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RPPR Final Report
as of 03-Jan-2019

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Major Goals: Objective: Metal Organic Framework (MOF) materials are a highly porous class of materials with an unparalleled degree of tunability and range of chemical and physical properties. As a result they have a large potential for use as sensitive and selective chemical sensors particularly for the detection of gas and vapor phase analytes. These properties may be further enhanced is the MOF materials are formed into complicated 3D structures. Additive manufacturing (i.e. 3D printing) may prove to be a useful tool in the fabrication of MOF materials into optical shapes.

The specific goal of this project is to develop methods, materials and processes to 3-Dimensionally (3D) Print Metal Organic Framework (MOF) materials onto substrates and into 3D structures.
During this proof-of-concept efforts methods will be developed to 3D print samples of MOF materials onto a suitable substrates and into 3D structures.

Task I: Material development
During this task we will develop methods to identify suitable binders for ink formulation, mixing, ratios, print speed and drying rates. Following method development, ECBC will provide candidate MOF materials for 3D printing, examples of these materials are UiO-66 MOF and HKUST-1 MOF.

Task II: 3D Printing using micro-dispensing technology
After suitable ink formulations and have been developed we will print the candidate materials onto a suitable substrate and into simple 3D structures (such as cylinders and cubes). The printing will be done using our nScrypt micro-dispensing printer. Exact size and shapes for 3D printing will be determined collaboratively between UDEL and ECBC.

Task III: Material Characterization
ECBC will characterize the printed materials by using Scanning Electron Microscopy (SEM) and studying the MOFs ability to degrade or capture PH3 gas. Follow-on work may be necessary to optimize binder selection, binder-to-mof ratios, MOF composition, reactivity or other parameters.

Accomplishments: 1. We successfully employed three different methods for sintering of UiO-66 MOF particles. Any one of these techniques has certain advantages depending of the target applications. Solvo-thermal and facile synthesis methods allow for uniform size particles, but due to strong cross-linking between also formed large clusters which were not easy to break. This made it difficult to disperse the MOF in a polymer solution. The green method has several important advantages: no harmful chemicals are used during the sintering process; sintering is less time consuming in comparison to other methods; it is quite easy to scale up to large volume production; and the cost of produced MOFs is much lower due to the low cost of the base chemicals. As a result, for future studies we recommend the green method as a first choice for large scale fabrication of MMMs.

2. We developed a technology for dispersing MOF particles within a polymer solution. During these experiments we overcame several technical challenges as described in Section 3 of this report. Due to the short time duration of this project we were unable to perform and test all possible modifications of MOF/polymer “ink” preparation technique. For the future additional equipment may be needed such as a rotational evaporator operating in vacuum and more powerful mixing devices such as strong vibrational mixer and ball milling shaker.
3. We proved that the 3D printing of MOF is possible. Depending on the specific application area we can advice on the use of the most appropriate MOF materials. For example, materials from series MOF-74 such as Co-MOF-74 and Mn-MOF-74 are best candidates for phosphine gas adsorption. Another matrix polymers also can be examined. For example the soluble thermoplastic polyimide Matrimid possesses very high glass transition temperature and excellent high temperature properties for use in structural composites which have to work at high temperature environment.

Training Opportunities: Nothing to Report

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Honors and Awards: Nothing to Report

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Technology Transfer: The work was done in collaboration with the Army's Edgewood Chemical Biological Center. The processes and results have been shared with the ECBC sponsor.

PARTICIPANTS:

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Person Months Worked: 1.00 **Funding Support:**
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RPPR Final Report
as of 03-Jan-2019

Final Technical Report
W911NF1720035

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Title of Project: **“**3D Printing of Metal Oxide Framework (MOF) Materials**”**

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1. Introduction

Metal organic frameworks (MOFs) have emerged as a new type of functional materials and can be constructed by an infinite number of metal/ligand combinations [1]. These materials are also known as porous coordination polymers (PCPs), class of crystallized porous polymeric materials formed by the coordination of metal ions/clusters and organic bridging ligands. The ability of coordination between the metal ions with different linker in MOF frameworks system generate high possibility to control the properties of the resulting MOF. Therefore, this is one factor that allows the MOF to be designed in accordance with the desired properties and applications [2]. Some applications of MOF has been widely reported, such as a hydrogen storage, the separation of gas molecules, and catalysts.

