1898
doi:10.1017/S1431927613011483
Microsc. Microanal. 19 (Suppl 2), 2013

3D X-Ray Microscopy (XRM) Technique for Evaluating the Porosity of the 3D Ordered Macroporous Materials by Colloidal Crystal Templating

Hongkun He[1], Jeff Gelb[2], Naomi Kotwal[2], Arno Merkle[2] and Krzysztof Matyjaszewski[1]

[1.] Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA.
[2.] Xradia, Inc., Pleasanton, CA 94588, USA.

Colloidal crystals have a structure of three-dimensionally (3D) periodic lattices, which are assembled from monodisperse spherical colloidal particles [1]. Because of their unique structures, colloidal crystals have been used as templates for making porous materials with highly ordered porous structures [2]. The pore size of the resulting porous materials can be measured by using the commonly used microscopy techniques, including scanning electron microscope (SEM), transmission electron microscope (TEM), and atomic force microscopy (AFM). However, it is a challenge to assess the quality of the 3D ordered macroporous (3DOM) structure, such as the interconnection of pores. Here, we utilize X-ray microscopy (XRM) to characterize the 3D structure of the porous polymers form by colloidal crystal templating and evaluate the influence of two different infiltration methods on the porosity of the affording materials.

The 3DOM polymers were prepared in a four step process (Figure 1): 1) preparation of colloidal crystals: the monodisperse poly(methyl methacrylate) (PMMA) spheres were synthesized by surfactant-free emulsion polymerization, and assembled via centrifugation approach [3]; 2) infiltration of polymer precursors: the PMMA colloidal crystals were used as the templates, which were infiltrated with an aqueous mixture of the monomer ((vinylbenzyl)trimethylammonium hydroxide (VBTMAOH)), the crosslinker (*N,N′*-(1,4-phenylenebis(methylene))bis(*N,N*-dimethyl-1-(4-vinylphenyl)methanammoinium) dihydroxide (PMVPMAOH)), as well as an azo initiator (VA-044); 3) polymerization: the precursor mixture was polymerized thermally in the void spaces formed between the PMMA spheres; and 4) removal of the templates: the PMMA spheres were eliminated by washing with THF and acetone to create the pores in the crosslinked polymer networks.

The 3D structures of the 3DOM polymers were characterized by nanoscale 3D XRM (Figure 2a,b,d,e), using an Xradia UltraXRM-L200. For the sample prepared through infiltration by filtration, a mixture of porous and non-porous structures was observed. Some areas of this material showed the honeycomb-like porous structure, while some areas showed dense bulk matter without pores. This was caused by the disturbance of the ordered structure of the PMMA colloidal crystals templates during the infiltration process aided by vacuum filtration, which generated many defects in their ordered structures. The defects between the PMMA spheres were filled with polymers to form non-porous blocks, resulting in poor interconnection between the pores. While for the sample prepared through infiltration by capillary forces, the continuous and homogeneous ordered porous structure was observed, and there were nearly no non-porous areas. This is because that infiltration by capillary forces is milder than by filtration, resulting in fewer defects in the templates and better interconnection of the pores in the products.

In addition, SEM was used to characterize the 3DOM polymers. As shown in Figure 2c,f, a striking contrast was also found between the samples prepared through different infiltration methods. These results are in good agreement with those obtained by XRM. However, the morphology observed by SEM was from the sample surfaces, and no internal structure could be seen. It reveals the advantage of using XRM for the characterization of both the external and internal structures of 3DOM materials.

In conclusion, we demonstrated that XRM is a powerful tool for the visualization of the 3D structures of 3DOM materials. The non-destructive XRM approach has the potential to enable time-dependent (4D) or *in situ* studies, as the porous structures are exposed to an environment or undergo any structural changes. The 3D XRM study of the porosity of the 3DOM polymers indicated that the infiltration of the polymer precursor solution into the colloidal crystal template by capillary force can greatly reduce the defects in the porous structure compared to the infiltration by filtration.

