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Microwave-assisted seeded growth of the submicrometer-thick and pure *b*-oriented MFI zeolite film using an ultra-dilute synthesis solution

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1. Experimental Details

1.1 Synthesis of silicalite-1 crystals

The silicalite-1 crystals sized at ca. 1.3 × 0.9 × 0.5 μm^3 were synthesized using the ingredient of 1TEOS/0.2TPAOH/90H_2O/4C_2H_5OH. Tetraethyl orthosilicate (TEOS, 98%, Tianjin Kewei Chemical Co. Ltd) was slowly added to a solution of tetrapropyl ammonium (TPAOH, 20%, Tianjin Guangfu Chemical Co. Ltd) under vigorous stirring. The clear gel was stirred at room temperature for 24 h and transferred to a Teflon-lined autoclave, followed by the hydrothermal reaction with stirring at 140 °C for 8 h. The collected silicalite-1 crystals were thoroughly washed with a copious amount of deionized distilled water (DI water) and dried at 120 °C overnight.

1.2 Preparation of *b*-oriented silicalite-1 monolayers

The manual assembly of zeolite monolayers on the bare glass plate and the supported layer of PVA or chitosan was performed according to our previous studies (Langmuir, 2008, **24**, 11942–11946). Before the preparation of chitosan and PVA thin layer, the glass plate (2 × 2 cm^2) was first treated by potassium dichromate solution, followed by ultrasonic treatment in acetone and being dried in a cleaned atmosphere for one day.

1.3 The seeded growth of silicalite-1 films

The microwave-assisted seeded growth was carried out at 423 K in a microwave oven (MDS-6, Sineo Microwave Chemical Technology Co., Ltd). The substrate was held by a Teflon holder with the supported silicalite-1 monolayer or the bare chitosan film upwards in the synthesis solution with the molar composition of 1TEOS:0.2TPAOH:800H_2O:4C_2H_5OH. Then, the autoclave was removed and cooled down to room temperature. The sample was removed, washed with DI water and dried in vacuum at 368 K.

The seeded growth under the conventional electric heating was carried out in an electric oven at 423 K for 2 h, where the substrate was held by a Teflon holder with the seed layer upwards in the synthesis solution loaded in a Teflon-lined autoclave.

1.4 Instrumentation

FE-SEM images were recorded on a FEI Nanosem 430 at an acceleration voltage of 5 kV and 10 kV. X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2500v/pc diffractometer using Cu Kα radiation (λ_1=0.1541 nm and λ_2=0.1544 nm at 40 kV and 200 mA).

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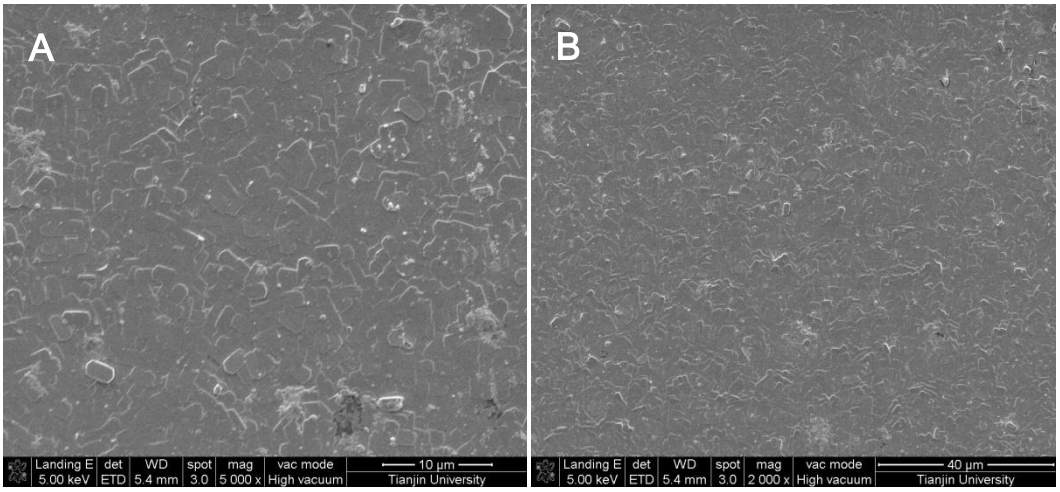

Fig. S1 Top-view FE-SEM images at the magnifications of ×5000 (A) and ×2000 (B) for the as-prepared silicalite-1 film after the microwave-assisted seeded growth for 1 h.

