A facile method for precise microstructure control of molecular sieve films remains a great challenge. In contrast to conventional hydrothermal methods, herein AEL molecular sieve films with preferred c-orientation are in situ fabricated through elaborate programming of the applied electric fields under ionothermal conditions. The approach developed here may pave a new avenue for designing and fabricating high quality molecular sieve films with diverse microstructures and functionality.

Molecular sieves in the form of films have shown great potential in separation,1–4 fluorescence,5,6 vapor sensing7,8 and anti-corrosion9–11 over the last few decades. Apart from the framework topology and chemical composition, performances of molecular sieve films are often strongly associated with their microstructures. Therefore, facile methods enabling precise microstructure control of molecular sieve films (like the preferred orientation) will greatly promote their potential applications.1

Secondary growth, which involves controlled deposition of molecular sieve seeds on the substrate prior to film growth,12,13 is deemed to be more appropriate for microstructural manipulation of molecular sieve films. Nevertheless, complicated procedures that require elaborate control of both substrate functionalization and seed deposition conditions have disfavored its widespread application in industry.14 On the other hand, in situ crystallization as a simpler method occasionally can realize controlled growth of molecular sieve films; nevertheless, this goal is in general achieved through trial and error rather than deliberate design.15,16

In general, the mechanism of molecular sieve synthesis involves the formation of inorganic–organic composite intermediate species which are self-assembled through attractive interactions between oppositely charged organic structure-directing agents (SDAs) and inorganic building blocks.17 Therefore, it becomes very attractive to regulate their motion behaviors in case an electric field can be applied during the synthesis of molecular sieve films. It should be particularly noted that their microstructures may be precisely tuned by rigorous manipulation of the related electric field parameters. To the best of our knowledge, electric field-driven in situ fabrication of molecular-sieve films with controlled microstructures has so far been rarely explored, although it has proven effective for oriented attachment of fibrous AlPO₄-5 building blocks on glass slides.18

An ionic liquid is considered as an ideal medium for overcoming several disadvantages of a conventional hydrothermal system due to its wide electrochemical window, high ionic conductivity and negligible vapor pressure.19,20 Benefits from both electric fields and ionic liquids have inspired us to apply electric fields to the ionothermal synthesis (the ionic liquids are used simultaneously as both the solvent and potential SDA, allowing highly efficient preparation of molecular sieve-type materials under ambient pressure21–23) of molecular sieve films.24 Very recently, we reported a facile one-step method for the electrochemical ionothermal synthesis of in-plane oriented and defect-free AlPO₄-11 (AEL framework topology) molecular sieve films on Al plates25 by applying a constant negative potential. In particular, an AEL framework is orthorhombic and belongs to the space group Imma (a = 13.534 Å, b = 18.482 Å, c = 8.370 Å) with 120 atoms per unit cell. It forms one-dimensional pores with a free diameter of 6.5 × 4.0 Å parallel to the crystallographic c-direction.

Nevertheless, several other benefits of electric fields, such as programmable operation parameters, a quick response and non-delayed feedback, are still waiting to be explored. Furthermore, the interplay between electric field parameters and microstructures of molecular sieve films is urgently awaiting elucidation. Herein, we demonstrate for the first time that
microstructures (in particular, with a preferred c-orientation) of AlPO₄-11 molecular sieve films could be easily designed and in situ fabricated by programming the related electric field parameters in an ionothermal system.

To achieve this goal, a three-electrode electrochemical cell with one aluminum panel as a working electrode as well as the substrate, another aluminum panel as a counter electrode and a Pt wire as a pseudo-reference electrode is used. The precursor solution solely consists of a phosphorus acid (H₃PO₄), mineralizing agent (HF) and ionic liquid 1-ethyl-3-methylimidazolium bromide ([emim]⁺Br⁻), its chemical structure is shown in Fig. S1, ESI†.

As mentioned above, an in-plane oriented AEL molecular sieve film could be in situ prepared on the working electrode by applying a negative potential of −0.2 V (vs. OCV). In this process, the electrode surface reacts with phosphorous acid and spontaneously changes to an AEL film with the assistance of the SDA at high temperature (190 °C), and its orientation is critically linked to the loose AEL nuclei and insufficient supply of the Al source obtained via chemical reactions at the electrode–solution interface. Nevertheless, it is impractical to prepare preferentially c-oriented AEL films simply by adjusting the potential values or ionothermal synthetic conditions alone (Fig. S2 and S3, ESI†).

