Highly Adsorptive, MOF-Functionalized Nonwoven Fiber Mats for Hazardous Gas Capture Enabled by Atomic Layer Deposition

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While metal-organic frameworks (MOFs) show great potential for gas adsorption and storage, their powder form limits deployment opportunities. Integration of MOFs on polymeric fibrous scaffolds will enable new applications in gas adsorption, membrane separation, catalysis, and toxic gas sensing. Here, we demonstrate a new synthesis route for growing MOFs on fibrous materials that achieves high MOF loadings, large surface areas and high adsorptive capacities. We find that a nanoscale coating of Al2O3 formed by atomic layer deposition (ALD) on the surface of nonwoven fiber mats facilitates nucleation of MOFs on the fibers throughout the mat. Functionality of metal-organic frameworks; fibers; atomic layer deposition; adsorption; polymer

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Abstract

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ABSTRACT

While metal-organic frameworks (MOFs) show great potential for gas adsorption and storage, their powder form limits deployment opportunities. Integration of MOFs on polymeric fibrous scaffolds will enable new applications in gas adsorption, membrane separation, catalysis, and toxic gas sensing. Here, we demonstrate a new synthesis route for growing MOFs on fibrous materials that achieves high MOF loadings, large surface areas and high adsorptive capacities. We find that a nanoscale coating of Al2O3 formed by atomic layer deposition (ALD) on the surface of nonwoven fiber mats facilitates nucleation of MOFs on the fibers throughout the mat. Functionality of MOFs is fully maintained after integration, and MOF crystals are well attached to the fibers. Breakthrough tests for HKUST-1 MOFs [Cu3(BTC)2] on ALD-coated polypropylene fibers reveal NH3 dynamic loadings up to 5.93 ± 0.20 mol/kg (MOF+fiber). Most importantly, this synthetic approach is generally applicable to a wide range of polymer fibers (e.g., PP, PET, cotton) and MOFs (e.g., HKUST-1, MOF-74, and UiO-66).
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1. Introduction

Hazardous gas adsorption has important implications for human health, industrial safety, and environmental protection. Traditional adsorbents including zeolites, activated carbons, and silica gels can abate hazardous gas emission, but there is growing need for materials with higher capacity and better selectivity, while simultaneously providing multifunctional performance (i.e., capture and alert capability). Metal organic frameworks (MOFs), composed of metal-containing units and organic bridging ligands, exhibit high surface area, good thermal stability, and have significant synthetic versatility, enabling structures with tunable pore sizes and adjustable internal functionality. MOF synthesis usually follows wet solvothermal batch methods, producing powders that require further manipulation and handling, and may be difficult to implement for some applications. Integration of MOFs on polymeric fibrous scaffolds could simplify handling, regeneration and deployment. It could also broaden practical use for filtration, separations, catalysis, sensing and other applications.

Several methods have been used to integrate MOF crystals on polymer fiber matrices, including encapsulation in electrospun fibers and immobilization on fibers via solvothermal synthesis, layer-by-layer method or microwave irradiation. Unfortunately, these methods generally lead to small MOF loading fractions, poor MOF crystal quality, and low Brunauer–Emmett–Teller (BET) surface areas—limiting applicability. For example, Kuesgens et al. grew HKUST-1 crystals on pulp fibers using direct solvothermal synthesis and found the surface area to be limited to 314 m$^2$/g. Wu et al. encapsulated HKUST-1 MOFs in electrospun fibers, and also only achieved a value of 311 m$^2$/g before repeating secondary growth. These values are at least 2 times lower than pure HKUST-1 powders grown solvothermally (692–1460 m$^2$/g). To date, no prior report has assessed the hazardous gas adsorption capacity for MOF-functionalized fibers.

In this work, we introduce a novel synthesis route for achieving high-quality MOF growth on polymer fibers. We use atomic layer deposition (ALD) to form a nanoscale-thick conformal coating on polymer fibers for nucleation of solvothermally grown MOF crystals. This approach is first demonstrated...
with HKUST-1 on ALD-Al₂O₃-coated polypropylene fibers. MOF nucleation on fibers is compared between untreated and ALD-coated substrates, while the quality of MOFs is benchmarked to pure powders. Hazardous gas (ammonia) adsorption capacity was characterized via breakthrough tests. We also show the general applicability of this technique to a wide range of polymer fibers (e.g., PP, PET, and cotton) and MOFs (e.g., HKUST-1, MOF-74, and UiO-66).

