Zr-Based UiO-66 MOF Thin-Film Synthesis on Silicone Substrate via Solvothermal Method

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Abstract

UiO-66 metal–organic framework (MOF) thin films have been increasingly attractive due to their potential in surface-integrated device applications. This study focuses on the solvothermal synthesis of Zr-based UiO-66 thin films directly on silicone substrates. Using modified conditions based on Miyamoto et al. (2015), the author aimed to develop a reproducible method to produce high-quality UiO-66 MOF thin films. Characterization by FTIR and XRD suggested the formation of UiO-66 powder. However, thin film formation remained incomplete, likely due to insufficient surface nucleation. Future work will explore substrate surface modification and advanced growth techniques to enhance thin film uniformity and adhesion.

INTRODUCTION

Metal–organic frameworks (MOFs) are materials composed of metal ions or clusters connected to organic linkers. These components are joined by coordination bonds to form an ordered, cage-like structure. This structure allows MOFs both highly porous and crystalline, giving them a very large internal surface area.[1]

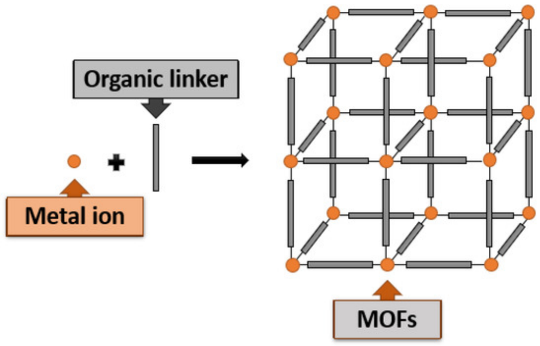

Figure 1. Schematic diagram of MOF synthesis process[3]

Their structures can also be adjusted through the coordination between metal ions and organic linkers, offering both structural versatility and functional adaptability.[2] This metal–linker coordination defines geometric properties (e.g. pore size, shape, framework structure) and chemical properties (e.g. polarity, affinity toward guest molecules, and potential for post-synthetic modification).[4] This tunability has led to the synthesis of thousands of MOF frameworks to date, supporting a wide range of applications, including gas storage and separation, adsorption, catalysis, chemical sensing, and membrane-based separations. By carefully selecting suitable metal-linker combinations, MOFs can be engineered to exhibit properties aligned with the demands of their intended applications.[2]

MOFs are most commonly synthesized via solvothermal methods, producing powder (bulk) materials. However, bulk powders face limitations for direct device integration due to their lack of controlled orientation and substrate contact. Consequently, recent research has increasingly focused on MOF thin films, which offer advantages such as controlled thickness, tailored crystal orientation, and well-defined interfaces. These characteristics are essential for surface-integrated applications, where performance depends heavily on interface quality. Achieving thin films with smooth surfaces and low defect densities has therefore become a central objective in MOF thin film fabrication.[4]

One limitation of many MOFs is their poor chemical stability, which depends largely on factors such as the metal-ligand bond strength, hydrophilicity/hydrophobicity, crystallinity, and nature of the metallic centres.[5] MOFs are commonly classified into families such as UiO, HKUST, MIL, and ZIF. Among these, the UiO series is notable for its exceptional chemical, mechanical, and thermal (up to 500 °C) stability, attributed to its zirconium-based framework. According to the hard-soft acid-base (HSAB) principle, the strong Zr–O bonds are due to the hard-acid of Zr(IV) and the hard-base of carboxylates, yielding a high bond strength.[6] UiO-type MOFs also exhibit versatility through post-synthetic modification and incorporation of functional guest molecules. In particular, UiO-66, formed from $ZrCl_4$ and terephthalic acid (H_2BDC), features the $[Zr_6O_4(OH)_4(BDC)_6]$ cluster. Due to zirconium having a +4 charge, it requires negatively charged ligands to balance the charge. These ligands link zirconium atoms together into a strong, tightly packed framework. This highly interconnected network shields the zirconium from reactive species, thus providing excellent structural stability.[7]

MOF thin films formation approaches include layer-by-layer (LBL) deposition, reactive electrodeposition, microwave-assisted thermal deposition, and hydro/solvothermal synthesis. These approaches aim to create a continuous film with randomly oriented grains. In contrast, oriented thin-film methods, such as Langmuir–Blodgett and liquid–air interfacial assembly, focus on aligning MOF crystals along a specific crystallographic direction.