The primary principle for secondary growth of oriented molecular sieve films involves an early stage for controlled deposition of molecular sieve seeds on the substrate followed by a second stage for epitaxial growth of molecular sieve films. By analogy, our strategy for controlling the preferred orientation of AEL molecular sieve films is associated with precise manipulation of the related electric field parameters, complementary to the low-temperature process for in situ seeding, followed by a higher temperature process for epitaxial film growth (schematically illustrated in Scheme 1). Owing to the relatively low reactivity between the substrate and H₃PO₄ in the low-temperature seeding process, the number of AEL nuclei generated solely from the ionothermal reactions may be insufficient. Alternatively, an electrochemical oxidation process realized by exerting a positive current may release a considerable number of Al³⁺ ions (Scheme 1b). Nevertheless, in the case of positively charged substrates, [emim]⁺ cations that act as the SDAs may be electrostatically repelled, thus severely inhibiting the AEL nucleation. In order to alleviate the contradiction between providing an aluminum source and attracting SDAs, alternating electric fields, in which electric currents are tuned from positive to negative repeatedly, are employed. It is thus anticipated that a controlled release of Al³⁺ ions by electrochemical oxidation coupled with preferential adsorption of SDAs by exerting a negative current (Scheme 1c) may greatly promote the nucleation of AEL seeds (Scheme 1d). It should be particularly noted that positive and negative currents should be recycled to ensure full coverage of AEL seeds on the substrate (Scheme 1e). In the next step, a constant negative potential is applied to the working electrode at higher temperature to warrant a sufficient supply of SDAs during the c-oriented epitaxial growth of AEL molecular sieve films (Scheme 1f).

A positive current with +12 mA cm⁻² for 20 s followed by a negative current with −12 mA cm⁻² for 5 min at 160 °C has proved sufficient for providing the Al³⁺ source and adsorbing SDAs for in situ nucleation of AEL seeds. After recycling 35 times, a substantial number of nucleation centers were readily formed (Fig. 1b). In the next step, maintaining a constant negative potential under given ionothermal conditions (170 °C for 8 h) further promoted epitaxial growth of rod-like AEL seeds along the c-direction. Not only the strong (002) reflection peak in the XRD pattern (Fig. 1c) but also the SEM image (Fig. 2a) convincingly indicated that the one-dimensional ten-membered ring channels in AEL crystals were preferentially

Scheme 1 Synthetic strategy for c-oriented AEL molecular sieve films. (a) The working electrode served as the substrate; (b) aluminum source was provided by electrochemical oxidation of the Al plate using a positive current. (c) Under the negative current, SDA cations were electrically adsorbed on the substrate; (d) AEL nuclei formed during the reaction between Al³⁺ and phosphate anions with [emim]⁺Br⁻ ionic liquid as the solvent and template; (e) the AEL seed layer was obtained after several cycles; (f) c-oriented epitaxial growth of AEL molecular sieve films under a negative potential.

Fig. 1 XRD patterns of (a) a randomly oriented AEL molecular sieve film; (b) the AEL seed layer obtained by an alternating electric field at 160 °C and (c) the c-oriented AEL film prepared by applying a constant negative potential after secondary growth.
oriented perpendicular to the substrate. Moreover, the cross-sectional SEM image (Fig. 2b) of AEL films further revealed that the neighbouring vertically aligned AEL crystals have intergrown well with each other.

