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3D printing of mixed matrix films based on metal-organic frameworks and thermoplastic polyamide 12 by selective laser sintering for water applications

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ABSTRACT. The fabrication of metal-organic framework (MOF)-based macro-materials is considered a promising strategy toward the practical applications of powder MOF crystals. In this study, selective laser sintering (SLS), an advanced three-dimensional (3D) printing method, is employed to fabricate MOF-polymer mixed matrix films (MMFs), and sintering parameters are examined systematically to investigate the universality of the SLS method, particularly for water applications. Diverse MMFs based on thermoplastic polyamide 12 (PA12) and MOF fillers with various mass loading and grid patterns are fabricated. The thickness, specific surface area, hydrophilia, water flux and mechanical stability of as-prepared MMFs are then investigated. The results show that MMFs with high porosity can be manufactured with high permeate flux which accelerate the contact between the MOF fillers and external ambient. They also possess the combined inherited features of the PA12 film including mechanical stability, free-standing

characteristic and flexibility as well as the MOFs including high specific surface area and hydrophilicity. As a proof-of-concept demonstration, methylene blue adsorption experiments in aqueous solutions are carried out using NH₂-MIL-101(Al)-PA12 MMFs with different sized grid patterns. The results confirm that the MMFs are effective adsorbents which can be easily regenerated, and the MOF components retain their good adsorption capacity. Overall, the present work provides an insight into the utilization of advanced 3D printing technology to manufacture macroscopic MOF-polymer materials for practical applications.

1. INTRODUCTION

Metal-organic frameworks (MOFs) are promising porous materials for wide applications in adsorption, separation, gas storage, catalysis, molecular recognition, etc. due to their intriguing characteristics of high surface areas, highly dispersed metal sites and versatile organic functional groups.¹⁻⁹ Moreover, the achievement of large-scale MOF production has indicated their great potential for applications, such as in the

domains of catalysis and environmental control.¹⁰⁻¹² However, the difficult collection and secondary pollution of MOF powder materials have restricted their adaptation in field applications so far. A mitigation strategy which has been proposed in the literature is to load MOF crystals into various useful and shapeable bulk materials, especially film materials with good flexibility and large permeability.¹³⁻¹⁹ Thus, the possible application of MOF-based films has been widely studied in environmental pollution control in recent years.²⁰⁻²⁹

Three-dimensional (3D) printing is a disruptive innovative technology with high precision and controllability to manufacture macroscopic objects with complex shapes and geometries.³⁰⁻³⁵ Selective laser sintering (SLS) is one of the most important 3D printing techniques, by which a 3D solid matrix is built through the layer-by-layer sintering of hot-melt powdered material (including thermoplastic polymers, ceramics and metals) using a program-controlled laser beam.³⁶⁻³⁹ So far, this new technique has been mainly used to manufacture mechanical components in the automotive, aerospace,

military and healthcare industries, as well as function materials in the environmental, biomedical, electrical and magnetic fields.³⁶⁻⁴²

In the SLS process, voids may be formed when powder particles are sintered or melted rapidly by utilizing transient laser heating. When polymer particles and MOF fillers are mixed for SLS process, formed voids can provide MOF fillers embedded in the polymer matrix opening channels and increase the contact area between the fillers and the external ambient. The number and size of the voids can be conveniently controlled by adjusting such laser sintering parameters as laser power, laser scanning speed and laser hatching space. In addition, the SLS technique has distinct superiority over other large-scale manufacture approaches including electrostatic spinning and hot pressing to realize multi-layer structures with certain surface patterns.

We report here the introduction of the SLS printing technique into the fabrication of both single-layer and multi-layer MOF-polymer complexes. This research work focused on single-layer MOF-polymer complexes with grid patterns that have large specific surface area so as to possess high wetting efficiency and thus high adsorption rate. Such single-layer

MOF-polymer complexes are simply called mixed matrix films (MMFs). Scheme 1 and

Video 1-7 show the procedure for printing MOF-polymer MMFs with a grid pattern.

A commercial thermoplastic polymer (polyamide 12, denoted as PA12) which has been widely applied in the SLS process was used as a support material. Based on their morphology, size, functional group, powder density and thermostability, five different types of MOFs (ZIF-67, NH₂-MIL-101(Al), MOF-801, HKUST-1 and ZIF-8) were systematically investigated to understand the universality of this manufacture method for the fabrication of MOF-based MMFs. Eventually, we obtained a series of MOF-based MMFs with different types of MOF materials, mass loadings (10 wt.%, 20 wt.%, 30 wt.% and 40 wt.%) and laser sintering patterns (uniformly distributed square holes with the dimensions of 3 mm×3 mm, 2 mm×2 mm and 1 mm×1 mm). The corresponding MMFs were denoted as MOF-PA12-*X*-*Y*, with *X* representing the mass loading of MOFs (10, 20, 30 and 40) and *Y* representing the hole dimension (3×3, 2×2 and 1×1). These printed MMFs were endowed with the combined features of the filled MOFs (high

specific surface area and hydrophilia) and the PA12 film (high porosity and permeate flux, high mechanical stability, free-standing characteristic and flexibility).

