

Fabrication of highly *b*-oriented MFI monolayers on various substrates

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By surface modification of MFI microcrystals with *sec*-butanol and pre-coating the substrate with a temporary water layer, a convenient process is developed to directly assemble anisotropic MFI microcrystals into highly *b*-oriented monolayers on various substrates with different surface conditions.

The self-assembly of building blocks of all length scales into complex structures has received great attention in many research areas. Driven by their abundant host-guest properties, assembly of molecular sieve crystals into two- and three-dimensionally organized structures has attracted much attention in recent years. In particular, oriented molecular sieve monolayers can be further tailored so that they are suitable to be used in a variety of fields, such as separation membranes,^{1–3} selective sensors⁴ and optic materials.⁵ Many approaches, including *in situ* growth,^{6,7} chemical-bonding induced assembly,⁸ convective assembly,⁹ dip-coating¹⁰ and electric-field-driven assembly,^{11,12} have been used to prepare oriented molecular sieve monolayers, and some extensive review articles^{13–15} have been published that summarize the new advances in this field.

Among all the molecular sieves, the formation of oriented anisotropic zeolite (such as MFI type zeolites) monolayers is especially fascinating but also challenging. To date, to fabricate high-quality *b*-oriented MFI zeolite monolayers, the most feasible method is chemical-bonding induced assembly,^{5,8} developed by K. B. Yoon *et al.* from Sogang University, Korea. But during the whole process, the experimental conditions need to be accurately controlled, *e.g.* a humidity-free environment has to be maintained during the process, and an environmentally unfriendly organic solvent is used as the reaction medium. Moreover, for all these self-assembly methods, substrates with very flat surfaces and abundant functional groups (such as glass plates, silica plates and metal plates) are most frequently used. However, the direct organization of zeolite microcrystals on substrates with unfavorable surface conditions (such as rough surface morphology and few functional groups) is rarely reported. With expanding applications found to be appropriate for the application of oriented zeolite layers or films, it is highly desirable to develop a simple, efficient and environmentally friendly process to directly organize zeolite microcrystals, on various substrates with different surface conditions, with a preferred orientation.

In this communication, referring to the concept of the LB technique, we developed a novel method to directly assemble anisotropic MFI zeolite microcrystals into a monolayer with *b*-orientation on various substrates. The process can be described as follows: firstly, a thin layer of water is spread onto the substrate surface to serve as a temporary soft substrate; secondly, a calculated amount of a suspension composed of *sec*-butanol molecules and *sec*-butanol-modified zeolite microcrystals (zeolite microcrystals with *sec*-butoxy groups chemically anchored on the outer surface) is slowly and unceasingly injected onto the water layer to form a zeolite monolayer. After controlled evaporation of the temporary liquid layer (The self-assembly process is conducted at 25 °C under controlled humidity of 60% RH), a zeolite monolayer with *b*-orientation on the substrate is obtained.†

The MFI monolayer thus formed with a glass plate as substrate is subject to SEM characterization. As is shown in Fig. 1a, the as-prepared zeolite monolayer is highly oriented and continuous. With a closer look at samples (Fig. 1b), it can be observed that nearly every zeolite microcrystal anchors to the glass plate with its large facets and contacts closely with its neighbours. XRD characterization confirms strong *b*-orientation of zeolite monolayer, and [0*k*0] reflections dominate in the diffraction pattern, as shown in Fig. 1c.

It has been well-documented that alcohol molecules can directly react with the zeolite surface *via* an esterification

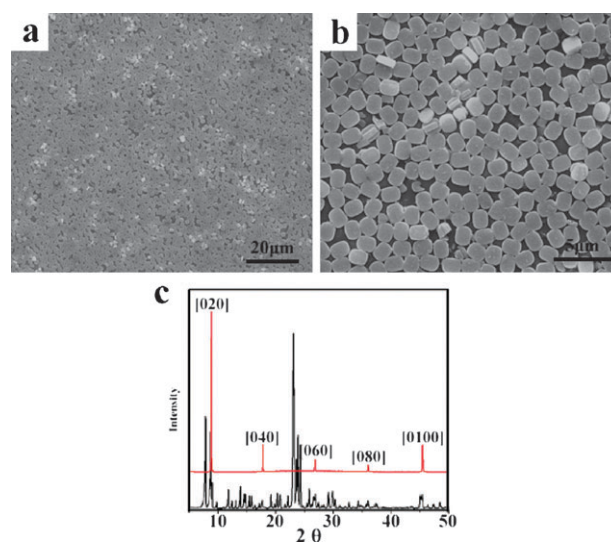


Fig. 1 (a) SEM images of as-prepared MFI monolayer with *sec*-butanol as dispersant, (b) an enlarged image of (a), and (c) an XRD pattern of the as-prepared *b*-oriented MFI monolayer with *sec*-butanol as dispersant (top), and XRD pattern for random oriented powders of Silicalite-1 (bottom).

