



MnCo₂S₄ nanozymes with dual enzyme-mimicking activities for catalytic degradation and optical monitoring of organic pollutants

Thinh Viet Dang^{a,1} , Duc Loc Sai^{b,1} , Moon Il Kim^{a,*}

^a Department of BioNano Technology, Gachon University, 1342 Seongnamdaero-ro, Sujeong-gu, Seongnam, Gyeonggi, 13120, Republic of Korea

^b School of Chemistry and Life Science, Hanoi University of Science and Technology, No. 1 Dai Co Viet Road, Hanoi, Viet Nam

ARTICLE INFO

Keywords:

MnCo₂S₄ nanozyme
Dual enzyme-mimicking activity
Catalytic degradation
Optical monitoring
Transition metal sulfide

ABSTRACT

Nanozymes have attracted considerable attention as robust catalytic alternatives to natural enzymes for catalytic degradation and monitoring of environmental pollutants. Herein, we report manganese cobalt sulfide nanozymes (MnCo₂S₄ NZs) exhibiting dual peroxidase- and laccase-like activities. The coexistence of Mn and Co active sites enables both reactive oxygen species (ROS)-mediated and ROS-independent catalytic pathways, resulting in enhanced catalytic efficiency and excellent operational stability across a broad range of pH and temperature conditions. The peroxidase-like activity of MnCo₂S₄ NZs efficiently catalyzes the degradation of organic pollutants, including Neutral Red and Crystal Violet, achieving approximately 99% removal within 20 min through the generation of highly reactive hydroxyl radicals (•OH), as confirmed by radical scavenger experiments. In addition, their intrinsic laccase-mimicking oxidation activity enables the transformation of the hazardous aromatic compound *o*-phenylenediamine (OPD) into 2,3-diaminophenazine (DAP), which serves as both a chromophoric and fluorescent product. The formation of DAP allowed convenient optical monitoring of the catalytic transformation through absorbance and fluorescence signals over a broad concentration range. Furthermore, MnCo₂S₄ NZs maintained high catalytic activity in tap water and river water spiked with OPD, demonstrating their practical applicability in complex aqueous matrices. Owing to their high catalytic activity, stability, reusability, and optical monitoring capability, MnCo₂S₄ NZs represent promising multifunctional NZs for the catalytic degradation and analysis of organic pollutants.

1. Introduction

The rapid expansion of industrial activities has led to the large-scale discharge of synthetic dyes and hazardous aromatic compounds into aquatic environments. It is estimated that the global production of synthetic dyes exceeds 7×10^5 tons annually, and approximately 10–15% of these dyes are released into wastewater during industrial processes [1,2]. These dye-containing effluents pose serious environmental concerns due to their high toxicity, chemical stability, and resistance to natural degradation. Moreover, their complex aromatic structures and high water solubility make efficient removal from wastewater particularly challenging [2,3]. In addition to synthetic dyes, *o*-phenylenediamine (OPD) is another hazardous aromatic compound frequently detected in industrial effluents. It is widely used as a precursor in the production of dyes, pesticides, polymers, and anticorrosive agents [4,5]. However, excessive exposure to OPD can cause severe

health problems, including respiratory disorders, digestive damage, and even DNA mutations or carcinogenic effects [6–8]. Therefore, the efficient removal, transformation, and monitoring of such pollutants remain highly desirable for environmental remediation and pollution control.

Various physical, chemical, and biological methods have been developed for the treatment of dye-contaminated wastewater, including membrane filtration, adsorption, advanced oxidation processes, and enzymatic degradation [3]. Among these approaches, enzymatic oxidation using natural enzymes such as laccase, peroxidase, and oxidase has attracted considerable attention because of its high catalytic selectivity and environmentally benign reaction pathways [9,10]. However, the practical application of natural enzymes is limited by their high production cost, low operational stability, susceptibility to denaturation, and poor recyclability, which restrict their large-scale use in wastewater treatment [11,12].

To overcome the limitations of natural enzymes, nanomaterials with

* Corresponding author.

E-mail address: moonil@gachon.ac.kr (M.I. Kim).

¹ These authors contributed equally to this work.

enzyme-like catalytic properties, known as nanozymes (NZs), have emerged as promising alternatives because of their facile synthesis, high stability, tunable catalytic activity, and good reusability [13,14]. In particular, multicomponent NZs have attracted increasing attention owing to synergistic interactions between different metal species, which can significantly enhance catalytic performance and enable multiple catalytic pathways [15–17]. Among these NZ systems, transition metal-based NZs have been extensively investigated because of their diverse redox properties and catalytic versatility [18–20]. Compared with other transition metals commonly used in nanozyme systems, manganese and cobalt offer multiple accessible oxidation states, excellent redox versatility, and high catalytic adaptability, making them attractive catalytic centers for enzyme-mimicking reactions. Manganese-based NZs have attracted considerable attention owing to their low cost, low toxicity, and rich valence states ($\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$), which enable diverse enzyme-mimicking activities, including peroxidase-, oxidase-, catalase-, superoxide dismutase-, and laccase-like activities, through flexible interconversion between oxidation states, which facilitates efficient electron transfer during catalytic reactions [21–24]. Similarly, cobalt-based NZs exhibit tunable redox activity and high catalytic efficiency, enabling multiple enzyme-mimicking activities, including peroxidase-, oxidase-, catalase-, laccase-, and superoxide dismutase-like activities [25–27]. Despite recent progress, solely Mn- or Co-based NZs remain constrained by relatively limited catalytic efficiency and functional versatility because they lack the cooperative redox interactions available in bimetallic systems. In addition, the catalytic mechanisms of multimetallic nanozymes remain insufficiently understood, and their performance in complex sample matrices requires further improvement. To address these challenges, transition metal sulfides have recently attracted considerable attention because they often exhibit superior catalytic and electronic properties compared with their oxide counterparts owing to their higher electrical conductivity, expanded lattice structures, and narrower band gaps [28–30]. Rational integration of manganese and cobalt into a single sulfide nanostructure is therefore expected to generate strong synergistic redox interactions, overcome the limitations of single-metal systems, and enhance the overall enzyme-mimicking performance. However, manganese–cobalt sulfide NZs have rarely been explored as multifunctional catalysts for environmental pollutant degradation.

In this study, manganese cobalt sulfide nanozymes (MnCo_2S_4 NZs) were synthesized via a simple hydrothermal strategy and investigated as multifunctional catalysts. The MnCo_2S_4 NZs exhibit dual enzyme-mimicking activities, including peroxidase- and laccase-like catalytic behavior. Benefiting from the synergistic interactions between Mn and Co active sites, the MnCo_2S_4 NZs show high catalytic efficiency and excellent stability over a wide range of pH and temperature conditions. The catalytic performance of MnCo_2S_4 NZs was further evaluated for the degradation of industrial dyes and the oxidation of OPD into 2,3-diaminophenazine (DAP), a chromophoric and fluorescent product. The resulting optical signals enabled convenient monitoring of the catalytic transformation. These findings demonstrate the potential of MnCo_2S_4 NZs as multifunctional catalytic NZs for pollutant degradation and monitoring applications.

2. Experimental section

2.1. Materials

Manganese(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, thiourea, *o*-phenylenediamine (OPD), Crystal Violet (CV), Neutral Red (NR), and 3,3',5,5'-tetramethylbenzidine (TMB) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Superoxide dismutase (SOD), sodium azide (SA), terephthalic acid (TA), ascorbic acid (AA), histidine (His), horseradish peroxidase (HRP), and laccase from *Trametes versicolor* were also obtained from Sigma-Aldrich. Hydrogen peroxide (H_2O_2 , 35%) was purchased from Junsei Chemical Co. (Japan). All chemicals

were of analytical grade and used without further purification. Milli-Q water was used for all experiments.

2.2. Synthesis and characterization of MnCo_2S_4 NZs

MnCo_2S_4 NZs were synthesized via a hydrothermal method based on a previously reported procedure [31]. Briefly, 0.6125 g of manganese acetate tetrahydrate and 1.2455 g of cobalt acetate tetrahydrate were dissolved in 75 mL of distilled water and stirred for 20 min. Subsequently, 1.5 g of thiourea was added, and the mixture was further stirred for 20 min. The resulting solution was transferred into a Teflon-lined autoclave and heated at 200 °C for 12 h. After naturally cooling to room temperature (RT), the products were collected by centrifugation ($10,000 \times g$, 10 min), washed several times with distilled water and ethanol, and dried under vacuum at 60 °C for 10 h. Control samples with different Mn/Co ratios were prepared to obtain $\text{Mn}_x\text{Co}_{(3-x)}\text{S}_4$ compositions ($0 \leq x \leq 3$).

The crystal structure of MnCo_2S_4 NZs was characterized by X-ray diffraction (XRD, D/MAX-2500, Rigaku, Tokyo, Japan). The elemental composition and oxidation states were analyzed using X-ray photoelectron spectroscopy (XPS, Sigma Probe, Thermo Scientific, WI, USA). The specific surface area and pore size distribution were determined by Brunauer–Emmett–Teller (BET, ASAP 2020, Micromeritics, USA) analysis based on N_2 adsorption–desorption isotherms. The morphology and microstructure of MnCo_2S_4 NZs were examined using scanning electron microscopy (SEM, Hitachi S-4700, Japan) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai, OR, USA). The elemental distribution was further analyzed by energy-dispersive X-ray spectroscopy (EDS) mapping.

