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COMMUNICATION

Green Synthesis of MOF-based textile composites for the degradation of a chemical warfare agent simulant

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A green synthesis of UiO-66-NH₂ embedded in chitosan and deposited on textiles has been investigated for the degradation of chemical warfare agents. This method requires no heating or use of toxic solvents. The composite synthesized presents an interesting efficiency in detoxifying common simulant of chemical warfare agents, such as DMNP. In parallel, resistance and permeability tests were also realized in order to confirm the suitability of the composites for further applications.

Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal ions or clusters joined by organic linkers. With their very high porosity (up to 7000 m²/g) and versatile composition, they have been studied for a large array of applications, from gas storage to catalysis.¹ More specifically, Zr-based MOF are known as stable MOF with excellent results in terms of capture and degradation of a large variety of threatening species, like chemical warfare agents.^{2, 3} For example, organophosphorus nerve agents have shown impressive detoxification degree using these MOFs, thanks to the presence of Zr^{IV} nodes, which catalyses organophosphorus hydrolysis.^{4, 5} However, powder MOFs are hardly implementable at industry scale.⁶ Therefore, their incorporation to industrial materials, such as textile fibers, is an attractive route for practical applications.^{2, 7}

In the actual context of emission reduction and environmental preoccupation, we turned our attention to a new green deposition method of MOF/chitosan composites on

textile surfaces (Figure 1). Green synthesis of MOFs has been developed increasingly these last years, by replacing the toxic organic solvents by water or decreasing the synthesis temperature.⁸ Due to its efficiency against organophosphorus species and relatively easy synthesis route, we selected the MOF compound, UiO-66-NH₂, as the catalyst to study the dimethyl 4-nitrophenyl phosphonate (DMNP) degradation, a common simulant of nerve agents in a chemical warfare context. The use of a base (e.g. N-ethylmorpholine – NEM) have already been showed to improve the catalytic degradation of the DMNP.⁷ In the continuous investigations of the green chemistry field, we focused our interest on chitosan, a natural biopolymer containing hydroxyl (-OH) and amino (-NH₂) groups that could interact with the MOF and the support fiber (Fig. 1). Indeed, these functions must interact by metal-chitosan coordination (H₂N→Zr and HO→Zr), as previously observed with HKUST-1@Chitosan aerogels.⁹

Finally, the preparation method has been developed using no toxic solvents and no heating steps. The principal aim of these synthetic conditions is to prove the efficiency of a green composite against chemical hazards. For this study we have selected cotton, polyester (polyethylene terephthalate, PET) and polyamide (PA/Nylon 6,6) as textile support.

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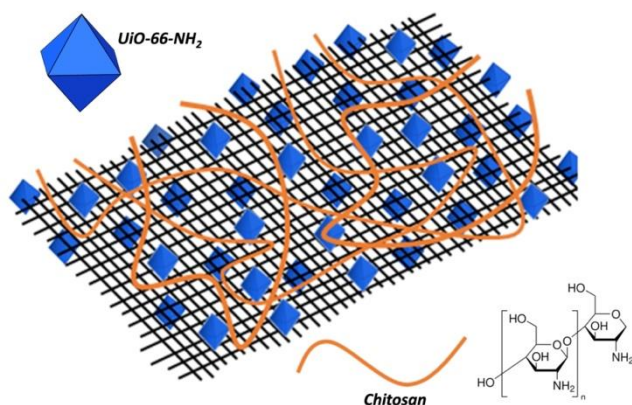


Figure 1. UiO-66-NH₂/Chitosan deposited on textile

UiO-66-NH₂/chitosan/fabric composites were prepared by an original green synthesis (see experimental section). First, a chitosan solution is mixed with zirconium tetrachloride. Then, the fabric is impregnated with precursor solution for 24h. After this step, the fiber is transferred in a second solution containing the MOF ligand (aminoterephthalic acid), the modulator to improve the crystallinity (formic acid), and the solvent (ethanol). After the complete evaporation (24 to 72h), the composite is washed thoroughly with ethanol and dried under air at room temperature.

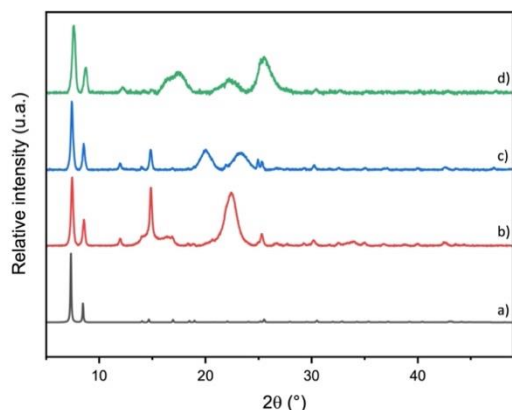


Figure 2. Powder XRD patterns of UiO-66-NH₂ reference (a), and UiO-66-NH₂/Chitosan composites deposited on the surface of cotton (b), polyamide (c) and polyester (d) fabrics (wavelength: copper radiation).

