Crystal Growth of Metal–Organic Framework-5 around Cellulose-Based Fibers Having a Necklace Morphology

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ABSTRACT: Herein, metal–organic framework (MOF)-5 crystals were grown on cellulose-based substrates including paper and cotton. Dopamine was used as a surface modification agent to improve the compatibility between MOF-5 crystals and the used substrates. The formed polydopamine film promoted the growth of MOF-5 crystals, which were bonded to the substrates. Besides dopamine, the structure of the substrate also played a major role in the crystal growth. In the case of paper, which had a structure with fibers closely packed to each other, MOF-5 crystals grew only on the surface of fibers (one side) and could easily fall off. Unlike paper, the cotton bulb had a looser structure and MOF-5 crystals grew around the fibers, forming a stable “necklace” morphology. The effects of dopamine modification on the crystal growth and the formation of “necklace” morphology were investigated using scanning electron microscopy analysis. The crystalline structure of MOF-5 was confirmed using X-ray diffraction. To determine how firmly crystals were attached to the cotton fibers, the substrates were exposed to a constant and strong air flow. It was found that the dopamine-modified cotton increased the strength of MOF-5 crystals attached to fibers. This work demonstrated the firm attachment of MOF-5 crystals onto the substrate, facilitating various potential applications.

INTRODUCTION

Metal–organic frameworks (MOFs) are a class of crystalline porous materials made by linking metal ions and organic ligands. Because of their well-defined structure and functionality, these porous materials have received a great research attention over the recent years.1–3 Their large and accessible surface area up to 7000 m2 g−1 is one of the most important characteristics.4 Tunable pore properties, various active sites, and thermal stability offer MOF materials’ potential applications for gas storage and separation,5,6 catalysis,7,8 and drug delivery systems.9 Applying MOFs for filtration of toxic gases and for air purification has become a hot research topic because of the increasing global air pollution.10–13 Despite all of the properties that MOFs possess, these materials are usually obtained as powders and this form limits their applications. To overcome this, many methods to process the MOF crystals into various structures were reported, that is, MOF thin films14 and membranes.15 Recently, it became more popular to grow MOF crystals from the surface of different fibers made by electrospinning processes.16–19 Supporting MOF crystals onto commercially available, cost-effective, and eco-friendly substrates provides an effective approach to expand their potential applications. One of the best candidates is cellulose-based substrates.

Cellulose is one of the widely used, renewable, and natural polymers. Cellulose fibers, whiskers, or cellulose nanocrystals have a broad range of applications in filtration, textile industry, biomedicine, and as a reinforcing filler in adhesives.20–22 Good mechanical properties, low cost, abundance, good processability, and easy recycling ensure their use in the fabrication of various composite materials. However, because of cellulose polar and hydrophilic nature, cellulose compatibility with nonpolar and hydrophobic materials is limited.23 To improve adhesive properties of cellulose-based substrates and ensure the growth of MOF crystals, the surface must be modified.24 Dopamine (DA) has been used as a surface modification agent for various substrates, and it is inspired by the chemistry of proteins in marine mussels.25–27 The ability of mussels to attract foreign objects is originated from proteins, which are rich in catechol groups from 3,4-dihydroxy-L-phenylalanine and lysine (amine) groups.28,29 The same functional groups can be found in small-molecule DAs which can polymerize under mild conditions and can be applied to almost all kinds of surfaces via amine and catechol functional groups.30 Although the mechanism of DA self-polymerization into polyDA (PDA) is complex and is yet to be understood,31 an effective surface modification can be achieved by simple treatment of substrates with buffered DA solution at ambient temperature. On the
surface of treated substrates, a thin polymer film is formed and its thickness is a function of immersion time. Our group has reported the use of DA for surface modification of various substrates and the growth of MOF-5 thin films on PDA as a nucleation center.25 PDA coated onto the surface of substrates significantly promoted the growth of MOF-5 crystals, facilitating the attachment of MOF crystal seeds to the substrate surface. Except for the adhesive ability to attach MOF-5 crystals, catechol groups on polymerized DA can bind with metal ions and form a metal–catecholate coordination complex.28,33,34 This simple fabrication of MOF-5 films was accomplished by simply immersing substrates into a MOF-5 mother solution.