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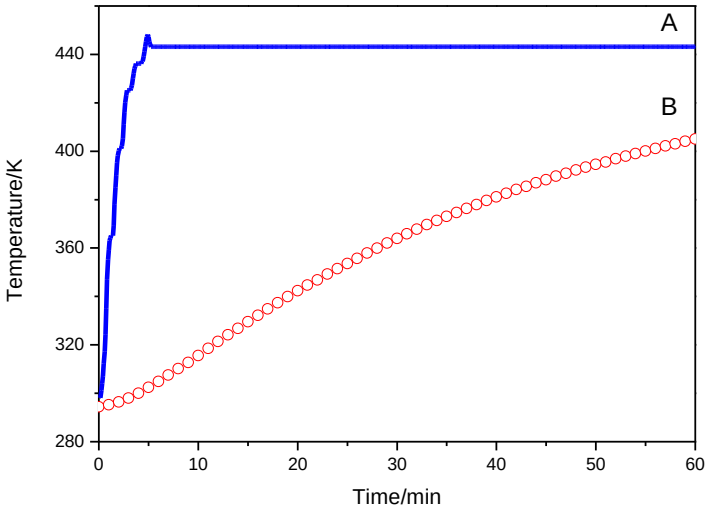

Fig. S2 Variation of temperature with time for the synthesis solution under the microwave-assisted heating (A) and the conventional electric heating (B).

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Table S1. Comparison of submicrometer-thick and uniformly *b*-oriented silicalite-1 films prepared by the seeded growth with TPA^+ as the structure-directing agent from literature reports and our work.

No.	H_2O/Si	H_2O/TPAOH	Synthesis time, h	Twin crystals on the film surface	Integrity	Heating method	Refs
1	200	1000	2*+3	rare	continuous	conventional	[1]
2	165	3300	3	a few	continuous	conventional	[2]
3	165	515.6	3	abundance	continuous	conventional	[2]
4	800	4000	1 h	no	continuous	microwave	This work

[1] Y. Liu, Y. S. Li and W. S. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 1768–1769.

[2] X. Li, Y. Peng, Z. Wang and Y. Yan, *CrystEngComm*, 2011, **13**, 3657–3660.

* pretreating the synthesis solution hydrothermally.

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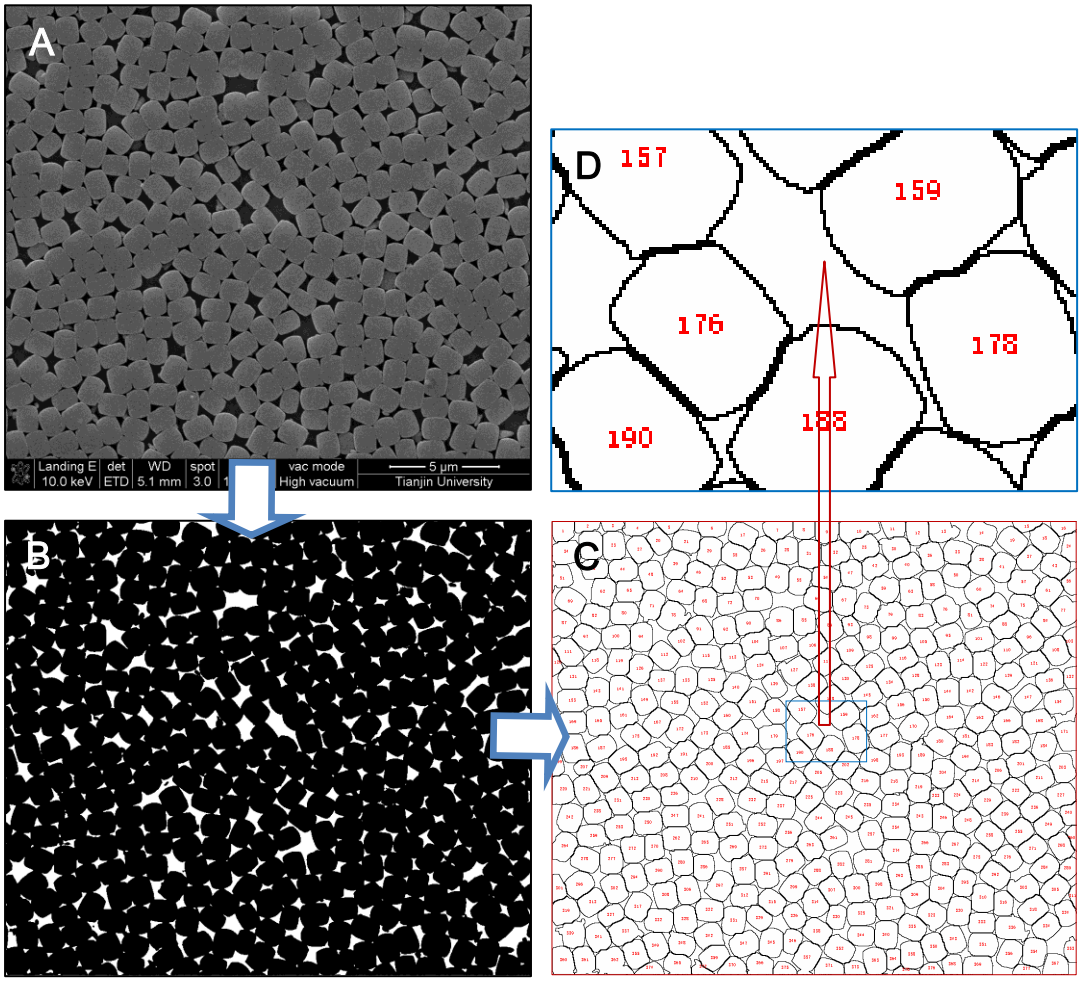

