Composite Materials

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Biological Chitin–MOF Composites with Hierarchical Pore Systems for Air-Filtration Applications

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In memory of Zoran Kljajić

Abstract: *Metal–organic frameworks (MOFs) are promising materials for gas-separation and air-filtration applications. However, for these applications, MOF crystallites need to be incorporated in robust and manageable support materials. We used chitin-based networks from a marine sponge as a non-toxic, biodegradable, and low-weight support material for MOF deposition. The structural properties of the material favor predominant nucleation of the MOF crystallites at the inside of the hollow fibers. This composite has a hierarchical pore system with surface areas up to 800 $m^2 g^{-1}$ and pore volumes of 3.6 $cm^3 g^{-1}$, allowing good transport kinetics and a very high loading of the active material. Ammonia breakthrough experiments highlight the accessibility of the MOF crystallites and the adsorption potential of the composite indicating their high potential for filtration applications for toxic industrial gases.*

Metal–organic frameworks (MOFs) are a new class of high performance materials with specific surface areas up to 7000 $m^2 g^{-1}$.[1,2] They are synthesized by self-assembly of metal ions or clusters and organic ligands. The crystalline networks exhibit well-ordered pore systems on the micro- and mesoscale. They offer a number of chemically reactive sites, including the metal centers as well as the functional groups of the ligands. Applications of MOFs in gas storage and gas separation as well as in heterogeneous catalysis have been a major topic of interest during the last few years.[3–11]

The majority of MOF syntheses describe the preparation of small- or medium-sized crystallites, resulting mostly in powders. However, specifically shaped materials are necessary for industrial applications. Thus, increasing efforts currently concentrate on attaching MOFs onto support materials to make them suitable for applications in membranes, filters, or columns. Suitable support materials need to be shapeable, cost-efficient, and chemically inert. They have to ensure robust attachment of a high amount of the active material without changing its functional properties. To date, MOFs have been supported on a wide range of materials, including self-assembling monolayers, metal and metal-oxide surfaces, silica or magnetic particles. However, these composite materials still suffer from low active mass loadings.[6,7,12,13]

Three-dimensional polymeric networks as support materials are a promising approach for the use of MOFs, especially in gas separation. MOFs have been deposited on synthetic polymers in the form of monoliths or fibers.[14–17] High loadings can be achieved using additional adhesion layers for the fixation of the active material. Zhao et al. recently deposited Cu_3BTC_2 (HKUST-1) on polypropylene fibers coated with an alumina adhesion layer, and achieved loadings up to approximately 80% with a specific surface area of 695 ± 76 $m^2 g^{-1}$.[18] For other polymers, such as polybutylene terephthalate or cotton, lower surface areas of 485 $m^2 g^{-1}$ and 121 $m^2 g^{-1}$, respectively, were reported.[18] Polydopamine was also discussed as an adhesion layer.[19]

As conventional polymers are based on the dwindling petroleum resources, biopolymers are becoming an increasingly important alternative. Polysaccharides, proteins, and nucleic acids show important advantages compared to synthetic polymers: They can be produced from renewable raw materials, are usually non-toxic and ideally bio-degradable. Most biopolymers intrinsically contain a number of functional groups which may be suitable for the binding of molecules or metal ions, whereas most synthetic polymers are chemically rather inert.

However, to our knowledge, only a few attempts have been published concerning MOF deposition on biological polymers. Cu_3BTC_2 was attached to cellulose fibers yielding a loading of 20% (w/w) and a specific surface of up to 314 $m^2 g^{-1}$.[20] Cu_3BTC_2 on cellulose tissue resulted in a loading of 1.7% (w/w, recalculated from copper content of 0.5%).[21] Abbasi et al. deposited Cu_3BTC_2 and López-Maya et al. deposited UiO-66 on silk fibers. Both obtained a loading of approximately 50% (w/w) on silk fibers.[22–24]

One of the most abundant and stable polysaccharides is chitin. Chitin and its deacetylated derivative, chitosan are widely used for adsorption, filtration, and water-cleaning