As a proof-of-concept demonstration for water applications, the experiments for methylene blue (MB) adsorption were conducted. The results indicated that the NH₂-MIL-101(Al)-PA12 MMF with the grid pattern of the smallest pore size could act as an easy-to-collect adsorbent with satisfactory adsorption capacity and rate. The present work explores new opportunities for advanced 3D printing technology to fabricate MOF-polymer materials in practical water applications, thus contributing to both chemistry and manufacturing domains with focus on MOF materials and SLS printing process.

2. RESULTS AND DISCUSSION

A CO₂ laser system (Figure S1a) was used to conduct the SLS process for the fabrication of MOF-PA12 complexes and the wavelength of the laser was about 10.6 μm .³⁷ The Fourier transform infrared (FTIR) spectrum of the PA12 powder showed that the peaks related to C-N bonds in PA12 around 1000 cm⁻¹ fall within the radiation band

of the CO₂ laser with a wavelength of 10.6 μm , indicating an effective energy absorption (Figure S2a). The melting temperature of the PA12 powder was around 180 °C.⁴⁴ The thermogravimetric analysis (TGA) analysis shows its decomposition temperature around 332 °C (5% decomposition) under air atmosphere (Figure S2b). When the laser beam focused into a spot with a high energy density, PA12 particles melt and coalesced with each other. The laser energy absorption of the powder particles attenuated from the top surface of the powder bed along the layer thickness direction. Thus, each layer formed in a multi-layer MOF-polymer complex generally consisted of two portions: a densely sintered top portion and a porous bottom portion which was partially sintered.⁴³

Figure 1 shows a three-layer HKUST-1-PA12 complex with 10 wt.% mass loading and uniform 2 mm×2 mm grid pattern, which was printed at the scanning speed of 1.78 m s⁻¹ and the laser power of 9.6 W with the laser defocus of 3 mm. This result demonstrates the feasibility of the SLS method in the fabrication of MOF-PA12 materials with 3D structures. As a single-layer film is more suitable for adsorption application due to its good flexibility and large permeability, it is the focus of this research work.

In order to determine the optimal sintering process parameters for MOF-PA12 MMFs, single-layer PA12 films were first studied. The fastest laser scanning speed (1.78 m s^{-1}) and different laser powers (8.4 W, 9.6 W, 10.8 W, 12 W and 13.2 W) were used to obtain single-layer PA12 films that could possess minimally sintered top portions while maintain both sufficient flexibility and mechanical strength. The SEM images of a single-layer PA12 film sintered with the laser scanning speed of 1.78 m s^{-1} and the laser power of 9.6 W show a densely sintered top portion and a porous bottom portion (Figure S3).

The top, bottom and cross-sectional microphotographs of the laser-sintered PA12 films (Figure 2) together with their X-ray diffraction (XRD) patterns (Figure S4a) demonstrate their printability and unchanged semicrystalline structures under an appropriate laser power. When the laser power was greater than 9.6 W, surface yellowing occurred to the films (Figure 2f-j) and was exacerbated as the laser power further increased. The surface yellowing was caused by the thermo-oxidative degradation of aliphatic polyamide and could lead to a reduction in tensile strength. On the other hand, however, a suitable increase of the laser power could result in a more

densely sintered film and thus an increase in its tensile strength. The thickness, mass and tensile strength of these laser-sintered PA12 films generally increased with the increasing laser power (Figure S5 and Table S1). Therefore, the laser power of 9.6 W was selected for the subsequent printing of MOF-PA12 MMFs in order to achieve minimally sintered top portion for more voids while maintain sufficient mechanical strength.

Five types of MOFs including ZIF-67, NH₂-MIL-101(Al), MOF-801, HKUST-1 and ZIF-8 were carefully selected as fillers to print a series of MOF-PA12 MMFs. The information of the MOF fillers is given in Table 1. The SEM images show that the sizes of the PA12, ZIF-67, NH₂-MIL-101(Al), MOF-801, HKUST-1 and ZIF-8 powder particles were 50-100, ~0.3, 0.2-0.5, 0.5-5, 1-2 and 1-10 μm , respectively (Figures 3 a1-f1). The XRD patterns of these as-synthesized MOF materials confirmed the crystalline structures of their corresponding MOFs (Figure 4a and Figures S6a,7a,8a,9a).⁴⁵⁻⁴⁸

The mass loading of the MOF fillers was initially set to be 10 wt.% for the printing of MOF-PA12 MMFs via SLS. All printed MOF-PA12 MMFs could be folded or shaped,

thus demonstrating their flexibility and free-standing characteristics (Figures 3 a2-f2).