In this work, we report a facile method to grow MOF-5 crystals around cellulose-based fibers. The growth of MOF crystals on cellulose fibers by various methods has been reported in the literature. Deposition of HKUST-1 crystals on pulp fibers was reported through in situ synthesis of MOF in the presence of pulp fibers.35 Different degrees of surface coverage were obtained depending on the chemical composition of fibers. Reynolds et al.36 reported immobilization of CuBTC crystals on cotton substrates via functionalization of the cotton surface with carboxylate linkers and immersing the modified substrate in a MOF mother solution. It was demonstrated that the modification played a vital role in the coverage of the substrate surface. Hinestroza et al.37 presented chemical attachment of MOF-199 onto cotton fibers. All of these works showed that MOF crystals grow on the surface of cellulose-based substrates. However, to the best of our knowledge, there has been no report on a “necklace” morphology, that is, the growth of crystal around cotton fibers. MOF-5 crystals were firmly attached to the fiber, whereas the large surface of the crystals remains free.

## EXPERIMENTAL SECTION

### Materials

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 98%), terephthalic acid (98%), DA hydrochloride, and tris(hydroxymethyl)aminomethane (Tris, 99.8%) were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF, 99.8%) was purchased from Caledon, CA. All chemicals were used without further purification. Deionized water was used throughout all the experiments.

Two different substances were used in the experiments: paper strips and cotton bulbs. The paper was a coffee filter paper (GK Connaisseur 03-2644637 from Dollarama in CA). Commercially available cotton balls made for medical uses were used.

### Substrate Modification

Paper was cut into rectangular strips, and cotton was washed with acetone and dried at room temperature. DA solution was made by dissolving DA hydrochloride in 200 mL of Tris aqueous solution (10 mM). The amounts of DA dissolved in 200 mL of Tris were 400 and 1000 mg. The substrates were immersed in the two DA solutions having different concentrations and left at room temperature for 24 h. The modified paper and cotton were washed with deionized water and ethanol three times to remove residual DA and dried in a vacuum oven at 65 °C for 24 h. To compare how MOF-5 crystals were attached to substrates without PDA, pristine paper and cotton were used. The paper strips and cotton bulbs were only washed with acetone and dried at room temperature.

### Preparation of MOF-5 Mother Solution

MOF-5 mother solution was prepared as follows. First, 4.239 g of Zn(NO$_3$)$_2$·6H$_2$O and 0.9072 g of terephthalic acid were dissolved in 135 mL of DMF. Transparent mother solution was then heated to 65 °C and kept for 48 h. After temperature was raised to 105 °C, the mother solution was left for additional 72 h at the temperature. The mother solution stayed transparent where generated MOF crystals were settled at the bottom of the beaker (Figure S1A, Supporting Information). MOF-5 crystals were cooled down to room temperature, washed with DMF, and dried in vacuo at 65 °C.

### Preparation of MOF@Paper Structures

The modified paper was immersed in the MOF-5 mother solution and remained for 3 days at 65 °C. After that, the sample was rinsed with DMF and dried in vacuo at 65 °C.

### Preparation of MOF@Cotton Structures

The modified cotton was immersed in the MOF-5 mother solution and kept in the mother solution for 3 days. In one set of experiments, the temperature was 65 °C, whereas in the other, it was increased to 105 °C and left for 72 h. Prepared MOF crystals were attached to the cotton bulb (Figure S1B, Supporting Information), and the mother solution stayed transparent. All samples were washed with DMF and dried in vacuo at 65 °C.

### Characterization

JEOL JSM 7000 scanning electron microscopy (SEM) was used to characterize morphologies of the obtained structures. Fourier transform infrared (FTIR) characterization was done on Thermal Nicolet 6700. Samples were scanned 64 times, and spectra were obtained with wavelengths from 4000 to 500 cm$^{-1}$. Gas sorption data were collected using a Quantachrome Instrument (v 5.2) at 77 K measuring nitrogen adsorption. Samples were previously degassed for 24 h at 393 K. Thermogravimetric analysis (TGA) was performed using a Mettler TGA/DSC 3+ thermogravimetric analyzer. Thermograms were recorded at a heating rate of 10 °C/min between 37 and 600 °C in a flow of argon at 20 mL/min. X-ray diffraction (XRD) of MOF@substrate structures was carried out on a Bruker D8 ADVANCE powder diffractometer with a scan speed of 1° 20 s$^{-1}$, a step size of 0.01°, and a 2θ range of 2–45°.

