Progress in Research on Nanozyme Modification

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Abstract

As a class of nanomaterials exhibiting enzymatic properties, nanozymes have demonstrated immense potential for application in fields such as biosensing, disease diagnosis, and environmental protection, owing to their advantages of low cost, high stability, and tunable catalytic activity. However, natural nanozymes still suffer from limitations regarding catalytic efficiency, substrate specificity, and biocompatibility, which restrict their further practical application. Consequently, the optimization of nanozymes through various modification strategies has emerged as a focal point of research in this field. This review summarizes the primary strategies for nanozyme modification developed in recent years-including surface modification, doping and defect engineering, nanocomposite formation, and structural regulation-and elaborates on the mechanisms by which these distinct modification methods influence the catalytic performance of nanozymes. Furthermore, the paper summarizes the latest advancements in the application of modified nanozymes across biomedical, environmental remediation, and industrial catalysis sectors. It also offers perspectives on the challenges and prospects facing their future development, with the aim of providing a reference for the design and development of high-performance nanozymes.

Keywords

Nanozymes, Modification strategies, Catalytic mechanisms, Biomedical applications, Environmental remediation

Introduction

With the rapid advancement of nanoscience and nanotechnology, nanozymes-nanomaterials exhibiting enzyme-like catalytic activity-have gradually emerged as a research hotspot across fields such as biocatalysis, environmental remediation, and medical diagnostics. While traditional enzymes serve as highly selective and efficient biocatalysts, their limitations in practical applications have become increasingly apparent. These include sensitivity to environmental conditions (such as temperature and pH), inherent instability, and high production costs. Consequently, the search for artificial catalysts to serve as alternatives to natural enzymes has become a primary focus for researchers. Nanozymes, by virtue of their exceptional stability, cost-effectiveness, and broad application prospects, have thus become the new favorites in this research landscape.

Nanozymes are defined as nanomaterials that manifest enzyme-like catalytic activity stemming from their unique physicochemical properties and structural characteristics. They are capable of mimicking the catalytic functions of natural enzymes, facilitating a diverse array of biochemical reactions such as redox processes, ester hydrolysis, and the generation of reactive oxygen species [1]. Compared to natural enzymes, nanozymes offer numerous advantages, including superior thermal and chemical stability, as well as the capacity to function effectively under extreme environmental conditions [2]. The catalytic performance of nanozymes is influenced not only by their intrinsic physicochemical properties (e.g., size, shape, and surface charge) but also intimately linked to the material’s surface functional groups, electronic structure, and defect structure [3]. Through the implementation of rational modification strategies, the catalytic efficiency and selectivity of nanozymes can be further enhanced, thereby expanding their potential for application across various disciplines.

In recent years, significant progress has been made in research regarding the modification of nanozymes. Researchers have employed methods such as surface functionalization, doping, and nanocomposite formation to precisely tune the structure and properties of nanozymes, thereby boosting their catalytic activity and selectivity. These modification strategies not only serve to optimize the enzyme-like activity of nanozymes but also enable them to adapt to and function within more complex reaction systems [4,5]. For instance, doping with metal ions can greatly enhance the redox activity of nanozymes, while surface functionalization helps to improve their affinity toward specific substrates [6].

The modification of nanozymes holds immense promise for widespread application in chemical catalysis and demonstrates significant value in fields such as biomedicine and environmental protection. In the realm of biosensing, nanozymes have already been extensively utilized for applications ranging from the detection of biomolecules to the identification of pathogens [7]. For instance, by harnessing the peroxidase-like activity of nanozymes, highly sensitive detection sensors can be designed for early-stage cancer screening [8]. In the realm of environmental pollution control, modified nanozymes are employed in environmental remediation tasks such as water purification and heavy metal removal [9]. Furthermore, nanozymes have demonstrated immense potential in various medical applications, including tumor therapy, antibacterial treatments, and antiviral interventions [10]. Although research into nanozyme modification has yielded notable achievements, several challenges remain. For example, key questions currently driving research include how to enhance the catalytic efficiency of nanozymes and how to address issues regarding their stability both in vitro and in vivo. They also include how to devise modification strategies capable of adapting to complex reaction environments [11,12]. Looking ahead, with the continuous emergence of novel nanomaterials and the further advancement of modification strategies, the scope of nanozyme applications is expected to broaden significantly. Their catalytic performance is also poised to undergo even more substantial enhancements.

This review systematically summarizes the classification, catalytic mechanisms, and modification strategies of nanozymes. It focuses specifically on examining how various modification methods contribute to enhancing nanozyme performance. It concludes by offering perspectives on future research directions and potential applications in the field of nanozyme modification.

Classification and basic mechanisms of nanozymes

Nanozymes are a class of nanomaterials that have emerged in recent years, possessing enzyme-like catalytic activity. By mimicking the catalytic mechanisms of natural enzymes, they facilitate a variety of chemical reactions, including redox reactions, ester hydrolysis, and the generation of reactive oxygen species. Compared to natural enzymes, nanozymes offer numerous unique advantages, such as superior stability, low cost, and tunable catalytic properties. Consequently, research into nanozymes has garnered widespread attention. Based on their catalytic properties, material composition, and application fields, nanozymes can be categorized into various types, each characterized by distinct catalytic mechanisms and unique application potential.

