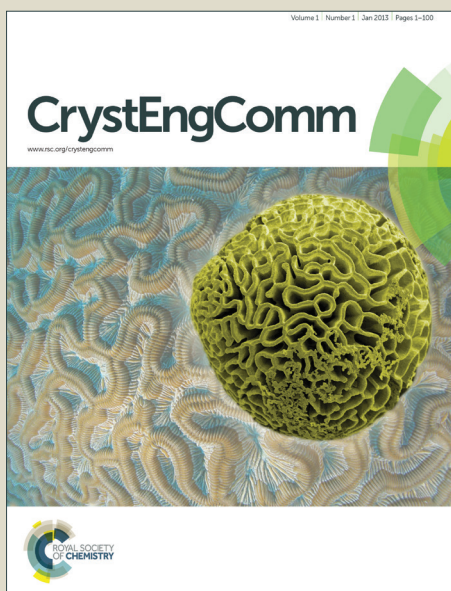


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COMMUNICATION

In situ solvothermal growth of highly oriented Zr-based metal organic framework UiO-66 film with monocrystalline layer

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A highly oriented UiO-66 film, with a monocrystalline layer, was successfully prepared by solvothermal method. Acetic acid, which served as a modulator, was essential to achieve high film orientation. Water played an important role on promoting the intergrowth of UiO-66 crystals.

Metal organic frameworks (MOFs) or porous coordinated polymers are a new class of crystalline porous materials that consist of organic linkers and inorganic nodes.¹ Furthermore, they feature extremely high specific surface areas and pore volumes. Over the last decade, numerous MOFs have been synthesized and demonstrated to exhibit great potential for many applications, such as adsorption², catalysis³, chemical sensing⁴ and membrane separation⁵, owing to their exceptionally broad chemical and structural diversity.⁶ However, poor chemical stability is one of the major disadvantages of MOFs. The stability of the frameworks is mainly dependent on the inorganic node and the strength of chemical bonding between the inorganic node and linker. Among the numerous MOFs synthesized to date, Zr-based MOFs are one of the most chemically stable MOFs that were first reported by Cavka et al.⁷ UiO-66 is a typical Zr-based MOF. The framework consists of Zr₆O₄(OH)₄ clusters and 1,4-benzenedicarboxylate (BDC) with octahedral and tetrahedral cavities (11 and 8 Å in diameter, respectively). Access to the cavities is provided by triangular windows with diameters of ~6 Å. This material features remarkably high chemical stability in organic solvents and water under a wide pH range (HCl and NaOH aqueous solutions), as well as high thermal stability up to 375°C in air.⁸ Accordingly, owing to their high chemical and thermal stability, UiO-66 and its derivatives have generated great interest for use in diverse fields such as catalysis⁹ and separation of hydrocarbons, aromatics, and CO₂.¹⁰

MOFs are typically used in microcrystalline powder form. However, MOF thin films have generated interest owing to their wider applications such as in electronic devices and membrane

separation. Accordingly, the formation of MOF thin films has been extensively investigated. Several approaches, e.g., layer-by-layer, reactive electrodeposition, and microwave-induced thermal deposition, have been proposed to date. Furthermore, oriented MOF films can be prepared using the Langmuir–Blodgett¹¹ and liquid–air interfacial assembly¹² techniques. However, solvothermal growth methods, including secondary growth, are typically employed for thin film or membrane preparation because the solvothermal method is easy to implement and does not require any specific equipments. The preparation of UiO-66 thin films via electrophoretic deposition was reported by Hod et al.¹³ Additionally, the preparation of two-dimensional and three-dimensional-oriented films via liquid–air interfacial assembly techniques was reported by Lu et al.¹⁰ Recently, the preparation of UiO-66 films on FTO (fluorine-doped tin oxide) substrates using solvothermal methods was reported for the first time by Fei et al.¹⁴ However, the prepared UiO-66 films were thick (2–5 μm) and randomly oriented. And the films consisted of monodisperse UiO-66 crystals, similar to those reported by Hod et al.¹³ More specifically, for membrane separation applications, the preparation of thin films with oriented and/or closely packed crystals obtained by intergrowth mechanism is desirable. Crystal intergrowth can prevent the formation of grain boundaries that are responsible for reduced membrane selectivity owing to the development of non-desirable permeation paths. Furthermore, coordinating the pore size of membrane surface obtained by favourable orientation of the film results in desirable selectivity.¹⁵ Therefore, controlling the film orientation and morphology of MOFs is of great interest. Here, we report the *in situ* solvothermal formation of a highly oriented UiO-66 thin film, featuring a very uniform monocrystalline layer, on a silicon substrate.