### Stability Test

To investigate the stability of MOF@cotton structures, the structures were exposed to a constant airflow at 18 L/min, three times for 20 s until a constant mass was reached (Supporting Information, Table S1). The present of the saved mass was calculated using the following equation

$$P = \frac{m_1 (\text{MOF@cotton})}{m (\text{MOF@cotton})} \times 100\%$$

where $m_1$ (MOF@cotton) was the mass of structures before air blow, and $m$ (MOF@cotton) was the mass of structures after exposure to air flow 3 × 20 s.

## RESULTS AND DISCUSSION

Two commercially available cellulose-based substrates, namely, paper strips (paper) and cotton bulbs (cotton), were treated with DA to modify the surface of the substrates and to ensure adhesion of the MOF-5 crystals. MOF-5, as one of the most studied MOFs, was chosen for the crystal growth onto the substrates because of its thermal stability and large and accessible surface area.38,39 This isoreticular MOF is inexpensive and easy to synthesize in various ways.38,40,41 The structure of the modified cellulose substrates has a significant effect on the attachment of MOF-5 crystals nurtured from a mother solution to the fibers. It was found that MOF-5 crystals could grow only on the paper surface (one side of the
paper substrate) and were easy to fall detached, whereas in the case of cotton, stable crystalline structures around individual fibers were formed. Apart from the substrate structure, the influences of DA solution concentration and MOF-5 nurture temperature on the crystal growth and morphology were studied. The morphology of MOF-5@substrate structures was investigated using SEM, and the crystal structure of MOF-5 was confirmed by XRD. Quantitative measurements were performed to determine how firmly MOF-5 crystals were attached to the cellulose-based fibers.

The fabrication of MOF-5@substrate structures is schematically represented in Figure 1. For simplicity, the schematic displays fabrication steps using the cotton bulbs (Figure 1A) and the same procedure was applied to the paper strips. The first step was substrate modification by DA hydrochloride solutions of two different concentrations (Figure 1B). The DA solutions were prepared by dissolving DA hydrochloride in 200 mL of Tris aqueous solution (10 mM). The prepared concentrations of DA in Tris were 2 and 5 mg/mL. Cotton bulbs were treated with DA solution for 24 h at room temperature. Upon treatment, the modified bulbs were dried in vacuo at 65 °C for 24 h (Figure 1C). For control experiments, nonmodified substrates were used after being rinsed with acetone and dried at room temperature. An obvious difference in observation of the substrates, treated with and without DA, was the change of their color from white to dark gray (Figure S1C, Supporting Information). This change in color indicated that PDA was formed and coated the cellulose-based substrates.

In the next step, we prepared MOF-5 mother solution through a straightforward method, using the recipe reported by Fischer et al. Zinc nitrate hexahydrate and terephthalic acid were dissolved in DMF. The final step was the growth of MOF-5 crystals onto paper and cotton substrates (Figure S2A,B respectively). The substrates were immersed in MOF-5 mother solutions and kept for 3 days, at 65 °C (Figure 1D). To investigate the temperature effect on the crystal growth, another set of substrates was kept in MOF-5 mother solution at 105 °C. In both cases, the prepared samples were rinsed with DMF and dried in vacuo at 65 °C for 24 h, after which MOF-5 crystals could be observed on the substrates by the naked eyes (Figure 1E).

The effect of DA solution concentration on MOF-5 crystal growth and their binding to the substrate were investigated. The results showed that the pristine paper substrate (no DA) treated with MOF-5 mother solution (Figure 2A) was almost free of MOF-5 crystals, that is, very few crystals were formed on the paper surface. On the other hand, the DA-modified paper substrate was densely covered with MOF-5 crystals of more than 100 μm in size, as it can be seen by the SEM image in Figure 2B. The modification with DA and consequently formed PDA clearly improved compatibility of the paper substrates with MOF-5, which promoted the crystal growth. The hydrophilic character of cellulose was reduced by reaction between hydroxyl groups on the surface and catechol groups of DA. The formed PDA layer on the surface of substrates also became a nucleation site of MOF-5 crystals. Although DA contributed to the greater coverage of the paper surfaces, it was difficult, if not impossible, to grow MOF-5 crystals around fibers of the cellulose paper because of space limitation effects. The paper substrate had a dense structure where fibers were close to each other and crystals could not grow within the fibers. Consequently, MOF-5 crystals could easily fall off the paper substrates, regardless of the modification with DA. In contrast, the experiments performed with the cotton bulbs gave a very different morphology. The loose fibrous structure of the cotton bulbs proved to be a better choice for the nucleation and growth of MOF-5 crystals.

