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Authors: Elmeri Lahtinen, Rafaella Precker, Manu Lahtinen, Evamarie Hey-Hawkins, and Matti Haukka

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COMMUNICATION

Selective Laser Sintering of Metal-Organic Frameworks: Production of Highly Porous Filters by 3D Printing onto a Polymeric Matrix

E. Lahtinen [a], R.L.M. Precker[b], M. Lahtinen[a], E. Hey-Hawkins*[b] and M. Haukka*[a]

Abstract: Due to their unique and well-defined pore structures Metal-Organic Frameworks (MOFs) have raised a lot of interest especially as adsorbing materials. One of the main challenges in the utilization of MOFs is their crystalline and powdery nature, which makes their use inconvenient in practice. Three-dimensional printing has been suggested as a potential solution to overcome this problem. In the current paper we used Selective Laser Sintering (SLS) to print highly porous flow-through filters containing the MOF copper(II) benzene-1,3,5-tricarboxylate (HKUST-1). These filters were printed simply by mixing HKUST-1 with easily printable Nylon-12 polymer matrix. By using SLS, powdery particles were fused together in such a way that the structure of the printed solid material resembles the structure of a powder bed. The MOF additive is firmly attached only on the surface of partially fused polymer particles and therefore remains accessible by fluids passing through the filter. Powder X-ray analysis of the printed object confirmed that printing did not have any negative impact on the structure of the MOF. CO_2-adsorption studies also showed that the activity of the MOF was not affected by the printing process. SLS offers a straightforward and easy way to fabricate tailor-made MOF-containing filters for practical applications.

In the past decade the field of ordered porous hybrid materials has been growing very rapidly, with a focus on new structures and compositions, but also on the introduction of new or optimized functionalities.[1] Metal-organic frameworks (MOFs) provide a widely used class of nanoporous materials, whose properties can be readily tuned by varying the molecular building blocks.[2] A variety of MOFs with a range of metals and linking ligands have been developed for different applications due to their adjustable porous structures. The capabilities of MOFs to store molecular species have led to their use in range of different applications, such as catalysis[1–3], hydrogen storage[4,5], CO_2 sequestration[6], separations[7–9], sensors[10], water treatment[11] and drug delivery[12,13]. One of the key properties of MOFs is their high and controllable porosity that can be up to 90% of the crystal volume. From an application point of view another important factor is high surface area (up to several thousand $m^2\ g^{-1}$).[14],[15] However, the wide spread industrial use of MOFs has been hindered by the challenges faced in the introduction of MOFs into industrial environment as they are typically crystalline solids. Most applications would benefit, if the MOF materials could be anchored onto a suitable supports without destroying their unique properties. Quite recently Rezaei *et al.* used extrusion-based 3D-printing for preparing MOF-containing objects by mixing MOFs with bentonite clay and polyvinyl alcohol (PVA).[16] However, this approach requires preparation of the extrusion paste and also post-processing to obtain the final object.

Powder-based Selective Laser Sintering (SLS) 3D printing provides an alternative 3D-printing tool for printing MOFs. Sample preparation is facile and no post-processing of the object is required. This technique uses small particles, typically around 50–100 µm diameter, as printing material. During the SLS printing process the particles are partially sintered together. The level of sintering can be controlled by fine-tuning the printing parameters including laser power, exposure time, printing temperature, and cooling rate, which then allows control over the physical properties of the object such as porosity.[17–20] When the printing conditions are carefully optimized, the sintered polymer particles are not completely melted but retain their particle-like appearance. Such process results in a solid, porous, powder-bed-like object that contains accessible voids between the partially sintered polymer grains. The porous structure allows fluids to pass through the object even if no specific flow channels are added in the structure. Any functional additive that is mixed with the printing matrix is attached only on the surface of the sintered particles,

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and is therefore available for interactions with the fluid passing through the material. This SLS approach has been previously used for printing selective filters for scavenging precious metals from aqueous solutions.[21]

Currently, SLS 3D printing is one of the most used techniques for fabricating printed objects with desired mechanical properties or aesthetic features. However, incorporation of chemical functionalities in the objects has been largely ignored. This is the case even if chemical functionality can be added easily by using for example functionalized polymers as printing material. Chemical functionality can also be added by mixing the active additive with suitable easily printable matrix. The additive can be for example another polymer, resin, oxide, crystalline material or even salts or molecular compounds. Nylon-12 provides an example of a functional printable polymer. It has been used to print selective filters for scavenging gold from acidic media.[22] Another example of a hybrid material is a mixture of polypropylene and type-I anion exchange resin as functional component.[21]