Fig. S3 (A) Top-view FE-SEM image of the as-prepared silicalite-1 monolayer on the supported chitosan,(B) the corresponding image with black (covered) and white (void) areas, (C) the digital image with covered and void areas, and (D) the enlarged digital image for the selected area.

Table S2. Comparison of monolayer on chitosan supported glass and bare glass by the image analysis software (ImageJ) [1]

Substrates	Number of crystals*	Void ratio (%)
bare glass plate	368	9.9
supported chitosan layer	367	11.2
supported PVA layer	365	13.3

*For counting the number of crystals, only crystals with area larger than 0.5 μm^2 are counted.

[1] Rasband, W. Image Processing and Analysis in Java, http://rsb.info.nih.gov/ij.

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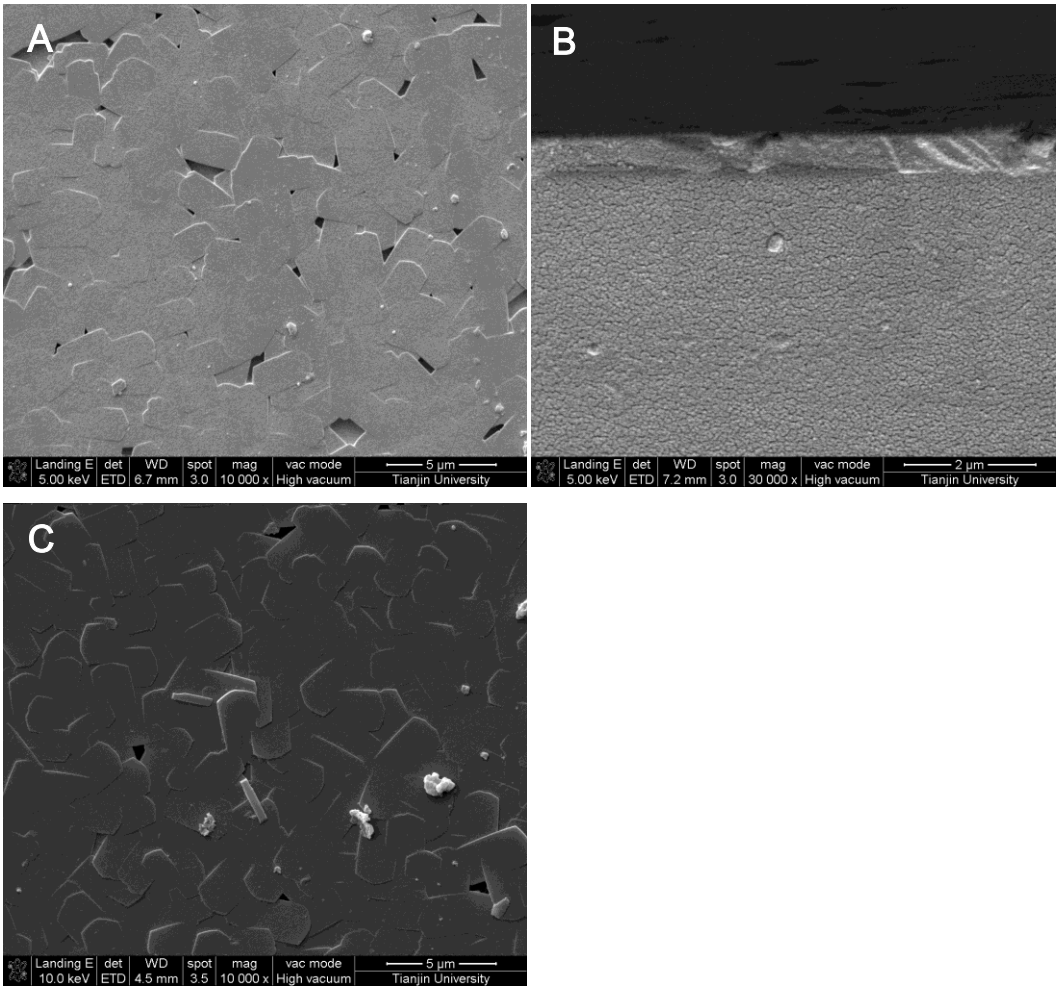

