Supporting information

Highly oriented neutral and cation-free $AlPO_4$ LTA: from seed crystal monolayer to molecular sieve membrane

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Experimental methods

1. Materials

Chemicals were used as received: phosphoric acid (H_3PO_4, 85%, Merck), aluminium oxide (Al_2O_3, PURAL®SB, Condea), hydrofluoric acid (HF, 48% in water, Merck); polyethyleneimine (PEI, Fluka); 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (K222, 98%, Acros); doubly distilled water. Glass plates (10 x 10 x 0.5 mm) and porous α-Al_2O_3 disks (Fraunhofer IKTS, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness) were used as substrates.

2. *Synthesis of $AlPO_4$ LTA crystals*

LTA $AlPO_4$ crystals with different crystals size were synthesized according to our previous procedure. [1] For a typical synthesis, 0.62 g H_3PO_4 and 0.35 g Al_2O_3 powder were mixed with 10.91 g doubly distilled water. The mixture was stirred for at least 16 h at room temperature before adding 0.5 g K222 and 0.08 g HF. The final mixture was again stirred for 30 min at room temperature and then introduced into a Teflon-lined stainless steel autoclave. After crystallization of 4 h at 473 K in an air conditioned oven, the autoclaves were cooled down. The solids were filtered, washed with distilled water and dried at 373 K.

3. *Assembly of oriented* $AlPO_4$ LTA *monolayer*

A certain amount of $AlPO_4$ LTA crystals suspended in PEI water solution (5.0 Wt. % in 0.2 g PEI and 10 g distilled water) was dropped onto the substrates. Then an ultrasonic treatment of the $AlPO_4$ LTA suspension was applied at RT for 5 min to yield a highly oriented $AlPO_4$ LTA monolayer on the substrates.

4. Secondary growth of oriented $AlPO_4$ LTA membrane

For the secondary growth of oriented $AlPO_4$ LTA membrane, the synthesis gel was prepared according to the procedure reported elsewhere. [2] After crystallization times of 5 h at 473 K in an air conditioned oven, the autoclaves were cooled down, the solution was decanted off and the membrane was washed with deionized water, and then dried at 373 K overnight. Finally, the as-synthesized membrane was calcined at 573 K for 24 h in O_3/air (about 100 ppmv of O_3 in air) to remove the template using 0.2 K/min heating and cooling rates.

4. *Characterization of $AlPO_4$ LTA monolayer and membrane*

SEM micrographs were taken on a JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10 μA. The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 VANDANCE X-ray diffractometer with CuKa radiation at 40 kV and 40 mA.

5. *Permeation of single gas and separation of mixed gases*

For the single gas and mixture gas permeation, the activated α-Al_2O_3 supported $AlPO_4$ *LTA* membrane was sealed in a permeation module with silicone O-rings. The feed gases were fed to the side of the membrane, and sweep gas was fed on the permeate side to keep the concentration of permeating gas low providing a driving force for permeation. The total pressure on each side of the membrane was atmospheric. For both single and mixture gas permeation, the fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromotograph (HP6890) was used to measure the gas concentrations, as shown in Figure S7. The separation factor $\alpha_{i,j}$ of a binary mixture permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i,j) in the feed, as show in Eq. 1.

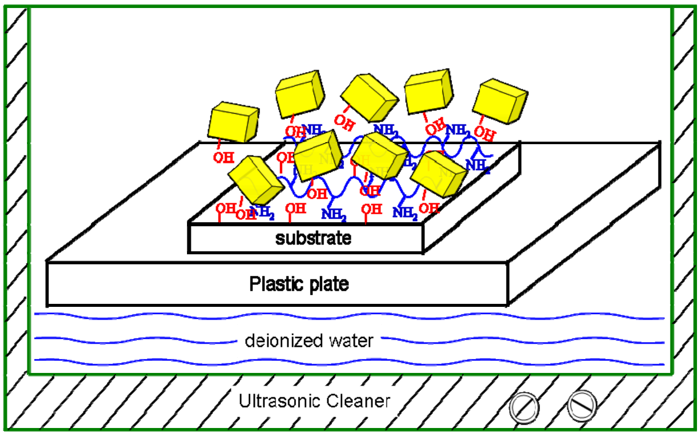
$$\alpha_{i/j} = \frac{y_{i,Perm} / y_{j,Perm}}{y_{i,\mathrm{Ret}} / y_{j,\mathrm{Ret}}} \qquad (1)$$

