

Scalable and Template-Free Aqueous Synthesis of Zirconium-Based Metal–Organic Framework Coating on Textile Fiber

Kaikai Ma,^{†,‡®} Timur Islamoglu,^{‡®} Zhijie Chen,^{‡®} Peng Li,^{‡®} Megan C. Wasson,^{‡®} Yongwei Chen,[‡] Yuanfeng Wang,[†] Gregory W. Peterson,^{⊥®} John H. Xin,^{*,†} and Omar K. Farha^{*,‡,§®}

[†]Research Centre for Smart Wearable Technology, Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Kowloon 999077, Hong Kong SAR

[‡]Department of Chemistry and International Institute of Nanotechnology and [§]Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

¹U.S. Army Combat Capabilities Development Command Chemical Biological Center, 8198 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010, United States

Supporting Information

ABSTRACT: Organophosphonate-based nerve agents, such as VX, Sarin (GB), and Soman (GD), are among the most toxic chemicals to humankind. Recently, we have shown that Zr-based metal-organic frameworks (Zr-MOFs) can effectively catalyze the hydrolysis of these toxic chemicals for diminishing their toxicity. On the other hand, utilizing these materials in powder form is not practical, and developing scalable and economical processes for integrating these materials onto fibers is crucial for protective gear. Herein, we report a scalable, template-free, and aqueous solution-based synthesis strategy for the production of Zr-MOF-coated textiles. Among all MOF/fiber composites reported to date, the MOF-808/polyester fibers exhibit the highest rates of nerve agent hydrolysis. Moreover, such highly porous fiber composites display significantly higher protection time compared to that of its parent fabric for a mustard gas simulant, 2-chloroethyl ethyl sulfide (CEES). A decreased diffusion rate of toxic chemicals through the MOF layer can provide time needed for the destruction of the harmful species.



INTRODUCTION

Nerve agents, extremely toxic organophosphonate-based volatile chemicals, covalently bind to the active site of acetylcholinesterase (AChE), resulting in the loss of muscular control in the body and death by asphyxiation.¹ Recent reports of the use of toxic phosphonate-based nerve agents have motivated researchers to develop new materials for fast decontamination.²⁻⁴ To this end, metal-organic frameworks (MOFs), composed of a metal node and organic linkers, have emerged as highly effective and versatile heterogeneous catalyst candidates due to their tunable structure.^{5–10}

We and others have recently demonstrated that Zr₆-based MOFs can efficiently catalyze the hydrolysis of nerve agents as well as their simulants at ambient temperature.¹¹⁻¹⁵ Rational tuning of the pore aperture,¹⁶ particle size,¹⁷ linker functionalization,^{18,19} and zirconium node connectivity²⁰ have been demonstrated to be crucial for high catalyst activity. We have reported that MOF-808, a Zr-based MOF constructed from a 6-connected node and trimesic acid, can destroy dimethyl-4-nitrophenyl phosphate (DMNP), a nerve agent simulant, with a half-life of less than 1 min using <3 mol % catalyst.²⁰ Similarly, we have also observed that UiO-66-NH₂, another Zr-based MOF with up to a 12-connected node (when no defects present) and 2-aminoterephthalic acid,

showed unprecedented catalytic activity toward the hydrolysis of DMNP.¹⁹ However, the vast majority of these studies were performed using MOF powders; practical applications for the employment of these materials as protective layers requires integrating these materials on a fabric.

Flexible and air-permeable textiles have been suggested as inexpensive and readily accessible supports for MOFs. Several methods have been developed for the functionalization of textiles by Zr-MOFs.²¹⁻³¹ For example, Parsons and Peterson et al. have reported the functionalization of nanofibers or commercial nonwoven textile substrates with a metal oxide layer using atomic layer deposition (ALD) to serve as nucleation sites for Zr-MOF growth on the fiber.^{21,26} Navarro et al. have integrated Zr-MOF onto nanofibers with electrospinning to form a fibrous mat.³¹ Despite high catalytic efficacy for hydrolysis of the agents by these MOF/fiber composites, the scalability of utilizing such methods that require expensive equipment is challenging. Thus, a straightforward, complementary, and extendible methodology of installing MOF coatings on supports is essential and still sought after for practical and bulk applications.