In the current work the same approach has been used to incorporate the MOF copper(II) benzene-1,3,5-tricarboxylate (HKUST-1)[23] into an SLS 3D-printed object. The goal was to investigate if the MOF component can be printed in the form of a flow-through filter without destroying its structure or functional properties. One of the most commonly used printing polymers, Nylon-12, was chosen as the supporting polymer matrix. The structure and physical properties of the printed objects were characterized by using Helium Ion Microscopy (HIM) and powder X-ray diffraction analysis (PXRD).

The powder mixture for the SLS 3D printing was prepared by mixing (10 wt-%) of commercial HKUST-1 with Nylon-12 (N12) powder. The mixture was used for SLS 3D printing of the objects without any additional pretreatment. The printable objects were design to be shaped like a filter disk (Fig. 1) and were printed using a Sharebot SnowWhite SLS 3D printer operating at 170 °C during the printing process. The detailed printing parameters are summarized in the supporting information.

The printing conditions were tuned in such a way that the printed material retained its particle-like structure. The final objects were rigid and durable solids with high porosity. Due to the chosen printing conditions the HKUST-1 additive was firmly attached on the surface of the partially fused polymer particles (Fig. 2). This ensures that the functional component is not encapsulated by the polymer matrix and remains accessible for contact with fluids passing through the porous filter. The mechanical properties, porosity, shape and size can then be fine-tuned to match requirements by the environment the objects will be used in.

Figure 1. Image of the SLS 3D printed MOF/N12 disks with 20 mm diameter and 1.5 mm thickness.

The physical properties and the anchoring of the MOF crystals into the polymeric network were studied using HIM, which enables imaging of nonconductive samples without any additional pre-treatment of the sample.[24] Microscopic images confirmed that the 3D printed objects consist of partially sintered N12 polymer beads with voids between the particles. The MOF crystals are attached on the surface of the beads and are not encapsulated by the N12 matrix (Fig. 2). Furthermore, the MOF crystals have retained their characteristic orthogonal shape indicating that they are still intact after the printing process (Fig. 2). Thus, the MOF remains available for chemical reactions. In addition to HIM imaging, SEM-EDX analysis was performed to further confirm the macroporous structure of the object and the even distribution of the object (Fig. S1 and S2). Due to the low porosity of the polymer matrix, which has also been shown previously[21,25], the surface area of the supporting framework is small and therefore, the surface area of the printed object is dominated by the properties of the additive. This was confirmed by analysing the BET surface area of the 3D printed MOF/N12 object. The analysis resulted in surface area of roughly 40 m^2/g (Fig. S3) for the printed object.

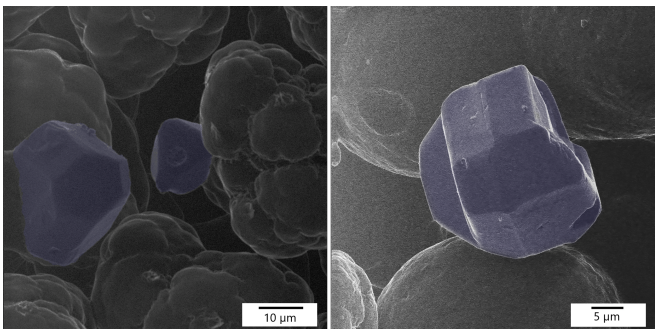

Figure 2. HIM images of the surface of the 3D-printed MOF/N12 disks. MOF crystals have been highlighted for clarity.