The specific goal of this project, supported by Edgewood Chemical Biological Center (ECBC), was to develop methods, materials and processes to 3-Dimensionally (3D) Print Metal Organic Framework (MOF) materials onto substrates and into 3D structures. The targeted application for the MOF composites is phosphine gas absorption. Our preliminary literature search showed that the best candidates for this application are materials from the series MOF-74, especially Co-MOF-74 and Mn-MOF-74 [3]. During our initial discussions with the sponsor we decided to start our study effort using UiO-66 MOF material as filler in the composites in order to proof the possibility of 3D printing. UiO-66 is an archetypal zirconium-based metal−organic framework (MOF) that is constructed from hexanuclear zirconium oxide clusters as secondary building units (SBUs) and 1,4-benzenedicarboxylate (bdc) linkers. The main reason for this choice was that this material is widely studied, both as methods of synthesis and procedures for fabrication of Mixed-Matrix Membranes (MMMs) using different types of polymers.

2. UiO-66 samples preparation and characterization

During this effort we experimented with three different methods for sintering UiO-66, described in the literature. For some methods minor modifications were made to the process in order to improve the MOF/Polymer mixing properties.

All reagents and solvents unless otherwise stated were obtained from commercial sources (Fisher Scientific, Alfa Aesar and Sigma Aldrich) and were used without further purification.

2.1. Solvothermal method for synthesis

Zirconium(IV) chloride (ZrCl4) (61 mg, 0.26 mmol) and terephthalic acid (43 mg, 0.26 mmol) were dissolved in 15 mL DMF with 0.447 mL glacial acetic acid in a 20 mL vial. The capped vial was placed in an oven and heated to 120 °C for 24 h. Product was collected by centrifugation, washed three times with DMF, and soaked in methanol at 60 oC for three days with replacing the soaking solvent every 24 hours to exchange DMF. After cooling to room temperature, the particles were collected by centrifugation (fixed-angle rotor, 4000 rpm, and 30 min), washed with

3×10 mL portions of MeOH (each time for 24 hours), and dried under vacuum at room temperature [4]. It is seen that this sintering method is quite time consuming. The yield of single run is approximately 40-50 mg UiO-66 per one vial. Initially we used 2 vials for one run and it took 4 weeks to obtain enough sample for XRD and SEM characterization (Sample S1). Later we used 8 vials and the yield increased up to ~300 mg per run (Samples S2-S6). For these samples we performed XRD studies as shown in Figure 1 to evaluate their chemical compositions. All six samples show the expected spectral features for pure UiO-66 MOF structure. One of the spectra (for sample S1) is presented in Figure 1, together with samples S7,S8, and S9, which will be described in 2.2 section of this report.

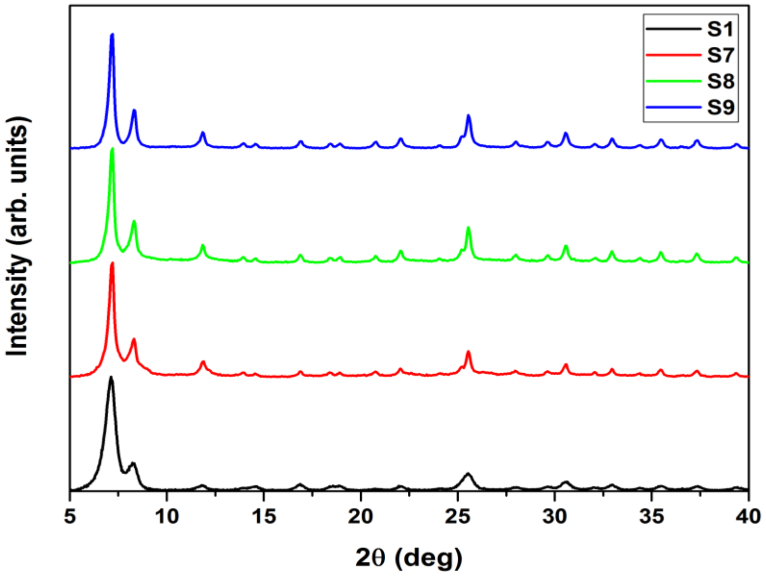

Figure 1. XRD spectra of 4 UiO-66 samples, described in the report (see text)

2.2 A facile synthesis of UiO-66

A scalable, reproducible method of synthesizing UiO-66 type MOFs, entailing the addition of HCl to the reaction mixture, has been described in reference [4]. The new sintering protocol requires a fraction of the time in comparison to solvothermal method, yields exceptional porosities, and works with a range of linkers. The later could be very useful for fabrication of MMM structures. We employed this method for fabrication of UiO-66, but did not explore linker's technique as described in the article. This may be done in a next stage of MMM fabrication if it will be required by the sponsor.

