

# A spray-drying strategy for synthesis of nanoscale metal–organic frameworks and their assembly into hollow superstructures

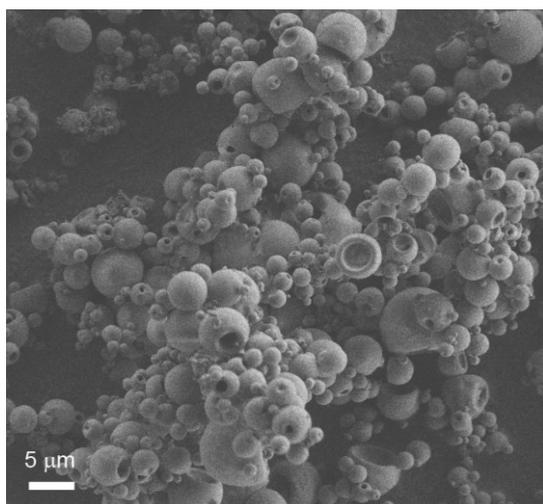
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Miniaturization to the nanometer scale regime is a very prolific strategy for the development of new materials with novel and often enhanced properties compared to traditional materials. In such a context, nanoscale Metal-Organic Frameworks (also known as nanoMOFs) can also show size-dependent properties that are expected to expand the scope of MOFs in numerous practical applications, including drug-delivery, contrast agents, sensor technology and functional membranes and thin-films, while opening up novel avenues to more traditional storage, separation and catalysis applications and to



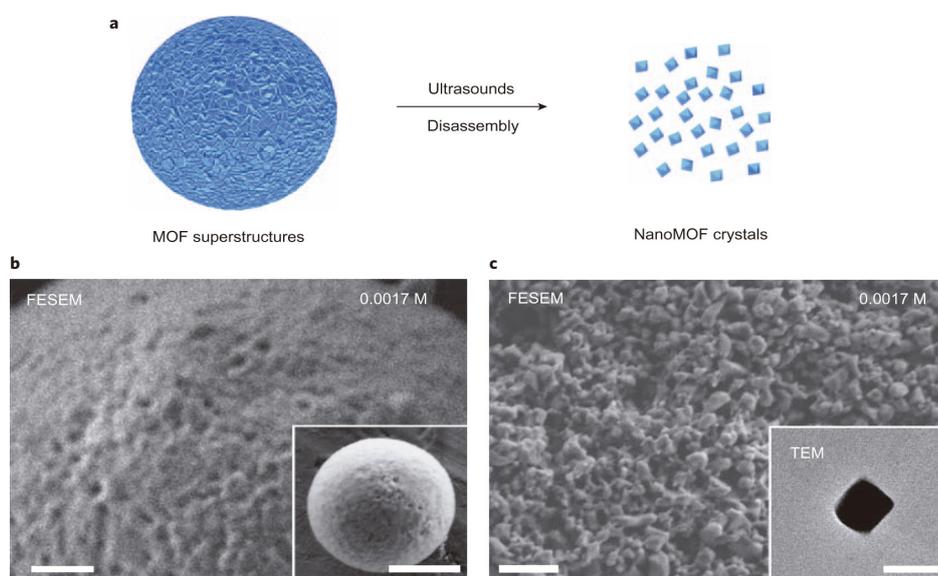
**Figure 1.** Hollow MOF superstructures obtained by spray-drying.

functional self-assembled MOF superstructures of higher complexity.<sup>1</sup> Today, the growing interest in nanoMOFs demands advanced, low-cost and scalable methodologies for their general synthesis and self-assembly. This is crucial if one wants to start imaging their use for practical applications in a near future.

Herein, we show that spray-drying technique can be exploited as a general, low-cost, rapid and scalable method for the synthesis and self-assembly of nanoMOFs.<sup>2</sup> It enables massive production of sub-5  $\mu\text{m}$  hollow, spherical MOF superstructures from the localized crystallization of nanoMOFs on the surfaces of atomized droplets of a MOF precursor solution upon heating (Fig. 1). In this method, the atomized droplets produced in spray-drying are used as individual reactors to confine the fast synthesis and assembly of nanoMOFs at a large scale. The resulting superstructures are robust and, following disassembly via sonication, afford well-dispersed, discrete nanoMOFs (Fig. 2).

Importantly, this strategy is applicable to a broad range of MOFs that covers most known porous MOF subfamilies (HKUST-1, Cu-bdc, NOTT-100, MIL-88A, 43 MIL-88B, MOF-14, MOF-74 [M = Zn(II), Ni(II) and Mg(II)], UiO-66, ZIF-8, Prussian blue analogues, MOF-5 and IRMOF-3), drastically reduces their production times and costs, and enables continuous and scalable nanoMOF synthesis as well as solvent recovery. Furthermore, this spray-drying strategy also enables the construction of MOF superstructures comprising multiple nanoMOFs assembled together, and the encapsulation of guest

species, such as fluorescent dyes and inorganic nanoparticles, within these superstructures. We anticipate that this will provide new routes to capsules, reactors, composite materials, and advanced adsorbents. As a first proof-of-concept, we show how the entrapment of magnetic nanoparticles within hollow HKUST-1 superstructures results in advanced adsorbents that can be used for magnetic solid-phase removal of the organosulfur dibenzothiophene (DBT) fuel contaminant.



**Figure 2.** a, Schematic showing the disassembly of the HKUST-1 superstructures upon sonication to form well-dispersed, discrete nanoHKUST-1 crystals. b, Representative FESEM and TEM (insets) images of the HKUST-1 superstructures (b) and corresponding disassembled nanoHKUST-1 crystals (c).

## References

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- [2] A. Carné, I. Imaz, M. Cano-Sarabia, D. Maspoch, *Nature Chemistry* **2013**, DOI: 10.1038/NCHEM.1569.