Hot Press Synthesis of MOF/Textile Composites for Nerve Agent Detoxification

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Metal Organic Framework, Nerve Agent, Cotton Fabric, UiO66-NH_2, Hot-press.

ABSTRACT: Chemical nerve agents employed in warfare can induce paralysis and death within minutes of exposure. Zirconium based metal-organic frameworks (MOFs), such as UiO-66-NH_2, show promise for the fast and efficient decontamination of nerve agents, which motivates their incorporation into textiles as protective layers. Few scalable methods to produce MOF/textile composites for personal protective applications have been developed, however, they mainly require use of toxic and flammable solvents. Here, we describe a scalable, single-step method to synthesize UiO-66-NH_2 on cotton fabrics by hot pressing the monomers onto the fabric samples. The use of a pre-formed hexanuclear zirconium benzoate cluster with 1,8- bis(dimethylamine)naphthalene as a non-nucleophilic base improved the quality of MOFs synthesized from the hot press method, as determined by an increase in their surface area and crystallinity. Pre-activation of the cotton fabric with carboxylic acids provided UiO-66-NH_2/cotton composites of high MOF loadings with homogeneous coverage, which demonstrated efficient decontamination of a nerve agent simulant, dimethyl-4-nitrophenyl phosphate (DMNP).

The use of chemical warfare agents after World War I has necessitated the development of counteractive compounds. The importance of detoxification methods persists because of toxic chemicals continue to be used against civilians by terrorists and in state-sponsored assassinations,[1,2] despite international laws that forbid their production, accumulation, and use.[3] Organophosphorous nerve agents (NAs) comprise a particularly problematic class of chemical warfare agents because they are among the most acutely toxic substances.[4] Organophosphorus NAs inhibit the acetylcholinesterase, an enzyme essential to the degradation of choline ester-based neurotransmitters, and disrupt the necessary process of neurotransmission, which ultimately results in paralysis and death. These dangerous and painful effects occur rapidly after skin or respiratory exposure to NAs.[5] Current detoxification strategies include neutralization of NAs with strongly basic solutions or by incineration. These strategies can be useful for destroying stockpiles but are not feasible for protective garments.[6,7] Therefore, efficient and rapid protection methods must focus on the development of solid composite materials.

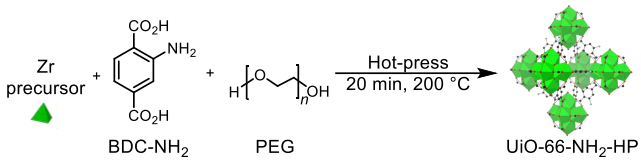
Recently, a new class of counteractive materials based on metal-organic framework (MOF) scaffolds have shown promising detoxification properties.[8] MOFs are crystalline coordination polymers comprised of metal nodes linked by organic monomers.[9] A zirconium-based MOF, UiO-66-NH_2, exhibits excellent thermal and hydrolytic stability relative to other MOFs and efficiently hydrolyzes a NA simulant, dimethyl-4-nitrophenyl phosphate (DMNP).[10] Despite its promise, UiO-66-NH_2 and most other MOFs are isolated as insoluble solids, which complicates subsequent textile processing steps required to produce NA-protective clothing. This challenge motivated us to develop efficient methods to integrate UiO-66-NH_2 into cotton fabrics.

Previous studies have incorporated MOFs into cotton by attaching pre-synthesized MOFs onto textiles or forming MOFs directly onto fabrics in situ via solvothermal synthesis.[11,12] Both methods, however, require organic solvents and time-intensive processing steps that preclude their usage in large-scale manufacturing applications. Given these limitations, hot pressing, a method commonly used in the fabric industry, was introduced by Chen *et al*. to incorporate different MOFs onto various substrates in a single step.[13,14] Here we build upon this approach by functionalizing cotton fabric with carboxylic acid groups to ensure a high degree of UiO-66-NH_2 loading onto the substrate. We also improved the quality of the MOF prepared under hot press conditions through the use of a non-nucleophilic base and a pre-formed zirconium benzoate cluster. In this study, we demonstrate that UiO-66-NH_2/cotton composites prepared via a scalable hot press method are promising materials for use as PPE against NAs. Our sorption, PXRD, SEM and reactivity tests showed that UiO-66-NH_2 crystals are accessible.

