Supplementary Information

Synthesis of highly *b*-oriented zeolite MFI films by suppressing twin crystal growth during the secondary growth

Xianming Li,[a] Yong Peng,[a] Zhengbao Wang,*[a] and Yushan Yan[a, b]

[a] Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China, and [b] Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA

*Corresponding author. Fax/Tel: +86-571-8795-2391; E-mail: zbwang@zju.edu.cn

1. Experimental Details

1.1 Synthesis of MFI seed crystals

Pure silica zeolite MFI (silicalite-1) seed crystals were synthesized as follows. The synthesis solution of molar composition 1TEOS: 0.32TPAOH: 165H_2O was made by slowly adding TEOS to a solution of TPAOH and water under stirring. A clear synthesis solution was obtained after stirring at room temperature for 4 h. Then the synthesis solution was directly loaded into a Teflon–lined stainless steel autoclave. Sequently, the autoclave was sealed and placed in a rotation convection oven at 175 ^{o}C for 2 h. In the rotation convection oven, the autoclave was fixed in a stationary barrier, which could rotate with the axis under 20 rpm. After the synthesis, the mixture was quenched. Then the sample was recovered, thoroughly washed with deionized water, and dried at 60 ^{o}C. Finally SDA included in the crystals was removed by calcination at 500 ^{o}C with the ramp speed of 1 ^{o}C/min. The size of the seed crystals ($a \times b \times c$ axis) was 700 × 300 × 900 nm^3.

1.2 Preparation of *b*-oriented seed monolayer

Silicon wafers were used as the substrates in this work. Before seeding, the substrates were immersed in hydrogen peroxide solution for 45 min, then rinsed with deionized water, and dried at 60 ^{o}C. Perfect *b*-oriented MFI seed monolayers formed on silicon wafers by rubbing seeds on the substrates with a finger in latex gloves.

1.3 Secondary growth

During the secondary growth, various synthesis solutions with different TPAOH concentrations were used. A synthesis solution of molar composition 1TEOS: xTPAOH: 165H_2O was made by slowly adding TEOS to a solution of TPAOH and deionized water under stirring. To accelerate the hydrolization of TEOS, the minimum molar ratio of OH^-/TEOS was kept at 0.10 by adding NaOH to the synthesis solution at low TPAOH concentration ($x < 0.10$). A clear synthesis solution was obtained after stirring at room temperature for 4 h. This clear solution was then loaded into a Teflon–lined autoclave. A seeded substrate was vertically placed with a Teflon holder at the bottom of the autoclave. The autoclave was then sealed and placed in a convection oven at 150 ^oC for 3 h. After the synthesis, the mixture was quenched. Finally, the sample was recovered, thoroughly washed with deionized water, and dried at 60 ^oC.

1.4 Characterization of samples

The morphology of silicalite films synthesized was examined by a field-emission scanning electron microscopy (FE-SEM) at 8 kV, using a Carl Zeiss ULTRA 55 microscope.

X-ray diffraction (XRD) patterns were collected on a Panalytical X' PertPro diffractometer using CuKα radiation.

2. MFI films synthesized with various TPAOH concentration (x=0, 0.005, 0.1 and 0.2)

The seed layer changed little after the secondary growth using a synthesis solution containing no TPAOH (Fig. S1a). At low TPAOH concentration ($x = 0.005$), the seeds grew to elongated crystals and some defects were found (Fig. S1b). At high TPAOH concentration ($x = 0.1$ and 0.2), continuous films were obtained. However, lots of twin crystals were observed, and the amount of twin crystals increased with TPAOH concentration (Fig. S1c and d).

