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3D Reconstruction and Porosity Study of a Hierarchical Porous Monolithic Metal Organic Framework by FIB-SEM Nanotomography

E. L. Solla[1], L. Micheron[2], P. Yot[3], J. Méndez[1] and P. Horcajada[2]

[1.] Servicio de Microscopía Electrónica, CACTI, Universidade de Vigo, Vigo, Spain.
[2.] Institut Lavoisier, Université de Versailles Saint-Quentin-en-Yvelines, Versailles, France.
[3.] Institut Charles Gerhardt Montpellier, Montpellier, France.

Porous metal-organic frameworks (MOFs) belong to a fascinating class of porous crystalline materials and currently receive much attention in regard to their potential applications in strategic domains [1]. Typically obtained as crystalline powders, MOFs need to be suitably shaped for their industrial application without affecting their textural properties. An interesting recent route is the formation of aerogel [2], which can provide additional porosity. In particular, the benchmarked cubic UiO-66 solids (UiO for Oslo University) [3], built up from $Zr_6O_4(OH)_4$ oxoclusters and terephthalate anions bearing different functional groups, appears to be a good candidate in storage, separation, catalysis and biomedicine [4]. UiO-66 exhibits tetrahedral and octahedral cages (6 and 11 Å) accessible through microporous windows (~4-6 Å), leading to a high porosity (BET surface area ~ 1200 m^2/g; pore volume ~ 0.47 cm^3/g) combined with a high thermal, chemical and mechanical stability.

A gel based on small and monodispersed nanoparticles (~40 nm) of the zirconium aminoterephthalate (UiO-66_NH_2) was initially prepared [5] and then dried using supercritical CO_2 leading to the formation of monolithic pieces with hierarchical porosity.

In order to perform a 3D reconstruction of the hierarchical porosity of the monolithic UiO-66_NH_2 material a FIB-SEM slice & view experiment was carried out with a Dual Beam FEI Helios Nanolab 600. FIB milling with Ga+ ions was performed at a current of 0.28 nA at 30 kV, keeping a distance of 20 nm between consecutive slices. SEM images were acquired with a 5 kV beam at a working distance of 4 mm. Fig. 1 presents a high magnification image of the ion beam polished material face, showing the nanoparticles that comprise the gel together with interparticle pores of different sizes.

The obtained image stack was subsequently aligned and processed with FEI Amira Resolve RT in order to produce a 1.30 x 1.08 x 2.88 µm 3D model of the porous MOF, presented on Fig. 2. Once the 3D model was obtained, it allowed performing further calculations to gather a deeper insight of the material. Therefore, a pore size distribution calculation was performed on FIJI [6] using the plugin developed by B. Münch *et al.* [7], yielding a total porosity of 53 % and the distribution in the 0 to 50 nm range presented on Fig. 3.

Interestingly, when the monolithic UiO-66_NH_2 material was subjected to Hg intrusion (Prior the collection, sample outgassed during 15 min. up to a P~6.5 Pa. Density and particle size distribution were determined in the pressure range from 0.1 to 200 MPa using a Micromeritics Autopore 9240 at room temperature) and N_2 adsorption porosimetry (Sample was previously outgassed at 150 °C overnight. N_2 sorption isotherm at 77 K performed using a Berlsorp Mini-Bel Japan apparatus), a porosity of around 54% was found with a pore size distribution disclosed on Fig. 4. If we examine the variation of pore volume with respect of pore radius (dV/dR) on Fig 3, it clearly shows two abrupt jumps at nearly the 100 and 200 Å, respectively. Likewise, the N_2 adsorption exhibited a bimodal distribution at nearly the

same pore size values, therefore validating the calculations performed purely on the 3D reconstructed model. In conclusion, the 3D reconstruction by means of FIB-SEM nanotomography has been revealed as a highly valuable tool to estimate the textural properties of complex hierarchical porous solids.