Fig. 1 shows the UiO-66 thin film prepared on the silicon substrate via solvothermal synthesis at 393 K using a precursor solution comprising acetic acid and water. Successful coverage

of the UiO-66 crystals on a large area of the silicon substrate was observed (Figs. S1a and b), and the synthesized UiO-66 film layer comprised intergrown octahedral crystals. In the densely packed regions, the surface was very smooth and few grain boundaries were observed, though large grain boundaries were observed in other regions. Interestingly, a film thickness corresponding to a monocrystalline layer was obtained even after three solvothermal treatments were applied. In other words, the UiO-66 crystals did not stack along the thickness direction; contrarily, only the density of crystals increased during the repeated solvothermal processes. Furthermore, the final crystal size remained unchanged following repeated solvothermal treatments, and some small octahedral crystals were observed as indicated by the blue circles in Fig. S1c. These findings indicated that repeated solvothermal treatments promoted nucleation of UiO-66 rather than crystal growth onto previously formed crystals. X-ray diffraction (XRD) analysis (Fig. 2) revealed that the obtained film (after the third solvothermal treatment) was highly oriented owing to the well-defined dominant diffraction peak at 2θ 7.4° that was attributed to the (111) surface. In contrast, the film obtained after the first solvothermal treatment displayed random orientation. The ratio of the intensity of the (111) and (200) peaks increased from 5.8 (after the first solvothermal treatment) to more than 2500-fold (after the third solvothermal treatment). This finding clearly indicated that repeated solvothermal treatments enhanced the (111) orientation of the film. Monocarboxylic acid and water are believed to strongly influence the crystal growth of UiO-66.¹⁶

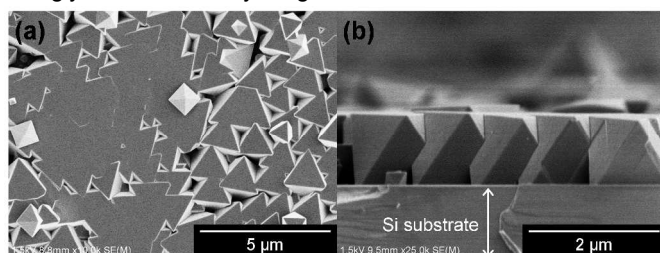


Fig. 1. Scanning electron microscopy (SEM) images of the (a) surface and (b) cross-sectional area of UiO-66 thin film on Si substrate obtained after three repeated solvothermal treatments using a precursor solution with a molar composition of 1.0 ZrCl₂: 1 BDC: 1 H₂O: 500 acetic acid: 1500 DMF (*N,N*-dimethylformamide).

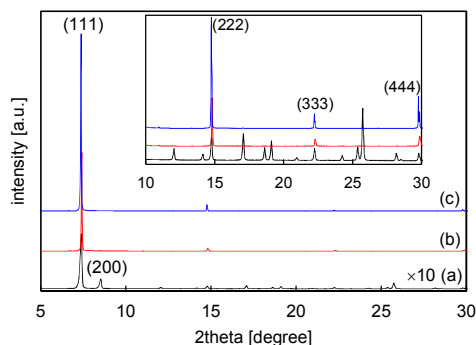


Fig. 2. XRD patterns of UiO-66 thin films on Si substrate obtained after (a) one, (b) two, and (c) three solvothermal treatments using a precursor solution with a molar composition of 1.0 ZrCl₂: 1 BDC: 1 H₂O: 500 acetic acid: 1500 DMF. Inset shows the magnified patterns.

The monocarboxylic acid ligands, with only one coordination site, can compete with the organic linkers for coordination to the metal site, resulting in crystal growth in a preferred direction. This mechanism, so-called coordination modulation method, was proposed by Kitagawa et al.¹⁷ The authors demonstrated that acetic acid directly influenced the coordination equilibria and controlled the crystal growth of nano-sized $[\{Cu_2(ndc)_2(dabco)\}_n]$ (*ndc* = 1,4-naphthalene dicarboxylate; *dabco* = 1,4-diazabicyclo[2.2.2]octane). Furthermore, the crystalline formation of UiO-66 via this mechanism was reported by Schaate et al.¹⁶ In this study, benzoic acid was used as a modulator, and the crystal size could be enlarged by increasing the number of equivalents of benzoic acid that led to favourable in situ formation of complexes between zirconium cations and benzoic acid. Additionally, the authors reported that acetic acid could act as a modulator, similarly to benzoic acid. In our investigation, the increasing added amounts of acetic acid enhanced the crystallinity from the XRD measurements (Fig. S2) and resulted in the formation of larger crystals, and monodisperse octahedral micrometer-sized crystals were obtained with >300 equivalents of acetic acid with respect to ZrCl₄ (Fig. S3), as consistent with the literature report by Lu et al.¹² More specifically, in the latter study, monodisperse microcrystals of UiO-66 with uniform shape and size assembled accordingly to generate (111)-oriented monocrystalline films with the (111) facets contacting the substrate. Additionally, Kitagawa et al. elucidated the important role of the modulator in determining the selective growth of particular crystal surface throughout the crystal growth process and concluded that the modulator controlled the population of preorganized secondary building unit by influencing the reaction kinetics to form a coordination bond between metal and organic linker.¹⁸ Based on these results, it can be concluded that acetic acid played an important role in inhibiting crystal growth in the (111) direction, resulting in octahedral crystalline structures consisting of (111) triangular surfaces owing to relatively high crystal growth rate in the (100) direction. A similar monodisperse microcrystalline film of UiO-66 was prepared by solvothermal synthesis using benzoic acid.¹⁴ However, the obtained film, interestingly, did not display any preferred orientations. This finding further highlights the significant effect of acetic acid on the orientation of UiO-66 films.

