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From wastes to interconnected porous monolith: upcycling of Al-based Metal Organic Framework via Pickering emulsion template

Fabrice LORIGNON^{ab}, Alban GOSSARD^{b*}, Michaël CARBONI^{a*}, Daniel MEYER^a

^a ICSM, CEA, Univ Montpellier, CNRS, ENSCM, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

^b CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France

Abstract

An Al-based Metal-Organic Framework (MOF) obtained from Li-ion battery wastes as an upcycled material has been shaped as a hierarchically porous solid monolith. This original method is based on the stabilization of a Pickering High Internal Phase Emulsion (HIPE) by MOF particles that conducts to the formation of a monolith after polymerization of the aqueous continuous phase and elimination of the organic internal phase of the emulsion. The presence of a small amount of additive polymers rigidifies the monolith structure and an adhesive binder is used to improve the final network porosity of the materials by creating pore throats. This makes the MOFs accessible at the internal surface of the monolith after shaping and keeps some of their original properties. A screening of the different parameters is proposed to optimize the ratio MOF/Polymer/Adhesive binder and retains at best the original properties of the MOFs. This work shows the great ability of MOFs to stabilize Pickering emulsions and to conduct to a solid polymer-MOF composite monolith with interesting properties. We assume that this method can be generalized to other MOFs materials.

Keywords: Metal-organic frameworks; Shaping; Pickering emulsion; Upcycling; Li-ion battery waste; Interconnected porosity

Corresponding information:

* michael.carboni@cea.fr / tel: (+33) 466 339 204 / ICSM, UMR 5257, Bât 426, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

* alban.gossard@cea.fr / tel: (+33) 466 339 134 / CEA, ISEC, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

Introduction

Porous materials (carbon, silica or even coordination polymers) have attracted lot of attention these past years due to their formidable properties for many applications [1]. In particular, MOFs, constructed from the assembly of organic and inorganic compounds in a crystalline structure, are probably the most promising of these porous materials due to the different possibilities of structure [2]. However, for a broad applicability, producing MOFs (generally obtained as powder) as handleable materials is crucial and the literature is lacking in efficient, simple and economic shaping procedures that do not alter the material properties (mainly porosity and crystallinity) [3]. Consequently, numerous routes to fix MOFs onto monolithic supports have been studied [4]. The simplest involves mechanical treatments of pre-synthesized MOFs. Unfortunately, the compacting process drastically reduces the powder porosity and is not suited to the shaping of macroporous materials. MOFs can also be shaped into solid materials by pressing, granulation, extrusion, spray drying and even 3D printing [4].

Recently, Pickering emulsions have shown their interest to shape MOFs as monolith [5]. By growing a solid skeleton in the continuous phase of the emulsion and eliminating the internal phase, a monolithic material can be obtained containing macropores as a replica of the emulsion droplets and MOFs covering the macroporous surface area. For that purpose, we have recently shown that MIL-96(Al) particles, obtained as an upcycled materials from Li-ion batteries [6], can stabilize paraffin-in-water Pickering emulsions due to their amphiphilic properties [7]. In this work we now aim to use this emulsion as a template for hierarchically porous materials synthesis.