2.3. Peroxidase- and laccase-like activities of MnCo_2S_4 NZs

The peroxidase-like activity of MnCo_2S_4 NZs was evaluated using the oxidation of TMB in the presence of H_2O_2 . The reaction was carried out in 10 mM sodium acetate buffer (pH 6.5) containing 1 mM TMB, 10 mM H_2O_2 , and 0.1 mg/mL MnCo_2S_4 NZs at 37 °C for 5 min. The reaction mixture was centrifuged ($8000 \times g$, 2 min), and the absorbance of the supernatant was measured at 652 nm. Kinetic parameters were determined by varying the concentration of TMB or H_2O_2 while keeping the other constant. The catalytic activity was analyzed using the Michaelis–Menten equation: $V = (V_{\max} \times [S]) / (K_m + [S])$, where V is the initial reaction rate, K_m is the Michaelis constant, $V_{\max}$ is the maximum reaction rate, and $[S]$ is the substrate concentration. The turnover number (k_{cat}) was calculated according to: $k_{\text{cat}} = V_{\max} / [E]$, where $[E]$ represents the molar concentration of MnCo_2S_4 NZs. The NZ concentration was estimated based on the average particle size obtained from TEM analysis, assuming a spherical morphology and using the bulk density of MnCo_2S_4 (detailed calculation is provided in the Supplementary Information).

The laccase-mimicking oxidation activity was evaluated using epinephrine as a substrate. The reaction was conducted in 50 mM MES buffer (pH 6.8) containing 0.1 mg/mL epinephrine and 0.1 mg/mL MnCo_2S_4 NZs at 37 °C for 1 h. The absorbance of the oxidized product was measured at 485 nm. Kinetic parameters were determined similarly by varying epinephrine concentrations.

To further investigate the catalytic mechanism, radical scavenging experiments were performed by introducing specific scavengers into the reaction system, including SOD, AA, TA, SA, and His. Each scavenger was added to the standard reaction mixture under identical conditions, and the catalytic activity was evaluated by monitoring the absorbance change. The involvement of different reactive species was inferred from variations in catalytic activity in the presence of these scavengers. Electron paramagnetic resonance (EPR) measurements were performed using a Bruker EMX premium X-band spectrometer (Bruker Corporation, MA, USA) to identify radical intermediates formed in the peroxidase-like and laccase-mimicking oxidation reaction systems. All experiments were

performed in quintuplicate ($n = 5$), and data are presented as mean $\pm$ standard deviation (SD).

2.4. Dye degradation using peroxidase-like activity of MnCo_2S_4 NZs

Crystal Violet (CV) and Neutral Red (NR) were used as model dyes. For peroxidase-like catalytic degradation, MnCo_2S_4 NZs (0.8 mg/mL) and H_2O_2 (0.1 M) were added to dye solutions with a final dye concentration of 0.4 mg/mL. The reaction mixtures were incubated at 37 °C for 20 min, and the absorbance of the supernatants was measured at 590 nm and 523 nm for CV and NR, respectively. For comparison, dye degradation via laccase-mimicking oxidation activity was conducted under identical conditions without the addition of H_2O_2 . Dye removal efficiency was calculated using the following equation: Removal (%) = $\{(A_0 - A)/A_0\} \times 100$, where A_0 and A represent the initial and final absorbance, respectively.

2.5. Oxidation and optical monitoring of OPD using laccase-mimicking oxidation activity of MnCo_2S_4 NZs

The oxidation of OPD was carried out in 50 mM MES buffer (pH 6.8) containing 0.1 mg/mL MnCo_2S_4 NZs. After incubation at 37 °C for 2 h, the formation of 2,3-diaminophenazine (DAP) was monitored by measuring the absorbance at 425 nm. Fluorescence spectra of DAP were recorded at an excitation wavelength of 417 nm, and the emission intensity was monitored at 569 nm.

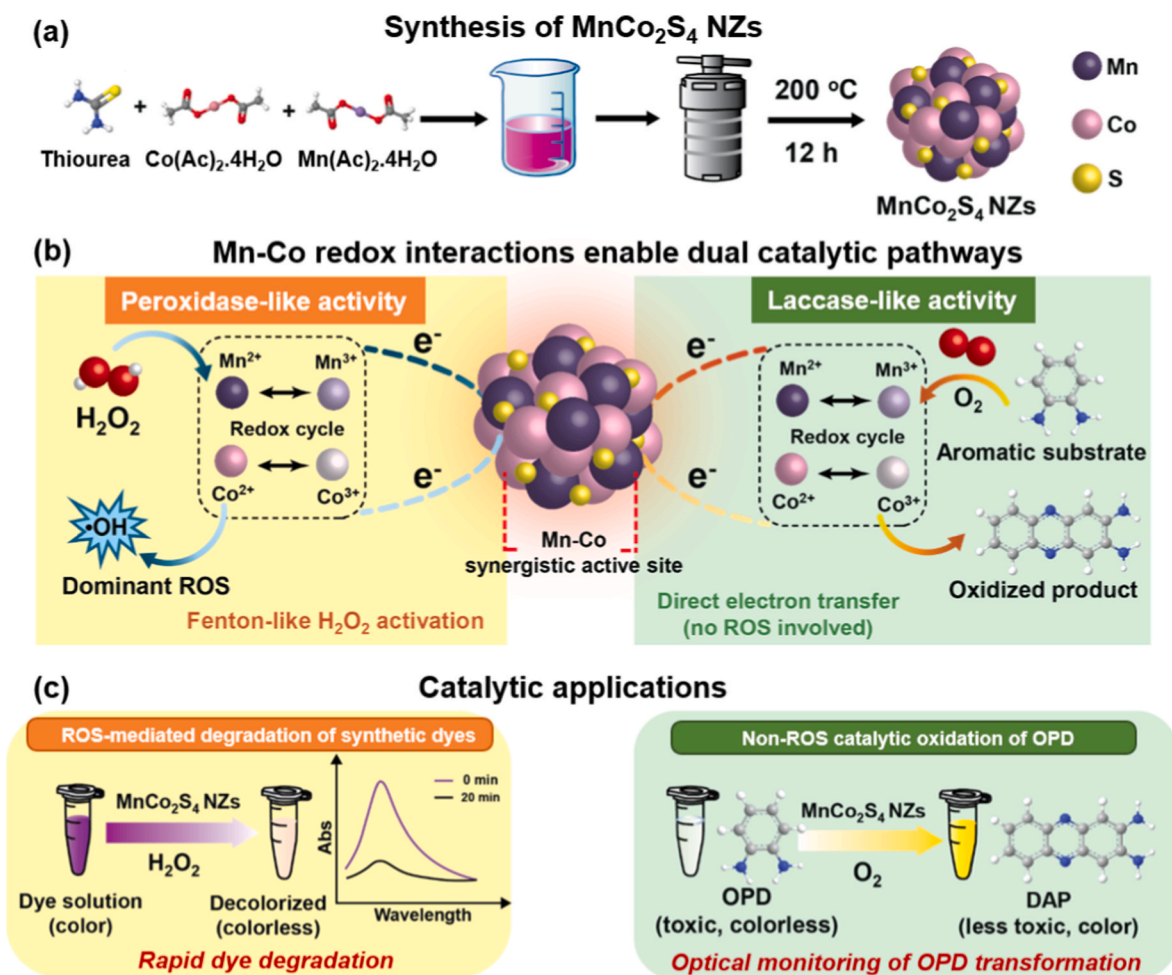
To evaluate practical applicability, tap water and river water samples were collected locally and filtered through a 0.22 μm membrane prior to use. The samples were spiked with known concentrations of OPD and subjected to the same reaction conditions. The catalytic oxidation efficiency and optical response were evaluated based on the absorbance and fluorescence signals of DAP.

3. Results and discussion

3.1. Construction and characterization of MnCo_2S_4 NZs

To address the limitations of conventional catalysts that typically operate through a single reaction pathway, MnCo_2S_4 NZs were designed to enable both reactive oxygen species (ROS)-dependent and ROS-independent catalytic processes. As illustrated in Scheme 1, the MnCo_2S_4 NZs exhibit dual enzyme-mimicking activities arising from synergistic redox interactions between Mn and Co active sites. In the peroxidase-like pathway, MnCo_2S_4 NZs activate H_2O_2 via a Fenton-like mechanism to generate $\bullet\text{OH}$ radicals, which act as the dominant oxidizing species for rapid degradation of organic dyes. In contrast, the laccase-like pathway proceeds through a direct electron-transfer mechanism, in which electrons are transferred from substrates to molecular oxygen via reversible Mn/Co redox cycling without the involvement of free ROS. These dual catalytic pathways enable efficient degradation and detoxification of environmental pollutants.

The crystal structure of MnCo_2S_4 NZs was confirmed by XRD



Scheme 1. Schematic illustration of MnCo_2S_4 NZs and their dual catalytic mechanisms. (a) Hydrothermal synthesis of MnCo_2S_4 NZs. (b) Dual enzyme-mimicking catalytic pathways: peroxidase-like activity via a Fenton-like mechanism generating $\bullet\text{OH}$ radicals, and laccase-mimicking oxidation activity via direct electron transfer without ROS involvement. (c) Applications in catalytic degradation of organic dyes and optical monitoring of OPD transformation.