References:

[1] Y. N. Xia, *et al*, Adv. Mater. **12** (2000), p. 693.
[2] A. Stein, *et al*, Chem. Mater. **20** (2008), p. 649.
[3] H. He, *et al*, Energy Environ. Sci. **6** (2013), p. 488.

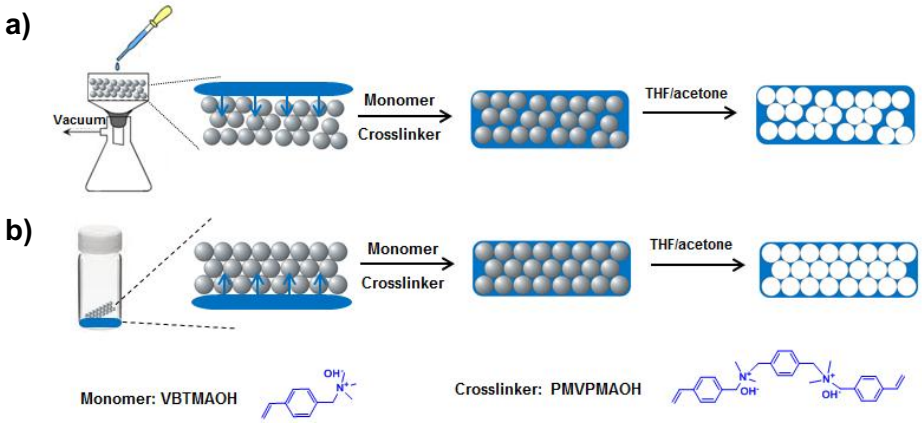

Figure 1. Preparation of the 3DOM polymers by PMMA colloidal crystal templating with different infiltration methods (by filtration (a) and by capillary force (b)).

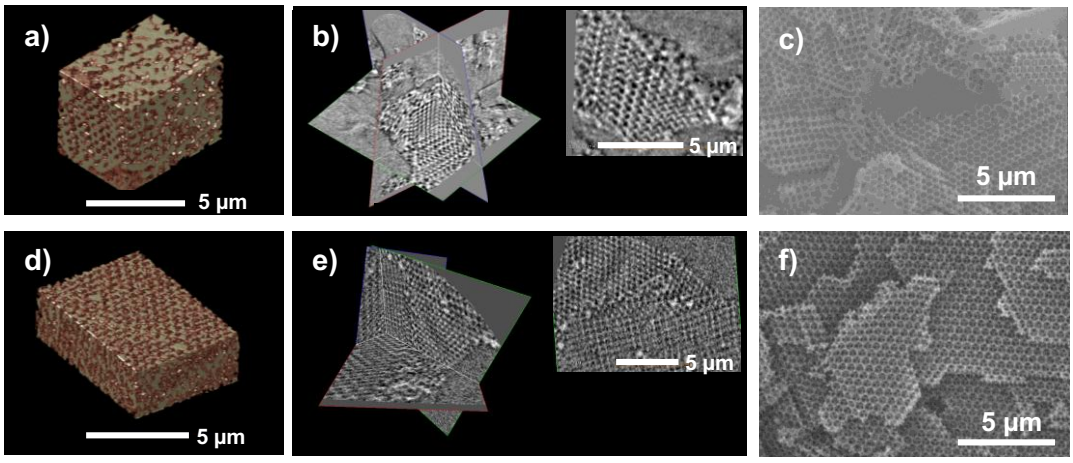

Figure 2. 3D XRM (a,b,d,e) and SEM (c,f) images of the 3DOM polymers prepared via different infiltration methods (by filtration (a-c) and by capillary force (d-f)): (a,d) the surface view of the structure, (b,e) the virtual slices through the imaging volume (the insets are the enlarged images of selected areas), and (c,f) SEM images of the surface structure.

https://doi.org/10.1017/S1431927613011483 Published online by Cambridge University Press