

CHEMISTRY

AN ASIAN JOURNAL

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Chem. Asian J.* 10.1002/asia.202000111

Link to VoR: <http://dx.doi.org/10.1002/asia.202000111>

A Journal of



A sister journal of *Angewandte Chemie*
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Single-Mode Microwave Heating-Induced Concurrent Out-of-Plane Twin Growth Suppression and In-Plane Epitaxial Growth Promotion of *b*-Oriented MFI Film under Mild Reaction Condition

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Dedication ((optional))

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Abstract: In this study, single-mode microwave heating was applied in epitaxial growth of *b*-oriented MFI seed monolayer prepared by facile manual assembly, resulting in the formation of well-intergrown and highly *b*-oriented MFI film with few twins exhibiting precise molecular sieving property at reaction temperature no higher than 100 °C within 2 hours, therefore making it possible for easy operation in an open environment. The capability for concurrent suppression of undesired out-of-plane twin growth and promotion of in-plane epitaxial growth rate under much milder reaction condition was attributed to obvious superiority of single-mode microwave heating in comparison with conventional multi-mode microwave heating in aspects of microwave field uniformity and intensity. Our research indicated that single-mode microwave heating technique could potentially be a useful tool for improving the microstructure and therefore the performance of diverse zeolite films.

Suppression of twins in *b*-oriented MFI film during the epitaxial growth has proven to be effective for reduction in diffusion path length of guest molecules and elimination of grain boundary defects.^[1] Recent decades have witnessed great efforts on the preparation of *b*-oriented MFI films with few twins.^[2] Diverse methods like multi-mode microwave heating,^[2a] precursor solution pretreatment,^[2b] employing specifically designed template (trimer-TPAOH),^[1a] vapor phase transformation,^[2c,2d] solvent-free epitaxial growth^[2e] and additive addition (like ammonia salts,^[2f] sodium tungstate^[2g] and 1,2-dihydroxybenzene^[2h]) have proven effective for twin suppression.

Among these methods, multi-mode microwave heating has been recognized as a potent tool for the preparation of zeolite films showing noteworthy superiority in aspects of reaction time, thickness and grain size uniformity.^[2a,3] Moreover, our previous research suggested that twin growth of *b*-oriented MFI films could be successfully avoided, owing to the well-recognized nucleation-related bottleneck effect.^[2a] From a practical perspective, however, it is anticipated that *b*-oriented MFI film with few twins could be prepared by hydrothermal synthesis at temperatures no higher than 100 °C, therefore making it possible to operate in an open environment.

In contrast to multi-mode microwave heating, potential applications of single-mode microwave heating in zeolite film

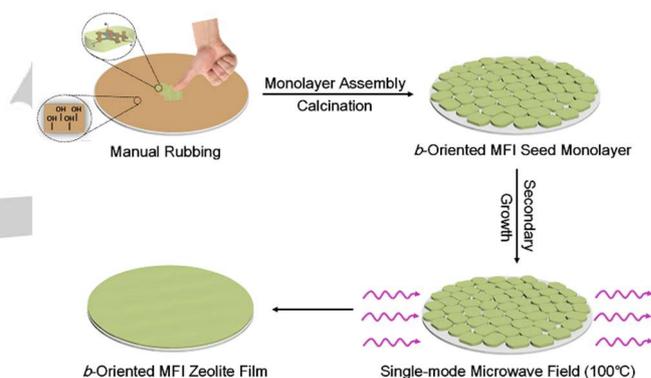


Figure 1. Schematic illustration of the as-synthesized *b*-oriented MFI zeolite film fabrication process.

synthesis have been rarely explored, although being quite effective in modulating the microstructure of NH₂-MIL-125(Ti) membranes.^[4] Taking into consideration the fact that single-mode microwave heating has obvious superiority over its multi-mode counterpart in aspects of microwave field uniformity and intensity,^[4,5] it is anticipated that notably enhanced nucleation-related bottleneck effect and higher in-plane epitaxial growth rate can be attained simultaneously, which may potentially result in the fast formation of well-intergrown MFI films with few twins under much milder hydrothermal conditions.

In this study, highly *b*-oriented MFI film was prepared by combining oriented seeding and controlled in-plane epitaxial growth. Initially, a well-established manual assembly method was employed for oriented deposition of uniform MFI seed monolayer; consequently, single-mode microwave heating was applied in the epitaxial growth of MFI film (Figure 1). It is noteworthy that with this method not only undesired twin growth could be suppressed with effect but also well-intergrown MFI film could be prepared on diverse substrate from a diluted aqueous precursor solution at 100 °C within 2 hours, thus making it attractive for easy operations in an open environment (e.g. by refluxing).

