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Enzyme Mimics as Sustainable Alternatives to Natural Enzymes in Green Catalysis

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Abstract: *Catalytic systems that reduce environmental effect while maintaining high efficiency and selectivity are of great interest due to the quest of sustainable and green chemical processes. Although natural enzymes are among the most effective catalysts known, their practical use in large-scale and industrial chemical processes is frequently restricted by their high production costs, limited operational pH and temperature ranges, poor thermal and chemical stability, and challenges with recovery and reuse. To address these restrictions, enzyme mimics, often referred to as artificial enzymes or nanozymes, have emerged as promising sustainable alternatives. The search for sustainable and environmentally friendly chemical processes has led to a significant deal of interest in catalytic systems that minimize environmental impact while retaining high efficiency and selectivity. Although natural enzymes are among the most effective catalysts known, their practical use in large-scale and industrial chemical processes is frequently restricted by their high production costs, limited operational pH and temperature ranges, poor thermal and chemical stability, and challenges with recovery and reuse. To solve these limits, enzyme mimics, frequently referred to as artificial enzymes or nanozymes, have emerged as viable sustainable alternatives. Active-site modelling, electron transfer pathways, and substrate–catalyst interactions are highlighted in the important discussion of the mechanistic elements underlying enzyme-mimetic catalysis. Additionally, important uses of enzyme mimics in green catalysis are explored, such as ecologically friendly industrial processes, oxidation reactions, pollutant degradation, and sustainable organic transformations. Finally, current problems and future possibilities are outlined, highlighting the need for enhanced selectivity, reduced toxicity, and scalable synthesis to fully realize the potential of enzyme mimics as viable substitutes for natural enzymes in sustainable catalytic technologies.*

Keywords: Enzymes, Enzyme mimics, sustainable, nanozymes, Artificial Enzymes.

I. INTRODUCTION

The world's shift to environmentally friendly and sustainable technologies has been sped up by the growing environmental effect of conventional chemical manufacture. Based on the ideas of green chemistry, green catalysis seeks to eliminate dangerous materials, lower energy use, improve atom economy, and support renewable feedstocks. Because they directly affect reaction efficiency, selectivity, and waste production, catalysts are essential to accomplishing these goals. Although natural enzymes have become highly effective biocatalysts because of their exceptional specificity and ability to function in mild environments, their use in large-scale industrial processes is still limited by inherent drawbacks like low thermal stability, denaturation susceptibility, high production costs, and restricted operating windows. Enzyme mimics, also known as artificial enzymes or biomimetic catalysts, have drawn a lot of interest as environmentally friendly substitutes for natural enzymes in green catalysis in order to overcome these difficulties. These manufactured systems offer improved resilience, tunability, and economic viability while simulating the structural and functional properties of biological enzymes. Enzyme mimics attempt to duplicate key enzymatic characteristics such active-site layout, substrate recognition, transition-state stabilization, and catalytic turnover by combining ideas from materials science, coordination chemistry, nanotechnology, and molecular engineering.The highly ordered three-dimensional protein structures that natural enzymes use to accurately position substrates and stable reaction intermediates allow them to attain remarkable catalytic efficiency. But since they depend on fragile tertiary and quaternary structures, they are vulnerable to non-physiological factors like high temperatures, organic solvents, mechanical stress, and extremely high pH. Furthermore, the expenses of the entire process are frequently greatly increased by the purification, immobilization, and storage of enzymes. Despite their inherent environmental benefits, these limitations prevent their wider industrial implementation.

By using sturdy inorganic, organic, or hybrid scaffolds that maintain catalytic functioning without relying on delicate protein structures, enzyme mimics get around several of these problems. For instance, catalysts based on nanomaterials (nanozymes) have excellent thermal and chemical durability and behave like enzymes. Metal-organic frameworks (MOFs) offer porous structures that can be adjusted to accommodate catalytic centers that resemble enzyme active sites. Through custom binding cavities, molecularly imprinted polymers (MIPs) provide selective substrate recognition, and artificial metalloenzymes combine synthetic or biological frameworks with transition-metal catalytic centers to obtain great selectivity in sustainable reactions. When combined, these systems combine the selectivity of enzymes with the robustness of synthetic catalysts, bridging the gap between biocatalysis and homogeneous catalysis.

The catalytic efficiency and selectivity of enzyme mimics have been greatly enhanced by recent developments in computer modeling, sensible catalyst design, and nanoscale engineering. The full replication of the dynamic conformational flexibility found in biological systems, the regulation of intricate multi-step reaction pathways, and the attainment of enzyme-level precision still present difficulties. To maximize structure–activity connections and broaden the application of enzyme-mimetic catalysis in sustainable chemical transformations, further multidisciplinary research is necessary.