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HKUST-1 is one of the most intensively studied MOFs due to its ability to adsorb small gas molecules such as H_2 and CO_2.[26–29] It has been demonstrated that HKUST-1 is sensitive to moisture and eventually loses its adsorption capabilities due to the collapse of its crystal structure. The water content also has an impact on the appearance of the material. At lower temperatures at ambient conditions the color of the material is turquoise (Fig. S4 and S5). If it is heated up or activated in vacuum the color changes to violet or dark blue due to loss of water.[29] This behavior is reversible at least to some degree and was observed also with the printed HKUST-1 (Fig. S4 and S5). The MOF/N12 powder was heated up to 170 °C during the printing process and a CO_2 laser was used to selectively sinter the MOF/N12 mixture, thus forming the 3D-printed object. The color of the mixture was violet indicating that HKUST-1 was in its activated form during printing. When the printed object was cooled to room temperature the color of the object turned to turquoise (or pale greenish blue), indicating that the MOF was able to adsorb water from the air even when it was in the printed object. Additionally, when the printed object was heated up to 120 °C for 15 minutes in an oven the object turned again violet (Fig. 3a). Almost immediately after removing the MOF/N12 from the oven, the color started to change towards turquoise as the MOF adsorbed water from the ambient air. After 5 minutes, the object had returned to its initial turquoise color (Fig. 2 b). The process could be repeated several times. The impact of water adsorption could also be shown by placing a small droplet of water on the 3D printed MOF/N12 object immediately after the object was removed from the oven. The water droplet caused an instant color change within the droplet area (Fig. 3 c). The impact of water on the color is a clear indication that the printed MOF is fully functional even in the printed material.

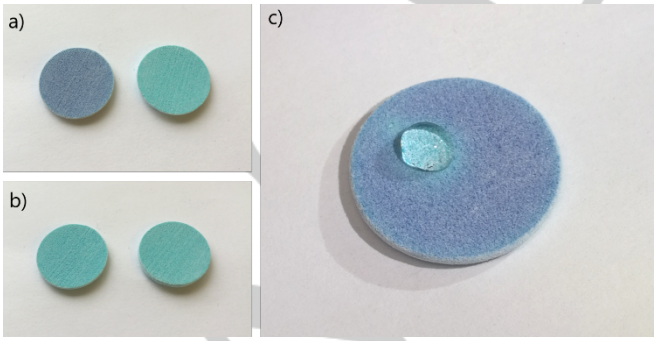

Figure 3. a) Image of the MOF/N12 disk after placing it in the oven (120 °C) for 15 minutes (left) and reference disk that was in ambient air the whole time (right). b) Image of the same two disks after 5 minutes exposure to air. c) Picture of MOF/N12 disk after removing it from the oven and placing a droplet of water on top of it.

Thermal stability of the MOF/N12 object was also analysed by performing thermogravimetric analysis (Table S1 and Fig. S6). The results that the composite material shares the thermal characteristics of the starting materials. The HKUST-1 can be seen to thermally decompose between 276 – 368 °C, which is in line with the reported thermal stability of the HKUST-1.[30] This also suggests that the printing conditions shouldn't negatively affect the structure of the HKUST-1, since the SLS 3D printing process for this specific composite material was performed at 170 °C.

To confirm that the structure of HKUST-1 survived the printing process the printed objects were further studied by variable-temperature powder X-ray diffraction (VT-PXRD). By comparing the PXRD patterns of the unprinted MOF powder and 3D-printed MOF/N12 object (Fig. 4), it can be seen that the printing has not changed the structural properties of the MOF, as consistently similar structural changes (caused by the desorption-adsorption process of water) of HKUST-1 were monitored both on bulk powder sample as well as on a printed MOF/N12 object (Fig. S4 and S5). The samples were heated up in air to 115 °C at 10 °C/min and at that temperature, structural changes induced by removal of water are indicated by subtle changes in the diffraction peak positions and their intensities. When the sample was cooled to room temperature, the original diffraction pattern was restored (Fig. 4); this is a reversible process. This is a further evidence that MOFs like HKUST-1 can be converted to functional objects by utilizing SLS printing.

Investigation of how the 3D printing process affects the activity of the MOF was done by measuring the CO_2 adsorption capacity of the 3D printed MOF/N12 object and the bulk MOF powder. Both of them were first activated by heating them up to 150 °C for 30 minutes under N_2 atmosphere. This resulted in removal of 15 wt-% of water from the bulk powder and 1.2 wt-% of water from the 3D printed object. The samples were then exposed to CO_2 flow inside the TG/DSC analyzer. The introduction of CO_2 lead to increase of roughly 6 wt-% and 0.6 wt-% in mass, respectively (Table S2 and Fig. S7). This is perfectly in line with the fact that the 3D printed object only contains 10 wt-% of the active MOF. The result also shows that the 3D printing method does not negatively affect the activity of the MOF.