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In this work, we developed a facile, scalable, and templatefree aqueous solution-based synthesis approach to yield Zr-MOF-coated textiles without the need of prior pretreatment that is applicable across different fiber surfaces (Figure 1).



Figure 1. Schematic illustration of template-free aqueous synthesis of Zr-MOF coating on fiber.

Such MOF-coated textiles exhibited high catalytic activity for the hydrolysis of a highly toxic nerve agent, GD, and its commonly used simulant, DMNP. Additionally, the developed composites provided a protection time significantly higher than that of the parent fabric for CEES, a simulant for the blister agent mustard sulfur. By slowing down CEES diffusion, the MOF layer afforded the necessary contact time for the destruction of the toxic chemicals (Scheme 1). We envision that the advantageous method developed herein can realize the practical application of MOFs as protective layers.

RESULTS AND DISCUSSION

To study the growth process of Zr-MOFs on fiber, MOF-808 was selected as a model due to the framework's robust chemical stability³² and high catalytic activity for the hydrolysis of GD and DMNP.^{20,33} To the best of our knowledge, this is the first study investigating the coating of MOF-808 on a fibrous surface. Briefly, the MOF-coated fiber was obtained by heating the textile in an aqueous solution containing the MOF precursors. Polyester fabrics (4 pieces, $4 \text{ cm} \times 4 \text{ cm}$), trimesic acid (2 mmol, 0.42 g), and ZrOCl₂·8H₂O (4.5 mmol, 1.45 g) were added to a mixture of deionized water (20 mL) and trifluoroacetic acid μ (TFA) (10 mL), which was sonicated for 30 min and heated in an oven at 100 °C for 2 h. Systematic characterizations indicated that MOF-808 growth on fiber is via a three-stage process: (1) aggregation of an amorphous coordination polymer on the fibrous surface (0-10 min), (2) formation of MOF-808 nucleation sites (10-20 min), and (3) growth into a continuous MOF coating (>30 min). After 10 min of reaction, a very thin gel layer was observed on the fiber's surface in the scanning electron microscopy (SEM) images (Figure 2b). It is inferred that this period served as a

Scheme 1. Representative Illustration of MOF-Fiber Composites for the 2-Chloroethyl Ethyl Sulfide (CEES) Capture and Soman (GD) Detoxification



pseudotemplating period during which reagents were adsorbed on the surface of the fiber and quickly formed an amorphous coordination polymer. The noncrystalline nature of the layer was verified by powder X-ray diffraction (PXRD) measurements, and the presence of Zr in the gel coating was confirmed by energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) (Table S1). Proton nuclear magnetic resonance spectroscopy (¹H NMR) of the digested sample indicated the presence of the BTC linker in the gel coating (Figure S1). After 20 min, the fiber's surface transitioned from a template site for reagent coverage to a nucleation site that formed small octahedral MOF particle seeds (Figure 2c). The newly formed seeds were identified as MOF-808 by PXRD (Figure 3a), and the increased porosity of the coating was evidenced through N2 sorption isotherm studies (Figure 3b,c).³² During the subsequent reaction time, the seeding MOF-808 particles grew larger and interconnected into a continuous layer on the fiber (Figure 2b-f). After 2 h reaction, the fiber's surface was thoroughly covered by intergrown MOF-808 particles. The characteristic elements of the MOF-808 coating were confirmed by EDS mapping analysis (Figure S2). SEM images of the fibers' edges showed a MOF layer thickness of approximately 1 μ m (Figure S3).