Reference

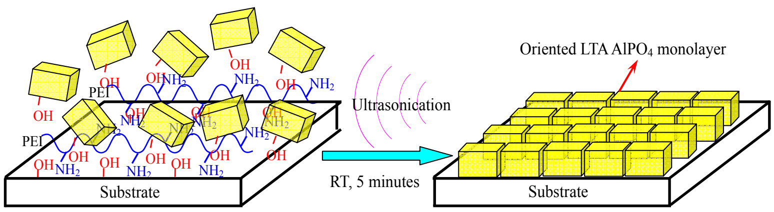
[1] A. Huang and J. Caro, *Micropor. Mesopor. Mater.*, 2010, 129, 90.

[2] A. Huang, F. Liang, F. Steinbach, T. M. Gesing and J. Caro, *J. Am. Chem. Soc.*, 2010, 132, 2140.

Figure S1



(a)



(b)

Figure S1. Scheme for the sonication set up (a) and the assembling of $AlPO_4$ LTA microcrystals by ultrasonication using polyethyleneimine (PEI) as mediator between the $AlPO_4$ LTA crystals thus forming a highly oriented seed crystal monolayer (b).

Figure S2

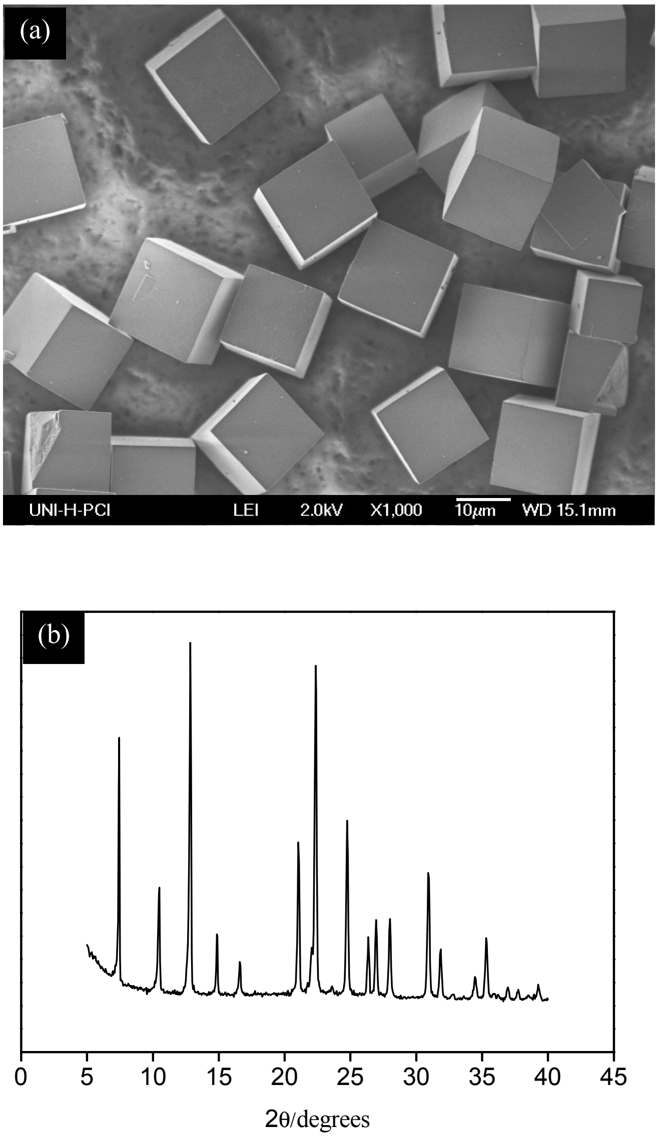


Figure S2. SEM image (a) and XRD pattern (b) of the LTA $AlPO_4$ crystals used for assembly of monolayer.