In our first attempt (Sample 7) we examined the utility of concentrated hydrochloric acid (HCl) in the formation of UiO-66 type MOF. Reproducible results were obtained when a half-filled 20 dram vial containing a 1: 1.4 molar ratio of ZrCl4 (1.1 mmol pre-dissolved in 5:1 v : v DMF:HCl) to benzene-dicarboxylic acid (H2BDC; pre-dissolved in 20 mL DMF) was heated at 80^0C overnight. A fine white powder starts settling after several hours and is well settled after 24 hours period of heating. Thus, removing a sufficient part of the solvents is much easier just soaking them by appropriate pipette. Most probably the role of the HCl is either to condition the solvent (N,N-dimethylformamide, (DMF) by neutralizing basic impurities (amines) and/or to assist in forming hexa-Zr clusters prior to linker binding. Next 3 samples (S8, S9 and S10) were obtained by 20-fold scaling up the sintering process. No noticeable charge in product crystallinity or porosity were exhibited (see XRD spectra in Figure 1). XRD spectra of these samples were independedly measured by the sponsor's team (ECBC). Results are practically the same as ours.

Shapes and size distribution of UiO-66 obtained in this experiment were examined by SEM. The pictures obtained at different magnifications are shown in Figure 2 and Figure 3 for sample S7 and and S10, respectively. It is clearly seen that single particles are submicron size and spherical shape. Large number of particles tend to cluster of much larger sizes (see top pictures on both figures) doe to linking between their polymeric cores This behavior is well known and commented in the literature.