By controlling the reaction time during the final growth stage, the mass loading of the MOF-808 on fiber was modulated. Zirconium elemental analysis by ICP-OES revealed that mass loadings ranged from 6.5 to 22% when the reaction time was prolonged from 0.5 to 2 h (Table S1). Importantly, these particles were intact even after vigorous washing, attributed to robust intercrystallite interactions as well as strong binding between crystallites and fiber. Nitrogen adsorption at 77 K confirmed the formation of the highly porous MOF (Figure 3b and Figure S4); Brunauer–Emmett–Teller (BET) surface area of the composite material increased from 2 to 480 m²/g after 2 h of MOF-808 growth (Figure 3c and Table S1). Importantly, the normalized BET surface area of the MOF-808 coating is about 2200 m²/g after 0.5 h, in agreement with previously reported values of MOF-808



Figure 2. SEM images illustrating the PET fiber surface change. Pristine PET fiber (a), after reaction of 10 min (b), 20 min (c), 30 min (d), 60 min (e), and 120 min (f). All scale bars are 5 μ m.



Figure 3. (a) PXRD patterns, (b) N_2 sorption isotherms, and (c) BET surface areas of composite materials.

powders^{20,32} to indicate the high quality of MOF coating obtained.

When MOF-fiber composites are prepared using solvo/ hydrothermal methods, the yield of the resulting coating can indicate how much MOF formed on the fiber as opposed to free powder in solution. Our protocol showed negligible free MOF particles in solution after the reaction, which implies that MOF-808 nucleation selectively started on the fiber's surface. This can be attributed to a preconcentration effect because the fiber provides an interface for precursor adsorption during the first growth stage, eliminating the necessity of the surface's pretreatment prior to MOF growth.³⁴ Following the reaction, the precursor mixture was reused in a new synthesis process, highlighting potential for efficient mass production. A coating with similar morphology and slightly lower loading (18%) was obtained from this reused precursor mixture (Figure S5). Previous solvothermal methods of MOF-coated fibers yielded 5-20 times more free MOF particles in reaction media compared with the amount that coated onto the fiber's surface.²¹ Therefore, our highly efficient method reported here could lower the cost of production and minimize the environmental impact.

The use of TFA as a modulator in the synthesis played a critical role for creating a uniform surface coverage of fibers. Notably, when other organic acids such as acetic acid and formic acid were used as modulators, aggregated islands of particles were formed on the fiber surface instead of uniform surface coverage achieved by TFA (Figure S6). Moreover, crystallization generally occurred in the solvent rather than on the fiber surface when using other modulators. We hypothesized that the higher acidity of TFA slowed down the crystallization to yield a continuous coating.³⁵ Additionally, TFA volume below 29% prevented total coverage of fiber by the MOF coating, emphasizing the importance of modulator concentration (Figure S7). Though both 33 and 50% TFA yielded complete surface coverage, safety and cost considerations render 33% TFA as the selected condition for the reliable growth of MOF-808 on fiber.

To ensure that our developed MOF on fiber synthesis is amenable to a variety of final applications, we probed the efficacy of the synthesis with different fibers. Therefore, we also coated polyacrylonitrile (PAN, 500 nm) nanofiber and polypropylene (PP, 2 μ m) microfiber in addition to PET fiber. The dense and continuous MOF coating on these fiber substrates was observed via SEM imaging, whereas the high-quality MOF-808 coating was confirmed by PXRD and N₂ sorption of the composite (Figure S8). Importantly, the aqueous synthesis method developed here offers unique applicability to some polymeric fibers, which are soluble in polar organic solvents such as dimethylformamide (DMF). For example, PAN nanofiber dissolved within 5 min in a typical MOF-808 synthetic procedure using DMF as a solvent (Figure S9).

In order to demonstrate the compatibility of the current method with other MOF systems, we coated PET fiber with UiO-66-NH₂, another Zr-based MOF that previously achieved exceptionally high hydrolysis rates of nerve agents. After 4 h reaction, a coating with continuous morphology was observed on the UiO-66-NH₂/PET composite with SEM imaging, and PXRD indicated good agreement of the composite material crystallinity with simulated UiO-66-NH₂ (Figure 4). PXRD patterns suggested the presence of missing cluster defects that form an 8-connected reotopology. Such defects have been shown to increase catalytic activity by increasing substrate diffusion inside the crystals as well as exposing more Zr active sites 36,37 High porosity of the UiO-66-NH₂ coatings was verified with a N₂ sorption test (Figure 4d). An observed color change of the white pristine fabric to a pale yellow after reaction completion (Figure S10) was rationalized as a visual indication of UiO-66-NH2 deposition. ICP-OES determined the MOF mass loading on the fiber as 8 and 27% after 1 and 4 h reactions, respectively, and the thickness of the coating after a 4 h reaction is about 1.5 μ m (Figure S11).

