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## COMMUNICATION

## Control of the nucleation and growth processes of metal-organic frameworks using a metal ion-doped polymer substrate for the construction of continuous films

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**We herein demonstrate a novel concept for the one-pot synthesis of metal-organic framework (MOF) films on a metal ion-doped polymer substrate based on control of the nucleation and growth processes. This strategy allows the ready fabrication of densely-packed uniform MOF films.**

Metal-organic frameworks (MOFs), a class of highly ordered porous materials, have drawn considerable attention in many applications such as gas storage,<sup>1</sup> separation,<sup>2</sup> catalysis,<sup>3</sup> and sensing,<sup>4</sup> due to their unique properties. A key aspect of MOF chemistry is a modular construction based on the self-assembly of frameworks, and this allows for control of the pore structures and network topologies.<sup>5</sup> Moreover, individually controlling the nucleation and growth processes of MOFs can provide further opportunities to fully realise the potential of MOF crystals,<sup>6</sup> since modulation of the crystal growth process enables control of the crystal structure parameters, such as the crystal size, morphology, and crystallinity.<sup>7</sup> The ability to control the nucleation and growth processes of MOF crystals is also important for the construction of MOF films with specific and desirable properties. As MOF films exhibit unique properties based on the efficient use of pore space and the integration of specific functions, increasing attention has recently focused on the preparation of MOF films.<sup>8</sup> For this purpose, sequential processes of uniform nucleation on a substrate and growth of the nuclei are essential for the preparation of continuous MOF films free from cracks or intercrystalline gaps. However, the preparation of continuous MOF films is challenging using thermodynamic-based conventional synthetic approaches, since the equilibration reaction for the formation of MOF crystals tends to lead to a preferential nuclei growth process. Therefore, the development of a general and

straightforward method to control the nucleation and growth processes on the substrate could pave the way for an improved understanding of the growth mechanism of framework materials and the construction of high-performance MOF films.

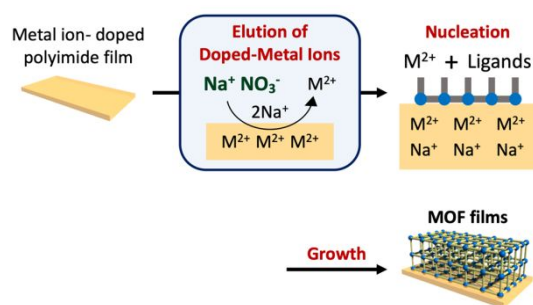
Thus, we herein propose a promising new strategy for the preparation of uniform MOF films. This strategy is based on the independent control of the nucleation and growth processes. In a previous study, we demonstrated an interfacial growth approach for the fabrication of MOF films using a metal ion-doped polyimide substrate to act not only as a support substrate, but also as a metal source for the formation of MOF crystals.<sup>9</sup> This approach is based on an ion-exchange reaction between metal ions doped into the polyimide substrate and the protons of organic ligands bearing carboxylic acid groups. Although this system provides a simple and rational reaction process for the fabrication of MOF films, control of the nucleation and growth processes is difficult since the carboxylic acid-bearing organic ligands have two roles, namely the elution of doped metal ions from the polyimide substrate and framework complexation, thereby limiting this synthetic process in the context of producing continuous MOF films. In this work, we report our investigation into the individual modulation of the elution of doped metal ions from a polyimide substrate and framework complexation through the use of sodium nitrate as a promoter that facilitates the ion-exchange reaction of doped metal ions, in addition to the use of organic ligands free from carboxylic acid groups (Scheme 1). Furthermore, using our proposed strategy, we investigate the growth mechanism of MOF crystals on the substrate.