2. Results and Discussion

Figure 1a–c illustrates the process scheme for the case of HKUST-1 grown on ALD-Al₂O₃-coated polypropylene fibers. Polypropylene (PP) fibers (Figure 1a) in a nonwoven mat were conformally coated with ALD Al₂O₃ (200 cycles at 60 °C), creating a core/shell “PP/ALD” structure with hydroxyl surface termination (Figure 1b). This ALD coating can change wettability of fibers for thorough permeation of solvothermal solvents (Figure S1), and improve reactivity of the fiber surfaces for MOF nucleation. Depending on the the deposition conditions, ALD coatings can increase surface roughness, which may also promote MOF nucleation. HKUST-1 [Cu₃(BTC)₂] was grown onto ALD-coated fibers solvothermally using copper nitrate trihydrate and 1,3,5-benzenetricarboxylic (BTC) acid as precursors in a water/ethanol (50/50 vol%) solution (Figure 1c). Fiber mats were placed in a Teflon-lined pressure vessel and immersed in the liquid reagents which readily wetted the coated fiber substrates. The vessel was sealed, and MOF growth proceeded under the optimal condition at 120 °C for 20 hours (optimization shown in the Supporting Information). Figure 1d shows HKUST-1 crystals grown densely and conformally on an ALD-coated PP fibers. This resulting MOF-functionalized fiber mat is referred to as “MOF-PP/ALD”.

In Figure 2 we compare the growth of HKUST-1 on untreated and ALD-coated PP fiber mats. MOFs grown on the untreated PP fibers (referred to as “MOF-PP”) show macroscopic non-uniformity and appear to have nucleated homogeneously (i.e. in solution) throughout the fiber matrix (Figure 2a). When coated with ALD Al₂O₃, the fiber mats show uniform MOF coverage indicative of heterogeneous nucleation on the fiber surface (Figure 2b). X-ray diffraction data in Figure 2c confirms HKUST-1 crystal formation for both structures.

Figure 2d shows the percent mass increase after MOF growth on untreated and ALD-coated PP fiber substrates. Mass increase percentage (Δm/m₀) is 336 ± 38% for PP/ALD, and 228 ± 83% for untreated PP respectively. The results show that the ALD treatment enhances both the amount and uniformity of MOF growth. Normalizing the MOF mass loading per unit substrate external surface area, we find Δm = 14.78 mg/cm² on PP/ALD to be 54% larger than on untreated PP (Δm = 9.61 mg/cm²). Mass gain is also more reproducible on the ALD-Al₂O₃-coated fiber mats, as indicated by the boxplot's interquartile range (IQR) = 69% for PP/ALD vs 145% for untreated PP. Figure 2e shows results from N₂ isotherms and Brunauer–Emmett–Teller (BET) surface area analysis. The MOF-PP/ALD fiber mats show an average surface area (SA_MOF+fiber) of 695 ± 76 m²/g (MOF+fiber), which is ~60% higher than that of MOF-PP fibers (434 ± 198 m²/g (MOF+fiber)). This is consistent with the higher MOF mass gain on PP/ALD substrates. The surface area of MOF-PP/ALD fiber mat is also >2x larger than prior reports for MOFs on fibers.[8,9]

We compare the quality of the MOFs nucleated on fibers to that of pure powders. The surface area of the MOF component in the MOF-fiber material (SA_MOF) is given by:

\[ \text{SA}_{\text{MOF}} = \text{SA}_{\text{MOF+fiber}} - \text{SA}_{\text{fiber}} \]
Synthesized high quality HKUST-1 crystals,[13–17] and essentially our lab shows MOF-PP/ALD. HKUST-1 powders similarly produced in our lab (7.23 mol/kg) and consistent with the reported values.[16] The similar values for the NH3 dynamic loadings indicate the fore strength of sorption. Figure 3 shows that the breakthrough time for MOF-PP/ALD is up to 58% longer than MOF-PP. Control PP mats without MOFs exhibit immediate breakthrough. From the breakthrough results, the ammonia dynamic loadings are 5.28 ± 0.40 mol/NH3/kg (MOF+fiber) for MOF-PP/ALD and 4.57 ± 0.27 mol/NH3/kg (MOF+fiber) for MOFs on untreated fibers. Calculation results show the NH3 dynamic loading for the MOF component in MOF-PP/ALD fiber mats is 6.9 ± 0.5 mol/kB(MOF), similar to that for pure MOF powders synthesized in our lab (7.23 mol/kg) and consistent with the reported values.[16] The similar values for the NH3 dynamic loadings indicate the adsorption takes place in the bulk MOF crystals on the fibers.