The as-synthesized Zr-MOF coating contained coordinated organic acid modulators on the Zr node, confirmed by the NMR spectra of the digested samples. After the composite material was treated with diluted HCl in acetone solution (0.12 M), the peak corresponding to trifluoroacetic acid nearly vanished, revealing the successful removal of the residual modulator bound to the Zr cluster (Figures S12 and S13).³⁸ The crystallinity and porosity of the MOF coating was still retained after the treatment.

In addition to illustrating the generality of our current protocol by varying the identity of fibers and/or MOFs, we probed the scalability through a larger proof of concept synthesis. A piece of PET fabric (about 10 cm \times 120 cm) was coated with MOF-808, and the representative larger composite featured surface morphology and loading (20%) comparable to that previously obtained with smaller pieces of fabrics (Figure 5). The BET area of the MOF-808 layer coated on fiber was approximately 2200 m²/g, demonstrating the high porosity of MOF-808 coating obtained from the scaled-up synthesis.

After the high quality of Zr-MOF coatings on the PET fiber was confirmed, the catalytic hydrolysis of the nerve agent simulant DMNP was first tested in aqueous *N*-ethylmorpholine buffer (0.45 M, pH 10) media. Reaction conversion was monitored by ³¹P NMR spectroscopy by comparing the integration of the ³¹P peak for DMNP ($\delta = -4.4$ ppm) and that of the hydrolysis product, dimethyl phosphate anion ($\delta = 2.8$ ppm).²⁰ MOF-808/PET composites with MOF loadings of 6.5, 12, and 22%, denoted as MOF-808_{6.5%}/PET, MOF-808_{12%}/PET, and MOF-808_{22%}/PET, were probed for their catalytic activity, and the same amount of MOF-808 was used



Figure 4. SEM images of UIO-66-NH₂ coating on fiber after reaction of 1 h (a) and 4 h (b). Scale bars: 5 μ m. PXRD patterns (c) and N₂ sorption isotherms (d) of related samples.

in all catalytic tests (normalized based on Zr amount in the composite).

The corresponding initial half-lives for MOF-808_{6.5%}/PET, MOF-808_{12%}/PET, and MOF-808_{22%}/PET are <0.5, <1, and 3 min, respectively. Total conversion of DMNP is achieved after approximately 1.5 min for MOF-808_{6.5%}/PET, 5 min for MOF-808_{12%}/PET, and 10 min for MOF-808_{22%}/PET (Figure 6a and Figures S14–S16 and Table S2). Significantly enhanced



Figure 5. Optical photograph (a), SEM image (b), PXRD patterns (c), and N₂ sorption isotherm (d) of samples from scale-up PET fabric coating (about 10 cm \times 120 cm). Scale bar: 10 μ m.

hydrolysis rates with lower MOF loading compared to higher loadings was attributed to the accessibility of Zr_6 node active sites (1.5 μ mol in total).³⁹ We found that the reaction immediately stopped after the removal of the MOF/fiber composite from the reaction mixture, confirming the heterogeneous nature of the reaction (Figure 6b and Figure S17). After catalysis, SEM and PXRD indicated the adhesion of the MOF layer to the polyester fiber, and its catalytic activity was fully recovered after being washed with water (Figures S18



Figure 6. (a) Catalytic reaction of DMNP and GD hydrolysis. Kinetic profiles for hydrolysis of (b) DMNP and (c) GD using MOF-coated fibers as the catalyst: 1.5 μ mol of catalyst; 25 μ mol of simulant.

and S19). Moreover, the catalytic activity remained unchanged after 6 months of air exposure or 24 h of stirring (400 rpm) in water (Figure S20), demonstrating the excellent durability of the composite material. Additionally, we performed the reaction with UiO-66-NH₂/PET, with a MOF loading of 8%, which demonstrated a half-life of 5 min (Figure 6b and Figure S21). The faster reaction rate in the case of the MOF-808/ fiber was attributed to the lower connectivity on the Zr node (6-connected), which affords more open Zr sites available for the reaction, in agreement with our previous findings with free MOF.²⁰ As a control, the background reaction of DMNP hydrolysis with fiber only in the buffer solution showed negligible conversion over 20 min (Figure 6b and Figure S22).

