

## IN-SITU GROWTH OF METAL-ORGANIC FRAMEWORKS VIA METAL-OXIDE RECRYSTALLIZATION: A NEW APPROACH OF MOF@POLYHIPE DESIGN

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### ABSTRACT

HKUST-1(Cu) and MOF-5(Zn)@polyHIPE hybrid materials were synthesized using the in-situ metal-organic framework (MOF) growth through a secondary recrystallization from the CuO- and ZnO-nanoparticles. A new synthesis approach enables high MOF loading within the polymer matrix and moreover high micropore accessibility. MOF phase within the hybrid materials exhibits superior structure hydrostability and durable CO<sub>2</sub> adsorption capacity under the humid conditions.

Keywords: metal-organic framework, MOF composites, CO<sub>2</sub> sorption, MOF hydrostability

### INTRODUCTION

Metal-organic frameworks (MOFs) are, over the last few decades, established as an important group of materials which can be applied in various fields of physical and chemical processing. Their structural and compositional versatilities, high porosity and ability to tune their functionalities make MOFs promising particularly for applications in gas storage and separations, heterogenous catalysis, sensing or drug delivery.<sup>[1-3]</sup> Prerequisite for further implementation is material's chemical stability, which turned out to be an important issue for numerous MOFs. Secondly, shaping into a proper macroscopic form, such as beads, membranes, monoliths, foams or thin films, is also an important requirement allowing easier handling and utilization of MOFs. The studies on the field of MOF science addressing the above mentioned challenges are therefore more and more focused in the development of composites.<sup>[4]</sup> Integration of MOFs with other active substrate can synergistically combine the advantageous properties of both components and thus enhance the MOF's performances or even access new physical or chemical properties which are not available for the pristine components.<sup>[5,6]</sup> In this manner, MOF/polymer composites have a great potential in various fields, due to the broad selection polymer types that can be used possessing variety of possible functionalities, their light weight, chemical stability and high flexibility of shaping.

Herein, we present the new concept of MOF@polyHIPE hybrid recrystallization from pre-formed metal-oxide@polyHIPE nanocomposites in the presence of appropriate organic ligands.

### EXPERIMENTAL

#### *Preparation of metal-oxide nanoparticles (NPs)*

ZnO and CuO nanoparticles with the average size of 50 nm (Sigma) were modified with oleic acid (OA) by suspending them in the OA solution and ethanol and sonicating for 10 min.

Preparation of the microcellular nanocomposite foams ( $\mu$ CNF)

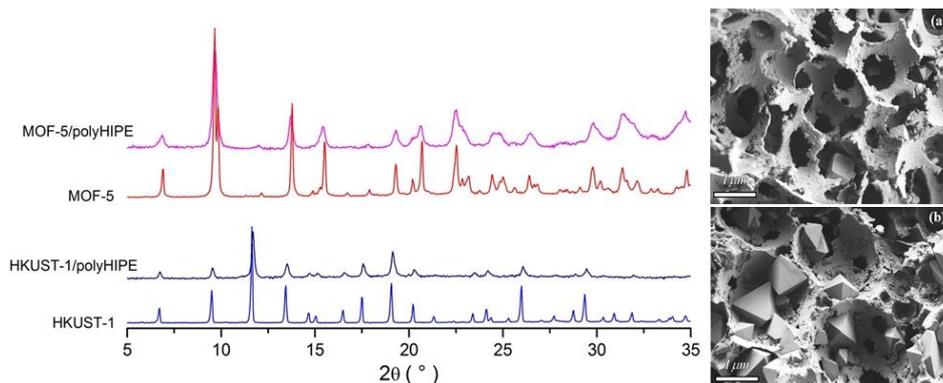
The 1.3 g of dicyclopentadiene monomer (DCPD), 0.136 g of Pluronic® L121, 50 $\mu$ L toluene and 30wt % of metal-oxide nanoparticles (ZnO or CuO) were stirred for 5 min. During the stirring 5.5 mL of deionized water was added drop-wise over about 1 h. Afterwards 1.3 mg of the initiator M2 dissolved in toluene (0.25 mL) was added and the emulsion was stirred for further 5 min. Subsequently, the emulsion was transferred to an appropriate mould (i.e. glass vials). The filled moulds were cured at 80 °C for 4 h which resulted in the formation of rigid monoliths in all cases. The specimens were purified by Soxhlet extraction with acetone for 24 h and subsequently dried in a desiccator under vacuum (10 mbar) until the weight was constant.

