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Recent advances in the applications of nanozymes for the efficient detection/removal of organic pollutants: a review

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Global concern regarding the environmental threat of organic pollutants is growing, which requires the development of efficient and environmentally friendly detection/removal techniques. Biological methods, especially those relying on enzymatic processes, have shown excellent performance in alleviating the environmental problems of organic pollutants. However, natural enzymes have certain limitations and drawbacks, such as strict reaction conditions, poor stability, and high cost. To overcome these issues, nanozymes, *i.e.*, nanomaterials with enzyme-like activities, possessing the advantages of low cost, mass production and high stability, have become popular in recent years. This review focuses on recent advances and challenges in the applications of nanozymes for the efficient detection/removal of organic pollutants. Four typical types of nanozymes including peroxidase-like nanozymes, oxidase-like nanozymes, catalase-like nanozymes and superoxide dismutase-like nanozymes are comprehensively evaluated, especially in terms of their catalytic processes and capacities. Moreover, the mechanisms in the nanozyme-driven processes for the detection/removal of organic pollutants are illustrated. Further, key factors such as size, shape, morphology, pH, temperature and other secondary factors are discussed and the ecological effect of nanozymes is briefly summarized. Finally, future research directions in this field and conclusions are indicated. Overall, this review provides a promising and comprehensive environmental perspective on the latest nanozyme-related techniques in the detection/removal of organic pollutants.

Environmental significance

With the rapid development of industrialization and urbanization, various environmental problems have emerged. A broad range of organic pollutants, such as phenolic compounds, polychlorinated biphenyls, dyes, pesticides and antibiotics, seriously threaten human health and the environment. Finding suitable methods for the efficient detection/removal of organic pollutants is essential. Nanozymes, possessing the characteristics of nanomaterials and the activities of natural enzymes, show the advantages of low cost, high stability and high activity. The excellent properties of nanozymes endow them with outstanding application prospects in the detection/removal of organic pollutants. Previous studies have mainly focused on nanozyme use in tumor treatment, biomedical applications and other aspects as opposed to environmental applications. To fill this gap, this review highlights the applications of nanozymes in the rapid detection and removal of environmental organic pollutants. Four typical types of nanozymes, namely peroxidase-like nanozymes, oxidase-like nanozymes, catalase-like nanozymes and superoxide dismutase-like nanozymes, are comprehensively evaluated, especially their catalytic processes and capacities. This review indicates the key mechanisms and influencing factors in nanozyme-driven processes for the detection/removal of organic pollutants. Particularly, this review highlights the ecological effect of nanozymes for their impact assessment on local ecosystems. Further, this review provides useful guidelines and environmental perspectives for the detection/removal of organic pollutants using nanozymes, which is novel and interesting for readers in the environmental field.

1. Introduction

In recent years, with the rapid development of industrialization and urbanization, various environmental problems have emerged, which threaten human health and the environment.[1–3] A broad range of organic pollutants, such as phenolic compounds, polychlorinated biphenyls, dyes, pesticides and antibiotics, are produced *via* anthropogenic activities and primary sources such as paper mills and the plastic, leather, printing and food industries.[4,5] As a result of their wide use and disposal, organic pollutants enter the environment and are mainly recognized as persistent, bio-accumulative, carcinogenic and/or poisonous

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chemicals. For their transformation and degradation, diverse methods have been developed, such as chromogenic reactions, chemical precipitation, ion exchange, coagulation, oxidation, biodegradation and physical adsorption.[6–9] However, their problems of relatively low efficiency and the formation of by-products have not been fully addressed.[10] Thus, it is essential to find suitable methods for the efficient removal of organic pollutants. Meanwhile, certain refractory organic pollutants have been found to be resistant to degradation using existing technologies, and thus real-time and effective detection methods are necessary for their accurate monitoring.[11] Particularly when their concentrations exceed the environmental threshold and threaten the survival of humans, animals and plants, appropriate methods should be applied to lower the degree of contamination.[12]

With the development of technology, biological techniques have been proven to exhibit excellent performance for the rapid and sensitive detection of organic pollutants.[13] Furthermore, in comparison to traditional chemical and/or physical methods, biological techniques are more environmentally friendly, and promote the biotransformation of organic pollutants into less toxic products.[14] Common biological techniques, such as enzymatic methods, fermentation, anaerobic digestion and composting, have been widely studied.[15,16] Among them, enzymatic methods, which can lower the activation energy of reactive systems and have the advantages of high catalytic efficiency and strong specificity, have drawn increasing attention.[17,18] Research on enzymes has been conducted for about two centuries.[19] Enzymes are suitable candidates for environmental, medical, agricultural and industrial applications.[20–22] For example, Kalaiarasan *et al.* studied the removal of phenols from an acidic environment using horseradish peroxidase (HRP).[23] Guan *et al.* studied bacterial laccases for industrial applications.[24]

However, natural enzymes require strict reaction conditions and their catalytic activities are easily influenced by environmental factors such as pH and temperature. Moreover, natural enzymes have poor stability and are scarce and expensive.[20,25] Thus, to overcome these drawbacks, Yan's group found that Fe_3O_4 nanoparticles (NPs) had peroxidase-like activities in 2007, and since then, hundreds of nanomaterials have been proven to exhibit enzyme-like activities.[26,27] Subsequently, the "nanozyme" concept was developed as "nanomaterials with enzyme-like activities".[28–31] Given the current development in this field, nanozymes can be defined as nanomaterials that can catalyze the conversion of enzyme substrates to products and follow enzymatic kinetics (*e.g.*, Michaelis–Menten) under physiologically relevant conditions, even though the molecular mechanisms of the reactions may be different between nanozymes and the corresponding enzymes.[27,32,33] Nanozymes not only have the characteristics of nanomaterials, but also have the activities of natural enzymes with the advantages of low cost, high stability and high activity.[34–36] The excellent properties of nanozymes mentioned above endow them with outstanding performances in many fields.[37–39] The published studies mainly introduced the composition, characteristics, and properties of nanozyme materials applied in a variety of fields such as tumor treatment,[40–42] biomedical application[43] and other aspects rather than environmental application.[38,39] However, due to the rapidly increasing serious problems of organic pollution, it is very important to detect and remove organic pollutants using new nanozyme technologies (Fig. 1a and b).

In this review, the classification and catalytic processes of four common nanozymes are introduced. Furthermore, the use of nanozymes to detect/remove organic pollutants is highlighted. Then, the key factors in nanozyme-driven processes are discussed and the ecological effect of nanozymes is illustrated. Moreover, previous studies mainly focused on tumor treatment, biomedical applications and other aspects rather than the environmental application of nanozymes. Thus, to fill this gap, this review highlights the application of nanozymes in the rapid detection and removal of environmental organic pollutants that pose a serious threat to human life and the survival of biological species. For the future practical application of nanozymes in the real environment, this review indicates the following research

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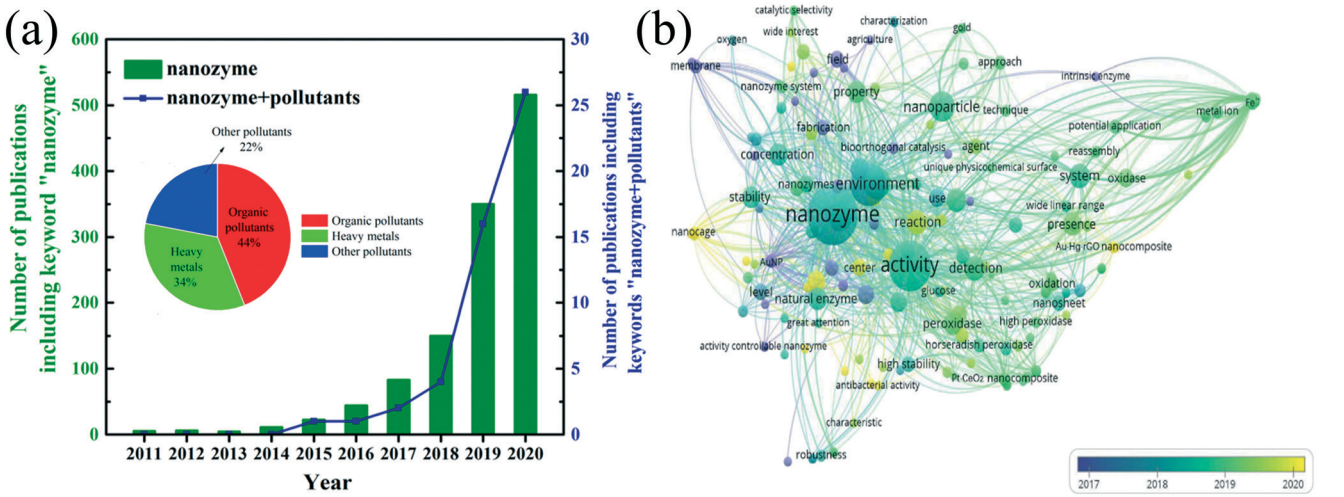

Fig. 1 (a) Evolution of the number of publications in indexed journals including the keyword "nanozyme" and keywords "nanozyme + pollutants" from 2011 to 2020. (b) Overlay visualization of the application of nanozymes in the environment in the past ten years.

directions and their application possibility in the detection and removal of pollutants. The key factors in the nanozyme-driven processes are divided into the main internal factors, external environmental factors and other secondary factors, which are firstly introduced the influence factors in the environmental field. Especially, this review firstly introduces the ecological effect when applying nanozymes in the real ecosystem, which is novel and interesting for readers in the environmental field. Further, in the prospects part, this review provides useful guidelines on the detection/removal of organic pollutants *via* the use of nanozymes.

2. Classification and catalytic processes of nanozymes

In recent years, nanozymes have been proven to be great enzyme mimics because of their low cost, mass production and high stability.[34] Especially, the inherent structures of nanozymes endow them with stable activities regardless of the change in ambient conditions. In general, depending on their catalytic mechanisms, nanozymes can be mainly divided to four categories including peroxidase-like nanozymes, oxidase-like nanozymes, catalase-like nanozymes and superoxide dismutase-like nanozymes, which have been applied in different fields with specific properties (Table 1).[44–57] In particular, catalase-like nanozymes and superoxide dismutase-like nanozymes have been mainly applied in tumor treatment and immunoassay, and also the detection of Hg^{2+}, GSH, H_2O_2 and glucose instead of organic pollutants.[58–60] Therefore, catalase-like nanozymes and superoxide dismutase-like nanozymes are introduced briefly in the following detection/removal parts. The inherent connections of these four types of nanozymes are shown in Fig. 2.[61] In terms of nanomaterial composition, the typical nanozyme materials include noble metals (*e.g.*, Au, Ag, Pt, and Pd), metal oxides (*e.g.*, Fe_3O_4, Co_3O_4, CeO_2, and MnO_2), carbon materials (*e.g.*, carbon nanotubes (CNTs), carbon nanodots, and graphene oxide), metal–organic frameworks (MOFs) and covalent organic frameworks (COFs).[62–66] The catalytic processes of these four types of nanozymes are discussed in detail in the following section.

