Applications of nanozymes in the environment

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Abstract: Nanozymes are inorganic nanopaticles that mimic the enzyme-like properties in redox reactions, processing both unique properties of nanomaterials and a catalytic function. Because of high catalytic activity, stability and multifunctionality, nanozyme are of increasingly wide interest in the fields of environmental science and technology. In this article, we review the most recent advances of nanozyme research for environmental pollutant detection and treatment. Nanozymes can be used to detect ions, molecules and organic compounds both qualitatively and quantitatively. They have also been applied for destruction multi-drug resistant bacteria and the degradation of various organic pollutants. Despite the apparent potential of nanozymes in environmental science and technology, current research and application is still limited, and so future challenges and research prospects have been highlighted.

Keywords: nanozyme; heavy metals; organic pollutants; antibacterial substances; organic pollutant degradation

1. Introduction

1.1 Definition of nanozyme

Most life processes in nature involve "enzymes". Natural enzymes are a class of biomolecules that process catalytic functions.[1] They are mainly proteins, and their catalytic activity on the substrate can be very efficient and high specific.[2] However, since most natural enzymes are inhibited and denatured by non-physiological or adverse conditions, such as heat, acids, and alkalis, they are prone to degeneration and can lose their function.[3-5] With the rapid development of nanoscience, nanotechnology and the development of nanomaterials have entered various branches of the life sciences.[6, 7]

In early research, the superoxide dismutase (SOD) mimicking activities of fullerene derivatives was discovered.[8, 9] Subsequently it was found that the inorganic nanomaterial Fe_3O_4 processed a biological activity similar to that of the natural enzyme, horseradish peroxidase (HRP).[10, 11] Since then, the "nanozyme" concept has developed and the subyear of increasing numbers of research publications.[12-24]

Nanozymes are inorganic nanopaticles that mimic enzyme-like properties in redox reactions, therefore processing both unique properties of nanomaterials and a catalytic function.[14, 23, 25-27] Because of high catalytic activity, stability and multifunctionality, nanozymes have found increasingly wide potential applications in fields, such as medicine, chemical engineering, agriculture and the environment.[21, 22, 28-32] In fact, nanomaterials were originally considered as being a chemically inert material with no intrinsic biological effects, a nanozyme was originally defined as an enzyme or enzymic catalytic group associated with the nanomaterial surface and termed a nanomaterial hybridizing enzyme.[33, 34] For example, azacrown was modified onto gold nanoparticles (AuNP) by chelation with Zn^{2+} to imbue catalytic activity in shearing phosphodiester bonds mimicking the function of RNase[35]. Thus the catalytic activity arises from surface-modified components and not from the nature of the nanomaterials themselves. However, with the further development and application of nanomaterials, several nanomaterials have been found to process inherent enzymic catalytic properties, and therefore, the definition of nanozyme has become broader to include all nanomaterials that possess intrinsic enzyme-like activities.[36]

1.2 Classification and catalytic mechanisms of nanozyme

Nanozymes vary in structure and composition, and include metal oxides,[37-52] metals,[17, 53-71] and carbon-based nanomaterials.[72-78] However, most of the catalytic reactions mediated by nanozymes employ the following four kinds of enzymic reactions: oxidase (OXD), peroxidase (POD), catalase (CAT) and superoxide dismutase (SOD) (Table 1).

Table 1 Current nanomaterials as enzyme mimics and their typical applications and representative references (GO: graphene oxide, PANI: polyaniline, rGO: reduced graphene oxide, C-dots: carbon dots, NPs: nanoparticles, CAT-NP: catalytic nanoparticles, Dex-NZM: dextran-coated iron oxide nanoparticles termed nanozymes, GQD: Graphene quantum dot, MNP@CTS: ferromagnetic chitosan nanozyme, OXD: oxidase, POD: peroxidase, CAT: catalase, SOD: superoxide dismutase, HRP: Horseradish Peroxidase)

Application	**Nanomaterial**	**Enzyme type**	**Reference**
Detection of ions	MoS_2	POD	104
	Fe_3O_4	POD	105
	Au	POD	106
	CoO_xH-GO	POD	108
Detection of organic pollutants	PdAu	POD	112
	PANI/rGO	CAT	115
	MnO_2	OXD	117
Antimicrobial and antifouling treatments	MoS_2	POD	133
	C-dots	OXD	134
	C_3N_4@AuNPs	POD	123
	CAT-NP with Fe_3O_4	POD	135
	CuO NPs	POD	138
	CuO nanorods	POD	139
	Nanoceria	SOD and CAT	140
	Dex-NZM	POD	136
	CeO_{2-x} nanorods	HRP	141
	GQD	POD	72,143
Treatment of organic pollutants	MNP@CTS	POD	149
	MnP	POD	150
	LiP	POD	153
	ZnO/CuO	POD	157
	Au/TiO_2	POD	158
	Nano-eco-enzyme	POD	159,160

Natural OXDs are enzymes that catalyze an oxidation-reduction reaction, especially those involving dioxygen (O_2) as the electron acceptor.[79] Nanozymes based on gold[80-86] and copper[87, 88] are typical representatives of OXD mimic enzymes.[34] The proposed mechanism of molecular activation for AuNP catalysis is shown in Figure 1. The hydrated glucose anion is first adsorbed onto the surface of the AuNP, and the interaction with gold surface atoms forms an electron-rich gold species which effectively activates molecular oxygen by nucleophilic attack and produces a dioxo-gold intermediate. The Au^{+}-O_2^{-} or Au^{2+}-O_2^{2-} couples of the dioxo-gold intermediate serve as a bridge to transfer electrons from glucose to dioxygen. Finally, gluconic acid and H_2O_2 are produced.[33, 34]

