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To be cited as: *Chem. Asian J.* 10.1002/asia.202100507

Link to VoR: https://doi.org/10.1002/asia.202100507

A Journal of
ACES
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Fabrication of a kagomé-type MOF membrane by seeded growth on amino-functionalized porous Al_2O_3 substrate

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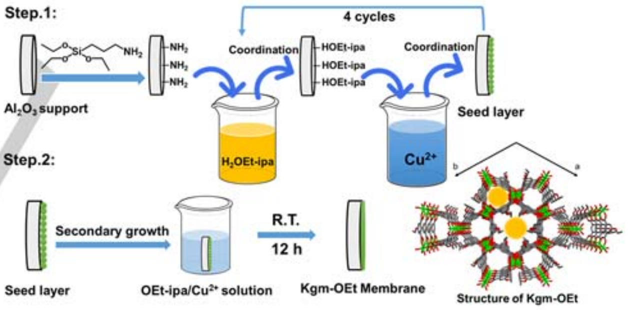
Abstract: In this study, we report the efficient fabrication method for the membrane of a metal-organic framework (MOF) (Kgm-OEt) which is one kind of kagomé-type MOF with a two-dimensional (2D) sheet structure having one-dimensional (1D) channels suitable for separation of H_2 from other larger gases. Kgm-OEt seed layer was created on a Al_2O_3 substrate using layer-by-layer (LBL) growth, then a membrane was fabricated by the secondary growth. The membrane on a 3-aminopropyltriethoxysilane (APTEs)-treated substrate obtained in this method was continuous and defect-free with the crystal orientation suitable for gas transportation, while the membrane grown on an unmodified substrate was loosely packed with the unfavorable crystal orientation.

Metal-Organic Frameworks (MOFs) are a new class of crystalline porous solid materials for gas storage,[1,2] separations,[3,4] heterogeneous catalysis,[5] drug delivery[6] and so on. Their structures are one, two, or three-dimensional periodic networks formed by the bridging of metal ion-based nodes and organic ligands. An important essence of MOFs is the large specific surface area and tunable pore size, structure and functionality.[7-9] In the past few decades, MOF membranes for gas and liquid separations have been extensively studied.[10-12] However, it remains challenging to prepare a continuous and high-quality MOF membrane for practical gas separation applications, owing to the low affinity between the MOFs and substrates. For example, the direct growth of MOF membranes by immersing substrates in the solution of metal ions and organic ligands is the primary fabrication method.[13] However, it often leads to heterogeneous nucleation of MOF crystals resulting in the formation of defects, although chemical modification of substrates sometimes can improve it.[14,15] Instead of direct growth, the secondary growth method, where MOF membrane is grown from the substrate with seed MOF crystals, is regarded as a promising method. In the secondary growth method, the fabrication of a continuous seed layer is one of the key processes. Nevertheless, the preparation of a homogeneous seed layer is not easy due to the poor adhesion bond between MOF particle and surface of common substrate materials such as Al_2O_3. Some methods have been developed so far to prepare a uniform seed layer.[16-19] 3-aminopropyltriethoxysilane(APTEs) is used to chemically modify substrates to enhance the interaction between the substrate surface and MOF.[20,21] The layer-by-layer (LBL) growth method is a commonly used technique to fabricate thin MOF films known as surMOF by immersing the substrate into solutions of ligands and metal ions repeatedly.[22-24] However, the studies on the preparation of two-dimensional (2D) MOF membrane by LBL growth are still limited since 2D MOF has high aspect ratio of crystals, which often prevents dense packing of crystals.

In this study, a new membrane based on [Cu(OEt-ipa)] (Kgm-OEt, OEt-ipa = 5-Ethoxyisophthalate) was prepared by secondary growth method on Al_2O_3 substrate. Kgm-OEt having an infinite kagomé-type 2D sheet structure.[25-27] Kgm-OEt is formed through the connection between Cu paddle-wheel units by the OEt-ipa ligands. The 2D sheets create two kinds of one-dimensional (1D) infinite channels along the c axis; one channel is triangular and contains only coordinated water molecules on the paddle wheel SBUs. Another pore has hexagonal geometry and contains all the alkoxy groups pointed towards the pore center. The cross-sectional size of the two channels is around 3.5 Å after the removal of coordinated solvent molecules. The channel is larger than the kinetic diameter of H_2 (2.89 Å) and smaller than those of N_2 (3.64 Å), CH_4 (3.80 Å) and C_2H_4 (4.20 Å). In this study, we employed a combination of surface modification of Al_2O_3 substrate and LBL seeding method to fabricate seed layer followed by the secondary solvothermal crystal growth forming continuous Kgm-OEt membrane (Scheme 1).



