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Environmental remediation with nanozymes

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21.1 Introduction

Nanozymes are nanomaterials possessing enzyme-like catalytic properties and distinctive physicochemical characteristics (Wong et al., 2021; Chai et al., 2023; Wu et al., 2024). Since 2007, when Gao et al. reported that iron oxide (Fe_3O_4) nanoparticles exhibit peroxidase-mimicking activity (Gao et al., 2007), numerous studies have focused on synthesizing new nanozymes and comprehending their mechanisms of action (Huang et al., 2019a; Wang et al., 2019a). With advancements in nanotechnology, an increasing array of nanomaterials with natural enzyme-mimicking activities, including peroxidase (POD), catalase (CAT), oxidase (OXD), glucose oxidase, superoxide dismutase (SOD), laccase, ascorbate oxidase, and glutathione peroxidase, has been reported (Huang et al., 2019a; Wu et al., 2024; Xin et al., 2023).

Nanozymes can be classified as metallic (e.g., Au, Ag, Pt, and Cu) (Jv et al., 2010; Jiang et al., 2012; Hu et al., 2013; Jin et al., 2017; Mansur et al., 2022), metal oxide (e.g., ZnO, CuO, MnO_2, and CeO_2) (Biparva et al., 2014; Xu and Qu, 2014; Qu et al., 2021; Mansur et al., 2022), carbon-based (e.g., carbon nanotubes (CNTs), modified graphene oxide (GO-COOH), and carbon quantum dots (CQDs)), and hybrid nanostructures (Song et al., 2010a,b; Singh et al., 2018; Wong et al., 2021; Mansur et al., 2022; Li et al., 2023). Compared to natural enzymes, which exhibit low thermal stability and operate within a limited temperature and pH range, coupled with high production costs, the nanozymes offer low cost, straightforward preparation, controllable activity, high stability, and durability (Wong et al., 2021; Wu et al., 2023; Chai et al., 2023). Therefore, nanozymes have been widely used in fields, such as biological imaging (Sharma et al., 2014; Liang and Han, 2020; Chai et al., 2023), environmental remediation (Gao and Yan, 2016; Li et al., 2018; Chai et al., 2023), and disease diagnosis and treatment (Duan et al., 2015; Jeyachandran et al., 2023).

Environmental problems unquestionably stand out as one of the primary challenges confronting living organisms today. Such issues include heavy metals, pesticides, herbicides, fertilizers, oil spills, airborne pollutants, industrial wastes, sewage, and organic compounds (Khan and Ghoshal, 2000; Vaseashta et al., 2007). Environmental remediation

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is crucial in safeguarding human health and ecosystems, ensuring compliance with regulations, fostering sustainable development, and contributing to the overall well-being of regions and the planet. A variety of materials can be employed for this purpose. The complexity, high volatility, and low reactivity of the materials make the capture and degradation of environmental pollutants challenging. Therefore, recent studies have focused on developing nanomaterials for new environmental remediation technologies (Tratnyek and Johnson, 2006). Among them, nanozymes are considered excellent contributions to the improvement of both traditional and advanced wastewater treatment processes (Long et al., 2021). It has been demonstrated that nanozymes exhibit catalytic properties similar to peroxidase and oxidase, which are involved in the natural breakdown of pollutants by enzymes (Zhang et al., 2020; Chai et al., 2023). Nanozymes can overcome the limitations of traditional enzymes in terms of production cost, recyclability, reaction rate, and operating range (pH and temperature) (Huang et al., 2019a; Meng et al., 2020; He and Liang, 2020). They are commonly used, particularly in the removal of persistent organic compounds, such as phenolic compounds, pesticides, dyes, and organophosphates, due to their effectiveness in environmental remediation (Diao et al., 2024).

21.2 Types of nanozymes used in environmental remediation

The classification of nanozymes offers a comprehensive framework for understanding the diverse functional and structural attributes, facilitating environmental remediation. Wong et al. classified nanozymes into four categories according to their mimicry of natural enzyme behavior. These categories include type I nanozymes, functioning similarly to active metal centers; type II nanozymes, predominantly exhibiting peroxidase-like activity; type III nanozymes, comprising metal or metal oxides integrated with carbon materials, MOFs, or bimetallic alloys; and type IV nanozymes, characterized by their three-dimensional nanostructures (Wong et al., 2021). Here, we classified nanozymes as metal-based, carbon-based, and hybrid nanostructures. Fig. 21.1 illustrates the widespread utilization of nanozymes across diverse environmental monitoring and remediation applications.

In the class of metal-based nanozymes, there are transition metal compounds (metals with oxygen, sulfur, or nitrogen) (Fang et al., 2020; Xie et al., 2019; Tang et al., 2021), metal nanoparticles (gold, silver, copper, platinum or palladium, iridium) (Huang et al., 2021a; Li et al., 2021a; Geng et al., 2021), and mono-, bi- and multi-metallic alloys (Zhou et al., 2022a; Song et al., 2022a; Xu et al., 2020). An initial instance of such nanozymes is provided by Fe_3O_4 nanoparticles, as reported by Gao et al. in 2007, demonstrating peroxidase-like activity akin to the natural horseradish peroxidase (HRP) enzyme, which catalyzes the oxidation of chromogenic substrates, including 3,3′,5,5′-tetramethylbenzidine (TMB), 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), and *o*-phenylenediamine dihydrochloride (OPD), in the presence of hydrogen peroxide (H_2O_2). Cerium oxide (CeO_2) nanoparticles act as a nanozyme due to their similarity in structure and, primarily,

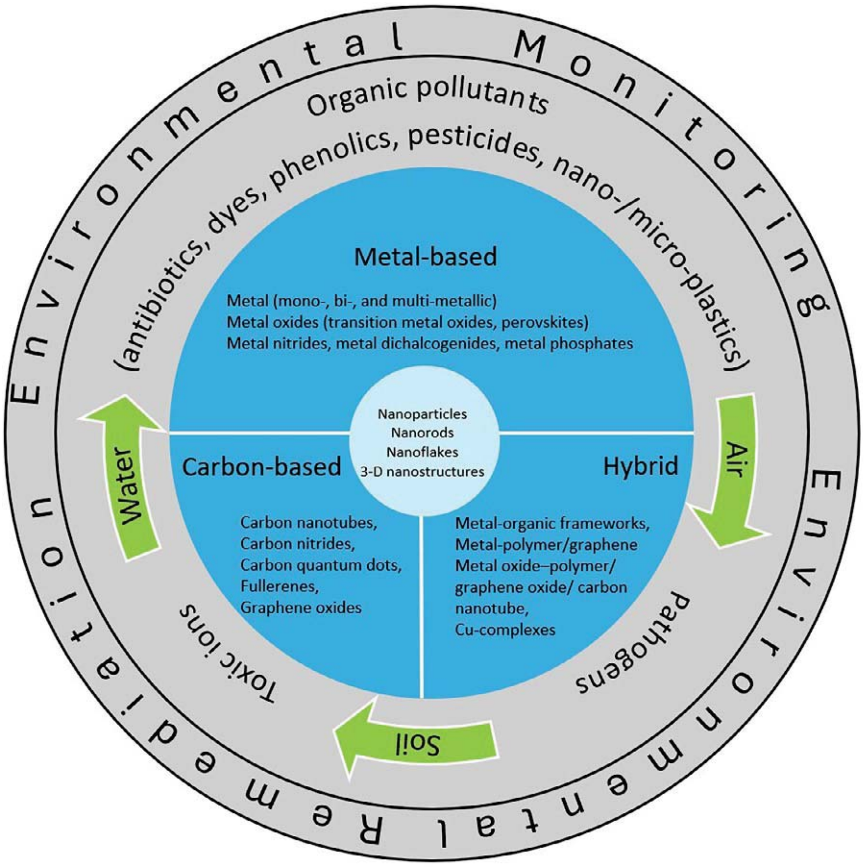

FIG. 21.1 Types of nanozymes used in environmental monitoring and remediation.

their affinity to proteins in terms of biochemical properties, resembling iron ions. Their catalase-like activity by decomposing hydrogen peroxide H_2O_2 into O_2 and H_2O, superoxide dismutase-like activity by converting $O_2^{\bullet-}$ into O_2 and H_2O_2, and peroxidase-like activity by facilitating various peroxidation reactions make them multifunctional catalysts (Wong et al., 2021).