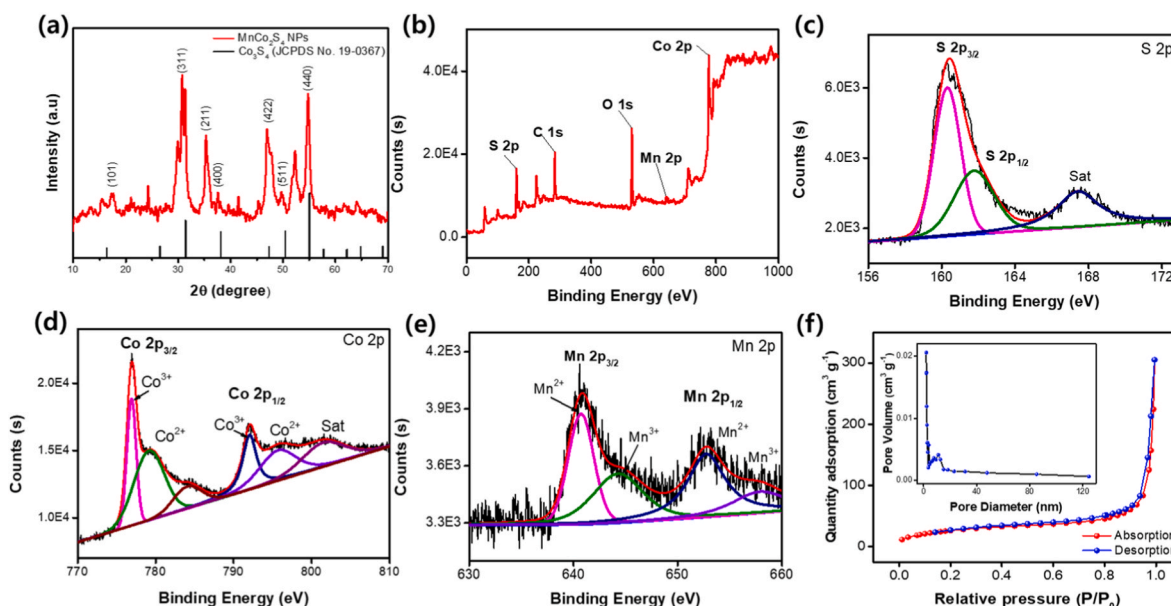


Fig. 1. (a) XRD pattern; XPS spectra including (b) survey scan, (c) S 2p, (d) Co 2p, and (e) Mn 2p; and (f) N_2 adsorption-desorption isotherms with pore size distribution (inset) of $MnCo_2S_4$ NZs.

(Fig. 1a). The diffraction peaks at 30.9° , 38.1° , 47.0° , 50.3° , and 55.1° correspond to the (311), (400), (422), (511), and (440) planes of cubic Co_3S_4 (JCPDS No. 73-1703) [32], consistent with previous reports on $MnCo_2S_4$ [32,33]. This indicates that the incorporation of Mn ions does not substantially alter the cubic sulfide framework. Minor peaks at 17.98° and 35.9° were assigned to the (101) and (211) planes of Mn_3O_4 (JCPDS No. 24-0734), suggesting partial surface oxidation [34]. The sharp and intense diffraction peaks indicate the high crystallinity of the synthesized material.

The XPS spectrum (Fig. 1b) confirms the presence of Co, Mn, and S in the $MnCo_2S_4$ NZs. Peak fitting was performed using a Shirley-

type background subtraction and Gaussian-Lorentzian (70% Gaussian/30% Lorentzian) line shapes, and the detailed parameters were provided in Table S1. The S 2p spectrum (Fig. 1c) shows two prominent peaks at 160.4 and 161.9 eV, corresponding to S $2p_{3/2}$ and S $2p_{1/2}$, respectively. The Co 2p and Mn 2p spectra were deconvoluted into spin-orbit doublets, indicating the coexistence of divalent and trivalent oxidation states [33]. In the Co 2p spectrum (Fig. 1d), the peaks at 779.2 and 795.7 eV are assigned to Co^{2+} , whereas those at 776.9 and 792.0 eV correspond to Co^{3+} [35]. Similarly, the Mn 2p spectrum (Fig. 1e) shows peaks at 640.8 and 652.7 eV assigned to Mn^{2+} , along with additional peaks at 644.6 and 657.6 eV corresponding to Mn^{3+} .

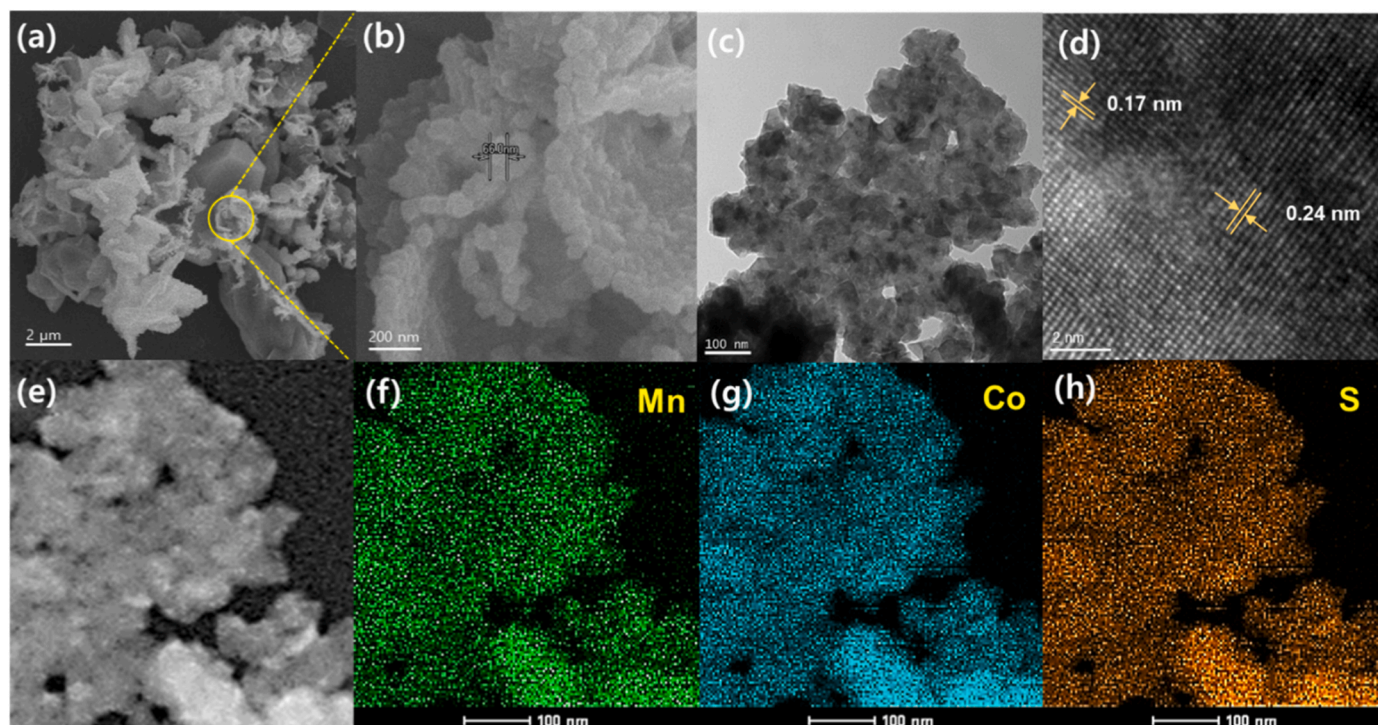


Fig. 2. Morphological characterization of $MnCo_2S_4$ NZs: (a, b) SEM images; (c) TEM image; (d) HRTEM image; and (e-h) EDS elemental mapping.

[36]. The coexistence of $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ suggests the presence of mixed-valence redox centers, which can facilitate electron transfer during catalytic reactions.

BET analysis was performed to evaluate the specific surface area and pore structure of MnCo_2S_4 NZs. The N_2 adsorption–desorption isotherm (Fig. 1f) exhibits a type II isotherm with an H3 hysteresis loop, indicating the presence of mesoporous/macroporous structures, consistent with the pore size distribution and previous reports [31,37,38]. The relatively large specific surface area of $50.4 \text{ m}^2 \text{ g}^{-1}$ provides abundant accessible reaction sites, which is beneficial for enhancing enzyme-like catalytic activities. SEM and TEM images (Fig. 2a–c) show spherical nanoparticles with an average diameter of approximately 66 nm. HRTEM analysis (Fig. 2d) reveals distinct lattice fringes with interplanar spacings of approximately 0.24 and 0.17 nm, corresponding to the (400) and (440) planes of MnCo_2S_4 , respectively [32,33,39,40]. EDS elemental mapping (Fig. 2e–h) further confirms the homogeneous distribution of Mn, Co, and S throughout the synthesized material.

3.2. Dual enzyme-like activities of MnCo_2S_4 NZs and their catalytic mechanism

The peroxidase-like activity of MnCo_2S_4 NZs was evaluated by monitoring the oxidation of TMB in the presence of H_2O_2 , which produces a blue-colored product with a characteristic absorbance peak at 652 nm (Fig. 3a). Among the $\text{Mn}_x\text{Co}_{(3-x)}\text{S}_4$ series and the natural enzyme counterpart HRP, MnCo_2S_4 NZs exhibited the highest catalytic activity (Fig. 3b). Notably, the activity was maintained near neutral pH, which is uncommon for many conventional peroxidase mimics and advantageous for practical applications (Fig. S1).

The laccase-mimicking oxidation activity of MnCo_2S_4 NZs was confirmed using epinephrine as a substrate. Upon oxidation, the reaction solution changed from colorless to orange, with a corresponding absorbance peak at 485 nm, consistent with natural laccase activity (Fig. 3c). To confirm the role of molecular oxygen in the laccase-mimicking pathway, the catalytic oxidation of epinephrine by

MnCo_2S_4 NZs was evaluated under O_2 -rich, normal, and O_2 -depleted conditions. As shown in Fig. S2, the reaction efficiency was strongly dependent on O_2 availability, being markedly enhanced in the O_2 -rich environment and nearly abolished under O_2 -free conditions, supporting the proposed role of molecular oxygen as the terminal electron acceptor in the laccase-mimicking electron-transfer mechanism. The absence of H_2O_2 generation during the reaction (Fig. 3d) indicates that the catalytic process does not follow an oxidase-like pathway but instead mimics laccase behavior. Furthermore, among the $\text{Mn}_x\text{Co}_{(3-x)}\text{S}_4$ series and natural laccase, MnCo_2S_4 NZs exhibited the highest laccase-mimicking oxidation activity (Fig. 3e). Based on these results, MnCo_2S_4 NZs were selected as the primary catalyst for subsequent experiments.