Uniform coffin-shaped MFI seeds (0.9×0.45×1.2 μm³, Figure 2a) were prepared by facile hydrothermal growth.^[6] Prior to oriented

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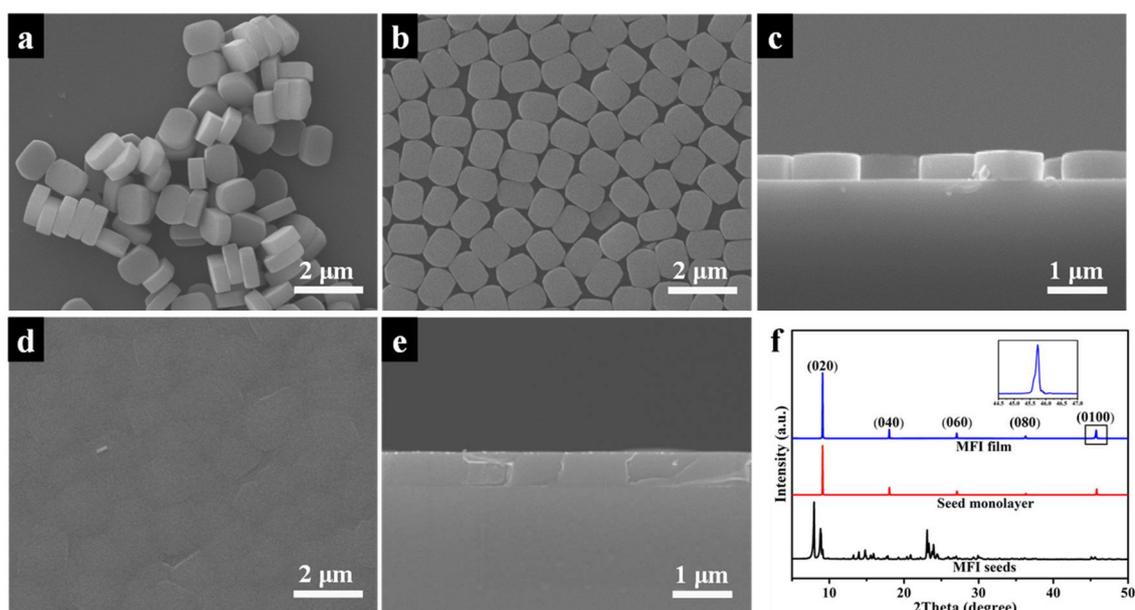


Figure 2. SEM images of (a) MFI seeds, (b) *b*-oriented MFI seed monolayer and its (c) cross-sectional image, (d) prepared MFI film after secondary growth on seeded glass plate and its (e) cross-sectional image; (f) XRD patterns of MFI seeds, MFI seed monolayer and the obtained MFI film. Inset: Enlarged image of (0 10 0) diffraction peak. Note: the $K\alpha_2$ line was removed from XRD patterns.

deposition, a thin layer of PVA was utilized to enhance the binding strength between MFI seeds and the substrates.^[7]

The next step involved oriented deposition of MFI seed monolayer. As well reported in the literature, manual rubbing was employed for the organization of MFI seed monolayer on polyvinyl alcohol (PVA) thin layer-modified glass substrate.^[8] SEM results indicated that prepared MFI seed monolayer (Figure 2b and c) was uniform and compact. XRD patterns further confirmed the dominance of a preferred *b*-orientation since only (0*k*0) diffraction peaks were observed (Figure 2f).

Finally, controlled epitaxial growth was conducted on *b*-oriented MFI seed monolayer. As mentioned in our previous study, it turned out to be very difficult to balance twin suppression and film continuity in case of conventional heating, even if the synthetic condition had been fully optimized.^[4] This could be ascribed to intrinsically high nucleation rate of MFI crystals in the bulk precursor solution and low epitaxial growth rate of *b*-oriented MFI seed monolayer. It therefore became essential to concurrently suppress the bulk nucleation of MFI crystals and promote the epitaxial growth rate of *b*-oriented MFI seed monolayer during the secondary growth.

Our recent research indicated that relying on the unique nucleation-related bottleneck effect of multi-mode microwave heating, the undesired twin growth could be suppressed with effect under optimized reaction conditions.^[2a] Nevertheless, further lowering the reaction temperature to ~100 °C without significantly degrading the microstructure as well as prolonging the reaction time has remained impractical. Considering the obvious superiority of single-mode microwave heating in aspects of microwave field uniformity and intensity, single-mode microwave heating was herein applied in epitaxial growth of *b*-oriented MFI film. SEM images (Figure 2d) indicated that well-intergrown MFI film with few twins had been formed after microwave heating at 100 °C within 2 h. Cross-sectional image (Figure 2e) showed that prepared MFI film was ~0.6 μm-thick. Corresponding XRD pattern (Figure 2f) showed strong (0*k*0)

reflections, which unambiguously confirmed that prepared MFI film remained dominantly *b*-oriented.