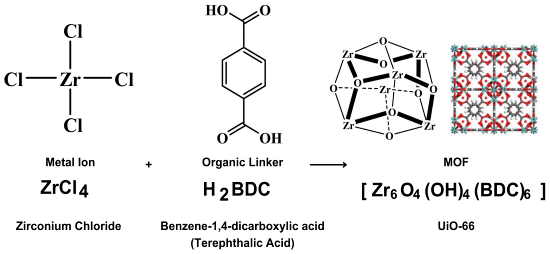

Figure 2. Schematic Diagram of the structure and synthesis of UiO-66 (Modified from Ref [8])

Among all techniques, hydro/solvothermal synthesis is most common due to its simplicity, minimal equipment requirements, and ability to produce highly crystalline films.[1] It involves dissolving metal precursors and organic linkers in a solvent, then heating the sealed mixture under high temperature and pressure for several hours to days. This allows for control over solvent choice, temperature, and reaction time.[7] The use of modulators, often carboxylic acids, such as acetic acid, competes with the linker for coordination sites, slowing nucleation and stimulating the growth of larger, more crystalline particles.[5] Particle size, defects, and crystallinity can be further tuned by modulating other factors such as temperature and the metal:linker ratio.[9]

While UiO-66 MOF powder synthesis is well established, there are few studies on UiO-66 MOF thin films. This study aims to develop a reproducible solvothermal method for high-quality Zr-based UiO-66 MOF thin films on silicone substrates.

MATERIALS AND METHODS

The synthesis followed the solvothermal growth approach of Miyamoto et al. (2015) with minor modifications, producing UiO-66 MOF thin films. $ZrCl_4$ (26.6 mg), H_2BDC (18.6 mg), acetic acid (3.21 mL), and water (2.02 µL) were dissolved in 13.02 mL of DMF to obtain a precursor solution with a molar ratio of 1 $ZrCl_4$: 1 H_2BDC : 500 acetic acid : 1 water : 1500 DMF. $ZrCl_4$, H_2BDC, and DMF were first mixed on a magnetic stirrer until fully dissolved. Afterwards, acetic acid and water were added and the solution was stirred further.

Silicone wafers, used as substrates, were cleaned sequentially with acetone, isopropanol (PLA), electronic laboratory (EL) acetone, and EL isopropanol, then stored in a desiccator to avoid moisture adsorption. The wafers were placed (glossy side facing up) in a pressure-resistant container, and the precursor solution was added. The sealed pressure-resistant container was heated at 120 °C for 12 hours in an electric furnace. After cooling to room temperature, the substrates were removed, rinsed gently with DMF, and dried in open air.

RESULTS AND DISCUSSION

The solvothermal treatment yielded a white paste. To separate the white paste from the solvent, the mixture was centrifuged at room temperature for 20–25 minutes at 8000 rpm. The recovered white paste was then dried at 50 °C for 5 hours to obtain the final product of a dried white paste.