Preparation of the MOF@polyHIPE hybrid materials

MOF@polyHIPE hybrid materials were solvothermally crystallized from  $\mu$ CNF precursors. In the case of MOF-5@polyHIPE, the ZnO@pDCPD monolith (0.25 g) was immersed in the solution containing 42 mg of terephthalic acid in 10 ml of *N,N*-dimethylformamide and 0.01 ml of water. Hybrid material was solvothermally treated in the sealed vial at 60 °C for 2 days. Similar procedure was used for the synthesis of HKUST-1@polyHIPE: 0.25 g of CuO@pDCPD was placed in the solution containing 8 ml of ethanol and 2 ml of water. Recrystallization was taking place at 120 °C for 2 days. The products were recovered by rinsing with acetone and drying at room temperature.

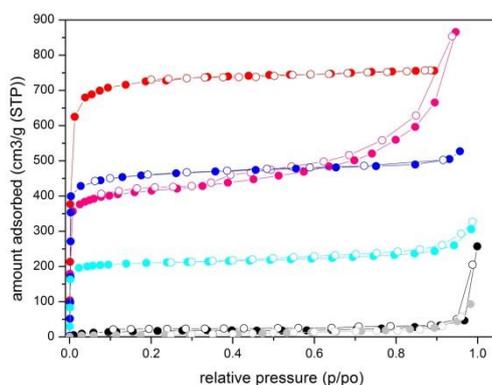
## RESULTS AND DISCUSSION

HKUST-1(Cu)/polyHIPE and MOF-5(Zn)/polyHIPE were recrystallized under hydrothermal conditions from the corresponding metal oxide-based composites as can be indicated by XRD measurements (Fig. 1, left). Metal oxide nanoparticles seem to be completely recrystallized into MOF phase since there are no visible diffraction peaks belonging to the corresponding metal oxides in neither case. The weight contribution of MOF phases within the composites were determined by TG analysis (not shown here) and found to be 75.4 wt.% and 55.1 wt.% for HKUST-1(Cu)/polyHIPE and MOF-5(Zn)/polyHIPE materials respectively. Additional information about structural correlations between MOF and polyHIPE phases can be provided by SEM analysis (Fig. 1, right). SEM micrographs of the monolith cross-sections clearly show the presence of the MOF crystals, which are more or less homogeneously located within the bulk monolith and seem to grow from the walls of the polymer matrix. As it was already determined by TG, the contribution of MOF crystals is higher in the case of HKUST-1/polyHIPE than in the case of MOF-5/polyHIPE. It is apparent that the MOF crystals are located within the macroporous cavities of the polymer and that they tend to grow from the polyHIPE walls.



**Figure 1:** XRD patterns of the composite and pristine MOF materials (left) and SEM micrographs of the MOF-5/polyHIPE (upper right) and HKUST-1/polyHIPE monoliths (lower right).