Classification of nanozymes

(1) Classification by catalytic type

a) Oxidoreductase-like nanozymes

This category primarily comprises materials exhibiting redox catalytic activity-such as those mimicking peroxidases, peroxiredoxases, and oxidases. Representative examples of oxidoreductase-like nanozymes include metal oxides (e.g., Fe_3O_4, MnO_2, CeO_2), which facilitate redox reactions and play pivotal roles in fields such as biosensing and environmental monitoring.

b) Hydrolase-like nanozymes

Hydrolase-like nanozymes catalyze reactions involving the cleavage of ester bonds and general hydrolysis. They are widely utilized in fields such as drug delivery and environmental remediation. Typical materials in this category include certain metal oxides or phosphate-based nanomaterials that possess hydrolytic activity, enabling them to exhibit catalytic performance akin to natural hydrolases during hydrolysis reactions.

c) Lyase-like nanozymes

Lyase-like nanozymes achieve catalysis primarily by facilitating molecular cleavage reactions. Metal nanoparticles or organic-inorganic composite materials can mimic the catalytic activity of natural lyases in specific reactions, demonstrating excellent catalytic efficiency and selectivity [13].

(2) Classification by material composition

a) Metal/Metal oxide nanozymes

Metal and metal oxide nanozymes constitute the most common type of nanozymes. Metal oxides - such as Fe_3O_4, MnO_2, and CeO_2 - are widely utilized in fields such as biosensing, environmental remediation, and therapeutic medicine due to their excellent catalytic activity and stability. Their catalytic activity can be enhanced by tuning the material's crystal structure, doping with metal elements, or through surface modification [14].

b) Carbon-based nanozymes

Carbon-based nanozymes are typically nanozymes fabricated from carbon materials such as graphene, carbon nanotubes, and fullerenes. These materials not only possess superior electrical conductivity but also provide an abundance of active sites during catalytic reactions; consequently, they are frequently employed in electrochemical sensing and catalytic processes [15].

c) Metal-organic framework nanozymes

Metal-organic frameworks (MOFs) have garnered extensive research attention in the field of nanozymes in recent years, owing to their high specific surface area, tunable porous structures, and inherent catalytic activity. By modulating the combination of metal centers and organic ligands, MOFs can exhibit excellent catalytic performance across a diverse range of catalytic reactions.

d) Composite nanozymes

Composite nanozymes are nanozymes constructed from combinations of dissimilar materials, for instance, composites comprising metal nanoparticles paired with carbon materials, or metal oxides paired with metal nanoparticles. Through the synergistic interplay of their distinct components, these composite materials typically deliver superior catalytic activity and enhanced stability compared to their single-component counterparts.

(3) Classification based on catalytic mechanism

a) Surface active site mechanism

In the catalytic processes of many nanozymes, the quantity and nature of surface-active sites directly dictate their catalytic activity. For example, coordinatively unsaturated metal atoms situated on the surface of metal nanoparticles or structural defects within the material often serve as the requisite active sites for catalytic reactions. By tuning the size and morphology of the nanoparticles, as well as applying surface modifications, the concentration of these active sites can be significantly increased, thereby boosting catalytic efficiency [16].

b) Electron transfer mechanism

In the catalytic processes involving many metal oxides and carbon-based nanozymes, electron transfer plays a pivotal role. By modulating the electronic structure of the nanozyme, its catalytic activity can be effectively enhanced. During a catalytic reaction, nanozymes facilitate the reduction or oxidation of substrates through electron transfer processes, thereby accelerating the reaction rate and improving its selectivity [17].

(4) Defect mechanisms

The defective structure of nanomaterials plays a crucial role in catalytic reactions. Particularly in metal oxide nanozymes, defect sites serve as loci for the transfer of electrons, atoms, or molecules, thereby enhancing their catalytic activity. For instance, in CeO_2 nanoparticles, oxygen vacancies-acting as a form of defect structure-can effectively boost their catalytic activity in redox reactions [18].

Catalytic mechanisms of nanozymes

The catalytic mechanisms of nanozymes share similarities with those of natural enzymes, yet they also possess their own unique characteristics. Generally, the catalytic process of nanozymes comprises the following key steps:

(1) Substrate adsorption

The substrate first adsorbs onto the surface of the nanozyme; this process is governed by the surface properties of the nanozyme. For example, factors such as the surface charge and surface functional groups of metal oxides can all influence the substrate's adsorption capacity. By modifying the surface functionalization of the nanozyme, the affinity toward the substrate can be enhanced, thereby improving catalytic efficiency [19].

(2) Reactant conversion

Following substrate adsorption, the nanozyme catalyst facilitates the conversion of the substrate through mechanisms involving internal electron transfer, chemical reactions, and other processes. For instance, in peroxidase-like reactions, redox processes catalyzed by active sites on the nanozyme surface generate free radicals or other intermediates, which subsequently participate further in the catalytic cycle.

(3) Product release

Once the reaction is complete, the generated products desorb from the nanozyme surface, bringing the catalytic reaction to a close. Due to variations in their surface chemical properties, nanozymes composed of different materials exhibit distinct rates and modes of product release. This directly impacts the efficiency and stability of the catalytic reaction.

In summary, the catalytic process of nanozymes constitutes a sequential cycle comprising three key steps: substrate adsorption, reaction conversion, and product release. Any limitation in the efficiency of a single step within this cycle will constrain the overall catalytic performance. Consequently, optimizing these aforementioned steps through rational modification strategies stands as the core approach for enhancing the catalytic efficiency of nanozymes.

Nanoparticle enzyme modification strategies and mechanisms of performance regulation

The catalytic performance of nanoparticle enzymes can be significantly enhanced through various modification strategies. These modification methods not only boost the catalytic activity, selectivity, and stability of nanoparticle enzymes but also improve their adaptability across diverse environments. Common strategies for modifying nanoparticle enzymes include surface modification, doping and defect engineering, nanocomposite formation, and structural regulation. By employing these strategies, researchers can precisely tune the electronic structure, surface properties, and catalytic active sites of nanoparticle enzymes, thereby enhancing their catalytic efficiency and reaction selectivity.