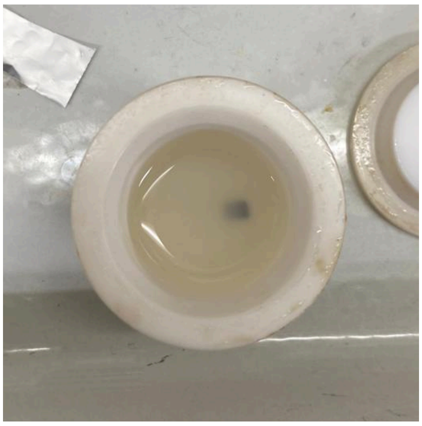

Figure 3. Substrate and Solvent After Solvothermal Treatment

Figure 4. White Paste After Solvothermal Treatment

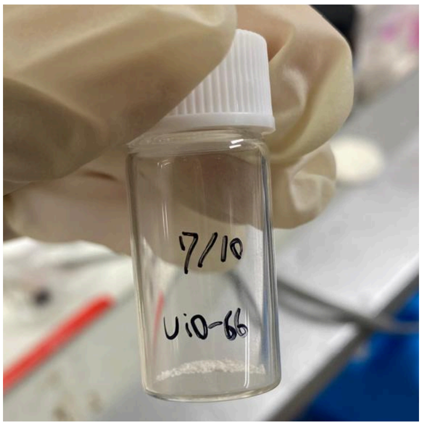

Figure 5. Dried White Paste After Solvothermal Treatment

After the solvothermal treatment, the obtained samples were characterized using Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). FTIR was used to identify functional groups by analyzing characteristic absorption peaks in the transmittance spectra, which reveal the types of chemical bonds present. XRD was employed to determine the crystalline structure of the synthesized UiO-66 thin films.

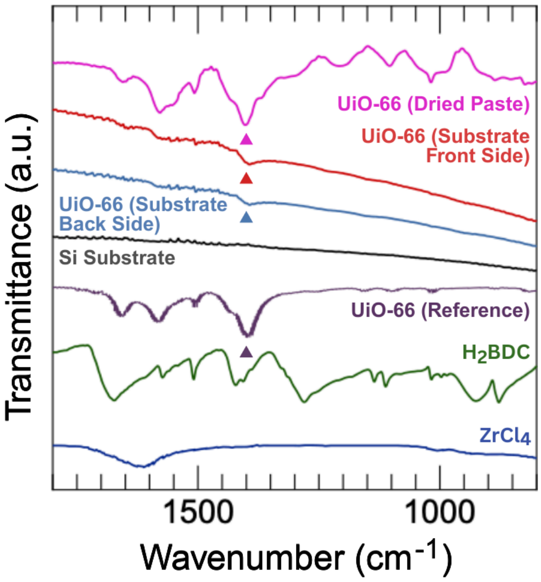

Figure 6. IR Spectra of UiO-66 Trial 1 with a molar composition of 1 $ZrCl_4$: 1 H_2BDC : 500 acetic acid : 1 water : 1500 DMF

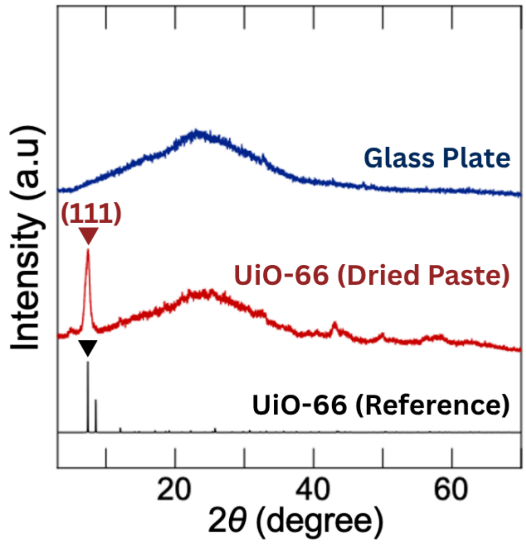

Figure 7. XRD pattern of UiO-66 Trial 1 with a molar composition of 1 $ZrCl_4$: 1 H_2BDC : 500 acetic acid : 1 water : 1500 DMF