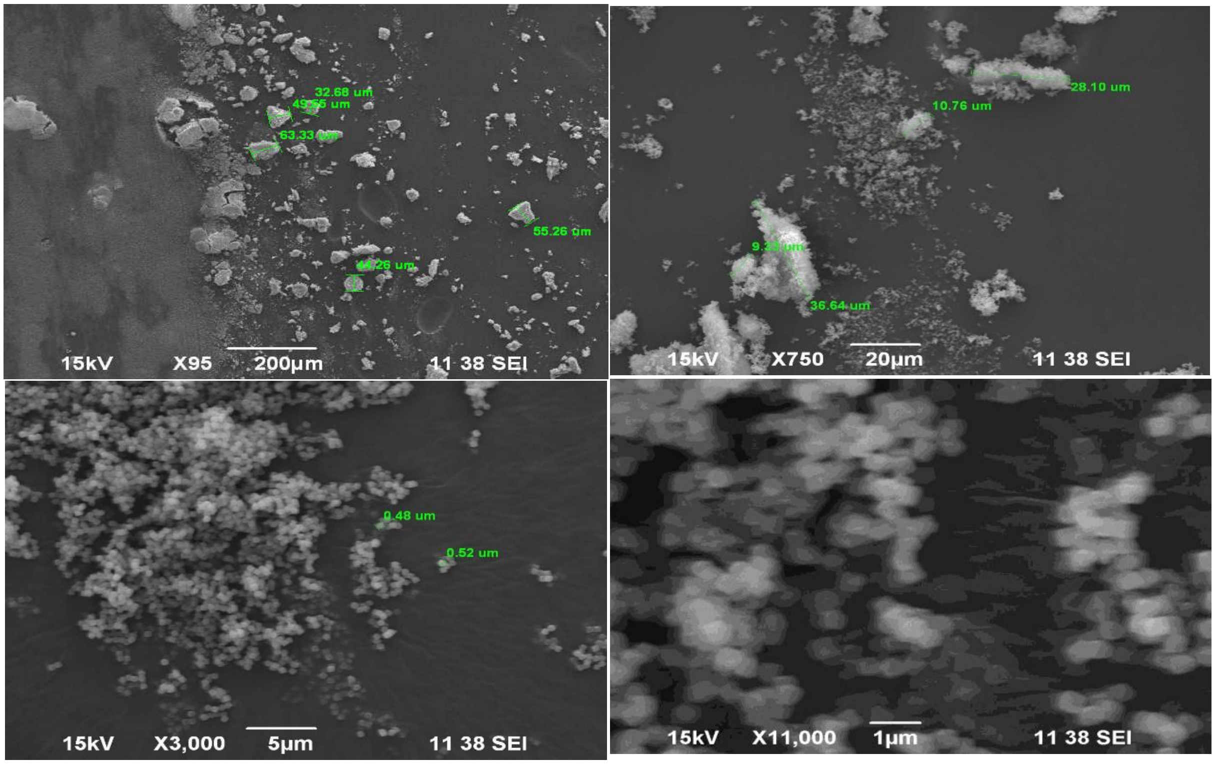

Figure 2. SEM images of S7 sample particles at different scales

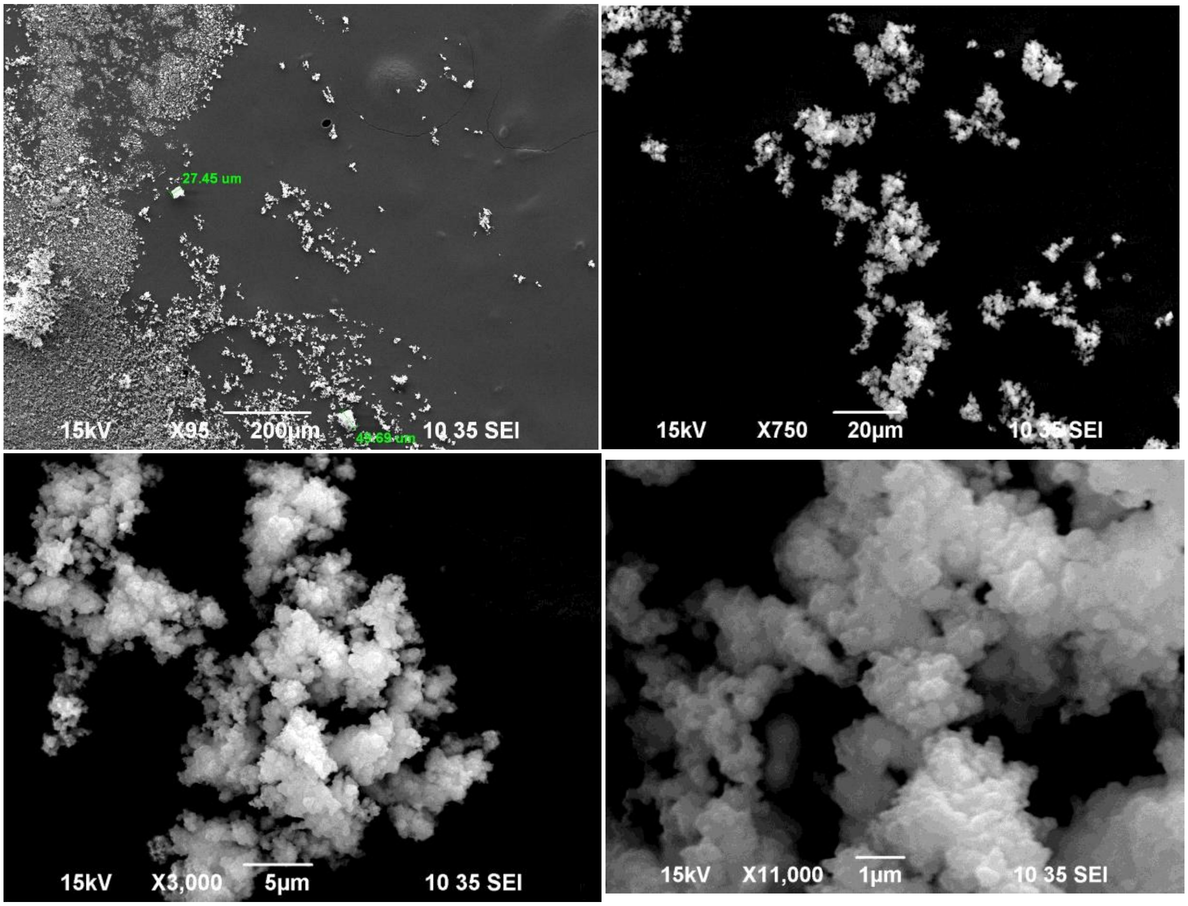

Figure 3. SEM images of S10 sample particles at different magnification scales

Unfortunately, particle's clustering causes serious problems when one try to embed them in a polymer solution matrix in order to produce ink for 2D or 3D printing. We will address this issue further in this report

2.3 Green Synthesis of UiO-66

Distilled deionized water is a reaction medium for this synthesis. The major drawback of the sintering methods based on use of DMF and similar solvent is that the employed amides are flammable, toxic and teratogenic. The main advantage of green synthesis techniques, in comparison to methods described above, is that the transfer of MOFs is easier because multiple washing procedures are no longer needed. In addition this method is more scalable to large volume MOF manufacturing. Lastly, the run time is significantly shorter, allowing for an increase in productivity.