The catalytic performance of MnCo_2S_4 NZs was further evaluated using the Michaelis–Menten model and compared with that of natural enzymes. Kinetic analysis (Fig. S3 and Table 1) revealed lower K_m values and significantly higher k_{cat} values than those of the corresponding natural enzymes, indicating strong substrate affinity and superior catalytic efficiency. This enhanced performance is attributed to the large surface area of MnCo_2S_4 NZs, which provides abundant accessible active sites, as well as the synergistic redox interactions between Mn and Co centers.

To elucidate the catalytic mechanisms, radical scavenging experiments were performed (Fig. 4). Various scavengers were introduced into the reaction system, including SOD as a quencher of $\bullet\text{O}_2^-$ [46], AA as a broad-spectrum scavenger for $\bullet\text{OH}$, $\bullet\text{OOH}$, and $\bullet\text{O}_2^-$ [47], TA as a selective $\bullet\text{OH}$ scavenger [48], SA as a quencher for $^1\text{O}_2$ [49], and His as a quencher for both $\bullet\text{OH}$ and $^1\text{O}_2$ [50]. For the peroxidase-like activity, significant inhibition was observed in the presence of TA and AA (Fig. 4a), confirming that $\bullet\text{OH}$ radicals are the dominant reactive species and supporting a Fenton-like H_2O_2 activation mechanism [51]. The addition of SOD and SA resulted in only slight decreases in activity, suggesting minor contributions from $\bullet\text{O}_2^-$ and $^1\text{O}_2$, respectively. In contrast, the laccase-mimicking oxidation activity was not significantly affected by the ROS scavengers (Fig. 4b), indicating that the reaction proceeds through a direct electron-transfer pathway without ROS

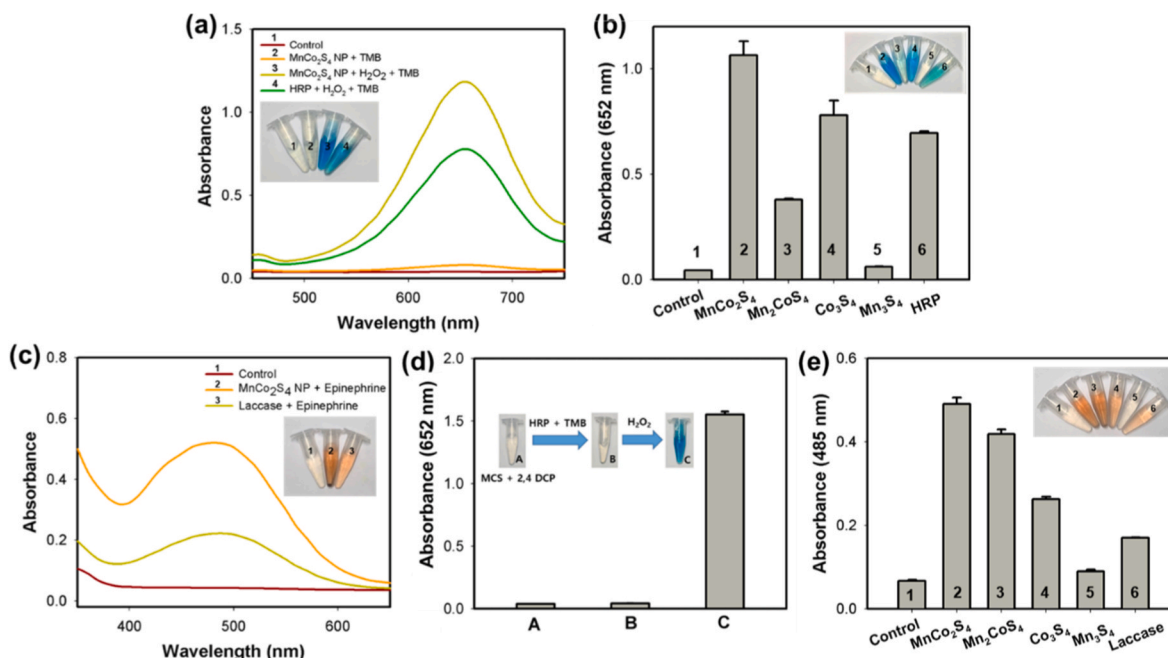


Fig. 3. Peroxidase- and laccase-like activities of MnCo_2S_4 NZs. (a) UV–vis spectra of TMB oxidation under different conditions; inset shows corresponding color changes. (b) Comparison of peroxidase-like activity of $\text{Mn}_x\text{Co}_{(3-x)}\text{S}_4$ (0 ≤ x ≤ 3) and HRP at 652 nm. (c) UV–vis spectra of epinephrine oxidation by MnCo_2S_4 NZs and laccase; inset shows corresponding color changes. (d) Verification of laccase-like activity using 2,4-dichlorophenol (2,4-DCP), indicating no H_2O_2 generation unless externally added. (e) Comparison of laccase-mimicking oxidation activity of $\text{Mn}_x\text{Co}_{(3-x)}\text{S}_4$ (0 ≤ x ≤ 3) and laccase at 485 nm. Data are presented as mean ± SD (n = 5 independent experiments).

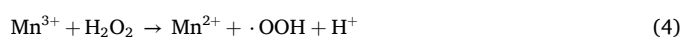
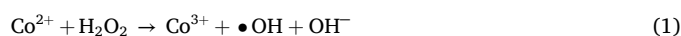
Table 1

Kinetic parameters (K_m , V_{max} , and k_{cat}) of $MnCo_2S_4$ NZs toward peroxidase substrates (TMB and H_2O_2) and the laccase substrate (epinephrine), compared with natural enzymes and representative nanozymes.

Catalysts	Substrates	[E] (M)	K_m (mM)	V_{max} ($10^{-8}M s^{-1}$)	k_{cat} (s^{-1})	Ref.
$MnCo_2S_4$ NZs	TMB	1.26×10^{-12}	0.224	2.60	2.1×10^4	This study
	H_2O_2	1.26×10^{-12}	1.798	3.07	2.4×10^4	
HRP	TMB	2.5×10^{-11}	0.434	10.00	4.0×10^3	[41]
	H_2O_2	2.5×10^{-11}	3.70	8.71	3.48×10^3	
$CoFe_2O_4$	TMB	3.6×10^{-6}	0.14	48.04	0.13	[42]
	H_2O_2	3.6×10^{-6}	0.11	37.65	0.10	
$MnFe_2O_4$	TMB	3.6×10^{-6}	0.16	23.35	6.41	
	H_2O_2	3.6×10^{-6}	0.037	16.05	4.41	
$CuFe_2O_4$	TMB	-	0.14	6.99	-	[43]
	H_2O_2	-	6.23	9.11	-	
$MgFe_2O_4$	TMB	-	0.67	2.09	-	[44]
	H_2O_2	-	4.61	13.46	-	
$MnCo_2S_4$ NZs	Epinephrine	3.15×10^{-12}	0.48	66.3	2.1×10^5	This study
Laccase	Epinephrine	1.03×10^{-6}	0.71	38.5	3.74×10^{-1}	This study
CH-Cu MOFs	Epinephrine	3.15×10^{-10}	0.58	45.7	1.19×10^3	[45]

involvement. To further investigate the radical generation pathways associated with the two catalytic reactions, EPR spectroscopy was employed. As shown in Fig. S4a, the peroxidase-like reaction with H_2O_2 produced a strong radical signal characteristic of $\bullet OH$ radicals, supporting the proposed ROS-mediated pathway. In contrast, no detectable radical signal was observed during the laccase-mimicking oxidation reaction with epinephrine, even in the presence of $MnCo_2S_4$ NZs (Fig. S4b). This absence of signals strongly suggests that the laccase-mimicking oxidation activity proceeds predominantly through a direct electron-transfer mechanism, in which electrons are proposed to be transferred directly from the substrate to the nanozyme surface and subsequently to molecular oxygen via reversible Mn/Co redox cycling, without the involvement of free reactive oxygen species. This behavior is consistent with natural laccase catalysis, in which substrate oxidation is coupled to the reduction of molecular oxygen through a multi-electron transfer process [52,53]. These results clearly demonstrate the dual peroxidase- and laccase-like catalytic nature of $MnCo_2S_4$ NZs.

To elucidate the proposed bimetallic synergistic mechanism underlying the peroxidase-like activity of $MnCo_2S_4$ NZs, the stepwise redox reactions involved in H_2O_2 activation are summarized as follows. The activation of H_2O_2 is proposed to be initiated by low-valence Co^{2+} and Mn^{2+} through Fenton-like reactions, generating highly reactive $\bullet OH$ radicals (Reactions 1 and 2). Subsequently, the oxidized Co^{3+} and Mn^{3+} species are regenerated through intermetallic electron transfer between adjacent Co and Mn redox pairs (Reaction 3), thereby promoting continuous recycling of catalytically active sites. In addition, Mn^{3+} may further react with H_2O_2 to generate $\bullet OOH$ radicals (Reaction 4), which could also contribute to the overall radical pool. This proposed synergistic redox cycle facilitates H_2O_2 activation and is consistent with the coexistence of Co^{2+}/Co^{3+} and Mn^{2+}/Mn^{3+} redox pairs observed by XPS (Fig. 1d and e), as well as the radical scavenging results indicating that $\bullet OH$ is the dominant reactive species during the peroxidase-like reaction (Fig. 4a).



A key advantage of nanozymes over natural enzymes is their enhanced stability under various environmental conditions. $MnCo_2S_4$ NZs exhibited excellent stability for both peroxidase- and laccase-like activities (Fig. 5). The catalytic activities were maintained above 90% across a wide pH range, whereas the corresponding natural enzymes showed significant activity loss. Similarly, $MnCo_2S_4$ NZs retained high activity at elevated temperatures, while HRP and laccase were rapidly deactivated. Furthermore, the NZ maintained stable activity after two weeks of storage, highlighting its robustness for practical applications.