2.1. Peroxidase-like nanozymes

Peroxidase-like nanozymes, such as Fe_3O_4, Co_3O_4, Au, Pt, CNTs, and some hybrid nanozymes,[63,67] can catalyze the oxidation of substrates by peroxides.[68] The common peroxides are H_2O_2 and organic hydroperoxides (R-OOH). Their catalytic processes conform to the following equations (eqn (1) and (2)).[69] H_2O_2 is commonly applied in the catalytic reactions of peroxidase-like nanozymes. In general, peroxidase-like nanozymes firstly react with H_2O_2 to form hydroxyl radicals ($^{\cdot}OH$), which can oxidize the substrate to produce an oxidized product and H_2O.

Glutathione peroxidase (GPx), an important peroxidase, exhibits catalytic activity due to its selenium-cysteine catalytic center, which catalyzes H_2O_2 with the assistance of glutathione (GSH). In the reactive process, H_2O_2 can be transformed to $^{\cdot}OH$ initially, and finally H_2O is produced. As shown in Fig. 3a, a novel Fe_3O_4/MIL-88-H_2O_2-methylene blue (MB)-peroxidase nanozyme was applied for the colorimetric detection of GSH. The possible mechanism was that the Fe^{2+} of the MOF reacted with H_2O_2 to produce $^{\cdot}OH$, catalyzing MB to form reactive products. When GSH was added to the Fe_3O_4/MIL-88-H_2O_2-MB system, GSH could react with the Fe^{3+} of the MOF to produce glutathione disulfide (GSSH) and Fe^{2+}. Meanwhile, MB would fade.[70]

$$2AH + H_2O_2 \xrightarrow{\text{Peroxidase}} 2A + 2H_2O \quad (1)$$

$$2AH + ROOH \xrightarrow{\text{Peroxidase}} 2A + ROH + H_2O \quad (2)$$

2.2. Oxidase-like nanozymes

Oxidase-like nanozymes, such as Au, Pt, MnO_2 and some hybrid nanozymes, can catalyze the oxidation of substrates by O_2.[55,71]

Table 1 Applications of nanozymes with different enzyme-like activities

Nanozyme	Nanomaterials	Crystalline structure	Size	Synthetic method	Applications	Ref.
Peroxidase	Cubic boron nitride (c-BN)	Irregular-particle shape	420 nm	Modified by ion implantation and thermal annealing	Dihydroxyl radicals detection and rhodamine B removal	44
	NH_2-MIL-88B(Fe) MOF	Needle-shaped morphology	800 nm	Microwave heating with a yield of *ca.* 30%	Methylene blue degradation	45
	Au/CuS composite	Hexagon shape	500–700 nm	Sophisticated solvothermal method	Degrading rhodamine 6G	46
	Plasmonic gold nanoparticles (AuNPs)	Nanoparticles	13 nm	The Turkevich method with minor alterations	Proteolytic biomarker determination	47
	Fe_3O_4–TiO_2/reduced graphene oxide (FTG)	Agglomerated form	9 ± 0.2 nm	One-step simple hydrothermal technique	Detection and photodegradation of pesticide	48
	Fe_3O_4 nanoparticles	Granular shape	11 nm	Modified coprecipitation method	Phenolic pollutants detection	49
	Boron nitride quantum dots anchored porous CeO_2 nanorods (BNQDs/CeO_2)	Porous nanorods	0.21–0.32 nm	A two-step hydrothermal treatment	Kanamycin detection	50
Oxidase	Copper-containing carbon dots (Cu-CDs)	Spherical particles	9.7 nm	One-pot hydrothermal method	Hydroquinone detection	51
	MnO_2 nanosheets	2D and ultrathin plane with occasional folds and crinkles	—	Exfoliating the bulk δ-MnO_2 material in BSA aqueous solution according to a literature method, with slight modifications	Glutathione detection	52
	Heparin sodium stabilized platinum nanoparticles (HS-PtNPs)	Face-centered cubic shape	4.8 ± 0.6 nm	Basic chemical method	Isoniazid detection	53
	Graphene-like molybdenum disulfide (MoS_2)/multi-walled carbon nanotubes (MWCNTs) porous nanohybrid network (MoS_2/MWCNTs)	Nanohybrid network	—	Dispersed method	Carbendazim detection	54
	Ce/Zr-UiO-66 MOFs	Organic framework	0.20–1.45 nm	Basic chemical method	Oxidation of cysteine and glutathione	55
Catalase	Bovine serum albumin (BSA) and Bi_2Se_3–MnO_2 nanocomposites (Bi_2Se_3–MnO_2@BSA)	Spherical morphology	38 nm	Biomineralization method	Tumor radiotherapy sensitization	56
Superoxide dismutase	NiO nanoflowers	Flower-like structure	2.9 nm	A template-free solvothermal method	—	57

In this process, the substrate loses an electron to form the oxidized product. Meanwhile, O_2 is reduced to generate H_2O, H_2O_2, or $^{\bullet}O_2^-$ (eqn (3) and (4)).[72] The catalytic processes of oxidase-like nanozymes usually include several steps. In general, oxidase-like nanozymes firstly combine with O_2 to form an intermediate, and then utilize this intermediate for the catalytic oxidation of the substrate. Taking Au oxidase as an example, it combines with O_2 to form Au^+–O_2^- or Au^{2+}–O_2^{2-} couple intermediates for the oxidation of the substrate.[73] Glucose oxidase (GOx) plays an important role in many processes and has been mostly applied in the detection of glucose. For instance, Chen *et al.* prepared a novel oxidase by encapsulating Au nanoparticles in Au nanoclusters (AuNP@AuNCs) for sensing glucose. AuNP@AuNCs with GOx-like activity could catalyze glucose to produce H_2O_2 and gluconic acid in the presence of O_2. Further, utilizing TMB, the chromogenic reaction could be employed to detect the concentration of glucose indirectly.[74] Furthermore, a 2-dimensional Co_3O_4-stabilizing Rh nanocomposite (2D Co_3O_4@Rh NC) with oxidase-like activity was used to detect urea and *p*-aminophenol (*p*-Ap). As shown in Fig. 3b, with the addition of urea and *p*-Ap, the color of the reactive system changed quickly. Urea caused oxTMB to produce brown yellow products, while *p*-Ap caused oxTMB to fade to colorless.[75]

$$AH + O_2 \xrightarrow{\text{Oxidase}} A + H_2O \quad (3)$$

$$AH + O_2 + H_2O \xrightarrow{\text{Oxidase}} A + H_2O_2 \quad (4)$$

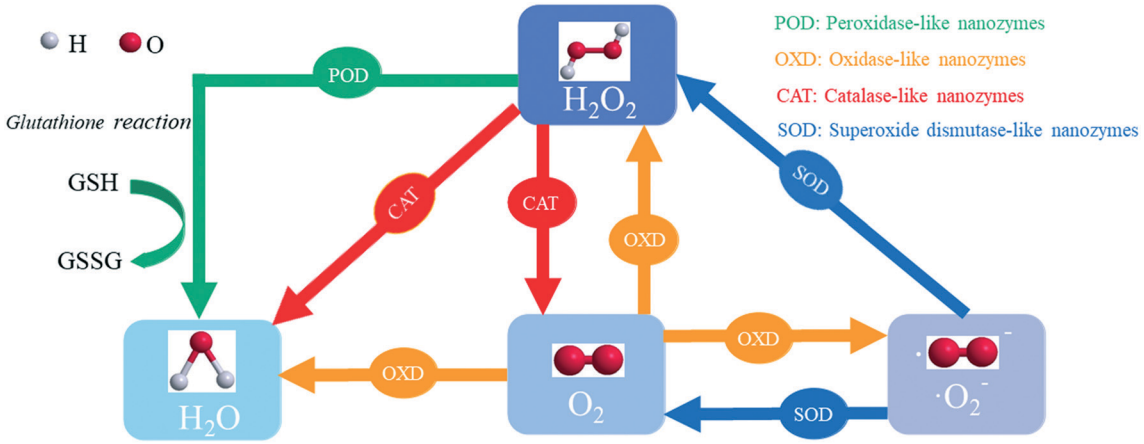

Fig. 2 Inherent connections of the four main nanozymes. Adapted with permission from ref. 61. Copyright 2020, Elsevier.

2.3. Catalase-like nanozymes

Catalase-like nanozymes, as great antioxidants, can effectively decompose H_2O_2 into H_2O and O_2 (eqn (5)). Many nanomaterials have been proven to exhibit catalase-like activity, such as Prussian blue (PB), Co_3O_4, CeO_2, MOFs and some hybrid nanozymes.[6–78] Catalase-like nanozymes combine with H_2O_2, where some reactions firstly produce O_2, and then the H_2O is generated, while others do the opposite depending on their properties.[79] According to the study by Ghibelli's group, the possible catalytic mechanism of CeO_2 catalase-like nanozymes was illustrated as follows. Firstly, CeO_2 reacts with H_2O_2, contributing to the transformation of Ce^{4+} to Ce^{3+}, and H_2O_2 is oxidized to produce O_2 simultaneously. Subsequently, another H_2O_2 can combine with the produced Ce^{3+} to release H_2O with the oxidation of Ce^{3+} to Ce^{4+} (Fig. 3c).[80] In contrast, taking Co_3O_4 NPs as an example, Mu *et al.* reported that Co^{2+} of Co_3O_4 firstly reacts with H_2O_2 to form Co^{3+} and H_2O, and another H_2O_2 reacts with the formed Co^{3+} to produce O_2 finally.[81] Moreover, Xu *et al.* produced a new Fe_3O_4@Cu/GMP-GOx nanozyme, which was constructed by assembling Cu^{2+} and guanosine 5-monophosphate (GMP) on magnetic nanoparticles and encapsulating glucose oxidase (GOx) *in situ*. The nanozyme could mimic both catalase- and laccase-like activity for the colorimetric detection of glucose and β-arbutin.[82] Besides, Zhang *et al.* found that $Co_2V_2O_7$ with intrinsic catalase-like activity could decompose H_2O_2 to produce O_2, which could be detected using a dissolved oxygen meter. Further, $Co_2V_2O_7$ exhibited ultrahigh sensitivity toward H_2O_2 and could successfully detect GSH and glucose.[83]