Scheme 1. Schematic diagram for the preparation of the membrane and the structure of Kgm-OEt. Atoms are colored as follows: Cu, green; O, red; C, gray.

The LBL method was applied to synthesize Kgm-OEt seed layer. Firstly, a layer of APTEs was deposited on an Al_2O_3 substrate through the reaction of ethoxysilane of APTEs and hydroxyl groups on the surface of Al_2O_3. Secondly, the seed layer was construted by soaking the substrate into the solutions of H_2OEt-ipa and $Cu(NO_3)_2$ repeatedly. After the first seeding cycle, strong XRD peaks indicate the formation of Kgm-OEt crystals on the APTEs-modified substrate, while the weak XRD peaks suggest that almost no crystals were formed on the unmodified Al_2O_3 substrate (Figure S1). In addition, SEM images show that MOF crystals can grow on the surface of APTEs-modified substrate, while only the substrate surface is seen on the unmodified Al_2O_3 substrate (Figure S2). Optical images of the substrate also show that the color of the seed layer from the APTEs-modified substrate was green which was far deeper than that from the unmodified substrate (Figure S3). These results indicate that APTEs modification can promoted the crystal nucleation.

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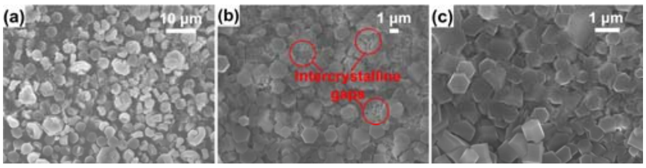

Figure 1. SEM images of Kgm-OEt crystals of (a) powder sample and seed layer on (b) unmodified and (c) APTEs-modified Al_2O_3 substrate.

As the seeding cycle times increased, the intensity of XRD peaks in APTEs-modified Al_2O_3 substrate increased (Figure S4), indicating that denser Kgm-OEt seed layer was fabricated by LBL cycles. The intensity of XRD peaks was almost unchanged between four and five LBL cycles, and the SEM image shows that the seed layer completely covered the APTEs-modified substrate, thus four cycles can be enough for the deposition of the seed layer. In contrast, uncovered Al_2O_3 is still visible on the unmodified substrates even after seeding for four cycles (Figure 1). Notably, APTEs modification not only improves the nucleation rate of Kgm-OEt, but also results in the generation of particles with smaller sizes than those on unmodified substrate (400 nm and 1.2 μm, respectively, Figure S5). The nucleation rate on the APTES-modified substrate might be faster than that on the unmodified one due to the higher density of ligand on the surface by $-NH_2$ groups, which may lead to the formation of smaller particles on the APTES-modified substrate.[28,29] The smaller particle size of the seed layer would be advantageous to form a continuous MOF membrane after the secondary growth, while larger particles tend to produce binary gaps between particles.

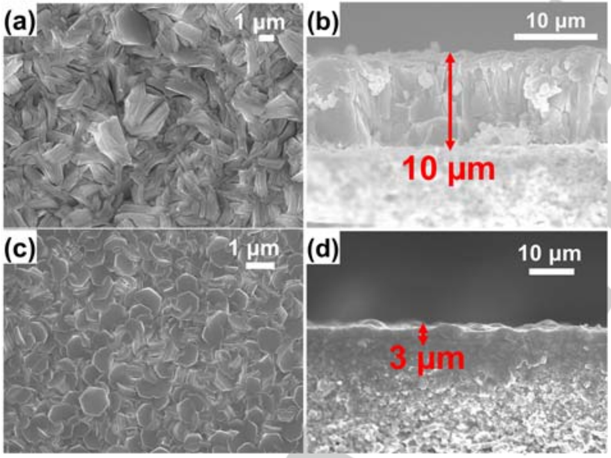

Figure 2. Top and cross-sectional view SEM images of Kgm-OEt membranes synthesized on the (a, b) unmodified and the (c, d) APTEs-modified substrate at different magnifications.