Metal-based nanozymes have been used, especially in the detection and degradation of toxic ions, such as Fe^{2+}/Pb^{2+}(Xie et al., 2019), Hg^{2+} (Fang et al., 2020; Cao et al., 2020), As^{3+} (Xue et al., 2021), As^{5+} (Zhong et al., 2019), and Cu^{2+} (Luo et al., 2020); antibiotics, such as kanamycin (Tang et al., 2021; Chen et al., 2020) and streptomycin (Wei et al., 2020), dyes (Geng et al., 2021; Wang et al., 2023a), and phenolic compounds (Xu et al., 2020; Ma et al., 2022); and pesticides (Sun et al., 2021a; Li et al., 2022a) and pathogens, such as *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus,* and *Bacillus cereus* (Mirhosseini et al., 2020; Fuentes et al., 2021) by mimicking peroxidase, oxidase, and/or catalase.

Carbon-based nanomaterials, including fullerenes and their derivatives, carbon quantum dots, carbon nanotubes, and graphene oxide, among other nonmetallic nanozymes, can mimic enzymes, such as peroxidase, catalase, and oxidase due to their structural and catalytic properties. For example, it has been reported that increased electron density and mobility in carbon quantum dots result in peroxidase-like catalytic activity. The modification processes of C-based nanozymes (such as carboxyl groups and N or B atoms) have been indicated to enhance the catalytic activities of nanozymes (Wong et al., 2021).

C-based nanozymes have been utilized in the determination of toxic ions, such as Cr^{6+} (Goswami et al., 2022) and Al^{3+} (Song et al., 2022b) and pathogens like *Yersinia enterocolitica* (Savas and Altintas, 2019) and *E. coli* (Loukanov et al., 2022). On the other hand, the use of C-based nanozymes in detecting and degrading toxic organic molecules, such as dyes, phenolic compounds, and antibiotics, remains an open area of research.

Hybrid nanozymes are composed of a combination of metal- and carbon-based nanostructures that can mimic multiple enzymes. For instance, the adenine phosphate-Cu complex exhibited noteworthy peroxidase, laccase, and oxidase mimicking activities through the coordination of Cu ions with specific nitrogen sites (N3, N6, N7, and N9) on the adenine phosphate. Furthermore, it is applied to the degradation of phenolic compounds and used in colorimetric sensing methods for detecting H_2O_2, epinephrine, and glutathione with high sensitivity and selectivity (Chai et al., 2023).

As an eco-friendly alternative, the fungal chitosan–copper nanocomposite (CsCu) showed laccase activity to oxidize various phenolic compounds in synthetic and real wastewater (Mekonnen et al., 2023). A detailed study by Wu et al. revealed that most literature focuses on copper-based laccase-mimicking nanozymes. For noncopper laccase mimics, MnO_2 ultra-thin film was proposed for the detection of o-, m-, and p-dihydroxybenzene isomers and the direct differentiation of tetracycline and its derivatives (e.g., chlortetracycline, oxytetracycline) (Wu et al., 2024).

The enhanced enzyme-like activity observed in metal, metal compound, and carbon-based nanozymes stems from their expansive surface area, achieved via either size (typically in the tens of nanometers range for metal or metal compound-based nanozymes) or intricate porous frameworks (characteristic of carbon-based nanozymes) (Wong et al., 2021).

21.3 Applications of nanozymes in environmental treatment

Nanozymes represent a revolutionary approach to environmental applications, including soil, air, and water treatment, by seamlessly integrating the benefits of traditional chemicals and biocatalysts. These innovative catalysts offer unparalleled attributes, including superior stability, recyclability, ease of manufacturability, cost-effectiveness, prolonged storage stability, and environmental compatibility. As a result, they emerge as promising candidates for diverse environmental applications spanning various domains. Specifically, nanozymes exhibit tremendous potential in ecological monitoring and remediation, where their unique properties enable effective pollution mitigation and restoration of ecosystems. Furthermore, their versatility extends to toxic ion sensing, detection and degradation of organic compounds, antibacterial treatments, and beyond, making them invaluable tools for addressing pressing environmental challenges with efficiency and efficacy.

21.3.1 Toxic ions

Cases of inorganic ion contamination have led to detrimental effects on both the environment and human health worldwide. In affected regions, ecosystems have been disrupted, leading to the decline of biodiversity and loss of habitat for various species. Additionally, contaminated water sources pose a significant risk to human populations, causing acute and chronic health problems upon ingestion or exposure. Table 21.1 lists the commonly used modified or functionalized metal-based, carbon-based, and hybrid nanozymes that have been employed to enhance the binding affinity toward target ions, thus further improving sensitivity in detection applications. These modifications involve the surface functionalization of nanozymes with specific ligands, receptors, or functional groups tailored to interact specifically with the target ions of interest, particularly for Hg^{2+} and Cr^{6+}. In a representative study, the initially low peroxidase-like activity of ferromagnetic particles modified with cysteine (Cys-Fe_3O_4) because of Cys-Fe interaction has been enhanced in the presence of Hg^{2+}, forming a stronger coordination with Cys-Hg^{2+}-Cys. Thus, the environmental nanosensor demonstrated high accuracy and selectivity in detecting trace levels of Hg^{2+} in both environmental and biological fluids, achieving a detection limit (LOD) of 5.9 pM (Niu et al., 2019). Mao et al. obtained exceptional catalytic activity by synthesizing SA-Fe/NG, a peroxidase mimetic comprising single-atom iron anchored onto two-dimensional nitrogen-doped graphene. The detection mechanism is based on the use of 8-hydroxyquinoline (HQ) (as the inhibitor to prevent the oxidation of TMB, and the recovery of the blue color through the interaction between Cr(VI) and 8-HQ. The optimized colorimetric method, with an LOD of 3 nM for Cr(VI) and high selectivity for various other metal ions, has been successfully employed in detecting Cr(VI) in both tap water and tuna samples (Mao et al. 2021). The primary detection method used is colorimetric, but other techniques, such as electrochemical, optical, and surface-enhanced Raman spectroscopy (SERS), have also been employed. While POD mimics of nanozymes are predominantly utilized in the detection of toxic ions, other nanozyme activities, such as OXD, dual POD-OXD, CAT, SOD, phosphatase, and laccase-like activities, are also employed.