$$H_2O_2 \xrightarrow{\text{Catalase}} O_2 + 2H_2O \quad (5)$$

2.4. Superoxide dismutase-like nanozymes

Superoxide dismutase-like nanozymes, such as CeO_2 and fullerene, can remove excess reactive oxygen species (ROS), which is beneficial to reduce the damage to living systems.[84] $^{\cdot}O_2^-$, $^{\cdot}OH$ and H_2O_2 are common ROS while most applications involve $^{\cdot}O_2^-$. Specifically, $^{\cdot}O_2^-$ can undergo a dismutation process catalyzed by superoxide dismutase-like nanozymes to produce O_2 and H_2O_2 (eqn (6)).[85] Further, for this dismutation process to occur, it has been reported that it is necessary for some different valence metal ions such as $Cu^{1+/2+}$, $Mn^{2+/3+}$, $Fe^{2+/3+}$ and $Ni^{2+/3+}$ to be involved.[86] For instance, Zhang *et al.* synthesized novel bio-inspired Cu–TCPP MOF nanodots (denoted as CTMDs). This novel MOF could both mimic the catalytic activities of superoxide dismutase and GPx. The Cu active sites of the MOF were similar to natural superoxide dismutase and the ordered channels of the MOF could serve as substrate channels with the ability of superoxide enrichment. Therefore, $^{\cdot}O_2^-$ could be removed efficiently and the H_2O_2 could also be transformed to generate H_2O. Meanwhile, endotoxemia, a pathophysiological manifestation caused by the release of massive endotoxins by several relevant bacteria in the blood and lesions or the input of a large amount of endotoxin-contaminated fluid, could be alleviated in the experimental mouse (Fig. 3d).[87]

$$2^{\cdot}O_2^- + 2H^+ \xrightarrow{\text{Superoxidase Dismutase}} O_2 + H_2O_2 \quad (6)$$

In the detection/removal of organic pollutants by nanozymes, researchers usually try to design various nanomaterials by mimicking the functional mechanism of enzymes. For example, when a nanomaterial has peroxidase-like activity, studies focus on whether the detection/removal processes are according to the catalytic mechanism of peroxide such as whether H_2O_2 is present and H_2O is produced in the reactive systems. Moreover, it is also important to note the similarities between nanozymes and natural enzymes.

3. The detection of organic pollutants by nanozymes

Traditional technologies for the detection of organic pollutants include gas chromatography (GC), high-performance liquid

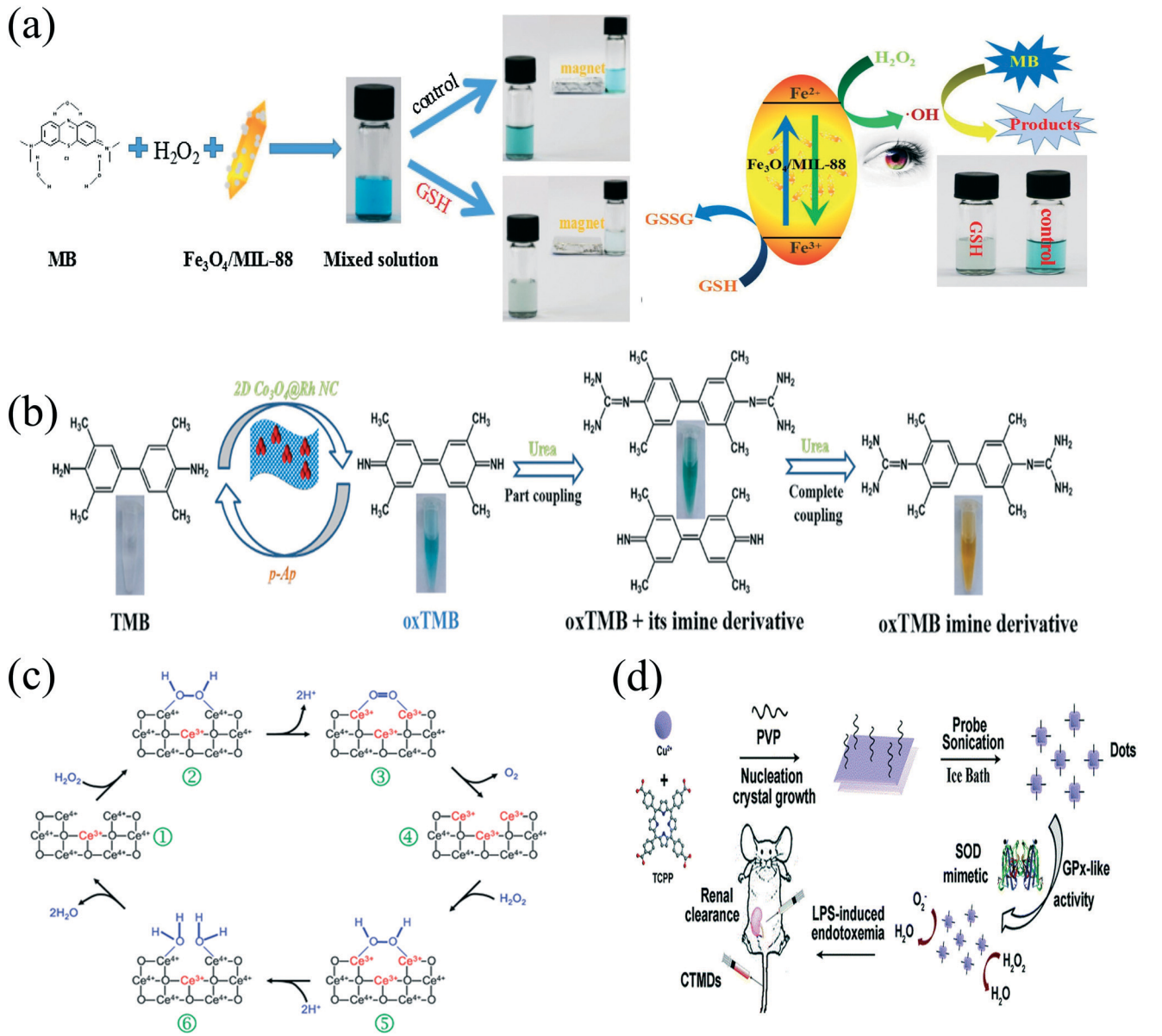

Fig. 3 (a) Highly sensitive and selective colorimetric detection of glutathione *via* magnetic metal organic frameworks. Reproduced with permission from ref. 70. Copyright 2018, Elsevier. (b) Schematic illustration of the 2D Co_3O_4@Rh NC-TMB system applied for the simultaneous determination of urea and *p*-Ap. Reproduced with permission from ref. 75. Copyright 2021, Elsevier. (c) Proposed mechanism of a nanoceria-based catalase mimic. Reproduced with permission from ref. 80. Copyright 2011, the Royal Society of Chemistry. (d) Schematic illustration of the synthesis of CTMDs. Reproduced with permission from ref. 87. Copyright 2019, the Royal Society of Chemistry.

chromatography (HPLC), ion-exchange chromatography, mass spectroscopy (MS), ICP-mass spectrometry, LC-MS and GC-MS.[88–90] For example, Xu *et al.* utilized HPLC for the detection of polycyclic aromatic hydrocarbons (PAHs), fluoroquinolones (FQs), and sulfonamides (SAs). The detection ranges were 0.24 to 0.33 ng mL^{-1} for FQs, 0.04 to 0.38 ng mL^{-1} for PAHs, and 0.63 to 1.31 ng mL^{-1} for SAs. However, the limit of detection (LOD) of these three organic pollutants was not mentioned, which limited the detection capacities.[88] Compared to these traditional technologies, the detection of organic pollutants by nanozymes is environmental-friendly and applied widely, which can detect various organic pollutants such as pesticides, antibiotics and phenolic compounds.[91] For example, Xiao *et al.* synthesized 2D Cu–TCPP(Fe) with peroxidase-like activity for the detection of sulfonamide. This detection system had a wide detection range (1.186–28.051 ng mL^{-1}) and satisfactory accuracy and precision (recoveries, 64–118% and CV, 2.16–7.27%) with a low LOD of 0.395 ng mL^{-1}.[92] Both examples showed that nanozyme detection technology has wider linear ranges compared with traditional detection technologies.[88,92]

The detection of organic pollutants using nanozymes is popular and has been extensively researched.[49,93,94] The typical organic pollutants and detection methods using nanozymes are summarized in Table 2.[11,49,54,92,95–102] The

Table 2 Summary of the application of nanozymes for the detection of organic pollutants

Detection methods	Published papers	Advantages	Disadvantages	Nanozyme	Enzyme-like activity	Organic pollutants	Linear range	LOD	Ref.
Colorimetric method	437	• Convenient • Low cost • Fast	• Serious interference • Low sensitivity • Substrates need to be of high purity	Gold nanoclusters	Peroxidase	Tetracycline	1.5–30.0 μM	0.2 μM	95
				Fe_3O_4 NPs	Peroxidase	Phenolic pollutants	1.67 μM–1.2 mM	3.79 μM	49
				CuS/g-C_3N_4	Peroxidase	Ibuprofen	0–100 mg L^{-1}	16.1 mg L^{-1}	96
				Pd@AuNRs	Peroxidase	Malathion	0.005–200 μg mL^{-1}	0.005 μg mL^{-1}	97
				Cu–N–C SAzymes	Peroxidase	OPs	1–300 ng mL^{-1}	0.60 ng mL^{-1}	98
				MIL-101(Fe)	Peroxidase	OPs	8–800 ng mL^{-1}	1 ng mL^{-1}	99
Fluorescent method	83	• High sensitivity • Low LOD	• Low stability • Fluorescent substrates	MIL-101(Fe)	Peroxidase	Carbaryl	2–100 ng mL^{-1}	1.45 ng mL^{-1}	100
Electrochemical method	107	• High sensitivity • High accuracy • Wide ranges • Automation	• Poor selectivity • Short life span	2D Cu–TCPP(Fe)	Peroxidase	Sulfonamide	1.186–28.051 ng mL^{-1}	0.395 ng mL^{-1}	92
				$CoFe_2O_4$	Peroxidase	Kanamycin	1 pM–1 μM	0.5 pM	101
				MoS_2/MWCNTs	Oxidase	Carbendazim	0.04–100 μM	7.4 nM	54
Photoelectrochemical method	6	• Digitalization • High precision • Fast	• Poor adaptability • Weak signal	PtNi nanozyme	Peroxidase	Chloramphenicol	0.1 pM–100 nM	26 fM	11
Chemiluminescence method	29	• High sensitivity • High specificity	• Low stability • Short luminous time	MOF-Pt	Catalase	Chlorpyrifos	0.5 ng mL^{-1}–1.0 μg mL^{-1}	0.21 ng mL^{-1}	102

