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Biomimetic catalysts designed on macromolecular scaffolds

Yanzhen Yin[a,b], Zeyuan Dong[a], Quan Luo[a], Junqiu Liu[a,*]

[a] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, PR China
[b] College of Chemistry and Chemical Engineering, Qinzhou University, Qinzhou 535000, PR China

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ABSTRACT

Enzyme, an efficient and sophisticated biocatalyst, evolves into unique biomacromolecule with three-dimensional structure consisting of a linear sequence of amino acids and plays a crucial role in catalyzing biologically chemical reactions with high efficiency and selectivity in living system. For understanding the relationships between the enzyme structures and functions, the enzymatically catalytic mechanism, as well as for the potential applications, various biomimetic catalysts have been constructed to simulate the catalytic behavior of native enzymes. According to the wide studies in this area, the substrate recognition, specifically supramolecular interactions, and the cooperativity between the catalytic sites and substrate-binding sites have been regarded as pivotal factors for designing an efficient artificial enzyme. Up to now, large numbers of artificial enzymes have been constructed on various different scaffolds ranging from small molecular compounds, polymers, biomacromolecules to supramolecular assemblies and nanomaterials. Although most of the artificial enzymes showed moderate catalytic activities, encouragingly, some of them exhibited exciting high efficiency and selectivity. Compared to other scaffolds, macromolecules with their own advantages can endow enzyme models with enriched catalytic sites as well as the easy-achieved cooperation of the catalysis and recognition. This review will give an overview of the construction of artificial enzymes using macromolecules as scaffolds in the past decades, wherein various macromolecules containing copolymers, dendrimers, hyperbranched polymers, polymer microgels, supramolecules, imprinted polymers and biomacromolecules have been developed as scaffolds of artificial enzymes.

Contents

Abbreviations: ArSH, 3-carboxy-4-nitrobenzenethiol; CD, cyclodextrin; CDNB, 1-chloro-2,4-dinitrobenzene; CoCyc, Co(III) complex of cyclen; CPA, carboxypeptidase A; CTAB, hexadecyltrimethylammonium bromide; CUOOH, hydroperoxide; Dap, L-2,3-diaminopropionic acid; DTT, dithiothreitol; Fe(ToCPP), iron(III)-α,α,α,β-meso-tetrakis(ortho-carboxyphenyl)porphyrin; Gbn, γ-globulin; GPx, glutathione peroxidase; GR, glutathione reductase; Grx1, *E. coli* glutaredoxin 1; 6HDNO, 6-hydroxy-D-nicotineoxidase; GSH, glutathione; GST, glutathione transferase; HVA, homovanillic acid; LCST, lower critical solution temperature; NPA, p-nitrophenyl acetate; NPP, p-nitrophenyl phosphate; PAMAM, poly(amidoamine); PCD, poly(chloromethylstyrene-co-divinylbenzene); PEI, polyethylenimine; PhSeSePh, diphenyl diselenide; PNIPAM, poly(N-isopropylacrylamide); PNPP, p-nitrophenyl picolinate; PQQ, pyrrolinoquinoline quinine; PVCL-Vim, poly(N-vinylcaprolactam-co-1-vinylimidazole); ROOHs, hydroperoxides; ROS, reactive oxygen species; sGDH, soluble glucose dehydrogenase; SMCs, smooth muscle cells; SOD, superoxide dismutase; TC, 1,5,9-triazacyclododecane; TCPP, tetra(4-carboxyphenyl) porphine; tren, tris(2-aminoethyl)amine; TSAs, transition-state analogs.

* Corresponding author. Fax: +86 431 85193421.
E-mail address: junqiuliu@jlu.edu.cn (J. Liu).

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1. Introduction

As a kind of sophisticated proteins, enzymes catalyze a myriad of reactions in complex cellular fluids, maintaining the internal metabolic balances quite well in living system in Nature [1]. Enzymes evolve into unique biomacromolecules with three-dimensional structures consisting of a linear sequence of amino acids and exhibit the characteristic of large molecules: their size and structure let reactions occur inside a hydrophobic and nonaqueous region of the protein while the outside of the protein has polar groups and is compatible with the aqueous solvents [2,3]. As known, enzyme catalyzes chemical reactions with tremendously high catalytic efficiency and selectivity. Compared to the non-catalytically chemical reactions the typical rate enhancements are 10^{10} to 10^{15} folds, at the identical condition the enzyme-catalyzed chemical reactions can be accomplished in 1 s but 300–30,000,000 years without enzymes [4]. There are some agreements that both the microenvironment provided by the three-dimensional structures and the dynamics of the segment motion in the structure of enzyme can contribute to the high catalytic efficiency [2]. Considering that enzymes play a biologically crucial role in catalyzing chemical reactions with high efficiency and selectivity in living systems, the researchers are allowed to use man-made materials to construct artificial enzymes for simulating the catalytic functions demonstrated by natural enzymes, and for overcoming the limitations of natural enzymes such as instability to heat, incompatibility with organic solvents, inapplicability to abiotic reactions. The design and preparation of artificial enzymes which possess high catalytic activities and selectivities being comparable to native enzymes become a long-term aim. Up to now, some of artificial enzymes have been endowed with high catalytic efficiency and selectivity and have been used as efficient catalysts in complex cellular fluids. At the same time, some other artificial enzymes would be mainly used as industrial catalysts which catalyze a key target reaction in chemical reactor and will not be required to select substrates from many hundreds in the same solution, whereas enzymes routinely do in the cells [5]. Therefore, as successfully artificial enzymes, they should exhibit appropriate catalytic efficiency and selectivity to act as satisfactory catalysts for applications in complex cellular fluids as well as in industrial process.

To obtain more information about native enzymes, researchers pioneered in characterization of the structures of native enzymes [6–9], exploration of the properties of catalytic mechanisms [4–12]. However, the construction of artificial enzymes offers a unique opportunity to understand enzymatic catalysis in detail by systematically varying and simplifying the functional groups in the active sites [13–18]. In fact, many useful insights into the structures, functions, and kinetics of enzymes were revealed by the contribution of the successful construction of artificial enzymes. Among these insights, several features of enzyme catalysis are particularly important for the design and redesign of artificial enzymes. Firstly, the hypothesis that the powerful catalytic behavior of enzymes could be explained by strong binding to the transition state species was reported by Pauling over 60 years ago [10] and discussed more in detail by Jencks [19]. According to the transition state theory, the enzyme active-site structure is most complementary to the transition state structure of the substrate. The additional binding interactions presenting in the transition state lowers the activation energy of the reaction. Secondly, as an