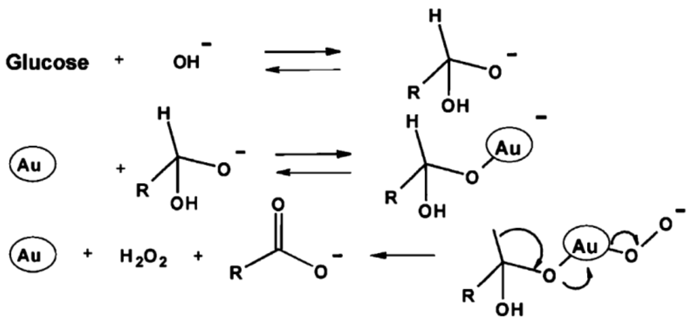

Fig. 1 Gold nanoparticles exhibit a catalytic mechanism that mimics glucose oxidase (reproduced with permission from ref. 86, Copyright 2006 Wiley-VCH).

PODs can commonly attack peroxides.[89] Fe_3O_4 magnetic materials process intrinsic POD properties[10] and these have been applied for the detection of both H_2O_2 and glucose.[90] Other iron oxide-based POD mimics have also been studied, including Fe_3O_4,[91, 92] Fe_2O_3,[93, 94] and doped ferrites.[95] Since POD-like iron oxide has a Fenton and/or Haber-Weiss reaction mechanism (possibly involving ·OH / HO_2·), nanozymes can be used for organic pollutant degradation by combining free radical production with magnetic properties of iron oxide.[34]

CATs catalyze the decomposition of hydrogen peroxide to water and oxygen.[96] CeO_2 NPs can serve as CAT mimic enzymes.[97] A series of catalytic effects is achieved by a redox reaction that forms catalytically effective Ce^{4+}. Ce^{4+} is reduced by H_2O_2 to form Ce^{3+} and produces protons and O_2. After that, another H_2O_2 molecule can combine with the oxygen vacancy in reaction ⑤, oxidizing Ce^{3+} to

Ce^{4+}, and releasing H_2O (Fig. 2).[33, 98]

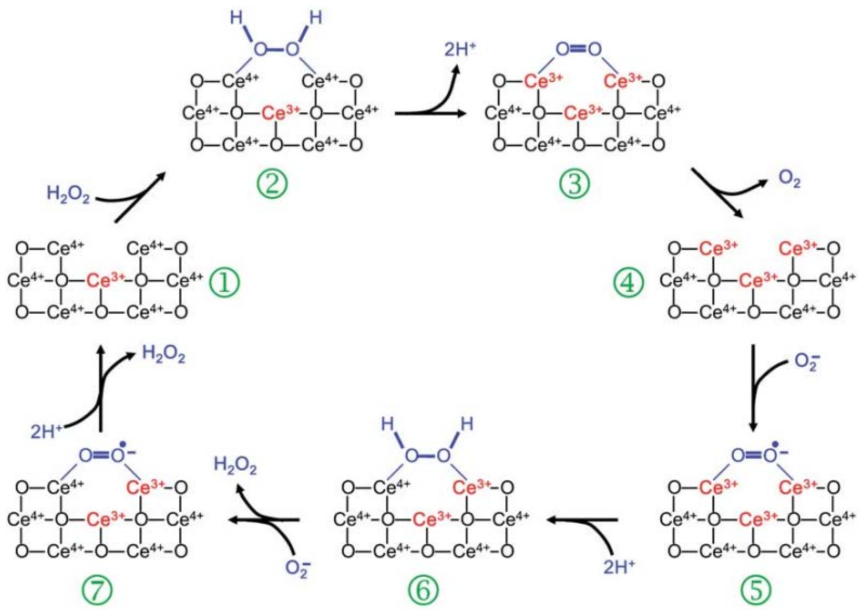

Fig. 2 Mechanism of CeO_2 nanoparticles acting as catalase mimic enzymes (reproduced with permission from ref. 98, Copyright 2011 Royal Society of Chemistry).

SOD is an enzyme that alternately catalyzes the dismutation (or partitioning) of the superoxide ($O_2^{-}\cdot$) radical into either molecular oxygen (O_2) or hydrogen peroxide (H_2O_2).[99] Taking Cu SOD as an example, as a reducing agent, $O_2^{-}\cdot$ is finally turned into O_2: Cu^{2+}-SOD + $O_2^{-}\cdot \rightarrow Cu^{+}$-SOD + O_2.[100]

These kinds of redox reactions can produce (or eliminate) free radicals and regulate levels of reactive oxygen species (ROS). Because ROS can attack nucleic acids, proteins, polysaccharides, lipids and other biological molecules, ROS releasing nanozymes can have excellent antimicrobial properties.[101] In addition, POD-mimic nanozymes can produce hydroxyl radicals with oxidative properties. Due to these characteristics, nanozymes have been widely applied to environmental problems. Nanozymes can detect the presence of certain pollutants, and also be used for effective treatment.

