METAL-ORGANIC FRAMEWORKS FUNCTIONALIZED MULTIFUNCTIONAL TEXTILES

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ABSTRACT

Textile substrates with additional qualities, functions, or capacities beyond their core textile features are known as functional textiles. Multifunctional textiles are gaining attention due to their ability to fulfill multiple applications, like hydrophobicity, hydrophilicity, flame-retardancy, microbial inhibition, odor adsorption, etc. Different nanomaterials, polymers, carbon materials, and inorganic and organic compounds are being reported to impart various functionalities to textile substrates.

The rapid growth of industrialization, global warming, and modern lifestyle are responsible for the emergence of many environmental hazards. The presence of pollutants, volatile organic compounds (VOCs), and malodors in the ambient air degrades the quality of life. Similarly, UV radiation from the Sun and microbial infections also seriously threaten human health. Further, the problem of fabric malodors is very challenging as many unpleasant smells are caused by the biotransformation of non-odorous chemicals (called "odor precursors") by certain microorganisms. Most smells emanating from the human body are examples of this biotransformation. Similarly, the increased levels of particulate matter, nitrous oxides, sulfur oxides, carbon oxides, and other toxic VOCs are of major concern for air pollution. These pollutants have adverse effects on human health. The presence of a small amount of these VOCs in the air can cause unpleasant odors and toxicity. Also, long-term exposure to these pollutants/odors, even at levels of a few parts per million, can cause life-threatening respiratory diseases, like asthma, eye and throat irritations, and even cancer. Therefore, developing innovative, multifunctional smart textiles is essential to mitigate the adverse effects of these hazards.

Metal-Organic Frameworks (MOFs) are an emerging class of materials that can be potential candidates for developing innovative, multifunctional, and smart textiles to mitigate the adverse effects of the above-discussed hazards. MOFs consist of two components: organic and inorganic. The organic part is known as bridging ligands or linkers. On the other hand, the inorganic elements are metal ions or clusters.

MOFs have gained importance due to their high adsorption capacities and open metal sites. Natural fiber-based textiles also seem to be very promising substrates for MOFs to expand their different applications. Among the various MOFs, MOF-5, MOF-199, ZIF-8, and ZIF-67 are relatively easier to synthesize and are widely studied in the literature for their different applications.

In this study, a facile and rapid approach for in-situ surface functionalization of the cellulosic textiles with MOF-5, MOF-199, ZIF-8, and ZIF-67 MOF structures. The carboxymethylation was performed to facilitate the growth/attachment of MOFs on the cotton fabric. The in-situ process was found to be facile, rapid, and commercially viable. All the MOF structures were grown on the fabric by in-situ technique. It was also found that carboxymethylation and deprotonation of the linker are essential for rapid growth, high add-on, and high wash durability. FESEM analysis revealed the morphology of different MOF crystals. MOF-5 crystals showed flake-type morphology, the MOF-199 crystals showed octahedral morphology, the ZIF-8 crystals were of distorted spherical shape, displaying indistinct hexagonal characteristics, and the ZIF-67 crystals exhibited cubic and tetragonal shapes. FESEM analyses confirmed the uniform coverage of the fabric by MOF structures, and the XRD studies confirmed the crystal structures of the grown MOFs. The chemical characteristics of the MOF-functionalized cellulosic textiles were analyzed using ATR-FTIR and XPS techniques. Based on N_2 adsorption, the BET surface areas were calculated for the carboxymethylated and all MOF-functionalized cotton fabrics. The modified fabrics showed significantly high surface areas as compared to the pristine fabric. The BET surface area was the highest for ZIF-8@CMC at 77.78 m^2/g, followed by ZIF-67@CMC fabric at 57.64 m^2/g. Surprisingly, the surface areas of the MOF-5@CMC and MOF-199@CMC were just 1.43 m^2/g and 4.03 m^2/g, respectively. It was observed that there was no significant change in the strength and breaking elongation of the cotton fabrics after the MOF growth.

The MOF functionalized cotton fabrics were investigated for pollutant adsorption, malodor/VOCs adsorption, UV-blocking, and antimicrobial properties. The MOF functionalized fabrics showed rapid adsorption of significantly high amounts of three model aromatic pollutants: aniline, benzene, and styrene. Further, all the MOF functionalized textiles also showed adsorption of high amounts of malodor up to 1000 ppm. Interestingly, all the MOF functionalized samples showed nearly 99.9% antimicrobial activity against *E. coli* and *S. aureus*. Additionally, MOF-199@CMC and ZIF-67@CMC showed high UPF values of 238 and 149, respectively. A comparative study of these multifunctional fabrics in terms of ease of growth, surface area, wash durability, malodor adsorption capacity, UV-blocking properties, antimicrobial activities, and commercial viability has been reported. These MOF functionalized textiles can be used as highly effective protective textiles.

The study also demonstrates the development of a ZIF-8 NPs-based finish for polyester textiles for malodor adsorption and to prevent microbial growth. ZIF-8 NPs with an average size of

~60 nm were synthesized by a water-based procedure at ambient temperature and applied in small concentrations on a PET fabric using a commercial polyurethane binder and crosslinker. The ZIF-8 functionalized polyester fabric (ZIF-8@PET Fabric) was characterized for its morphology and functionalities.

In comparison to the control PET fabric, the ZIF-8@PET fabric has a significantly higher surface area. The reported fabric exhibited outstanding wash durability, malodor adsorption, and antibacterial activity. The fabrics were found to adsorb high concentrations of three odor-causing model compounds, such as isovaleric acid, indole, and nonenal, and could effectively inhibit the bacterial growth of *E. coli* and *S. aureus*. Further, the fabric functionality was retained even after several wash cycles and could be reused repeatedly.