number of published papers was collected from Web of Science using the keywords "nanozyme + respective detection methods". As shown in Table 2, the detection methods usually include the colorimetric method, fluorescence method, electrochemical and photoelectrochemical method and chemiluminescence method.[50,97,102] For example, Liu *et al.* developed a robust ratiometric fluorescent nanosensor based on bifunctional Fe-based metal–organic frameworks (NH_2-MIL-101(Fe)) for the high-performance determination of pesticides.[100] Tang's group designed a novel self-powered photo-electrochemical (PEC) aptasensor for the determination of chloramphenicol (CAP). In this biosensor system, the PtNi nanozyme with excellent peroxidase-like activity could catalyze the oxidation of 4-chloro-1-naphthol to generate an insoluble precipitate, leading to an obvious decrease in photocurrent and further realizing signal amplification. Depending on the relationship between the CAP concentration and the PEC signal, this PEC biosensor could achieve the ultrasensitive detection of CAP.[11] Lu *et al.* constructed a long-lasting chemiluminescence (CL) imaging sensor for the detection of OPs. The method was based on *N*-(4-aminobutyl)-*N*-ethylisoluminol/Co^{2+}/chitosan (ABEI/Co^{2+}/CS) hydrogels, where metal organic framework materials (MOF-Pt) with catalase-like activity were selected as catalysts to significantly improve the sensitivity.[102] Particularly, the colorimetric method and electrochemical method are mostly applied in the detection of organic pollutants using nanozymes according to the number of published papers, as shown in Table 2. Moreover, the main organic pollutants detected by nanozymes include pesticides, antibiotics and phenolic compounds, as presented in Table 2. Therefore, a summary focusing on the mechanisms for the detection of organic pollutants by nanozymes is essential (Fig. 4).

3.1. Colorimetric method

The colorimetric method is the most common detection method for the detection of organic pollutants by nanozymes.[48,97] This method is convenient and usually allows the indirect determination of the concentration of organic pollutants based on the change in the color of common chromogenic substrates (*e.g.*, TMB, *o*-phenylenediamine (OPD), and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS)) in catalytic processes employing nanozymes. Because of the different concentrations of organic pollutants and different properties of various organic pollutants, the reaction systems between organic pollutants and nanozymes exhibit obvious trends in color depth. Actually, some organic pollutants especially phenolic compounds can be oxidized to produce colored products directly, and thus it is not necessary to utilize chromogenic substrates. The colorimetric method is easy because the naked eyes can be used to qualitatively determinate whether the catalytic reaction happens. With the help of UV-vis spectroscopy, the quantitative determination of the final products is also possible.

Common organic pollutants, such as pesticides, antibiotics, dyes, and phenolic compounds, can be detected *via* colorimetric methods.[103,104] By introducing chromogenic substrates in the reaction system during the catalytic oxidation process by nanozymes, organic pollutants can be detected sensitively and quickly. For example, Tang's group prepared boron nitride quantum dot-anchored porous CeO_2 nanorods (BNQDs/CeO_2) as a novel peroxidase-like nanozyme and utilized a nanozyme–aptamer system for the colorimetric detection of kanamycin (KAN). The aptamer could obviously improve the catalytic activity of BNQDs/CeO_2, which oxidized TMB to form oxidized oxTMB. Conversely, KAN could restrain this catalytic enhancement through the aptamer-target recognition event (Fig. 5a).[50] Similarly, Zhao *et al.* studied a gold nanoparticle (AuNP) nanozyme for the colorimetric detection of streptomycin, and the chromogenic substrate was ABTS.[105] Singh *et al.* found that Pd@AuNR peroxidase mimetics could allow the colorimetric detection of malathion excellently with OPD as the reactive chromogenic substrate.[97] Moreover, phenolic compounds can be detected well due to the bright colors of the resulting products. Wu *et al.* prepared small-sized Fe_3O_4 NPs with peroxidase-like activity, which

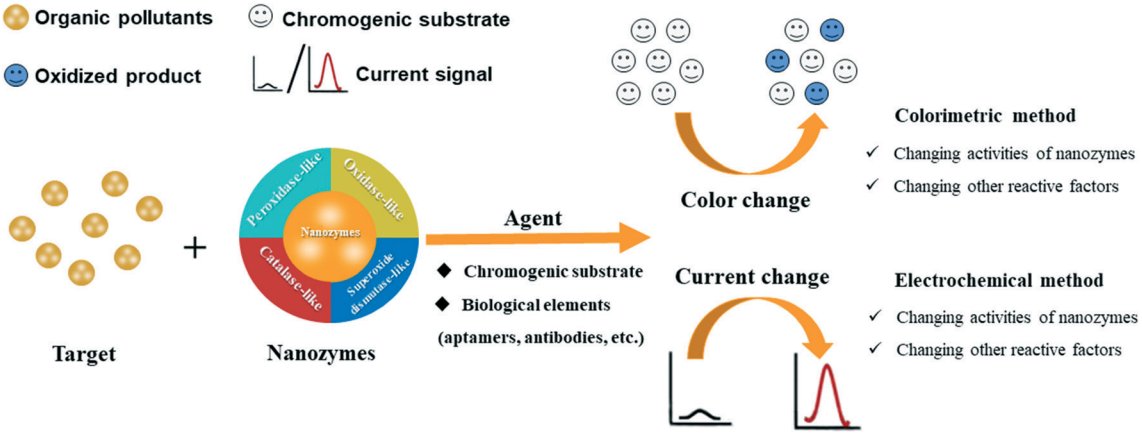

Fig. 4 The detection of organic pollutants by nanozymes.

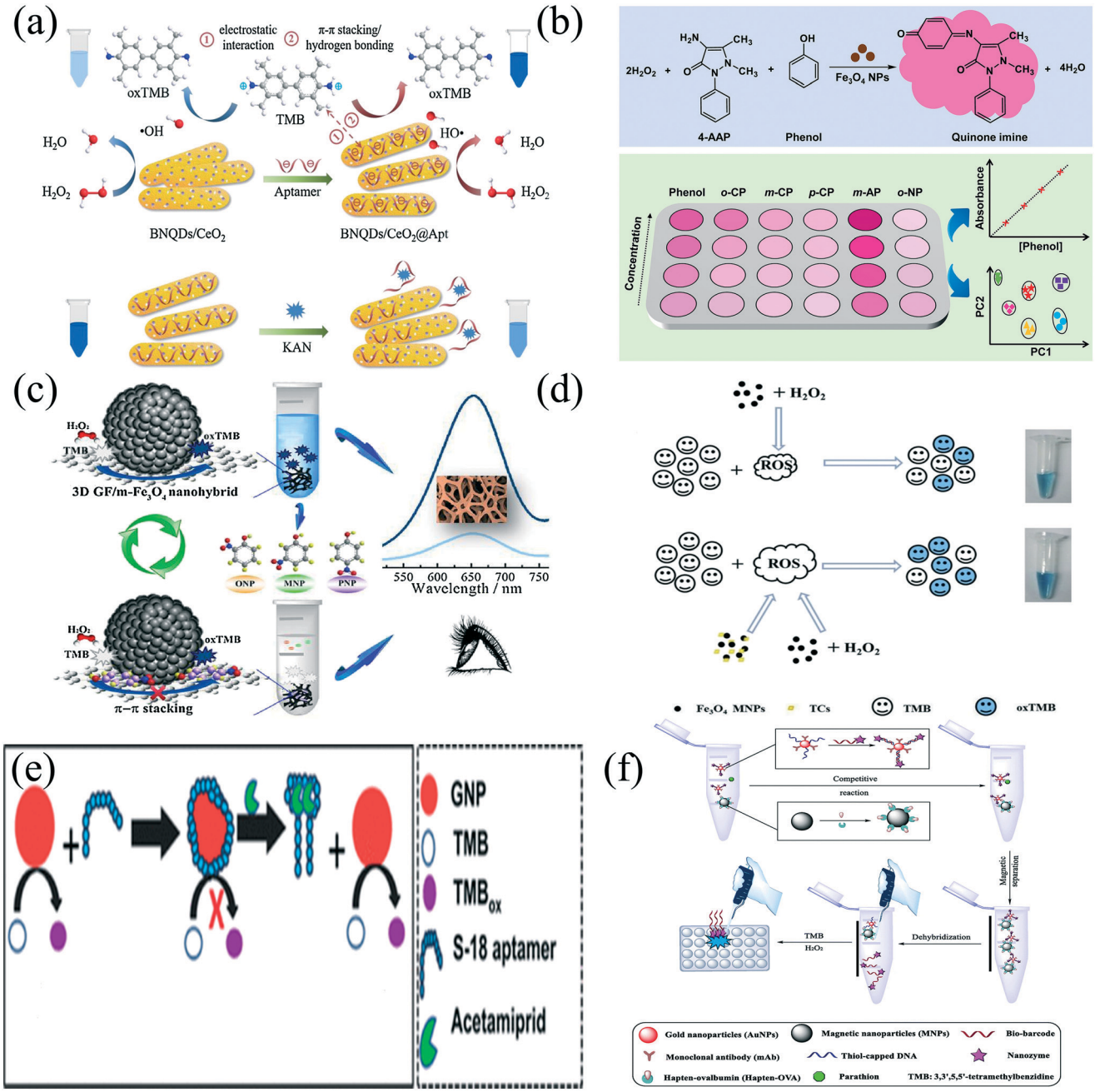

Fig. 5 (a) Mechanism of the aptamer-enhanced peroxidase-like activity of the BNQDs/CeO_2 nanozyme for the colorimetric detection of KAN. Reproduced with permission from ref. 50. Copyright 2021, Elsevier. (b) Illustration of the reaction of phenol, 4-AAP and H_2O_2 catalyzed by peroxidase-like Fe_3O_4 NPs and the fabricated sensor array for the colorimetric quantification and discrimination of phenolic pollutants. Reproduced with permission from ref. 49. Copyright 2020, Elsevier. (c) Schematic representation of the selective colorimetric determination of *p*-nitrophenol (PNP) based on the 3D GF/*m*-Fe_3O_4 nanohybrid nanozyme. Reproduced with permission from ref. 107. Copyright 2018, Elsevier. (d) Schematic illustration of the TC assay based on the enhancement of the Fe_3O_4 MNPs–TMB–H_2O_2 reaction. Reproduced with permission from ref. 111. Copyright 2016, Elsevier. (e) Schematic representation of the reversible inhibition of the nanozyme activity of GNPs using an acetamiprid-specific S-18 ssDNA aptamer. Reproduced with permission from ref. 114. Copyright 2014, the American Chemical Society. (f) Schematic representation of the colorimetric bio-barcode immunoassay for parathion based on amplification using platinum nanoparticles as a nanozyme. Reproduced with permission from ref. 117. Copyright 2019, Springer-Verlag GmbH Austria.