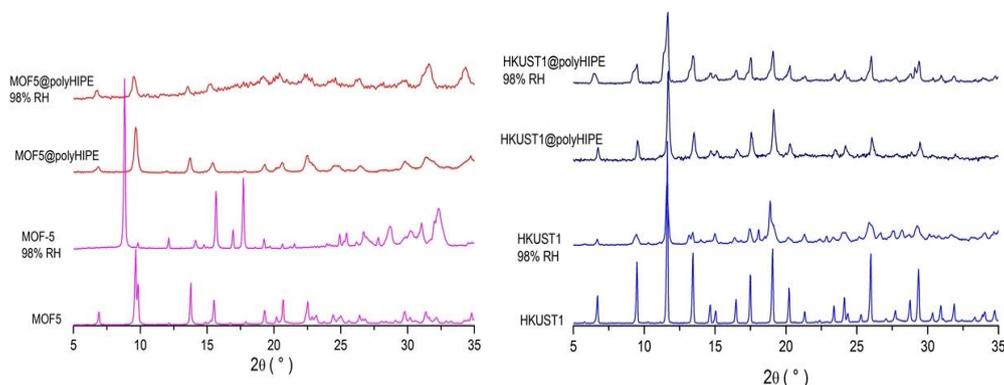
To evaluate the accessibility for hosting molecules more reliably, N<sub>2</sub> sorption analysis was performed within the composites. Pure HKUST-1 and MOF-5 powders show typical type I isotherm with the S<sub>BET</sub> values of 1211 and 2501 m<sup>2</sup>/g, respectively. Starting ZnO/polyHIPE and CuO/polyHIPE composites have negligible surface areas with no microporosity. After the recrystallization of metal-oxide composites into MOF/polyHIPEs the specific surface area increases significantly. In both cases, S<sub>BET</sub> shows about half of the values as were measured for the parent MOF materials, i.e. 794 and 1298 m<sup>2</sup>/g for the HKUST-1@polyHIPE and MOF-5@polyHIPE, respectively. MOF-5/polyHIPE shows also gradual increase of N<sub>2</sub> uptake in the p/p<sub>0</sub> region between 0.8 and 1, probably due to the formation of mesopore voids between MOF-5 and polyHIPE matrix or cracks which could occur on MOF-5 crystals. On the other hand, this effect is much less pronounced in the case of HKUST-1/polyHIPE, which could suggest that either better contact between MOF crystals and polyHIPE matrix is established.



**Figure 2:** N<sub>2</sub> isotherms of ZnO/polyHIPE (black), MOF-5/polyHIPE (pink), pristine MOF-5 (red), CuO/polyHIPE (gray), HKUST-1/polyHIPE (light blue) and pristine HKUST-1 (dark blue). Adsorption points are marked as full circles, whereas desorption points as empty circles.

MOF-5 and HKUST-1 structures are known to exhibit high structure sensitivity towards moisture, which in large extent limits their applicability in various physical or chemical processes. Hydrostability was investigated for the synthesized hybrids in order to evaluate their functionalities in humid conditions. The hybrid materials and the parent MOFs were exposed to 98 % of relative humidity for 3 days at room temperature (Figure 3). The parent HKUST-1 notably loses its structure integrity with the appearance of additional nonporous phase. On the

other hand, the parent MOF-5 underwent complete hydrolysis, leading to recrystallization into the nonporous phases already after 24h. On the other hand, the HKUST-1 and MOF-5 phases within the hybrid materials remained unchanged. Slight decrease of the reflection intensities and broadening of the peaks indicate partial amorphization of the MOF phase, however, nonporous hydrous phase which commonly forms from the bulk MOF-5 did not occur. The reason for such a profound improvement of the MOF hydrostability is due to the inherently hydrophobic nature of the poly(DCPD) polyHIPE matrix which repels the water vapour and protects the MOFs.



**Figure 3:** XRD patterns of the as-prepared materials and after exposure at 98% RH for (a) MOF-5 pristine and corresponding composite and (b) HKUST-1 and corresponding composite.

## CONCLUSIONS

A new synthetic route to prepare MOF@polyHIPE hybrid materials via secondary recrystallization of the pre-synthesized metal-oxide@polyHIPE nanocomposites is disclosed. This synthetic approach overcomes the issues of limited loadings, chemical instability and micropore clogging associated with the MOF phase once incorporated into the polymer framework. Referring to the advantages of the secondary recrystallization approach, the HKUST-1@polyHIPE and MOF-5@polyHIPE hybrid materials were synthesized and exhibit high MOF phase loading with pronounced micropore accessibility. Both hybrid materials further show improved structure resistivity upon water vapour exposure, offering the functionality of the water-sensitive MOF hybrid materials in humid conditions.

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