Results and Discussion

Synthesis of Hot Pressed MOFs. Amongst five Zr sources, a hexanuclear zirconium benzoate cluster ($Zr_6O_4(OH)_4(C_6H_5COO)_{12}$) was the most effective precursor to prepare UiO-66-NH_2 in the hot press method. A finely ground mixture of Zr_6 cluster, 2-aminoterephthalic acid (BDC-NH_2), and polyethylene glycol (PEG) was wrapped in aluminum foil and heated at 200 °C for 20 min using a hot

press to afford a dark brown powder (Scheme 1, Table S1). This powder was washed with DMF/acetone and characterized by powder x-ray diffraction (PXRD) (Figure S1) which confirmed the formation of UiO-66-NH_2. MOF prepared from the Zr benzoate cluster exhibited the highest degree of crystallinity, as indicated by the PXRD peaks at 7.4° and 8.5° that correspond to the (111) and (200) planes of UiO-66-NH_2, respectively.[15] PXRD patterns of UiO-66-NH_2 samples prepared from other Zr sources ($Zr(acac)_4$, $ZrO(NO_3)_2$, $ZrCl_4$, and $ZrOCl_2$), however, either exhibited a broadened peak at 7.4° or lacked the peak at 8.4°. Based on previous reports that show the pre-formed hexanuclear zirconium benzoate clusters allow access to UiO-66 MOFs under mild conditions (i.e., solvent-free or ambient temperatures),[16,17] we suspect that the zirconium benzoate cluster helps drive ordered network extension through ligand exchange with BDC-NH_2 in the hot press method, resulting in the formation of a more crystalline MOF.



Scheme 1. Synthesis of UiO-66-NH_2 using the hot press method.

In traditional solvothermal synthesis, the hydrolysis of DMF forms dimethyl amine, which acts as a base to deprotonate carboxylic acid groups on the linker and promote exchange with the benzoic acids on the Zr cluster.[18] Since the hot press method does not use solvent, we speculated that adding an external base would promote the exchange and improve MOF quality. Nucleophilic bases, however, are undesirable because they might hinder network formation. To circumvent this problem, a non-nucleophilic external base, 1,8-bis(dimethylamino)naphthalene (proton sponge, PS), was added during the hot press synthesis. To investigate the effect of PS in facilitating benzoic acid exchange between the linker and Zr benzoate cluster, we independently prepared UiO-66-NH_2 in the presence (UiO-66-NH_2-PS) and absence of PS and analyzed the MOF's composition through digestion experiments. UiO-66-NH_2 samples were digested in concentrated aqueous sodium deuteroxide (NaOD), and the quantity of residual reactants (i.e, benzoic acid from the Zr benzoate cluster and BDC-NH_2 linker) were determined via ^{1}H-NMR spectroscopy (Figure S2 and Table S3). Based on this spectroscopic data, UiO-66-NH_2-PS contained higher incorporation of the linker as compared to the UiO-66-NH_2 prepared without PS (73% and 58% of BDC-NH_2 incorporation, respectively). Additionally, UiO-66-NH_2-PS exhibited a PXRD pattern with sharper peaks at 7.4° and 8.5° than UiO-66-NH_2 prepared in absence of PS (Figure 1a), consistent with the formation of a more crystalline MOF. Further, we determined the surface area of UiO-66-NH_2 prepared with and without PS using N_2 isotherms at 77K to give an apparent Brunauer-Emmett-Teller surface area (S_{BET}) of 650 and 435 $m^2\ g^{-1}$, respectively (Figure 1b). Although their values are lower than those obtained from solvothermal methods (1290 $m^2\ g^{-1}$),[19] the increase in surface area of UiO-66-NH_2-PS suggests that the addition of PS improves the quality of the MOF.