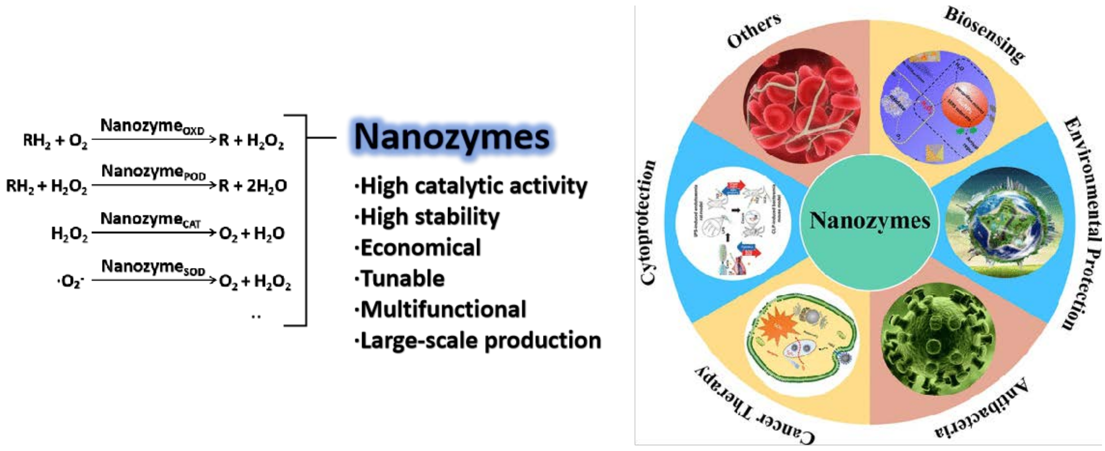

Fig. 3 Natural enzymic properties, advantages and applications of nanozymes (R: substrate, OXD: oxidase, POD: peroxidase, CAT: catalase, SOD: superoxide dismutase) (reproduced with permission from ref. 33, Copyright 2019, American Chemical Society).

Table 2 Nanomaterials for detection as enzyme mimics and their targets and agents (PANI: polyaniline, rGO: reduced graphene oxide, OXD: oxidase, POD: peroxidase, CAT: catalase) (adapted from refs.104-108,112,115,117)

Nanomaterial	Enzyme type	Agent	Target
MoS_2	POD	2, 3-diaminophenazine	Fe^{2+}
Fe_3O_4	POD	4-chloro-1-naphthol	Ag^{+}
Au	POD	4-nitrophenol	Hg^{2+}
CoO_xH-GO	POD	Amplex Red	CN^{-}
PdAu	POD	O-phenylenediamine	Malathion
PANI/rGO	CAT	Electrical signal	Kanamycin
MnO_2	OXD	Oligonucleotides	Ochratoxin A

2. Nanozymes for the detection of environmental pollutants

Nanozymes can be used in place of natural enzymes for environmental monitoring. By employing the catalytic activity of POD nanozymes, the content of hydrogen peroxide in rainwater, acid rain, and heavy metals, including mercury, can be detected in environmental samples. Such nanozyme detection methods are also suitable for operation under various environmental conditions and are relatively simple and inexpensive, and can be easily applied to screening of, e.g. pesticides, organophosphorus compounds, and other substances.

Whether the pollutants are ions, metals or organic compounds, nanozymes can only detect them indirectly. The basic principle of detection is that the target activates a reaction between the nanozyme and the agent, or the presence of the nanozyme causes the target to undergo a change in chemical properties and reacts with the agent to be detected (Fig. 4). An agent is usually a colorimetric sensor although there is some use of sensors such as electric current monitors (Table 2).

2.1 Detection of Ions

In the field of environmental pollution, the term heavy metals, mainly refers to such potentially biotoxic elements as mercury, cadmium, lead, chromium and arsenic. Heavy metals cannot be degraded, only transformed into different chemical species by abiotic or biotic mechanism, and they can be biologically amplified through food webs, causing harm to ecosystems and organisms, including humans. [102, 103]

A novel layered molybdenum disulfide (MoS_2) nanosheet POD mimetic-based fluorescent catalytic biosensor was developed for the sensitive and selective detection of Fe^{2+} over the range of 0.005-0.20 μM.[104] The catalyst MoS_2, was synthesized from $Na_2MoO_4 \cdot 2H_2O$, and exhibits POD activity. O-phenylenediamine acts as the substrate and was converted to 2, 3-diaminophenazine by MoS_2 in the presence of Fe^{2+}, becoming an indicator of fluorescence detection. Since the fluorescence intensity was proportional to the Fe^{2+} concentration, Fe^{2+} was successfully detected with high selectivity and sensitivity.