Compared to those of their pure MOF counterparts, the XRD patterns of these MOF-PA12 MMFs all showed an extra broad peak at $2\theta \approx 21^\circ$, which was consistent with that of pure PA12 powder (Figure 4a and Figures S6b,7b,8b,9b).⁴⁹ This indicated that the MMFs were all formed from the mixture of MOFs and PA12, and the structure of each component in the MMFs remained during the SLS process. As seen in Figures 3 b3-f3, Figure 4b and Figures S6c-h,7c-h,8c-h,9c-h,10a-d, the MOF fillers were loaded into and partially filled the network channels of the PA12 matrix. These results confirmed the feasibility and flexibility of printing MOF-PA12 MMFs using the SLS technique.

Subsequently, MOF-PA12 MMFs with the five different MOF types and four different loading amounts (10, 20, 30 and 40 wt.%) were printed for analysis. The photographs of the as-obtained MMFs, the micrographs of their top surfaces and cross-sections, and the SEM images of their top surfaces verified the maximum mass loading of each type of MOF that could be added as fillers in MMFs (Figures S11-14). In particular, the powder density of a MOF, which is related to its structure, component, particle size and

specific surface area, was an important factor for the MOF-PA12 MMF (Table 1 and Figure S15), and their volume percentages for the five MOFs were 26, 50, 23, 46 and 57 vol. %, respectively (Table 2). Theoretically, the usage of MOFs with high powder density was easier to form MMFs with high mass loading. Among the MOF-PA12 MMFs, those MMFs filled by NH₂-MIL-101(Al) with lowest powder density (0.136 g cm⁻³) had a relatively low mass loading (20 wt.%), while those filled by ZIF-8 and HKUST-1 with higher powder density (0.273 g cm⁻³) had the maximum loading capacity (40 wt.%) and relatively high mass loading (30 wt.%), respectively (Table 2).

However, the MMFs filled by MOF-801 with highest powder density (0.461 g cm⁻³) had a relatively low loading (20 wt.%). After further analysis of the SLS approach, we found that the maximum mass loading was also influenced by the CO₂ laser heat absorption capacity, content of adsorbed water molecules and framework decomposition temperature of the filler. Irradiated by laser, both PA12 and MOFs in the MOF-PA12 mixed powders adsorbed the laser energy, as confirmed by FTIR spectra (Figures S2a, S16). The infrared absorption, appearing at ~1000 cm⁻¹, can be associated with (i) C-O

stretching and symmetric stretching vibrations of carboxylate groups, (ii) C-N stretching of aromatic amines and imidazole, and (iii) in-plane bending of the imidazole ring and the stretching of entire imidazole ring. Thus, all five MOFs could absorb the CO₂ laser energy to some extent. The CO₂ laser heat absorption capacity was also positively correlated to the number and types of functional groups inside the MOFs.

Upon irradiation, some of the laser heat energy was consumed and the remaining was transferred to the particles around the laser spot. The less the remaining heat energy was, the thinner the formed MMFs would become. The consumed laser energy made the PA12 melted and remodeled as well as the water molecules adsorbed in the metal clusters of MOFs desorb, which could be verified by the color change (from sky blue to deep purple) of HKUST-1-PA12-10 powder in the SLS process (Videos 5-7). The TGA curves (Figure 4c and Figures S6i,7i,8i,9i) show that the maximum weight loss of MOF-801 was up to about 37 wt.% of its total mass before the initial decomposition temperature (340 °C), indicating that a significant percentage of the water molecules were adsorbed in the MOF-801. Thus, the MOF-801-PA12 MMF was typically thin and

even difficult to be formed. This can also explain why the MMF filled by HKUST-1 (containing 28 wt.% adsorbed water molecules) showed a lower mass loading (30 versus 40 wt.%) than that filled by ZIF-8 (containing only 2 wt.% adsorbed water molecules), although both had the same powder density (0.273 g cm^{-3}).

Moreover, MOFs with poor thermostability were easy to be decomposed by the laser energy output. Thus, they consumed an excessive amount of laser heat energy, leading to the increased carbonization effect of the top surface of MMFs (Figure S11). Hence, with MOFs having poor thermostability, it was not suitable to improve the loading capacity by increasing the laser energy output. As shown in Figure S11, HKUST-1-PA12-10.8W MMFs showed severe carbonization in the top surface of MMFs due to the low decomposition temperature of HKUST-1 (290°C).

In summary, MOFs with poor heat absorption capacity, low content of adsorbed water molecules, good thermostability and high powder density were more suitable to be filled into the voids of the MMFs with a high mass fraction in the SLS process. The thickness and tensile strength of these MOF-PA12 MMFs are summarized in Table S2. Irradiated

by the same laser energy, PA12 with a higher volume percentage in the powder mixture could capture more laser heat energy, resulting in that the MMFs would be thicker and easier to shape. Hence, for the same type of MOF filler, the tensile strength and thickness of MMFs decreased with an increasing MOF mass loading. For different types of MOF fillers, the tensile strength and thickness of MMFs were both proportional to their maximum loading capacities.