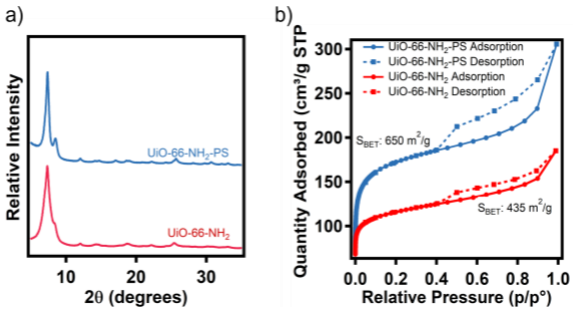
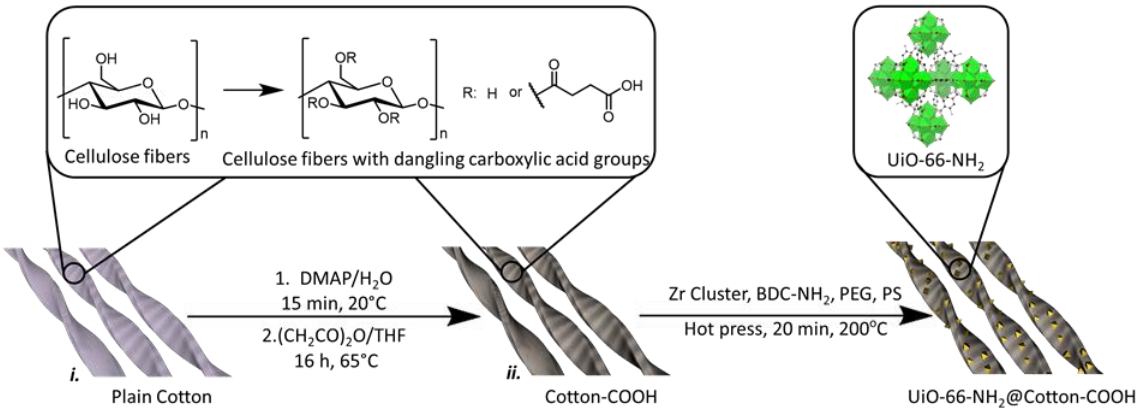


Figure 1: a. PXRD patterns of UiO-66-NH_2 prepared with proton sponge (PS) (blue) and without PS (red) via hot press method. b. Nitrogen adsorption isotherm of UiO-66-NH_2 prepared with PS (blue) and UiO-66-NH_2 without PS (red).

Fabric Functionalization and MOF/Textile Composite Fabrication. Cotton fabrics are ineffective at anchoring Zr-based MOFs due to lack of surface functionalities; thus, we sought to modify cotton with carboxylic acid groups to serve as attachment/nucleation points for MOF growth. Previously reported methods employ chloroacetic acid along with concentrated sodium hydroxide solutions to functionalize cotton fibers.[20,21] However, we observed that this method irreversibly damages the structural integrity of the cotton and caused fraying of the fabric sample. In contrast, we found that succinic anhydride is an effective reagent to modify cotton fabric without damaging the fibers. We developed a two-step procedure whereby cotton fabrics were first soaked in a solution of 4-dimethylaminopyradine (DMAP) in water (1.6 mM) and then treated with succinic anhydride in tetrahydrofuran (80 mL, 0.2 M) at 65 °C for 16 h (Scheme 2i). Subsequent water washes of the functionalized cotton fabrics (cotton-COOH) removed all unbound materials. Finally, the functionalized fabrics were air dried at room temperatures. FT-IR spectroscopy of cotton-COOH qualitatively indicated successful modification of the cotton fabric. Characteristic C-O and O-H stretches for carbohydrates at 1060 cm^{-1} and 3340 cm^{-1} and the appearance of a strong carbonyl C=O mode at 1726 cm^{-1} confirmed the incorporation of the carboxylic acid groups on the cotton fabric (Figure 2a and S3). Digestion experiments quantified the extent of carboxylic acid incorporation in cotton-COOH. Cotton-COOH samples were treated with saturated aqueous lithium carbonate solutions to exchange acidic protons with lithium, and then digested with nitric acid to analyze the resultant elemental composition with inductively coupled plasma optical emission spectroscopy (ICP-OES).[22] Cotton-COOH contained an average of 1.29 ± 0.33 mmol of COOH per gram of fabric, which corresponds to functionalization of ca. 7.0 ± 1.8% of the cellulose hydroxyl groups, corresponding to 1 succinic acid groups per 4.8 ± 1.2 glucose units of the cellulose. PXRD of the cotton-COOH revealed that the crystallinity of the cellulose was not lost during functionalization, as evidenced by the retention of characteristic cellulose diffraction peaks at 14.6°, 22.5°, and 34.3° (Figure 2b and S4). This was corroborated by scanning electron microscopy (SEM), which revealed