Experimental

MIL-96(Al) was obtained as an upcycled material from Li-Ion battery wastes as previously reported [6]. Different monoliths have been synthesized to evaluate the concentrations of MOFs, the polymeric precursors (acrylamide, noted AM, and methylene bisacrylamide) and the presence of adhesive binder (polyvinyl alcohol, PVA) on the porosity. Each monolith are designed as $M_{[MOFs]/[AM]/[PVA]}$. For example, $M_{100/10/0.5}$ corresponds to a material obtained with a $[MOFs]=100 \text{ mg.mL}^{-1}$ in H_2O , $[AM]=10 \text{ wt. \%}$ relative to H_2O and $[PVA]=0.5 \text{ wt. \%}$ relative to H_2O . To prepare $M_{100/10/0.5}$, 375 mg of MIL-96(Al), 375 mg of acrylamide, 18.75 mg of methylene bisacrylamide and 18.75 mg of KPS (Potassium Persulfate) are introduced into a beaker. After addition of 3.02 mL of water, homogenization is performed using an IKA Ultra Turrax T25 homogenizer with a single rotor (S25N-10 G) at 15.000 rpm. 0.73 mL of PVA is added while still under agitation as well as oil (paraffin) with a fixed ratio of 0.75 v/v, i.e. 11.25 mL. Agitation is maintained at 15.000 rpm for 2 min to obtain the emulsion, which is then placed at 80 °C to polymerize for 24 hours. The polyHIPE (for emulsion-templated polymers obtained within high internal phase emulsion) is finally washed using a Soxhlet extractor with ethanol for 48 hours to remove the oil, the polymer precursors in excess and PVA, and the material is dried under vacuum at 100 °C.

Results and discussion

The MOFs particles are oval like grains of rice and the material revealed a high crystallinity with a specific surface area of $655 \text{ m}^2 \cdot \text{g}^{-1}$ (**Figure S1**). In HIPEs, droplets are organised in a compact network and the continuous phase separating the oil droplets is a thin film of liquid, which favours the formation of an interconnected porous network. Polymer precursors are added to the emulsion to create a solid skeleton. As they are water-soluble, polymerization occurs in the continuous phase. PVA is known to be a particle adhesive. PVA is used to hold MOFs particles together at the oil-water interface and therefore contributes to the stabilisation of the emulsion [8].