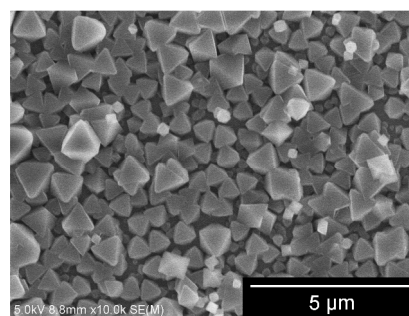


Fig. 3. SEM image of UiO-66 thin film prepared on Si substrate obtained after three repeated solvothermal treatments in the presence of acetic acid only.

When the solvothermal synthesis was carried out in the presence of acetic acid only, the resulting UiO-66 film predominantly consisted of monodisperse octahedral crystals (Fig. 3), though intergrowth of UiO-66 crystals was observed in some parts of the film (Fig. S4). XRD analysis of the film, obtained after three successive solvothermal treatments in the presence of acetic acid only, revealed that the formed UiO-66 crystals were oriented to the (111) surface (Fig. S5), but the ratio of the intensity of the (111) and (200) peaks (i.e., 547) was lower than those of the films synthesized in the presence of acetic acid and water, as expected from the SEM observations (Figs. 1 and 3). In the presence of water only, complete coverage and intergrown UiO-66 films, consisting of hundred nanometre-sized cubic crystals, were obtained following successive solvothermal treatments as shown in Fig. 4. The presence of water inevitably enhanced the hydrolysis of the Zr precursor, resulting in higher formation nuclei rates.¹⁹ Indeed, the size difference in crystals which implies the heterogeneous nucleation was observed by addition of water with >100 equivalents of acetic acid with respect to $ZrCl_4$ for powder synthesis (Fig. S6) compared with those in the presence acetic acid only (Fig. S3). Therefore, though complete coverage of the substrate was not achieved after the first solvothermal treatment, the content of crystals following subsequent solvothermal treatments was considerably higher than that synthesized in the presence of acetic acid only (Fig. S7). Furthermore, water is likely to promote the intergrowth of UiO-66 crystals though this requires further clarification. The current highly intergrown UiO-66 film is expected to find application in membrane separation using porous substrates as supports. XRD analysis (Fig. 5) revealed that the film, obtained after three successive solvothermal treatments in the presence of water, was randomly oriented owing to the small (111)/(200) peak intensity ratio (i.e., 7.8). Therefore, acetic acid is essential to achieve high orientation of the film. Considering the investigation reported by Schaate et al.¹⁶, This coordination modulation method by adding acetic acid can be extended to prepare the oriented other Zr based MOFs such as UiO-67 thin films. However, the influence of water on the intergrowth of the other Zr-based MOF films needs to be further investigated.

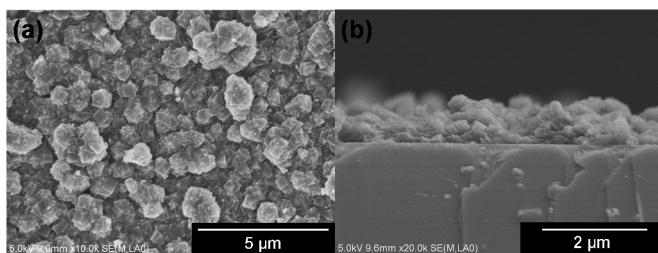


Fig. 4. SEM images of the (a) surface and (b) cross-sectional area of UiO-66 thin film on Si substrate obtained after three repeated solvothermal treatments in the presence of water only.