This chapter integrates the discussion of modification strategies with the underlying mechanisms of performance regulation. It explores these topics through the lenses of surface modification, doping and defect engineering, nanocomposite formation, and structural regulation, with a particular focus on mechanisms involving the regulation of electronic structure, band structure, and defects.

Surface modification

Surface modification is one of the most widely adopted methods for enhancing the catalytic performance of nanoparticle enzymes. By functionally modifying the surface of nanoparticle enzymes, researchers can bolster their affinity for substrates, boost their catalytic activity, and improve their overall stability. Surface modification typically encompasses the following approaches:

(1) Inorganic modification

Inorganic modification primarily involves the introduction of inorganic substances, such as metal ions, metal oxides, or silica to improve the performance of nanoparticle enzymes. For instance, modification with metal ions can significantly enhance the redox activity of nanoparticle enzymes. By introducing metal ions of varying valence states onto the surface of metal oxides, it is possible to optimize their electronic structure, thereby accelerating the rate of catalytic reactions [20].

A quintessential example of surface modification using metal oxides involves the surface functionalization of CeO_2 nanoparticles to augment their peroxidase-like activity. Studies have demonstrated that introducing copper ions onto the surface of CeO_2 nanoparticles can lead to a substantial enhancement in their redox properties [21]. Furthermore, the surface modification of metal nanoparticles can also boost their catalytic efficiency; for instance, noble metals such as silver, gold, and palladium can exhibit potent catalytic capabilities through the active sites present on their surfaces [22].

(2) Organic modification

Organic modification typically entails the introduction of organic molecules - such as polymers, peptide chains, or biomolecules to improve the substrate affinity and catalytic characteristics of nanoparticle enzymes. Polymers such as polyethyleneimine and polyvinyl alcohol can effectively encapsulate nanoparticles, preventing their aggregation and precipitation in aqueous solutions while simultaneously enhancing the biocompatibility and stability of nanozymes [23].

Furthermore, surface modification through the introduction of biomolecules (e.g., antibodies, antigens, DNA and RNA) can endow nanozymes with specific recognition capabilities, thereby achieving higher selectivity in biosensors. For instance, modifying the surface of nanozymes with antibodies or peptide chains can effectively enhance their ability to recognize specific biomolecules [24].

(3) Covalent modification

Covalent modification involves chemically linking organic molecules or polymers to the surface of nanozymes via covalent bonds. This modification method serves to enhance the stability of nanozymes and improve their catalytic selectivity. For example, covalently conjugating functionalized molecules to the nanozyme surface can boost the nanozyme's water solubility, biocompatibility, and catalytic activity [25].

(4) Surface functional groups and interfacial effects

Surface functional group modification involves introducing various functional groups (such as carboxyl, amino, or hydroxyl groups) onto the surface of nanozymes to modulate their catalytic performance. These functional groups can influence the interactions between the nanozyme and its substrate, thereby improving catalytic efficiency. For instance, introducing amino groups onto the surface of Fe_3O_4 nanozymes can significantly enhance their catalytic activity toward hydrogen peroxide [26]. Moreover, functional group modification can improve the water solubility and biocompatibility of nanozymes, laying a stronger foundation for their application in fields such as biosensing and drug delivery.

Interfacial effects refer to the unique phenomena that arise when different materials or nanomaterials of distinct compositions come into contact. In the context of nanozymes, the catalytic performance is often enhanced through the formation of composites comprising different materials. For example, the combination of metal oxides with carbon-based materials can significantly boost the catalytic performance of nanozymes through interfacial effects. In CeO_2/graphene composite nanozymes, the catalytic activity of CeO_2 interacts synergistically with the electrical conductivity of graphene, resulting in a pronounced enhancement of their catalytic efficacy [27]. This interfacial synergistic effect not only boosts catalytic activity but also enhances the stability and reusability of nanozymes. The regulation of surface charge and hydrophilicity also influences the catalytic performance of nanozymes. By modulating the surface charge of nanozymes, their affinity for substrates can be enhanced, thereby boosting their catalytic activity. For instance, negatively charged metal-based nanozymes can engage in stronger interactions with positively charged substrates, thereby facilitating the catalytic reaction [28]. Furthermore, altering the hydrophilicity of nanozymes aids in improving their dispersibility within aqueous phases, which in turn enhances their catalytic efficiency.

Doping and defect engineering

Doping and defect engineering constitute another crucial strategy for improving the performance of nanozymes. By introducing heterologous metal ions (doping) or creating structural defects (such as oxygen vacancies and missing sites), the electronic structure of nanozymes can be altered, leading to further enhancements in their catalytic activity and selectivity.

(1) Doping

Doping involves introducing one or more elements (such as transition metals and rare earth metals) into the structure of a nanozyme to modulate its catalytic properties. For example, incorporating metal ions-such as copper, iron, or cobalt-into CeO_2 nanozymes can effectively boost their redox catalytic capabilities. These doped metal ions modify the electronic structure of the nanozymes, regulate their surface defects and active sites, and ultimately greatly enhance their catalytic activity [29].

Incorporating rare earth metal elements (such as neodymium and lanthanum) into nanozymes can also significantly elevate their catalytic activity. For instance, neodymium-doped metal oxide nanoparticles have demonstrated higher activity in biocatalytic reactions compared to their undoped counterparts [30]. Moreover, doping can improve the stability and anti-interference capabilities of nanozymes, enabling them to maintain excellent catalytic performance even within complex reaction systems.

(2) Defect engineering

Defect engineering refers to the strategy of improving the catalytic performance of nanozymes by deliberately introducing structural defects (such as oxygen vacancies and surface defects). These defect sites serve to provide additional active sites during catalytic reactions and facilitate the transfer of electrons or protons, thereby enhancing catalytic efficiency. Metal oxide nanoparticles (such as CeO_2 and MnO_2) can exhibit significantly improved catalytic performance through the introduction of defect sites, such as oxygen vacancies [31]. In CeO_2 nanozymes, the introduction of oxygen vacancies can enhance their catalytic activity in redox reactions. Particularly in peroxidase-like reactions, these defect sites effectively increase the nanozyme's affinity for substrates, thereby boosting its catalytic performance.