Fig. S4 (A) Top-view FE-SEM image of as-prepared MFI film on the bare glass plate after the microwave-assisted seeded growth for 1 h, (B) The corresponding cross-sectional image of (A), (C) Top-view FE-SEM image of as-prepared MFI film on the bare glass plate after the microwave-assisted seeded growth for 2 h.

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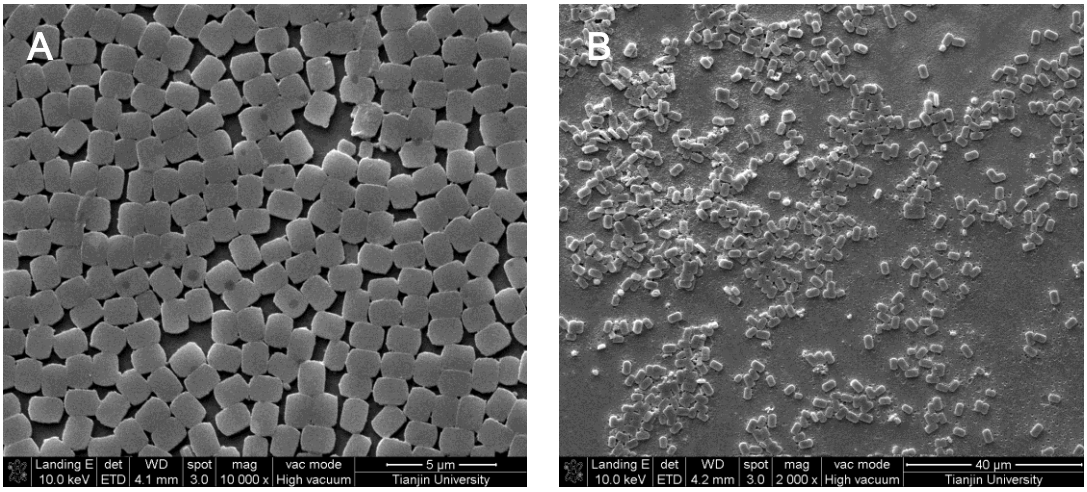

Fig. S5 Top-view FE-SEM images of the as-prepared silicalite-1 monolayer on the supported PVA layer (A) and the MFI zeolite film after the microwave-assisted seeded growth for 1 h (B).

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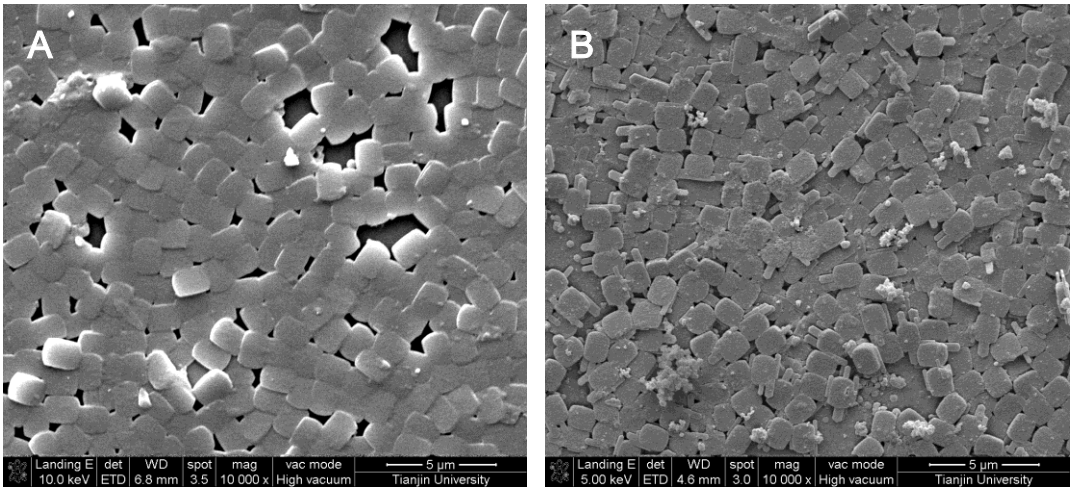

Fig. S6 Top-view FE-SEM image of as-prepared MFI film on the supported chitosan layer after the seeded growth for 2 h by the conventional electric heating at 150 °C (A) and 180 °C (B).