Finally, we evaluated the chemical stability of the oriented UiO-66 film prepared in the presence of acetic acid and water. From the XRD measurements, the peak intensity of the (111) surface was unchanged through the acid and base treatment for the UiO-66 film as shown in Fig. S8. For UiO-66 powder, while

the crystallinity was stable after the acid treatment, the peak intensity of the (111) surface after the base treatment decreased to 74% (Fig. S9), which shows a good agreement with the previous report by Valenzano et al.²⁰ Those results implies that the chemical stability of UiO-66 film was higher than UiO-66 powder, though the chemical stability of UiO-66 film needs to be further investigated. This high chemical stability of UiO-66 films are expected to an advantage for the application in liquid separation such as pervaporation.

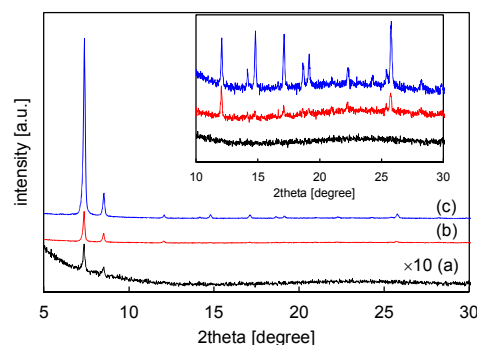
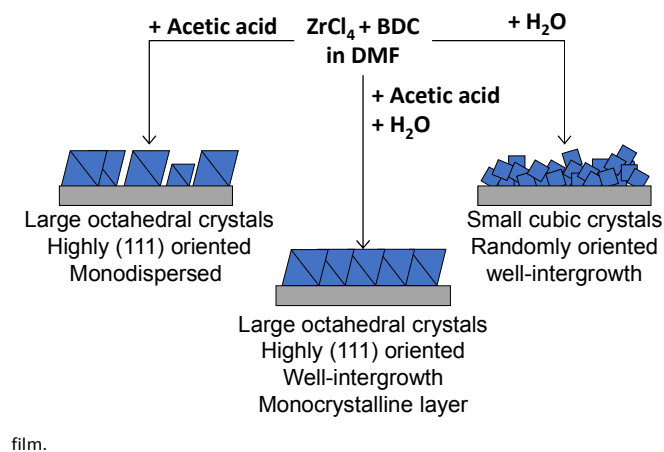


Fig. 5. XRD patterns of UiO-66 thin films on Si substrate obtained following (a) one, (b) two, and (c) three repeated solvothermal treatments in the presence of water only. Inset shows the magnified patterns.

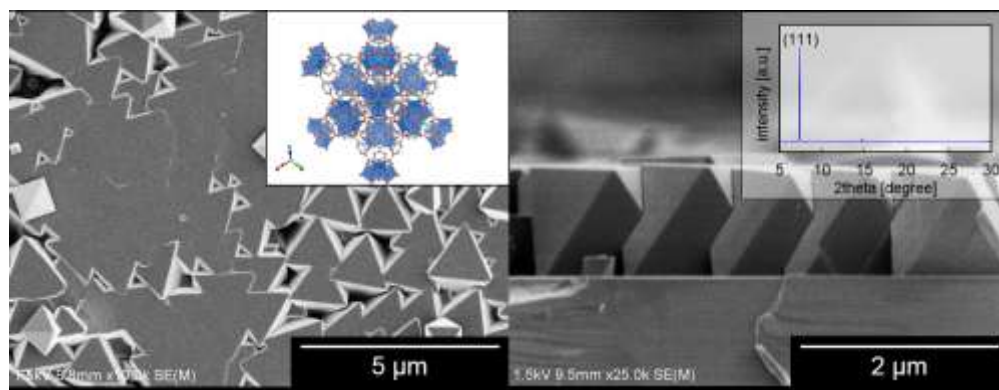
Scheme 1. Influence of acetic acid and water on the crystal growth of UiO-66



In conclusion, the influence of acetic acid and water is summarised in Scheme 1. A UiO-66 thin film was successfully prepared by solvothermal synthesis. The addition of acetic acid and water during synthesis led to the formation of a highly oriented UiO-66 film with monocrystalline layer. Acetic acid, which acted as a modulator to control the rate of crystal growth, was essential to achieve high film orientation. Conversely, water, which acted as an accelerating agent for the hydrolysis of Zr precursor, enhanced the intergrowth of UiO-66 crystals, but did not influence the orientation of the UiO-66 film.

Notes and references

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- † Electronic Supplementary Information (ESI) available: Experimental, SEM images of UiO-66 films and crystals, and XRD patterns. See DOI: 10.1039/c000000x/
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