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Communication

Controlled Two-Dimensional Alignment of Metal−Organic Frameworks in Polymer Films

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ABSTRACT: Controlling the alignment of metal−organic framework (MOF) particles is valueable for fully exploiting the anisotropic properties and porous structure of these materials. Herein, we propose a simple, one-step method that can control the two-dimensional (2D) alignment of MOF particles over large areas. Orientational control is achieved without consideration of the underlying lattice parameters or the need for particle surface modification, but instead was achieved by selection of the casting solvent on a water surface. Two distinct types of MOF particles, a hexagonal bifrustum morphology of MIL-96 and an octahedral morphology of the UiO-66 family were aligned and captured in a polydimethylsiloxane (PDMS) matrix using this approach. This work provides opportunities for studying and utilizing the anisotropic properties of MOFs in thin film applications.

Metal−organic frameworks (MOFs) are commonly found as crystalline polyhedral particles and can possess anisotropic pore structures along different crystal facets, which makes their physicochemical properties different depending on the crystallographic direction. Recently, exploiting directional anisotropy in MOFs has attracted attention as a strategy to complement other approaches to modulating the characteristics of MOFs, such as conductivity,[1−5] wettability,[6,7] selectivity,[8−11] and permeability.[8−10,12] In order to fully utilize the directional anisotropy of MOFs, it would be of value to control the alignment of MOFs and to be able to fix that alignment in a robust manner. Most studies on the alignment of MOFs have focused on utilizing a variety of substrates with specific lattice parameters or surface functionalization that guides the directional growth of MOFs.[4,12−21] However, in order to induce directional growth in MOFs, substrates with different MOF−substrate interfacial interactions must be prepared or growth conditions must be reoptimized, both of which are time-consuming. In addition, these approaches cannot be readily generalized to other MOFs, further limiting their versatility.

Novel strategies for controlling the alignment of MOF particles can be derived from the self-assembly of other inorganic polyhedral nanoparticles (NPs) into two-dimensional (2D) arrays. With these NPs, orientational control is often achieved by tailoring surface tension between NPs and liquid phases.[22−27] The alignment of polyhedral NPs (including MOFs) has generally required altering the surface tension of the NP interactions using surfactants or other surface modifications.[22−25] An alternative, simpler approach is utilizing different casting solvents, which can directly affect the surface tension and hence control the alignment of the NPs. If the alignment of the polyhedral NPs can be controlled by the casting solvent without changing the surface chemistry of the nanoparticles (including surface modification with surfactants), and maintained after evaporation or mixing, this would prove to be an attractive strategy to easily control the alignment of polyhedral particles, including MOFs.

Herein, we report a one-step strategy to control the 2D assembly of nanoporous polyhedral MOF crystals through simple changes in the casting solvent and subsequent immobilization of these oriented particles in large area polymer films. A key aspect of the present strategy is including a heat-curable polydimethylsiloxane (PDMS) in the casting solvent, which not only maintains MOF alignment controlled by the casting solvent, but also allows for preservation and transfer of the aligned film to other substrates (Figure 1). For this proof-

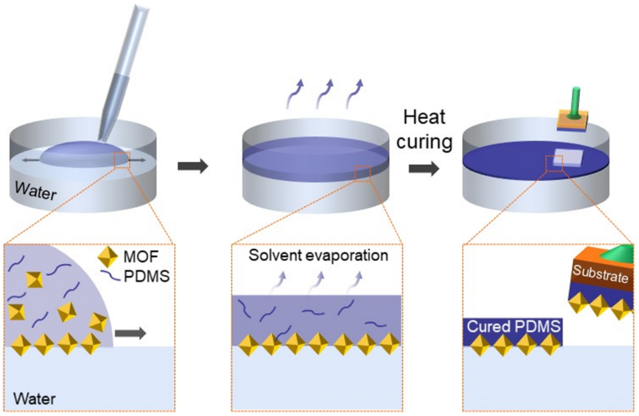

Figure 1. Schematic illustration for the preparation of aligned polyhedral MOF−PDMS films.