It is noteworthy that the employment of single-mode microwave heating is essential to obtain the desired microstructure under lower reaction temperature (~100 °C). As a comparative experiment, we also tried preparing well-intergrown *b*-oriented MFI films via conventional and multi-mode microwave heating under similar reaction conditions (the reaction temperature was set to 100 °C). Nevertheless, in both cases the grain size of MFI seeds only slightly increased (Figure 3a and c). Moreover, there still existed substantial inter-crystal defects in aspects of conventional and multi-mode microwave heating, even though the reaction period had been further extended to 12 h and 4 h, respectively (Figure 3b and d). Particularly, a substantial amount of twin crystals were formed concurrently using conventional heating (Figure 3b). Obviously, the large microstructural disparity between MFI films prepared under single-mode microwave heating and conventional/multi-mode microwave heating could be ascribed to the significantly enhanced microwave field uniformity and intensity, which ultimately led to much higher in-plane epitaxial growth rate of MFI seeds even at lower reaction temperature. In addition, it was noted that the mother liquor after single-mode microwave treatment remained clear and color-less, and no appreciable sedimentation could be observed at the bottom of the vessel (Figure S1), which demonstrated that undesired secondary nucleation in the bulk solution was effectively suppressed simultaneously.

Our method was not only adapted to MFI seeds with specific morphology. For instance, besides 1.2 μm-sized MFI crystals, uniform and regular-shaped MFI seeds with smaller grain size (~0.4 μm, shown in Figure S2a) were successively prepared and assembled into high-quality MFI seed monolayer (Figure S2b and d) via facile manual assembly. Moreover, well-intergrown *b*-oriented MFI film with few twins (Figure S2c and d) were readily obtained after single-mode microwave heating at 100 °C for 2 h.

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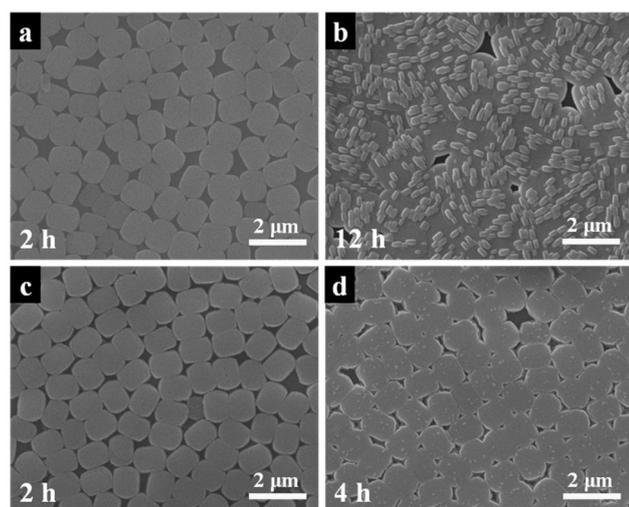


Figure 3. SEM images of MFI films prepared by (a, b) conventional heating and (c, d) multi-mode microwave heating in a TPA-containing gel (1TEOS:0.15TPAOH:135H₂O) at 100 °C for different time. The number marked at the bottom left corner denoted the epitaxial growth duration

In addition, we further prepared 4.0 μm-sized MFI seeds, which could still be easily organized into uniform and closely packed MFI seed monolayer with the manual assembly method (Figure S3a). Nevertheless, it became impractical to fabricate well-intergrown MFI film with single-mode microwave heating under mild reaction conditions (Figure S3b) possibly due to excessively large gaps between neighboring seeds and insufficient nutrient supply during the epitaxial growth. We therefore conclude that MFI films with desired microstructures can be obtained under mild reaction conditions on the premise that the grain size of MFI seeds is not excessively large.

To further verify the generality of this method, besides smooth glass plates, coarse stainless-steel plates and inert Pt electrodes (Figure S4a and b) were used as substrates of MFI films. Our results indicated that regardless of their surface properties, MFI seed monolayers (Figure S4c and d) and films with desired microstructures (Figure 4a, S4e, S4f and S5) could also be easily prepared, which was quite beneficial to expand their application areas.