The creation, categorization, workings, and uses of enzyme mimics as environmentally friendly substitutes for natural enzymes in green catalysis are examined in this study. Their design approaches, catalytic capabilities, environmental advantages, and new opportunities for industrial application are highlighted. The study demonstrates, via rigorous examination, how enzyme mimics are changing the field of sustainable catalysis and advancing ecologically friendly chemical technology.

II. LITERATURE REVIEW

Metal-organic framework-based nanozymes: types, activity regulation and analytical applications

When compared to natural enzymes, nanomaterial-based enzyme-mimetic catalysts have garnered a lot of attention because of their exceptional physicochemical stability and versatility under a variety of operating settings. Among these materials, metal–organic frameworks (MOFs) have become interesting prospects for nanozyme research. MOFs are a family of highly organized crystalline porous structures made from metal ions or metal clusters coordinated with organic linkers. They are especially well suited for creating catalytic systems that resemble enzymes because of their structural tunability, compositional diversity, and functional variability resulting from configurable metal nodes and organic ligands.Even though this field is growing quickly, there are still few thorough talks that concentrate on methods for improving the catalytic activity of MOF-based nanozymes. We first give a thorough summary of exemplary MOF-based nanozymes in this study, coupled with in-depth analyses of their catalytic processes. We then highlight important strategies used to enhance and modify their enzyme-mimicking activity. The practical relevance of these materials is subsequently demonstrated by examining their analytical applications. In order to support the logical design and high-performance development of next-generation MOF-based nanozymes, we conclude by providing a critical assessment of the present difficulties and prospects for the future. [1]

Nanomaterials with enzyme-like characteristics (nanozymes): next-generation artificial enzymes (II)

A type of nanomaterials known as nanozymes has catalytic qualities similar to those of enzymes (Chem. Soc. Rev., 2013, 42, 6060–6093). They were initially created to address the drawbacks of conventional artificial enzyme systems and natural enzymes. Since the release of the seminal review in 2013, the field of nanozymes has made significant strides due to the quick advancements in nanotechnology, biotechnology, catalysis, and computational modeling.This review starts by classifying various nanozyme types and detailing typical nanomaterials, together with their suggested

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catalytic processes when accessible, in order to highlight these advancements. The several strategies for controlling and improving nanozyme activity and specificity are then described. The diverse uses of nanozymes are then discussed, including environmental cleanup, theranostic platforms, and biological diagnostics and imaging. The review concludes by outlining the main obstacles that now limit nanozyme performance and suggesting possible future paths to advance this field of study. This article's overall goals are to give a thorough summary of the current status of nanozyme research and to encourage more advancements and creativity in the area. [2]

Nanoceria-Based Artificial Nanozymes: Review of Materials and Applications

Because of their strong stability, high catalytic efficiency, and affordability, nanozymes—nanostructured materials that resemble enzymes—have garnered a lot of interest. Cerium oxide nanomaterials (CeO_2 NMs) are distinct from other nanozymes due to their inherent enzyme-like properties and special physicochemical properties. They can mimic a variety of natural enzymes, such as phosphatase, nuclease, photolyase, oxidase (OXD), peroxidase (POD), catalase (CAT), and superoxide dismutase (SOD).CeO_2 NMs' ability to mimic enzymes is closely related to their surface chemistry, namely the existence of oxygen vacancies (OVs) and the reversible transition between Ce^{4+} and Ce^{3+} states. Their catalytic activity and redox behavior are greatly influenced by these characteristics. Furthermore, surface engineering can greatly increase or decrease their catalytic activity by adding metal ions, tiny organic molecules, or polymeric coatings.CeO_2 nanoparticles have emerged as intriguing candidates for a variety of biochemical applications, including biocatalytic processes, environmental pollutant degradation, antimicrobial treatment, biosensing, and therapeutic interventions, because of these adaptable qualities. The development of CeO_2-based enzyme mimics is reviewed, along with their catalytic processes, surface modification techniques, and applications as natural enzyme replacements in various biochemical settings. In order to offer insightful information for the logical development and useful application of these cutting-edge artificial enzyme systems, we also discuss current constraints and potential future developments. [3]

Enzyme mimics in-focus: Redefining the catalytic attributes of artificial enzymes for renewable energy production