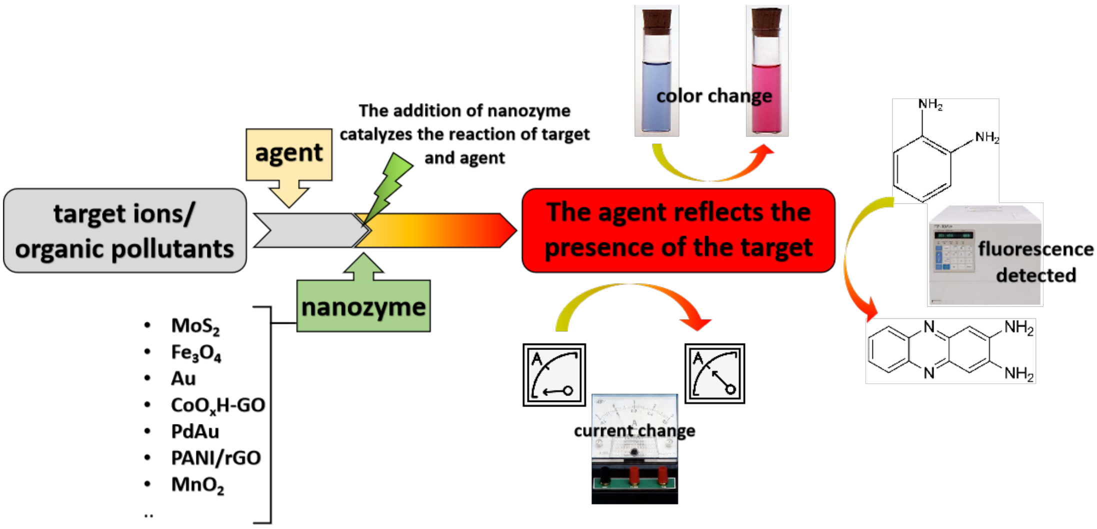

Fig. 4 The basic principle of nanozyme detection of ions/organic compounds (PANI: polyaniline, rGO: reduced graphene oxide) (adapted from refs.104-106,108,112,115,117)

Based on the POD-like properties of histidine-modified Fe_3O_4 (his-Fe_3O_4) nanozyme, a simple, low-cost means to detect Ag^+ was developed with ultralow detection limit of 18 fg/mL.[105] An electron transfer sensor was conjugated to the highly active nanozyme his-Fe_3O_4 in the presence of Ag^+ via a specific reaction. 4-chloro-1-naphthol was used as the substrate, nanozyme his- Fe_3O_4 was used as the catalyst, and H_2O_2 was used as an oxidant. When Ag^+ was present, the POD enzyme activity of his-Fe_3O_4 was activated and this changed the substrate to generate insulating precipitation of benzo-4-chlorohexadienone. The insulating products attenuate the photocurrent signal which reflected the presence of Ag^+. His-Fe_3O_4 nanozymes could make photoelectrochemical immunoassays chemical easier and less expensive.

Mercury in the environment exists in many chemical forms, with divalent mercury being one of the most stable. Because of the toxicity and bioaccumulation potential of mercury, detection in the environment is very important. One approach harnessed the strong affinity between AuNP and Hg^{2+}, meaning that mercury can attach to the surface of gold nanozymes to form a gold amalgam. As a POD nanozyme, AuNP activity was further enhanced by precipitation of Hg^{2+}, and $NaBH_4$ supplied as a reducing agent, reduce the substrate 4-nitrophenol more quickly. 4-nitrophenol reduction produces a colour change with ultra-high sensitivity to Hg^{2+} and detection limits down to 1.45 nM. This AuNP nanozyme was stable and recyclable. [106, 107]

A cobalt oxide/oxide-modified graphene oxide (CoO_xH-GO) nanozyme having POD-like catalytic activity has been used as an effective detecting agent for CN^- (selectivity>100-fold).[108] The principle relied on the significant inhibitory effect of CN^- on the catalytic activity of the CoO_xH-GO nanozyme. When Amplex Red was used as a substrate and colorimetric reagent, with the CoO_xH-GO nanozyme as catalyst and H_2O_2 as oxidant, the increase in CN^- concentration was clearly reflected by a decrease in red colour. This method can also be applied to complex wastewaters (e.g. sea water) at low cost.

2.2 Detection of organic pollutants

There are several kinds of organic pollutants in the environment, and many are difficult to detect. Nanozymes can be used to detect pesticides, antibiotics and other toxic organic compounds. [109-111]

Pesticide pollution refers to pollution caused by pesticides, and their toxic metabolites, degradation products and impurities remaining in organisms, agricultural by-products and the environment after pesticide use has exceeded the maximum residue limits. The toxicity of residual pesticides to living organisms is called the pesticide residue, and this can contaminate the soil, atmosphere and groundwater. In order to detect pesticide residues, various nanozymes have been examined. For example, O-phenylenediamine was used as the substance to be oxidized, and palladium-gold (PdAu) bimetallic nanozyme as the catalyst. Because the POD activity of nanozyme was selectively quenched with increasing concentrations of malathion, is PdAu nanozyme could be used for detection of is low-toxic insecticide. This assay was highly sensitive (60 ng/ml) and of low cost.[112-114]

Kanamycin is an antibiotic which can be detected by an innovative gas pressure-based biosensing platform.[115, 116] A polyaniline nanowire functionalized reduced graphene oxide (PANI / rGO) framework was used as a CAT-like nanozyme that catalyzed the reduction of hydrogen peroxide to produce oxygen. The existence of kanamycin triggered strand displacement amplification which affected the CAT nanozyme and reflected the presence of kanamycin as an electrical signal which increased with increasing kanamycin concentration.[115, 116]