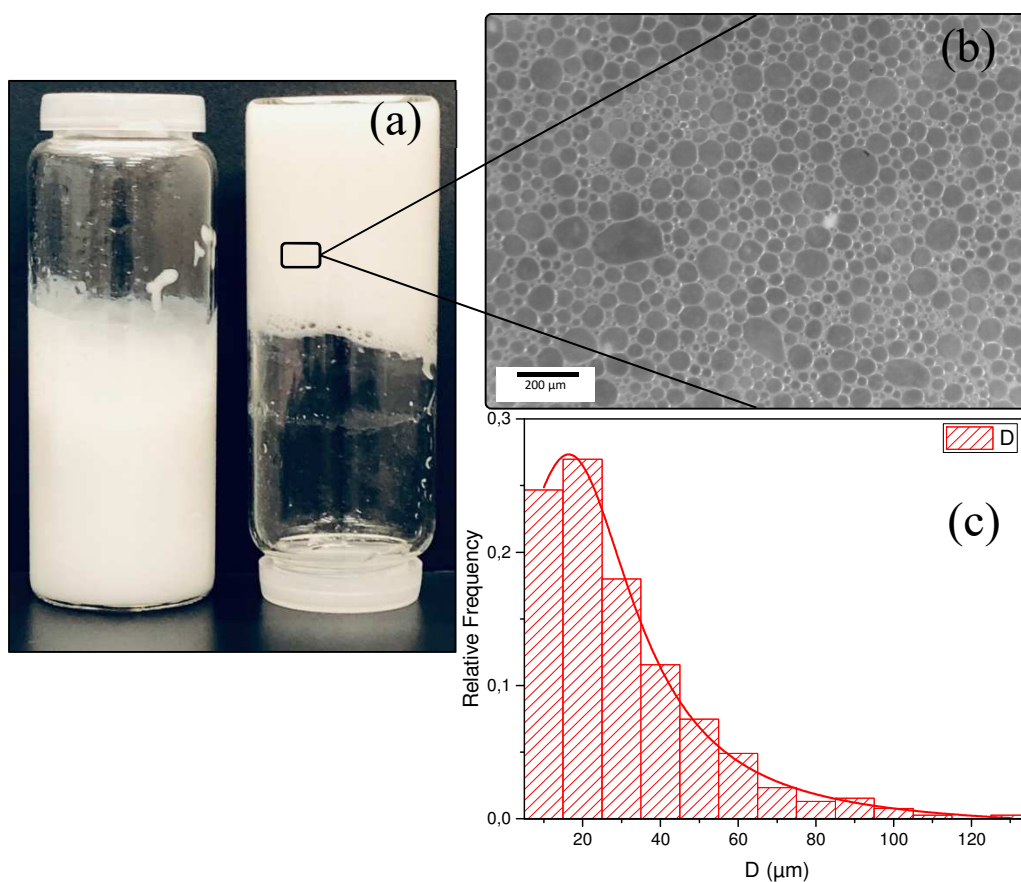


Figure 1: (a) Photograph of Pickering emulsions precursor of $M_{100/10/0.5}$; (b) Optical micrographs of the emulsion droplets and (c) Droplet size distribution in the emulsion.

Figure 1a exhibits the HIPE template before polymerization and shows that emulsion behaves a gel. The droplet size distribution is relatively homogeneous with droplets diameters centred around 20 μm . The presence of polymers has only a slight impact on the rheological properties, but PVA induces in the thickening of the continuous phase (**Figure S2**).

After polymerisation and elimination of the oil, a modification of the skeleton as well as the porosity is observed. TGA analyses have been performed to prove that no residual oil, polymer precursor or PVA remain in the final monolith (**Figure S3**). The synthesis of polyHIPEs leads to the formation of macropores as a replica of the oil droplets and small porosity due to the space between the particles. As observed on **Figure 2**, as an illustrating example, the $M_{100/10/0.5}$ monolith is white with visible macropores on the surface. The SEM analyses reveals the presence of a network of interconnected pores with various sizes. MIL-96(Al) particles can be identified over the entire internal surface of the pores where the droplets were located, confirming the Pickering-stabilization mechanism. Note that some MOFs particles are also irregularly present outside the pores (**Figure 2e**), probably because these particles aggregate in the continuous phase during formulation and are trapped in the walls during polymerisation [7]. PXRD (**Figure S4**) and FTIR (**Figure S5**) analyses are performed on pristine MOFs as well as on monoliths and show that the MOFs structure is retained in the final composites.