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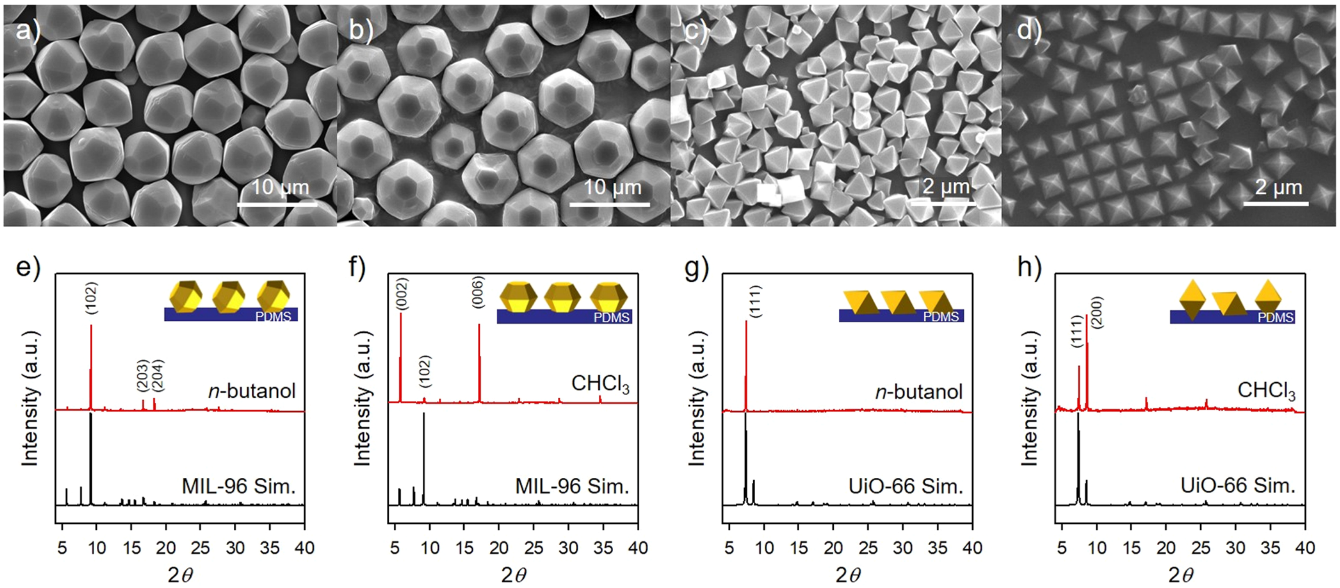

Figure 2. SEM images of the bottom surface of an aligned MIL-96-PDMS thin film prepared using (a) *n*-butanol and (b) $CHCl_3$. SEM images of the bottom surface of an aligned UiO-66-PDMS thin film prepared using (c) *n*-butanol and (d) $CHCl_3$. PXRD patterns of aligned MIL-96-PDMS thin films prepared using (e) *n*-butanol and (f) $CHCl_3$, compared with simulated diffraction patterns of randomly oriented MIL-96. PXRD patterns of an aligned UiO-66-PDMS thin film prepared using (g) *n*-butanol and (h) $CHCl_3$, compared with simulated patterns of randomly oriented UiO-66.

of-concept study, two types of polyhedral MOFs particles were used: a hexagonal bifrustum morphology of MIL-96 and an octahedral morphology of UiO-66 and UiO-66-NH_2. To the best of our knowledge, this represents the first example of controlling the alignment of MOFs with a simple change of casting solvent, which eliminates the need for complex surface chemistry or other synthetic modifications of the MOF.