could catalyze the oxidation of coupling phenolic species and 4-aminoantipyrine (4-AAP) with the assistance of H_2O_2, generating a remarkable color change (Fig. 5b).[49] Based on the detection principle, various common phenolic pollutants were detected sensitively.[106]

To deeply understand the inherent differences of the presented colors in various nanozyme-chromogenic substrate-organic pollutant systems, several studies have been reported.[107,108] In general, in the catalytic processes of nanozymes, the detection mechanisms of the reactive systems

can be mostly divided to two types. One is the combination of the nanozyme and organic pollutant to change the activities of the nanozyme, and the other is directly changing other reactive factors to influence the properties of the nanozyme in reactive systems (*e.g.*, the activity of acetylcholinesterase (AChE)).[109] In the former mechanism, monitoring each factor of the nanozyme–chromogenic substrate–organic pollutant-H_2O_2/O_2 system is necessary.[110] As shown in Fig. 5c, three-dimensional graphene/mesoporous Fe_3O_4 (3D GF/*m*-Fe_3O_4) with peroxidase-like activity could catalyze TMB to form remarkable oxTMB. When adding *p*-nitrophenol (PNP) to this reactive system, PNP was adsorbed on the catalytic sites of the 3D GF/*m*-Fe_3O_4 nanozyme by π–π stacking, which inhibited the combination of nanozyme and TMB, leading to the disappearance of the chromogenic reaction of TMB. The fading of the reactive system was a signal of the participation of PNP in the catalytic nanozyme system.[107] Conversely, Wang *et al.* found that using the combination of Fe_3O_4 MNPs and TCs, the catalytic activity of the Fe_3O_4 MNPs was improved, resulting in a deeper color of reactive system (Fig. 5d).[111] In the latter mechanism, the direct changes in other factors that influence the properties of nanozyme systems were shown by Zhang's group. Acetylthiocholine (ATCh) can react with AChE to produce high thiocholine (TCh). TCh, a thiol-containing compound with reducibility, reduced the degree of polyacrylic acid-coated cerium oxide nanoparticle (PAA-CeO_2)-catalyzed oxidation of TMB. Therefore, the oxidase-like activity of PAA-CeO_2 decreased. However, in the presence of organophosphorus pesticides (OPs), the enzymatic activity of AChE was inhibited, which produced a low amount of TCh, leading to a deepened color after the oxidation of TMB.[109] Similarly, Liang *et al.* utilized GeO_2 with peroxidase-like activity for the effective detection of OP. In the presence of OP, the production of TCh was blocked and more TMB could be oxidized to oxTMB.[112]

Moreover, in terms of the colorimetric detection of organic pollutants by nanozymes, the use of biological elements (aptamers, antibodies, *etc.*) is also common strategy due to their strong stability and high selectivity.[113–117] For example, Weerathunge *et al.* constructed a new colorimetric biosensing assay for the detection of acetamiprid pesticide. In this system, gold nanoparticles (GNPs) with peroxidase-like activity could combine with the acetamiprid-specific S-18 aptamer, which inhibited the enzyme-like activity of GNPs, preventing the oxidation of TMB. However, in the presence of the target acetamiprid pesticide, the S-18 aptamer combined with acetamiprid, restoring the peroxidase-like activity of GNPs. Meanwhile, the bare GNPs oxidized the colorless TMB into oxidized oxTMB (Fig. 5e).[114] Chen *et al.* utilized a novel colorimetric method for the detection of parathion. In the reactive system, there were three types of probes for the detection of parathion residues. (1) An AuNP probe was modified with monoclonal antibodies (mAbs) and thiolated single-stranded DNA (ssDNA); (2) a magnetic nanoparticle (MNP) probe was functionalized with ovalbumin coupled with parathion hapten (OVA-hapten); (3) a PtNP probe was modified with the complementary thiolated ssDNA (C-ssDNA). Firstly, the MNP probe and parathion competitively reacted with the AuNPs probe to form a probe complex (MNPs-AuNPs), and then the complexes reacted with the PtNP probe. Finally, the PtNP probe was released from the complex by the addition of dithiothreitol (DTT) and was used to catalyze TMB. This system had a linear range from 0.01–50 μg L^{-1} and its LOD was 2.0×10^{-3} μg L^{-1} (Fig. 5f).[117]

3.2. Electrochemical method

The electrochemical method is also a common method for the detection of organic pollutants by nanozymes.[11,54] Its core is the electrochemical signal change especially the current change. In general, the mechanisms of the electrochemical method can be divided into two categories, namely changing activities of nanozymes and changing other factors. For the first way, Xiao *et al.* designed a novel electrochemical immunosensor for ultrasensitive detection of sulfonamides (SAs), in which the synthesized 2D Cu–TCPP(Fe) with peroxidase-like property was used as a nanozyme and directly modified on the electrode surface. Meanwhile, the structure of 2D Cu–TCPP(Fe) could be destroyed by the polyethyleneimine (PEI) from PEI-GO@Ab_2 due to the stronger affinity between PEI and Cu^{2+}, leading to a change in the activity of the prepared nanozyme. When H_2O_2 was introduced in the system, the electrochemical current significantly declined owing to the decrease in the peroxidase activity of 2D Cu–TCPP(Fe), which led to signal amplifications (Fig. 6a).[92] The second way is changing other reactive factors such as the activity of AChE. Wu *et al.* used manganese dioxide nanosheets (MnNS) with oxidase-like property for the detection of OPs. In their study, ATCh was specifically hydrolyzed into reductive TCh, which decomposed MnNS into Mn^{2+} and decreased the amount of MnNS, subsequently preventing MnNS from catalyzing the oxidation of TMB. Consequently, TMB was not affected and contributed to a large current. However, upon incubation with OPs, the irreversible inhibition of the production of TCh suppressed the decomposition of MnNS by declining the enzyme-like activity of AChE. More TMB could be catalytically oxidized by MnNS, resulting in a decrease in electrochemical signal. Based on the changes in the electrochemical signal, the concentration of OPs could be detected accordingly. Hence, although TCh could decompose MnNS into Mn^{2+}, there was little possibility for this process to proceed because of the presence of OPs. Therefore, the MnNS oxidase nanozyme would not be gradually exhausted during the detection and the method was reproducible at the laboratory level (Fig. 6b).[118] In further practical applications, the real environment had little effect on this detection system in the absence of OPs.

Especially, in terms of the electrochemical method for the detection of organic pollutants by nanozymes, utilizing the specific recognition of biological elements (aptamers, antibodies, *etc.*) is common strategy.[92,119,120] In general, the

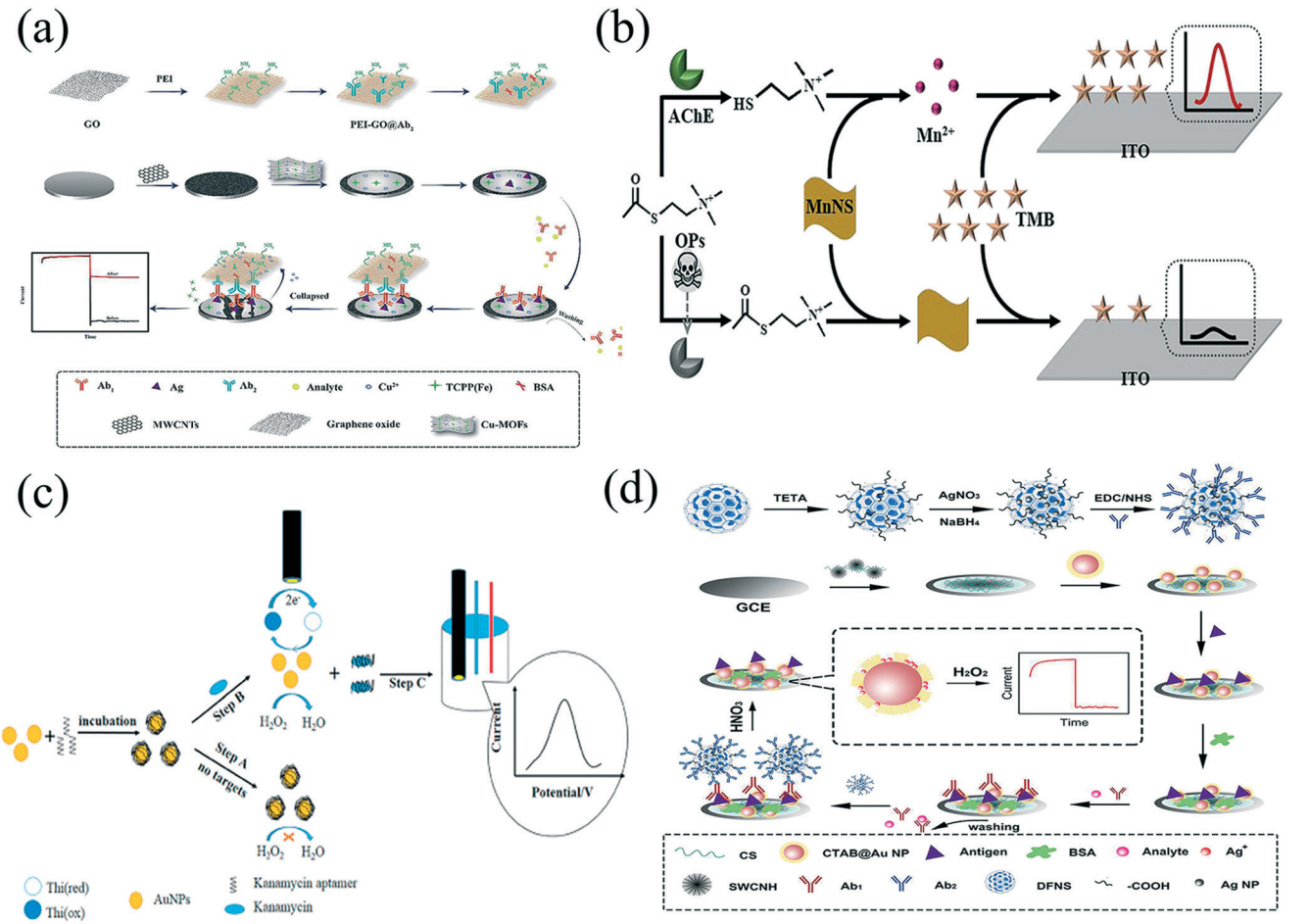

Fig. 6 (a) Schematic illustration of the electrochemical immunosensor for the detection of sulfonamides. Reproduced with permission from ref. 92. Copyright 2019, Elsevier. (b) Diagrammatic sketch of the MnNS-based homogeneous electrochemical sensor for OPs. Reproduced with permission from ref. 118. Copyright 2021, the American Chemical Society. (c) Schematic illustration of the electrochemical detection of kanamycin based on aptamer and nanozyme. Reproduced with permission from ref. 119. Copyright 2016, Elsevier. (d) Schematic illustration of the competitive immunosensor based on Ag^+@CTAB-AuNPs for detecting SMZ. Reproduced with permission from ref. 120. Copyright 2019, Elsevier.