As a proof-of-concept, we focus on a zeolitic imidazole framework,  $[\text{Zn}(\text{MeIM})_2]_n$  (ZIF-8; MeIM = 2-methylimidazole) because of its high stability and simple preparation under ambient conditions.<sup>10</sup> Importantly, we note that as the MeIM ligand has no proton release capability in solution prior to the formation of ZIF-8 crystals, it cannot induce elution of the doped metal ions from the polyimide substrate. Thus, the  $\text{Zn}^{2+}$ -doped polyimide substrate<sup>11</sup> was immersed in a mixture of  $\text{H}_2\text{O}$ /methanol (1000 mL) containing 500

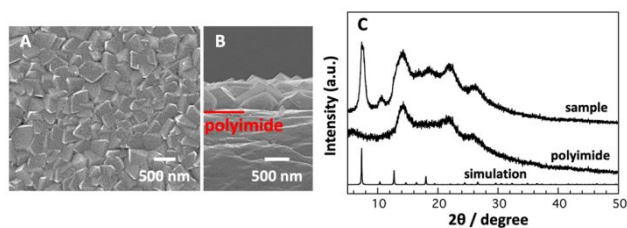
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Electronic Supplementary Information (ESI) available: [Experimental procedure, SEM image of obtained samples; Time course analysis; XRD pattern of obtained samples]. See DOI: 10.1039/x0xx00000x



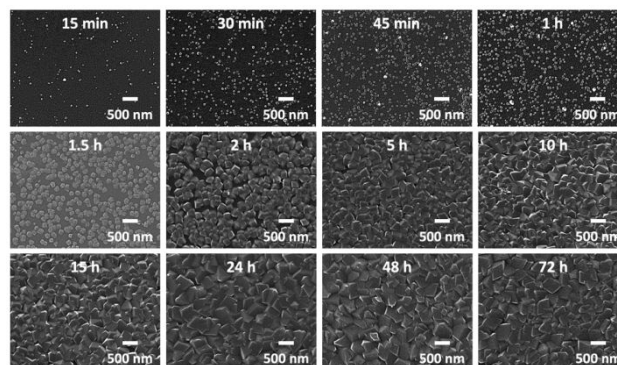
**Scheme 1.** Schematic illustration of the present strategy based on independent control of the elution of doped metal ions and the complexation of frameworks for fabricating the continuous MOF films.



**Figure 1.** (A) SEM image, (B) cross-sectional SEM image, and (C) XRD pattern for the ZIF-8 crystals formed on the polyimide substrate.

mM MeIM ligand and 100 mM NaNO<sub>3</sub> as a promoter for elution of the doped Zn<sup>2+</sup> ions. The resulting solution was then stirred at room temperature for 72 h to yield the ZIF-8 crystals on the polyimide substrate, in which the MeIM concentration was sufficient to immediately react with the eluted Zn<sup>2+</sup> ions. As shown in Figure 1A, scanning electron microscopy (SEM) observations of the obtained samples indicated that adequately intergrown polycrystalline MOFs with rhombic dodecahedral structures were densely packed on the substrate. Additionally, a cross-sectional SEM image shows that a uniform single-layered MOF crystal film was formed on the polyimide substrate, indicating the construction of a continuous MOF film (Figure 1B). Furthermore, X-ray diffraction (XRD) measurements of the products confirmed the formation of ZIF-8 crystals on the polyimide substrate; all peaks observed for the obtained crystals were assigned to the simulated ZIF-8 pattern and the halo pattern of the polyimide (Figure 1C).