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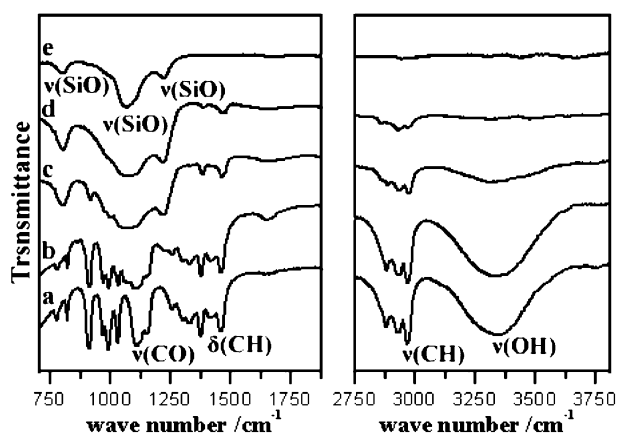


Fig. 2 Attenuated total reflection (ATR)-IR spectra of (a) *sec*-butanol and *sec*-butanol treated MFI zeolites dried for (b) 0 min, (c) 10 min, and (d) 60 min, and (e) ATR-IR spectrum of untreated MFI microcrystals.

reaction, leading to their covalent attachment to the zeolite surface.¹⁶ Fig. 2 shows the attenuated total reflection (ATR)-IR spectra of the MFI *sec*-butanol suspension, which were repeatedly recorded upon exposure to air over a period of 1 h. After drying at 25 °C for 10 min, the O–H bond vibrations of the *sec*-butanol molecules (wide peaks from 3100 cm⁻¹ to 3700 cm⁻¹) greatly weakened, and MFI characteristic peaks (at 795 cm⁻¹, 1060 cm⁻¹ and 1215 cm⁻¹) became dominant (see Fig. 2c), indicating that most of the *sec*-butanol molecules had evaporated. After 1 h drying, O–H bond vibrations are no longer visible. However, C–H bond vibrations (stretching vibrations from 2800 cm⁻¹ to 3000 cm⁻¹, bending vibrations from 1250 cm⁻¹ to 1500 cm⁻¹) and C–O bond vibrations (between 1000 cm⁻¹ and 1250 cm⁻¹) are still clearly visible (see Fig. 2d). Based on these observations, we propose that the –OCHCH₂(CH₃)₂ group might anchor onto the surface of the MFI microcrystals *via* interactions between *sec*-butanol molecules and the terminal –OH groups of zeolite particles, and that's why they can float at air–water interface. Similar results have also been reported by another research group recently.¹⁷

Besides *sec*-butanol, other kinds of alcohols, including ethanol, *n*-propanol, *iso*-propanol, *iso*-butanol and *n*-butanol, are also used here as dispersants in the experiment. However, it is found that all of them suffer from problems of the loss of compactness or insufficient *b*-orientation. Satisfactory explanations to this phenomenon is still not clear; here, we suppose that it may be attributed to the different hydrolysis rate of these functional groups anchored on surface of zeolite particles, which has been proved by well-documented articles.¹⁸ Further investigation to this unexpected phenomenon is still needed.

In order to investigate the applicability of this method, a stainless-steel plate, a ceramic mixed oxide disk (such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}), and a porous α -alumina disk were also utilized as substrates instead of the glass plate (Fig. 3). Fig. 3a illustrates the surface morphology of the stainless-steel plate. Grooves and cracks can be observed spreading through its surface. Unaffected by these unfavorable surface conditions, the MFI monolayer with good coverage and *b*-orientation was still formed (Fig. 3b). The same result was