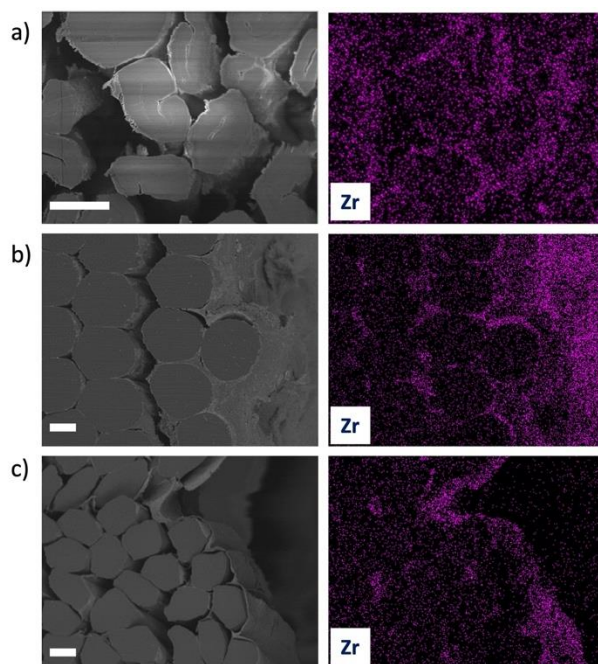
This relatively long process of impregnation and evaporation at room temperature is mandatory for the evaporation-induced self-assembly of MOF in a large amount. This simple strategy, involving fiber wetting and drying, should be scalable at the industrial level, since it is strongly inspired from the usual approach for fabric dyeing.¹⁰

For each fabric, the precipitation of UiO-66-NH₂ is confirmed by the presence of the characteristic Bragg peaks at 7.5° and 8.7° (2θ) from the analysis of powder XRD patterns (Fig. 2). The intense peaks at higher angle (8–9°), are assigned to the support fiber and may hide other expected characteristics expected Bragg peaks related to UiO-66-NH₂. Without chitosan, the MOF does not settle and no crystallization is detected by powder XRD

on the surface of the fabrics. The Zr-chitosan interaction was also identified by ¹³C solid state NMR (see supplementary information). For the signal associated to chitosan, the carbon atoms closest to the involved complexing functions (-OH, -NH₂) are those showing the most significant shift, compared to pristine chitosan.

This point confirms that the polysaccharide chitosan acts as binding intermediate between the fiber and the MOF. mixture SEM pictures (Fig. 3) indicate a homogeneous covering and as well as a good adhesion of chitosan and UiO-66-NH₂ at the surface and within the fabric of cotton and polyamide fibrils. Based on BET (Kr, 77 K) and ICP analyses, the deposition seems to be slightly more efficient for cotton (2.6 m²/g for the composite, % of Zr in the composite = 6.4 wt.% Zr) compared to polyamide (2.6 m²/g, 4.6 wt.% Zr).

Air permeability test indicates that the deposition of chitosan and UiO-66-NH₂, slightly decrease the breathability of cotton (-12%) and polyester-based (-22%) composites, compared to the pristine fabrics (see supplementary information). However, the composite fabricated with polyamide becomes almost impermeable to air after the chemical process. This loss is explained by the good solubility of polyamide in formic acid (used in low quantity for the MOF synthesis), leading to the



merging of the polyamide yarns.

Figure 3. SEM-BSE (Back Scattered Electron) images (left) and EDS (Electron Dispersive X-ray spectroscopy) mapping of UiO-66-NH₂/chitosan/fabric composites. A) Cotton, b) Polyamide, c) Polyester. The white bar corresponds to a length of 10 μm.

Finally, while chitosan is covering the surface of polyester fabric, the chitin derivative is not adhering well to this fabric since discontinuity are observed between the two materials (see Fig 3c). Furthermore, this weak affinity results in a low diffusion of chitosan within the fabric, and consequently a low amount of MOF in the final composite (0.4 m²/g, 1.9 wt.% Zr).

The low and inhomogeneous deposition on the surface of polyester fiber is assigned to the relative inertia of this synthetic fabric, whereas cotton or polyamide are functionalized by chemical groups (-OH or -NH), enabling the anchorage of nanomaterials. The BET surfaces measured for the different composite are also relatively low compared to the values reported in the literature for similar combination (Fabric/Polymer/MOF), usually above 50 m²/g.¹¹ Due to the very good embedding of UiO-66-NH₂ within chitosan, we suppose that MOF cages are obstructed by the polymer, limiting the access to the internal porosity.