The ultimate tensile strengths and elastic moduli of MOF-PA12-10 MMFs, shown in Figure S17 and Table S2, revealed that these MMFs remained robust enough to withstand significant mechanical stresses, even though the filling of MOFs into the voids of the PA12 matrix reduced their strength and stiffness to different degrees. Among these shaped MMFs, those filled by ZIF-8 with high powder density and thermostability exhibited the largest thickness and strongest mechanical properties. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the ZIF-8-PA12-40 MMF was measured to be about $332 \text{ m}^2 \text{ g}^{-1}$, indicating that the porosity of ZIF-8 was retained substantially in the printed MMF after the SLS process (Figure S18). We further conducted X-ray photoelectron

spectroscopy (XPS) to figure out the possible interaction between PA-12 matrix and MOF fillers (Figure S19). In the high-resolution spectrum of ZIF-8-PA12-40 MMF, the peak of N1s at 399.7 eV to acylamino group from PA-12, whereas the peak at 398.9 assigned to 2-methylimidazole from ZIF-8. Furthermore, the binding energies of O1s and Zn 2p in ZIF-8-PA12-40 MMF showed obvious shifts in contract to those of PA-12 and ZIF-8, respectively. The above results indicated the existence of chemical bonds of Zn-O/Zn-N between ZIF-8 and PA-12. The loss of specific surface area of ZIF-8-PA12-40 MMF may be attributed to the partial adsorption of PA12 on the surface of ZIF-8 which could block some of the pores.

Due to their large surface area, uniform and tunable pore size as well as abundant specific adsorption sites, the use of MOFs for the adsorptive removal of inorganic contaminants (such as heavy metal ions and fluorides)⁵⁰⁻⁵³ and organic contaminants (such as dyes and pharmaceuticals)⁵⁴⁻⁵⁵ from waste-water, as well as harmful gases (such as H₂S, SO₂, CO₂, CO, NH₃ and NO)⁵⁶⁻⁵⁷ from waste gases is now under active investigation. Hence, MOF-based macro-materials can potentially be used as effective adsorbents for direct removal of gaseous and water pollutant.^{13,24}

In this study, due to its large specific surface area and high thermostability, NH₂-MIL-101(Al) was chosen as a representative type of filler to manufacture the MOF-PA12-10

MMFs for a demonstrative water application. The S_{BET} of pure $\text{NH}_2\text{-MIL-101(Al)}$ was measured to be $1751 \text{ m}^2 \text{ g}^{-1}$ (Figure S10e,f). In addition, through a series of adsorption experiments (Figures S20,21), its adsorption capacity for MB was calculated to be about 222 mg g^{-1} . With the combination of excellent adsorption performance as well as the free-standing characteristic and high permeate water flux (up to $24813 \text{ L m}^{-2} \text{ h}^{-1}$ under low pressures with gravity, see Figure 4d and Figure S22) of the PA12 film, the $\text{NH}_2\text{-MIL-101(Al)-PA12}$ MMF was judged to be suitable for the direct application as removable adsorbents for dye pollutants in water.

As a proof-of-concept application, 3 mg $\text{NH}_2\text{-MIL-101(Al)}$ powder, 30 mg $\text{NH}_2\text{-MIL-101(Al)-PA12-10}$ MMF, 30 mg $\text{NH}_2\text{-MIL-101(Al)-PA12-10-3}\times\text{3}$ MMF, 30 mg $\text{NH}_2\text{-MIL-101(Al)-PA12-10-2}\times\text{2}$ MMF, 30 mg $\text{NH}_2\text{-MIL-101(Al)-PA12-10-1}\times\text{1}$ MMF and 60 mg PA12-1 $\times$ 1 film were employed as adsorbents for the MB adsorption in 4 mL 5 ppm MB solution at room temperature (25 °C) (Figure 5 and Figure S23). The color change of MB solutions with these films were observed directly in the experiments, showing that all MMFs could adsorb MB. The MB solution with $\text{NH}_2\text{-MIL-101(Al)-PA12-10-1}\times\text{1}$ MMF

reached the adsorption equilibrium at the fastest rate (about 3 h), while PA12-1×1 film showed very little adsorption of MB.

The fastest adsorption rate of the grid-patterned NH₂-MIL-101(AI)-PA12-10-1×1 MMF might be due to a larger accessible external surface area being exposed in the film, which further increased the wetting speed in aqueous solution and thus enhanced the adsorption rate. Although the adsorption rate was not as good as that of powder NH₂-MIL-101(AI) directly, these films adsorbed with MB could be easily removed for regeneration. As shown in Figure 4e, no wear-out was observed on this film even after being stirred at 800 rpm for 30 min in 100 mL deionized water, which confirmed that the free-standing NH₂-MIL-101(AI)-PA12-10 MMF could maintain its high flexibility and mechanical stability for adsorption applications.

The ability of spontaneous absorption of pollutant molecules from water for the NH₂-MIL-101(AI)-PA12-10 MMF could be attributed to the loading of viable adsorbents. SEM images and energy-dispersive X-ray spectroscopy (EDS) data both show that NH₂-MIL-101(AI) nanoparticles were distributed on the film surface and in the network channels

of the PA12 matrix (Figure S24). Even though the voids inside the PA12 film were filled by NH₂-MIL-101(Al) particles, the NH₂-MIL-101(Al)-PA12-10 MMF still maintained high porosity with high water permeate flux at room temperature driven by low pressures with gravity only, reaching up to 15401 L m⁻² h⁻¹ (Figure 4d). The water contact-angle tests (Figure 4f) revealed that the NH₂-MIL-101(Al)-PA12-10 MMF was hydrophilic (89.15°) compared to the hydrophobic PA12 film (107.75°) and PA12 powder (131.66°), which was attributed to the loading of highly hydrophilic NH₂-MIL-101(Al) (10.23°), which enhanced the water permeate flux of this film.