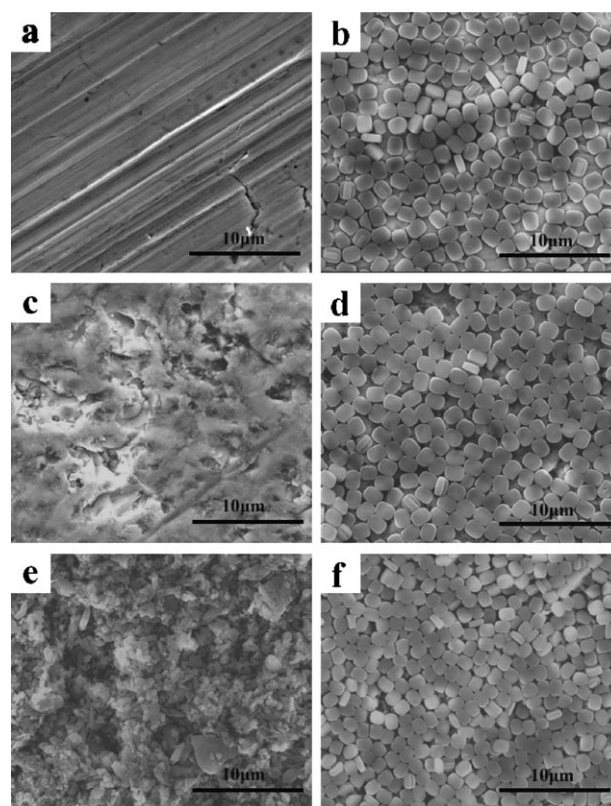


Fig. 3 SEM images of (a) stainless-steel substrate, (b) stainless-steel substrate with MFI monolayer, (c) Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} substrate, (d) Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} substrate with MFI monolayers, (e) porous α -Al₂O₃ substrate, and (f) porous α -Al₂O₃ substrate with MFI monolayer.

observed when Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} disk was used as the substrate (Fig. 3c and d). Taking into consideration of the fact that none of these substrates possess abundant hydroxide functional groups to facilitate the interactions with zeolite microcrystals, we conclude that the method introduced here can directly organize zeolite microcrystals onto various substrates with preferred orientation, regardless of their unfavorable surface properties. Aiming at the application in membrane fabrication, a home-made symmetric porous α -Al₂O₃ substrate (Fig. 3e) was also tested. A compact and highly *b*-oriented MFI monolayer formed on the rough α -Al₂O₃ surface (Fig. 3f). Based on this result, we maintain that oriented zeolite separation membranes on different substrates can be prepared using the secondary growth method, which has been developed by our group.

Compared with conventional self-assembly approaches, we can find some distinct features from this method. Generally speaking, two different processes can be distinguished here during the formation of the oriented zeolite monolayer: formation of an oriented monolayer of zeolite microcrystals, and its attachment to support. Conventional self-assembly methods (*in situ* growth, convective assembly *etc.*) tend to couple these processes together. Consequently, the properties of substrate have to be taken into consideration because of their great influence on the final morphology of zeolite monolayer. But, the new approach we introduce here does decouple these two processes completely, owing to the introduction of a

water layer as a temporary “soft” substrate. So not only can we exert more controls over this process, but also simultaneously do we make it less dependent on the surface properties of substrate; as a result, many pre-treatment process may be omitted if not necessary.

In conclusion, a novel method is developed to organize MFI microcrystals into a continuous and highly *b*-oriented monolayer. With the introduction of water layer as temporary soft substrate, we can self-assemble *sec*-butanol pre-treated MFI particles into monolayer on various substrates. No other organic solvents are used except *sec*-butanol. This approach is simple, effective and environmentally friendly. More importantly, this method may be illustrative to the oriented self-assembly of other particles with regular shapes.

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Notes and references

† Experimental details.

A glass plate ($2 \times 2 \text{ cm}^2$) was washed with DDI water, immersed in piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 2/1$) and heated to 90°C to remove organic impurities. After 1 h, it was taken out and washed with DDI water for three times, and then immersed in pure ethanol solution. Before use, it was taken out and dried in air. The stainless-steel plate, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ disk (home-made), and porous α -alumina disk (home-made), were cleaned with liquid detergent to remove impurities on their surface, and then they were washed with DDI water before use.

MFI (Silicalite-1) microcrystals were synthesized according to the well-documented procedure,¹ but with slight modification. 7.626 g TPAOH (20 wt.%, Aldrich) and 7.5 g TEOS (98 wt.%, Kermel) were mixed with 60 g DDI water. The mixture was further stirred at room temperature for 24 h, and then transferred into a Teflon-lined vessel. It was then placed in an oil bath with stirring. The temperature was maintained at 130°C . After 12 h, it was taken out and quenched to room temperature. Zeolite microcrystals were then centrifuged (6000 r/min) and washed three times. After that, they were air-dried in an oven overnight and ready for use. As-prepared MFI particles had the coffin shape with an average size of $2 \mu\text{m}$.