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purposes, in the food industry, and for medical applications.[25–31] Chitin is chemically extremely resistant and dissolves only under very harsh conditions.[26] Owing to its high content of hydroxy and acetamido groups, it is an excellent adsorbent for metal ions.[28,32,33] Chitosan, the deacetylated derivative of chitin, is generally regarded as an even better sorbent for metal ions.[34,35] However, in contrast to chitin, chitosan is soluble in acidic media and chemically less stable.[26] Both biopolymers are enzymatically degradable.[36–38]

A natural chitinous material in the form of two- or three-dimensional fibrous networks is produced by sponges from the order *Verongida*. It serves as a skeleton and as a matrix for cell growth. This chitinous material can be extracted from the sponge in a simple and cost-effective procedure. It is mechanically stable but flexible.[39,40] Chitinous networks from sponges have already been used for the deposition of zirconium dioxide nanoparticles or silica nanoparticles, but so far the application potential of these materials has not been demonstrated.[41,42]

Chitinous skeletons were extracted from the dried marine sponge *Aplysina aerophoba (A. aerophoba)* using sodium hydroxide solution and diluted acetic acid.[40] The remaining white chitinous material is a porous fiber network which strongly swells in water (Figure S1a in the Supporting Information). It has a specific inner surface area of about 18 $m^2 g^{-1}$ after supercritical drying. Presumably, this surface area is due to the structure of the fibers which consist of concentric rings of chitinous material with a hollow core.[40] The surface area is reduced to 5 $m^2 g^{-1}$ when the chitinous network is dried in air because of the collapse of the internal structure.[43]

It has been hypothesized that the core of the fibers is filled with proteins and/or cellular tissue in the native state.[40] This can be shown by staining the cleaned chitin fibers with Coomassie Blue, a sensitive stain for proteins.[44] After washing, the staining occurs mainly in the hollow channels of the fibers and between the chitin layers (Figure 1). It is very likely that small amounts of proteins remain in these cavities even after the extraction with sodium hydroxide and acetic acid.

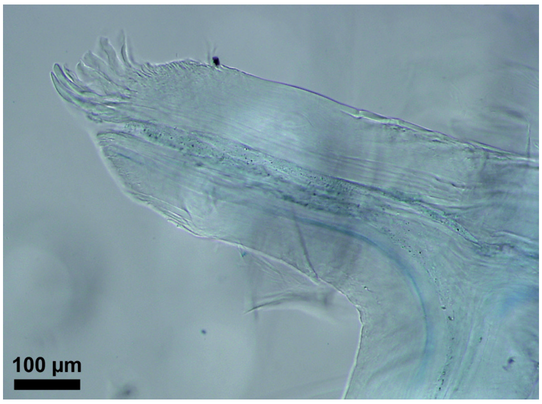

Figure 1. Chitin fibers stained with Coomassie Blue. The stain is located in the hollow cores of the fibers, indicating the presence of proteins.

The cleaned chitinous network was incubated in a $Cu(NO_3)_2$ solution. The color of the network changed from white to light blue, visually confirming the Cu^{II} loading (Figure S1b). The loaded network was incubated in a mixture of water and ethanol containing $Cu(NO_3)_2$ and benzene-1,3,5-tricarboxylic acid. The conditions of the reaction were the same as those used for homogenous synthesis of Cu_3BTC_2. The blue color of the network became more intense after this treatment, though not entirely uniform, indicating an inhomogeneous deposition of Cu_3BTC_2. Powder XRD measurements confirmed the formation of the desired Cu_3BTC_2 phase without any crystalline by-products (Figure S2).

SEM and microscopic images indicate that MOF crystal formation takes place predominantly inside the hollow fibers and to a lower extent on the outer surface (Figure 2). Crystals are also formed homogeneously in solution. However, they are easily washed away during the work-up. The preferential formation of MOFs inside the fibers might be explained by the remaining proteins inside the channels. Proteins interact with metal ions by their various functional groups. These interactions would add to the chitin–copper interactions of pure chitin,[45–47] resulting in predominant nucleation of the MOF crystallites inside the hollow fibers and encapsulation into a highly stable biogenic material. Mechanical deformation and abrasion do not cause any substantial loss of the active material.