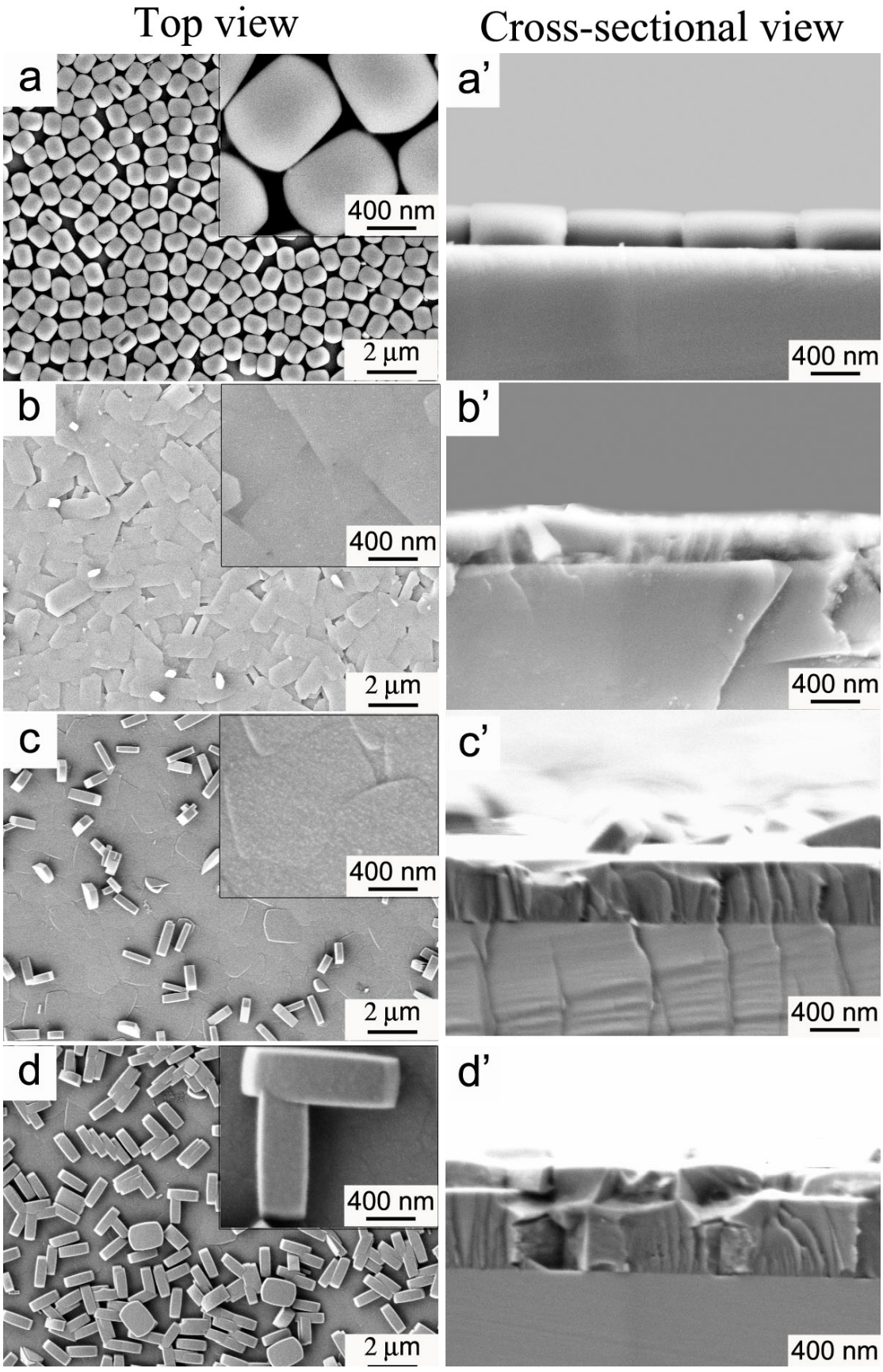

Fig. S1 SEM images of the films synthesized with various TPAOH concentration (x). (a) x = 0, (b) x = 0.005, (c) x = 0.1, and (d) x = 0.2.

3. Recycle of the synthesis solution

A synthesis solution (solution-1) of molar composition 1TEOS: 0.05TPAOH: 0.05NaOH: 165H_2O was used. The solution was clear after stirring at room temperature for 4 h and then was loaded into a Teflon–lined autoclave with a seeded substrate. Sequently, the autoclave was sealed and placed in a convection oven at 150 ^oC for 3 h. After the synthesis, the mixture was quenched. A clear solution (solution-2) and the sample (film-1 (Fig. 1c)) were recovered.

Solution-2 was used with a fresh seeded substrate in the first repeated experiment. And the secondary growth was carried out as mentioned above. After the secondary growth, a clear solution (solution-3) and the sample (film-2 (Fig. S2a)) were recovered.

Solution-3 was used with a fresh seeded substrate in the second repeated experiment. And the secondary growth was carried out as mentioned above. After the secondary growth, a clear solution (solution-4) and the sample (film-3 (Fig. S2b)) were recovered.

As shown in Fig. S2, no significant changes were observed among the three samples, film-1 (Fig. 1c), film-2 (Fig. S2a), and film-3 (Fig. S2b). Moreover, all solutions recovered after the secondary growths were clear. The results showed that the synthesis solution was reusable.

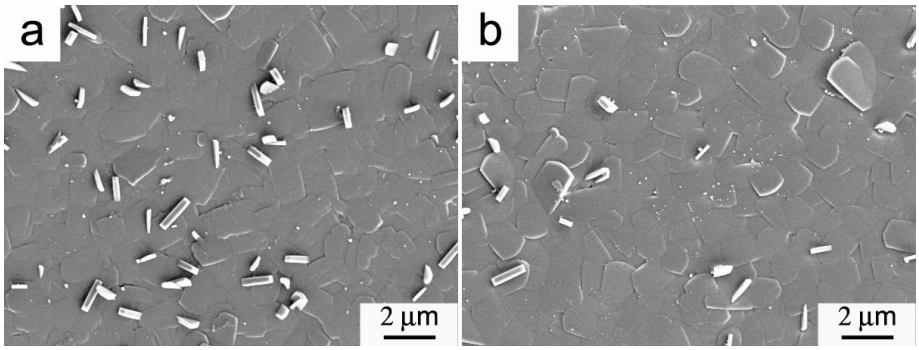

Fig. S2 SEM images of the films synthesized in the repeated experiments: (a) film-2 and (b) film-3.