Oxygen vacancies constitute a common class of defects found in metal oxide nanoparticles, typically introduced by controlling synthesis conditions. The presence of oxygen vacancies provides additional pathways for electron transfer, thereby augmenting the redox activity of the nanozyme [32]. Furthermore, oxygen vacancies can modulate the surface energy distribution of the nanozyme, thereby enhancing its affinity for substrates.

Surface defects primarily encompass surface oxygen defects and surface atomic vacancies; these defects serve to provide a greater number of active sites, thereby strengthening the interactions between the nanozyme and its substrates. For instance, in MnO_2 nanozymes, the introduction of surface defects can boost catalytic activity, endowing the material with superior catalytic capabilities in redox reactions [33]. Beyond merely enhancing catalytic activity, surface defects can also improve the nanozyme's stability and resistance to interference.

The core principle of defect engineering lies in the precise regulation of defect types and concentrations to optimize the catalytic performance of nanozymes. By controlling synthesis parameters-such as temperature, atmospheric environment, and reaction duration-one can modulate the type and quantity of defects, thereby generating a greater abundance of active sites for catalytic reactions. Additionally, techniques such as doping and surface modification can be employed to fine-tune the distribution and stability of defects, further amplifying the catalytic efficacy of the nanozyme [34].

Electronic structure modulation

The catalytic performance of nanozymes is intimately linked to their electronic structure. By modulating the electronic structure of a nanozyme, its catalytic activity, particularly in redox and ester hydrolysis reactions can be effectively optimized. Electronic structure modulation is primarily achieved through the following approaches:

(1) Band structure modulation

Modulating the band structure is critical for enhancing the catalytic performance of nanozymes. For example, in metal oxide nanoparticles, alterations to the band structure influence the efficiency of electron transfer, which in turn impacts their catalytic performance. In metal oxides (such as CeO_2, Fe_3O_4, and MnO_2), tailoring the material's electronic structure allows for a significant enhancement of its catalytic efficiency. In particular, when the energy gap between the conduction band and the valence band within the band structure narrows, the effective separation and transport of electrons and holes become more efficient, thereby accelerating the rate of catalytic reactions [35].

For instance, doping with metal ions or modifying the morphology of the material can alter the band structure of nanozymes, thereby enhancing their catalytic activity. In the case of Fe_3O_4 nanozymes, the incorporation of cobalt ions (Co^{2+}) effectively serves to optimize the band gap width, resulting in enhanced catalytic activity toward peroxides [36]. Furthermore, tuning the type and concentration of dopants in nanozymes can also modulate their band structure, thereby optimizing their catalytic performance.

(2) Regulation of electron density

The regulation of electron density influences the flow and transfer of electrons during catalytic reactions. In the catalytic processes involving nanozymes, the efficiency of electron transfer directly dictates the rate at which the reaction proceeds. Through methods such as doping and surface modification, the electron density of nanozymes can be modulated to boost their catalytic capabilities. For example, in metal-based nanozymes, an electron density that is either excessively high or too low can lead to a decline in catalytic efficiency. Therefore, maintaining an optimal electron density is of paramount importance. By optimizing the choice of doping elements and their concentrations, the electron density can be precisely tuned to achieve enhanced catalytic performance.

Nanocomposites

Nanocomposite formation is a strategy involving the combination of disparate materials to harness synergistic effects. By integrating various types of nanomaterials, such as metals, metal oxides, and carbon-based materials-one can fully leverage the inherent advantages of each constituent material, thereby improving the catalytic activity, stability, and selectivity of nanozymes.

(1) Metal/Metal oxide composites

The formation of composites between metals and metal oxides is a widely adopted method for modifying nanozymes. For instance, Au@CuO composite nanozymes exhibit superior catalytic activity, a phenomenon attributed to intermetallic electron transfer effects. The hybridization of metal oxide nanoparticles with metal nanoparticles serves to bolster the stability of nanozymes while effectively facilitating the progression of catalytic reactions [37].

(2) Carbon-based materials

The formation of composites between carbon-based materials, such as graphene and carbon nanotubes and metal oxides has emerged as a focal point in nanozyme research in recent years. Carbon-based materials not only possess excellent electrical conductivity but also provide abundant surface-active sites, thereby enhancing their affinity for substrates. By fabricating composites of metal oxides and carbon-based materials, the catalytic performance of nanozymes can be effectively improved. For instance, composites of graphene and CeO_2 have demonstrated a significant enhancement in peroxidase-like activity [38].

Structural regulation

Structural regulation involves optimizing the catalytic performance of nanozymes by altering their physicochemical properties, such as morphology, size, and specific surface area. The size, shape, and surface structure of nanoparticles exert a significant influence on their catalytic performance. For example, smaller nanoparticles possess a larger specific surface area and a greater number of active sites, thereby contributing to enhanced catalytic efficiency [39].

Furthermore, the shape of nanozymes also has a profound impact on their catalytic performance. For instance, nanoparticles with morphologies such as nanorods or nanosheets possess a higher density of edge sites compared to spherical nanoparticles, resulting in enhanced catalytic activity [40].

Regulation of other properties

In addition to electronic structure, defect engineering, surface modification, and interfacial effects, other regulatory approaches also exert a significant influence on the catalytic performance of nanozymes. For example, the synthesis methods and reaction conditions (such as solvent, temperature, and pH) employed for nanozymes can also affect their catalytic performance. By optimizing synthesis methods, nanozymes with superior catalytic activity and enhanced stability can be obtained [41].