Although several nanozymes are used to detect toxic ions, only a few are employed in degrading them. Wang et al. designed dendrimer-like macroporous silica nanoparticles (DMSNs)@AuPtCo tri-metal nanozymes with peroxidase and catalase-like activities that effectively removed (>95%) the excessive H_2O_2 in H_2O_2 sewage (Wang et al., 2020). Su et al. examined how microbial sensitivity regulation mechanisms (MSRM) function in response to common heavy metal pollutants (As^{3+} and Cr^{6+}) in paddy fields. They employed nanoMn_3O_4-coated microbial populations (NMCMP) and found that Flavoisolibacter and Arthrobacter are key bacteria involved in the remediation of As^{3+} and Cr^{6+} pollution.

Table 21.1 Detection of toxic ions by nanozymes.

Nanozyme		Toxic ions	Activity	Detection mode	Detection range	LOD	Ref.
Metal-based	Citrate-capped Cu nanoparticles	Hg^{2+}	POD	Colorimetric	0.100–6.000 μM	0.052 μM	Li et al. (2019)
	Cys-Fe_3O_4		POD	Colorimetric	0.02–90 nM	5.9 pM	Niu et al. (2019)
	CuS hallow nanospheres		POD	Colorimetric	0–1000 ng/L	50 ng/L	Fang et al. (2020)
	Ag nanowires		OXD	Colorimetric	25–5000 μg/L	19.9 ng/L	Cao et al. (2020)
	Pt nanoparticles		POD	Colorimetric	20–3000 nM	10.5 nM	Li et al. (2021a)
	Fe-MoS_2@AuNPs		POD	Electrochemical	0.5–200 nM	0.2 nM	Dai et al. (2022)
	Ag Nanoparticles		POD	Optical	0.008–83.3 μM	0.44 nM	Hu et al. (2023)
	MnO_2	Fe^{2+}/Pb^{2+}	CAT	Colorimetric	0.001–0.02 mM 0.05–0.4 mM	0.5 μM 2 μM	Xie et al. (2019)
	Tannic Acid@Au NPs	Pb^{2+}	POD	Colorimetric	25–500 ng/mL	11.3 ng/mL	Serebrennikova et al. (2021)
	AuRu aerogels	Fe^{2+}	POD, OXD	Colorimetric	5–250 μM	0.7 μM	Xu et al. (2022a)
	$MoSe_2$@Fe	Fe^{3+}	POD	Colorimetric	25–300 μM	1.97 μM	Lin et al. (2022a)
	FeOOH	As^{5+}	POD	Electrochemical	0.04–200 μg/L	12 ng/L	Zhong et al. (2019)
	CoOOH	As^{3+}	POD	Electrochemical	0.1–200 μg/L	56.1 ng/L	Wen et al. (2019)
	Au nanoparticles		POD	Colorimetric	0.01–11.67 mg/L	0.008 mg/L	Xue et al. (2021)
	GdOOH	Cr^{3+}	Phosphatase	Colorimetric	5.0–200 μM	0.84 μM	Xiong et al. (2021)
	Nano-UO_2	Sn^{2+}	POD	Colorimetric	0.5–100 μM	0.36 μM	Yang et al. (2019)
	MMoO (M = Co, Ni)	Cu^{2+}	POD	Colorimetric	0.1–24 μM	0.024 μM	Luo et al. (2020)
	Nanoceria	Al^{3+}	Phosphatase	Electrochemical	30–3.5 × 10^3 nM	10 nM	Tian et al. (2020)
	MnO_2 nanosheets	Ag^+	OXD	Colorimetric	0.02–1.0 μM	6.7 nM	Zhang et al. (2021a)
	R-$MnCo_2O_4$/Au nanotubes	F^-	POD	SERS	0.1–10 nM	0.1 nM	Wen et al. (2020)
	AgPt-Fe_3O_4		POD	Colorimetric	50–2000 μM	13.73 μM	Qiu et al. (2022)
	Ag_3Cit	Cl^-, Br^-, I^-	OXD	Colorimetric	–	26, 12, 7 nM	Wang et al. (2021)
Hybrid	MVC-MOF	Hg^{2+}	OXD	Colorimetric	0.05–6 μM	10.5 nM	Wang et al. (2018)
	CS-$MoSe_2$NS		POD, OXD	Colorimetric	0.1–4.0 μM	3.5 nM	Huang et al. (2019b)
	Ag_2S@GO		OXD	Colorimetric	5.0–120.0 × 10^{-8} M	9.8 × 10^{-9} M	Zhao et al. (2021)
	Au nanoparticle-hydrogel		POD	Colorimetric	0.008–20 μg/mL	1.10 ng/mL	Ko et al. (2021)

Hybrid	MXene/DNA/Pt Nanocomposites	Hg^{2+}	POD	Colorimetric	50–250 nM	9.0 nM	Shi et al. (2022)
	L-cysteine@GO nanoarchitectonics		POD	Colorimetric	0–200 µg/L	5 µg/L	Tian et al. (2022)
	AuPt@DSN		POD	Colorimetric	0.1–10^3 nM	8.58 pM	Zhou et al. (2022a)
	His-Au Nanoclusters		OXD	Colorimetric	0.05–0.8 µM	8 nM	Fu et al. (2022)
	AuPd@UiO-67		POD	Electrochemical	1–10^6 mM	0.16 nM	Wang et al. (2022a)
	C-dots/Mn_3O_4 Nanocomposites	Fe^{2+}	OXD	Colorimetric	0.03–0.83 µM	0.03 µM	Honarasa et al. (2020)
	NCD/UiO-66 Nanocomposites	Fe^{3+}	POD, SOD	Colorimetric	0–0.1 mM	–	Zhao et al. (2022)
	Pd-DTT	As^{3+}	OXD	Colorimetric	33–3.333 × 10^5 ng/L	35 ng/L	Xu et al. (2019)
	CuS-frGO	Cr^{6+}	POD	Colorimetric	0–200 nM	26.60 nM	Borthakur et al. (2019)
	PEI-Ag nanoclusters		OXD	Colorimetric	–	1.1 µM	Xue et al., 2020
	Ni/Al–Fe$(CN)_6$ LDH		POD	Colorimetric	0.067–10 mM	0.039 mM	Amini et al. (2020)
	MOF		OXD	Colorimetric	0.1–30 µM	20 nM	Shi et al. (2021)
	SA-Fe/NG		POD	Colorimetric	30–3 µM	3 nM	Mao et al. (2021)
	Cu-PyC MOF		POD	Colorimetric	0.5–50 µM	0.051 µM	Kulandaivel et al. (2022)
	$CuFe_2O_4$/rGO	Cr^{3+}	POD	Colorimetric	0.1–25 µM	35 nM	Yi et al. (2022)
	E-ChlCu/ZnO	Cu^{2+}	POD	Colorimetric	0–1/1–15 µM	0.024 µM	Hu et al. (2022)
	MoS_2/g-C_3N_4HNs	S^{2-}	POD	Colorimetric	0.1–10 µM	37 nM	Liu et al. (2020)
	GMP-Cu		Laccase	Colorimetric	0–220 µM	0.67 µM	Huang et al. (2021b)
	PDA@Co_3O_4 NPs		CAT	Colorimetric	4.3–200 µM	4.3 µM	Vu et al. (2022)
	His@AuNCs/RGO	NO_2^-	POD	Electrochemical	2.5–5700 µM	0.5 µM	Liu et al. (2019a)
	AuNP-CeO_2 NP@GO		OXD	Colorimetric	100–5000 µM	4.6 µM	Adegoke et al. (2021)
	MB@ZrHCF	PO_4^{3-}	POD	Colorimetric	10–200 µM	2.25 µM	Zhang et al. (2022b)
	MA-Hem/Au-Ag	H_2O_2	POD	Colorimetric	0.010–2.50 mM	2.5 µM	Liu et al. (2019b)
	Pt/CeO_2/NCNFs		CAT	Electrochemical	0.0005–15 mM	0.049 µM	Guan et al. (2020)
Carbon-based	CD/g-C_3N_4	Cr^{6+}	POD	Colorimetric	0.3–1.5 µM	0.31 µM	Goswami et al. (2022)
	Single-atom Ce-N-C	Al^{3+}	Laccase	Colorimetric	5–25 µg/mL	22.89 ng/mL	Song et al. (2022b)