4. Effects of the synthesis time

In order to measure the correlation between the size of seed crystals and the crystallization time, non-continuous *b*-oriented seed layer was prepared on the silicon wafer substrate. A synthesis solution of molar composition 1TEOS: 0.32TPAOH: 165H_2O was used. The results are shown in Fig. S3. It is observed that the size in *c*-direction increased sharply with the synthesis time, but the size in *b*-direction increased slowly after the synthesis time of 2.5 h. The twin crystals already

appeared even at the synthesis time of 1 h 40 min (Fig. S4a). New *b*-oriented layer could be observed on the naked substrate surface (without seed crystals) after 2 h (Fig. S4b).

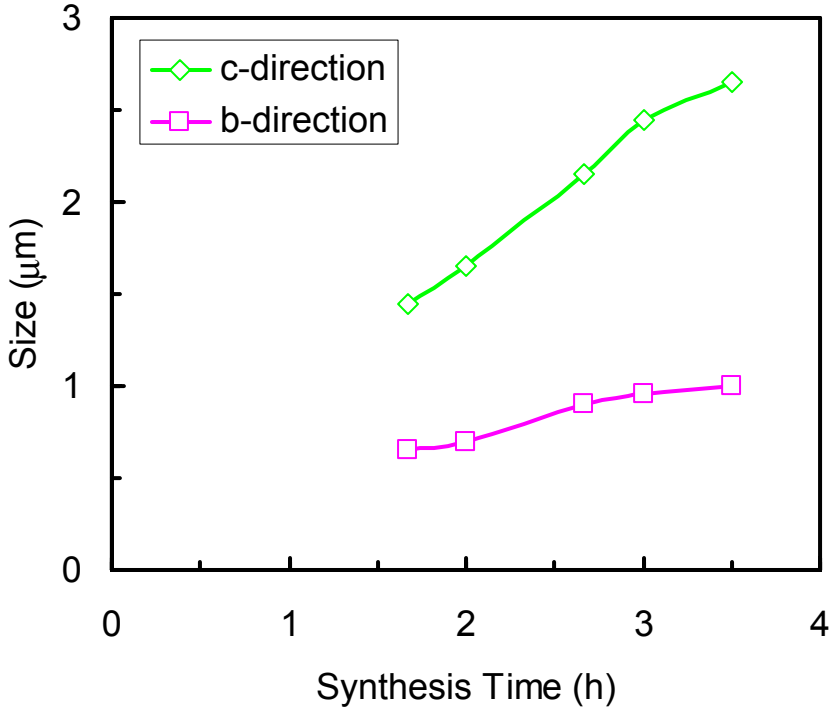

Fig. S3 The crystallization curve for the synthesis solution of 1TEOS: 0.32TPAOH: 165H_2O.

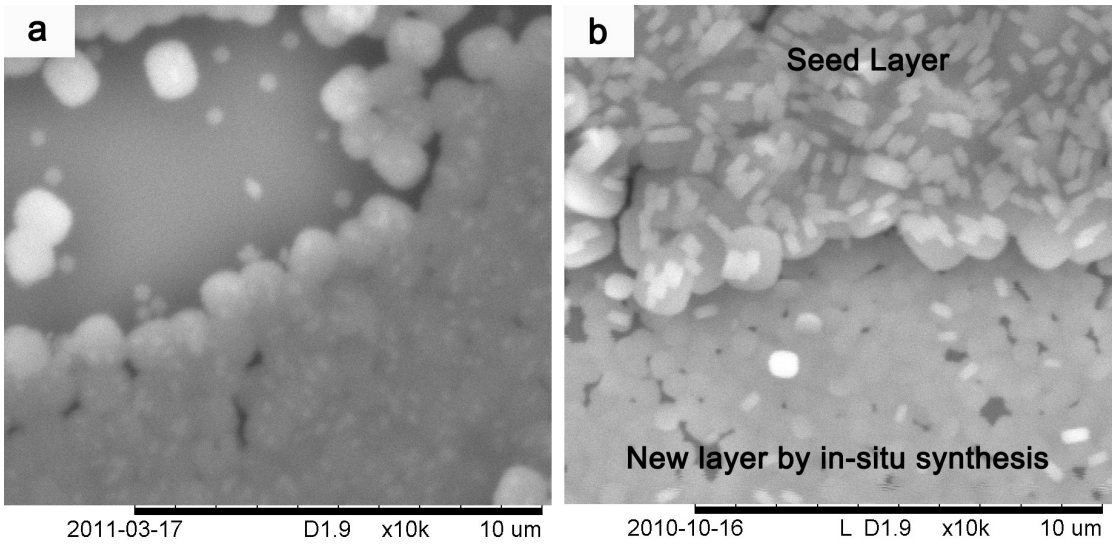

Fig. S4 SEM images of the seed growth after the synthesis time of (a) 1 h 40 min, (b) 2 h. The synthesis solution of molar composition 1TEOS: 0.32TPAOH: 165H_2O.