Progress in nanozyme applications

As research into nanozymes continues to deepen, these materials have demonstrated immense potential for application across numerous fields, particularly in biosensing, environmental protection, catalytic reactions, and biomedicine. Due to their exceptional catalytic performance, robust stability, low cost, and tunability, nanozymes have emerged as a vital tool, finding widespread application in a diverse array of detection and catalytic systems. The following sections provide a detailed overview of the progress made in applying nanozymes across various disciplines.

Biosensing and detection

In the realm of biosensing, researchers frequently employ specific strategies to enhance detection sensitivity and selectivity. These strategies often involve modifying surface functional groups to boost the affinity between the nanozyme and its substrate or recognition probe, or doping the nanozyme with metal ions to optimize its electronic structure, thereby improving its catalytic efficiency. Furthermore, nanocomposite strategies can leverage interfacial synergistic effects to further amplify detection signals, enabling the detection of target analytes at concentrations as low as the pg/mL level.

Biosensors achieve the rapid, sensitive, and selective detection of target molecules by integrating biomolecules with sensing materials. Nanozymes have emerged as ideal alternative materials for biosensors, owing to their catalytic properties which mimic those of natural enzymes - as well as their superior stability and lower production costs. The applications of nanozymes in biosensing primarily encompass the following areas:

(1) Targeted detection

Nanozymes have been extensively utilized in the detection of various biomolecules and biological targets, such as DNA, proteins, and cells. Through surface modification or doping techniques, nanozymes can be engineered to achieve highly efficient recognition of specific targets. For instance, by harnessing the peroxidase like activity of nanozymes, researchers have designed a variety of detection platforms for the analysis of DNA, RNA, and antigens. By conjugating nanozymes with appropriate probes, such as antibodies, aptamers, or primers researchers can efficiently capture target molecules and generate detectable signals [42].

For example, nanocomposites formed by combining metal oxide nanozymes (e.g., Fe_3O_4, MnO_2) with antibodies can be employed for antigen detection. These systems generate signals via redox reactions triggered by the presence of hydrogen peroxide, thereby endowing the platform with high sensitivity and selectivity within the context of immunoassay applications [43].

(2) Environmental pollutant detection

Nanozymes are also widely applied in the detection and monitoring of environmental pollutants. Given their excellent catalytic properties, nanozymes can generate signals correlated with pollutant concentrations through catalytic reactions, thereby enabling the rapid detection of hazardous substances in the environment. For instance, in water quality monitoring, nanozymes have been employed to detect heavy metal ions (such as Pb^{2+}, Cu^{2+} and Hg^{2+}) and organic pollutants (such as aniline compounds) [44].

Metal oxide nanozymes, such as MnO_2 and Fe_3O_4 have been utilized for the rapid detection of environmental hazards due to their highly efficient catalytic capabilities. Studies have demonstrated that MnO_2 nanozymes can catalyze the degradation of certain organic pollutants, thereby enable the determination of their concentrations and facilitate real-time water quality monitoring [45].

(3) Clinical diagnostics

Nanozymes hold significant value in the field of clinical diagnostics. By specifically binding to disease biomarkers, nanozymes enable the rapid in vitro detection of disease-associated molecules, thereby aiding in early clinical diagnosis. Currently, nanozymes are widely applied in the detection of tumor markers, pathogenic nucleic acids, inflammatory factors, and similar analytes.

In the realm of tumor diagnostics, the peroxidase-like activity of nanozymes can be harnessed to design colorimetric sensors for detecting common tumor markers, such as carcinoembryonic antigen (CEA) and alpha-fetoprotein (AFP). For example, when antibody-modified Fe_3O_4 nanozymes bind to specific target antigens, they catalyze a rapid color-generating reaction involving 3,3’,5,5’-tetramethylbenzidine (TMB). This allows for accurate quantitative detection based on color changes, achieving detection limits in the pg/mL range and providing a powerful tool for early tumor screening [46].

Regarding the diagnosis of infectious diseases, nanozymes are also utilized for the rapid detection of viruses and bacteria. For instance, an immunochromatographic test strip based on Au@Pt nanozymes can detect SARS-CoV-2 antigens within 15 minutes, offering the advantages of high sensitivity and operational simplicity. Furthermore, nanozymes can be integrated with CRISPR technology to achieve highly specific detection of nucleic acid biomarkers, demonstrating immense potential for the rapid diagnosis of diseases such as hepatitis and HIV/AIDS.

In the field of Point-of-Care Testing (POCT), nanozymes are particularly well-suited for disease screening in resource-limited settings, owing to their high stability and the fact that they do not require cold-chain transportation. Researchers have developed portable, nanozyme-based detection devices capable of transmitting readable signals via smartphones, enabling the rapid detection of metabolites such as blood glucose, uric acid, and cholesterol. This innovation offers a novel solution for home healthcare and primary care settings.

Environmental protection and pollution control

As industrialization continues to advance, environmental pollution has become an increasingly severe issue; consequently, effectively mitigating environmental pollution stands as one of the major challenges facing the globe today. As a novel class of catalysts, nanozymes have demonstrated immense potential in the field of environmental pollution control. The following sections outline several key applications of nanozymes in environmental protection and pollution remediation.

In environmental remediation applications specifically to meet the catalytic demands of complex aquatic or atmospheric environments researchers frequently employ doping and defect engineering techniques to modulate the electronic structure and active site density of nanozymes. This approach serves to enhance their catalytic stability under extreme pH conditions or high-salinity environments. Concurrently, nanocomposite strategies can endow nanozymes with recyclability, thereby resolving issues related to their reusability in practical treatment processes and effectively lowering application costs.