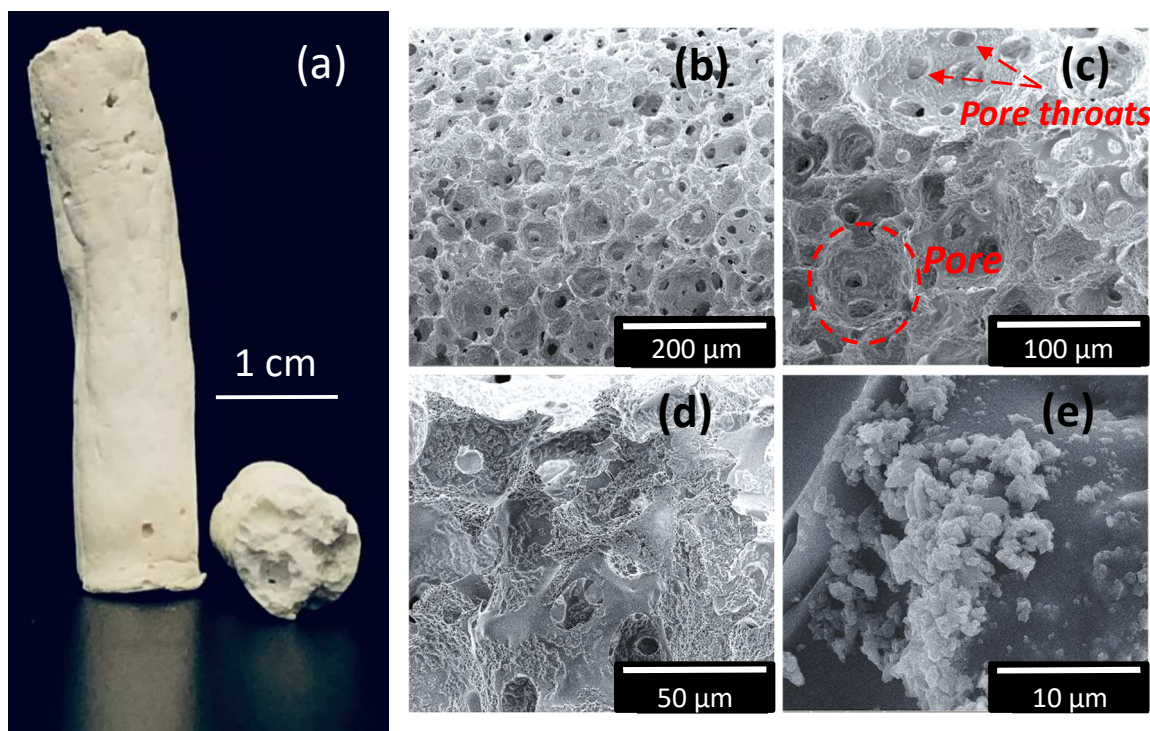


Figure 2: (a) Photograph of the $M_{100/10/0.5}$ monolith, seen from the front and from below; (b-e) SEM images of the $M_{100/10/0.5}$ monolith at different magnifications

The influence of the concentrations of MOFs, polymeric precursors and PVA on the porosity was evaluated. As observed on **Figure 2c**, the porous network of the monoliths is a combination of pores and throat pores connecting the pores. The **Figure 3** presents the evolution of the pores and pore throats for different formulations. Both pores and pore throat diameters decrease as the PVA concentration increases. Particularly, the pore diameter is divided by approximately 5 when the PVA

increases from 0 wt. % to 0.5 wt. %. Indeed, PVA is a surface active component and can thus participate to the stabilization mechanism of the emulsion. The PVA also interposes itself among the droplets and creates open windows (pore throats) between the pores after polymerization. In this way, the presence of PVA in the emulsion formulation promotes the formation of pore throats and thus improves interconnectivity of the porous network. Note that, the variation of MIL-96(Al) amount has only a small impact on pore size at PVA= 0.5 wt. % .