We made two attempts to accomplish green synthesis of UiO-66. Initially 2.4 g (13.3 mmol) 2-aminoterephthalic acid (H2BDC), 7.1 g (20 mmol) Zr(SO4)2·4H2O, 100 mL H2O and 1 mL formic acid were heated at 94^{0}C for 16 h in a pyrex glass bottle placed in an oil bath. After cooling down to room temperature, the mixture was filtrated, washed with water and acetone and dried under ambient conditions. The yield of this synthesis method was 8.6 g. In a second run we doubled the amounts of all chemicals and were able to double the yield.

The green synthesis experiment was carried out at the very end of the contract period. As a result, we were unable to perform any structural or morphology studies on these two samples (marked as S11 and S12 respectively) by XRD and SEM. However, these two samples were delivered to the sponsor at ECBC for further characterizations.

3. MOF-polymer mixed matrix membranes (MMMs) and "inks" for 2D casting and 3D printing.

Our goal in this task was to embed the UiO 66 MOF powder within a polymer solution forming an appropriate ink for 2D casting and 3D printing. Based on the thermo-plastic properties and suggestions found in the literature we used polyvinylidene fluoride (PVDF) as a basic polymer for ink formation.

The process began by first preparing a polymer solution by dissolving 15 mg PVDF in 200 ml of DMF (7.5 wt% PVDF). The mixture was then sonicated for 45 min in 60^{0}C water bath or until the material became completely transparent. Next, 150 mg of dry MOF powder was dispersed in 5 mL of acetone with bath sonication for 30 min in a scintillation vial. Then 1.0 g of PVDF solution was added to the MOF suspension so that the final MOF:PVDF ratio was 2:1 w/w. The combined MOF/PVDF suspension was then sonicated for 30 min in an ultrasonic bath, after which the acetone was removed by evaporation, resulting in a MOF 'ink' (MOF and PVDF in DMF).

The ink was hand casted onto films of Al foil, Al sheet, or glass substrates by drawdown coating with a glass rod using a spacer thickness of 300-400 µm. The coated films were then heated to remove any remaining solvent (1 h in an isothermal oven set at 70 °C). It should be noted, that immersion in solvent (acetone or MeOH) resulted in rapid delamination of the MMMs. Delamination of the film in the aforementioned solvents is likely due to swelling of the PVDF, resulting in a morphological change at the MMM/substrate interface and consequent release. Sufficient roughening of the substrate surface prior to film deposition enhances substrate adhesion of the film, effectively inhibiting delamination.

For all attempts to fabricate MMM samples we used the MOF sintered by the facile synthesis method. Two SEM images of the top surface of one of the first films based on approximately 66 wt% of S8 UiO-66 powder in PVDF is presented in Figure 4. It is seen that the film is not perfect. There are several defect features, which need to be addressed in order to improve the quality of the ink, especially when it will be used for 3D printing:

a) Particle distribution is not uniform;

b) Some agglomeration of particles in relatively large clusters is seen;

c) Some micro cracks are formed most probably due to the shrinkage of the film during drying.