By redefining catalytic functionality and investigating the usage of artificial enzymes (AEs) in energy-related applications, this work demonstrates the advantages of enzyme mimetics. In the field of biocatalysis, nanozymes' intrinsic enzyme-like catalytic qualities have drawn more and more interest. The conventional knowledge of catalytic activity has been expanded by the emergence of AEs, opening up new avenues for biotechnology and sustainable energy technologies.One of the main forces behind the development of contemporary society is energy. Significant greenhouse gas emissions from the past 50 years' heavy reliance on fossil fuels have had a negative impact on the environment and public health. Coal, oil, and natural gas accounted for around 84% of the world's primary energy supply in 2019. This significant reliance highlights how urgently the world must move toward sustainable and renewable energy sources, such as biofuels and biohydrogen, in order to guarantee cleaner energy generation.However, there are a number of difficulties in using natural enzymes in renewable energy systems. Large-scale implementation is hindered by their high production costs, sensitivity to severe environments, and low operating stability. An appealing substitute in this situation is provided by artificial enzymes, which are synthetic or inorganic materials with clearly defined structures that mimic the catalytic properties of natural enzymes. Enzyme mimics, while still in the early stages of development, overcome many of the drawbacks of traditional enzymes. Through increased robustness, effectiveness, and affordability, they have a great deal of potential to boost the production of renewable energy. With a focus on their function in developing renewable energy technologies, this paper offers a thorough summary of artificial enzymes' potential as biocatalysts. [4]

Biodegradable enzyme-mimicking nanocatalysts: From degradation behavior to theranostic applications

A class of nanomaterials known as "nanozymes" has drawn interest as appealing alternatives to normal enzymes due to their innate enzyme-like characteristics. Low production costs, exceptional structural stability, tunable catalytic performance, and viability for large-scale manufacturing are some of their benefits. Interest in synthetic enzymes has grown significantly since the first discovery of nanomaterials with peroxidase-like activity, propelling significant advancements in nanomedicine research. However, safety difficulties, specifically nanotoxicity from long-term storage in biological tissues, have limited the therapeutic usage of nanozymes.The creation of biodegradable nanozymes has offered a practical way to get around these restrictions without sacrificing therapeutic effectiveness. Expanding their uses in diagnosis and treatment requires a deep comprehension of their catalytic mechanisms. To improve biocompatibility and reduce possible immunological reactions, it is equally crucial to elucidate their metabolic routes and breakdown behavior in vivo.The degradation mechanisms of biodegradable nanozymes, their enzyme-like catalytic capabilities and underlying reaction mechanisms, and current advancements in biomedical applications, such as therapeutic approaches and diagnostic imaging, are the three main topics that are methodically covered in this study. Furthermore examined are the technical challenges and present prospects in the development of biodegradable enzyme-mimicking nanocatalysts. By looking at these important aspects, the review hopes to encourage the logical development of biodegradable nanozymes with enhanced safety profiles, which will make it easier for them to go from precision medicine research to clinical use.While maintaining the catalytic properties of enzymes and providing stable, cost-effective substitutes for natural enzymes, biodegradable nanozymes offer a promising means of reducing the toxicity linked to persistent nanomaterial accumulation. This review thoroughly assesses their degradation mechanisms, catalytic principles, and medical uses in light of recent biomedical breakthroughs. It also draws attention to the obstacles that still stand in the way of successful clinical translation and optimal design. A better understanding of their catalytic action and degradation mechanisms will aid in the creation of safer and more effective precision medicine nanozyme-based devices. [5]

MOF nanozymes: active sites and sensing applications

The porous hybrid materials known as metal–organic frameworks (MOFs) are made up of metal ions and organic ligands. They have a lot of active sites that enable them to mimic the actions of natural enzymes, which makes them very appealing for sensing applications. This article provides a thorough overview of current developments in the use of MOFs to provide catalytically active sites for the production of nanozymes. MOFs use organic linkers and metal centers as catalytic sites, and their porous structures allow for the arrangement and stabilization of many functional units.Furthermore, MOFs can be chemically converted into derivatives such nanostructured metal compounds and porous carbon materials, which can increase their catalytic efficacy and broaden their use as nanozymes. The paper also looks at how MOF-based nanozymes are used in analytical sensing across several catalytic pathways, showing how they can increase the dynamic range, sensitivity, and specificity of detection. The importance of various active sites in influencing sensing performance is emphasized, as are methods for creating and assembling MOFs to optimize catalytic efficiency.The study provides guidelines for the logical design of next-generation catalytic nanomaterials by outlining future possibilities for MOF-based nanozyme research and highlighting important issues that must be resolved to advance the area.[6]

III. FUTURE SCOPE

A promising family of artificial enzyme mimics, Metal-Organic Framework (MOF)-based nanozymes have gained attention because of their high catalytic potential, modular chemistry, and adjustable porosity. Even though there has been a lot of development, there are still a number of areas for further study that could improve their sustainability, performance, and usefulness.