Kgm-OEt membrane was grown from the seed layer by the secondary growth at room temperature. Top view SEM image of the membrane on the unmodified substrate shows that the crystals are loosely packed and poorly intergrown (Figure 2(a)). The SEM cross-sectional images indicate that the thickness of the membrane prepared on the unmodified substrate was about 10 μm. The continuity of the membrane was relatively poor, and small gaps between MOF particles were observed (Figure 2(b)). On the other hand, the surface was densely covered with hexagonal plate crystals merged tightly with each other forming the intergrowth structure on the APTEs-modified substrate and the thickness of the membrane on APTEs-modified substrate was about 3 μm (Figure 2(c)-(d)), which was about 3 times thinner than that by unmodified substrate, and the membrane was grown very compact without observable gaps between the intercrystalline boundary. It should be noted that the 2D sheet MOF crystals on the unmodified substrate tend to grow nearly vertical to the substrate surface after the secondary growth. On the other hand, most hexagonal particles were parallel to the APTEs-modified substrate, which can be suitable for gas transportation.

The difference in the growth direction of Kgm-OEt could be explained by the van der drift growth model.[30,31] The morphology of these Kgm-OEt crystals is a 2D hexagonal sheet structure with the order of crystal dimensions $L_b = L_a > L_c$, where L_i denotes the crystal length along the i axis (Figure S6). As the crystals grow larger, they collide with each other, and the orientation of the crystals change to get sufficient space for the crystal growth. On the unmodified substrate, the *a*- and *b*- axes growth of the crystal is faster than that of the *c*-axis, so the *a*- and *b*- axes are oriented to be perpendicular to the substrate. On the APTEs-modified Al_2O_3 substrate, as the particle sizes of the membrane were smaller, the collision of the crystals and the change of the crystal growth direction were greatly suppressed.

Figure. 3(a) shows the XRD patterns of the simulation of Kgm-OEt, powder, seed layer, membranes on unmodified and APTEs-modified substrate. All of the peak positions of membrane samples well match with the simulation, indicating the no impure phase. To analyze the orientation of the membranes, we compared the XRD of the membranes on APTEs-modified and unmodified substrate (Figure S7). Figure 3(b) shows the crystal plane of Kgm-OEt. The (001) plane is parallel to the hexagonal crystal. The 001 peak of membrane on unmodified substrate is almost absent, indicating the crystal orientation vertical to the hexagonal plane. For the membrane on APTEs-modified substrate, the 001 peak is clearly visible, indicating that the vertical growth is suppressed. EDX mapping analysis further revealed the boundary between the Kgm-OEt membrane and the APTEs-modified Al_2O_3 substrate (Figure 4(a), (b)). Optical images of the APTEs-modified Al_2O_3 substrate, seed layer and membrane also showed in Figure 4(c). In short, we tuned microstructure by deposition of amino groups on Al_2O_3 substrate and successfully prepared high-density and continuous Kgm-OEt membrane.

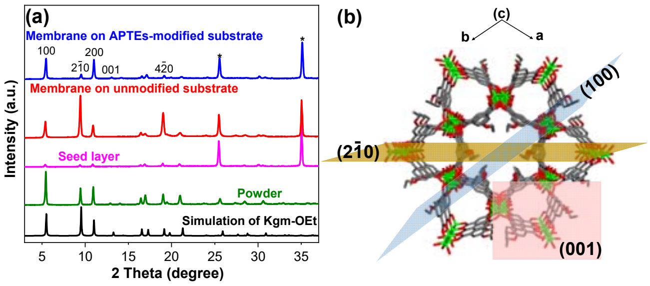

Figure 3. (a) XRD patterns of the simulation of Kgm-OEt, powder, seed layer and membranes. The asterisks (*) indicate the peaks derived from Al_2O_3 substrate. (b) Crystal plane of Kgm-OEt.