detection process of organic pollutants by aptamers includes several steps. Firstly, aptamers bind to the surfaces of nanozymes, leading to a decline in the activities of the nanozymes. Then, with the addition of organic pollutants, the organic pollutants preferentially combine with specific aptamers, causing them to detach from the surface of the nanozymes. Meanwhile, the activities of nanozymes are restored. For example, Wang *et al.* utilized an electrochemical method to detect kanamycin precisely. In the presence of kanamycin, AuNPs with peroxidase-like activity could stay away from their aptamers and excellently catalyze the reaction between H_2O_2 and reduce thionine to generate oxidized thionine, which showed an apparent reduction peak (Fig. 6c).[119] Utilizing antibodies for the efficient detection of organic pollutants is also a common method. For instance, Yang *et al.* developed an electrochemical immunosensor for the ultrasensitive detection of sulfamethazine (SMZ) based on AuNPs with peroxidase-like activity. Cetyltrimethylammonium bromide-capped AuNPs (CTAB-AuNPs) were used as a signal amplifier and electrode matrix and coated with an antigen–antibody ($Cag–Ab_1$) specific binding system as a recognition unit for the target compound. Silver nanoparticle labels were functionalized with dendritic fibrous nanosilica (DFNS@AgNPs) and decorated on chitosan/single-walled carbon nanohorn (CS/SWCNH)-modified glass carbon electrodes (GCEs). Under acidic conditions, the massive amount of Ag^+ bound to the surface of the AuNPs dissolved, and then formed Ag^+@CTAB–AuNP complexes, which resulted in a distinct improvement in peroxidase-like activity and enhanced current response. Furthermore, after treating the established electrode with acid solution, the resistance of the destroyed $Ab_1–Ab_2$-DFNS conjugation decreased due to the loss of labels, which led to the amplification of the electrochemical signals (Fig. 6d).[120]

Considering the advantages and disadvantages and choosing appropriate methods for practical application are necessary. At present, the colorimetric method is still popular owing to its convenience and low cost. Also, the electrochemical method exhibits high sensitivity and wide linear ranges. However, the development of new detection

methods is necessary for better improving the detection ranges and detecting more organic pollutants. Combined with the experimental application scenarios, choosing the optimal detection method is also important.

Further, based on the existing theoretical research mentioned above, in the field of practical application using nanozymes for the detection of organic pollutants, exploring convenient and fast detection devices will be a promising research direction. Although most of the current studies are still in the laboratory stage, the unveiling of the relative mechanisms has promoted the research and development of nanozyme-based contaminant detection devices. At present, the common nanozyme-based contaminant detection device is smartphone-based. The image information of the kit captured *via* a smartphone can be transduced to a hue intensity, which provides a directly quantitative tool to detect relevant organic pollutants. Meanwhile, due to the widespread availability of smartphones worldwide, it has been reported that numerous smartphone-based contaminant detection devices are promising.[118–122] For example, Wei *et al.* utilized nanoceria nanozyme-assisted technology for the detection of organophosphorus pesticides. A dual-mode method including smartphone-based colorimetric and spectroscopic strategies was rationally developed. In appropriate conditions, the detection method could well-detect methyl-paraoxon with an LOD of 0.42 μmol L^{-1}. Further, this present dual-mode method based on two different mechanisms could be applied for the detection of environment samples, even those with complex substances.[123] Moreover, Jin *et al.* designed a real-time nanozyme detection device using a smartphone, which could detect oxalate well with an LOD of 8.0 μmol L^{-1}. In this detection system, MnO_2 nanosheets were employed as the nanozyme. A smartphone biosensor was also successfully applied directly as a quantitative tool and achieved the requirements of routine screening and disease prevention.[122] Although pilot-scale research and subsequent large-scale research have not been carried out in detail, we believe that with the deepening of the research in this field, once the existing problems are solved including improving the detection range of organic pollutants, reducing the LOD, reducing the interference of multiple organic pollutants and lowering the cost of practical application, the commercial value of nanozymes for the detection of organic pollutants will be immeasurable.

4. The removal of organic pollutants by nanozymes

The methods for the removal of organic pollutants by nanozymes mainly include degradation processes. The typical organic pollutants such as phenolic compounds, polychlorinated biphenyls, dyes, pesticides and antibiotics can be removed *via* degradation processes (Table 3).[93,124–128] Traditional degradation technologies such as Fenton oxidation technology, ozone oxidization technology, photocatalytic oxidation technology, ultrasonic oxidation technology and persulfate oxidation technology have been applied for the degradation of organic pollutants.[129–131] For example, Kavitha *et al.* reported the degradation of phenol *via* the Fenton method. They found that the maximum mineralizing efficiency for phenol was 41%.[132] However, these traditional degradation technologies easily produce by-products and cause secondary pollution. Further, these catalytic processes require significant energy and are not environmental-friendly. In contrast, nanozymes can catalyze organic pollutants efficiently and their degradation efficiency is relatively high.[93] For example, Jiang *et al.* constructed a recyclable ferromagnetic chitosan nanozyme (MNP@CTS) for the decomposition of phenol. The degradation efficiency was higher than 95% after 5 h.[127] Wang *et al.* reported Au/Pt/Co tri-metal nanozyme with peroxidase-like and catalase-like activity for the degradation of phenol. The nanozyme was capable of degrading 90% phenol within 60 min and the removal efficiency was over 99% when the treatment time was over 24 h.[133]

In general, the processes for the degradation of organic pollutants utilizing nanozymes are complex, which are accompanied by several intermediate reactions and can produce many intermediate products. In these catalytic processes, nanozymes can catalyze the degradation of organic pollutants to form some intermediates, and finally produce degraded products (CO_2 and H_2O are produced when the organic pollutants are degraded completely). As shown in Fig. 7, the degradation processes are summarized as substrate binding, oxidation, electron transfer and decomposition (eqn (7)–(10)).[134–138] Firstly, nanozymes combine with organic pollutants to form coupling products.[139] Then, the process of oxidation occurs, which produces several free radicals.[140] Next, electron transfer occurs.[141] Electron transfer usually refers to the movement of electrons between two atoms or other chemical substances, such as molecules. For example, Sun *et al.* found that free radicals were extremely unstable due to their unpaired electrons and these radicals could take electrons from neighboring molecules to become a new free radical, which tended to grab an electron. As a result of this chain reaction, the macromolecular organic pollutants were degraded stepwise. When all the reactions accomplished, the organic pollutants were transformed to generate degraded products, even CO_2 and H_2O by the decomposition process.[130,142]

$$\text{Nanozymes} + \text{Organic pollutants} \xrightarrow{\text{Substrate Binding}} \text{Coupling products} \quad (7)$$

$$\text{Coupling products} \xrightarrow{\text{Oxidation}} \text{Oxidation radicals} \quad (8)$$

$$\text{Radicals} \xrightarrow{\text{Electron Transfer}} \text{Intermediates} \quad (9)$$

$$\text{Intermediates} \xrightarrow{\text{Decomposition}} \text{Degraded products} + \text{Nanozymes} \quad (10)$$

Furthermore, Wang *et al.* investigated a bioinspired laccase-mimicking nanozyme for the removal of phenolic

Table 3 Summary of the application of nanozymes for the removal of organic pollutants

Nanozyme	Enzyme-like activity	Organic pollutants	Removal methods	Removal mechanisms	Removal efficiency	Removal time	K_m[a]	V_{max}[b]	pH	Temperature	Substrate concentration	Ref.
Tb-OBBA-hemin[c]	Peroxidase	17β-Estradiol	Degradation	Electron transfer and decomposition	88.00%	60 min	7.65 μM	13.27 μM s^{-1}	5.00	—	10 μM	93
FDGs[d]	Peroxidase	Simazine	Degradation	Substrate binding, oxidation, electron transfer and decomposition	98.60%	50 min	0.089 mM	0.056 μM s^{-1}	4.80	25 °C	0.1 mM	124
Cu/H_3BTC MOF[e]	Oxidase	Dye AB-10B	Degradation	Electron transfer and decomposition	90.00%	60 min	67.98 μM	94 μM min^{-1}	6.80	30 °C	100 mg mL^{-1}	125
CNPs[f]	Peroxidase	Methyl orange	Degradation	Oxidation and decomposition	93.00%	60 min	550 μM	3.8 μM min^{-1}	5.00	30 °C	50 ppm	126
MNP@CTS[g]	Peroxidase	Phenol	Degradation	Oxidation and decomposition	95.00%	300 min	—	—	4.00	40 °C	100 μM	127
$W_{18}O_{49}$	Peroxidase	MB	Degradation	Oxidation, electron transfer and decomposition	91.00%	60 min	8.734 mM	1.123 μM s^{-1}	5.00	45 °C	20 mg L^{-1}	128

[a] K_m = Michaelis constant. [b] V_{max} = maximum reaction rate. [c] OBBA = 4,4′-oxybisbenzoic acid. [d] FDGs = Fe_3O_4 nanoparticles decorated functionalized rGO sheets. [e] H_3BTC = 1,3,5-benzene tricarboxylic acid. [f] CNPs = cellulose incorporated magnetic nano-bio-composites. [g] MNP@CTS = ferromagnetic chitosan nanozyme.