As shown in Figure 5, slight peaks (marked by triangles) appear on the substrate's both front and back sides, as well as in the dried paste, all corresponding to the symmetric carboxylate (COO^-) peak characteristic of UiO-66. In Figure 6, the XRD pattern of the dried paste shows a single prominent peak, the (111) reflection, matching the UiO-66 reference. From both IR and XRD observations, the results indicate a possible UiO-66 synthesis, with the white dried paste being consistent with UiO-66. This suggests that the paste showed partial adhesion to the silicone substrate, but coverage was uneven, which is possibly due to an insufficient $ZrCl_4$:H_2BDC molar ratio that limited nucleation. To improve coverage, subsequent trials increased the molar ratio to 2:2 (trial 2) and 5:5 (trial 3). According to Shearer et al. (2014), increasing the ratio may enhance nucleation.

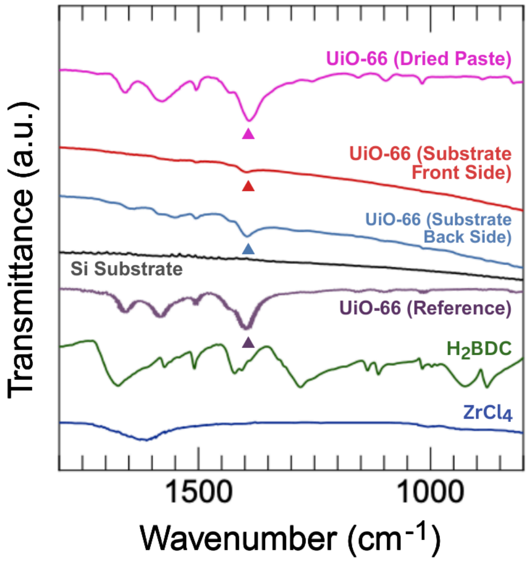

Figure 8. IR Spectra of UiO-66 Trial 2 with a molar composition of 2 $ZrCl_4$: 2 H_2BDC : 500 acetic acid : 1 water : 1500 DMF

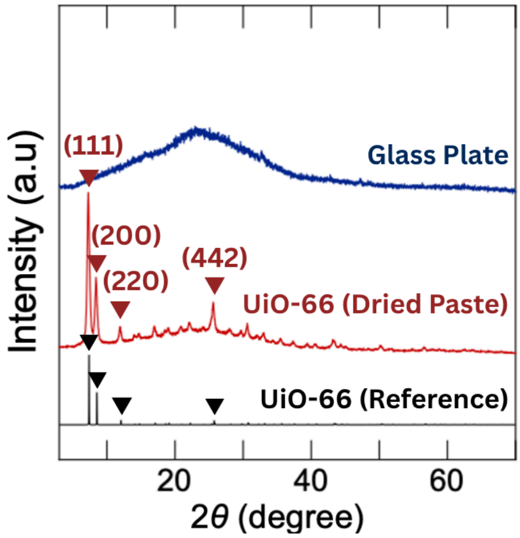

Figure 9. XRD pattern of UiO-66 Trial 2 with a molar composition of 2 $ZrCl_4$: 2 H_2BDC : 500 acetic acid : 1 water : 1500 DMF

As shown in Figure 7, IR spectra again reveal slight peaks (marked by triangles) for both substrate surfaces and the dried paste, corresponding to the symmetric carboxylate (COO^-) peak of UiO-66. The XRD pattern exhibits four peaks, namely (111), (200), (220), and (442), consistent with the UiO-66 reference, showing improved crystallinity compared to Trial 1.