Figure S3

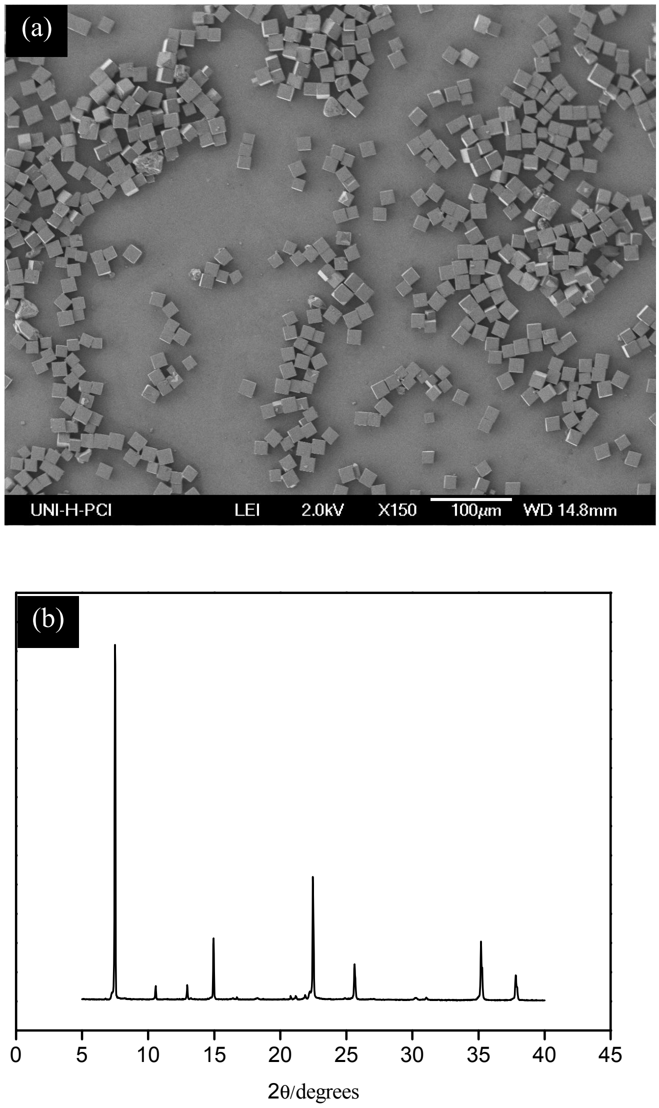


Figure S3. SEM image (a) and XRD pattern (b) of the LTA $AlPO_4$ layer in the case of assembling PEI-free suspension.

