



Recent advances in enzyme immobilization techniques: Metal-organic frameworks as novel substrates



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Contents

1. Introduction	30
2. Metal-organic frameworks (MOFs)	31
2.1. Synthesis of MOFs	31
2.2. Properties and applications of MOF	32
3. Recent emergence of MOFs as novel enzyme immobilization substrates	32
3.1. Protocols of synthesizing enzyme-MOF matrices	33
3.2. Surface immobilization	33
3.3. Diffusion into the pores of MOF	36
3.4. <i>In-situ</i> encapsulation of enzyme within MOF	37
4. Critical assessment of the different MOF-enzyme processes	38
5. Conclusions	39
Acknowledgments	39
References	39

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ABSTRACT

In the past few years, metal organic frameworks (MOFs) have drawn increasing research interest as bio-immobilization support materials. The unique properties of MOFs, including tunable porosity, desirable functionality, extremely high surface area, and chemical/thermal stability, have motivated a considerable interest in exploiting them as a potential matrix for enzyme immobilization. Improvements in the biocatalyst efficiency, promising recyclability, enhanced accessibility to active sites, and a high loading capacity are the main features of the novel MOF-enzyme supports. This review aims to cover the recent progress in the application of MOFs as enzyme immobilization supports. We discuss different approaches used in the development of MOF-enzyme biocatalytic supports, such as surface adsorption, diffusion, and *in-situ* encapsulation. The trends in current developments and the significance of each strategy are critically reviewed in this paper.

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1. Introduction

Metal organic frameworks (MOFs) are porous crystalline organic-inorganic hybrid materials with an architecture quite similar to zeolites, but with additional flexibility. Two components, i.e., metal

ions and multidentate ligands, assemble in different combinations through coordinate bonds to form versatile 3-D extended structures exhibiting novel topologies with exceptional intrinsic properties [1]. The morphology and functionality of MOFs can be tailored for desired applications unlike other nanoporous materials such as zeolites, silica, and carbonaceous materials. Over the past two decades, unparalleled growth in the number of research and review publications related to various aspects of MOFs has occurred [2–7]. The related developments have now very well established the MOFs as advanced functional materials with exceptional properties such as ultrahigh porosity, diverse functionality, and incredibly large surface area (even up to 6000 m²/g) [8,9]. Their optical, catalytic,

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magnetic, and electrochemical properties have attracted enormous research attention [6,10–12]. The MOFs have been developed and explored in diverse technological areas including molecular sensing, gas-storage, gas and molecular separation, catalysis, bio-imaging, and drug delivery [6,11,13–23]. MOFs have also been explored extensively as guest-responsive bio-immobilization substrates due to their large surface area, well-defined porosity, and the presence of rich palettes of functional groups [14,24]. Different bioactive molecules like DNA, drugs, enzymes, and other proteins have been immobilized on MOFs and have been demonstrated in a variety of applications [25–27].

Enzymes are natural catalysts that have been exploited by humans since ancient times. The ancient Egyptians produced beer and wine through fermentation processes, which were facilitated by enzymatic reactions [28]. Enzymes are three dimensional proteinaceous molecules made up of folded linear chains of amino acids. The sequence of amino acids then determines the structure along with functional catalytic activity of enzyme [29]. The size of enzymes may range from 62 (e.g., monomer of 4-oxalocrotonate tautomerase) to over 2500 amino acid residues. The presence of enzymes increased the reaction rate substantially (e.g., by order of 10^6) without changes in the reaction equilibrium [30]. They can indeed accelerate biochemical reactions by lowering the activation energy without being actually consumed in the reaction [31]. The activity of an enzyme, i.e., 'enzyme unit (U)', is thus quantitatively expressed as the amount of enzyme (1 U) that catalyzes the reaction of 1 nmol of substrate per min. Enzymes have replaced chemical catalysts in many processes due to their excellent properties including high specificity, easy production, and green chemistry [32]. As advances in knowledge and technology have widened the understanding of enzymatic processes, it has become possible to produce enzymes with analytical grade purity in a cost effective manner. This has accelerated their uses in health care, chemical, and food industries [28].

The widespread application of enzymes is still thwarted by their instability in harsh operational conditions, low shelf-life, and difficulty in recycling [33]. The immobilization of enzymes on solid supports is very important for overcoming these problems. As compared with the solubilized form, immobilized enzymes provide a high enzyme to substrate ratio, efficient digestion, and easy handling [32]. Therefore, the development of robust, stable, and efficient biocatalytic support platforms has become a major research avenue. Various types of materials, e.g., inert polymers and inorganic materials have been investigated as immobilization supports for enzymes by employing different experimental strategies [28,32,33]. MOFs are the latest entry in this list of support materials. Despite the relatively small related research output to date, they are emerging rapidly as alternative candidates due to their extreme utility in various biocatalytic applications.