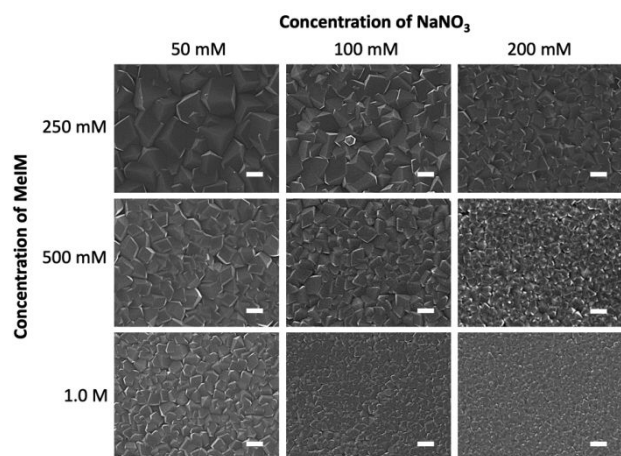
To investigate the temporal evolution of the obtained films, a time-course analysis of the crystal growth process was performed through SEM observations (Figure 2). In this case, we monitored the evolution of the crystal number and size as a function of the reaction time (Figure S1). During the first hour of the reaction, the crystal number clearly increased, while the crystal size increased only slightly, indicating that the nuclei were preferentially generated during this time. In contrast, the crystal size drastically increased during the subsequent hour, which was accompanied by a decrease in the crystal number. This was attributed to the fusion of neighbouring crystals during the early growth process, which was in



**Figure 2.** SEM images of the ZIF-8 films obtained after different reaction times.

turn caused by the high surface energy of the small crystals. After allowing the reaction to proceed for a further hour, the crystal size gradually increased without any apparent crystal fusion. It was therefore clear that nucleation of the ZIF-8 crystals took place preferentially during the initial hour of the reaction, while crystal growth proceeded slowly beyond this point, with the fusion of small crystals occurring only in the early stages of the growth process. It should be noted here that the nucleation of ZIF-8 crystals on the substrate is based on the elution behaviour of doped Zn<sup>2+</sup> ions from the polyimide substrate in the presence of NaNO<sub>3</sub>. As shown in Figure S2, the doped Zn<sup>2+</sup> ions rapidly elute from the polyimide substrate within the first hour, followed by gradual elution only after this time. This was attributed to the concentration difference of Na<sup>+</sup> ions between the reaction solution and the polyimide substrate in the initial stages. However, as a high reaction volume of 1000 mL was used to facilitate elution of the doped metal ions from the polyimide substrate, the concentration of Zn<sup>2+</sup> ions in the polyimide substrate (the concentration of Zn<sup>2+</sup> ions after 1 h of reaction = ca. 1 M in the polyimide layer) was significantly higher than that of the reaction solution, thereby slowing the elution of Zn<sup>2+</sup> ions from the substrate. This elution behaviour consisting of faster elution in the early stage of the reaction and slower elution after 1 h is key to the sequential process of preferential nucleation on the substrate and growth of the resulting nuclei. When the elution rate is fast, nucleation takes place preferentially due to the high concentrations of Zn<sup>2+</sup> ions and MeIM ligands at the interface between the reaction solution and the polyimide substrate. After 1 h, crystal growth proceeds through the slow feeding of Zn<sup>2+</sup> ions from the polyimide substrate. These results therefore indicate that control of the elution rate through the use of NaNO<sub>3</sub> as a promoter for the ion-exchange reaction can lead to kinetically-dominated nucleation on the substrate in the initial reaction stage, followed by thermodynamically-favoured crystal growth in the subsequent stage.

Since the elution of doped Zn<sup>2+</sup> ions can be induced by an ion-exchange reaction with the Na<sup>+</sup> ions of NaNO<sub>3</sub>, we attempted the preparation of ZIF-8 films with varying NaNO<sub>3</sub> concentrations (i.e., 50–200 mM, MeIM concentration = 500 mM) to elucidate the effect of the metal ion elution rate on the formation of MOF crystals. The



**Figure 3.** SEM images of the ZIF-8 films obtained after 72 h of reaction at different concentrations of  $\text{NaNO}_3$  and MeIM. The scale bars are 500 nm.

