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Tiling Silicalite Nanoslabs into 3D Mosaics

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Nanoslabs with the Silicalite-1 structure type [1] are prepared through hydrolysis of tetraethylorthosilicate (TEOS) in concentrated solution of tetrapropylammonium hydroxide (TPAOH). Silicalite-1 nanoslab formation is directed by TPA cations. The nanoslab size, which can be monitored with low angle X-ray scattering, dynamic light scattering and electron microscopy, is controlled by the synthesis conditions [2]. The preparation departs from a basic suspension of nanoslabs with dimensions of 1.3 x 2.0 x 4.0 nm. Aggregation of these nanoslabs into an open structure is achieved by addition of an aqueous solution of cetyltrimethylammonium bromide (CTAB), a surfactant known to favour formation of uniform mesoporous channel structures [3]. For imaging of the structure a low intensity electron beam is applied. Because of the very large unit cell dimensions and our interest in the nanoslab tiling rather than in the internal structure of the nanoslabs, the images are mostly taken at large underfocus conditions. In this regime the resolution is not limited by the spherical aberration of the microscope and the contrast is determined by the focus. This is a regime where the "projected charge density" approximation of Cowley and Moodie is valid [4]. As a consequence, underfocus will image tunnels as bright dots.

The HREM of Zeotile-1 shows the presence of two types of pores, revealed by a different brightness (Fig.1b). The schematic mosaic structure of Zeotile-1 is superimposed in blue on the HREM image (Fig.1b bottom right). Nanoslabs are forced into face sharing, double units, measuring 2.6 x 2.0 x 4.0 nm and then linked in a hexagonal symmetry pattern. This tiling generates hexagonal and triangular channels, respectively (Fig.1b blue overlay). HREM image simulations for different focus values and different crystal thickness have been performed based on the proposed nanoslab tiling; the result for a large defocus value of 550 nm is shown in Fig.2. The overlay in fig. 2b of the projected silicate framework and the HREM simulated image clearly indicates the one to one correspondence between the tunnels in the projected structure and the bright dots in the HREM image. The simulation is in striking agreement with the experimental image, as illustrated by the white-framed inset in Fig.1b.

At least four other phases, with different lattices and different symmetries, have been analysed as well. The fine structure within a nanoslab however could not be resolved with HREM because of electron irradiation damage of the weak Si-O bonds. The FT of the HREM images only show information on the nanoslab tiling; no reflections related to the internal nanoslab structure are detected.

Mesoporous materials obtained from non-structured silica sources typically have a single type of channel, determined by the template properties. The presence of different channels in the same Zeotile, i.e. Zeotile-1 with triangular and hexagonal channels (Fig.1b) and Zeotile-3 with two differently sized square channels, is a direct consequence of tiling of slabs with rigid and uniform shape. Zeotiles are unexpectedly robust materials combining the advantages of micro- and mesoporous silicate materials. The four newly discovered Zeotiles illustrate the structural diversity of the material. From a structural point of view, other combinations are equally possible.

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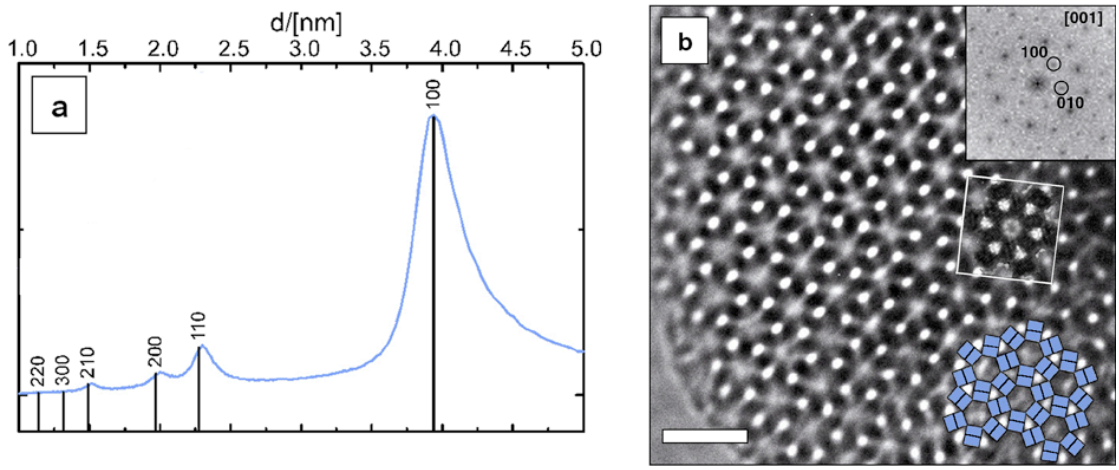

Figure 1. a) XRD pattern of Zeotile-1. b) HREM (scale bar = 10 nm) with Fourier transform and simulated HREM image (white-framed insert). A structural model is overlaid on the HREM image.

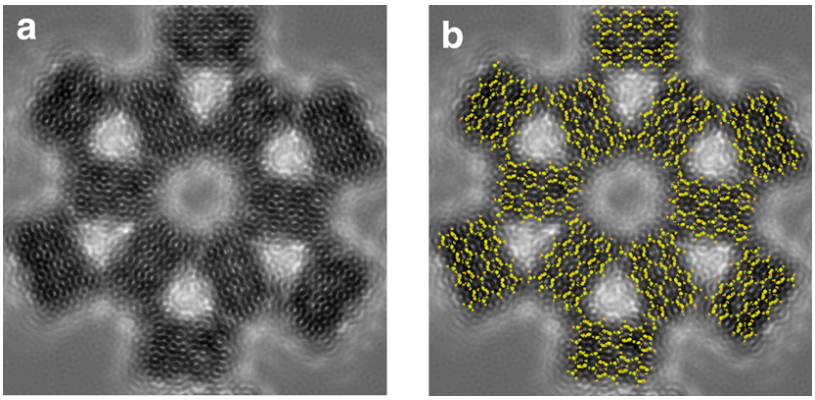

Figure 2. a) HREM image simulation of Zeotile-1 at a focus of –550 nm and a crystal thickness of 16 nm; b) Superposition of the projected silicate framework on the simulated HREM image of.a).

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