Figure S4

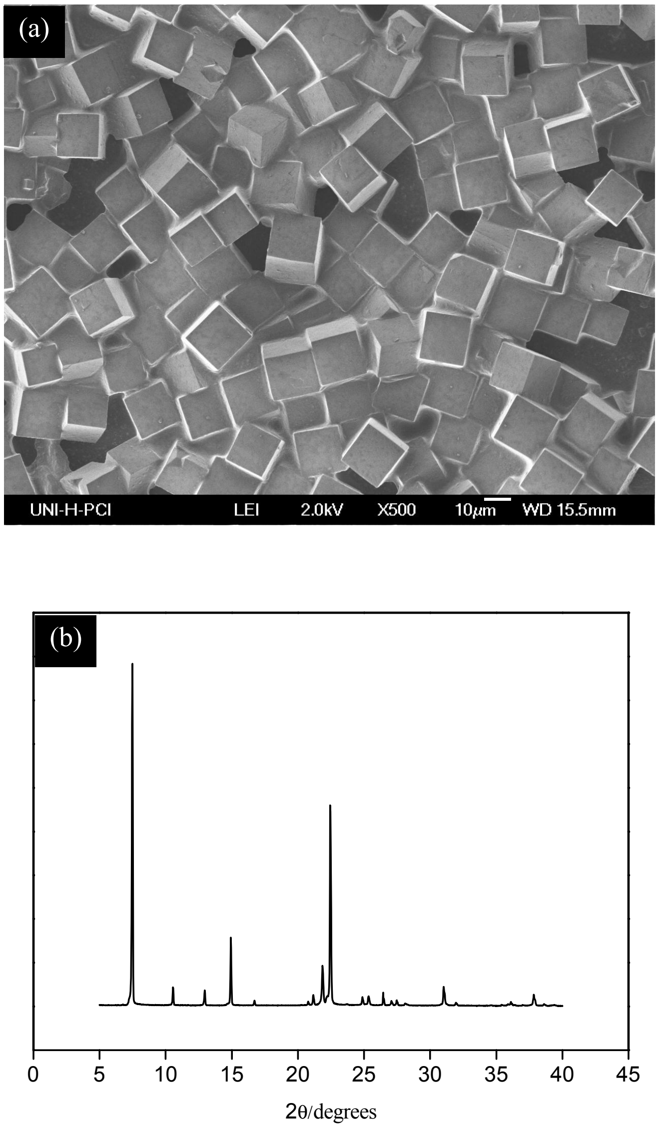


Figure S4. SEM image (a) and XRD pattern (b) of the LTA $AlPO_4$ layer in the case of ultrasonic-free treatment.

Figure S5

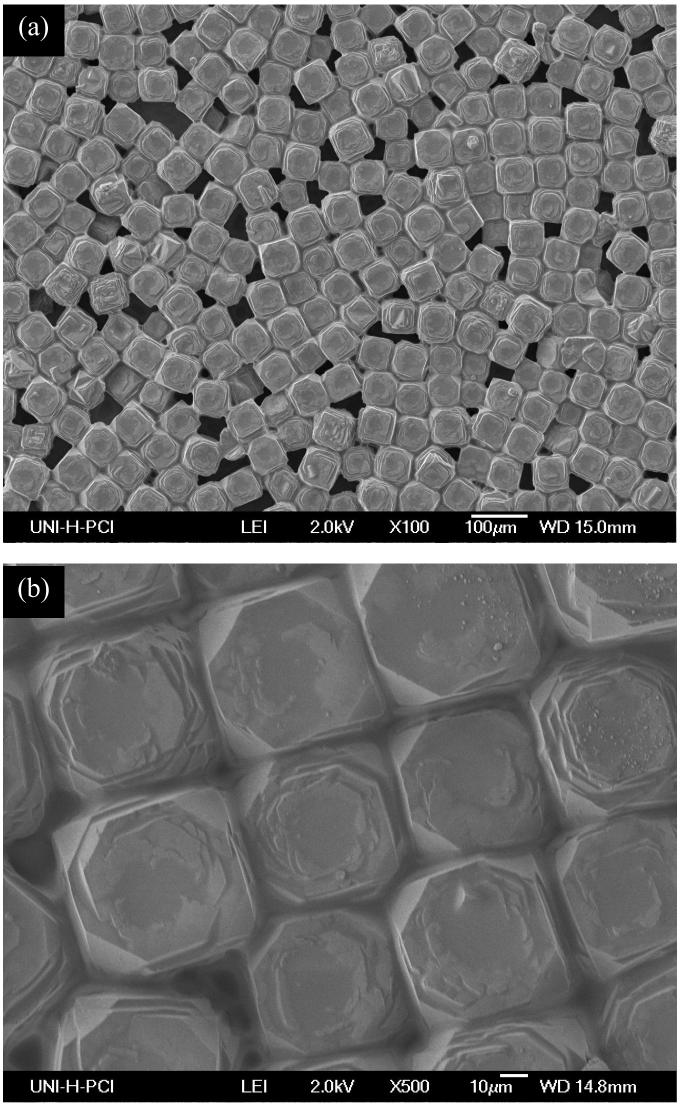


Figure S5. Low (a) and high (b) magnification SEM images of the oriented LTA $AlPO_4$ monolayer with crystals size of larger than 60 μm.