1. Customized Active Site Architecture and Mechanistic Understanding

To maximize enzyme-like activity, future studies should concentrate on the logical design of catalytic centers inside MOFs. Certain catalytic activities, such oxidase- or peroxidase-like activities, can be enhanced via structural engineering that aims to precisely position metal nodes and ligands. Deeper mechanistic insights and the conversion of

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empirical optimization into predictive design will result from a better theoretical knowledge of structure–activity correlations. [11]

2. Improving Reusability and Stability

Structural instability under harsher conditions or multiple catalytic cycles is a major drawback of many MOF nanozymes. Future research must create frameworks that are both highly active and more durable. Multiple cycles of integrity and catalytic performance can be maintained with the use of techniques like derivatization, post-synthetic modification, and composite creation. [12]

3. Green and Scalable Synthesis Techniques

The majority of MOF nanozyme synthesis techniques used today are complicated, expensive, and challenging to scale, which restricts their commercial viability. Future research should focus on scalable and environmentally friendly production techniques that use low-cost precursors, low-energy or solvent-free synthesis approaches, and continuous manufacturing technology. This will increase the economic viability of MOF nanozymes for use in industrial settings. [13]

4. Combining Smart Technologies

A new horizon for practical applications is the sophisticated integration of MOF nanozymes with smart platforms including point-of-care diagnostic systems, biosensors, and Internet of Things (IoT) devices. MOF nanozymes can be integrated into automated and portable devices to enable real-time monitoring in biomedical and environmental settings, enhancing remote sensing and quick diagnoses. [14]

5. Cascade Catalysis and Multifunctionality

MOF nanozymes can be designed to imitate natural metabolic pathways by emulating cascade catalytic events or multi-enzyme mimicking activity. In mild and sustained conditions, this could allow for one-pot conversions in complex chemical syntheses. [15]

6. Biomedical Translation and Biocompatibility

MOF nanozymes have enormous promise for use in biological fields such oxidative stress management, biosensing, and targeted therapies. To enable safe clinical translation, future studies should concentrate on pharmacokinetics, biocompatibility, and in vivo stability.

7. Remediation of the Environment and Sustainable Catalysis

Green environmental processes like pollution degradation, greenhouse gas conversion, and sustainable chemical production can benefit greatly from the employment of MOF nanozymes. Investigating nanozymes for resource recycling, air purification, and water treatment will connect catalytic design with global sustainability issues.

IV. CONCLUSION

In conclusion, in green catalysis, enzyme mimics in particular, nanozymes and other biomimetic catalysts have shown great promise as sustainable substitutes for natural enzymes. Artificial enzyme mimics use designed nanomaterials to provide strong catalytic activity under a variety of challenging conditions, in contrast to natural enzymes, which are frequently constrained by low stability, high production costs, and limited operational ranges. In addition to retaining a large portion of the catalytic effectiveness and selectivity of real enzymes, nanozymes, metallic complexes, MOF-based systems, and other artificial catalysts frequently outperform them in terms of stability, scalability, and ease of synthesis.Transition metal oxides, carbon-based materials, noble metal nanoparticles, and metal-organic frameworks (MOFs) are examples of nanomaterials with enzyme-like properties. These materials have demonstrated a variety of enzyme-mimicking activities, including oxidase, peroxidase, and catalase, and have been effectively used in biochemical conversions, pollutant degradation, biosensing, and environmental remediation. The performance of natural enzymatic systems can be approached by MOF nanozymes, which combine the high surface area, variable pore structure, and diversity of active sites of MOFs with biomimetic catalytic function. They also add the benefits of heterogeneous catalysis and recyclability.The range of green catalytic applications is further expanded by these enzyme mimics, which make it easier to construct sophisticated catalytic systems for energy-related activities, selective transformations, and cascade reactions. The efficiency, selectivity, and practical value of artificial enzymes can be greatly improved by strategic alterations, such as surface functionalization, bimetallic synergy, and the addition of photocatalytic or stimuli-responsive capabilities.Notwithstanding these developments, there are still important obstacles to overcome, such as the requirement to enhance substrate selectivity, attain more sophisticated control over reaction processes, and further reduce the performance gap with natural enzymes in terms of catalytic specificity. To fully exploit the potential of enzyme mimic catalysis, ongoing interdisciplinary efforts combining computational design, mechanistic insights, sustainable synthesis techniques, and application-oriented research will be crucial. However, the creation of synthetic enzyme mimics represents a revolutionary step in green chemistry, providing environmentally friendly, economical, and adaptable substitutes for natural biocatalysts in a variety of catalytic applications. [7][8][9][10]

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