Scheme 2. Schematics of i) Pre-activation of cotton fabric with carboxylic acid using succinic anhydride and ii) in-situ growth of UiO-66-NH_2 on activated cotton fabric via hot press method.

undamaged fibers in cotton-COOH after the succinic anhydride modification procedure (Figure 2c and S5).

Cotton composites containing UiO-66-NH_2 were prepared with unmodified cotton and cotton-COOH by evenly applying a mixture of the Zr benzoate cluster, BDC-NH_2, PS and PEG on the substrate (Table S2). The fabric was folded in half, wrapped in aluminum foil and hot pressed at 200 °C for 20 min. Residual unbound MOF materials were removed by a DMF/acetone washing process to yield UiO-66-NH_2/cotton composites (Scheme 2ii, Video S1). Additionally, we performed identical acid digestion experiments of the two MOF/cotton composites as described above and quantified the amount of Zr incorporated onto unmodified cotton or functionalized cotton-COOH fabrics. The UiO-66-NH_2@cotton-COOH composites contained over three times more Zr compared to UiO-66-NH_2@cotton (7.9 ± 1.9 mg/g and 2.1 ± 0.9 mg/g, respectively). Higher incorporation of the MOF in the cotton-COOH demonstrates that the carboxylic acid groups promote the formation and attachment of the MOF onto the cotton fabric. The FT-IR spectra of the MOF/cotton composites contained the typical carbohydrate peak located around 1100 cm^{-1} as well as a new C=O stretch band at 1650 cm^{-1} originating from UiO-66-NH_2, which suggests successful formation of the MOF onto the cotton fabric. Furthermore, UiO-66-NH_2@cotton-COOH exhibited an additional peak at 1730 cm^{-1} that corresponds to the carbonyl C=O stretch of the carboxylic acid group on the functionalized cotton-COOH material (Figure 2d, and 2g). PXRD analysis of the MOF/cotton composites also indicated successful incorporation of UiO-66-NH_2, in which the characteristic (111) plane of MOF appeared at 7.4° and 7.2° for UiO-66-NH_2@Cotton and UiO-66-NH_2@Cotton-COOH, respectively. Moreover, the cellulose remained intact as indicated by features at 14.6°, 22.5°, and 34.3° (Figures 2e and 2h). From the SEM images of the MOF/cotton composites, we observed more homogeneous coverage of MOF on cotton-COOH as a direct result of the carboxylic acids serving as anchoring points (Figure 2h and 2i). We demonstrated successful functionalization of cotton fabrics with carboxylic acid groups under mild reaction conditions while preserving the cotton fibers' crystallinity and their macroscopic appearance, allowing high loading and homogeneous coverage of UiO-66-NH_2 in the MOF/cotton composite.