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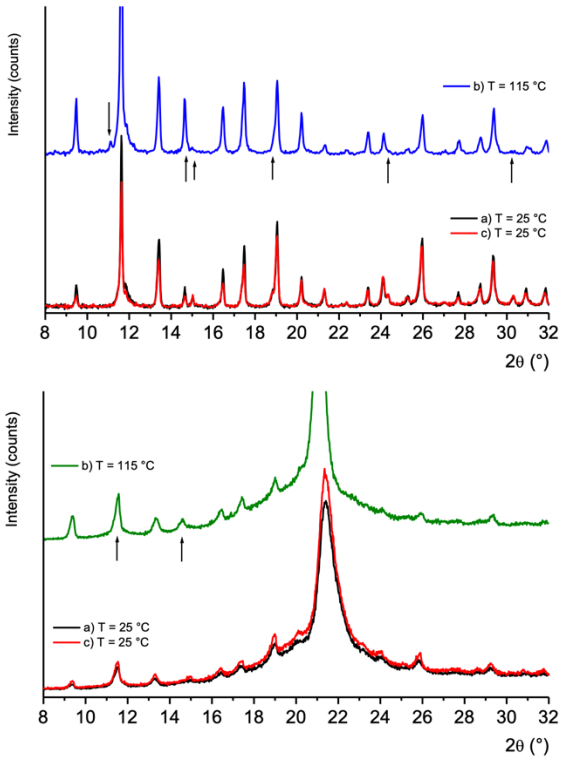

Figure 4. TOP: PXRD patterns of HKUST-1 bulk powder recorded a) at 25 °C, b) at 115 °C and c) again after cooling at 25 °C. Below: PXRD patterns MOF/N12 recorded a) at 25°C, b) at 115 °C, and c) again after cooling at 25 °C. Major changes between the patterns at room temperature and 115 °C are pointed out by arrows.

Even though in this work Nylon-12 was used as the supporting polymeric matrix, a wide variety of other printable polymeric materials could be used to modify the properties of the printed objects even further. For example, biodegradable and biocompatible polymers could be used as the supporting polymer. This could be exploited for example in the design of a new type of MOF-mediated drug delivery systems. Simply by using polymers with a more flexible backbone the mechanical properties of the objects could be modified further. Furthermore, by employing polymers with functionalities of their own multi-functional objects could be obtained. Similarly, it could be possible to use more than one-type of MOFs in the same object or to use other active additives together with MOFs. The advantage of SLS printing is that it requires only little effort and hardly any post-processing to prepare the printed material. Obviously, the advantage of printing in general is that the shape, size, mechanical properties and flow-properties of the object can be tailor-made for the reaction environment and thus directly designed for the end-user.

Whether the SLS printing together with supporting matrix has any impact on the stability of the MOF structure and more detailed adsorption properties of the 3D-printed objects are currently being investigated.

Conclusions

Here we have shown that Selective Laser Sintering 3D printing can be utilized to produce solid but highly porous objects containing HKUST-1. During the printing process, Nylon-12 served as supporting polymeric matrix for the MOF crystals. VT-PXRD analysis, combined with HIM imaging, and CO_2 adsorption studies confirmed that the HKUST-1 is unharmed by the 3D printing process. Due to the SLS 3D printing technique, the MOF crystals remained active and readily accessible for adsorption processes. The work shows that SLS 3D printing can open up new ways to utilize MOFs by anchoring them into a customizable polymeric networks. As long as the MOF is stable enough to be printed, it can be converted into a wide range of practical objects and devices which can be tuned to fit specific applications. The ability to easily manufacture highly customizable macroscopic objects with the MOF embedded into the structure, broadens the scope of possible applications for MOFs.

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The authors declare no conflict of interest.

Keywords: adsorption • laser sintering • metal-organic frameworks • porosity • polymers

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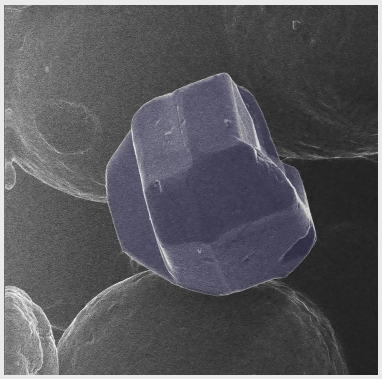
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Selective Laser Sintering 3D printing was used to prepare macroscopic objects, where MOF crystals are firmly anchored onto a polymeric support structure. The MOF retains its functional properties throughout the 3D printing process. This represents a pioneering approach to MOF chemistry.



E. Lahtinen, R.L.M. Precker, M. Lahtinen, E. Hey-Hawkins, M. Haukka**

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