The adsorption capacity of NH₂-MIL-101(Al)-PA12-10 MMF was 133 mg g⁻¹ calculated through the adsorption experiments at 25 °C (Figure S25). TGA analysis was also performed to estimate the actual NH₂-MIL-101(Al) loading amount (~8.93 wt.%) (Figure 4d), and the adsorption capacity of NH₂-MIL-101(Al)-PA12-10 MMF was corrected to 149 mg g⁻¹. A handful of MOF materials wrapped into the top dense sintered portion led to a small amount of effective mass loss. A KOH etching experiment showed that the yellow film turned white and its surface appeared yellowish (Figure S26), indicating

most of the $\text{NH}_2\text{-MIL-101(Al)}$ could be etched quickly by 1 M KOH with a small part of the $\text{NH}_2\text{-MIL-101(Al)}$ remaining unattachable. This further confirmed that although part of the $\text{NH}_2\text{-MIL-101(Al)}$ particles in this film inevitably lost its usefulness, most of $\text{NH}_2\text{-MIL-101(Al)}$ particles was accessible and easily wetted.

To investigate the regenerating and reusing of the $\text{NH}_2\text{-MIL-101(Al)-PA12-10-1}\times 1$ MMF, desorption experiments were also carried out (Figure 6a). 30 mg $\text{NH}_2\text{-MIL-101(Al)-PA12-10-1}\times 1$ MMF was putted into 4 mL 5 ppm MB solution. After soaking for 3 h, the MMF was taken out and put into methanol for several minutes to desorb the MB. After 5 cycles of absorption-desorption experiments (Figure 6b), the MB removal efficiency was still high at 81.3%, showing the good recyclability and durability of $\text{NH}_2\text{-MIL-101(Al)-PA12-10-1}\times 1$ MMF as an effective adsorbent.

3. CONCLUSION

In this study, we applied the SLS method to fabricate MOF-PA12 MMFs and investigated their laser-sintered behaviors. MMFs made up of various MOF components

with a controllable loading amount and designable grid patterns exhibited multiple advantages including free-standing characteristic, flexibility, large accessible surface area, highly permeable, hydrophilia, good mechanical stability, recyclability and durability. As a demonstration for water applications, the grid patterned NH₂-MIL-101(Al)-PA12-10-1×1 MMF was found capable of effectively adsorbing MB in aqueous solutions with satisfactory maximum adsorption capacity and rate. The used film can be directly regenerated in methanol for reuse.

We also applied the SLS technique to print a three-layer HKUST-1-PA12-10-2×2 complex to verify the feasibility of constructing a 3D architecture. Limited by the amount of MOFs synthesized in the laboratory, the fabrication of a larger-scaled MOF-polymer complex was not demonstrated. However, it can be expected that the advancement in 3D printing technology will enable the manufacturing of macroscopic-scale 3D structures based on powder materials and thermoplastic polymers for wide practical applications in the near future.

Moreover, many thermoplastic materials such as polyurethane (PU), polypropylene (PP), polyethylene (PE), polyaryletherketone (PAEK), polybutylene terephthalate (PBT), polystyrene (PS), polycarbonate (PC) and thermoplastic elastomers (TPEs) can be used for SLS to fabricate MOF-thermoplastic macro-materials, which further widened their application range.³⁷ Various functional MOFs and thermoplastics as well as 3D printed structures will endow 3D MOF-thermoplastic complexes more application prospects in such domains as electrocatalysis,⁶⁰ oil/water separation⁴³ and gas separation²⁶ as well as photo-, electrical- and thermo-responsive applications.⁶¹

4. METHODS AND EXPERIMENTS

4.1 Materials. Thermoplastic polyamide 12 (PA12, PA2200 from EOS GmbH, Krailling, Germany) with the mean diameter of 50~100 μm and the mean powder density about 0.45 g cm^{-3} was employed as binder phase. Its melting point is 184°C . Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 2-Melm), 1,3,5-benzenetricarboxylic acid ($\text{C}_6\text{H}_3\text{O}_6$, H_3BTC), 2-aminoterephthalic acid ($\text{C}_8\text{H}_7\text{NO}_4$, $\text{H}_2\text{N-BDC}$) were purchased from

Sigma-Aldrich. N,N-dimethylformamide (DMF), methanol (MeOH), ethanol (EtOH) and acetone were purchased from VWR International SAS (Fontenay sous bois, France).

Methylene blue trihydrate ($C_{16}H_{18}ClN_3S \cdot 3H_2O$, MB) was purchased from Alfa Aesar.