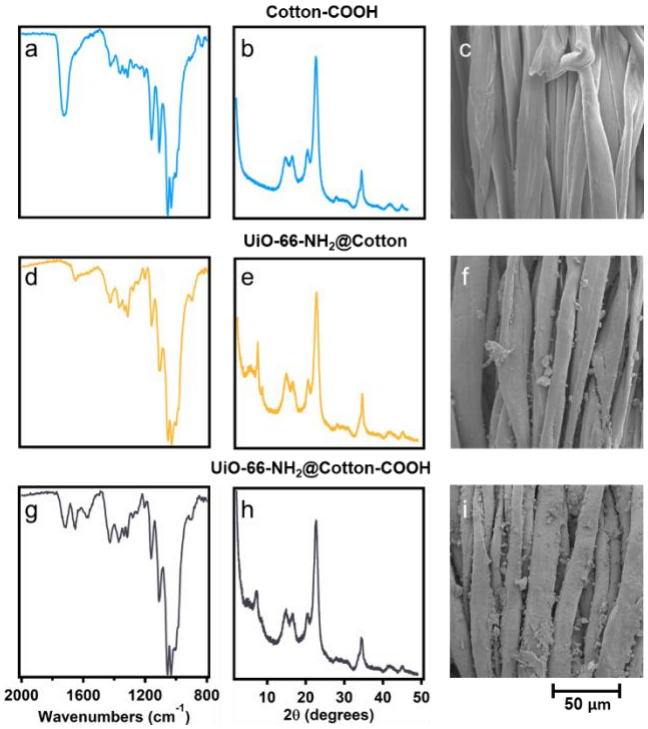


Figure 2. a. FT-IR spectrum, b. PXRD pattern, and c. SEM image of Cotton-COOH (blue). d. FT-IR spectrum, e. PXRD pattern, and f. SEM image of UiO-66-NH_2@Cotton (orange). g. FT-IR spectrum, h. PXRD pattern, and i. SEM image of UiO-66-NH_2@Cotton-COOH (black).

Hydrolysis of a Nerve Agent Simulant. To investigate the ability of MOF and MOF/cotton composites prepared using hot press method to hydrolyze phosphoester bond, we performed the catalytic hydrolysis of a NA simulant, dimethyl-4-nitrophenyl phosphate (DMNP) (Scheme S1). As-prepared MOFs demonstrated that UiO-66-NH_2-PS exhibits superior catalytic activity towards phosphoester hydrolysis compared to analogs prepared without added base. DMNP (4 µL) was treated with 3 mg (6 mol %) of MOFs. Powder samples of the UiO-66-NH_2-PS achieved 98%

conversion within 30 min, whereas base-free UiO-66-NH_2 plateaued at 75% conversion after 60 min (Figure 3a). Furthermore, samples of UiO-66-NH_2-PS catalyzed DMNP hydrolysis faster than those prepared without added base, as evidenced by the corresponding first-order rate constants (k) for UiO-66-NH_2-PS and UiO-66-NH_2 (k = 0.134 ± 0.007 min^{-1} and 0.049 ± 0.003 min^{-1}, respectively; Figure S6). These rate constants correspond to DMNP half-lives of 5.2 ± 0.3 min for UiO-66-NH_2-PS and 14.2 ± 1.0 min for UiO-66-NH_2 without PS (Table S4). These findings further corroborate the important role of PS to promote better framework formation through more effective linker exchange, which improves the MOF's performance towards catalytic hydrolysis of DMNP. Overall, the optimized hot press conditions using Zr benzoate cluster and PS produced UiO-66-NH_2 with efficient DMNP hydrolysis performance, validating the promise of the hot press method for UiO-66-NH_2 preparation.

The promising activity of the as-prepared MOFs was retained in the fabric composites. A hydrolysis study of DMNP indicated that UiO-66-NH_2@Cotton-COOH had improved degradation efficiency compared to UiO-66-NH_2@Cotton. The loading of UiO-66-NH_2 was kept constant (3.0 mg, 6 mol %) by adjusting the amount of MOF/cotton composite based on their Zr incorporation wt%. DMNP (4 μL) was treated with 32.9 mg of UiO-66-NH_2@Cotton-COOH and 83.8 mg of UiO-66-NH_2@Cotton. Although the fabric mass was 2.5 times less, UiO-66-NH_2@Cotton-COOH exhibited 1.5 times higher DMNP conversion than UiO-66-NH_2@Cotton after 240 min (68% and 47%, respectively, Figure 3b). As a control, we tested the hydrolysis of DMNP using the Cotton-COOH and observed negligible catalytic activity with conversion under 10% at 4 h; this indicated that the presence of MOF embedded onto the fabric constitutes the most to the decomposition of DMNP. Additionally, the respective first-order rate constants and half-lives (Figure S7 and Table S5) of UiO-66-NH_2@cotton-COOH (k = 0.012 ± 0.0013 min^{-1} with a half-life of 59.6 ± 6.6 min) and UiO-66-NH_2@cotton (k = 0.0065 ± 0.00047 min^{-1} with a half-life of 107.3 ±7.8 min) demonstrated that UiO-66-NH_2@Cotton-COOH hydrolyzes DMNP more rapidly. These results illustrate that UiO-66-NH_2 in the composites are active catalysts for DMNP hydrolysis. Moreover, UiO-66-NH_2@Cotton-COOH exhibits greater and faster hydrolysis performance than UiO-66-NH_2@Cotton which reduces the amount of fabric required for DMNP degradation, highlighting the importance of carboxylic acid anchors.