3.3. Dye degradation via peroxidase-like activity of $MnCo_2S_4$ NZs

The practical applicability of $MnCo_2S_4$ NZs was demonstrated through the degradation of NR and CV via their peroxidase-like activity. In the presence of H_2O_2 , $MnCo_2S_4$ NZs efficiently generate $\bullet OH$ radicals through a Fenton-like process, leading to rapid oxidative degradation of dye molecules.

Dye degradation was quantitatively assessed by monitoring the decrease in characteristic absorbance at 523 nm for NR and 590 nm for CV. Negligible changes were observed in control systems lacking either $MnCo_2S_4$ NZs or H_2O_2 , whereas a pronounced decrease in absorbance occurred when both components were present, confirming their essential roles in catalytic degradation (Fig. 6a and b). Under optimized

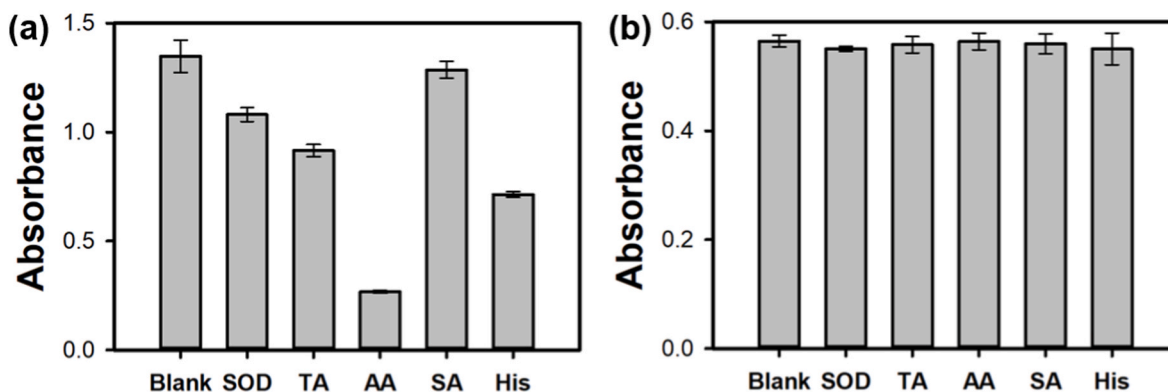


Fig. 4. Radical scavenging analysis of $MnCo_2S_4$ NZs. (a) Radical scavenging assay for the peroxidase-like activity of $MnCo_2S_4$ NZs in the presence of different scavengers. (b) Radical scavenging assay for the laccase-mimicking oxidation activity of $MnCo_2S_4$ NZs under identical conditions. Data are presented as mean $\pm$ SD ($n = 5$ independent experiments).

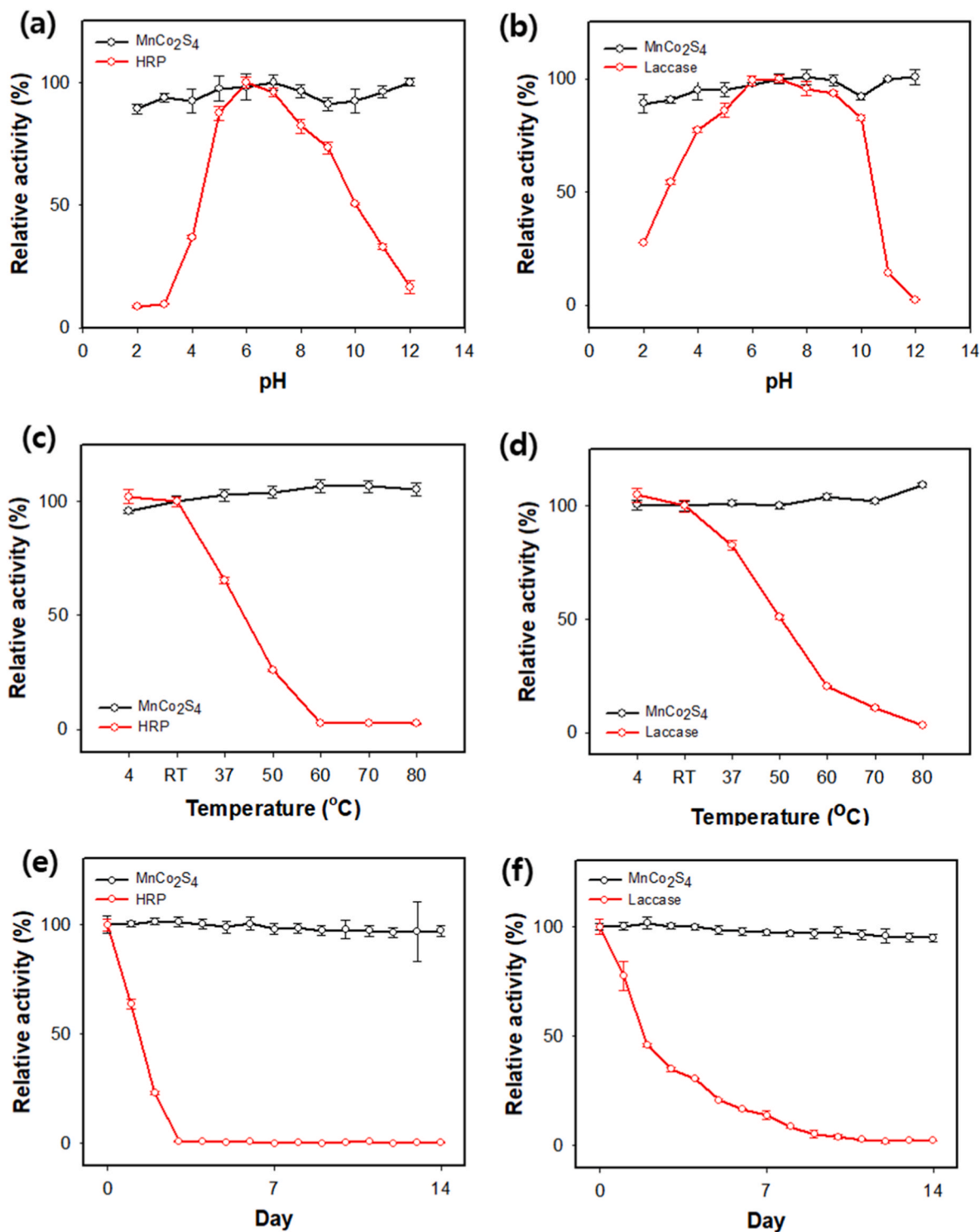


Fig. 5. Stability of MnCo₂S₄ NZs compared with natural enzymes under various conditions: pH (a, b), temperature (c, d), and long-term storage (e, f). Data are presented as mean $\pm$ SD ($n = 5$ independent experiments).

conditions, nearly complete degradation of both dyes (>98%) was achieved within 20 min (Fig. 6c and d), demonstrating the high efficiency of MnCo₂S₄ NZs. Compared with laccase-like pathways, the ROS-mediated peroxidase-like process enabled significantly faster degradation kinetics (Fig. S5). Optimization studies (Fig. S6) showed that degradation efficiency increased with temperature, catalyst loading, and H₂O₂ concentration, reaching optimal performance at 37 °C, 0.8 mg mL⁻¹ MnCo₂S₄ NZs, and 0.1 M H₂O₂. These results indicate that MnCo₂S₄ NZs can rapidly degrade industrial dyes under relatively mild

conditions.

3.4. Catalytic oxidation and optical monitoring of OPD using laccase-mimicking oxidation activity of MnCo₂S₄ NZs

The laccase-mimicking oxidation activity of MnCo₂S₄ NZs was further applied to the oxidative transformation of OPD into DAP, a less toxic product that exhibits both chromophoric and fluorescent properties. Unlike the peroxidase-like pathway, this oxidation is proposed to