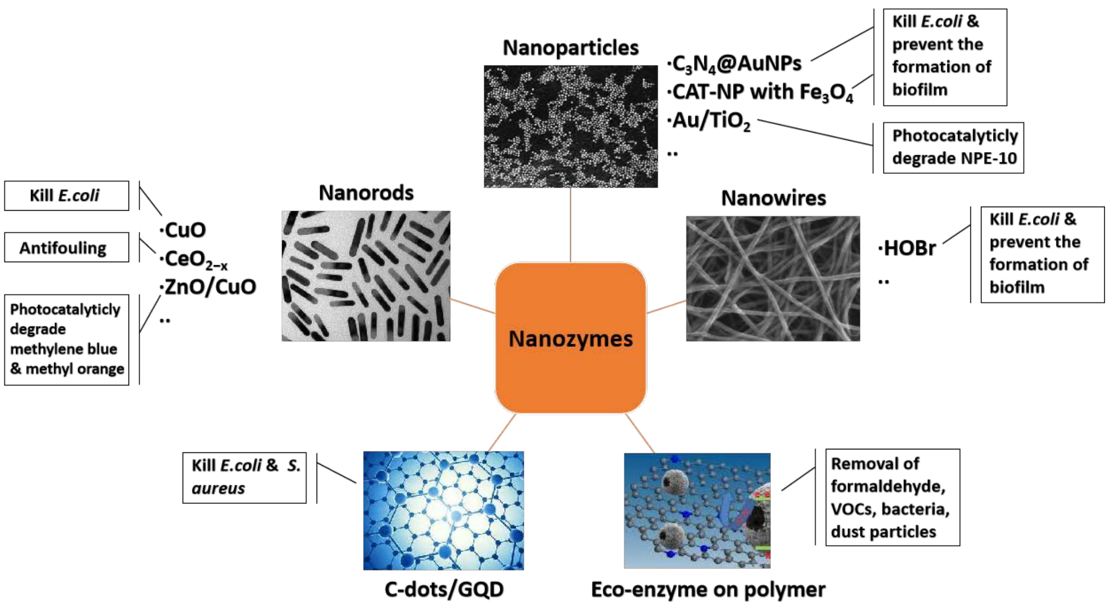

Fig. 5 Different forms of nanozymes and their applications in environmental biotechnology (C-dots: carbon dots, NPs: nanoparticles, CAT-NP: catalytic nanoparticles, GQD: Graphene quantum dot, *E.coli: Escherichia coli*, *S.aureus: Staphylococcus aureus*, NPE-10: nonylphenyl poly (oxyethylene) ethers, VOCs: volatile organic compounds) (adapted from refs. 72, 133-141,149-160).

Ochratoxin is a mycotoxin that has attracted worldwide attention. It is one of a group of important, food-contaminating mycotoxins produced by seven species of *Aspergillus* and six species of *Penicillium*, four of which are the most toxic and widely distributed in the agricultural products. The most widely polluting and damaging to human health is ochratoxin A (OTA). One detection method was based on the biotin-streptavidin reaction.[117, 118] Here, 3, 3', 5, 5'-tetramethylbenzidine (TMB) was used as a substrate and a colorimetric reagent, and MnO_2 nanosheets were used as an OXD nanozyme to oxidize TMB to a blue colour TMB Ox. However, when OTA was present, acid-2-phosphate was converted to ascorbic acid, which reduced the MnO_2 nanosheet to Mn^{2+} which cannot oxidize TMB. Theis method for detecting OTA possessed high sensitivity, with a limit of detection being 0.069 nM.[117, 118]

3. Application of nanozymes in environmental treatment

3.1 Nanozymes as antimicrobial and antifouling agents

Environmental antibiotic resistance is a rapidly increasing problem in recent years. Abuse of antibiotics can lead to the emergence of multi-drug resistant bacteria as well as causing environment pollution. Therefore, it is important to develop new antimicrobial agents that are highly effective, environmentally-friendly and which avoid or minimize drug resistance. Effects of antibacterial nanomaterials are multifaceted, which can make it difficult for bacteria to develop drug resistance. Compared with traditional nanomaterials, nanozymes have possess higher biosafety and show promise as an effective antibacterial material.[119, 120]

Reactive oxygen species (ROS) play an important role in cellular defence against pathogen invasion[121, 122], and nanozymes have the ability to regulate level of ROS free radicals.[123] This ability confers an antibacterial function. For instance, hydrogen peroxide is a commonly used disinfectant because it can be decomposed to generate free radicals, thereby attacking cellular components of bacteria, such as membranes, proteins and nucleic acids.[124, 125] However, the efficiency of generating free radicals is low, and the addition of a catalyst greatly accelerates the reaction. Nanomaterials with POD mimicking enzyme activity can be used as such a catalyst to improve the transformation of hydrogen peroxide to free hydroxy radicals and thus enhance sterilization.[126-129]It was found that in the presence of low concentrations of hydrogen peroxide, trace amounts of nanozymes could kill 100% *Escherichia coli* (*E. coli*), while the sterilization efficiency of hydrogen peroxide alone was less than 15%.[130]This study also found that vanadium pentoxide nanowires with vanadium haloperoxidase activity effectively inhibited formation of biofilm. In the presence of hydrogen peroxide, this substance can oxidize bromide ions to produce hypobromous acid (HOBr) and singlet oxygen, which has strong antibacterial activity. Applying vanadium pentoxide nanowires to the surface of stainless steel inhibited microbial adhesion, thus effectively preventing the formation of biofilm, and therefore has potential in antifouling applications, e.g. for ship hulls.