Unlike the crystals that grew only on fibers at the paper surface, the crystals grown on fibers of the cotton bulb (inside-out of the bulb) wrapped the fibers, forming a unique morphology with the crystals firmly attached to the fibers (Figure 2C). To the best of our knowledge, there has been no work reported on growing MOF crystals around cotton fibers. The MOF-5 crystals were strung by the cotton fibers as a MOF-5 "necklace" (Figure 2D). In both cases, the truncated cubic shape of the crystals was formed at 65 °C. This MOF-5 was made of dicarboxylic linkers and metal ions that together created a three-dimensional cubic unit cell. In general, the

Figure 1. Schematic representation illustrating the steps involved in the MOF-5@substrate preparation, taking cotton bulbs as an example. (A) Pristine cotton bulb, (B) treatment with DA solution, (C) modified cotton bulb (gray color represents a color change of the substrate upon treatment with DA), (D) treatment with MOF-5 mother solution, and (E) cotton bulb with MOF-5 crystals.

Figure 2. SEM images of MOF-5@substrate (temperature of the crystal growth was 65 °C). (A) MOF-5 crystals on the pristine paper (no DA), (B) MOF-5 crystals on the paper modified with DA, (C) MOF-5 growing around cotton fibers, and (D) "necklace" morphology (the scale bar is 100 μm).
crystal shape is related to its internal structure,\textsuperscript{44} it is a reflection of the unit cell shape, and thus the shape of MOF-5 crystals was expected to be cubic. All of the crystals formed had the same truncated cubic shape.

To examine how temperature affects the crystal shape, another set of experiments were performed, in which the substrates were kept in the mother solution for 3 day at 105 °C. As a substrate in this set of MOF-5 growth, only cotton bulbs were used because it was proven that the crystals could be firmly attached to the fibers. The crystal shape could be controlled by changing the synthesis conditions.\textsuperscript{45} In this case, an increase of temperature led to a change of MOF-5 crystal shape. It is evident in Figure 3 that the resulting MOF-5 crystals have the expected cubic shape. SEM analysis proved once again the importance of substrate modification with DA solution. The unmodified cotton bulbs (Figure 3A) were much less covered with MOF-5 crystals than the DA-modified substrates (Figure 3B–D). The formed PDA film on the surface of fibers provided more nucleation sites for MOF-5 crystals because of interactions of catechol groups of DA with metal ions of MOF-5. A better coverage of substrates with MOF-5 crystals was achieved. Moreover, as a result of having more nucleation sites on the surface of the fibers, smaller crystals were formed with a size of less than 100 μm. Once again, the “necklace” morphology was confirmed with the crystals wrapping cotton fibers, as it can be clearly seen from Figure 3D, with the red arrows pointing out to the fibers penetrating through the crystals.

Attenuated total reflection–FTIR spectra of pristine cotton, cotton modified in DA solution, and MOF-5@cotton structures obtained at 105 °C (Figure 4). PDA and cellulose in the structures have similar spectra. The bands between 3300 and 3400 cm\(^{-1}\) can be assigned to not only −OH group stretching modes but also to −NH from PDA. The presence of the quinine group in PDA can be confirmed with the peak at 1720 cm\(^{-1}\) that appeared in the case of DA-modified cotton with and without MOF-5 crystals. Furthermore, the spectrum for DA-modified cotton showed a broad and weak signal around 1600 cm\(^{-1}\), and it is assigned to −C═C stretching modes.\textsuperscript{36,47} However, in the case of MOF-5 grown around the fibers, the strong peaks around 1390 and 1600 cm\(^{-1}\) are assigned to the existence of organic linker, which is in the case of MOF-5 terephthalic acid.\textsuperscript{48}

XRD was used to confirm the crystal structure of pristine MOF-5 crystals and MOF-5 crystals grown on DA-modified and unmodified cotton at 105 °C. Unlike XRD patterns of MOF-5 truncated cubic crystals grown at 65 °C (Figure S3), Figure 5 shows a typical diffractogram of MOF-5 crystals as previously reported by Yaghi et al.\textsuperscript{38} All of the characteristic peaks were identified confirming the cubic shape of MOF-5 crystals observed in SEM analyses in Figure 5, as well as its crystallinity due to sharp diffraction peaks. Furthermore, the modification of cotton bulbs with DA did not affect the crystal structure of MOF-5, which could be observed by contrasting XRD patterns in Figure 5.