Additionally, NMCMP were shown to enhance the reduction of Cr^{6+} levels and suppress the release and rapid oxidation of As^{3+} during the repair process of $As_2H_2S_3$ (Su et al., 2022). A bimetallic mesoporous nanozyme called AgRu@β-CD co GO had a porous structure with hydroxyls and GO aromatic rings that effectively adsorb Hg^{2+} and Cl^- from water. The nanozyme achieved over 95.4% removal efficiency for Hg^{2+} and 93.8% for Cl^- (Yan et al., 2022).

21.3.2 Organic pollutants

Organic pollutants pose a significant threat to water and soil quality, presenting a long-standing challenge in their removal from these environments. Traditional methods for wastewater treatment, including physical, chemical, and biological approaches, encounter various obstacles, such as the generation of toxic byproducts, high costs of production, complex equipment requirements, nonselective oxidation reactions, and limited recyclability (Singh et al., 2023). Nanozymes offer advantages for both detecting and degrading organic pollutants present in wastewater and soil. We examined the types of nanozymes employed in the remediation of antibiotic residues, dyes, phenolic compounds, pesticides, and nano−/microplastics.

21.3.2.1 Antibiotic residues

Antibiotics are a class of compounds produced by microorganisms or synthesized chemically, typically used to inhibit the growth of or kill bacteria. Nevertheless, once antibiotics are introduced into animal or human systems, a significant portion of them is excreted via feces and urine, retaining their original structures or metabolizing into byproducts. The release of antibiotic residues into the environment poses risks, such as the proliferation of resistance genes. Some antibiotics can potentially interact with nanozymes, particularly if the nanozymes possess surface functional groups or catalytic sites that allow for chemical interactions. However, the specific nature of this interaction would depend on various factors, such as the chemical composition of the nanozymes, the structure of the antibiotics, and the conditions under which the interaction occurs. The utilization of nanozymes for detecting antibiotic residues is detailed in Table 21.2.

Tetracycline and kanamycin were mostly used in nanozyme-based antibiotic residue detection. A highly effective portable sensor utilizing a hybrid Cu-doped-g-C_3N_4 nanozyme has been developed for real-time visual monitoring of remaining tetracycline in milk, achieved through a π-π stacking-induced blocking mechanism. The Cu-doped-g-C_3N_4 nanocomposite demonstrated enhanced peroxidase-like activity (LOD: 31.51 nM) compared to free Cu^{2+} and g-C_3N_4 nanosheets, attributed to the synergistic effects of Cu^{2+} and g-C_3N_4 (Shen et al., 2022a). In addition to metal doping, incorporating recognition elements like aptamers can be utilized to develop aptasensors for the detection of antibiotics. Alsulami et al. designed a target-specific aptamer-conjugated nanocomposite comprising nonspherical gold nanoparticles and black phosphorus (BP-nsAu NPs), capable of detecting tetracycline with an LOD value of 90 nM. The advantages of hybrid

Table 21.2 Detection of antibiotic residues by nanozymes.

Nanozyme		Antibiotic residues	Activity	Detection mode	Detection range	LOD	Ref.
Metal-based	$CoFe_2O_4$ nanoparticles	Kanamycin	POD	Electrochemical	$1–10^{-6}$ μM	0.5 pM	Chen et al. (2020)
	WS_2 nanosheets		POD	Colorimetric	0.1–0.5 μM	0.06 μM	Tang et al. (2021)
	Aptamer-functionalized Fe/CeO_2 microcrystals		POD	Colorimetric	0.05–48.45 ng/mL	0.035 ng/mL	Chen et al. (2023)
	Au@Pt NPs	Streptomycin	POD	Lateral flow immunoassays	0.062–0.271 ng/mL	1 ng/mL	Wei et al. (2020)
	Co_3O_4	Chloramphenicol	POD	Electrochemiluminescence	5×10^{-13}–4×10^{-10} M	1.18×10^{-13} M	Li et al. (2021b)
	PtNi NCs	Sulfamethazine	POD	Photoelectrochemical	$0.05–10^3$ pg/mL	37.2 fg/mL	Song et al. (2022a)
	$Co(OH)_2$	Enrofloxacin	POD	Chemiluminescence immunoassay	0.0001–1000 ng/mL	0.041 pg/mL	Pei et al. (2021)
Hybrid	2D Cu-TCPP (Fe)	Sulfonamides	POD	Electrochemical	1.186–28.051 ng/mL	0.395 ng/mL	Xiao et al. (2020)
	Au@Pt@SiO_2	Sulfadiazine	POD	Biomimetic Immunoassay	100–500 mg/L	0.2 mg/L	He et al. (2020)
	FO@ZMFO@FMMOG	Norfloxacin	CAT OXD POD	Colorimetric	0.415–6.21 μM	52 nM	Sun et al. (2021b)
	MIL-53 (Fe)@MIP	Metronidazole	POD	Colorimetric	1–200 μM	53.4 nM	Zhang et al. (2021b)
	Hemin@Fe-MIL-88NH_2/PtNP	Kanamycin	POD	Colorimetric	0.01 to 100 ng/mL	2 pg/mL	Li et al. (2022b)
	Chitosan oligosaccharide-AuNPs	Enrofloxacin and ciprofloxacin	POD	Colorimetric	1.4–1400 nM	321.1 pM and 961.0 pM	Wang et al. (2023b)
	Cu-doped-g-C_3N_4	Tetracycline	POD	Colorimetric	0.1–50 μM	31.51 nM	Shen et al. (2022a)
	Fe_3O_4@MIP		POD	Colorimetric	2–225 μM	0.4 μM	Liu et al. (2022)
	MIL-101 (Fe/Co)		POD	Colorimetric	1–8 μM	0.24 μM	Zhu et al. (2022a)
	Fe–N–C nanoparticles		OXD, POD	Colorimetric	0.08–100 μM	62–88 nM	Wen et al. (2023)
	Aptamer-conjugated BP-nsAu nanocomposite		OXD	Colorimetric	0.2–1 μM	90 nM	Alsulami and Alzahrani (2024)

nanozymes, as well as the use of a free-radical scavenging ligand and rough surfaces (providing higher surface activation energy), were also highlighted (Alsulami and Alzahrani, 2024). Another recognition molecule, the molecularly imprinted polymer, is used for generating artificial cavities and binding sites for precise target recognition. Combining molecular imprinting with enzyme mimics not only retains the signal amplification capability of nanozyme catalysis but also addresses their lack of specific recognition. The proposed Fe_3O_4@MIP nanostructure possesses channels for substrate access, allowing it to mimic peroxidase activity and catalyze the oxidation of TMB. The MIP shell captures tetracycline molecules, partially blocking the channels and hindering the TMB reaction. This approach enables highly selective colorimetric detection of tetracycline with an LOD of 0.4 μM. Additionally, the magnetic properties of the nanozyme allow for easy recovery and reuse, making it suitable for recyclable sensing applications (Liu et al., 2022). While kanamycin was detected at the picomolar level using bimetallic oxide ($CoFe_2O_4$) nanozyme (Chen et al., 2020), sulfamethazine was detected at the femtomolar level using bimetallic PtNi nanozyme (Song et al., 2022a).