Oriented MOF films were prepared by a conventional drop-casting method with the addition of PDMS to the casting solvent containing the MOF particles (Figure 1). Briefly, the casting solution containing the dispersed MOF particles and PDMS was introduced onto a water surface. As the casting solvent spreads over the water surface, the suspended MOF particles are trapped with a preferred alignment at the water−solvent interface, with the PDMS diffusing freely throughout the casting solvent layer. As the casting solvent evaporates, the PDMS concentration increases, forming a thin, viscous layer that holds the aligned MOF particles in place. Finally, the PDMS layer is cured by heating to produce a thin film with MOF particles in a fixed orientation. The resulting film can be readily transferred to other substrates.

The solvent-dependent alignment of polyhedral MOF particles was first investigated utilizing hexagonal bifrustum-shaped MIL-96 particles and eight casting solvents: *n*-butanol, tetrahydrofuran, ethyl acetate, CH_2Cl_2, $CHCl_3$, toluene, hexane, and cyclohexane (Table S1). MIL-96 particles directly transferred to carbon tape and imaged by scanning electron microscopy (SEM) show randomly oriented and stacked particles (Figure S1). In contrast, the same particles assembled at a water interface, using *n*-butanol, tetrahydrofuran, or ethyl acetate as casting solvents, produced MOF−PDMS films with the trapezoidal facets of MIL-96 particles aligned upward as clearly observed by SEM (Figure 2a and Figure S2). This orientation corresponds to the ⟨*h*0*l*⟩ direction of MIL-96, which was verified by powder X-ray diffraction (PXRD) experiments, in good agreement with SEM images (Figure 2e, Figure S2). When the casting solvent is changed to CH_2Cl_2 or $CHCl_3$, the MIL-96-PDMS films show a completely different alignment with the hexagonal facets facing up, corresponding to the ⟨002⟩ orientation (Figure 2b,f; Figure S3). Use of toluene, hexane, or cyclohexane resulted in poor spreading over the water surface, producing MOF−PDMS aggregation instead of the desired thin films (Figure S4).

To explore the generality of this approach, octahedral particles of UiO-66 and UiO-66-NH_2 were subjected to the same film forming strategy. SEM images revealed that octahedral UiO-66 and UiO-66-NH_2 particles displayed a “facet up” and “vertex up” alignment using *n*-butanol and $CHCl_3$ as casting solvents, respectively (Figure 2c, d; Figure S5, Figure S6). These alignments correspond to preferred crystallographic orientations of the ⟨111⟩ and ⟨200⟩ faces with *n*-butanol and $CHCl_3$, respectively. PXRD measurements and quantitative measurement of the degree of crystal orientation using the crystallographically preferred orientation (CPO) index[9,28,29] verified the strong alignment of these particle films (Figure 2g,h, Figures S5−S8).

To understand how the casting solvent controls particle alignment, the correlation with various physical properties of the solvents was examined (Table S1, Figure S9). No correlation with solvent polarity, vapor pressure, or dielectric constant was consistent with the observed alignments in the thin film structure. On the other hand, the interfacial tension of the water-casting solvent, which affects the alignment of NPs at the interface between the two liquids,[22,26,30] appears to be correlated with the observed alignment trend of polyhedral MOF particles (Figure S9). For solvents that are are miscible with water or have a low interfacial tension, the alignment of the trapezoidal facet upward is dominant. However, as the interfacial tension increases, the alignment of the hexagonal facet upward becomes dominant. For interfacial tension values of 36.1 mN/m or higher, the solvents do not spread evenly on the water surface, resulting in MOF−PDMS aggregation.

These results suggest that solvent-dependent MOF alignment is closely related to the water−liquid interface environment created by the introduced casting solvent.

