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Review

Optimization protocols and improved strategies for metal-organic frameworks for immobilizing enzymes: Current development and future challenges

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ABSTRACT

Metal-organic frameworks (MOFs) are a type of porous material that have tunable porosity, desirable functionality, extremely high surface area, and chemical/thermal stability. MOFs consist of metal containing nodes and organic ligands linked through coordination bonds. Owing to the unique properties of MOFs, there is considerable interest in using them as a potential matrix for enzyme immobilization. Recent studies have focused on developing enzyme-MOF composites with potential applications. Many MOF-enzyme composites exhibit excellent catalytic performance, far outperforming free enzymes in many aspects. This review summarizes recent developments in enzyme-MOF composites with special emphasis on novel synthesizing strategies, process optimization, and improvement of catalytic performance of the enzyme-MOF composites over free enzymes.

Contents

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1. Introduction

In the past few decades, enzymes have been widely accepted in diverse sectors owing to their ease of production, substrate specificity and selectivity, and green chemistry. However, the use of soluble enzymes for industrial applications is often hindered by their low operational stability, difficult recovery, and lack of reusability under operational conditions [1–3]. Immobilization of the enzymes is one of the most attractive concepts to overcome these drawbacks [4–7]. Compared to soluble enzymes, immobilized enzymes exhibit improved operational stability, enhanced enantioselectivity, easier reactor operation and product separation [8–10]. Moreover, the immobilized enzymes can be recycled to reduce the cost of the production processes [11–14]. The improved properties of immobilized enzymes are due to prevention of subunit dissociation via multisubunit immobilization [15], prevention of aggregation, autolysis or proteolysis by proteases [4,16], rigidification of the enzyme structure via multipoint covalent attachment [13], and generation of favorable microenvironments [10]. In contrast, the selectivity improvements via immobilization can be summarized as follows: alteration of the geometry of the active center via immobilization [17], stabilizing enzyme conformation [18], and elimination of diffusion limitation [19]. Additionally, coupled immobilization/purification of enzymes via control of the immobilization process can be achieved [20,21]. At present, enzyme immobilization methods include carrier-bound and carrier-free [1,22]. These methods present advantages and drawbacks. For example, the enzymes immobilized on solid matrices offer more effective control of the reaction processes, facile separation from the product, and enhanced enzyme stability in storage and operational conditions [21,22]. Furthermore, the support with excellent properties is very important for enzyme immobilization [23]. However, the volumetric activity of the biocatalyst and productivity of the reaction can be reduced simply as a result of the presence of the noncatalytic mass of the carrier [24–26]. Compared to carrier-bound immobilized enzymes, carrier-free immobilized enzymes have no need for extra inactive mass as a carrier, resulting in high space time yields and volumetric and catalyst productivities [27,28]. However, carrier-free immobilized enzymes are too fragile for many industrial applications in almost any kind of reactor configuration, and it is difficult to handle and fully recover these particles [29–31]. Moreover, the internal mass-transfer limitations of the immobilized enzyme particles bring about a special accessibility problem for macromolecular substrates [32,33]. Furthermore, enzymes are exposed to the medium and may be inactivated by gas bubbles or proteolysis, etc [34]. Consequently, the choice of a suitable immobilization strategy depends on the chemical and physical properties of the enzyme and immobilization matrix.

Nanomaterials, such as nanoparticles, nanofibers, nanotubes, metal organic frameworks (MOFs), nanosheets and nanoflowers, have been used as novel supports for enzyme immobilization because of larger specific surface area and less diffusion limitation [35]. However, the conventional nanomaterials for enzymes are non-uniform, non-porous, have long-range ordering from the atomic to microscale, and require harsh conditions and extended periods of time for either material preparation or enzyme immobilization, thus leading to low protein-loading efficiency and severe reduction of enzymatic activity [35–37]. Unlike other nanomaterials, MOFs are compounds consisting of metal ions or clusters coordinated to organic ligands [38]. In the past few years, MOFs have been extensively applied for gas adsorption, separation, catalysis, and drug delivery [38,39]. Recently, MOFs have been considered to be promising candidates for the immobilization of enzymes because of their high surface area and pore volume, ease of pore size tuning, facile modification on both metal nodes and ligands, and mild synthetic conditions [40–42]. Moreover, MOFs are perfectly suited to stabilize conformation of enzymes through specific host-guest interactions and/or confinement effects [43,44]. In recent years, the number of studies regarding preparing enzyme-MOF composites per year has increased rapidly, and various combination approaches have been developed [45]. Various MOFs have been applied to an increasingly wide selection of hydrolases and oxidoreductases, such as organophosphorus acid anhydrolase [46], lipase [47,48], trypsin [49], glycerol dehydrogenase [50], glucose dehydrogenase [51], and urease [52,56]. However, there have been few reviews specifically on enzyme immobilization in MOFs. Although reviews of definition and scope, characteristic features, and applications of enzyme-MOF composites have been described [26,53–55], process optimization and novel improved strategies for preparing enzyme-MOF composites have hardly been reviewed. In this review, we focus on process optimization in preparing enzyme-MOF composites, new improved strategies of preparing enzyme-MOF composites and the latest advances in preparing enzyme-MOF composites. Moreover, we discuss the improvements that MOF immobilization offer enzymes: reusability, catalytic activity, and stability.

2. Introduction to metal-organic frameworks

MOFs are porous coordination polymers consisting of metal containing nodes and organic ligands linked through coordination bonds [57]. Generally, MOFs possess highly unique and/or exceptional properties such as tunable ultrahigh porosity (up to 90% free volume), large surface area (beyond 6000 m^2/g), diverse functionality, high thermal/mechanical stability, and good opto-electronic properties [58,59]. Because of their exceptional properties and the extraordinary degree of variability for both the organic and inorganic components of their structures, MOFs have become an area of focus in the fast-growing fields of storage, separation, catalysis, biomedical applications, and sensor materials [60]. For example, some MOFs have been used for storage of gases (e.g., H_2, CH_4, CO_2, and NO) without the usual requirements of high pressure and/or compression [61,62], and some MOFs have been employed for the separation of toxic organic compounds (e.g., tetrahydrothiophene, benzothiophene, benzene, and toluene) [63,64]. Typically, synthesis routes of MOFs can be classified as solvothermal, slow evaporation/direct precipitation, microwave assisted, electrochemical, mechanochemical, and sonochemical [65,66]. Synthetic-method development has played a major role in the applicability of MOFs. Accordingly, the choice of the synthesis method for the MOF is determined by the type of the metal, organic linker, and/or by the type of targeted application.

3. General strategies for synthesizing enzyme-MOF composites

In principle, enzyme immobilization on solid supports is achieved through the formation of bonding and non-bonding interactions between enzymes and supports. To the best of our