21.3.2.2 Dyes

The printing and dye industry has led to a surge in wastewater containing organic dyes, posing a threat to aquatic life due to its high toxicity and difficulty in biodegradation. Nanozymes, popular catalysts, are increasingly used to degrade various types of dyes, alongside other methods like adsorption. In general, two different catalytic reaction systems exist: nanozymes with peroxidase-like features are used to create Fenton-like systems for dye degradation, while they can also be integrated with advanced oxidation processes (AOPs) like peroxydisulfate (PDS) and peroxymonosulfate (PMS) activation to develop effective dye degradation (Diao et al., 2024). Specifically, PMS can be efficiently activated by specific catalysts, such as Fe-, Co-, and Cu-based nanozymes to generate reactive oxygen species (ROS), which play a crucial role in the degradation of organic pollutants. For instance, FeBi-NC single-atom nanozymes with dual active sites for both cascade catalysis and peroxymonosulfate (PMS) activation were fabricated by Chen et al. and used for RB degradation (Chen et al., 2022a). Table 21.3 lists the nanozymes and their efficacy in degrading dyes such as methylene blue (MB), rhodamine B (RB), methyl orange (MO), and malachite green (MG). In general, nanozymes achieve over 90% removal efficiency in dye degradation, and especially, Fe_3O_4-based nanozymes have efficiencies exceeding 99%.

21.3.2.3 Phenolics

Phenols pose serious risks to human health and the environment. These risks include carcinogenic effects, hormonal disruptions, and increased environmental pollution. Therefore, reducing and controlling the effects of phenols is of critical importance. Table 21.4 lists the types of nanozymes recently used for phenolic compounds. Studies have shown that nanozymes are an effective method for both detecting and degrading phenols. Among these compounds, 2,4-dichlorophenol is one of the most extensively studied. Laccase, a

Table 21.3 Degradation of dyes by nanozymes.

Nanozyme		Dyes	Activity	Removal Efficiency (%)	Ref.
Metal-based	$CoFe_2O_4$	MB	POD	91.2	Wu et al. (2018)
	MnO_2- and SiO_2@Fe_3O_4	MG	POD	99.5	Jangi et al. (2020)
	Copper nanozyme	MO	POD	93.0	Geng et al. (2021)
	Ag-Fe_3O_4	Triarylmethane	POD	>99.0	Wang et al. (2023c)
Hybrid	Cu/H_3BTC MOF	Amidoblack	Laccase	60.0	Shams et al. (2019)
	Fe_3O_4@C-Cu^{2+}	MG	Laccase	99.0	Li et al. (2020)
	Pd@ZnNi-MOF/GO	MB	POD	95.0	Su et al. (2021)
	Cu^{2+}-HCNSs-COOH	MB	POD	80.7	Zhu et al. (2021a)
	PdNPs/PCNF	MB	POD, OXD	99.64	Dadigala et al. (2022)
	Sulfur-doped graphdiyne nanosheets	RB	POD	>98.0	Zhang et al. (2022a)
	FeBi-NC SAzyme	RB	OXD	99.0	Chen et al. (2022a)
	Fe_3O_4@Gel	Indigo carmine	POD	99.0	Zha et al. (2022)
	CeO_2@ZIF-8	MO	POD	99.81	Yang et al. (2023a)

type of multicopper oxidase, is more commonly used in the reduction of phenolic compounds. It exhibits the ability to convert molecular oxygen into water while simultaneously oxidizing substituted phenols and aromatic amines. Therefore, laccase-like nanozymes are being explored as potential alternatives for laccase in practical applications. Based on the studies in the tables, the detection limit of phenols using nanozymes typically falls within the micromolar range. Ferromagnetic nanoparticles are preferred due to their abilities in the degradation of phenolic compounds. For instance, Jiang et al. examined the catalytic properties of ferromagnetic chitosan nanozymes (called as MNP@CTS), which promote the generation of ROS from H_2O_2.

The removal efficiency surpassed 95% within 5 h. In addition, hybrid nanozymes generally come to the fore, combining the advantageous aspects of metals, metal oxides, carbon-based materials, and polymers, and thus, higher efficiency and specificity can be achieved.

21.3.2.4 Pesticides

Pesticides are organic compounds widely used in modern agriculture to control and eliminate pests (Wong et al., 2021; Prasad et al., 2021). Pesticides significantly threaten human health and the ecosystem by causing environmental pollution and contamination in food and water sources. Due to their high toxicity, pesticides should not exceed a certain concentration in drinking and surface waters (Prasad et al., 2021). Traditionally, liquid or gas chromatography coupled with mass spectrometry (LC–MS, GC–MS) has been used to detect pesticides. However, these techniques have limitations as they are not suitable for rapid in-field detection of pesticides and involve challenging operating conditions (Hernández et al., 2005; Wong et al., 2021). Instead, nanomaterials mimicking enzymes,

Table 21.4 Detection and degradation of phenolics by nanozymes.

Nanozyme		Phenolics	Activity	Detection mode	Detection range/ LOD/removal efficiency	Ref.
Metal-based	Fe_3O_4@MnO_x	Chlorophenols	OXD	Colorimetric	10–1600 μM 0.85 μM	Xu et al. (2020)
	$Co_{1.5}Mn_{1.5}O_4$	Hydroquinone	OXD	Colorimetric	0.05–100 μM 0.04 μM	Liu et al. (2021a)
	$NiCo_2O_4$@MnO_2		POD, OXD	Colorimetric	0–24 μM 0.042 μM	Ma et al. (2022)
Hybrid	MNP@CTS	Phenol	POD	Colorimetric	>95.0%	Jiang et al. (2018)
	CH-Cu	2,4-Dichlorophenol	Laccase	Colorimetric	82.0%	Wang et al. (2019b)
	DMNS@AuPtCo	Phenol	CAT POD	Colorimetric	90.0%	Wang et al. (2020)
	Modified Fe-doped ceria/Au	2,4-Dinitrophenol	POD	Colorimetric	1–100 μg/mL 0.45 μg/mL (2.4 μM)	Adegoke and Daeid (2021)
	AMP-Cu	2,4-Dichlorophenol	Laccase	Colorimetric	0.1–100 μM 0.033 μM, 65.0%	Huang et al. (2021a)
	CA-Cu NPs	2,4-Dichlorophenol	Laccase	Colorimetric	90.0%	Xu et al. (2021)
	1-Methylimidazole/Cu	2,4-dichlorophenol, 3-methoxylphenol, p-aminophenol, resorcinol, and guaiacol	Laccase	Colorimetric	0.5–4 μg/mL 0.57 μg/mL	Lei et al. (2022)
	Fe_3O_4@COF	Hydroquinone	POD	Colorimetric	0.5–300 μM 0.12 μM	Sun et al. (2022)
	Aminopropyl-functionalized copper containing phyllosilicate	Hydroquinone	Laccase	Colorimetric	100%	Lv et al. (2022
	MnCo@C NCs	2,4-dichlorophenol	Laccase	Electrochemical	3.1–122.7 μM 0.76 μM	Zhu et al. (2022b)
	Fe1@CN-20	2,4-dichlorophenol	Laccase	Colorimetric	65.0%	Lin et al. (2022b)
	Cu-Cys@COF-OMe	2,4-dichlorophenol	Laccase	Electrochemical	>75.0%	Tang et al. (2022)

