometer scale to the micrometer scale. Due to the small quantity of material in ultra-thin films, the characterization of ultra-thin films of MOFs has proven difficult using typical laboratory methods (X-ray diffraction, electron microscopy, etc). To this end, we have employed a quartz crystal microbalance (QCM) to buttress current characterization methods. QCMs measure the frequency change of a piezoelectric quartz sensor that result from a change in the mass of the sensor. The relationship between frequency-shift and mass can be shown using the Sauerbrey equation. As a result, QCMs are capable of measuring mass changes on the nanogram scale, which allows us to monitor the mass change due to the growth of ultra-thin films of MOFs on a QCM sensor. Ultra-thin films of HKUST-1 were grown on a 6 MHz gold coated QCM crystal (Maxtek, Inficon USA). The gold coated surface of the QCM crystal was exposed to a .35 mM ethanolic solution of 11-mercapto-1-undecanol for 24 hours to grow a uniform thiol-based self-assembled monolayer (SAM). The HKUST-1 MOF was then grown on the SAM functionalized crystal via a solution-based LBL procedure.⁶ The substrate was first dipped in a 1mM solution of Cu (Ac)₂ for 30 minutes. After 30 minutes, the crystal was removed, rinsed with ethanol, and dried under nitrogen. Subsequently, the crystal was dipped in a 0.1 mM solution of benzene tricarboxylic acid in ethanol for 1 hr. After the 1 hr, the crystal was removed, rinsed with ethanol, and dried under nitrogen. The process was then repeated for thicker film growth (one cycle corresponds to 1/8 unit cell).

The growth of a quarter unit cell (2 cycles) thick film was performed on a QCM crystal. Frequency measurements were taken with the QCM before and after SAM and HKUST-1 growth. The closeness of the mass and density ratios suggest a near complete coverage of the SAM with HKUST-1. By extending growth times, we aim to increase the surface coverage. X-ray diffraction further supports the uniform growth of varying thicknesses of HKUST-1 on a SAM-modified surface.

Preliminary adsorption studies were then performed to test the viability of the QCM set up to analyze the interaction of sub-unit cell HKUST-1 with CWA simulants. Moving forward, we will perform studies with other CWA simulants under more controlled conditions to gain insight into adsorption and diffusion behavior as a function of film thickness.

Training Opportunities: Two graduate students worked on this 9-month project and both learned a great deal and underwent much training. Both students were trained in x-ray diffraction studies, vacuum techniques, scanning electron microscopy, and quartz crystal microbalance methods. Both of the students were very involved in the synthesis of the ZIF-8 and HKUST-1 MOFs.

Results Dissemination: We are currently preparing an archival journal article describing our results but the paper is not yet finished (we believe the paper will be submitted prior to the end of calendar year 2018).

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to report here yet but we think the work will eventually lead to technology transfer related to sensors for chemical warfare agents.

PARTICIPANTS:

Participant Type: PD/PI

Participant: Charles Buddie Mullins

Person Months Worked: 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Sungmin Han

Person Months Worked: 9.00

Project Contribution:

Funding Support:

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International Collaboration:
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Participant Type: Graduate Student (research assistant)

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Funding Support:

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Participants regarding ARO **Contract Number:** W911NF1710214

PI – Charles Buddie Mullins (no salary provided – worked part-time on the grant for 9 months)

Graduate Student – Mr. Sungmin Han (partially supported for 9 months – Mr. Han was also supported via a fellowship from UT-Austin during this period).

Graduate Student – Mr. Ryan Ciufo (fully supported for 9 months by this grant).