Figure S6

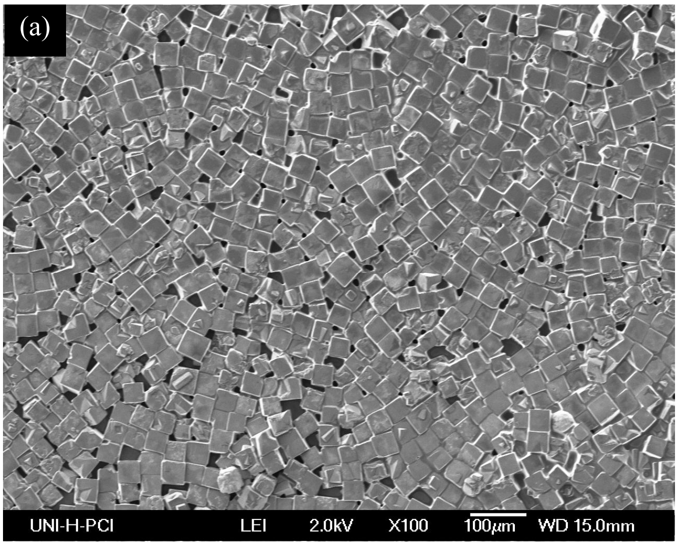


Figure S6. SEM image of the oriented aluminosilicate LTA (NaA) monolayer with crystals size of larger than 30 μm.

Figure S7

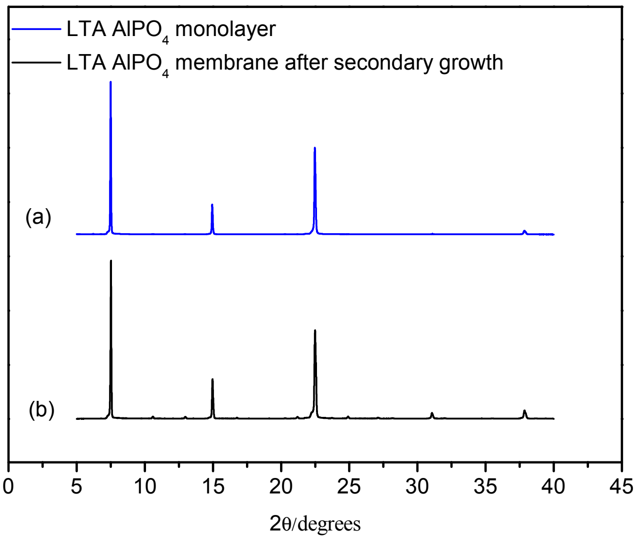


Figure S7. XRD pattern of the LTA $AlPO_4$ monolayer on porous Al_2O_3 support (a) and LTA $AlPO_4$ membrane on porous Al_2O_3 support after secondary growth (b).

Figure S8

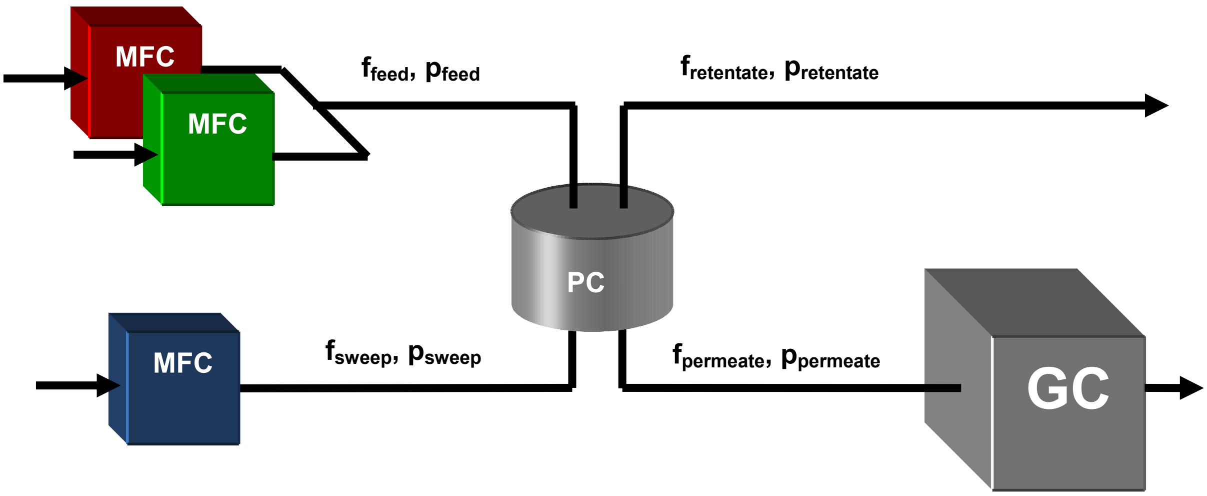


Figure S8. Measurement equipment for both single and mixed gas permeation.