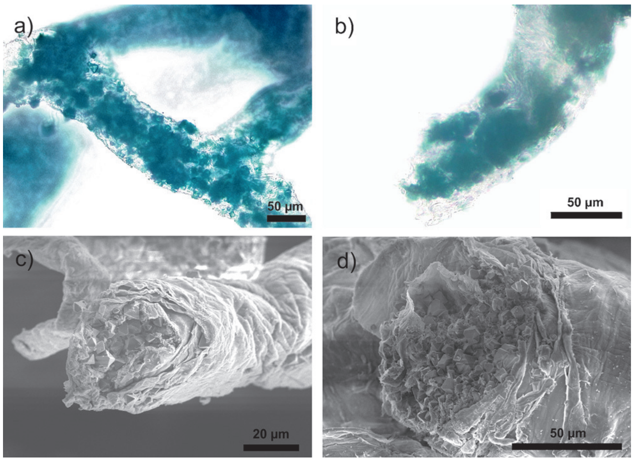

Figure 2. a,b) Stacked microscopic images and c,d) scanning microscope images of chitin fibers from *A. aerophoba* loaded with Cu_3BTC_2.

The composite was dried with supercritical carbon dioxide to avoid the collapse of the chitinous hollow fibers. The loading of the composite with Cu_3BTC_2 was determined by thermal analysis (TGA) and reaches up to 55% (w/w; Figure S3). This corresponds to the highest loading of MOFs reported for biological supports to date.[20,22,23]

^{13}C CP-MAS-NMR spectra (CP = cross polarization, MAS = magic angle spinning) of the composite material were recorded (Figure S4). Pure Cu_3BTC_2 shows very broad signals owing to the paramagnetic metal center. The identification of individual signals is thus difficult. Pure chitin networks from *A. aerophoba* show well-resolved signals.

The spectrum of the composite is dominated by the chitin signals. The Cu_3BTC_2 signals are hardly visible because of their huge line width. Only the strongest Cu_3BTC_2 signal at $\delta = 45–50$ ppm can be identified. The chitin spectrum only differs from pure chitin at the C3 and C5 positions, which are better resolved in the composite. The C5 position is even shifted to lower field by 0.2 ppm. However, these changes are rather small. Note that the chitin fibers in the composite are still present as bulk material with limited surface contact with the MOF. Interactions between the MOF and the chitin are therefore hardly detectable. ATR-IR spectra (ATR = attenuated total reflection) of the composite also show a superposition of vibrational bands from chitin and Cu_3BTC_2 (Figure S5).

The composite obtained shows a remarkably high surface area up to 800 $m^2 g^{-1}$ (Figure 3). This corresponds to a Cu_3BTC_2 loading of approximately 53 % (w/w) as can be calculated from the surface area of pure Cu_3BTC_2 which was prepared under the same conditions without any support (Table 1). The value is consistent with the loading value calculated by thermal analysis.

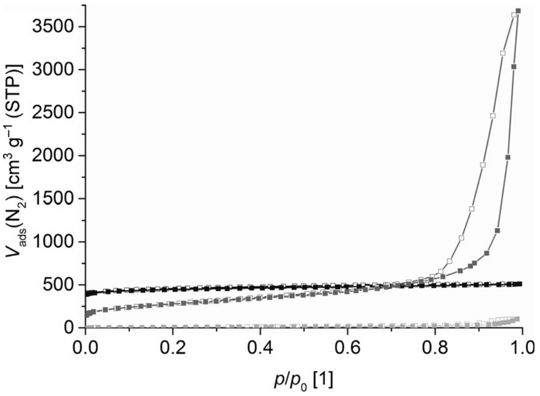

Figure 3. Nitrogen physisorption isotherms at −196 °C: pristine Cu_3BTC_2 (black), chitin fibers from *A. aerophoba* (pale gray) and composite material (gray).