Zirconyl (IV) chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) (98+%) was purchased from Acros Co.

Ltd. Polyvinylpyrrolidone (PVP-K30, M.W. ≈ 40000), Fumaric acid ($C_4H_4O_4$) (>99%)

were purchased from Tokyo Chemical Industry Co., Ltd. Formic acid (98/100%) was

purchased from Fisher Chemical Co. Ltd. All chemicals were used as received without further purification.

4.2 Synthesis of MOFs and Fabrication of MMFs.

Synthesis of ZIF-8. 44.64 g of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 60 mL DMF to form a clear solution. 49.2 g of 2-Melm was dissolved in 450 mL DMF to form another clear solution. The above two solutions were injected into a beaker respectively and stirred vigorously for 5 min. The resultant solution was transferred to a 1L Teflon-lined stainless-steel autoclave and heated in an oven at 120 °C for 48 h. After cooling, the

white solids were collected by centrifugation and washed with EtOH three times. The as-obtained white powder was vacuum dried overnight at 80 °C.

Synthesis of HKUST-1. Three beaker containing 35.52 g of PVP, 2.016 g of H₃BTC and 1.956 g of Cu(NO₃)₂·2.5H₂O were prepared, respectively. Then 180 mL of deionized water, 240 mL of DMF, 60 mL of deionized water were used to dissolve the Cu(NO₃)₂·3H₂O, PVP and H₃BTC, respectively. The copper nitrate solution and PVP aqueous solution were mixed and stirred at room temperature for 10 min, and then the H₃BTC solution was injected into the above mixed solution and stirred at room temperature for another 10 min. The resultant solution was transferred to a 1 L Teflon-lined stainless-steel autoclave and heated in an oven at 100 °C for 24 h. After cooling, the blue precipitates were collected by centrifugation and washed with EtOH three times. The as-obtained blue powder was vacuum dried overnight at 80 °C.

Synthesis of NH₂-MIL-101(Al). In a typical synthesis process,⁵⁸ 0.6 g of AlCl₃·6H₂O was dissolved in 70 mL DMF to form a clear solution. 0.643 g of H₂N-BDC was dissolved in 26 mL DMF to form another clear solution. The above two solutions were

injected into a beaker respectively and stirred vigorously for 10 min. The resultant solution was transferred to a 250 mL Teflon-lined stainless-steel autoclave and heated in an oven at 130 °C for 3 d. After cooling, the white solids were collected by centrifugation and washed with DMF one time and acetone twice. The as-obtained yellow powder was activated with methanol under reflux for 12 h and vacuum dried overnight at 100 °C.

Synthesis of ZIF-67. In a typical synthesis process,⁵⁹ 3.64 g (12.5 m mol) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in the mixed solution of 100 mL MeOH and 100 mL EtOH to form a clear solution. 4.11 g (50 m mol) of 2-Melm was dissolved in another mixed solution of 100 mL MeOH and 100 mL EtOH to form another clear solution. The above two solutions were injected into a glass bottle respectively and mixed vigorously for 30 s. The mixed solution was then incubated at room temperature for 22 h. The as-obtained purple precipitates were collected by centrifugation and washed with EtOH several times and finally dispersed in EtOH.

Synthesis of MOF-801. In a typical synthesis process,⁴⁷ 5.8 g (50 mmol) fumaric acid and 16 g (50 mmol) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in the mixed solution of 200 mL DMF and 70 mL formic acid. The resultant solution was transferred to a 1 L Teflon-lined stainless-steel autoclave and heated in an oven at 130 °C for 12 h. After cooling, the blue precipitates were collected by centrifugation and washed with EtOH three times. The as-obtained blue powder was vacuum dried overnight at 80 °C.

Preparation of MOF-PA12 mixed powder. 10 g composite powder containing 10~40 wt.% MOF and complementary PA12 was mixed in a beaker. After 30 min of continuous stirring inside a mixer, the mixed powder was sifted by fine sieves. The sieved mixture was further inspected by SEM (Figure S27) for its uniformity to be directly used in SLS process.

Fabrication of PA12 films, MOF-PA12 MMFs and three-layer HKUST-1-PA12 complex by SLS. A CO_2 laser (Epilog laser Helix, USA) was used to fabricate 3D MOFs/PA12 composite matrix membranes by SLS. Its maximum laser power is 60 watts and its maximum scanning speed is 1.78 m s^{-1} . Both its relative laser power and scanning

speed can be adjusted from 1% to 100%. The diameter of the focused spot size of the laser beam is 120 μm , which also represents the theoretical resolution of the focused system. In this work, 3 mm defocus was used to reduce the laser heat on the top surface, resulting in a larger laser spot and hence lower laser sintering resolution at about 180 μm (Figure S28).