In addition to ammonia, we also evaluated the performance of MOF-functionalized fibers for H2S removal. Compared with H2S adsorption by MOF powders,[22] the H2S dynamic loading for our MOF-fiber mats show good H2S loading capacity, demonstrating that the MOF-fiber constructs have functional capacity to adsorb hazardous gases beyond NH3.
We investigated the effect of ALD coating thickness, and find that MOF crystal size distribution and extent of growth into the fiber mat can be systematically changed with ALD thickness. Figure S7 shows top-view and cross-sectional SEM images of MOFs grown on PP fiber mats with 0, 50, 100, 200 and 500 cycles of Al$_2$O$_3$ ALD (roughly correspond to 0 nm, 6 nm, 12 nm, 24 nm, and 60 nm of Al$_2$O$_3$ respectively). MOF crystal size distributions analyzed from both top-view and cross-sectional SEM are plotted in Figure 4. Crystal size distributions were analyzed based on 50 measured crystal sizes on each corresponding SEM image. Mass increase of the fiber mats after MOF integration. BET surface area of the MOF-functionalized fiber mats and the surface area of MOF component in the fiber mats. NH$_3$ dynamic loading and NH$_3$ breakthrough time on MOF-functionalized fiber mats.

Figure 4. MOF-fiber mats with different ALD coating thicknesses. a) MOF crystal size distribution on the top surface. b) MOF crystal size distribution on the cross-section. c) Mass increase of the fiber mats after MOF integration. d) BET surface area of the MOF-functionalized fiber mats and the surface area of MOF component in the fiber mats. e) NH$_3$ dynamic loading on MOF-functionalized fiber mats. f) NH$_3$ breakthrough time on MOF-functionalized fiber mats.

We investigated the effect of ALD coating thickness, and find that MOF crystal size distribution and extent of growth into the fiber mat can be systematically changed with ALD thickness. Figure S7 shows top-view and cross-sectional SEM images of MOFs grown on PP fiber mats with 0, 50, 100, 200 and 500 cycles of Al$_2$O$_3$ ALD (roughly correspond to 0 nm, 6 nm, 12 nm, 24 nm, and 60 nm of Al$_2$O$_3$ respectively). MOF crystal size distributions analyzed from both top-view and cross-sectional SEM are plotted in Figure 4a,b and Figure S8. On the top layer of fibers (Figure 4a), MOF crystal sizes decrease from 24 ± 8 µm to 9 ± 3µm with narrowing distributions, as ALD coating thickness increases from 0 to 500 cycles. Similar trend is also found in the cross-sections of the MOF-fiber mats with different ALD thickness (Figure 4b). The amount of MOFs grown into the fiber mat rises as the number of ALD cycles increases to ~100 cycles (Figure S7), leading to the similar trends of MOF loading and BET surface area shown in Figure 4c,d. The NH$_3$ breakthrough tests, summarized in Figure 4e,f show that NH$_3$ adsorption capacity correlates closely with BET surface area, regardless of the different crystal size distribution.

In addition to ALD coating thickness, we also tested the effect of ALD chemistry. ALD ZnO and TiO$_2$ coated PP fiber mats were functionalized with HKUST-1 MOFs, and the results shown in Figure 5a,b are compared with MOFs on ALD Al$_2$O$_3$ coated PP. We find that MOF crystals on ZnO are small, whereas those on TiO$_2$ are generally larger than the MOFs on Al$_2$O$_3$. This indicates that MOF crystal morphology can be adjusted using different ALD coatings. We hypothesize that the wettability, surface roughness and isoelectric points (IEP) of different ALD coatings may all affect the nucleation of MOF crystals. The mechanism of MOF nucleation on different ALD materials is currently under investigation. The resulting mass increase, BET surface area, and NH$_3$ dynamic loading of these MOF-fiber materials are shown in Table 1. The NH$_3$ dynamic loading of MOF-PP/ALD(ZnO) (5.93 ± 0.20 mol/kg$_{\text{MOF-fiber}}$) represents the best adsorptive capacity of MOF-fiber materials so far. MOF-PP/ALD(TiO$_2$) fiber mats exhibit less adsorptive capacity than MOF-PP/ALD(Al$_2$O$_3$) and MOF-PP/ALD(ZnO). This may be explained with the low surface area of the MOF component in this material (~670 m$^2$/g$_{\text{MOF}}$), which may suggest the formation of impurities or the necessity of careful post-synthesis activation.