The fixation of Cu_3BTC_2 within the hollow chitin fibers results in the formation of a remarkably high interparticular volume, which can be shown by the hysteresis at high p/p_0 in the N_2-physisorption isotherm (Figure 3). A huge total pore volume of 3.6 $cm^3 g^{-1}$ is achieved. The interparticular space may act as a network of transport pores. The micropores of the MOF and the large *meso*- and macropores present in the composite material thus constitute a hierarchical pore system.

Table 1: Summary of the adsorption data.[a]

Sample	S_{BET} [$m^2 g^{-1}$]	V_{tot} [$cm^3 g^{-1}$]	m_{res} [%]	L_{NH_3} [$mg g^{-1}$]
Cu_3BTC_2	1370 ± 20	0.75 ± 0.06	35.36	97.0
chitin network	18 ± 9	0.15 ± 0.08	5.74	–
Cu_3BTC_2 on chitin	730 ± 70	3.6 ± 1.0	19.22	39.3

[a] BET-surface areas (S_{BET}) were determined at $p/p_0 = 0.3$, total pore volume (V_{tot}) at $p/p_0 = 0.98$, residual mass m_{res} from TGA traces at 800 °C and the ammonia capacity L_{NH_3} from break-through curves.

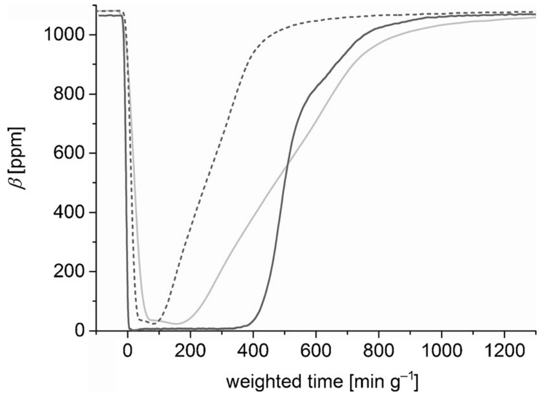

Figure 4. Ammonia break-through curves of pure Cu_3BTC_2 (black), of the composite material (gray, dashed), and of the composite normalized of the amount of Cu_3BTC_2 (gray). Time was set to zero when the gas flow started passing through the sample cell.

To test the suitability of the composite material for filtration applications for toxic industrial chemicals, ammonia break-through curves were recorded (Figure 4). The ammonia capacity of the composite of 39.3 $mg g^{-1}$ corresponds to approximately 40 % of that of the pure Cu_3BTC_2 (97.0 $mg g^{-1}$). Taking into account a Cu_3BTC_2 loading of 53 % (w/w), this implies that more than 75 % of the Cu_3BTC_2 crystals are accessible for ammonia vapor, although they are mostly present inside the fibers. This is most likely due to the huge space in between the particles which allows for diffusion of the target gas into the composite. The ammonia capacity is comparable to the highest reported for Cu_3BTC_2 on biogenic fibrous supports so far (Table S1).[18,48] Only Zhao et al. reported slightly higher capacities for Cu_3BTC_2 on alumina-coated polypropylene.[18]

In summary, chitinous networks from marine sponges, such as *A. aerophoba*, are highly promising biological support materials for MOFs in gas adsorption or filtration applications. This biopolymer has a high affinity for metal ions, which might even be enhanced by small residual amounts of protein. Very high loadings of up to 53 % (w/w) could be achieved. These loadings have so far only been found for synthetic fibrous polymers with additional adhesions layers.[18]

The structure of the chitinous network and the distribution of the remaining proteins induce the site-directed crystallization inside hollow channels. Thus, the MOF is effectively protected from mechanical stress and abrasion. The observed very high accessibility of the crystallites for gases is ensured by a network of macropores acting as transport pores. The composite is thus well suited as a robust adsorption material for toxic gases, for example, in air filters. The approach presented herein might easily be extended to other applications and metal–organic frameworks. Materials with other morphologies may be produced by extracting chitin networks from other *Verongida* species.[40]

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Keywords: chitin · Cu_3BTC_2 · marine sponge · metal–organic frameworks · NH_3 adsorption

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