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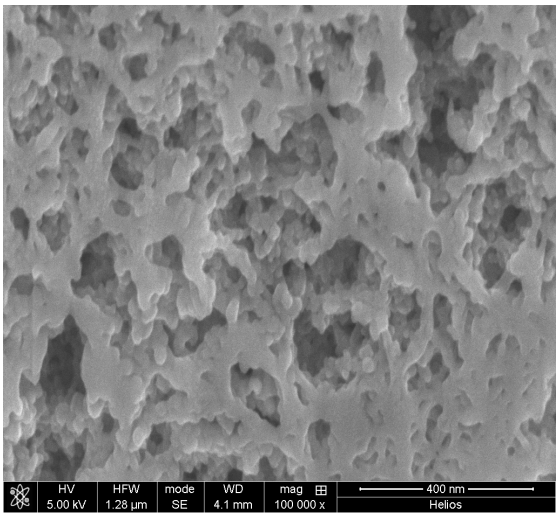

Figure 1. SEM image of the FIB polished material face.

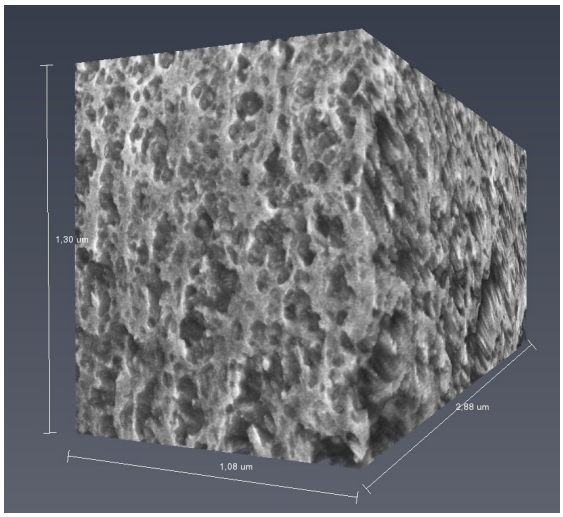

Figure 2. 3D Model of the porous MOF, reconstructed with the FIB-SEM image stack.

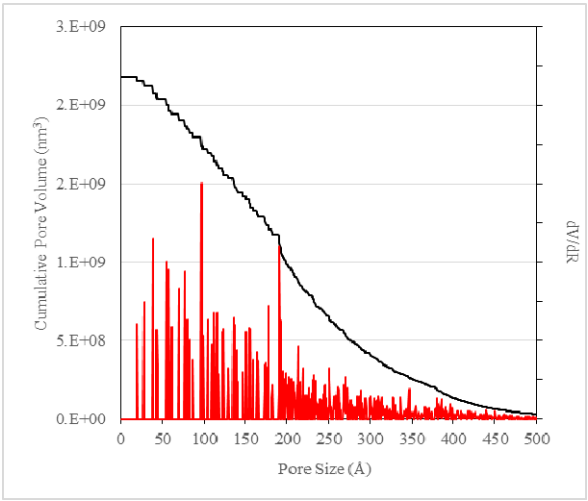

Figure 3. Pore size distribution and volume variation relative to pore radius calculated on the 3D structure.

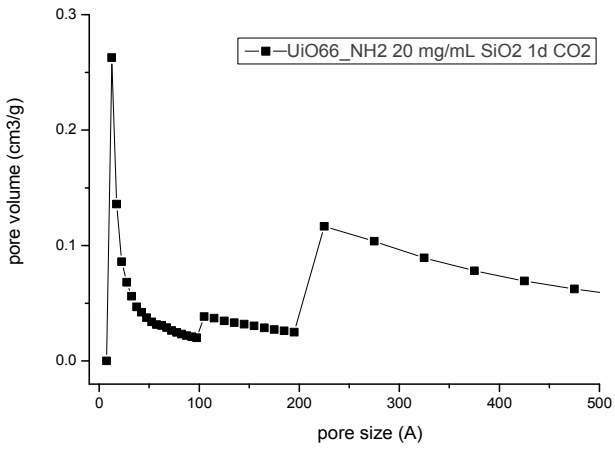

Figure 4. Pore size distribution obtained from the N_2 adsorption performed on the MOF.

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