Consequently, how the current profile had significantly influenced the microstructures of the prepared AEL seed layer was investigated in detail. The positive currents were first leveraged for a more precise control of the amount of Al\(^{3+}\) source released from the Al plate. It was found that a loose AEL seed layer (Fig. 3a, and Fig. S4, ESI†) was obtained at a low positive current (+1 mA cm\(^{-2}\)), indicating that the number of Al\(^{3+}\) ions provided by electrochemical oxidation was insufficient. In contrast, at higher positive currents, a non-porous AlPO\(_4\) impure phase would form. On the other hand, negative currents that contributed to the adsorption of positively charged SDAs also had a pronounced effect on the microstructure of AEL molecular sieve films. It was observed that an amorphous gel (Fig. 3b) instead of the AEL seed layer was obtained when the negative current was adjusted to −1 mA cm\(^{-2}\). Further increasing the current to −6 mA cm\(^{-2}\) led to the formation of an amorphous gel in which sparse AEL seeds were embedded (Fig. 3c and Fig. S5, ESI†). A compact AEL seed layer could be obtained by further increasing the negative current to −12 mA cm\(^{-2}\) (Fig. 3d). In addition, it was illustrated that the compactness of the AlPO\(_4\)-11 seed layer could be adjusted by controlling the number of alternating positive and negative electric field cycles (Fig. S6, ESI†). In summary, the application of alternating electric fields provided us with an effective approach to obtain a better match between Al\(^{3+}\) source dissolution rates and SDA adsorption rates in comparison with the conventional solvothermal growth.

In the next step, a constant negative potential (−0.3 V vs. OCV) was applied under ionothermal conditions (170 °C for 8 h) to adsorb positively charged SDAs. The c-oriented epitaxial growth of the AEL film during secondary growth could be explained by the “evolution selection” growth mechanism developed by Van der Drift for interpreting the preferred orientation of a vapor-deposited PbO layer.\(^{26}\) For anisotropic AEL crystals, in the early stage, the AEL nuclei evolved in all possible crystallographic axes. However, since the growth rate along the c-direction was much faster than those along other directions. Eventually, c-axis of AEL crystallites would survive and ultimately arrange in a direction perpendicular to the substrate. When two AEL crystallites met, the more steeply growing crystal would prevent the further growth of the less steeply growing crystal. Simultaneously, a sufficient supply of Al\(^{3+}\) sources in the precursor solution due to controlled release of Al\(^{3+}\) in an electrochemical oxidation process (Fig. S7, ESI†) as well as a relatively low reaction temperature further facilitated the c-axis oriented growth of AEL molecular sieve films (Fig. S8, ESI†).

The relationship between electric fields and microstructures of AEL seed layers in the \textit{in situ} seeding process is schematically illustrated in Fig. 4. In general, four types of microstructures (amorphous gel, amorphous gel + AEL seeds, loosely packed AEL seed layer and compact AEL seed layer) could be identified by tuning the values of current density. It was noted that only the amorphous gel was generated at a lower negative current density, while formation of the AEL phase was preferred at a higher negative current density. Furthermore, the value of growth rate slightly increased from 0.20 to 0.26 nm s\(^{-1}\) with...
increasing positive current density. However, a sharp increase from 0, 0.024 to 0.26 nm s\(^{-1}\) existed with the negative current density (Fig. S9, ESI†), indicating that the negative current density significantly affected the growth rates of molecular sieve seeds. For the aforementioned reason, we came to the conclusion that directional diffusion and adsorption of SDAs was the rate-limiting step that ultimately dominated micro-structural evolution of AEL seed layers.

In addition, during secondary growth, microstructures of AEL films were strongly associated with the negative current density. Lowering the negative current density was more beneficial for controlling the preferred orientation (both c- and in-plane oriented growth) of AEL molecular sieve films, whereas randomly oriented AEL films could be obtained at a higher negative current density (Fig. S10, ESI†). In a word, programming electric field parameters had enabled us to precisely control microstructures of molecular sieve films, which conventionally could be achieved solely by trial-and-error. We firmly believe that this strategy may pave an elegant way for designing and fabricating high quality molecular sieve films with desired microstructures.

In summary, herein an elegant alternating electric field method has been developed to achieve unprecedented control over microstructures of AEL molecular sieve films under ionothermal conditions. In particular, preferentially c-oriented AlPO\(_4\)-11 films could be \textit{in situ} fabricated on Al plates by exerting alternating positive and negative electric fields at lower temperature (\textit{in situ} seeding) followed by the application of a constant negative potential at higher temperature (oriented epitaxial growth). It is expected that by adjusting the types of ionic liquids or adding extra reagents, other molecular sieve films such as AFI and CHA could be easily obtained using this method. Moreover, the electrochemical approach may provide new insights into rational design and precise fabrication of molecular sieve films with desired microstructures and functionality.

This work was supported by the 100-Talent Project of CAS and the National Natural Science Foundation of China (Grant No. 21476223).

Notes and references