such as peroxidases, oxidases, and phosphatases, can be used to detect pesticides (Prasad et al., 2021). In addition to detecting pesticides, bioremediation strategies have been developed to reduce their environmental impact by transforming them into less toxic forms and facilitating their degradation. Table 21.5 lists metal-based and hybrid nanozymes used for the detection and degradation of pesticides. The detoxification of pesticides is provided by enzymes, such as oxidoreductases, hydrolases, and lyases (Zhu et al., 2020; Sharma et al., 2018). In recent years, it has been identified that nanozymes can be effectively utilized for monitoring and degrading pesticide residues in plants, soil, and water samples. Nanozymes mimicking phosphatase-like activity, such as CeO_2 (Sun et al., 2021a; Wei et al., 2019), are commonly used for pesticide degradation. Additionally, nanozymes based on peroxidase-like activity, such as Fe_3O_4-based nanoparticles (Chen et al., 2022b; Li et al., 2021c; Boruah and Das, 2020) or metal nanoparticles (Li et al., 2022a; Weerathunge et al., 2019; Shah et al., 2021), are used.

21.3.2.5 Nano/microplastics

Nano- and microplastics are significant carriers of pollution initially found in oceans. Their small size (<5 mm), abundance, and widespread distribution facilitate ingestion by marine organisms and their entry into the human body through food chains, posing severe health risks. Due to their challenging metabolization, un-excreted nano- and microplastics accumulate in the body, causing organ damage and diseases. Thus, removing and degrading these particles from water resources is crucial. Recently, nanozymes have been utilized for the degradation of nano- and microplastics (Diao et al., 2024; Zandieh et al., 2023). In a representative study, Kang et al. successfully conducted catalytic oxidation of microplastics by encapsulating manganese carbide nanoparticles within helical nitrogen-doped carbon nanotubes (Mn@NCNTs) through pyrolysis. Mn@NCNTs were both able to oxidize cosmetic plastic microbeads by catalytically activating PMS to generate reactive free radicals, achieving a removal rate of 50%, and the degradation intermediates could serve as nutrients for aquatic algae without harming microorganisms (Kang et al., 2019). Zandieh et al. showed that use of Fe_3O_4 nanoparticles, which is among the most studied nanozymes with peroxidase-like activities, allowed it to degrade microplastics with almost 100% efficiency when heated close to their melting temperature. Additionally, Fe_3O_4 nanoparticles were highlighted for their ability to be easily recycled thanks to their magnetic properties and excellent stability (Zandieh and Liu, 2022). In a supporting study poised to expand the application of artificial enzymes in combating microplastic pollution, researchers concentrated on merging the magnetic attributes of bare Fe_3O_4 nanoparticles with nanozyme technology to achieve near-complete removal and degradation of microplastics (Palliyarayil et al., 2023).

21.3.3 Pathogens

Infectious diseases are known to be responsible for more than a quarter of global deaths, and the primary causes are bacteria and viruses. Contaminated food and water are

Table 21.5 Detection and degradation of pesticides by nanozymes.

Nanozyme		Pesticides	Activity	Detection mode	Detection range/LOD/removal efficiency	Ref.
Metal-based	NiO-SPE	Parathion	OXD	Electrochemical	0.1–30 µM 0.024 µM	Khairy et al. (2018)
	MnOOH NWs	Dichlorvos	OXD	Colorimetric	0–15 ng/mL 3 ng/mL	Huang et al. (2019c)
	Ag-Nanozyme	Chlorpyrifos	POD	Colorimetric	35–210 mg/L 11.3 mg/L	Weerathunge et al. (2019)
	Nanoceria	Methyl-paraoxon	Laccase	Colorimetric	0.42–126 µM 0.42 µM	Wei et al. (2019)
	C-Au NPs	Parathion ethyl	POD	Colorimetric	11.6–92.8 ng/mL 5.8 ng/mL	Shah et al. (2021)
	CeO_2	Methyl-paraoxon	POD OXD	Electrochemical	0.1–100 µM 0.06 µM	Sun et al. (2021a)
	$NiFe_2O_4$	2,4-Dichlorophenoxyacetic acid	POD	Colorimetric	0.218–3.282 µg/mL 0.311 µg/mL	Omar and Jabbar (2022)
	Pt NP	Dimethoate	POD	Colorimetric	0.5–9 µg/mL 0.15 µg/mL	Li et al. (2022a)
	Porous Co_3O_4	Glyphosate	POD	Colorimetric	8–80 µg/L 2.37 µg/L	Wu et al. (2022a)
	CP@CA	Nicosulfuron	POD	UPLC-TOF-MS	96.25%	Yang et al. (2023b)
Hybrid	LDH@ZIF-8	Diazinon	POD	Colorimetric	0.5–300 nM 0.22 nM	Bagheri et al. (2019)
	MoS_2/MWCNTs	Carbendazim	OXD	Electrochemical	0.04–100 µM 7.4 nM	Zhu et al. (2020)
	Fe_3O_4-TiO_2/rGO	Atrazine	POD	Colorimetric	2–20 µg/L 2.98 µg/L 98.00%	Boruah and Das (2020)
	2D MnO_2	Paraoxon	OXD POD	Electrochemical	0.1–20 ng/mL 0.025 ng/mL	Wu et al. (2021)
	Ti_3C_2-MXene/BP	Naphthalene Acetic acid	OXD	Electrochemical	0.02–40 µM 1.6 nM	Zhu et al. (2021b)
	Fe_3O_4/C-dots@Ag-MOFs	Methyl-parathion		Electrochemical	5×10^{-11}–2×10^{-9} M 1.16×10^{-11} M	Li et al. (2021c)

NH_2-MIL-101(Fe)	Carbaryl	POD	Colorimetric	2–100 ng/mL 1.45 ng/mL	Liu et al. (2021b)
Fe_3O_4/DG	Simazine	POD	Colorimetric	2.24 µM 99%	Boruah et al. (2021)
AgNPs/MWCNTs/GO	Benomyl	OXD	Electrochemical	0.2–122.2 µM	Xu et al. (2022b)
SACe-N-C	Omethoate	POD	Colorimetric	100–700 µg/mL 55.83 ng/mL	Song et al. (2022c)
Au@PN	Glyphosate	POD	Colorimetric	0.5–20 nM 0.24 nM	Wang et al. (2022b)
Fe_3O_4@C_7/PB	Glyphosate	POD	Colorimetric	0.125–15 µg/mL 0.1 µg/mL	Chen et al. (2022b)
ZIF-8	Fipronil	POD	Colorimetric	0.2–4 µM 0.036 µM	Zhang et al. (2022c)
Fe-N/C SAzyme	Malathion	OXD	Colorimetric	0.5–10 nM 0.42 nM	Ge et al. (2022)

common sources of transmission of these diseases. As a result, the first step in managing infectious diseases is to identify pathogenic microorganisms. The use of nanozymes in biosensing has experienced significant growth in recent years, driven by advances in the development and synthesis of various nanozyme-based systems specifically designed for the detection of bacteria and viruses. Table 21.6 provides a summary of recently utilized metal-based, carbon-based, and hybrid nanozymes for the detection and degradation of various pathogens.