The single gas permeances of the Kgm-OEt membrane were measured at 10 kPa differential pressure and 25 °C using a Wicke-Kallenbach setup (Figure S8). As-prepared Kgm-OEt membranes were activated by N_2 sweeping at 100 °C prior to gas permeation experiments. The activation temperature was determined by TGA curve (Figure S9). The results are shown with the kinetic diameter of the gas molecules (Figure 5(a)). The membrane exhibits the highest permeance for H_2 (2.73×10^{-8} mol m^{-2} s^{-1} Pa^{-1}), and the permeances decrease with an order of $H_2 > CO_2 > N_2 > CH_4 > C_2H_4$, which corresponds to their kinetic diameters except for CO_2. The calculated ideal selectivities for H_2/CO_2, H_2/N_2, H_2/CH_4 and H_2/C_2H_4 are 5.2, 4.4 ,4.6 and 6.5, respectively. The experimental separation factors for H_2 over CO_2, CH_4, N_2 and C_2H_4 obtained by 1:1 binary-gas permeation tests are 5.0, 4.1, 4.4, and 6.2. All of the separation factors superpass Knudesen constant and C_2H_4 molecules have the lowest permeability, indicative of the sieving effect of the membrane. The stronger CO_2 adsorption of Kgm-OEt (Figure S10) can reduce the CO_2 mobility so that the membrane shows lower permeance of CO_2 than N_2 and CH_4.[32,33] H_2/CO_2 selectivity is also higher than those of polymer membranes based on Robeson (2008) and Robeson (1991) (Figure 5(b)).[34]

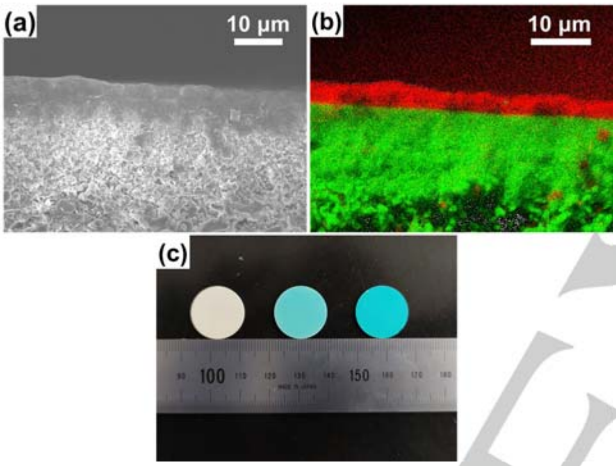

Figure 4. (a) SEM, (b) EDX mapping (Green: Al, red: Cu) of membrane on the APTEs-modified substrate. (c) Photograph of the APTEs-modified Al_2O_3 substrate: left, Kgm-OEt seed layer: middle and Kgm-OEt membrane: right.

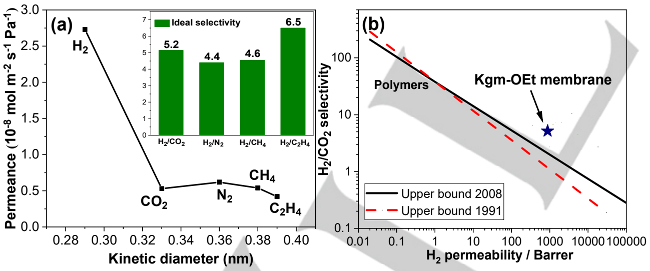

Figure 5. (a) Single gas permeances on the Kgm-OEt membranes at 25 °C and 10 kPa with the kinetic diameters. (b) H_2/CO_2 selectivity versus H_2 permeability for Kgm-OEt membrane at 25 °C and 10 kPa, compared with the upper bound lines for polymeric membranes are based on Robeson (2008) and Robeson (1991).

As a comparison, we tested the binary-gas permeation of Kgm-OEt membrane prepared on the unmodified Al_2O_3 substrate (Table S1). The separation factor for H_2 and other gases were lower than 2. This value is much lower than Knudsen constant, the reason can be attributed to the existence of pinholes or poor intergrowth of particles. The results clearly illustrate that APTEs improve the growth of Kgm-OEt on the Al_2O_3 substrate to form a defect-free membrane.