(1) Removal of heavy metal ions

Heavy metal contamination constitutes a significant aspect of environmental pollution; heavy metal ions possess high toxicity and can contaminate water sources, soil, and air. By harnessing the catalytic properties of nanozymes, researchers have developed a variety of methods for removing heavy metal ions from water. For instance, metal oxide nanozymes (such as Fe_3O_4, MnO_2, and CeO_2) can effectively catalyze the reduction of heavy metal ions into less toxic substances, thereby eliminating these pollutants from water [47].

Integrating these nanozymes with adsorbent materials can further enhance their efficiency in removing heavy metals. For example, CeO_2 nanoparticles can effectively remove lead ions from water through catalytic reactions; when combined with adsorbent materials, this removal efficacy is further amplified, thereby achieving the objective of water purification [48]. In recent years, magnetic nanozymes (e.g., $Fe_3O_4@SiO_2$) have demonstrated exceptional reusability in the treatment of heavy metal-laden wastewater, largely due to their ability to be rapidly separated from the medium via an external magnetic field. Studies indicate that functionally modified Fe_3O_4 nanozymes can achieve removal rates exceeding 95% for Pb^{2+}, Cd^{2+}, and Hg^{2+} ions, while retaining a removal efficiency of over 80% even after being reused five times.

(2) Pollutant degradation

Nanozymes are also widely applied in the degradation and removal of organic pollutants. For instance, by utilizing nanozymes to catalyze the oxidation of organic substances, such as aniline compounds, pesticides, and dyes, the degradation and detoxification of these harmful materials can be effectively achieved. In the field of water treatment, nanozymes have been employed to remove organic pollutants from water, including aniline compounds and dyes [49].

Metal oxide nanozymes, such as MnO_2 and Fe_3O_4, are capable of effectively degrading organic pollutants in water due to their excellent catalytic capabilities. Studies have demonstrated that MnO_2 nanozymes can decompose dyes through catalytic reactions, converting them into non-toxic or low-toxicity products. In recent years, significant progress has been made in the research of photo-responsive nanozymes (e.g., TiO_2/Fe_3O_4 composites). Under light irradiation, these materials generate abundant reactive oxygen species, thereby significantly enhancing the degradation efficiency of organic pollutants. For example, under ultraviolet light irradiation, TiO_2/CeO_2 composite nanozymes can achieve a degradation rate of over 98% for Rhodamine B, with the reaction time reduced to just 30 minutes.

Furthermore, nanozyme-based Fenton reaction systems have been widely adopted in the treatment of industrial wastewater. By combining Fe_3O_4 nanozymes with H_2O_2, recalcitrant organic pollutants-such as phenol and bisphenol A-can be efficiently degraded. The hydroxyl radicals generated during the reaction mineralize these organic substances into CO_2 and H_2O, thereby achieving complete purification.

(3) Air pollution control

Air pollution - particularly the emission of toxic gases has emerged as an increasingly serious environmental issue. The application of nanozymes in air pollution control primarily focuses on the removal of harmful substances from gaseous streams. For instance, by leveraging the catalytic properties of nanozymes, pollutants such as nitrogen oxides and sulfur dioxide can be effectively eliminated from gases.

Research indicates that CeO_2-based nanozymes can achieve a catalytic reduction efficiency of over 85% for NO_x, while also exhibiting excellent thermal stability. Additionally, noble metal nanozymes-such as those based on Pt and Pd-are utilized to catalyze the oxidation of volatile organic compounds (VOCs), including formaldehyde and benzene derivatives, converting them into harmless CO_2 and H_2O under low-temperature conditions. In recent years, researchers have also developed supported nanozyme-based air purification filters; by immobilizing MnO_2 nanozymes onto porous ceramic or fibrous materials, these filters are utilized for indoor air purification. They effectively remove formaldehyde and ozone, thereby offering novel technology for improving air quality.

Biomedical applications

The application of nanozymes in the biomedical field is primarily manifested in areas such as disease diagnosis, cancer therapy, and antimicrobial and antiviral treatments. Owing to their exceptional catalytic properties and biocompatibility, nanozymes have introduced numerous innovative therapeutic approaches to the biomedical sector.

In biomedical applications, surface modification of nanozymes serves as a pivotal strategy for enhancing their biocompatibility and extending their circulation half-life in vivo. By leveraging the specific characteristics of the tumor microenvironment, doping and defect engineering techniques can be employed to modulate the catalytic selectivity of nanozymes under weakly acidic conditions. This enables the precise elimination of cancer cells via chemodynamic therapy. Furthermore, nanocomposite strategies facilitate the construction of synergistic therapeutic platforms, which simultaneously amplify anti-tumor or antimicrobial efficacy while minimizing toxic side effects on normal tissues.

(1) Cancer therapy

The application of nanozymes in cancer therapy is primarily achieved through the selective elimination of cancer cells, mediated by their peroxidase-like activity and catalytic functions. For instance, nanozymes such as MnO_2 and CeO_2 can catalyze the generation of free radicals, which subsequently attack cancer cells and inhibit their proliferation [50]. Moreover, nanozymes can be combined with conventional chemotherapeutic agents to augment their therapeutic efficacy and enhance the targeting specificity and selectivity of the treatment.

In recent years, nanozyme-based chemodynamic therapy (CDT) has emerged as a focal point of research in cancer treatment. This therapeutic modality utilizes nanozymes to catalyze the conversion of endogenous H_2O_2 present within the tumor microenvironment into highly toxic hydroxyl radicals, thereby inducing apoptosis in cancer cells. Compared to conventional chemotherapy, CDT is characterized by its high selectivity and minimal toxic side effects. For example, Fe_3O_4 nanozymes can efficiently catalyze the Fenton reaction within the weakly acidic tumor microenvironment, generating copious amounts of reactive oxygen species (ROS) to effectively eradicate cancer cells.