The combination of MOFs and enzymes can simultaneously offer an enhanced loading/immobilization of biomolecules to help improve efficiency in many catalytic applications. As the MOFs have one of the best surface area properties amongst all the support materials, their potential in this particular area can be considered quite high. The availability of diverse approaches to synthesize an MOF-enzyme system (e.g. surface functionalization, diffusion into the pores, and *in-situ* entrapment during synthesis) can also broaden the chance for stable immobilization (fixing) of the enzyme. As enzymes are soluble molecules in their native form, their immobilization on solid supports (like MOFs) can greatly support their recovery (for reuse). The immobilized enzymes can also be easily separated from the reaction mixture by filtration or centrifugation. After separation from the reaction mixture, it can be easily washed off from the enzyme supports with suitable solutions/buffer reagents so that they can be purified and stabilized against deactivation.

Primarily, the MOFs with sufficiently large pore diameters (e.g., Cu-MOF (1.78 nm), Tb-TATB (3.9 and 4.7 nm), Mn-MOF (3.4 nm), and PCN-333 (4.2 and 5.5 nm)) have been investigated as potential candidates for the enzyme immobilization. The presence of functional groups on the surface of MOFs may aid to the desired adherence of enzymes. For example, MIL-101 (a Cr based MOF) possess pendent carboxylic groups of ligand, which can be used for covalent attachment of the enzymes. Lately, there have been some serious research efforts to synthesize the MOFs (e.g., ZIF-8, Tb-BDC, MIL-88, and HKUST-1) under room temperature/ambient conditions so as to help ensure the preservation of enzyme activity. The present review has been written to describe the latest developments in this particular scientific area with immense technological significance.

2. Metal-organic frameworks (MOFs)

The first modern-era report of metal-organic frameworks (MOFs) appeared in 1995 when Yaghi and Li showcased the synthesis of a cationic MOF with nickel and pyridine as the metal ion and organic linker, respectively [34]. Thereafter, as another important contribution, Li et al. reported the crystalline structure of MOF-5 in 1999 [35]. Since then, many categories of metal ions have been exploited, mainly including transition metals, *p*-block elements, alkaline earth metals, and actinides [36]. The co-ordination number of the metal component defines different possible molecular geometries, e.g. linear, T-/Y-shaped, square-planar, square-pyramidal, octahedral, trigonal-bipyramidal, trigonal-prismatic, and pentagonal-bipyramidal [37]. In the case of organic linkers, the use of multi-dentate organic ligands with varying size and structure enables control of the architecture and properties of the synthesized framework [5]. The most commonly used organic linkers include carboxylates, amines, nitrates, phosphates, and sulfonates. Among these, anionic carboxylates have higher affinity to metal ions as compared with the cationic ones. Typically, the MOFs possess highly unique and/or exceptional properties such as tailorable ultrahigh porosity, large surface area (even up to 6000 m²/g), diverse functionality, high thermal/mechanical stability, and good opto-electronic properties [38]. Some of recent advancements in securing the stability of MOFs in the aqueous phase and/or at high temperature conditions have helped widen their applicabilities further [39]. Fig. 1 summarizes the different aspects of MOF technologies including synthesis protocols, properties, and applications.

2.1. Synthesis of MOFs

In light of the immense applicability of MOFs, researchers around the globe have been exploring diverse routes for their synthesis that are cost-effective, green, and rapid. Such routes can be classified as solvothermal, slow evaporation/direct precipitation, microwave assisted, electrochemical, mechanochemical, and sonochemical methods [14,36,40]. Solvothermal approach is one of the widely used throughput methods for the synthesis of MOFs [36]. In contrast, slow evaporation approach is one of the most convenient routes of all available synthesis methods, as it does not require any external energy source [36]. However, the requirement of a long synthesis time (usually for several hours to days) is a major hurdle for such approach [41]. The microwave based method has been applied on chemically inert metal ions to improve the crystallinity of MOFs by increasing the temperature homogeneously in a localized zone [40]. The electrochemical and mechanochemical methods have also been suggested to offer additional degrees of freedom in the synthesis of MOF [42]. In the case of sonochemical technique, ultrasonic waves are also used to synthesize MOFs. The cavitation created by ultrasonic waves leads to a sudden rise or fall in the temperature/pressure conditions, creating hot spots to facilitate rapid crystallization of homogeneous crystals of MOFs [36]. In addition, MOFs can also

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