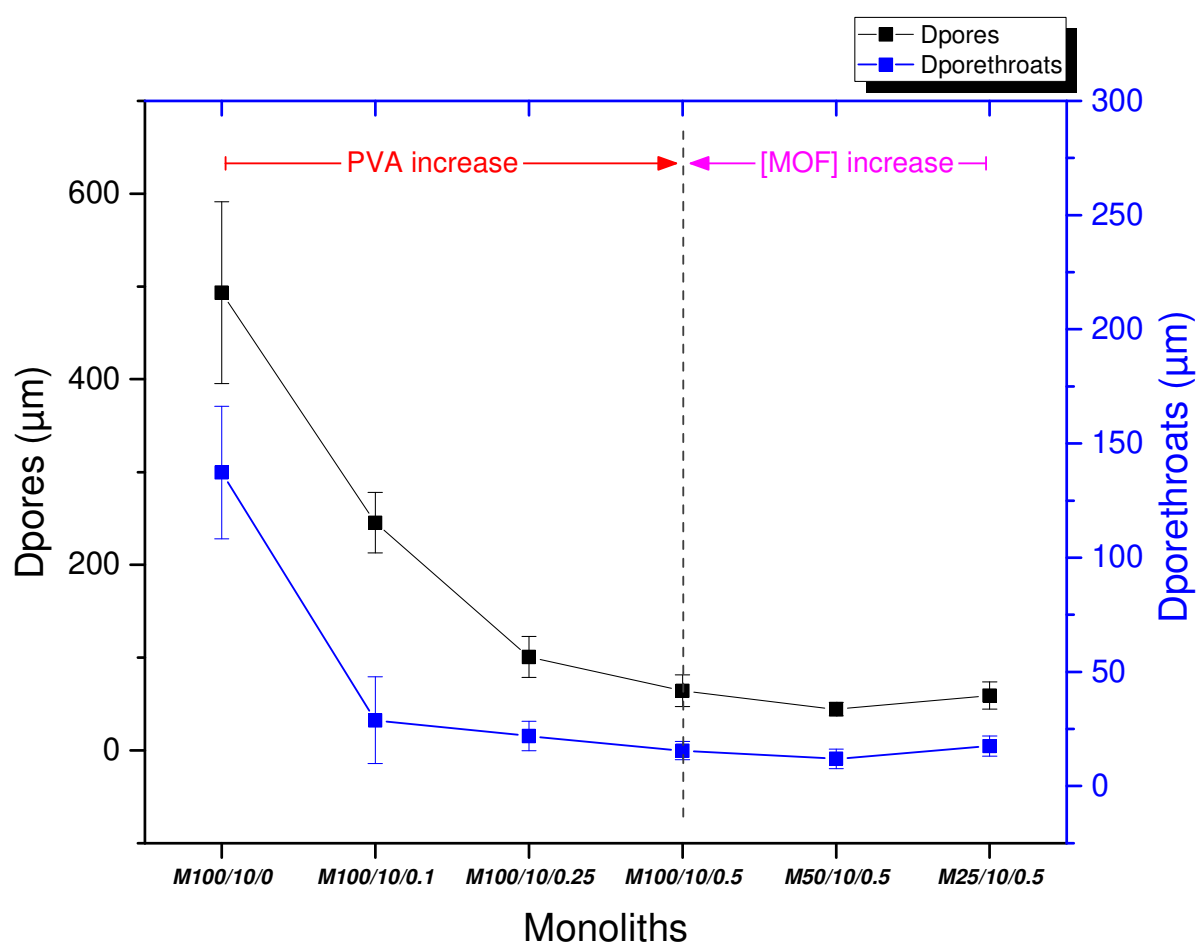


Figure 3: Average pore diameters (black) and pore throats (blue) of different monoliths.

The analysis of nitrogen adsorption and desorption (**Figure 4**) is in adequacy with the porous microstructure. Isotherms of the different monoliths present a typical behaviour of a macro and microporous network. The macroporosity comes from the droplets created during the emulsification step that subsequently forms the pores while the microporosity is a signature of the accessibility of the MIL-96(Al) into the material. The influence of the MOF concentration as well as the porogenic effect of PVA are highlighted through these analyses and particularly by the evolution of the specific surface area. First, adding more MOFs in the emulsion formulation induces a higher specific surface area. As the MOF concentration increases, more particles stabilize the droplet interface, resulting in an

abundance of MOFs in the pores. One part of these particles will be trapped in the polymer structure while the other part will be accessible. Furthermore, the presence of PVA induces the formation of pore throats and thus opens the porous network. This leads to a higher availability of MOFs in the composite, which is reflected by the increase of the specific surface between $M_{100/10/0}$ ($51 \text{ m}^2\cdot\text{g}^{-1}$) and $M_{100/10/0.5}$ ($91 \text{ m}^2\cdot\text{g}^{-1}$). By combining these results with those of the thermogravimetric analysis, the accessible surface of the particles in the monolith model $M_{100/10/0.5}$ can be evaluated. TGA presents a mass loss due to MIL-96(Al) about 60 wt. % (**Figure S3**) meaning that a maximum of surface area of $393 \text{ m}^2\cdot\text{g}^{-1}$ (instead of $655 \text{ m}^2\cdot\text{g}^{-1}$) can be obtained if the all MOFs porosity is accessible at the surface of the monolith. However, the specific surface area of the material is $91 \text{ m}^2\cdot\text{g}^{-1}$. The polymer support does not contribute to the specific surface area [9], this means that some particles are embedded in the polymer and a part of the surface area is lost. The ratio between the real and theoretical surfaces is thus $91/393 = 0.23$, so the shaping of the monoliths reduces the accessible surface of the powder by 77%.