The composites have been submitted to various normed resistance tests. The abrasion experiment, involving a contact pressure of 9 kPa and 1250 cycles of circular frictions on the surface of the fibers, leads to a final weight loss below than 2 wt % (Fig. S1), confirming the mechanical adherence of the impregnated phase in composites. A severe artificial aging test, mimicking drastic conditions, as also applied to the functionalized fibers: functionalized fabrics have been placed in an exposure chamber under UV irradiation (50W/m²), controlled temperature (30°C) and moisture (relative humidity = 60%) for 24 hours. Whereas SEM (Fig. S2) and XRD (Fig. S3) analyses did not show any apparent degradation of the three supports, the cotton-based composite has shown an important loss of porosity from 2.6 to 0.4 m²/g. Since the other compounds (polyester- and polyamide-based composite) are preserved, this loss of porosity is assigned to a lower resistance in the selected conditions of the composite synthesised with cotton.

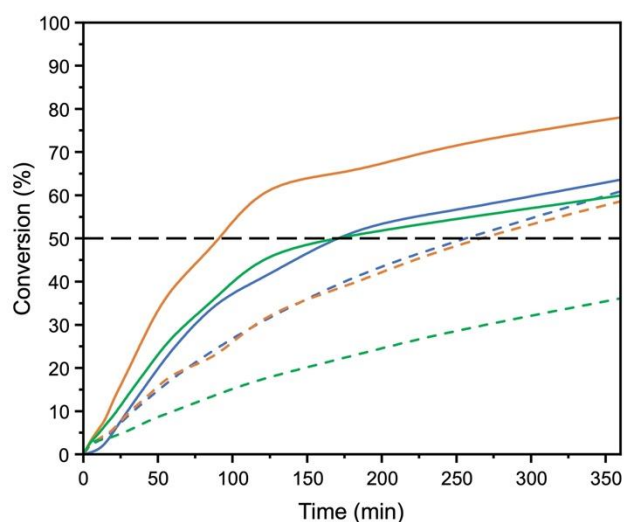


Figure 4. Kinetics of catalytic degradation of DMNP to p-nitrophenoxide using Zr-MOF/Chitosan composites (blue: cotton, orange: polyamide, green: polyester); full line: pristine composite; dashed line: composite submitted to the exposure chamber.

For this study we focus our work on dimethyl-4-nitrophenyl phosphate (DMNP, also called methyl-paraoxon), as model for organophosphorous species; less toxic than the usual chemical warfare agents (VX, Tabun, GB, etc) but showing very similar chemical organization and hydrolysis behaviour.³

The efficiency of the composite toward the degradation of DMNP has been evaluated in aqueous NEM (4-Ethylmorpholine) solution, as usually applied in the literature to measure the degradation efficiency of such materials against organophosphorous agents.¹² Herein, the best degradation (Fig. 4) was obtained with the polyamide composite, showing a half-life time ($t_{1/2}$) of 92 min (Fig. 4). The fibers incorporating cotton or polyester exhibit very similar efficiency for the hydrolysis of DMNP, with $t_{1/2}$ around 160 min. After severe ageing step (UV-steam-30°C, for 24h), the performances of all MOF-based fabrics for DMNP decomposition have dropped, exhibiting longer half-time (>250 min). Nevertheless, the degradation times calculated in this study are in agreement with the results from the literature, concerning composites with similar amount of Zr-based MOFs.² Typically, higher loading of zirconium deposited at the surface of the fiber will accelerate the decomposition of the organophosphorous agent, but also result in significant abrasion resistance decrease for the fabric.¹¹

In summary, the green MOF-fabric composites were synthesized at room temperature in aqueous solution and without any toxic chemicals used for the synthesis. In this process, chitosan was used for coating textile fabrics and to graft Zr-based UiO-66-NH₂. A satisfying covering of the fabrics by the MOF-chitosan phase is observed (especially with cotton and polyamide), highlighted by a homogeneous deposition of the porous material and the green polymer within the fabric. This good interaction between the fabric and the deposit provides an excellent resistance to abrasion and to severe ageing conditions, and still with very good permeability for cotton-based composite.

Thanks to the efficient immobilization of zirconium-based catalyst, the material also shows a good efficiency for DMNP decomposition ($t_{1/2}$ < 100 min for polyamide-based composite), despite relative low amount of UiO-66-NH₂ integrated to the fabrics.

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There are no conflicts to declare.

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