In summary, a continuous and defect-free MOF Kgm-OEt membrane has been successfully synthesized by the secondary growth approach on the APTEs-modified porous Al_2O_3 substrate surface. We applied an LBL method to construct the seed layer for this kagomé-type of MOF. It is shown that APTEs-modified Al_2O_3 substrate can form a fully covered seed layer. The particle size of the seed is smaller on the APTEs-modified substrate than the unmodified substrate. The microstructure of the membrane grew in the APTEs-modified substrate is greatly improved compared with the unmodified substrate. Our work would give a convenient method for the preparation of various types of MOF membranes, especially those based on metal carboxylates, which cause defects by the ordinary methods.

Acknowledgements

This work was supported by the PRESTO (Grant No. JPMJPR141C) and CREST (Grant No. JPMJCR17I3) of the Japan Science and Technology Agency (JST), and JSPS KAKENHI (Grant No. JP18K14043, JP19H02734, JP20H02575, and JP20K20564). X. Wang acknowledges the financial support from China Scholarship Council (No. 201806060138).

Keywords: Metal-organic framework 1 • MOF membrane 2 • Gas permeation 3 •

[1] H. Furukawa, M. A. Miller, O. M. Yaghi, *J. Mater. Chem.* **2007**, *17*, 3197-3204.
[2] S. Kusaka, A. Kiyose, H. Sato, Y. Hijikata, A. Hori, Y. Ma, R. Matsuda, *J. Am. Chem. Soc.* 2019, *141*, 15742-15746.
[3] L. Li, R. Lin, R. Krishna, H. Li, S. Xiang, H. Wu, J. Li, W. Zhou, B. Chen, *Science* **2018**, *362*, 443-446.
[4] H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata, S. Kitagawa, *Science* **2014**, *343*, 167-170.
[5] J. S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982-986.
[6] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Angew. Chem. Int. Ed.* **2006**, *45*, 5974-5978.
[7] Y. Ma, R. Matsuda, H. Sato, Y. Hijikata, L. Li, S. Kusaka, M. Foo, F. Xue, G. Akiyama, R. Yuan, S. Kitagawa, *J. Am. Chem. Soc.* **2015**, *50*, 15825-15832.
[8] G. E. Cmarik, M. Kim, S. M. Cohen, K. S. Walton, *Langmuir.* **2012**, *28*, 15606-15613.
[9] Y. Tan, Y. He, J. Zhang, *Inorg. Chem.* **2012**, *51*, 9649-9654.
[10] S. R. Venna, M. A. Carreon, *J. Am. Chem.* Soc. **2010**, *132*, 76-78.
[11] W. Wang, X. Dong, J. Nan, W. Jin, Z. Hu, Y. Chen, J. Jiang, *Chem. Commun.* **2012**, *48*, 7022–7024.
[12] S. Jiang, X. Shi, F. Sun, G. Zhu, *Chem. Asian J.* **2020**, *15*, 2371-2378.
[13] Y. Liu, Z. Ng, E. A. Khan, H.-K. Jeong, C.-b. Ching, Z. Lai, *Micropor. Mesopor. Mat.* **2009**, *118*, 296-301.
[14] A. Huang, W. Dou, J. Caro, *J. Am. Chem. Soc.* **2010**, *132*, 15562-15564.
[15] S. Tanaka, K. Okubo, K. Kida, M. Sugita, T. Takewaki, *J. Membr. Sci.* **2017**, *544*, 306-311.
[16] H. Yin, J.Wang, Z.Xie, J.Yang, J.Bai, J.Lu, Y. Zhang, D. Yin, J. Lin, *Chem. Commun.* **2014**, *50*, 3699-3701.
[17] S. Zhou, X. Zou, F. Sun, F. Zhang, S. H. Zhao, T. Schiestel, G. Zhu, *J. Mater. Chem.* **2012**, *22*, 10322-10328.
[18] Y. Sun, Y. Liu, J. Caro, X. Guo, C. Song, Y. Liu, *Angew. Chem. Int. Ed.* **2018**, *130*, 16320-16325.
[19] F. Zhang, X. Zou, X. Gao, S. Fan, F. Sun, H. Ren, G. Zhu, *Adv. Funct. Mater.* **2012**, *22*, 3583-3590.