Additionally, multifunctional nanozymes have been developed to facilitate synergistic therapeutic strategies. Researchers have successfully integrated photothermal therapy with chemodynamic therapy to construct $Au@Fe_3O_4$ composite nanozymes. Under near-infrared light irradiation, Au nanoparticles generate a photothermal effect that elevates local temperature; simultaneously, Fe_3O_4 nanozymes catalyze the generation of free radicals. The synergistic action of these two mechanisms significantly enhances their anti-tumor efficacy. In vivo experiments have demonstrated that this composite nanozyme achieves a tumor inhibition rate exceeding 90.0%, while exhibiting no significant toxic side effects on normal tissues.

(2) Antibacterial and antiviral applications

Significant progress has also been made in the application of nanozymes for antibacterial and antiviral purposes. By leveraging the redox catalytic functions of nanozymes, it is possible to effectively disrupt the structures of bacteria and viruses, thereby inhibiting their growth. For instance, utilizing the antibacterial properties of metal-based nanozymes, such as those derived from copper or silver enables effective antimicrobial action in fields ranging from water treatment to medical devices [51].

The primary antibacterial mechanisms of nanozymes include: the catalytic generation of reactive oxygen species (ROS) to disrupt bacterial cell membranes. The release of metal ions to interfere with bacterial metabolism; and the physical disruption of bacterial structures through direct contact. Studies indicate that Fe_3O_4 nanozymes can achieve a killing rate exceeding 99.9% against Staphylococcus aureus and Escherichia coli and remain equally effective against drug-resistant strains. Compared to conventional antibiotics, nanozymes are less prone to inducing drug resistance, thereby offering unique advantages in the fight against “superbugs”.

In the realm of antiviral applications, nanozymes have been employed to inhibit viral infection and transmission. For example, MnO_2 nanozymes can catalyze the generation of free radicals to disrupt viral envelopes, thereby effectively inactivating influenza viruses and coronaviruses. Furthermore, researchers have developed integrated nanozyme-based platforms that combine rapid detection with therapeutic intervention, enabling the in-situ elimination of viruses concurrently with their detection. This approach offers novel strategies for controlling viral infections.

Regarding wound healing, nanozymes are utilized in the fabrication of antibacterial wound dressings. By immobilizing nanozymes onto hydrogels or fibrous membranes, a continuous supply of reactive oxygen species can be generated at the wound site, effectively inhibiting bacterial infection while simultaneously promoting tissue regeneration. Animal studies have demonstrated that nanozyme-enhanced antibacterial dressings can significantly accelerate the rate of wound healing and minimize scar formation.

Industrial catalysis applications

In the field of industrial catalysis, nanozymes are gradually displacing traditional catalysts, owing to their high catalytic activity, excellent stability, and cost-effectiveness. Nanozymes are widely employed in various industrial reactions, such as hydrogen production, catalytic cracking of oil and gas, and green chemical synthesis.

In the field of energy catalysis, metal oxide nanozymes (e.g., CeO_2 and MnO_2) have been applied in environmentally friendly energy-related catalytic reactions, such as hydrogen production and organic synthesis [52]. For instance, Pt@CeO_2 composite nanozymes demonstrate excellent catalytic activity in the water-gas shift reaction, converting CO into CO_2 while simultaneously generating H_2. Their hydrogen production rate can exceed that of traditional catalysts by more than twofold. Furthermore, $NiFe_2O_4$ nanozymes exhibit promising catalytic performance in the oxygen evolution reaction (OER) during water electrolysis for hydrogen production, offering a novel solution for renewable energy conversion.

In the synthesis of fine chemicals, nanozymes are utilized to catalyze green organic reactions. For example, Pd nanozymes demonstrate high selectivity and conversion rates in Suzuki coupling reactions, making them suitable for the synthesis of pharmaceutical intermediates. Compared to traditional palladium catalysts, nanozymes exhibit superior recyclability, capable of being reused more than 10 times without any significant decline in catalytic activity.

In the petrochemical sector, nanozymes are employed in catalytic cracking and hydrodesulfurization reactions. Studies indicate that MoS_2 nanozymes can effectively remove sulfur-containing compounds from fuels during hydrodesulfurization, reducing sulfur content to below 10 ppm and thereby meeting clean fuel standards. Additionally, nanozymes show great promise for application in green chemical processes such as biodiesel production and biomass conversion.

As research into nanozymes continues to deepen, their applications in the field of industrial catalysis are expected to become even more widespread. In the future, the development of nanozyme catalysts possessing higher selectivity, greater stability, and enhanced recyclability will be the key to driving their industrial-scale application.

Challenges and future trends

Although nanozymes have demonstrated immense potential across numerous fields, their widespread application still faces several challenges, particularly regarding catalytic efficiency, selectivity, stability, and biocompatibility. Moving forward, with the continuous advancement of nanomaterials science and nanocatalysis technologies, nanozymes are expected to overcome these hurdles and open up new avenues for application. The following sections will discuss the primary challenges confronting the development of nanozymes and offer a prospective outlook on potential future research directions.

Challenges

(1) Enhancing catalytic efficiency

While nanozymes exhibit promising performance in many catalytic reactions, their catalytic efficiency is generally lower compared to natural enzymes. Natural enzymes often achieve extremely high-rate constants, whereas nanozymes may demonstrate slower catalytic rates in certain reactions. To boost the catalytic efficiency of nanozymes, researchers must further optimize their structures, for instance, by employing strategies such as doping, defect engineering, and surface modification to increase both the number and activity of catalytic sites.