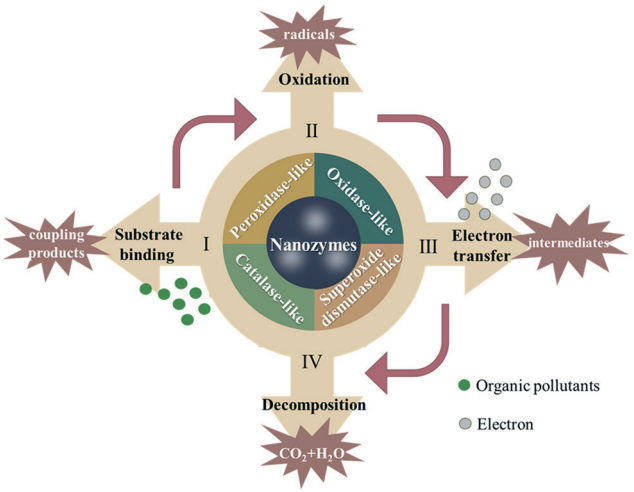

Fig. 7 The degradation processes of organic pollutants by nanozymes.

compounds (laccase is a type of oxidase). They prepared a new class of nanozyme with laccase-like activity *via* the coordination of Cu^{+}/Cu^{2+} with a cysteine (Cys)–histidine (His) dipeptide (CH–Cu). The catalytic mechanism of CH–Cu for the removal of phenolic pollutants included four steps, as follows: (1) substrate binding, (2) oxidation, (3) electron transfer and (4) O_2 reduction near the Cu–N site. Firstly, the active sites of the CH–Cu nanozyme combine with phenolic compounds (hydroquinone), where Cu^{+} binds to the thiol group through chemical binding. Then, the phenolic substrates are oxidized to benzoquinone by Cu^{+}, which is the primary electron acceptor site, with single-electron oxidation of the CH–Cu nanozyme owing to the higher oxidation ability of Cu^{+}. Next, the electrons are transferred through the Cys–His pathway to Cu^{2+} and Cu^{2+} is converted to Cu^{+} after accepting electrons. Besides, owing to the lack of protection of the surrounding chemical groups, Cu^{+} is oxidized to Cu^{2+} by oxygen in the system, which is the final electron acceptor *via* a four-electron reduction procedure and the CH–Cu nanozyme can be generated *via* the oxidation of Cu^{+}.[139] Further, Geng *et al.* investigated a novel copper nanozyme (CNZ) for the degradation of dyes. They found that CNZ with excellent reusability and storage stability could well-degrade methyl orange with a degradation rate of about 93%.[143]

Several nanozymes can simultaneously detect and remove organic pollutants owing to their unique structures.[124,144,145] For example, Boruah *et al.* utilized Fe_3O_4 nanoparticle-decorated functionalized rGO sheet (FDG) nanozymes for the detection and degradation of harmful triazine pesticides.[124] Wang *et al.* constructed a bioinspired laccase-mimicking nanozyme for the degradation and detection of phenolic pollutants.[139] In the future, the application of nanozymes for the simultaneous detection and removal of organic pollutants will increase.

Moreover, the use of nanozyme technology for full-scale/commercial-scale environmental remediation needs to be developed with the deeper research into nanozymes. At present, applying nanozymes for the removal of organic pollutants is limited to the laboratory level. Luckily, with the deepening of research, the theoretical basis of nanozymes for the removal of organic pollutants is relatively mature.[118–121] Developing nanozymes on the pilot scale, and then applying them to actual water environment are significant. Previous studies showed the possibility of the practical applications of nanozymes in the removal of organic pollutants. For instance, Xu *et al.* prepared a new laccase mimic (defined as CA–Cu) *via* the coordination of copper with a cysteine (Cys)–aspartic acid (Asp) dipeptide. The CA–Cu nanozyme exhibited great laccase-like activity and could catalyze the oxidation of a wide range of phenolic pollutants, such as 2,4-dichlorophenol, phenol, *p*-chlorophenol, 2,6-dimethoxyphenol, hydroquinone, *o*-nitrophenol and *o*-aminophenol hydroquinone, providing a promising environmental catalyst for the treatment of phenolic pollutants under high-salt or heavy metal ion conditions.[146]

Further, some nanozymes are not affected by the presence of multiple organic pollutants based on laboratory-level research. Taking an aptasensor as an example, the detection/removal system of organic pollutants by nanozymes is not affected due to the substrate specificity of aptamers. For example, Weerathunge *et al.* showed that the intrinsic peroxidase-mimic nanozyme activity of tyrosine-capped silver nanoparticles (Ag-nanozyme) could be exploited for the highly specific and rapid detection of chlorpyrifos. They designed an aptasensor based on the dynamic non-covalent interaction of the chlorpyrifos specific aptamer (Chl) with the nanozyme (sensor probe) and the pesticide target (analyte). The Chl aptamer ensured high specificity to chlorpyrifos, while the sensor remained unresponsive to other pesticides in the organophosphate and non-organophosphate groups.[115] In a real water environment, few studies have been reported to date. However, applying nanozyme technology for the removal of organic pollutants in real water is possible based on theoretical studies.[115,124–126] Therefore, the development of nanozyme technology on a pilot scale and even large-scale practical application should the focus of future research. Meanwhile, it is essential to explore more efficient nanozymes for the practical removal of organic pollutants. In the practical application of nanozymes, there are multiple organic pollutants in the real environment. Therefore, nanozymes that remove a single organic pollutant will not be suitable for practical application in the presence of hybrid systems consisted of multiple organic pollutants. Previous research indicated that nanozymes exhibit different catalytic activities for different types of organic pollutants. Although the catalytic activity of a specific nanozyme will not decrease, its interaction with multiple coexistent organic pollutants (*e.g.*, phenol, catechol, hydroquinone and naphthol) will cause different removal effects in real water or other environments.[139,146–148]

5. Key factors in nanozyme-driven processes

The detection/removal effects of organic pollutants by nanozymes tend to be influenced by several key factors. In

the process of the detection/removal of organic pollutants by nanozymes, the core mechanism is the change in the enzyme-like activities of nanozymes. Here, some important factors in the nanozyme-driven process are introduced. Size, shape and morphology play the main roles, contributing a direct internal influence on the enzyme-like activities of nanozymes.[27,149–151] Next, pH and temperature as external environmental factors can influence their enzyme-like activities to some extent.[118,124,144] Finally, in reactive systems for detection/removal of organic pollutants by nanozymes, other secondary factors such as type of organic pollutant, dosage of nanozyme catalyst and concentration of organic pollutant are discussed.[49,119,152]

5.1. Main internal factors

5.1.1. Size. The detection/removal of organic pollutants by nanozymes is size-dependent. The same type of nanozyme with different sizes usually presents different catalytic activities. In general, nanozymes with a smaller size have higher catalytic activities, which is attributed to three aspects.[153] Namely, an increase in the specific surface area, number of surface atoms and surface energy with a decrease in the size of nanozymes.[151] For example, Wu *et al.* investigated the use of $CoFe_2O_4$ with peroxidase-like activity for the degradation of MB. The pore diameters and specific surface areas of $CoFe_2O_4$ NPs obtained at 300 °C (CF300), 400 °C (CF400) and 500 °C (CF500) were compared, which possessed pore diameters of 4.47, 8.84, and 14.29 nm and specific surface areas of 204.10, 112.17 and 58.44 $m^2\ g^{-1}$, respectively. CF300 with the smallest size showed the highest specific surface area and catalytic activity and could well-degrade MB.[145] Similarly, Xi *et al.* studied the catalytic activities of palladium (Pd)–Ir core–shell nanoparticles (Pd–Ir NPs) with peroxidase-like activities at four different sizes (3.3, 5.9, 9.8 and 13.0 nm), and found that the Pd–Ir NPs with the largest size exhibited the lowest catalytic activity.[154] Also, with the particle diameters of 10, 2, and 1 nm, the surface atoms accounted for 20%, 80%, and 99%, respectively. Moreover, together with an increase in specific surface area and number of surface atoms, nanozymes with higher surface energies are extremely unstable and easily react with other substrates, therefore presenting strong catalytic activities.[151] Furthermore, an increase in Ce^{3+} improved the enzyme-like activities of nanoceria when its size was less than 5 nm.[155,156]

5.1.2. Shape and morphology. It is well known that the shape and morphology of nanomaterials play a critical role in their catalytic properties.[157–159] In the processes of the detection/removal of organic pollutants using nanozymes, nanozymes with different shapes and morphologies will present different catalytic activities, further influencing the effects of the detection/removal of organic pollutants. For example, Wan *et al.* compared the oxidase-like activities of MnO_2 nanomaterials with different shapes such as sheets, spheres, wires, complexes, and sticks. They found that although the nanospheres and nanowires exhibited the highest activities, the nanospheres were not stable, and thus only the MnO_2 nanowires were used for further bioanalysis.[160] Singh *et al.* compared the enzyme-like activities of different-shaped Mn_3O_4 NPs (*e.g.*, nanoflowers, flakes, cubes, polyhedra, and hexagonal plates). They found that the flower-shaped Mn_3O_4 exhibited the highest catalytic activities, which were chosen for further application.[161] Moreover, the activity of nanozymes is dependent on their morphology. This is because the atom coordination environment and dangling bonds are closely related to the crystal planes.[151] For instance, the coordination saturation follows the order of (001) facet > (010) facet > (100) facet. It has been shown that the glutathione peroxidase-like activity of V_2O_5 nanozymes follows the order of only (001) facet-bound nanowires < large (001) and minor (010) facet-bound nanosheets < major (010) and minor (001) facet-bound nanoflowers < two major (100), (010) facet-bound nanospheres.[150,162] Similarly, Liu *et al.* studied the morphology effects of Fe_3O_4 MNPs on their peroxidase-like activities. They found that the more active (220) planes of the triangular plates were responsible for their higher activities compared with the octahedrons with (111) planes.[163]

5.2. External environmental factors

5.2.1. pH. Different solution pH usually lead to different detection effects and removal efficiencies of organic pollutants in the presence of nanozymes. pH can obviously change the enzyme-like activities of several nanozymes, causing them to show multiple enzyme-mimicking characteristics and catalytic mechanisms at different pH.[151] For example, Li *et al.* demonstrated that Au, Ag, Pt and Pd nanomaterials exhibited peroxidase-like activities at acidic pH and catalase-like activities at basic pH.[164] Lin *et al.* indicated that under acidic conditions, AuNPs could be considered a peroxidase-like nanozyme. In contrast, in neutral or alkaline conditions, AuNPs presented catalase-like activity or superoxide dismutase-like activity.[165] This pH-switchable phenomenon was further investigated by Nie and co-workers using 1–2 nm platinum nanoparticles, which showed that the catalase-like activity was evident under basic conditions, while the peroxidase-like activity was more dominant under acidic conditions.[166] Moreover, Adeel *et al.* synthesized a novel Co-based two-dimensional (2D) metal framework nanosheet (MAF-5-CoII NS) nanozyme, which displayed a good redox activity in both neutral and alkaline media with the formation of the Co^{2+}/Co^{3+} redox pair.[167] Jiang *et al.* prepared a ferromagnetic chitosan nanozyme (MNP@CTS) for decomposing phenol. When the solution pH changed from acidic to alkaline, the highest catalytic activity of MNP@CTS was observed in acidic condition. The optimal pH was approximately 4.0 and over 95% phenol could be removed from the aqueous solution within 5 h.[127] Furthermore, He *et al.* found that $CoPW_{11}O_{39}$ with peroxidase-like activity exhibited catalytic activity at neutral pH. The proposed mechanism indicated that $CoPW_{11}O_{39}$ has

a surface with abundant negative charges from the intrinsic properties of the Keggin-structured polyoxometalate, which can attract positive-charged substrates by electrostatic interactions. Once the reactive pH changes to acidic condition, the H^+ in solution combines with the intrinsic negatively charged surface of $CoPW_{11}O_{39}$, which makes the charge of the nanozyme very weak in acidic solution. Correspondingly, the enzyme-like activity of $CoPW_{11}O_{39}$ decreases obviously.[168]