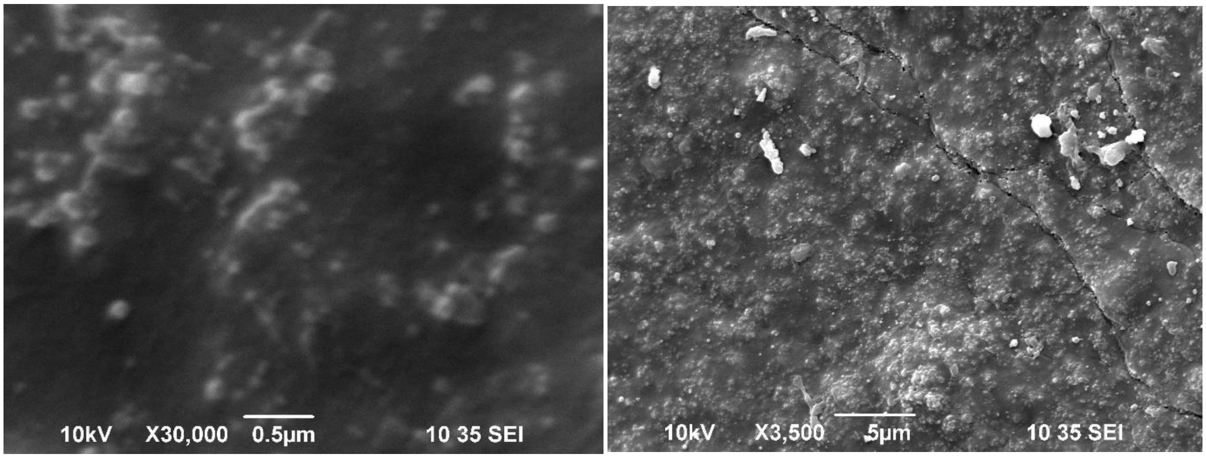

Figure 4. SEM images of top surface of casted film (made of S8 MOF particles) at different magnification.

This means that several modifications of our fabrication process must be done in order to achieve required properties of the ink for use in 3D printing process.

First, MOF particles mixing in acetone followed by mixing in polymer solution is not effective enough. As made MOF powder contains many particle clusters which are not broken during the mixing process. In order to achieve more homogenous mixing we used a high frequency powerful shaker for additional separation of particles in the clusters and uniformly distribution in the solvents.

Second, evaporation of acetone in the air is not effective. We are not able to achieve pure PVDF/MOF solution in DMF, dense enough for use in the 3D printing process. As result some cracks are formed in the casted films, due to the strong shrinkage of the deposited ink. Another undesired effect of the low density of the polymer mixture is the observed changes in the vertical powder distribution in the vials, because particles tend to settle down and form large clusters again. The thinner the ink is, the faster this cluster formation appear. In order to avoid this effect we tried to improve acetone evaporation process. The best way to do this is to use rotational evaporator in vacuum or lower pressure. Unfortunately, we did not have this technique available and tried to increase the ink density by heating the solution and mechanically rotate the vial tilted at approximately 45 degree of vertical. This lead to obtaining much dense ink suitable for printing.

Third, there are some issues in the printing process itself. As DMF evaporated very slowly at RT, we decided to use heated substrate. Other way the printing process will take a very long time as to deposit second layer, the first layer must be dry. This is especially necessary if small size structures are printed. But from the other side the heated substrate cause another kind of troubles – the printing syringe outlet get also heated and can be blocked by dense ink. In the first attempt substrate was heated up to 60^0C and we were able to deposit only one layer on the heated substrate. In our second experiment we prepare most dense ink and printed it on substrate heated just to 40^0C, achieving seven layers printed in the shape of small ring. The picture of printed ring is shown in Figure 5. Thus, we have proven that 3D printing is possible and we have the knowledge what to improve in the ink fabrication process in order to scale up 3D printing and make it robust and faster.

4. Conclusions and recommendations

We are confident that we successfully demonstrated the ability to synthesize MOF based inks useful for 3D printing. In future efforts we will work to improve the 3D printing methodology to create fine featured samples. Our experience working on the current effort can be summarized in the following conclusions and recommendations for the work in the future.

1. **We successfully employed three different methods for sintering of UiO-66 MOF particles.** Any one of these techniques has certain advantages depending of the target applications. Solvo-thermal and facile synthesis methods allow for uniform size particles, but due to strong cross-linking between also formed large clusters which were not easy to break. This made it difficult to disperse the MOF in a polymer solution. The green method has several important advantages: no harmful chemicals are used during the sintering process; sintering is less time consuming in comparison to other methods; it is quite easy to scale up to large volume production; and the cost of produced MOFs is much lower due to the low cost of the base chemicals. *As a result, for future studies we recommend the green method as a first choice for large scale fabrication of MMMs.*
2. **We developed a technology for dispersing MOF particles within a polymer solution**. During these experiments we overcame several technical challenges as described in Section 3 of this report. Due to the short time duration of this project we were unable to perform and test all possible modifications of MOF/polymer “ink” preparation technique. For the future additional equipment may be needed such as a rotational evaporator operating in vacuum and more powerful mixing devices such as strong vibrational mixer and ball milling shaker.
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