[20] B. Ghalei, K. Wakimoto, C.Y. Wu, A. P. Isfahani, T. Yamamoto, K. Sakurai, M. Higuchi, B. K.Chang, S. Kitagawa, E. Sivaniah, *Angew. Chem. Int. Ed.* **2019**, *58*, 19034-19040.

[21] L. Wan, C. Zhou, K. Xu, B. Feng, A. Huang, *Micropor. Mesopor. Mat.* **2017**, *252*, 207-213.

[22] B. Liu, O. Shekhah, HK. Arslan, J. Liu, C. Wöll, R. A. Fischer, *Angew. Chem. Int. Ed.* **2012**, *51*, 807-810.

[23] A. S. Münch, J. Seidel, A. Obst, E. Weber, F. O. R. L. Mertens, *Chem. Eur. J.* **2011**, *17*, 10958–10964.

[24] O. Shekhah, L. Fu, R. Sougrat, Y. Belmabkhout, AJ. Cairns a, EP. Giannelis, M.Eddaoudi, *Chem. Comm.* **2012**, *48*, 11434-11436.

[25] B. Garai, A. Mallick, A. Das, R. Mukherjee, R. Banerjee, *Chem. Eur. J.* **2017**, *23*, 7361-7366.

[26] O. Barreda, G. Bannwart, G. P. A. Yap, E. D. Bloch, *ACS. Appl. Mater. Interfaces.* **2018**, *10*, 11420-11424.

[27] F L. N. McHugh, M. J. McPherson, L. J. McCormick, S. A. Morris, P. S. Wheatley, S. J. Teat, D. McKay, D. M. Dawson, C. E. F. Sansome, S. E. Ashbrook, C. A. Stone, M. W. Smith and R. E. Morris, *Nat. Chem.* **2018**, *10*, 1096-1102.

[28] S. H. Jhung, T. Jin, Y. K. Hwang, J. S. Chang, *Chem. Eur. J.* **2007**, *13*, 4410-4417.

[29] X. Wu, Z. Bao, B. Yuan, J. Wang, Y. Sun, H. Luo, S. Deng, *Micropor. Mesopor. Mat.* **2013**, *180*, 114-122.

[30] Z. Zhong, J. Yao, R. Chen, Z. Low, M. He, J. Z. Liu, H.Wang, *J. Mater. Chem.A.* **2015**, *3*, 15715-15722.

[31] A. J. Bons, P. D. Bons, *Micropor. Mesopor. Mat.* **2003**, *62*, 9-16.

[32] N. Wang, A. Mundstock, Y. Liu, A. Huang and J. Caro, *Chem. Eng. Sci.* **2015**, *124*, 27-36.

[33] C. Liu, Y. Jiang, C. Zhou, J. Caro, A. Huang. *J. Mater. Chem.A.* **2018**, *6*, 24949-24955.

[34] L. M Robeson, *J. Membr. Sci.* **2008**, *320*, 390-400.

10.1002/asia.202100507

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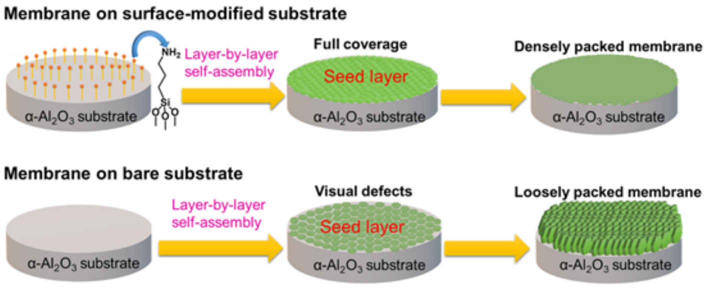

A simple chemical modification for Al_2O_3 substrate facilitates the preparation of more compact and better-oriented Kgm-OEt membrane.