Photocatalytic cooperation with nanozymes can kill bacteria very effectively.[131, 132] POD activity of a MoS_2 nanozyme was activated by lowering the pH which altered the surface charge of MoS_2 from negative to positive. The activated MoS_2 nanozyme catalyzed the decomposition of H_2O_2, and the resulting •OH destroyed cell integrity to achieve an antibacterial effect. The advantage of this method is that this antibacterial treatment can be accomplished simply by controlling the light.[133] Light-driven carbon dots (C-dots) were used as OXD nanozymes to kill *E. coli* and *S. aureus* by photosensitization, both ambient light and UV irradiation being tested.[134]

Ultra-thin graphite carbon nitride (g-C3N4) AuNPs can be used as POD to efficiently catalyze the decomposition of H_2O_2 into •OH to kill drug-resistant Gram-negative and Gram-positive bacteria. This method was also very effective in destroying and preventing biofilm regeneration.[123] Catalytic nanoparticles containing biocompatible Fe_3O_4 and dextran coated iron oxide NPs also have POD activity and can be used to decompose H_2O_2 to produce •OH. This method degrades the biofilm matrix and kills bacteria quickly. [135, 136]

Nano-CuO, as an artificial POD, is another kind of antibacterial material.[137] Nanozyme based hydrogel (nanozyme-gel) CuO NPs and CuO nanorods (NRs) can be used to catalyze the decomposition of H_2O_2 to kill *E. coli*. Interestingly, the catalytic activity of CuO NRs showed significant catalytic enhancement under visible light irradiation, allowing light control of antibacterial activity. [138, 139]

Nanoceria has a variety of enzymic properties. A nanoceria was discovered with both CAT and SOD properties, which was controlled by the Ce^{3+}/Ce^{4+} ratio.[140] When the Ce^{3+}/Ce^{4+} ratio and its activity are regulated, the cerium oxide nanozyme converts between these two properties. The superoxide anion is converted to H_2O_2 like SOD which is then further converted to H_2O and O_2 like CAT, and was effective in killing *E. coli* and *S. aureus*. CeO_{2-x} nanorods can somehow prevent biofouling in an aqueous environment because of haloperoxidase activity. One CeO_{2-x} NRs is stable in water, including marine environments, and can reduce bacteria adhesion by 70% compared to conventional PVA fibres. [96-99, 141, 142]

Graphene quantum dots (GQD) also have multiple enzymatic properties like nanoceria. GQD can exhibit POD properties, e.g. addition of GQD can significantly improve the antibacterial activity of H_2O_2, while GQD/AgNP hybrids can express an OXD function.[72, 143]

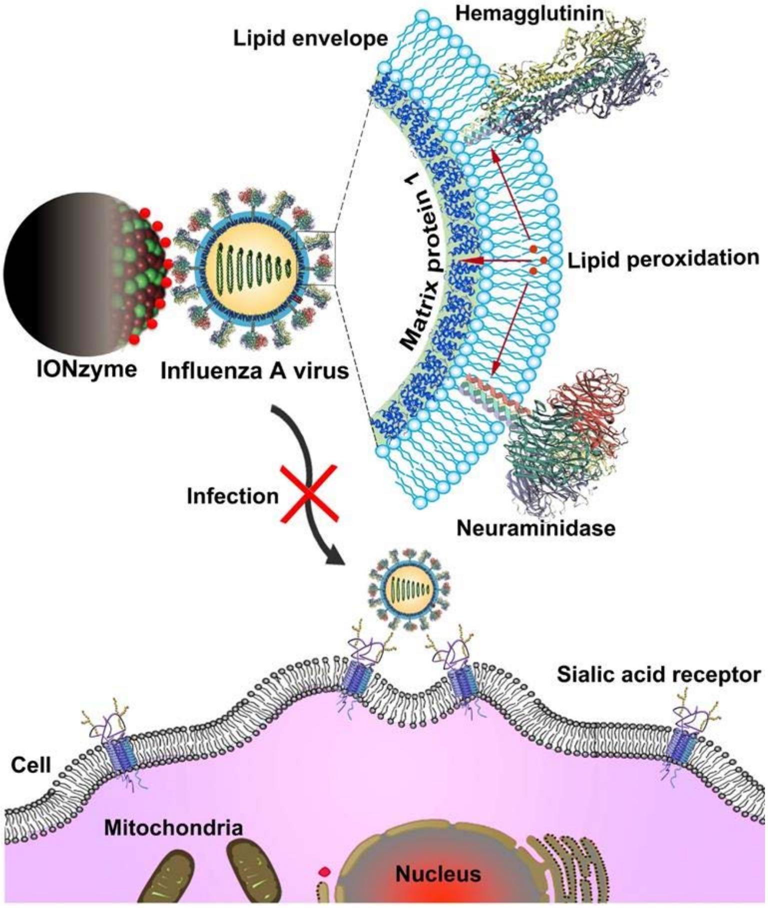

Fig.6 Schematic of viral lipid peroxidation by IONzymes for virus inactivation. IONzymes directly contact with IAVs particles and collapses the viral lipid envelope by enhancing the level of lipid peroxidation, which further produces free radicals to destroy neighbouring proteins, including haemagglutinin, neuraminidase, and matrix protein 1, and impaires various viral structures and functions resulting in failed infection. (IONzymes: iron oxide nanozymes, IAVs: inactivated A viruses) (reproduced with permission from ref. 144, Copyright 2019, Ivyspring International Publisher) .