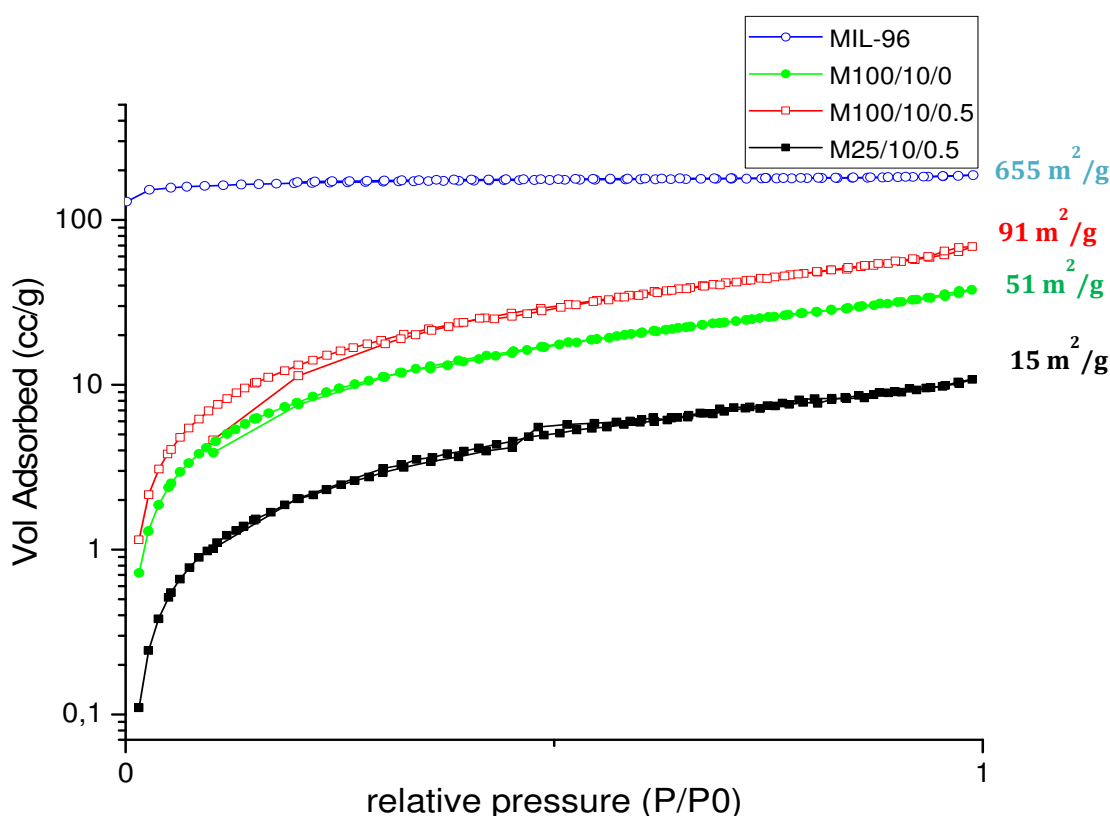


Figure 4: Nitrogen isotherm adsorption/desorption of the corresponding MIL-96(Al) powder, $M_{100/10/0.5}$, $M_{100/10/0}$ and $M_{25/10/0.5}$.

Finally, $M_{100/10/0.5}$ shows to have a good mechanical resistance until 1 kg (**Figure S6**).

Conclusion

We have demonstrated in this work the possibility to form monoliths of polymer-MOFs composites via a Pickering emulsion templating approach with addition of polymer and adhesive binder in the continuous phase of the emulsion. By optimizing the formulation of the emulsion, we are able to propose a best formulation keeping some porous properties of the pristine MOF in the range or higher than those observed in the literature with similar strategy [9–14]. As a perspective, we assume that this strategy can be transposed to other MOF materials and generalized as a way to shape powdery MOFs, which will increase their application fields.

Acknowledgements

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