Enzyme-powered micromotors based on hierarchical porous MOFs

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Bioinspired micro-/nano-motors are artificial micro-/nano-machines that can convert various forms of energy to propel their movement [1]. For example, the motion of some of these micromachines can be precisely controlled by application of external physical stimuli including magnetic, electric and acoustic fields [2, 3]. Inspired by the study of microorganisms, researchers have been exploring also the use of available chemical energy from the local environment to trigger and sustain self-propulsion [4]. Within this research direction, Metal-Organic Frameworks (MOFs) - a class of extended materials synthesized via a modular approach from inorganic (metal clusters or ions) and organic linkers [5] – offer excellent opportunities for the design and synthesis of self-propelled micromotors. MOFs typically possess ultra-high surface areas that allow facile access to densely populated catalytically active sites imbedded within their pore networks. Through careful design these catalytic sites can be exploited to convert chemical energy into kinetic energy resulting in self-propulsion of the MOF crystal [6]. In addition, rigidity, density, crystalline pore organization and pore size of MOFs can be optimized to carry out a swimming-type motion [7].

Recent advance in pore engineering combined with progress in enzyme immobilization in MOFs has enabled the fabrication of effective biocatalysts [8], and this progress was applied by Yang et al. [9] to design a MOF-based biocomposite that showed autonomous motion. In this study, the MOF-based micro-motors were powered by the enzyme catalase, which catalysts the decomposition of H_2O_2 to O_2 and H_2O, immobilized in a hierarchical porous Zirconium-based MOF. The authors prepared micro-sized MOF crystals, Zr-fcu-azo/sti-30%, by mixing 4,4′-azobenzenedicarboxylic acid and 4,4'-stilbenedicarboxylic acid linkers to $ZrCl_4$ in DMF under acidic, solvothermal conditions. Ozonolysis of the washed and dried crystals selectively oxidized the olefin functional group of the linker generating a hierarchically porous framework that possessed a pore size distribution of sufficient size to accommodate catalase (Cat, radius of gyration ca. 4 nm [10]). Subsequent to immobilizing catalase Cat-on-Zr-fcu-azo/sti-30% system, termed MOFtor, was immersed in an aqueous solution with H_2O_2 and surfactant (Triton X-100). Rapid decomposition of H_2O_2 by the catalase yielded O_2 gas that imparted ballistic propulsion. The authors suggested that the combined effects of porosity, surface defects and crystal aggregation in the MOFtors enhanced the accumulation O_2 bubbles for jet-like propulsion. It is noteworthy that the authors found high bubble production only in the presence of Triton X-100. They surmised that the surfactant facilitated both the formation and the stabilization of bubbles by reducing the surface tension of the liquid.

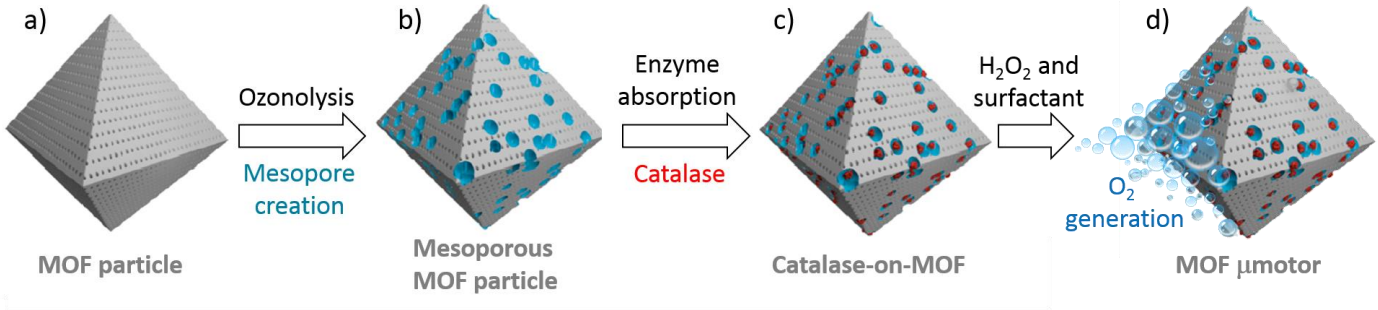

Fig. 1. Schematic representation of the multistep process used to synthesize the MOFtors. Copyright 2020, American Chemical Society [9].

Confocal analysis of the biocomposite revealed that catalase was spatially located within mesopores at the subsurface region of the MOF crystals. As a result the additional micro-pores of the MOFs remained available to adsorb guest molecules. To demonstrate the capacity of the biocomposites to adsorb additional cargo the authors exposed the MOFtors to rhodamine B. Remarkably, the adsorption capacity of rhodamine B within the catalase-powered MOFtor in the H_2O_2 and Triton X-100 solution exceeded that measured in pure water. This data suggests that enhanced guest uptake was induced by the motion of MOFtors and points towards the potential application of such systems in environmental detoxification.

In summary, Yang and co-workers have shown how an enzyme immobilized in a hierarchical porous MOF can yield a new generation of micromotors. Considering the rapidly increasing number of MOF materials, advances in pore engineering and structuralization, along with our growing understanding of enzyme in MOFs [8, 11, 12], it can be anticipated that this study will stimulate multidisciplinary research in the fabrication of MOF-based micromotors powered by enzymes. The pursuit of such chemistry will be motivated by the excellent promise that MOF materials show in areas such as drug delivery [13] and pollutant sequestration. [14]

Acknowledgments

P.F. acknowledges European Research Council under the European Union's Horizon 2020 Program (FP/2014–2020)/ERC Grant Agreement no. 771834 – POPCRYSTAL.

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Graphical Abstract

Enzyme-powered MOFtors with hierarchical porosity self-propelled by oxgen bubbles from Catalse immobilised in mesopores enhance uptake of dye molecules in micropores during propulsion.