The pore properties of both MOF-5 and MOF-5@cotton samples were analyzed using nitrogen physisorption at 77 K.
Figure 6 shows adsorption and desorption isotherms of the pristine MOF-5 and MOF-5@cotton. The measurements showed type I isotherm for both samples with a characteristic sharp increase at the low relative pressure (Figure S4, Supporting Information). Even though N2 adsorption slightly decreased in the case of MOF-5@cotton, the sample kept high porosity. The specific areas are 658.04 m²/g for MOF-5 crystals and 611.71 m²/g for MOF-5@cotton structure.

MOF crystals have been studied for various environmental applications.49,50 Combined with cellulose fibers, those structures would have certain advantages because of their green nature and low cost. However, there must be a strong attachment of MOF crystals on the substrate. In this work, we demonstrated that it is possible to bind MOF-5 crystals and cellulose fibers. However, how strong MOF-5 crystals were attached to cellulose fibers could be questioned. We quantitatively determined their strength by exposing MOF-5@cotton samples to a constant air blow, 18 L/min, three times for 20 s, or until a constant mass was reached (Figure 7A). The mass of the MOF-5@cotton structure was measured before and after the air blow. The percentage of MOF-5 crystals remaining attached to the fibers was calculated using the equation given in the experimental part.

The fabricated MOF-5@cotton structure proved to be quite resistant to the air blow effect, and the “necklace” morphology increased the stability of the MOF crystals stringed on the fibers. Figure 7B compares the results for cotton substrates modified and unmodified with two different DA concentrations. The percentage of MOF-5 crystals remaining attached to the unmodified cotton substrates was 91.9 ± 1.1%. For the substrate treated with 2 mg/mL of DA solution, this number was 94.8 ± 0.6%, whereas for 5 mg/mL, it was 96 ± 1.1%, which clearly indicated that DA improved the attachment of MOF-5 to the cotton fibers.

The TGA curves of cotton, MOF-5, and MOF-5@cotton structures are shown in Figure 8. A major weight loss in the case of pure cotton occurred between 180 and 430 °C because of decomposition of cellulose as the main component of cotton. The thermogram for pristine MOF-5 revealed its typical degradation mechanism with two weight losses. The first weight loss (5.51%) occurred because of solvent evaporation, whereas the degradation of MOF started around 400 °C. Finally, for the MOF-5@cotton sample, the first weight loss could be attributed not only to the evaporation of solvent (DMF) which was used for the synthesis of MOF-5 but also to the evaporation of adsorbed moisture in cotton fibers. Every additional weight loss before 430 °C was attributed to the degradation of cotton fibers, which was consistent with the results for pure cotton. Decomposition of the framework caused the final weight loss, and it started after 430 °C.51−53 The amount of char formed during thermal degradation was used to quantitatively determine the amount of MOF-5 incorporated. The char yield of pure cellulose at 600 °C was 11.3%, whereas in the case of MOF-5@cotton structures, the
number increased to 35.7%. Thus, the structures had 24.4% MOF-5 by mass.

**CONCLUSIONS**

In summary, a facile method to attach MOF-5 crystals to cellulose-based fibers and to fabricate stable morphologies is demonstrated. Paper and cotton fibers have been used in the experiments. In both substrates, DA was used as a surface modification agent, which promoted the growth of crystals. The surface was modified by simply immersing substrates in a DA solution. An important difference between the two substrates was in the way of crystals growth. Because of the dense structure of the paper, MOF-5 crystals could grow only on the surface of the substrate. In contrast, in the case of cotton substrates, the crystals grew throughout the whole body of a cotton bulb and were firmly attached to the fibers. MOF-5 crystals could grow around the surface of individual cellulose fibers, generating a stable “necklace” morphology. In this way, MOF-5 crystals were firmly attached to the fibers, which are desired in many applications. Apart from the structure of the used substrates, surface modification of the substrates with DA played a major role in the crystal growth. No matter what kind of substrate was used, all of the experiments showed that after DA modification, more crystals grew on the surface. The obtained MOF-5/cotton structure showed excellent stability when they were exposed to air blow as an external influence because of the strong attachment of the crystals and fibers.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02332.

Pictures of substrates before and after modification with DA, SEM images, XRD patterns, N2 sorption isotherms for low relative pressure, and table with experimental data (PDF)

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**Notes**

The authors declare no competing financial interest.

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