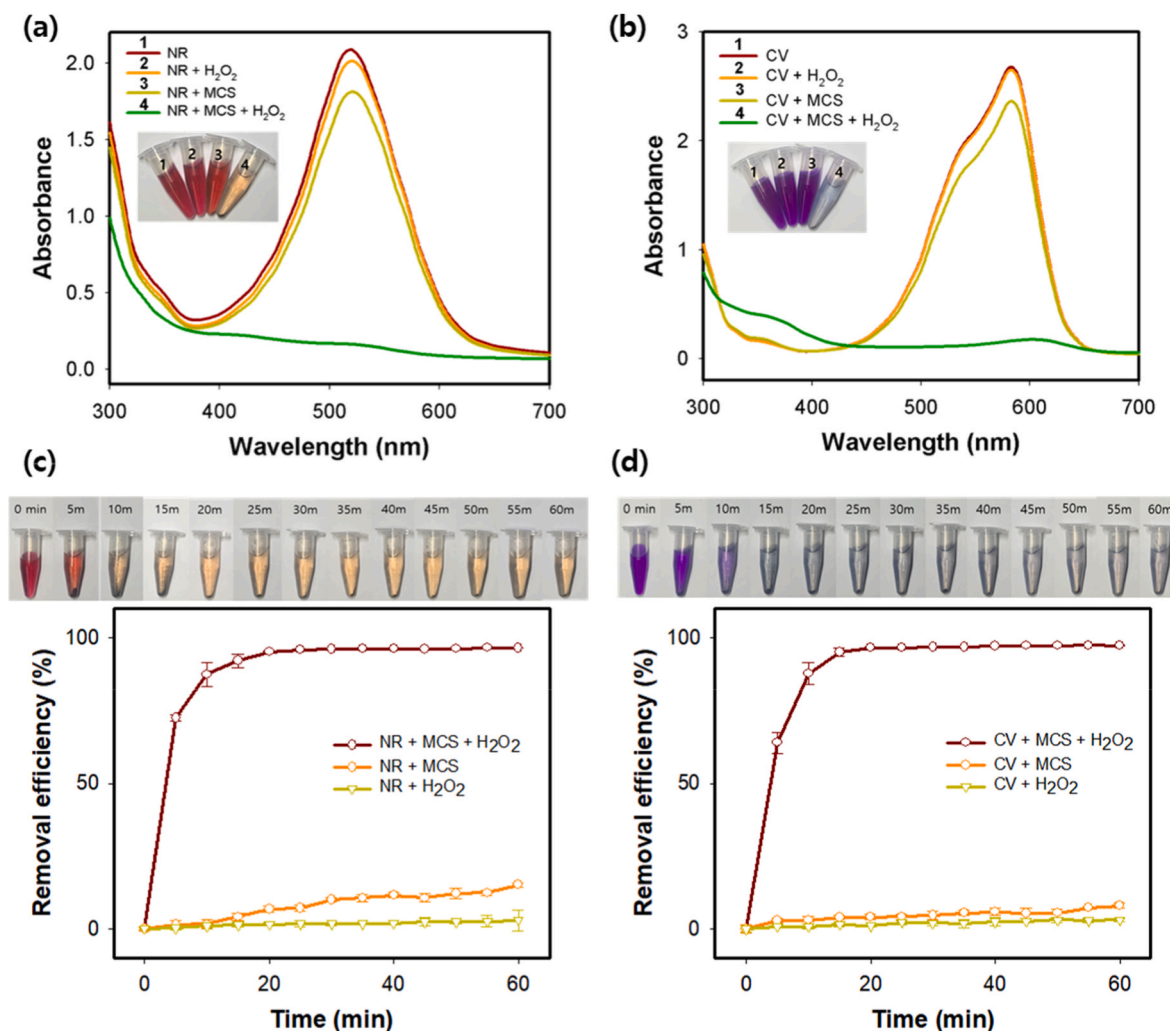


Fig. 6. Absorbance spectra of NR (a) and CV (b) under different reaction conditions (H₂O₂ only, MnCo₂S₄ NZs only, and MnCo₂S₄ NZs + H₂O₂). Time-dependent degradation profiles of NR (c) and CV (d). Data are presented as mean $\pm$ SD ($n = 5$ independent experiments).

proceed predominantly through a direct electron-transfer mechanism, with molecular oxygen serving as the terminal electron acceptor and without the involvement of diffusible reactive oxygen species. This interpretation is supported by the ROS scavenger experiments (Fig. 4b) together with the absence of detectable radical signals in the EPR spectra (Fig. S4b). Such a mechanistic distinction is expected to reduce interference from radical-scavenging species present in complex aqueous matrices, making this catalytic pathway particularly suitable for reliable optical monitoring in real water samples.

The oxidation process was accompanied by a distinct color change from colorless to yellow, corresponding to the formation of DAP (Fig. 7a). Negligible changes were observed in the absence of MnCo₂S₄ NZs, confirming the essential role of the catalyst. The formation of DAP was monitored over time, showing a gradual increase and reaching a maximum after 1 h (Fig. 7b), indicating efficient catalytic oxidation under mild conditions. The catalytic conversion efficiency increased with temperature and reached an optimum at 50 °C (Fig. 7c). The NZ also exhibited good reusability, retaining over 85% of its initial activity after five cycles (Fig. 7d), demonstrating its potential for repeated catalytic applications.

Since DAP is both chromophoric and fluorescent, OPD transformation can be conveniently monitored through absorbance and fluorescence signals. The formation of DAP was monitored through its characteristic absorbance at 425 nm and fluorescence emission (excitation: 417 nm, emission: 569 nm), exhibiting concentration-dependent

responses over a wide range of OPD concentrations (0.05–2.0 mM) for both signals (Fig. S7). These results demonstrate that the laccase-mimicking oxidation activity of MnCo₂S₄ NZs enables straightforward colorimetric and fluorometric monitoring of OPD transformation in aqueous systems.

Importantly, the catalytic oxidation of OPD by MnCo₂S₄ NZs was further validated in real water samples (Table 2). High conversion efficiencies of 98–104% were maintained in both tap water and river water, with low coefficient of variation values (<5%), indicating good reproducibility and robustness against matrix interference. These results demonstrate that MnCo₂S₄ NZs are highly effective for OPD transformation and optical monitoring in complex environmental water matrices.

4. Conclusions

In this study, MnCo₂S₄ NZs were successfully synthesized via a hydrothermal method and exhibited dual enzyme-mimicking activities arising from synergistic Mn–Co redox interactions. These complementary catalytic pathways enable the NZs to operate through both ROS-mediated and direct electron-transfer mechanisms. As a result, MnCo₂S₄ NZs demonstrated excellent catalytic performance toward organic pollutants, achieving approximately 99% removal of industrial dyes (Neutral Red and Crystal Violet) within 20 min via peroxidase-like activity. In addition, the laccase-mimicking oxidation activity of

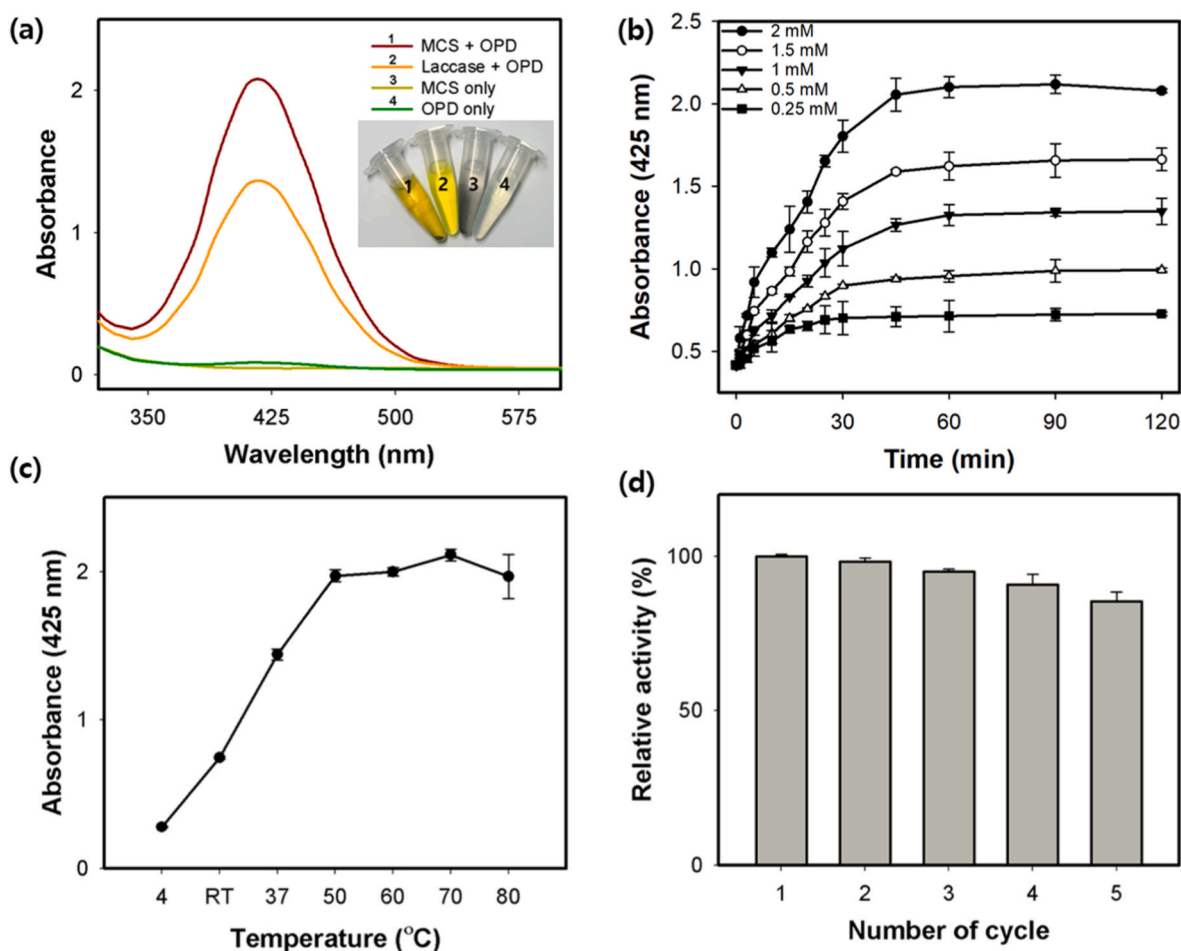


Fig. 7. (a) UV–vis absorbance spectra of OPD oxidation catalyzed by MnCo₂S₄ NZs and laccase for comparison. Time-dependent (b) and temperature-dependent (c) catalytic oxidation of OPD. (d) Reusability of MnCo₂S₄ NZs for OPD oxidation and monitoring. Data are presented as mean $\pm$ SD ($n = 5$ independent experiments).

Table 2

Catalytic oxidation and optical monitoring of OPD in real water samples using MnCo₂S₄ NZs, including reproducibility parameters such as standard deviation (SD) and coefficient of variation (CV).

Samples	Method	Original ^a (mM)	Added (mM)	Found ^b (mM)	Conversion rate ^c (%)	SD ^d	CV ^e (%)
Tap water	Colorimetry	ND ^f	0.2	0.196	98.20	2.07	2.11
			0.1	0.098	98.47	4.77	4.84
			0.05	0.051	101.78	3.60	3.54
	Fluorometry	ND	0.2	0.206	103.12	3.05	2.96
			0.1	0.1	100.42	2.07	2.06
River water	Colorimetry	ND	0.05	0.05	99.08	4.84	4.88
			0.2	0.2	99.77	3.79	3.80
			0.1	0.102	102.01	4.47	4.38
	Fluorometry	ND	0.05	0.05	100.99	4.72	4.67
			0.2	0.203	101.61	3.41	3.35
			0.1	0.1	99.67	4.58	4.59
			0.05	0.05	100.01	3.15	3.15

^a The original amount of target in real samples.

^b Mean value of five independent measurements.

^c Measured value/expected value $\times 100$.

^d Standard deviation of five independent measurements.