Nanozyme-mediated pathogen detection utilizes a range of detection modes, including colorimetric, fluorescence, and electrochemical detection. Savas et al. utilized graphene quantum dots (GQDs) (<5 nm) for the electrochemical detection of the *Y. enterocolitica*. The electronic interactions, enhanced electrical conductivity, and catalytic surface area between the Au electrode and GQDs were emphasized. Detection of the analyte was achieved through H_2O_2 reduction by GQDs and hindered electron transfer due to formation of the antigen–antibody complex (Savas and Altintas, 2019).

Nanozyme technology finds application in laboratory research methods like PCR and enzyme-linked immunosorbent assays, as well as point-of-care devices such as electronic biosensors and lateral flow detection strips, all of which serve as indicators for pathogen detection and identification (Songca, 2022). Recently, a novel label-free and dual-readout lateral flow immunoassay utilizing a multifunctional nanocomposite (Fe_3O_4@PDA@Pt) with magnetic-adhesion-color-nanozyme properties was reported by Dou et al. (2022). Fe_3O_4 magnetic core simplified separation processes and surface adherent polydopamine (PDA) films demonstrated robust adhesion to *E. coli* and provided colorimetric detection signal, and platinum nanoparticles (Pt NPs) acted as nanozymes to generate an additional catalytic signal for an LOD of 10^2–10 CFU/mL. In another study, a nanozyme chemiluminescence paper test was developed for the rapid and sensitive detection of the SARS-CoV-2 antigen. The Co-Fe@hemin-peroxidase nanozyme that facilitated chemiluminescence similar to natural peroxidase HRP, thereby enhancing the immune reaction signal and achieving the LOD of 0.1 ng/mL (Liu et al., 2021c).

In addition to the detection of pathogens, nanozymes are also being investigated for their potential as antibacterial agents. Zhou et al. defined the nanozyme-based antibacterial alternatives as "nanozybiotics" (Zhou et al., 2022b). For instance, a single-atom nanozyme based on Pt single atoms modified carbon nitride nanorod (SA-Pt/g-C_3N_4-K) demonstrated excellent biocompatibility and achieved a killing efficiency of over 99.99% against gram-negative bacteria (Fan et al., 2022). Apart from their antibacterial effects, nanozymes have emerged as a solution for preventing and removing marine biological fouling. Haloperoxidase mimicry, which involves the catalytic oxidation of halides by H_2O_2 to form hypohalous acids, has been reported in CeO_2-x nanorods (Herget et al., 2017), and chromium single atoms coordinated on carbon nitride (Cr-SA-CN) (Luo et al., 2022a).

While nanozymes are typically categorized for environmental applications related to toxic ions, organic pollutants, and pathogens, they are also utilized in air purification (Elkomy et al., 2024) and glucose biofuel cells (Guo et al., 2020).

Table 21.6 Detection and degradation of pathogens by nanozymes.

Nanozyme		Pathogens	Activity	Detection mode	Detection range/LOD/ removal efficiency	Ref.
Metal-based	Au@Co-Fe NPs	*Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus,* and *Bacillus cereus*	POD	Colorimetric	10^8 CFU/mL 99.9%	Mirhosseini et al. (2020)
	Au NRs	*E. coli*	OXD	Colorimetric	1.0×10^2–1.0×10^5 CFU/mL 22 CFU/mL	Zhou et al. (2020)
	Au-Pt dumbbell NPs	*E. coli*	POD	Colorimetric	10–10^7 CFU/mL 2 CFU/mL, 95%	Lu et al. (2021)
	w-SiO_2/CuO	*E. coli*	OXD	Colorimetric	90%	Fuentes et al. (2021)
	Pd@Pt	*E. coli* *Salmonella enteritidis*	POD	Lateral flow immunoassays	34 CFU/mL 20 CFU/mL	Cheng et al. (2017)
	Pd@Pt	*S. aureus*	POD	Lateral flow immunoassays	10–300 ng/mL 9.56 ng/mL	Wu et al. (2022b)
Hybrid	PAA-Cnp	*E. coli*	Phospholipase	–	>80%	Khulbe et al. (2020)
	IPs-Pt	*Salmonella typhimurium*	POD	Colorimetric	10^4–10^6 CFU/mL 10^3 CFU/mL	Hu et al. (2021)
	Co–Fe@hemin	SARS-CoV-2	POD	ELISA and colorimetric	0.2–100 ng/mL 0.1 ng/mL	Liu et al. (2021c)
	Cu-C_3N_4-TiO_2	*S. aureus*	POD	Photoelectrochemical	10–10^8 CFU/mL 3.40 CFU/mL	Luo et al. (2022b)
	$P_2W_{18}Fe_4$/PDA	*E. coli*	POD	Colorimetric	10^3–10^6 CFU/mL 4.2×102 CFU/mL	Zhang et al. (2021c)
	SA-Pt/g-C_3N_4-K	Gram-negative bacteria	POD	Colorimetric	>99.99%	Fan et al. (2022)
	Cu-anchored PDA	*Aspergillus flavus*	POD	Colorimetric and photothermal lateral flow immunoassay	Down to 0.45 and 0.22 ng/mL	Liang et al. (2022)
	Fe@PDA	*Listeria monocytogenes*	POD	Colorimetric and fluorescence	Absorbance 6.9–1.0×10^7 CFU/mL 2.3 CFU/mL Fluorescence 3.0–1.0×10^7 CFU/mL 1.0 CFU/mL	Shen et al. (2022b)
	Fe_3O_4@PDA@Pt	*E. coli*	POD	Lateral flow immunoassay	10^2–10 CFU/mL	Dou et al. (2022)
Carbon-based	Graphene quantum dots	*Yersinia enterocolitica*	POD	Electrochemical	1–6.23×10^8 CFU/mL, LOD (milk) = 5 CFU/mL, LOD (serum) = 30 CFU/mL	Savas and Altintas (2019)
	Histidine-containing carbon nanodots	*E. coli*	OXD	Colorimetric	80%	Loukanov et al. (2022)

21.4 Mechanisms of nanozymes

Nanozymes, mimicking enzymes like catalase, superoxide dismutase, peroxidase, and laccase—prominent in living organisms—are frequently employed for detecting and degrading heavy metals, along with organic pollutants like dyes, pesticides, and drugs. The catalytic performance of nanozymes can be impacted by factors like composition, size, morphology, solution pH, surface coverage, and surface chemistry (Navya and Daima, 2016; Singh et al., 2023).

The mechanisms of action for these nanozymes can be categorized as follows.

21.4.1 Catalase-mimicking functionality

Catalase is an enzyme that catalyzes the breakdown of H_2O_2 into water and oxygen. First, it was reported that the amine-terminated PAMAM dendrimers-Au nanoclusters mimic catalase activity (Liu et al., 2017). Subsequently, it has been noted that CeO_2, platinum, and manganese oxide nanoparticles exhibit nanozymes with catalase-like activity. At the molecular level, the nanozymes exhibiting catalase-like behavior occur through mechanisms, involving bi-H_2O_2 association, acid-like dissociation, or base-like dissociation (Guo et al., 2020).

