Electronic supporting information

Insights into the Interplay between Electric Fields and Microstructures of Molecular Sieve Films Under Ionothermal Conditions

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Methods

Chemicals: The phosphoric acid (85.0 wt.%), hydrofluoric acid (40 wt.%) were purchased from Sigma-Aldrich. The sodium carbonate (99.5 wt.%) was purchased from Tianjin Bodi Chemical Engineer Co. LTD. The sodium hydroxide (99.5 wt.%) was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. The chloroform (99.0 wt.%) was purchased from Beijing Chemical Works. The aluminum plane was purchased from McMaster-Carr Company. The ionic liquid 1-ethyl-3-methylimidazolium bromide ([emim]⁺Br⁻) was purchased from Shanghai Cheng Jie Chemical Co. LTD (China). This [emim]⁺Br⁻ was kept at high vacuum and elevated temperature for 15 hours to remove any residual water prior to use. A Basic solution was prepared by dissolving 2 g sodium hydroxide and 4 g sodium carbonate anhydrous in 500 ml DI water.

Preparation of precursor solution: The precursor solution was prepared by mixing H_3PO_4 and HF in [emim]⁺Br⁻ with a molar composition [emim]⁺Br/H₃PO₄/HF = 32:3:0.8 followed by vigorous stirring for 1 h at 90 °C.

Al electrode preparation: Al planes were pretreated by sonication in chloroform for 20 minutes and in deionized (DI) water for 15 minutes to dispose of oil, followed by sonication in DI water for another 5 minutes, in a basic solution for 5 minutes and DI water for 5 minutes. Then two Al planes were fixed vertically inside the precursor solution with the electrochemical cell as the cathod and anode as the substrate.

Preparation of AlPO₄-11 molecular sieve film: The electrochemical reaction was carried out in a three-electrode system. The pesudo-reference electrode was prepared in our laboratory as reported in the literature. The three-electrode cell was heated at 160 °C while simultaneously applying a current of $+12 \text{ mA/cm}^2$ for 20 seconds followed by a current of -12 mA/cm^2 for 5 minutes, which was defined as a current cycle. In total 35 current cycles were carried out. A new Al electrode was then substituted for the Al counter electrode after these cycles. Finally, the temperature was increased to 170 °C accompanied with a potential of -0.3 V vs open-circuit potential (OCV) for 8 hours. All three-electrode cells were equipped with a Solartron SI1287 Potentiostat/Galvanostat. After the synthesis, AlPO₄-5 film-coated Al plates were thoroughly washed with DI water, acetone and finally dried with compressed nitrogen gas.

Characterization: XRD patterns were recorded on a Rigaku D/MAX 2500/PC diffractometer with CuK_{α} radiation. SEM images were obtained on a FEI Quanta 200F or a Hitachi TM 3000 Scanning Electron Microscope.



Fig S1. The chemical structure of [emim]+Br-



Fig S2. SEM image of the AEL molecular sieve film with random orientation synthesized with the potential of -0.6 V(vs.OCV) for 4 h at 190 °C.



Fig S3. SEM image of the AEL molecular sieve film with random orientation synthesized with the potential of -0.2 V(vs.OCV) for 6 h at 190 °C.



Fig S4. The XRD pattern of an uncompact AEL seed layer synthesized by alternating electric fields in which the positive current density is +1 mA/cm² at 160 °C.



Fig S5. The XRD pattern of an uncompact AEL seed layer synthesized by alternating electric fields in which the negative current density is -6 mA/cm² at 160 °C.



Fig S6. SEM images of AEL molecular sieve seed layers synthesized by alternating electric fields with different cycles: a) 12 times; b) 30 times; c) 35 times. The compactness can be controlled by the cycle number.



Fig S7. SEM image of the AEL molecular sieve film with random orientation synthesized by alternating electric field method with less sufficient Al³⁺ source after recycling for 33 times and growth at the potential of -0.3 V(vs.OCV) for 6 h at 170 °C.



Fig S8. SEM image of the AEL molecular sieve film with random orientation synthesized by alternating electric field method with higher growth temperature after recycling 40 times and growth at the potential of -0.3 V(vs.OCV) for 6 h at 180 °C.



Fig S9. The interplay among electric fields, growth rates and microstructures of AEL molecular sieve seeds under ionothermal conditions at 160 °C.



Fig. S10. The interplay between electric fields and microstructures of AEL molecular sieve films under ionothermal conditions.