Legend:

MFC: Mass flow controller

PC: Permeation cell with mounted membrane

GC: Gas chromatograph

f: Volumetric flow rate

p: Pressure

Figure S9

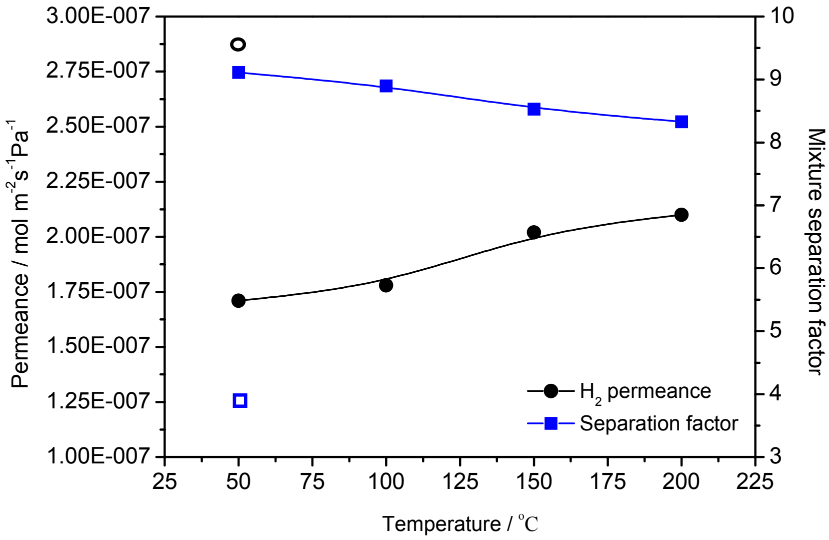


Figure S9. H_2/CH_4 mixture separation factor and the H_2 permeance of the oriented LTA $AlPO_4$ membrane as a function of the permeation temperature. The open symbols indicate H_2/CH_4 mixture separation factor (□) and the H_2 permeance (○) of the randomly oriented LTA $AlPO_4$ membrane.

Table S1 Comparison of gas separation performances of the oriented $AlPO_4$ LTA membrane in this study with other small pore-sized zeolite and MOF membranes from literatures.

Membrane	Pore size (nm)	Gas separation performances					Reference
		Selectivity				H_2 permeances ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	
		H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/C_3H_8		
DDR	0.36~0.44	3.5	/	/	/	7.9×10^{-6}	1
DDR	0.36~0.44	1.7 [a]	10 [a]	/	/	9.3×10^{-13}	2
Matrix $AlPO_4$	/	9.7	6.0	/	/	1.1×10^{-7}	3
SAPO-34	0.38	1.3	25	/	/	3.0×10^{-8}	4
NaA	0.4	5.3	4.2	3.6	6.6	$2.5 \sim 3.6 \times 10^{-7}$	5
NaA	0.4	9.2 [a]	9.4 [a]	5.0 [a]	/	5.0×10^{-8}	6
MMOF	0.32	/	23 [a]	/	/	1.2×10^{-7}	7
ZIF-8	0.34	4.5 [a]	11.6 [a]	11.3	/	5.1×10^{-8}	8
ZIF-7	0.3	6.5	7.7	5.9	/	$7.7 \sim 8.0 \times 10^{-8}$	9
ZIF-22	0.3	7.2	6.4	5.2	/	$1.6 \sim 1.9 \times 10^{-7}$	10
ZIF-90	0.35	7.2	12.6	15.9	/	$2.3 \sim 2.5 \times 10^{-7}$	11
LTA $AlPO_4$	0.4	10.9	8.6	8.2	142	1.9×10^{-7}	This study

[a] Ideal separation factor

Reference:

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