Different metal-oxide nanozymes exhibit catalase-like activity following one of the three proposed mechanisms. For instance, the catalytic activity of cobalt oxide nanoparticles can be better explained through the bi-hydrogen formation mechanism. In the case of CeO_2 nanoparticles, the process involves the initial adsorption and reaction of H_2O_2 on the nanoparticle surface, converting oxygen and CeO_2 into H_2-CeO_2. Subsequently, upon reacting with another H_2O_2 molecule, it further converts into water (Thao et al., 2023; Wang et al., 2019c).

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + O_2 + 2H^+$$

$$2Ce^{3+} + H_2O_2 + 2H^+ \rightarrow 2H_2O + 2Ce^{4+}$$

21.4.2 Superoxide dismutase-mimicking functionality

Superoxide radicals are fundamental components of ROS produced as byproducts during the metabolism of living systems. Superoxide radicals are closely associated with oxidative stress and readily convert into other ROS forms. Superoxide dismutase, an enzyme found in plants, animals, and microorganisms, exhibits a potent antioxidant property by catalyzing the conversion of superoxide anion radicals into H_2O_2 and oxygen (Thao et al., 2023). Since the report by Krusic and colleagues in 1991 (Krusic et al., 1991), stating that nanomaterial consisting of 60 carbon atoms possesses free-radical scavenging properties, nanozymes mimicking superoxide dismutase, mainly composed of transition metals, such as copper, iron, and cerium, and elements, such as nitrogen, oxygen, carbon, and sulfur, have been produced (Thao et al., 2023). The various carbon-based nanomaterials, including graphene oxide (GO), carbon nanotubes (CNTs), and carbon dots (CDs), have demonstrated superoxide dismutase-like activities. Among them, CeO_2, trimanganese tetraoxide (Mn_3O_4), and manganese dioxide (MnO_2) nanoparticles effectively mimic the superoxide dismutase. The catalytic activity mechanism of nanozymes, which mimics the superoxide dismutase exemplified by CeO_2 nanoparticles, is explained through the electron transfer model (Celardo et al., 2011). In this model, the $O^{\bullet-}$ molecule briefly binds to the reduced oxygen vacancy sites, releasing H_2O_2 through the absorption of two protons and the subsequent transfer of one electron from Ce^{3+}. In another theory, the superoxide dismutase activity of CeO_2 nanoparticles is attributed to defect regions forming at the interface due to the adsorption of $HO_2^{\bullet}$ species onto the nanoparticle surface, leading to H_2O_2 and oxygen (Wang et al., 2019c).

21.4.3 Peroxidase-mimicking functionality

Peroxidase enzymes facilitate the oxidation of an organic substrate by serving as an electron acceptor for H_2O_2. Since the initial report by Gao et al. in 2007 on the peroxidase-mimicking capability of Fe_3O_4 nanoparticles, various metal oxides, conductive polymers, metal–organic frameworks (MOFs), and carbon-based nanomaterials have been demonstrated to mimic peroxidase activity (Liu et al., 2021b). Nanozymes mimicking peroxidase exhibit catalytic activity through Fenton reactions, Fenton-like reactions, or electron transfer mechanisms, as Adeniyi et al. reported (Adeniyi et al., 2020). The peroxidase-mimicking activity of Fe_3O_4 nanoparticles has been associated with the production of $OH^{\bullet}$ and $O^{\bullet-}/HO^{\bullet}$ radicals due to the released metal ions. Wang et al. suggested that the degradation and mineralization of organic molecules, such as rhodamine B, are a result of the radicals generated by Fe_3O_4 nanoparticles (Wang et al., 2010). In subsequent studies, researchers suggested that peroxidase-like activity is more attributed to reactions occurring on the nanoparticle surface than to the released metal ions. Supporting this hypothesis, one study suggested the peroxidase-like activity of vanadium pentoxide nanotubes for surface properties rather than free orthovanadate anions (André et al., 2011).

21.4.4 Laccase-mimicking functionality

Laccases are sourced from diverse organisms, such as plants, insects, fungi, bacteria, and lichens. As a member of the multicopper oxidase family, laccases can oxidize a broad spectrum of phenolic (R-OH) and nonphenolic compounds (i.e., reactive dyes). In the catalytic reaction of laccases, oxygen is the electron acceptor, producing water as a by-product (Arregui et al., 2019). Currently, synthetic metal and metal-oxide nanozymes, such as Fe, Ag, Pd, PdPt, guanosine monophosphate (GMP-Cu), Cys-His dipeptide-Cu (CH-Cu), CeO_2, MnO_2, Fe_3O_4, and surface-modified nanomaterials, are actively utilized for the elimination and conversion of R-OH (Chen et al., 2019). In addition, the micro−/nano-sized CuO particles also exhibited peroxidase and laccase activities, as indicated by TMB and phenol degradation (Liu et al., 2014). Significantly, the nanosized CuO in the degradation of phenol, catechol, hydroquinone, and other byproducts has highlighted to act effectively than larger particle size of nanozyme, which has insufficient phenol degradation. The hypothesis has been proposed that the catalytic activity of CuO particles increases due to the increased surface area/volume in smaller particles. Laccase-mimicking nanozymes have been proposed to convert oxygen to water directly without generating H_2O_2. A study supporting this hypothesis employed CH-Cu for the removal of 2,4-dichlorophenol. After the reaction, adding ABTS and HRP to the supernatant did not induce any color change. However, the introduction of H_2O_2 into the environment resulted in an immediate shift in color to green, confirming the nanozyme's mimicking of laccase (Wang et al., 2019c).

The mechanism of R-OH transformation through metal and metal-oxide nanozymes involves surface reactions encompassing R-OH adsorption, diffusion, chemical transformation, and product desorption steps. Metal and metal-oxide nanozymes initially adsorb R-OH compounds onto their surfaces, forming surface complexes. Surface complexes undergo one-electron transfer to produce phenoxy radical intermediates, inducing a change in the metal redox state. The electrons in phenoxy radicals resonate with benzene rings, leading to covalent bonding reactions, forming dimers, trimers, tetramers, oligomers, and polymers. Simultaneously, the transfer of a solitary electron can result in the dehydrogenation, hydrolysis, and hydroxylation reactions of R-OH, generating small molecule species (Chen et al., 2019; Zhou et al., 2017; Wang et al., 2017).

21.5 Conclusion and future perspectives

Nanozymes are highly promising materials with numerous advantages, such as affordability, straightforward preparation, robust stability, and recyclability, for the determination and removal of metal ions with high sensitivity and selectivity, as well as the detection and degradation of toxic organic molecules, such as dyes, phenolic compounds, and antibiotics. Since their initial discovery, nanozymes have garnered increased research interest due to their catalytic properties and enhanced tolerance to challenging working and storage conditions compared to natural enzymes. They find applications across a wide range of fields, including health sciences and ecological studies, encompassing diagnosis and treatment, sensing, environmental monitoring, and remediation of environmental contaminants.

The majority of nanozymes exhibit peroxidase/oxidase-like activity in the presence of metal ions, and this activity can be enhanced. Peroxidase-like catalytic activity, especially in the degradation of environmental pollutants, such as phenols and dyes (MB, RhB), has been the most explored activity. Composite nanozymes containing Fe_3O_4 nanoparticles, especially on carbon materials or MOFs, have demonstrated higher catalytic efficiency compared to metal/metal-oxide nanozymes. However, recent studies suggest that the combination of nanozymes with natural enzymes may lead to positive synergistic effects in specific applications. Ongoing efforts to improve catalytic activity aim to support sustainable growth and increase the application of nanozymes in the environmental field.

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