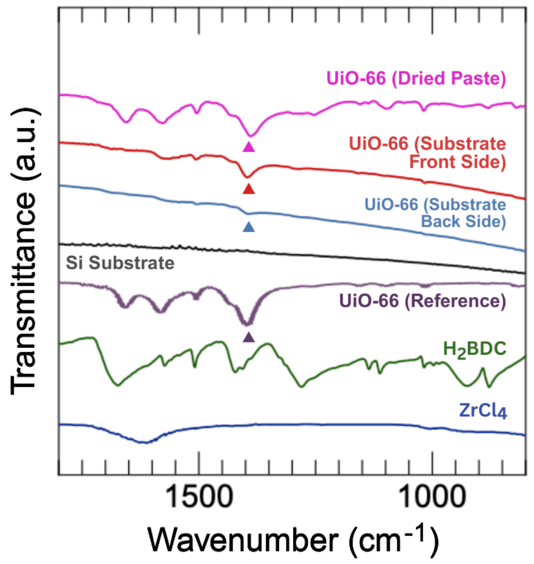

Figure 10. IR Spectra of UiO-66 Trial 3 with a molar composition of 5 ZrCl$_4$: 5 H$_2$BDC : 500 acetic acid : 1 water : 1500 DMF

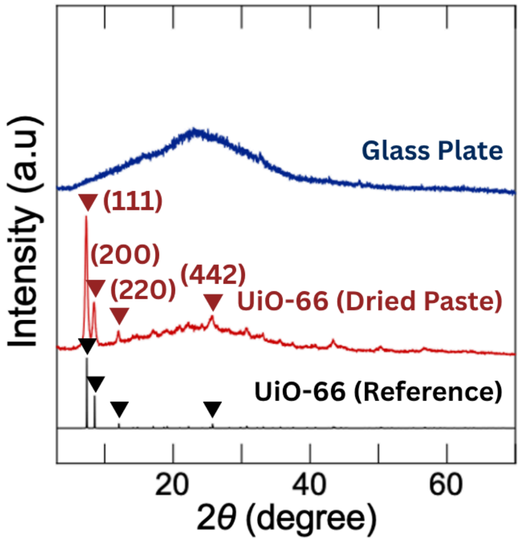

Figure 11. XRD pattern of UiO-66 Trial 3 with a molar composition of 5 ZrCl$_4$: 5 H$_2$BDC : 500 acetic acid : 1 water : 1500 DMF

Similarly, Trial 3 produced IR spectra consistent with UiO-66, as the IR spectra show the same symmetric carboxylate peaks (marked by triangles in the figure). The XRD pattern for Trial 3 also confirms the UiO-66 formation, displaying the (111), (200), (220), and (442) reflections consistent with the UiO-66 reference.

The FTIR and XRD results suggest the synthesis of UiO-66 powder, as evidenced by the characteristic symmetric carboxylate peaks and matching diffraction reflections. However, the dried white paste showed uneven adhesion on the silicone substrate, suggesting that continuous thin film formation was not achieved. This limited coverage may be affected by insufficient precursor molar ratio and limited nucleation. Increasing the ZrCl$_4$:H$_2$BDC molar ratio from 1:1 to 2 variants: 2:2 and 5:5 enhanced crystallinity, demonstrated by the presence of additional XRD peaks and a more clear IR peaks. Nonetheless, uniform film formation remained inadequate, indicating that factors beside precursor concentration play a role in thin film growth.

CONCLUSION AND FURTHER WORK

Further research should focus on the variation and optimization of parameters, such as the precursor molar ratios and modulators like acetic acid and water, may refine the synthesis process, as modulator components can influence nucleation and crystal growth of UiO-66 crystallinity.[1]

Further characterization techniques, such as SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy), are necessary to evaluate film morphology and uniformity. [1, 11] Moreover, the limited nucleation observed suggests substrate surface properties play a critical role in uniform film formation. Future work should explore substrate surface modification strategies, such as self-assembled monolayers (SAMs), alongside methods such as seeded or interfacial growth, to enhance adhesion and uniformity of the MOF thin film.[10, 11]

Preliminary attempts to synthesize related UiO-series MOFs, specifically UiO-67, have also been made, following similar solvothermal conditions adapted from Miyamoto et al. (2015). However, additional characterization is required for complete analysis.

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