^e Coefficient of variation (CV) = (SD/mean) $\times 100$.

^f Not detected.

MnCo₂S₄ NZs enabled the oxidation of OPD into DAP, generating both colorimetric and fluorescent signals that allowed convenient optical monitoring of the catalytic transformation. Furthermore, the NZs exhibited high stability, good reusability, and reliable performance in real water samples. The robust catalytic performance demonstrated in this study suggests that MnCo₂S₄ NZs may be applicable to a broader

spectrum of emerging environmental pollutants, including the oxidative fragmentation of microplastics and degradation of persistent antibiotic residues, both of which pose growing threats to aquatic ecosystems and public health. Furthermore, the integrated optical monitoring capability provides opportunities for developing multifunctional sensing and degradation platforms, while future studies on surface functionalization,

catalytic selectivity, and the toxicity assessment of degradation products will further facilitate their practical environmental applications. Overall, this work highlights MnCo_2S_4 NZs as multifunctional NZs for both catalytic degradation and optical monitoring of organic pollutants and provides a useful strategy for the development of integrated catalytic and optical monitoring platforms.

CRedit authorship contribution statement

Thinh Viet Dang: Conceptualization, Investigation, Methodology, Writing – original draft. **Duc Loc Sai:** Methodology, Validation. **Moon Il Kim:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (Ministry of Science and ICT [RS-2023-NR077205]) and the Basic Science Research Program through the NRF funded by the Ministry of Education (RS-2021-NR060117).

Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtchem.2026.103902>.

Appendix A. Supplementary material

Supplementary Information associated with this article can be found, in the online version.

Data availability

Data will be made available on request.

References

- W. Xiaoxuan, J. Jinming, G. Weijun, Reviewing textile wastewater produced by industries: characteristics, environmental impacts, and treatment strategies, *Water Sci. Technol.* 85 (2022) 2076–2096, <https://doi.org/10.2166/wst.2022.088>.
- A.P. Periyasamy, Recent advances in the remediation of textile-dye-containing wastewater: prioritizing human health and sustainable wastewater treatment, *Sustainability* 16 (2024) 495, <https://doi.org/10.3390/su16020495>.
- B. Balachandran, P.C. Sabumon, A comprehensive review on biodegradation of Azo dye mixtures, metabolite profiling with health implications and removal strategies, *J. Hazard. Mater. Adv.* (2025) 100834, <https://doi.org/10.1016/j.hazadv.2025.100834>.
- S. Zhang, F. Lin, Q. Yuan, J. Liu, Y. Li, H. Liang, Robust magnetic laccase-mimicking nanozyme for oxidizing o-phenylenediamine and removing phenolic pollutants, *J. Environ. Sci.* 88 (2020) 103–111, <https://doi.org/10.1016/j.jes.2019.07.008>.
- F. Vetr, Z. Moradi-Shoeili, S. Özkur, Oxidation of o-phenylenediamine to 2,3-diaminophenazine in the presence of cubic ferrites MFe_2O_4 ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$) and application in colorimetric detection of H_2O_2 , *Appl. Organomet. Chem.* 32 (2018) e4465, <https://doi.org/10.1002/aoc.4465>.
- T.G. Gichner, D.A. Stavreva, F. Van Breusegem, o-Phenylenediamine-induced DNA damage and mutagenicity in tobacco seedlings is light-dependent, *Mutat. Res.* 495 (2001) 117–125, [https://doi.org/10.1016/S1383-5718\(01\)00204-2](https://doi.org/10.1016/S1383-5718(01)00204-2).
- A. Nezamzadeh-Ejhi, Z. Salimi, Heterogeneous photodegradation catalysis of o-phenylenediamine using CuO/X zeolite, *Appl. Catal. Gen.* 390 (2010) 110–118, <https://doi.org/10.1016/j.apcata.2010.09.038>.
- M. Matsumoto, M. Suzuki, H. Kano, S. Aiso, K. Yamazaki, S. Fukushima, Carcinogenicity of ortho-phenylenediamine dihydrochloride in rats and mice by two-year drinking water treatment, *Arch. Toxicol.* 86 (2012) 791–804, <https://doi.org/10.1007/s00204-012-0800-z>.
- R. Ezra, G. Vanti, S. Masaphy, Sustainable, targeted, and cost-effective laccase-based bioremediation technologies for antibiotic residues in the ecosystem: a comprehensive review, *Biomolecules* 15 (2025) 1138, <https://doi.org/10.3390/biom15081138>.
- B. Thakur, A.K. Nadda, A. Kant, Recent advances in laccase-based nanobiocatalysts for sustainable bioremediation applications, *Biotechnol. Bioeng.* 123 (2026) 1432–1464, <https://doi.org/10.1002/bit.70210>.
- M.K. Al-Sakkaf, I. Basfer, M. Iddrisu, S.A. Bahadi, M.S. Nasser, B. Abussaud, Q. A. Drmash, S.A. Onaizi, An up-to-date review on the remediation of dyes and phenolic compounds from wastewaters using enzymes immobilized on emerging and nanostructured materials: promises and challenges, *Nanomaterials* 13 (2023) 2152, <https://doi.org/10.3390/nano13152152>.
- L.Y. Jun, L.S. Yon, N.M. Mubarak, C.H. Bing, S. Pan, M.K. Danquah, E.C. Abdullah, M. Khalid, An overview of immobilized enzyme technologies for dye and phenolic removal from wastewater, *J. Environ. Chem. Eng.* 7 (2019) 102961, <https://doi.org/10.1016/j.jece.2019.102961>.
- P. Mathur, R. Singh, M. Kumawat, S.P. Srinivas, H.K. Daima, Trends in designer-made metal oxide nanozymes for environmental applications, *Inorg. Chem. Commun.* (2025) 115190, <https://doi.org/10.1016/j.inoche.2025.115190>.
- S. Nayak, S. Hansdah, S.P. Palai, G.C. Malik, B. Singh, D. Fawcett, G.E.J. Poinern, P.K. Parhi, Nanozyme-based remediation of complex wastewater streams: a focus on emerging contaminants, *Inorg. Chem. Commun.* (2026) 116268, <https://doi.org/10.1016/j.inoche.2026.116268>.
- M. Cui, B. Xu, L. Wang, Recent advances in multi-metallic-based nanozymes for enhanced catalytic cancer therapy, *BMEMat* 2 (2024) e12043, <https://doi.org/10.1002/bmm.212043>.
- D. Sun, C. Ding, N. Wang, Q. Ding, W. Liu, X. Liu, H. Wei, J. Yang, Z. Cheng, S. Zhao, B. Hong, T. Zhao, Near-infrared responsive nanozyme-carboxymethyl chitosan/chondroitin sulfate composite hydrogel: multicomponent synergy optimizes bone defect microenvironment to enhance repair, *Int. J. Biol. Macromol.* (2025) 148646, <https://doi.org/10.1016/j.jbiomac.2025.148646>.
- J. Wang, Y. Liu, X. Zhang, Hydrogenated silicene nanosheet functionalized scaffold enables immuno-bone remodeling, *Explorations* 3 (2023) 20220149, <https://doi.org/10.1002/EXP.20220149>.
- L. Wang, P. Dai, H. Ma, T. Sun, J. Peng, Advancing biomedical applications of polyoxometalate-based metal-organic frameworks: from design to therapeutic potential, *Inorg. Chem. Front.* 11 (5) (2024) 1339–1365, <https://doi.org/10.1039/d3qj02414h>.
- Y. Peng, Y. Zhuang, Y. Liu, H. Le, D. Li, M. Zhang, K. Liu, Y. Zhang, J. Zou, J. Ding, Bioinspired gradient scaffolds for osteochondral tissue engineering, *Explorations* 3 (2023) 20210043, <https://doi.org/10.1002/EXP.20210043>.
- X. Li, J. Li, W. Wang, Z. Yue, T. Sun, Thermo-oxidative coupling amplification effect unleashed by tungsten-based polyoxometalate nanoreactors enables synergistic hyperthermia-chemodynamic therapy, *Part. Part. Syst. Char.* 43 (2026) e00192, <https://doi.org/10.1002/ppsc.202500192>. Particle & Particle Systems Characterization.
- M. Tang, Z. Zhang, T. Sun, B. Li, Z. Wu, Manganese-based nanozymes: preparation, catalytic mechanisms, and biomedical applications, *Adv. Healthcare Mater.* 11 (2022) 2201733, <https://doi.org/10.1002/adhm.202201733>.
- Y. Lin, Z. Zhu, Z. Xu, J. Chen, Z. Li, H. Huang, Y. Zhang, D. Chen, B. Liang, G. Wang, Triple-enzyme mimetic manganese nanozyme with redox-adaptive catalysis for synergistic MSU degradation and inflammation resolution in acute gout, *Adv. Healthcare Mater.* 14 (2025) 2502180, <https://doi.org/10.1002/adhm.202502180>.
- Q. Tian, S. Huangfu, G. Kang, H. Wang, H. Liu, X. Wang, A. Li, Y. Chen, K. Fan, L. Zhang, High-spin states of manganese (III) enable robust cold-adapted activity of MnO_2 nanozymes, *Adv. Sci.* 12 (2025) 2415477, <https://doi.org/10.1002/advs.202415477>.
- S. Deng, Y. Hao, L. Yang, T. Yu, X. Wang, H. Liu, Y. Liu, M. Xie, Construction of nanozyme based with mixed valence manganese oxide loaded on defective metal-organic frameworks for sensitive detection of biomarker procalcitonin, *Biosens. Bioelectron.* 278 (2025) 117339, <https://doi.org/10.1016/j.bios.2025.117339>.
- Y. Li, X. Hu, H. Deng, Cobalt-based nanozymes: design strategies, biomedical applications, and future challenges, *Colloids Surf. B Biointerfaces* (2025) 115032, <https://doi.org/10.1016/j.colsurf.2025.115032>.
- Y. Chen, B. Jiang, H. Hao, H. Li, C. Qiu, X. Liang, Q. Qu, Z. Zhang, R. Cao, D. Duan, S. Ji, D. Wang, M. Liang, Atomic-level regulation of cobalt single-atom nanozymes: engineering high-efficiency catalase mimics, *Angew. Chem.* 135 (2023) e202301879, <https://doi.org/10.1002/anie.202301879>.
- S. Li, X. Zhao, H. Ding, J. Chang, X. Qin, F. He, X. Gao, S. Gai, P. Yang, Advanced cobalt-ferrite layered double hydroxides sandwich-structured nanozymes for ROS-bloomed tumor therapy, *Chem. Eng. J.* 473 (2023) 145414, <https://doi.org/10.1016/j.ccej.2023.145414>.
- S. Ali, S.H.U. Bakhtiar, A. Ismail, P.M. Ismail, S. Hayat, A. Zada, X. Wu, A. N. Alodhayb, M. Zahid, F. Raziq, J. Yi, L. Qiao, Transition metal sulfides: from design strategies to environmental and energy-related applications, *Coord. Chem. Rev.* 523 (2025) 216237, <https://doi.org/10.1016/j.ccr.2024.216237>.
- H. Jia, L. Meng, Y. Lu, T. Liang, Y. Yuan, Y. Hu, Z. Dong, Y. Zhou, P. Guan, L. Zhou, C. Liu, M. Li, T. Wan, B.J. Ni, Z. Han, D. Chu, Boosting the efficiency of electrocatalytic water splitting via in situ grown transition metal sulfides: a review, *J. Mater. Chem. A* 12 (2024) 28595–28617, <https://doi.org/10.1039/d4ta06197g>.
- M. Zhu, D. Wang, Z. Ge, L. Pan, Y. Chen, W. Wang, N. Mitsuzaki, S. Jia, Z. Chen, Recent advances in transition metal sulfide-based electrode materials for supercapacitors, *Chem. Commun.* 61 (2025) 8314–8326, <https://doi.org/10.1039/d5cc01411e>.