Finally, we examined molecular sieving properties of *b*-oriented MFI film-coated Pt electrodes, which were employed as working electrodes in following electrochemical experiments. The cyclic voltammetry (CV) behavior of several redox species of different charge and size in aqueous solution, including [Ru(NH₃)₆]³⁺ (~5.5 Å) and [Fe(phen)₃]²⁺ (~13.0 Å), was tested. The pore size of MFI crystals along the *b*-axis is 5.5 Å, so it was expected that [Ru(NH₃)₆]³⁺ could diffuse through prepared *b*-oriented MFI film and experience redox reactions on the Pt electrode while [Fe(phen)₃]²⁺ would be excluded. As shown in Figure 4b, we found that in comparison with the bare Pt electrode, a much weaker and deformed CV signal was detected for [Ru(NH₃)₆]³⁺ on MFI film-modified electrode, while no CV response was detected for [Fe(phen)₃]²⁺ (Figure 4c). For the mixed [Ru(NH₃)₆]³⁺ and [Fe(phen)₃]²⁺, merely the redox signal for [Ru(NH₃)₆]³⁺ was detected (Figure 4d), which convincingly demonstrated the defect-free nature and precise molecular sieving property of MFI film.

To summarize, in this study we prepared well-intergrown *b*-oriented MFI film with few twins by employing single-mode

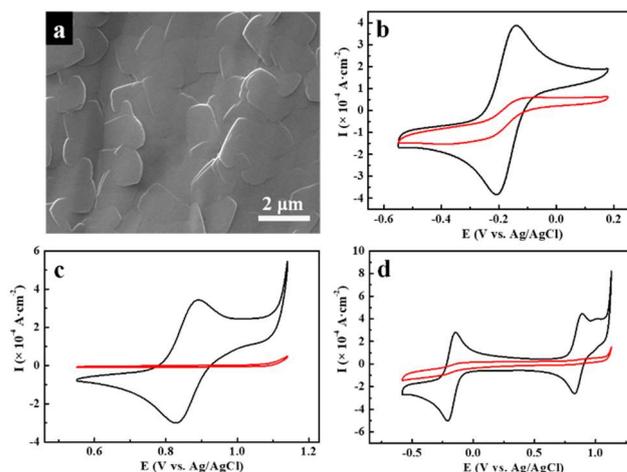


Figure 4. (a) SEM image of prepared MFI film on Pt electrode. Cyclic voltammograms of [Ru(NH₃)₆]³⁺ and/or [Fe(phen)₃]²⁺ in aqueous solutions. Black line: bare Pt electrode; red line: Pt electrode-supported *b*-oriented MFI film for (b) [Ru(NH₃)₆]³⁺, (c) [Fe(phen)₃]²⁺, and (d) [Ru(NH₃)₆]³⁺ + [Fe(phen)₃]²⁺. Supporting electrolyte: 0.5 M KCl. Reference electrode: Ag/AgCl electrode. Scan rate: 50 mV/s.

microwave heating for the epitaxial growth. Owing to its obvious superiority compared with multi-mode microwave heating in aspects of microwave field uniformity and intensity, MFI film with desired microstructures could be easily prepared. It was noteworthy that single-mode microwave heating not only effectively suppressed the undesired twin growth, but also significantly enhanced the in-plane epitaxial growth rate of MFI seeds even at much lower reaction temperature (~100 °C), therefore making it promising for easy operation in an open environment. Moreover, with this method high-quality MFI film could be easily prepared irrespective of surface properties of the substrate. CV experiment convincingly demonstrated the defect-free nature and precise molecular sieving property of prepared MFI film. It was expected that single-mode microwave heating technique could serve as powerful tool in improving the microstructure and performance of diverse zeolite films.

Acknowledgements

The authors are grateful to National Natural Science Foundation of China (21176231), Liaoning Revitalization Talents Program (XLYC1807084), the Thousand Youth Talents Program and the Technology Innovation Team of Dalian University of Technology (DUT2017TB01) for the financial support.

Keywords: microwave heating • zeolites • film • orientation • hydrothermal growth

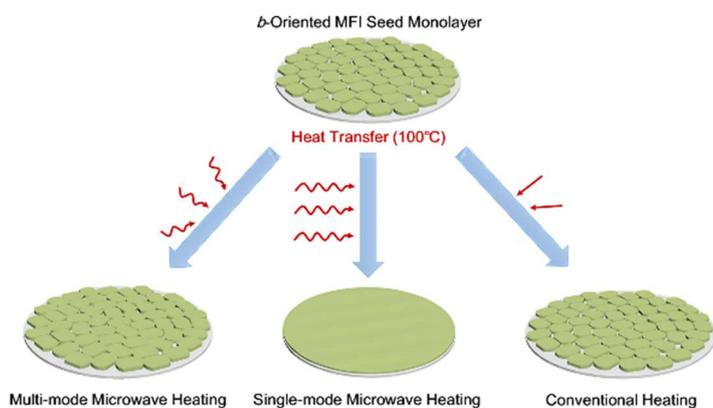
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Relying on the obvious superiority of single-mode microwave heating in terms of microwave field uniformity and intensity, well-intergrown and highly *b*-oriented MFI film with precise molecular sieving property was successfully prepared under much milder reaction conditions (at 100 °C within 2 hours), therefore making it promising for easy operation in an open environment.