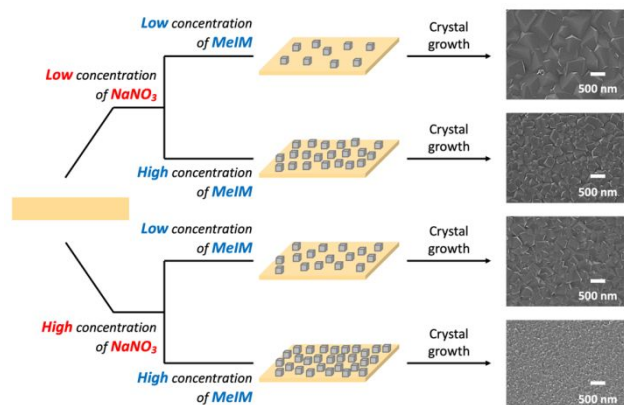
obtained SEM images are shown in Figure S3, while the variation in crystal number and size of the samples obtained during the 1 h reaction are presented in Figure S4. Nuclei were preferentially generated and the number of nuclei increased as a function of reaction time, while the nuclei size changed only slightly within the initial 1 h. These results indicate that preferential nucleation occurred on the substrate in the early stage of the reaction. As expected, the number of crystals obtained within the initial 1 h increased upon increasing the  $\text{NaNO}_3$  concentration. Consequently, the crystal domain size of the final obtained continuous ZIF-8 films after 72 h reaction was smaller at higher  $\text{NaNO}_3$  concentrations (Figure S5). These results were attributed to the different elution rates of doped  $\text{Zn}^{2+}$  ions from the polyimide substrates in the initial reaction stage. As shown in Figure S6, in the presence of a high  $\text{NaNO}_3$  concentration, the doped  $\text{Zn}^{2+}$  ions rapidly elute from the polyimide substrate, which leads to the rapid nucleation of ZIF-8 crystals on the substrate. It was therefore apparent that the  $\text{NaNO}_3$  concentration clearly influences the nucleation rate of ZIF-8 crystals on the polyimide substrate, resulting in the formation of continuous ZIF-8 films with different crystal sizes. However, the presence of excess  $\text{NaNO}_3$  (i.e., 200 mM) leads to insufficient growth of the initially-formed nuclei, resulting in the formation of MOF crystals bearing intercrystalline gaps. An appropriate balance between early stage nucleation and subsequent growth is therefore key to the formation of continuous MOF crystal films.

The effect of ligand concentration on MOF crystal formation was then investigated by varying the MeIM concentration between 250 mM and 1.0 M. Indeed, it was found that the crystal number increased in the early stage of the reaction (1 h) upon increasing the MeIM concentration, while there was no obvious difference in the crystal size (Figures S7 and S8). Following nucleation, the nuclei grew slowly to give larger crystals. However, faster nucleation was found to result in the formation of densely-packed continuous films consisting of smaller crystals since there was not sufficient space to

grow large crystals where a dense arrangement of nuclei was produced in the initial stage. Thus, the crystal size of the final products obtained after 72 h was smaller at higher MeIM concentrations (Figure S9). Although the elution rate of the doped  $\text{Zn}^{2+}$  ions remained constant at each MeIM concentration, different nucleation rates of the ZIF-8 crystals were observed on the polyimide substrate. This was attributed to the collision frequency between the eluted  $\text{Zn}^{2+}$  ions and the MeIM ligands. At high MeIM concentrations, the eluted  $\text{Zn}^{2+}$  ions can immediately react with MeIM, which induces fast nucleation and the formation of continuous ZIF-8 films with small crystals, such as those observed in the case of higher  $\text{NaNO}_3$  and lower MeIM concentrations. In contrast, the collision frequency decreases at low MeIM concentrations, suggesting that  $\text{Zn}^{2+}$  ions eluted from the polyimide substrate may diffuse into the reaction solution, although the concentration of these ions would be particularly low due to the high reaction solution volume employed. Therefore, after the initial hour of reaction, ZIF-8 crystals may be grown by the slow feeding of doped  $\text{Zn}^{2+}$  ions from the polyimide substrate and diffused  $\text{Zn}^{2+}$  ions present the reaction solution, which could lead to the formation of continuous ZIF-8 films with large crystals.