The self-assembly process was conducted at 25°C and 60% RH. The glass plate was placed onto a horizontal plane. Then 0.8 ml DDI water was injected onto the substrate. After the formation of a uniform water layer on glass plate, the zeolite suspension was slowly and continuously injected onto the water layer using an automatic injector (TJ-1A, Baoding Longer Precision Pump Co., Ltd.) at the

speed of $2 \mu\text{l min}^{-1}$. A monolayer was formed after injection of $75 \mu\text{l}$ suspension. With the evaporation of liquid layer, MFI microcrystals self-assembled into a continuous and highly *b*-oriented monolayer on the substrate. Identical procedures were employed to perform self-assembly process for stainless-steel plate, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\alpha\text{-Al}_2\text{O}_3$ disk.

- Z. P. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis and D. G. Vlachos, *Science*, 2003, **300**, 456; Z. P. Lai, M. Tsapatsis and J. P. Nicolich, *Adv. Funct. Mater.*, 2004, **14**, 716.
- W. H. Yuan, Y. S. Lin and W. S. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 4776.
- X. C. Xu, W. S. Yang, J. Liu and L. W. Lin, *Adv. Mater.*, 2000, **12**, 195; Y. S. Li, H. L. Chen, J. Liu and W. S. Yang, *J. Membr. Sci.*, 2006, **277**, 230; G. Q. Zhu, Y. S. Li, H. L. Chen, J. Liu and W. S. Yang, *J. Mater. Sci.*, 2008, **43**, 3279.
- S. Mintova, S. Y. Mo and T. Bein, *Chem. Mater.*, 2001, **13**, 901; S. Li, X. Wang, D. Beving, Z. W. Chen and Y. S. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 4122.
- J. S. Lee, H. Lim, K. Ha, H. Cheong and K. B. Yoon, *Angew. Chem., Int. Ed.*, 2006, **45**, 5288.
- S. Li, Z. J. Li, K. N. Bozhilov, Z. W. Chen and Y. S. Yan, *J. Am. Chem. Soc.*, 2004, **126**, 10732.
- X. D. Wang, B. Q. Zhang, X. F. Liu and Y. S. Lin, *Adv. Mater.*, 2006, **18**, 3261.
- S. Y. Choi, Y. J. Lee, Y. S. Park, K. Ha and K. B. Yoon, *J. Am. Chem. Soc.*, 2000, **122**, 5201; G. S. Lee, Y. J. Lee and K. B. Yoon, *J. Am. Chem. Soc.*, 2001, **123**, 9769; Y. S. Chun, K. Ha, Y. J. Lee, J. S. Lee, H. S. Kim, Y. S. Park and K. B. Yoon, *Chem. Commun.*, 2002, 1846; J. S. Park, G. S. Lee, Y. J. Lee, Y. S. Park and K. B. Yoon, *J. Am. Chem. Soc.*, 2002, **124**, 13366; J. S. Lee, J. H. Kim, Y. J. Lee, N. C. Jeong and K. B. Yoon, *Angew. Chem., Int. Ed.*, 2007, **46**, 3087.
- J. A. Lee, L. Meng, D. J. Norris, L. E. Scriven and M. Tsapatsis, *Langmuir*, 2006, **22**, 5217.
- L. C. Boudreau, J. A. Kuck and M. Tsapatsis, *J. Membr. Sci.*, 1999, **152**, 41.
- J. Caro, G. Finger, J. Kornatowski, J. R. Mendau, L. Werner and B. Zibrowius, *Adv. Mater.*, 1992, **4**, 273.
- J. C. Lin, M. Z. Yates, A. T. Petkoska and S. Jacobs, *Adv. Mater.*, 2004, **16**, 1944.
- K. B. Yoon, *Acc. Chem. Res.*, 2007, **40**, 29.
- M. A. Snyder and M. Tsapatsis, *Angew. Chem., Int. Ed.*, 2007, **46**, 7560.
- M. Zhou, B. Q. Zhang and X. F. Liu, *Chin. Sci. Bull.*, 2008, **53**, 801.
- C. H. Cheng, T. H. Bae, B. A. McCool, R. R. Chance, S. Nair and C. W. Jones, *J. Phys. Chem. C*, 2008, **112**, 3543.
- Z. Wang, L. H. Wee, B. Mihailova, K. J. Edler and A. M. Doyle, *Chem. Mater.*, 2007, **19**, 5806.
- G. C. Ossenkamp, T. Kemmitt and J. H. Johnston, *Chem. Mater.*, 2001, **13**, 3975.