5.2.2. Temperature. Unlike natural enzymes, nanozymes usually have excellent tolerance in various temperature ranges. However, a high temperature can influence the enzyme-like activities of nanozymes. In different reactive systems, there is an optimal temperature for the catalytic activities of nanozymes. Meanwhile, the efficiency for the detection/removal of organic pollutants by nanozymes is highest at the optimal temperature.[115] For instance, Wang *et al.* found that 55 °C was optimal for the application of $LaNiO_3$ perovskite nanocubes as peroxidase mimics.[169] Zhang *et al.* investigated the peroxidase-like activity of Fe-loaded MOF-545(Fe) under different temperature conditions. In their study, 20 °C was found to be the most appropriate temperature when the reaction temperature changed from 10 °C to 60 °C. At this temperature, the Fe-loaded MOF-545(Fe) nanozyme exhibited the greatest activity.[170] Furthermore, Geng *et al.* studied the influence of the reaction temperature for the degradation of MO by a CNZ nanozyme. The results showed that when the temperature increased from 20 °C to 60 °C, the activity of the CNZ nanozyme improved correspondingly.[143] Similarly, Wang *et al.* found that 100 °C was optimal for the degradation and detection of phenolic pollutants by a CH–Cu nanozyme.[139]

5.3. Other secondary factors

5.3.1. Type of organic pollutant. In the application of nanozymes for the detection/removal of organic pollutants, the type of targeted organic pollutant needs to be considered. Different types of organic pollutants usually have different linear detection ranges and LODs and the removal efficiencies of organic pollutants are also different in the presence of the same type of nanozymes. For example, Zhang *et al.* constructed a novel magnetic biomimetic nanozyme (Fe_3O_4@Cu/GMP (guanosine-5′-monophosphate)) with high laccase-like activity, which could remove various phenolic compounds (*e.g.*, phenol, catechol, hydroquinone and naphthol) with different efficiencies. In particular, the removal efficiency of naphthol increased to more than 95%.[148] Wu *et al.* utilized Fe_3O_4 NPs for the colorimetric detection of six phenolic species, namely phenol, *o*-CP, *m*-CP, *p*-CP, *o*-NP and *m*-AP. The Fe_3O_4 NPs exhibited favorable catalytic activity to promote the reaction of 4-aminoantipyrine, phenolic species and H_2O_2. Consequently, six phenolic species could trigger different chromogenic reactions, with a remarkable color change to indicate the level of the targeted pollutants. For instance, this approach provided a linear response for phenol in the concentration range of 1.67 μM to 1.2 mM and the LOD was 3.79 μM.[49]

5.3.2. Dosage of nanozyme catalyst and concentration of organic pollutant. The dosage of nanozyme catalyst and the concentration of organic pollutant are regarded as secondary factors in the detection/removal of organic pollutants by nanozymes. In a specific range, increasing the dosage of nanozyme catalyst can increase the catalytic active sites for improving the effects for the detection/removal of organic pollutants. For example, Hormozi *et al.* investigated SiO_2@Fe_3O_4 and MnO_2 nanozymes with a weight ratio of 2 : 1 (SiO_2@Fe_3O_4 : MnO_2) for the degradation of dyes. They found that the degradation efficiency reached the maximum value when 2.0 mg of the multi-nanozyme solid mixture was used, which was 99.5%. The inherent mechanism was easy to understand. Firstly, increasing the dosage of the nanozyme catalyst increases the number of catalytic active sites between the nanozyme and organic pollutant, causing more organic pollutant to react with the nanozyme. The degradation efficiency improves correspondingly. Then, the organic pollutant is almost completely degraded when the nanozyme dosage is optimal. As mentioned above, when adding excess nanozyme to the reactive system, the catalytic reaction could not continuously proceed due to the surplus of catalytic active sites.[152] Moreover, using the same catalytic system, with an increase in the concentration of organic pollutant, the detection effects and removal efficiencies present an increasing trend in the appropriate ranges. However, when the reaction conditions are optimized, a further improvement in the detection effects and removal efficiencies would be difficult to achieve due to the stable catalytic rate. For instance, Wang *et al.* utilized AuNPs with peroxidase-like activity for the electrochemical detection of kanamycin. A linear relationship between the concentration of kanamycin and the peak currents was observed. Also, with the further addition of kanamycin, the current production would slowly increase until ultimately becoming constant due to the decrease in the active sites in the nanozyme.[119]

Based on the above discussion, it is easy to find that nanozymes are influenced by multiple factors. Thus, in practical application, researchers can change some important influencing factors to improve the catalytic activities of nanozymes as much as possible. Meanwhile, the optimal reactive conditions should be considered by the comprehensive influence of various factors, rather than through a single factor.

6. Ecological effect

With the in-depth research on nanozymes, it is possible to apply nanozymes in the real environment. Nanozymes can detect organic pollutants sensitively and efficiently, and thus their application can remove various organic pollutants and alleviate the problem of environmental pollution. However, with the widespread application of nanozymes in the environment, their side effects on the ecosystem should be

considered, including three main aspects, *i.e.*, a decrease in biodiversity, the imbalance in the ecological system, and environmental pollution due to the function of the residue of the nanozyme reacting with organic pollutants in the ecosystem.[171,172] Previous research indicated that some nanozymes are toxic to local microbes and can damage the microbial community, in addition to causing pollution in the water, air and soil environments.[173] Thus, to promote the further popularization and utilization of nanozymes in the environment, it is essential to consider their ecological effects and find appropriate ways to avoid their adverse effects, such as producing low-toxicity nanozymes and controlling their dosage.[174]

7. Prospects

With the deepening of research and development of nanozymes, there are still some problems and several limitations of nanozymes that need to be solved efficiently. More efforts are urgently required to advance the following trends:

(1) Enhancing the enzyme-like activities and substrate specificities of nanozymes. The activities of nanozymes mainly depend on their surface area, active sites, shape and coated materials. Identical nanozymes obtained *via* different preparation methods may present diverse catalytic activities. Therefore, it is necessary to optimize the methods to synthesize nanozymes to enhance their enzyme-like activities. Moreover, the substrate specificities of nanozymes are poorer than that of natural enzymes. Thus, controlling the coordination structure of the active center atoms and improving the atom utilization of nanozymes will be beneficial for improving their enzyme-like activities and substrate specificities.

(2) Developing low-toxic nanozymes. Although many nanozymes have been applied in detecting/removing organic pollutants and have achieved excellent results, their intrinsic toxicities have been ignored. Thus, in the case of sustainable development, finding and developing low toxic nanozymes are also important.

(3) Developing novel nanozymes with multienzyme-like activities. Presently, many studies focus on the single enzyme-like activity of nanomaterials such as peroxidase-like activity, oxidase-like activity, catalase-like activity and superoxide dismutase-like activity. However, some nanomaterials have multiple functions and many environmental fields are contaminated with multiple organic pollutants. Thus, it is urgent to develop novel nanozymes with multienzyme-like activities for the detection/removal of organic pollutants.

(4) Exploring new enzyme-mimicking nanozymes and more reactive types. Many studies focus on nanozymes with peroxidase-like, oxidase-like, catalase-like and superoxide dismutase-like activity. However, nanomaterials with other types of enzyme-like activities need follow-up studies. Further, most of the existing catalytic reactions by nanozymes focus on redox-type reactions, except for a few based on hydrolytic reactions. However, due to the presence of various types of natural enzymes and organic catalysts, the current catalytic reactions of nanozymes do not represent all potential types of reactions. Thus, the development of nanozymes for new types of reactions will be another hot topic.

(5) Further revealing the detection/removal mechanisms of organic pollutants by nanozymes. To date, researchers have conducted many studies on detecting/removing organic pollutants by nanozymes. However, due to the limitation of technical tools and inherent properties of nanozymes, the underlying mechanisms in alleviating the environmental problems of organic pollutants *via* nanozymes are not fully understood. Hence, future research and increasing knowledge on nanozymes can serve as a foundation for evaluating and optimizing strategies for the detection/remediation of organic pollutants in the environment.

(6) Reducing the cost of nanozymes for their practical applications in the environmental field. Although the mass production of nanozymes has the advantage of being relatively inexpensive compared to natural enzymes, a further cost reduction is required for improving their widespread application instead of merely small-scale laboratory experiments.

(7) The development of nanozymes on a pilot scale, and then applying them in the actual environment. With the deepening of research, the theoretical basis of nanozymes for the detection/removal of organic pollutants is relatively mature. Thus, the next research direction is definitely to make the practical application of nanozymes in the detection/removal of organic pollutants possible.

8. Conclusions

In conclusion, we presented a comprehensive summary on the applications of nanozymes for the efficient detection/removal of organic pollutants. Four typical nanozymes, including peroxidase-like nanozymes, oxidase-like nanozymes, catalase-like nanozymes and superoxide dismutase-like nanozymes, and their catalytic processes were illustrated briefly. Furthermore, the detection methods and removal mechanisms of organic pollutants by nanozymes were introduced clearly. The key factors affecting nanozymes and their ecological effect were also discussed, which are of interest to readers in the environmental field. The development and enhancement of the applications of nanozymes in the detection/removal of organic pollutants will become a popular trend in the future. Combined with the existing research, it is convincing that nanozymes technology in the detection/removal of organic pollutants is also very promising for commercial application with the increase in deeper research on nanozymes.

Author contributions

All the authors contributed to this review. Qi Liu wrote the initial manuscript and made subsequent modifications. Xu Zhu, Linrui Zhong and Shoujuan Zhang proposed the conceptualization,

modified the structures of this review, and reviewed the manuscript. Xiaozhe Luo and Qian Liu supplemented the references. Lin Tang reviewed the manuscript. Yue Lu acquired the funding and directed the writing.

Conflicts of interest

The authors declare no competing financial interest.

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