These results indicate that the concentrations of  $\text{NaNO}_3$  and MeIM influence the nucleation rate of ZIF-8 crystals on the polyimide substrate. We therefore carried out a set of experiments in which the concentrations of  $\text{NaNO}_3$  and MeIM in the reaction solution were systematically changed. As shown in Figures S10 and S11, the crystal numbers obtained in the early stage of the reaction were larger at higher  $\text{NaNO}_3$  and MeIM concentrations, while the crystal sizes were comparable. In addition, when both concentrations were high, a large number of smaller ZIF-8 nuclei were densely formed in the early stage of the reaction. After 72 h, the crystal size decreased in the case when larger crystal numbers had been obtained after 1 h, and all resulting films were found to consist of densely-packed continuous ZIF-8 crystals (Figures 3, S12 and S13). These results confirm that continuous ZIF-8 films with systematically controlled crystal sizes could be readily prepared by modulating the nucleation rate.

The successful construction of uniform MOF films with tuned crystal sizes was therefore successfully achieved using our strategy through independent control of the nucleation and growth processes. Such control is generally difficult to achieve using conventional approaches since the thermodynamically-controlled reaction system induces a dominant growth process to construct thermodynamically stable MOF crystals with high crystallinities.<sup>12</sup> Moreover, the use of a kinetically-controlled reaction system based on a homogeneous reaction solution containing both metal ions and organic ligands generally results in the formation of aggregated coordination polymers containing an amorphous phase.<sup>13</sup> In contrast, our approach involves a heterogeneous system through the use of a metal ion-doped polymer substrate and a reaction solution containing only the desired organic ligands. In addition, the use of  $\text{NaNO}_3$  as a promoter leads to precise control of the elution rate of doped metal ions from the polyimide substrate, which allows for



**Figure 4.** Schematic representation of the proposed strategy for the formation of continuous ZIF-8 films with controlled crystal size based on independent control of the nucleation and growth processes.

separation of the nucleation and growth processes. Furthermore, as shown in Figure 4, the nucleation rate can be easily controlled by modulating the concentrations of  $\text{NaNO}_3$  and MeIM, since these factors influence the elution rate and the complexation rate, respectively. As such, by tuning these concentrations, the surface morphology of the resulting continuous ZIF-8 crystal films can also be controlled.

In summary, continuous MOF films with controlled crystal sizes were successfully prepared by ensuring a suitable rate for complexation of metal ions and organic ligands at the interface between a polyimide substrate and a reaction solution. In our strategy, the nucleation and growth processes were controlled using  $\text{NaNO}_3$  as a promoter to facilitate the elution of doped metal ions from the substrate. In addition, the nucleation rate was easily controlled by modulating the concentrations of  $\text{NaNO}_3$  and the MeIM ligand, which allowed for control of the crystal size of the ZIF-8 films produced on the polyimide substrate. This study would be expected to pave the way for the development of a fundamental understanding of the growth mechanism of MOF crystals on a substrate to ultimately produce continuous MOF films.

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## Conflicts of interest

There are no conflicts to declare.

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- In this report, to form densely-packed continuous ZIF-8 crystal-based films, a large amount of  $\text{Zn}^{2+}$  ions are doped into the polyimide substrate. When the ion loading is lower than that of utilized polyimide substrate in the present report, we cannot obtain the densely-packed, continuous ZIF-8 crystal-based films. On the other hand, at higher ion loading, the elution rate of adsorbed  $\text{Zn}^{2+}$  in the early stage of the reaction (within 1h) is almost the same, suggesting that the concentration of  $\text{NaNO}_3$  is a key factor for controlling the elution rate of adsorbed  $\text{Zn}^{2+}$  in the present experimental condition. This is because the concentration of  $\text{NaNO}_3$  is too higher than that of adsorbed  $\text{Zn}^{2+}$  in the polymer substrate.
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