Most recently, iron oxide nanozymes (IONzymes) have been demonstrated to effectively inactivate A viruses (IAVs) by inducing envelope lipid peroxidation and destruction of the integrity of neighbouring proteins, including haemagglutinin, neuraminidase, and matrix protein 1 (Fig. 6). Furthermore, IONzymes possess broad-spectrum antiviral activity against 12 subtypes of IAVs (H1~H12).[144]

3.2 Treatment of organic pollutants in water

Nanozymes have shown excellent qualities for the treatment of contaminated wastewater because they (i) can treat compounds that are normally difficult to biodegrade, (ii) can operate independently of the contaminant concentration, (iii) can operate over a wide range of pH, temperature and salinities, (iv) are not subject to inhibition from biofouling, (v) are relatively simple and easy to control, and (vi) possess high stability and are recyclable.[145-148]

Ferromagnetic chitosan nanozymes (MNP@CTS) has been synthesized which are more catalytically active than conventional ferromagnetic nanozymes for the degradation of phenol.[149] This type of nanozyme has excellent POD activity and can be prepared and regenerated easily at a lower cost than conventional horseradish peroxidase (HRP). MNP@CTS removed over 95% phenol from an aqueous solution within 5 h under the optimum conditions (pH range 2-10). What is more important is that the MNP@CTS are very stable and could be regenerated for reuse for at least ten cycles. In otherwork Mn(III)-chelate arising from manganese POD was pumped into a reaction vessel containing organic contaminants.[150] It was found that the Mn(III)-chelate efficiently oxidized 2, 4-dichlorophenol and 2, 4, 6-trichlorophenol. The Mn(III) was oxidized to Mn(III) at an initial rate of 78% under optimized conditions. This nanozyme had the advantage of retaining 88% of the initial MnP nanozyme activity after about 24 hours of continuous operation.

Aromatic compounds are a class of compounds possessing benzene ring structures. They are normally structurally stable, resistant to degradation, and often highly toxic, causing serious pollution to the environment and injurious to human health.[151, 152] Lignin peroxidase (LiP) from a variety of sources can degrade a variety of recalcitrant aromatic compounds including polycyclic aromatic and phenolic compounds. In addition to exhibiting the normal properties of POD, the enzyme can form a substrate cation radical with non-phenolic aromatic compounds and catalyze high-potential one-electron oxidation.[153, 154]

Dyes are still a major problem in water pollution.[155, 156] A new thermal-decomposition method was used to prepare ZnO nanorods and ZnO/CuO nanocomposites with different weight ratios (the maximum efficiency was observed for 5% CuO loaded on ZnO).[157] Organic dyes such as methylene blue and methyl orange were photocatalytically degraded by addition of composite catalyst under visible light irradiation. Preparation of this nanozyme is simple, rapid and economical.

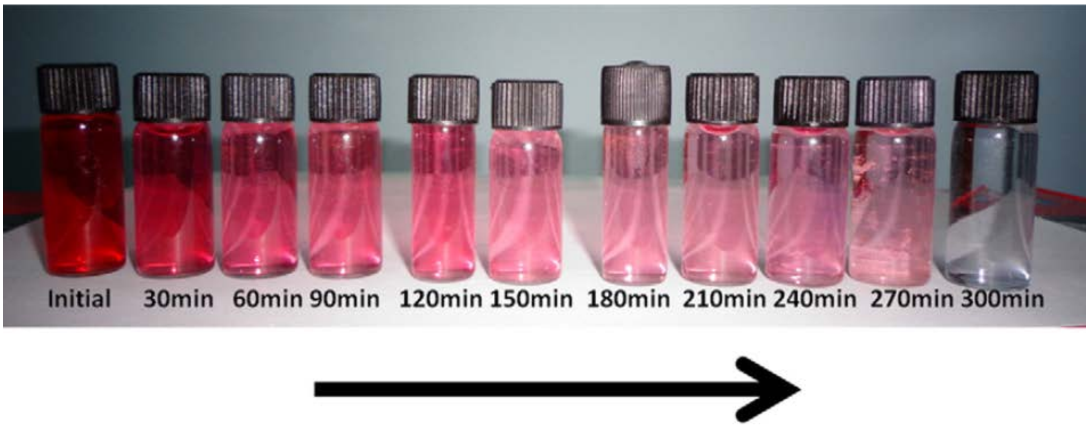

Fig. 7 Photography image represents change in colour of textile dyes using ZnO/CuO (95:5) catalyst for different exposure time under visible light irradiation.) (adapted from refs. 157).

In other research, Au/TiO_2 powder was prepared by a sol-gel method, and this could photocatalytically degrade nonylphenyl poly (oxyethylene) ethers (NPE-10) under sunlight illumination.[158] The degradation rate of NPE-10 after irradiation for 4h was 91.8%, while that of TiO_2-P-25% and undoped TiO_2 was 66% and 52.6%, respectively.