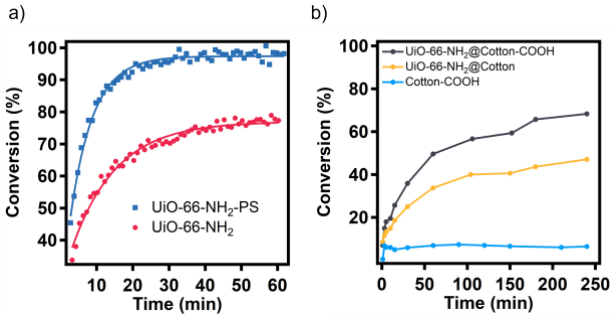


Figure 3. a. Hydrolysis of DMNP by UiO-66-NH_2 prepared using hot press method with PS (blue) and without PS (red). b. Hydrolysis of DMNP by the fabrics UiO-66-NH_2@Cotton-COOH (black), UiO-66-NH_2@Cotton (yellow), and Cotton-COOH (blue).

Conclusions

Hot pressing is a facile, rapid, and solvent-free method to obtain high-quality UiO-66-NH_2 composites with textile fiber. By using a pre-formed Zr benzoate cluster and a non-nucleophilic base, we improved MOF quality and enhanced its catalytic activity towards the hydrolysis of a NA simulant, DMNP. The pre-activation of cotton with carboxylic acids was a critical step in anchoring UiO-66-NH_2 to the fabric and achieving both higher loading and more homogenous MOF coverage. The UiO-66-NH_2@Cotton-COOH exhibited promising activity in the hydrolysis of DMNP, which highlights the UiO-66-NH_2/cotton composite as an active and effective material for potential use in personal protective equipment against NAs and provides a rapid and potentially scalable approach to prepare MOF/fabric composites.

ASSOCIATED CONTENT

Supporting Information. Experimental details, NMR and FT-IR spectra, N_2 adsorption isotherm, DMNP kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Declaration of competing interests
O.K.F. has a financial interest in the start-up company NuMat Technologies, which is seeking to commercialize metal-organic frameworks.

ACKNOWLEDGMENT

WRD acknowledges financial support from the Defense Threat Reduction Agency (HDTRA1 19 1 0010) and the National Science Foundation (NSF) through the Center for Sustainable Polymers (CHE-1413862). OKF acknowledges financial support from the Army Research Office (W911NF2020136). M.C.W. is supported by the NSF Graduate Research Fellowship under grant DGE-1842165. This work made use of the IMSERC, QBIC and NUANCE facilities at Northwestern University, which have received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the State of Illinois, and International Institute for Nanotechnology (IIN).

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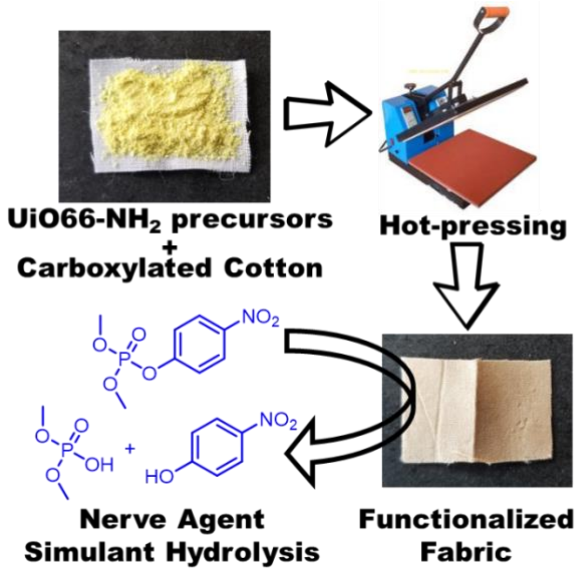
UiO66-NH2 precursors
+
Carboxylated Cotton
Hot-pressing
NO2
HO
OH
Nerve Agent
Simulant Hydrolysis
Functionalized
Fabric