Current research primarily focuses on enhancing catalytic efficiency through methods such as doping with metal ions, altering material morphology, and adjusting surface functional groups. However, the question of how to achieve truly high-efficiency catalysis remains a pressing issue awaiting resolution. In the future, the development of novel materials and highly efficient catalytic mechanisms is expected to further elevate the catalytic capabilities of nanozymes.

(2) Issues of selectivity

Although nanozymes have demonstrated good selectivity in certain catalytic reactions, their selectivity remains relatively poor within complex reaction systems. Low selectivity can lead to the occurrence of side reactions, thereby compromising both the efficiency of the catalytic process and the purity of the resulting products. To improve the selectivity of nanozymes, researchers are currently exploring various approaches including surface modification, functionalization, and molecular imprinting to facilitate highly selective catalytic reactions.

At present, the challenge of how to enhance selectivity toward target reactants while simultaneously maintaining high catalytic activity remains one of the most difficult hurdles in nanozyme research. By optimizing the surface properties of nanozymes, tuning the local environment of catalytic sites, and utilizing external stimuli (such as light, electricity, or temperature), it is anticipated that the selectivity of nanozymes can be significantly improved.

(3) Stability and reusability

The stability of nanozymes constitutes another major challenge in the context of their practical application. Although nanozymes are generally more stable than natural enzymes, their stability may still diminish during prolonged use or under extreme reaction conditions, leading to a decline in their catalytic activity. Furthermore, the reusability of nanozymes remains an issue that requires resolution. To overcome this challenge, researchers are currently employing strategies such as surface modification, polymer encapsulation, and nanocomposite formation to enhance the stability and interference resistance of nanozymes.

(4) Biocompatibility and safety

The biocompatibility and safety of nanozymes constitute a major bottleneck regarding their application in the biomedical field. While nanozymes have demonstrated excellent catalytic performance in vitro experiments, their safety and biocompatibility in vivo have not yet been fully evaluated. The size, shape, and surface properties of nanomaterials all exert an influence on their biocompatibility. Consequently, research into the safety of nanozymes is of paramount importance. To address this issue, future research must focus on developing nanozyme materials characterized by lower toxicity and superior biocompatibility. By optimizing the surface properties of these materials and incorporating highly biocompatible components, their safety within biological systems can be significantly enhanced.

Future trends

(1) Smart nanozymes

Driven by the rapid advancement of smart materials and smart sensors, future nanozymes are expected to possess self-regulating and adaptive characteristics. Smart nanozymes will be capable of automatically adjusting their catalytic activity under varying environmental conditions and responding to external stimuli-such as light, electricity, or temperature. For instance, smart nanozymes responsive to temperature, pH levels, or electric fields could selectively activate their catalytic activity under specific conditions, thereby enhancing both reaction efficiency and selectivity. Such intelligent nanozymes hold immense promises for widespread application in fields such as biomedicine and environmental monitoring.

(2) Multifunctional nanozymes

In the future, the development of nanozymes will trend toward multifunctionality. On one hand, the catalytic potency of individual nanozyme materials will be further enhanced. On the other hand, multifunctional nanozymes will be designed to simultaneously execute multiple catalytic functions, thereby enabling the synergistic catalysis of complex reactions. For example, the development of nanozymes endowed with multiple catalytic capabilities, such as redox activity, ester hydrolysis, and cleavage, is expected to provide highly efficient solutions for fields including environmental protection, energy conversion, and biomedicine. Research into multifunctional nanozymes is poised to become a pivotal direction in the future evolution of nanozyme technology.

(3) Commercial applications of nanozymes

As nanozyme technology continues to mature, the commercial application of nanozymes is poised to become a key direction for future development. Nanozymes hold extensive potential for application across fields such as biosensing, environmental monitoring, and drug delivery. In the future, nanozymes are expected to emerge as low-cost, highly efficient, and safe alternative materials, finding widespread application in industrial production. With the ongoing optimization of nanozyme preparation processes and the continuous enhancement of their performance, the market prospects for nanozymes are set to become even broader.

(4) Green synthesis and sustainability of nanozymes

Currently, the synthesis of nanozymes often relies on complex chemical processes or energy-intensive methods; consequently, future research will increasingly focus on the green synthesis and sustainability of nanozymes. Synthesizing nanozymes using biomaterials or green chemistry methods not only reduces production costs but also minimizes environmental pollution. For instance, employing natural methods, such as utilizing plant extracts or microbial synthesis to produce nanozymes enables low-pollution, high-efficiency manufacturing.

Conclusion

Nanozyme modification has evolved from a supplementary optimization approach to a core technology driving the advancement of nanozyme research and application. Surface modification, doping and defect engineering, nanocomposite construction, and structural regulation have successively broken through the bottlenecks of low catalytic efficiency, poor substrate specificity, and insufficient biocompatibility of natural nanozymes. This has endowed nanozymes with superior catalytic performance and environmental adaptability. At present, modified nanozymes have achieved remarkable application progress in biosensing, environmental remediation, biomedicine, and industrial catalysis, demonstrating huge potential to replace natural enzymes and traditional catalysts.

Nevertheless, challenges such as further improving catalytic efficiency and selectivity, enhancing in vivo stability and biosafety, and realizing large-scale green synthesis still restrict the commercialization and large-scale application of nanozymes. In the future, with the deep integration of nanoscience, materials science, and biomedicine, smart responsive nanozymes, multifunctional composite nanozymes, and green sustainable synthesis systems will become important research directions. It is believed that through continuous innovation of modification strategies and in-depth exploration of catalytic mechanisms, nanozymes will gradually move from laboratory research to industrial practical application. This will provide new technical solutions for solving major problems in the fields of health, environment, and energy.

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Authors' contributions

Keying Ling and Hongying Zhu contribute equally to the article.

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Conflicts of Interest

The authors declare no conflict of interest.

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