- [31] F. Zhang, M. Cho, T. Eom, C. Kang, H. Lee, Facile synthesis of manganese cobalt sulfide nanoparticles as high performance supercapacitor electrodes, *Ceram. Int.* 45 (2019) 20972–20976, <https://doi.org/10.1016/j.ceramint.2019.06.240>.
- [32] L. Abbasi, M. Arvand, S.E. Moosavifard, Facile template-free synthesis of 3D hierarchical ravine-like interconnected MnCo₂S₄ nanosheet arrays for hybrid energy storage device, *Carbon* 161 (2020) 299–308, <https://doi.org/10.1016/j.carbon.2020.01.094>.
- [33] Y.V. Lim, S. Huang, Q. Wu, D. Kong, Y. Wang, Y. Zhu, Y.X. Wang, H.K. Liu, S. X. Dou, Super kinetically pseudocapacitive MnCo₂S₄ nanourchins toward high-rate and highly stable sodium-ion storage, *Adv. Funct. Mater.* 30 (2020) 1909702, <https://doi.org/10.1002/adfm.201909702>.
- [34] L. Wang, L. Chen, Y. Li, H. Ji, G. Yang, Preparation of Mn₃O₄ nanoparticles at room condition for supercapacitor application, *Powder Technol.* 235 (2013) 76–81, <https://doi.org/10.1016/j.powtec.2012.10.010>.
- [35] H. Chen, J. Jiang, Y. Zhao, L. Zhang, D. Guo, D. Xia, One-pot synthesis of porous nickel cobalt sulphides: tuning the composition for superior pseudocapacitance, *J. Mater. Chem. A* 3 (2015) 428–437, <https://doi.org/10.1039/C4TA04420G>.
- [36] D. Li, X. Zhang, L. Pei, C. Dong, J. Shi, Y. Xu, High-performance supercapacitors and nonenzymatic electrochemical glucose sensor based on tremella-like NiS/CoS/NiCo₂S₄ hierarchical structures, *Inorg. Chem. Commun.* 110 (2019) 107581, <https://doi.org/10.1016/j.inoche.2019.107581>.
- [37] S. Yi, F. Dai, C. Zhao, Y. Si, A reverse micelle strategy for fabricating magnetic lipase-immobilized nanoparticles with robust enzymatic activity, *Sci. Rep.* 7 (2017) 1–9, <https://doi.org/10.1038/s41598-017-10453-4>.
- [38] S. Fu, Q. Fang, A. Li, Z. Li, J. Han, X. Dang, W. Han, Accurate characterization of full pore size distribution of tight sandstones by low-temperature nitrogen gas adsorption and high-pressure mercury intrusion combination method, *Energy Sci. Eng.* 9 (2021) 80–100, <https://doi.org/10.1002/ese3.817>.
- [39] H. Wang, K. Zhang, Y. Song, J. Qiu, J. Wu, L. Yan, MnCo₂S₄ nanoparticles anchored to N- and S-codoped 3D graphene as a prominent electrode for asymmetric supercapacitors, *Carbon* 146 (2019) 420–429, <https://doi.org/10.1016/j.carbon.2019.02.035>.
- [40] S. Liu, S.C. Jun, Hierarchical manganese cobalt sulfide core-shell nanostructures for high-performance asymmetric supercapacitors, *J. Power Sources* 342 (2017) 629–637, <https://doi.org/10.1016/j.jpowsour.2016.12.057>.
- [41] L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett, X. Yan, Intrinsic peroxidase-like activity of ferromagnetic nanoparticles, *Nat. Nanotechnol.* 2 (2007) 577–583, <https://doi.org/10.1038/nnano.2007.260>.
- [42] C. Xia, H. Zhang, M. Xie, J. Che, Q. Feng, Y. Zhang, H. Fan, Parallel comparative studies on composition-dependent peroxidase-like catalytic activity of ultrasmall ferrite nanoparticles, *J. Mater. Chem. B* 13 (2025) 8434–8445, <https://doi.org/10.1039/D5TB00626K>.
- [43] J. Cao, J. Lv, L. Zheng, Q. Bai, Y. Yin, M. Li, Z. Hou, Rational design of CuFe₂O₄ nanozyme with enhanced activity via bimetallic synergy for sensitive detection of alendronate sodium, *Microchem. J.* (2026) 116993, <https://doi.org/10.1016/j.microc.2026.116993>.
- [44] L. Su, W. Qin, H. Zhang, Z.U. Rahman, C. Ren, S. Ma, X. Chen, The peroxidase/catalase-like activities of MFe₂O₄ (M = Mg, Ni, Cu) MNPs and their application in colorimetric biosensing of glucose, *Biosens. Bioelectron.* 63 (2015) 384–391, <https://doi.org/10.1016/j.bios.2014.07.048>.
- [45] J. Wang, R. Huang, W. Qi, R. Su, B.P. Binks, Z. He, Construction of a bioinspired laccase-mimicking nanozyme for the degradation and detection of phenolic pollutants, *Appl. Catal. B Environ.* 254 (2019) 452–462, <https://doi.org/10.1016/j.apcatb.2019.05.012>.
- [46] A. Sannasimuthu, V. Kumaresan, M. Pasupuleti, B.A. Paray, M.K. Al-Sadoon, J. Arockiaraj, Radical scavenging property of a novel peptide derived from C-terminal SOD domain of superoxide dismutase enzyme in *Arthrospira platensis*, *Algal Res.* 35 (2018) 519–529, <https://doi.org/10.1016/j.algal.2018.09.028>.
- [47] D. Njus, P.M. Kelley, Y.J. Tu, H.B. Schlegel, Ascorbic acid: the chemistry underlying its antioxidant properties, *Free Radic. Biol. Med.* 159 (2020) 37–43, <https://doi.org/10.1016/j.freeradbiomed.2020.07.013>.
- [48] K. Xu, S. Pei, W. Zhang, Z. Han, P. Guan, L. Wang, Y. Zou, H. Ding, X. Ma, C. Liu, F. Zhang, Ce(III)-terephthalic acid metal-organic frameworks as highly efficient •OH radical scavengers for fuel cells and investigation of antioxidation mechanism, *Mater. Today Energy* 31 (2023) 101195, <https://doi.org/10.1016/j.mtener.2022.101195>.
- [49] B.C. Ma, S. Ghasimi, K. Landfester, F. Vilela, K.A. Zhang, Conjugated microporous polymer nanoparticles with enhanced dispersibility and water compatibility for photocatalytic applications, *J. Mater. Chem. A* 3 (2015) 16064–16071, <https://doi.org/10.1039/C5TA03820K>.
- [50] H.C. Kaboggoza, B. Bekdeser, R. Apak, Peroxyl radical scavenging activity measurement of antioxidants using histidine-stabilized and glutathione-capped fluorescent gold nanoclusters, *Spectrochim. Acta* 285 (2023) 121876, <https://doi.org/10.1016/j.saa.2022.121876>.
- [51] T.V. Dang, H.U. Lee, J.I. Park, J.S. Bae, M.I. Kim, Single-atom Cu–N/O aerogel nanozymes with dual enzymatic activities for point-of-care detection of multiple neurotransmitters, *Chem. Eng. J.* (2026) 174822, <https://doi.org/10.1016/j.cej.2026.174822>.
- [52] X. Xu, J. Wang, R. Huang, W. Qi, R. Su, Z. He, Preparation of laccase-mimicking nanozymes and their catalytic oxidation of phenolic pollutants, *Catal. Sci. Technol.* 11 (2021) 3402–3410, <https://doi.org/10.1039/D1CY00074H>.
- [53] J. Wang, R. Huang, W. Qi, R. Su, Z. He, Construction of biomimetic nanozyme with high laccase- and catecholase-like activity for oxidation and detection of phenolic compounds, *J. Hazard. Mater.* 429 (2022) 128404, <https://doi.org/10.1016/j.jhazmat.2022.128404>.