The anisotropic structure of the polyhedral MOF−PDMS films, which differs from those of the other MOF−polymer films where the MOF particles are homogeneously distributed and randomly oriented in the polymer matrix, reveals important insight into the interface environment in which the MOF particles are aligned. As shown in bottom, top, and cross-section SEM images of the aligned films (Figures S10−12), a thin PDMS layer is present over the monolayer of the aligned polyhedral MOF particles. This suggests that the casting solvent containing PDMS is present over the aligned polyhedral MOF particles and that the polyhedral MOF particles are aligned at the water−solvent interface rather than at an air−solvent interface. In control experiments of MOF alignment performed under same conditions without PDMS, MOF particles showed the same alignment regardless of the casting solvent. This is because the MOF particles are ultimately exposed to the same water−air interface upon evaporation regardless of the casting solvent (Figure S13). The aligned MOF particles subsequently rearrange at the water−air interface.[31]. In contrast, the use of PDMS prevents rearrangement of the MOFs upon evaporation of the casting solvent and also fixes the alignment of the MOF particles upon curing. Taken together, these results indicate that the alignment of the polyhedral MOF particles occurs at the water−solvent interface, which can be controlled by the casting solvent and maintained by the presence of PDMS.

Because the heat-cured PDMS is strong enough to fix the aligned polyhedral NPs,[17,23,24,32,33] large area MOF−PDMS films can be obtained in which the alignment of polyhedral MOF particles is preserved. The uniform alignment of MOF particles across one of these large area film (ca. 23 cm^2) was verified by SEM and PXRD measurements sampled at three different locations in the film (Figures S14 and S15). In addition, PDMS is well-known to adhere to various substrates via a van der Waals interaction. Consistent with this, the aligned MOF−PDMS films could be directly transferred to flat and curved glass, ductile aluminum foil, and flexible latex polymer substrates (Figure 3a). Aligned MOF−PDMS films transferred and adhered to these substrates could be further shaped without disrupting the MOF orientation (Figure 3b). The MOF−PDMS composites could also be isolated and suspended as freestanding films (Figure 3a).

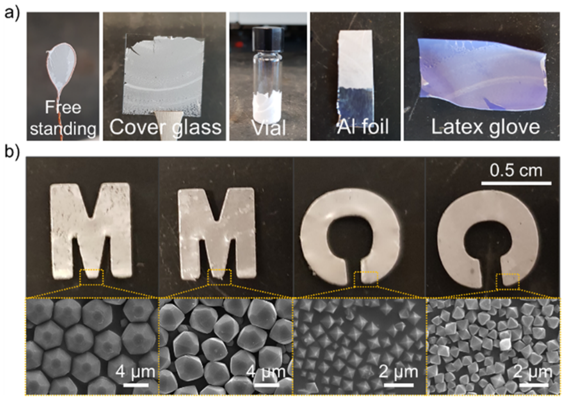

Figure 3. (a) Photographs of MIL-96-PDMS thin films prepared with $CHCl_3$ as the casting solvent as free-standing films or transferred to various substrates. (b) Photographs of four types of aligned MOF−PDMS films transferred to aluminum foil and further shaped into M and O characters.

Developing a novel strategy capable of controlling the alignment of MOFs is a significant challenge. In this work, we demonstrated that alignment of polyhedral MOF particles could be efficiently controlled by casting solvents at a water-casting solvent interface without surface modification of MOF or complex surface chemistry between substrates. Experimental validation of controlled alignment of MOF particles was successfully demonstrated with two distinct types of polyhedral MOFs, hexagonal bifrustum MIL-96 and octahedral UiO-66 and UiO-66-NH_2. By introducing PDMS into the casting solvent of the conventional drop-casting method, the controlled alignment of polyhedral MOF particles can be preserved in the MOF−PDMS film and transferred to various substrates. This work can serve as a starting point to accelerate the study of the anisotropic properties of MOFs that could be used in a variety of applications and will guide the development of a novel strategy to control the alignment of nanoparticles without surfactants.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c13459.

Experimental details, additional results presented in Table S1 and Figures S1−S15, and related references (PDF)

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Notes

The authors declare no competing financial interest.

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