Finally, we demonstrate our approach can readily extend to various fibers and MOFs. Figure 5d,e and Table 1 show HKUST-1 growth on ALD Al$_2$O$_3$ coated polyethylene terephthalate (PBT) and cotton fiber mats. Cotton cellulose has hydroxyl groups that promote ALD Al$_2$O$_3$ growth, but our results show HKUST-1 mass uptake on ALD treated cotton is less than on other ALD-modified fibers. Initial MOF loading on cotton/ALD fiber mats is comparable with that on PP/ALD and PBT/ALD fiber mats (Table 1), but MOFs grown on cotton/ALD fibers tend to show poor adhesion. We hypothesize that the ALD layer enhances nucleation, but nucleation attachment is less robust, possibly resulting from the smooth surface after ALD treatment. This is supported by Figures 5(e) and S9 showing MOF growth in the crevasses on the cotton fibers. The details of MOF nucleation on different surfaces are currently under investigation. Preliminary examples of Zn-MOF-74, Mg-MOF-74 and UiO-66 on ALD-coated...
nonwoven polymer fibrous substrates are given in Figure S10. Integration of these MOFs on nonwoven fiber mats could potentially broaden the practical use for filtration, separations, catalysis, sensing and other applications.

3. Conclusion

In conclusion, we have demonstrated a new synthesis route using ALD coatings to facilitate MOF nucleation on fibrous materials. Al₂O₃ ALD coatings improve the MOF macroscopic uniformity and its coverage on fiber surfaces. MOF-PP/ALD fiber mats exhibit higher BET surface areas and higher NH₃ dynamic loading capacities than MOFs grown on untreated PP fiber mats. These results significantly advance capability for functional MOFs on fiber substrates. Variations in ALD surface modification are found to affect MOF crystallite size and distribution but ultimately have minimal effect on ammonia removal performance. The process scheme presented here provides a robust platform technology for integrating various MOFs onto polymeric fibrous substrates for the use in human protection, industrial safety, and environmental preservation.

4. Experimental Section

Nonwoven polypropylene, polybutylene terephthalate and cotton fiber mats were used as received [23] (NCRC, NCSU) and coated with 200 cycles of ALD Al₂O₃ at 60 °C. HKUST-1 MOFs were synthesized using Cu(NO₃)₂·3H₂O (0.87 g, Aldrich, 99%) in ethanol (12 mL) and 1,3,5-benzene-tricarboxylic acid (0.42 g, Acros Organics, 98%) in deionized water (12 mL) as precursor solutions. Fiber mats were transferred in a Teflon-lined pressure vessel with the mixed precursor solution. MOF growth proceeded in the sealed vessel at 120 °C for 20 hours. After synthesis, the fiber mats were rinsed in ethanol, and dried in vacuum over at 120 °C for 12 hours. Scanning electron microscope (SEM) images were taken with an FEI Phenom bench-top SEM. Samples were sputter-coated with 5–10 nm of Au-Pd before imaging.

X-ray diffraction (XRD) was measured with a Rigaku SmartLab X-ray diffraction tool (CuKα X-ray source). BET surface areas were measured using a Quantachrome Autosorb-1C surface area and pore size analyzer. Samples were degassed at 120 °C for 12 h before measurement. BET surface areas were analyzed based on N₂ isotherm adsorption within the P/P₀ range of 0.05–0.31. Rapid micro-breakthrough analysis equipment (shown in Figure S6) was used to measure NH₃ adsorption (details and calculations are shown in the Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge funding from ECBC through grant #W911SR-07-C-0075 and from the Joint Science and Technology Office through Army Research Office grant #W911NF-13-1-0173.

Received: January 18, 2014
Revised: February 22, 2014
Published online: March 20, 2014

Table 1. Characterization of MOF-functionalized fiber mats: fiber mass gain (mg/cm²) after MOF integration, BET surface area (m²/g) of MOF-fiber materials and NH₃ dynamic loading (mol/kg) calculated from breakthrough curves.

<table>
<thead>
<tr>
<th>MOF-fiber Composites</th>
<th>Fiber Mass Gain (mg/cm²)</th>
<th>Total BET Surface Area (m²/g)</th>
<th>NH₃ Dynamic Loading (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-PP/ALD(ZnO)</td>
<td>25.21</td>
<td>764 ± 11</td>
<td>5.93 ± 0.20</td>
</tr>
<tr>
<td>MOF-PP/ALD(TiO₂)</td>
<td>12.85</td>
<td>509 ± 151</td>
<td>2.75 ± 0.02</td>
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<tr>
<td>MOF-PP/ALD(Al₂O₃)</td>
<td>14.78</td>
<td>694 ± 76</td>
<td>5.28 ± 0.40</td>
</tr>
<tr>
<td>MOF-PBT/ALD(Al₂O₃)</td>
<td>17.17</td>
<td>485</td>
<td>2.52 ± 0.23</td>
</tr>
<tr>
<td>MOF-Cotton/ALD(Al₂O₃)</td>
<td>13.59</td>
<td>121</td>
<td>1.70 ± 1.14</td>
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</table>