3.3 Treatment of indoor air pollution

Nano-ecological-enzyme air purification material, another kind of nanozyme, is a new type of functional material with high purification efficiency, low wind resistance and sterilizable. It can be used in air purifiers to remove indoor dust, microorganisms, formaldehyde and other volatile organic pollutants. The material is made of activated carbon fibre (ACF) and porous polymer composites and loaded with nano-silver and eco-enzyme catalyst.[159, 160] Eco-enzymatic catalysts are supported in the nanoporous carbon structure and become composite macromolecules with active oxygen carriers. Enzymatic catalysts in the nanopores combine with oxygen to form highly active superoxide ions and oxidation-reduction active sub-fields, similar to POD that are widely distributed in nature. The contact area between the eco-enzyme catalyst and adsorbed formaldehyde in the nanopores is very large. The active catalyst molecule quickly binds the formaldehyde molecule and, after a series of oxidation-reductase catalytic reactions, different intermediate peroxide molecules are formed. Finally, the formaldehyde is oxidized to water and carbon dioxide. The eco-enzyme catalyst quickly returns to its original state and can bind again to oxygen molecule in the atmosphere. This process of enzymatic oxidation-reduction can therefore be repeated multiple times (Fig. 8). Organic molecules such as formaldehyde and microbial propagules in the air can be absorbed by the nanopores through an autonomous cycle and thus maintain the long-term purification effect of the composite material. The average purification rate of formaldehyde in two hours is 91.9%.[159, 160]

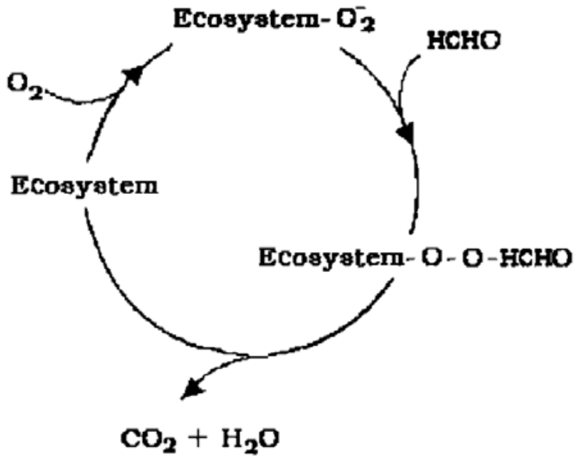

Fig. 8 Degradation of formaldehyde in air by nano-ecological-enzymes (adapted from ref.159).

4. Conclusions and research prospects

In the past 10 years, nanozyme research has been carried out in more than 220 laboratories in 26 countries (Fig. 7), and nanozyme applications have also extended to biology, medicine, agriculture, environmental protection and other fields.[36] In the field of environmental biotechnology, nanozymes have multi-functional applications ranging from pollutant detection to treatment. Nanozymes can not only achieve the specificity and efficiency of natural enzymes, but of function independently of various environmental factors that may affect biotic systems, e.g. extremes of temperature and pH.

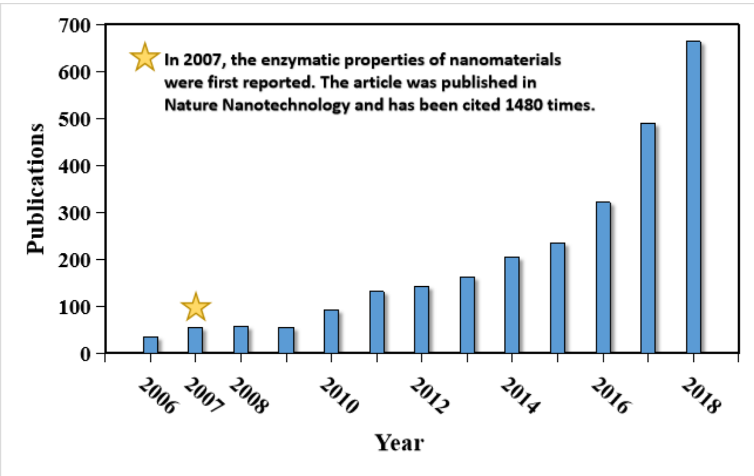

Fig. 9 The number of published papers on nanozymes has annually risen (source of data in the table: Google Scholar, December 31, 2018) (adapted from ref.36).

Nanozymes also have several limitations, although nanozymes overcome many restrictive factors active against natural enzymes, most catalytic activities of nanozymes are still much lower than the corresponding natural enzymes. At present, research on nanozymes mainly concentrates on redox enzyme mimics, such as OXD, POD, CAT and SOD, with much less attention given to other enzymes that may be important in the degradation of some polymers. In addition, although the efficiency of pollutant treatment is high, the cost of industrial treatment can be higher than traditional pollution treatment methods.

It is evident that nanozymes show good performance in small-scale experiments, but their application in environmental engineering is still limited, mainly because catalytic nanozyme devices require high precision technology, and an extended service life if such shortcomings can be overcome, applications of nanozymes for pollutant treatment industry may bring huge benefits. In addition, nanozymes can be combined with a variety of composite materials that allow application to changing environmental problems, which is also a challenging topic.[161, 162]

Although current research on nanozymes is still limited, the future of nanozyme technology seems promising. In the field of environmental biotechnology, research on nanomaterials is increasing and new nanozymes continue to emerge significant research questions include how to effectively kill bacteria under adverse conditions, and how to degrade very recalcitrant organic polymers. Integration of nanozyme technology in the fields of environment, biology, agriculture and medicine could result in multi-level benefits for industrial development and human health.

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