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

Inhar Imaz,¹ Amau Camé,¹ Mary Cano,¹ Daniel Maspoch¹²

¹CIN2 (ICN-CSIC), Catalan Institute of Nanotechnology, Esfera UAB, 08193 Bellaterra, Spain.
²Institució Catalana de Recerca i Estudis Avançats (ICREA), 08100 Barcelona, Spain

inhar.imaz@icn.cat, daniel.maspoch@icn.cat

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 functional self-assembled MOF superstructures of higher complexity.¹ 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.² It enables massive production of sub-5 µm 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

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