In this work, a series of parameter were set for the fabrication of PA12 films, MOF-PA12 (HKUST-1-PA12, NH_2 -MIL-101(Al)-PA12, MOF-801-PA12, ZIF-8-PA12, ZIF-67-PA12) MMFs and grid patterned NH_2 -MIL-101(Al)-PA12 MMFs with different macroscopic hollowing sizes (3 mm $\times$ 3 mm, 2 mm $\times$ 2 mm, 1 mm $\times$ 1 mm) . The scanning speed was fixed at 1.78 m s⁻¹ and the laser power was changed from 8.4 W to 13.2 W. The resolution of laser engraving was adjusted at 600 dots per inch (DPI).

The above-mentioned MOF-PA12 mixed powder were putted into a quartz slot (Figure S1b), in which the quartz sheet size was 20 cm $\times$ 5 cm $\times$ 3 mm and the slot size was 15 cm $\times$ 3 cm $\times$ 1 mm. The MOF-PA12 MMFs were fabricated using this CO₂ laser cutter system on the quartz slot with MOF-PA12 mixed powder at 100 % of scanning speed

(1.78 m s⁻¹) under 16 % of laser power (9.6 W) with the 3 mm defocus. Please see

Scheme 1 and Video 1-7 for the 3D printing procedure.

The three-layered HKUST-1-PA12 complex was produced inside a quartz slot with 2 cm×2 cm×1 mm slot size. The procedure of the first layer printing was the same as above-mentioned MOF-PA12 MMFs, and the subsequent ones were fulfilled by cycle procedure of loading powder and printing.

4.3 Material Characterization. Field-emission scanning electron microscopy (FESEM) images were acquired from a JEOL JSM-7600F scanning electron microscope with the electron beam voltage at 2 kV. Energy-dispersive X-ray spectroscopy (EDS) data was acquired from JEOL JSM-7600F scanning electron microscope at 15 kV to determine elemental composition of the sample. X-ray diffraction (XRD) patterns were recorded on Shimadzu 6000 X-ray diffractometer with Cu-K α radiation (λ = 0.154 nm) to investigate the crystalline structures of the samples. The thermal gravimetric analysis (TGA) data were obtained by TGA Q500 equipment (TA instrument, New Castle, DE, USA) on approximately 15 mg samples, which were heated from room temperature (25 °C) up to 800 °C at 10 °C min⁻¹ under air atmosphere.

The Fourier transform infrared (FTIR) spectra were obtained by a SHIMADZU (model IR Prestige-21) IR spectrometer in the range of 400-4000 cm^{-1} . N_2 adsorption/desorption isotherms and pore size distribution were measured by QuadraSorb SI BET automated surface area and pore size analyser. Micrographs were photographed under an Olympus SZX16 microscope. The magnification is $\times 2.5$ and $\times 4$ for all images, respectively. The concentrations of MB solution were conducted on a UV-1900PC spectrophotometer (AOE Instrument (Shanghai) CO., Ltd, China). Water contact angle was measured by a JC2000DS contact angle goniometer equipped with a CCD camera (Powereach Co., shanghai, China). Gravity driven water flux tests were conducted using a self-made device (Figure S21) with a porous stainless-steel holder (the diameter of film was 2.5 cm; the volume of water was about 200 ml). The results of tensile tests were analyzed on an Instron Universal Testing Machine equipped with a 500 N load cell. The extension rate was set at 0.005 mm s^{-1} . The size of films was 15 mm $\times$ 80 mm. The thickness of films was measured by an Olympus SZX16 microscope. The magnification was either $\times 2.5$ or $\times 4$ for all images.

4.4 Methylene Blue Adsorption Experiments. 20, 40, 100, 150, 200 mg MB was dissolved into 1000 mL deionized water for the preparation of MB solution of 20, 40, 100, 150 and 200 ppm, respectively (where the density of this solution was regarded as 1.0 mg L^{-1}). MB solutions of other concentrations (1-10 ppm) were prepared by the dilution of the MB solution of 200 ppm with deionized water, which were utilized for the construction of the MB calibration curve (Figure S18) by recording the MB absorption peak intensity (at 665 nm) in a UV-visible spectrophotometer.

The maximum adsorption capacity of $\text{NH}_2\text{-MIL-101(Al)-PA12-10}$ MMF and pure $\text{NH}_2\text{-MIL-101(Al)}$ were obtained by the adsorption experiments on a series of MB solutions of 10, 20, 40, 100, 150 and 200 ppm at 25°C . The change of the concentrations of MB solution was recorded by a UV-visible spectrophotometer.

In the adsorption experiments, the adsorbent ($\sim 50 \text{ mg}$ $\text{NH}_2\text{-MIL-101(Al)-PA12-10}$ MMF or $\sim 5 \text{ mg}$ pure $\text{NH}_2\text{-MIL-101(Al)}$) was weighed and put into a 20 mL MB solution with the concentration from 10 to 200 ppm. Then the MB solutions were magnetic stirred at 25°C and sampled at fixed time (10 min, 30 min, 1 h, 3 h, 7h, 12h/24h). After

separated by centrifugalization or a syringe filter (0.45 μm , Millex, Millipore), their MB concentrations were recorded by a UV-visible spectrophotometer. The experimental results fitted the Langmuir adsorption isotherm, which can be expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}a_L} + \frac{C_e}{Q_{\max}} \quad (1)$$

where C_e (ppm or mg L^{-1}) is the MB equilibrium concentration in solution, Q_e (mg g^{-1}) is the amount of adsorbed MB at equilibrium, $Q_{\max}$ (mg g^{-1}) is the maximum adsorption capacity of the adsorbent, and a_L (L mg^{-1}) is the Langmuir constant.