Encouraged by the high catalytic activity of the MOF/fiber composite for hydrolysis of DMNP, we explored the catalytic activity of these composite materials for the hydrolysis of an actual nerve agent, GD (Figure 6a and Table S2). MOF-808/ fiber and UiO-66-NH₂/fiber composites efficiently degraded GD with respective half-lives of 2 and 8 min, similar to those achieved by powders (Figure 6b). Remarkably, our MOF-808/ fiber composite exhibited the highest catalytic activity for DMNP and GD hydrolysis as compared with that of the previously reported composite materials (Table S2).

The diffusion of reactants and products through porous materials is an integral component of their catalytic activity.⁴⁰⁻⁴² Ideally, high retention time (contact time) of an agent is desired to facilitate ample time for the agent to react with the catalyst. In order to demonstrate the barrier properties of our MOF coating layer, we measured the permeation rates of our composite materials using CEES as an analyte in accordance with ASTM F739-12, where 300 mg/m³ CEES was fed across a fabric swatch (1 in. in diameter) at a flow rate of 300 mL min⁻¹. The exiting air streams were monitored using an Agilent 6890 gas chromatograph equipped with a flame ionization detector. The results indicated that full permeation of CEES through the uncoated PET sample occurred immediately, suggesting minimal blocking/adsorption capabilities from the pristine PET fabric (Figure 7).



Figure 7. CEES permeation through MOF/fiber materials.

According to ASTM F739-12 standard, protective clothing has effective protection function when the permeation rate of chemicals is under 0.1 μ g min⁻¹ cm⁻².⁴³ Strikingly, UiO-66-NH₂/PET (loading 27%) and MOF-808/PET (loading 22%) showed negligible (<0.1 μ g min⁻¹ cm⁻²) permeation over a considerably long time. According to ASTM F739-12 standard, UiO-66-NH₂/PET and MOF-808/PET had effective protection over 50 and 126 min, respectively.

CONCLUSION

Toward the practical implementation of MOF-based chemical warfare agent (CWA) catalysts, a facile, high yielding, low cost, scalable, template-free, and aqueous synthesis strategy was developed for the preparation of a continuous Zr-MOF coating on textile supports. A three-phase growth mechanism for MOF growth on fibers was optimized to yield high porosity composite materials with uniform coverage. These MOFcoated textiles exhibited the highest to date catalytic activity among composite materials for the hydrolysis of a nerve agent simulant DMNP and a nerve agent GD. Moreover, the highly porous MOF/fiber composite showed excellent capture performance for a mustard simulant, CEES, where the composite material exhibited considerable protection for over 2 h, implying a nearly defect-free surface coverage of the fiber, which is crucial for the current application. Importantly, these flexible MOF/textile composites could be conveniently tailored into different shapes, promising great potential for these materials to be incorporated into suits and masks as protective layers. Both the high catalytic activity and adsorption capacity of the MOF/fiber material observed herein invite further engineering to implement these materials as next-generation protective gear against multiple CWA contaminants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b07301.

Experimental details and supporting figures (PDF)

AUTHOR INFORMATION

Corresponding Authors

*tcxinjh@polyu.edu.hk

*o-farha@northwestern.edu

ORCID ©

Kaikai Ma: 0000-0003-0414-4397 Timur Islamoglu: 0000-0003-3688-9158 Zhijie Chen: 0000-0001-9232-7382

Peng Li: 0000-0002-4273-4577

Megan C. Wasson: 0000-0002-9384-2033

Gregory W. Peterson: 0000-0003-3467-5295

Omar K. Farha: 0000-0002-9904-9845

Notes

The authors declare no competing financial interest.

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