Scheme 1. Schematic procedure for printing MOF-PA12 MMFs with grid patterns and photographs of the PA12 film and MOF-PA12 MMFs with various MOF fillers.

Figure 1. A three-layer HKUST-1-PA12 complex with 10 wt.% mass loading and a uniform 2 mm×2 mm grid pattern printed at the scanning speed of 1.78 m s⁻¹ under the laser

power of 9.6 W with the laser defocus of 3 mm: (a) photograph and (b) cross-sectional micrograph.

Figure 2. PA12 films printed using a CO₂ laser at the scanning speed of 1.78 m s⁻¹ and various powers (13.2 W, 12 W, 10.8 W, 9.6 W and 8.4 W) with the defocus of 3 mm: (a-e) photographs; (f-j) micrographs of the top and bottom surfaces; (k-o) micrographs of the vertical cross-sections.

Figure 3. (a1-f1) SEM images of PA12, ZIF-67, NH₂-MIL-101(Al), MOF-801, HKUST-1 and ZIF-8 particles. The printed PA12 film and ZIF-67-PA12-10, NH₂-MIL-101(Al)-PA12-10, MOF-801-PA12-10, HKUST-1-PA12-10 and ZIF-8-PA12-10 MMFs printed at the

laser scanning speed of 1.78 m s^{-1} and the laser power of 9.6 W : (a2-f2) photographs; (a3-f3) SEM images of the top surfaces; (a4-f4) SEM images of the vertical cross-sections.

Figure 4. (a) XRD patterns of the synthesized NH₂-MIL-101(AI) powder and the printed NH₂-MIL-101(AI)-PA12-10 MMF. (b) SEM image of the top surface of the printed NH₂-MIL-101(AI)-PA12-10 MMF with the inset showing a magnified image. (c) TGA data of the PA12 powder, NH₂-MIL-101(AI) powder and NH₂-MIL-101(AI)-PA12-10 MMF. (d) Gravity-driven water flux results of the PA12 and NH₂-MIL-101(AI)-PA12-10 MMFs. (e) Mechanical stability testing results of the NH₂-MIL-101(AI)-PA12-10 and NH₂-MIL-

101(Al)-PA12-10-1×1 MMFs. (f) Water contact angles of the PA12 powder, NH₂-MIL-101(Al) powder, PA12 film and NH₂-MIL-101(Al)-PA12-10 MMF and the corresponding images of water droplets on the sample surfaces.

Figure 5. Photographs of the experimental results demonstrating the MB adsorption capacities of the PA12 powder, the printed various MMFs and the PA12 film.

Figure 6. (a) Photographs demonstrating the adsorption and desorption performance. (b)

Removal efficiency of the NH₂-MIL-101(Al)-PA12-10-1×1 MMF.

Table 1. Components, particle sizes, powder density, contents of adsorbed water molecules and decomposition temperatures of five types of MOFs.

MOF	ZIF-67	N H ₂ - MIL101(Al)	MOF-801	HKUST-1	ZIF-8
Metal center	Co	Al	Zr	Cu	Zn
Ligand
Particle size (μm)	~0.3	0.2-0.5	0.5-5	1-2	1-10
Powder density (g cm ⁻³)	0.175	0.136	0.461	0.273	0.273
Content of adsorbed water molecules (wt. %)	4	30	37	28	2

Decomposition temperature in air (°C)	320	460	340	290	410
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Table 2. The maximum mass and volume loadings of MOFs as fillers in MOF-PA12 MMFs and the thickness and ultimate tensile strength of the MOF-PA12-10 MMFs.

MOF-PA12 MMFs	ZIF-67- PA12 MMF	NH₂- MIL101(Al)- PA12 MMF	MOF-801- PA12 MMF	HKUST-1- PA12 MMF	ZIF-8- PA12 MMF
Maximum mass loading (wt.%)	10	20	20	30	40
Maximum volume loading (vol.%)	26	50	23	46	57
Thickness (μm)^a	242	278	311	300	343
Ultimate tensile strength (MPa)^a	0.034	0.138	0.768	0.246	0.915

^ameasured using MOF-PA12-10 MMFs.

ASSOCIATED CONTENT

Supporting Information.

Additional experimental data (PDF)

Additional videos (mp4)

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Notes

Any additional relevant notes should be placed here.

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BRIEFS. Metal-organic framework (MOF) films with grid patterns are fabricated based on the mixed powder of MOFs and polyamide 12 using a selective laser sintering (SLS) method. Diverse MOFs are systematically investigated to understand effect parameters and confirm the universality of SLS for the fabrication of MOF-based films, which are more suitable for practical applications compared with their powder counterparts.

SYNOPSIS

MOF-PA12 mixed matrix film