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Magnetic Flower-like Fe-Doped CoO Nanocomposites with Dual Enzyme-like Activities for Facile and Sensitive Determination of H₂O₂ and Dopamine

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ABSTRACT: He	rein, a new series of ma	anetic Fe-doped CoO	Oxidase

nanocomposites (Fe-CoO NCs) with dual enzyme-like activities (peroxidase and oxidase) were successfully synthesized. The molar ratio of Fe^{3+}/Co^{2+} salts during the solvothermal process determined the morphology and catalytic activity of the NCs. Among them, the flowerlike 0.15Fe-CoO NCs showed high peroxidase-mimicking activity over a wider pH range of 4-5 and a temperature range of 30-50 °C. Such nanozymes were applied for constructing a facile and sensitive colorimetric sensor to detect H_2O_2 and dopamine (DA) in the linear ranges of 6–20 and 2–10 μ M with limits of detection (LODs) of 4.40 and 1.99 μ M, respectively. The excellent magnetic separation performance and successful DA detection in human urine samples validated the promising application of CoO-based nanozymes in medical diagnosis.



The superior catalytic behaviors of 0.15Fe-CoO NCs could be ascribed to the high surface area, open mesoporous structure, increased surface active species, and the facile redox of Fe³⁺/Fe²⁺ and Co³⁺/Co²⁺. Based on the results of the fluorescent probe and radical trapping tests, the possible mechanism that Fe doping promoted the decomposition of H_2O_2 to produce hydroxyl radical (•OH) and superoxide radical (• O_2^-) was proposed.

INTRODUCTION

Natural enzymes are widely present in living organisms and play an important role in regulating the biological functions. They are the most effective catalysts for in vitro detection of various biomolecules owing to the merits of high sensitivity and excellent selectivity.¹ However, their applications were often limited owing to high price, low stability (>45 °C), and the difficulty to reuse.^{2,3} To replace natural enzymes, many kinds of artificial nanozymes have been developed, such as noble metals, metal sulfides and oxides, metal salts, and carbon materials.⁴ Among them, metal oxides, including Fe₃O₄ nanoparticles (NPs),^{1,5} Co₃O₄ NPs,⁶ V₂O₅ nanospheres,⁷ and CeO₂ nanorods,^{8,9} have attracted more interest thanks to their low cost, excellent stability, and reusability. Especially, open porous-structured nanomaterials always exhibited superior catalytic performance, attributing to the large working surface area and the convenient substrate transfer channels.^{6,10} Therefore, it is highly desirable to develop an effective metal oxide-based nanozyme with these advantages.

Various cobalt oxide (CoO) nanostructures have been studied in the fields of photo- and electrocatalysis because of their high stability, large surface area, and facile redox of $Co^{3+}/$ Co^{2+,11,12} Yet, pure CoO NPs exhibited poor electrical conductivity and tend to self-agglomerate to mask the active sites. Therefore, currently many efforts have been made to

further improve the catalytic properties of CoO NPs. For example, combining with carbon materials could effectively improve the electron-transfer efficiency and the dispersion of CoO NPs.^{13,14} The g-C₃N₄ with large surface area and twodimensional (2D) structure could prevent the agglomeration of CoO NPs and facilitate the separation of carriers in CoO/g- C_3N_4 .^{15,16} The introduction of CoO nanodots in nitrogendoped porous carbon increased the electron density on the carbon surface, thereby enhancing both radical and nonradical catalytic processes.¹⁷ Next, the construction of heterojunctions can create an interfacial electric field at the junction of two phases to fasten the electron transfer.^{18,19} The flower-like CoO@Bi₂S₃ heterojunction with multiple light reflection/ scattering channels and improved molecular diffusion kinetics provided more exposed active edges and greater light utilization efficiency.²⁰ The promising catalytic activity of the mesoporous CoO/CeO₂ could be attributed to the abundant surface defects and oxygen vacancies (OVs) introduced by the

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heterojunction interface of CeO₂ and CoO nanocrystals.²¹ Moreover, functional doping with a metal or metal oxide is also an effective way. For instance, the uniform doping of SiO₂ onto CoO nanorods significantly improved the intrinsic peroxidaselike activity of the latter.²² Suitable Ag decoration not only increased the surface active species but also promoted the separation of photogenerated electron—hole pairs of CoO NPs.²³ Nevertheless, only a few works about CoO-based catalysts as nanozymes have been reported. For this reason, it is still necessary to explore novel CoO-based nanozymes with special properties by a facile and green strategy.

Fe doping has been proved to be an efficient strategy to develop low-cost and highly active catalysts. For example, the doping of Fe³⁺ endowed 2D g-C₃N₄ nanosheets (NSs) with better catalytic property toward H2O2 in cancer cells to generate O_2 .²⁴ When doped with Fe³⁺, more OVs were generated to enhance the chemical absorption of O2 and generation of active oxygen species $(O^- \text{ and } O_2^-)$.^{25–27} Because of the coherent effect between the electrons of the Fe 3d orbitals and ZrO₂ intrinsic electronic states, the band gap of Fe-doped ZrO₂ NPs was narrowed to promote the charge transfer between the catalyst and the substrate.²⁸ Fe³⁺ (6%) doping obviously lowered the average size of CeO₂ NRs and created more surface defects (Ce³⁺ ions and OVs).²⁹ Notably, both Fe and FeO active centers hold strong magnetic moments and intrinsically drive the reactions through the radical mechanism.³⁰ Besides, the facile redox of $Fe^{3+} \leftrightarrow Fe^{2+}$ and $Co^{3+} \leftrightarrow Co^{2+}$ could provide reversible defect sites for the catalytic decomposition of H_2O_2 into free radicals.^{5,31,32} Inspired by these reports, we attempted to prepare the open porous-structured Fe-doped CoO NCs with a remarkable enzyme-like activity. The doping of Fe compounds may also endow CoO with excellent magnetic separation performance, which has never been reported for CoO-based nanozymes.

Herein, we have synthesized a new series of magnetic Fedoped CoO NCs by the simple one-pot solvothermal method followed by heat treatment. Especially, the flower-like 0.15Fe-CoO NCs possessed dual enzyme-like activities for quickly oxidizing the substrate 3,3',5,5'-tetramethylbenzidine (TMB) with H_2O_2 as an oxidant in 60 s. Owing to the magnetism of the composite catalyst, easy recyclability and reusability are important for the sustainable development. The roles of doped Fe compounds and CoO substrate were systematically investigated by the control and deoxygenation experiments. The catalytic behaviors of 0.15Fe-CoO NCs strongly relied on the solution pH and temperature and conformed to the Michaelis-Menten (M-M) kinetic model. According to the better peroxidase-mimicking activity of 0.15Fe-CoO, a colorimetric sensor was developed for rapid and sensitive determination of H₂O₂ and DA. The possible mechanism was investigated via fluorescent probe and radical trapping experiments.

EXPERIMENTAL SECTION

Reagents. Fe(NO₃)₃·9H₂O, Co(NO₃)₃·6H₂O, glycerol, isopropanol (IPA), *p*-benzoquinone (PBQ), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and *p*-phthalic acid (PTA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). TMB and dopamine hydrochloride (DA) were obtained from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and were used without further purification. Solutions were prepared with ultrapure water.

Fabrication of Fe-CoO NCs. A series of Fe-CoO NCs were fabricated by two-step routes including solvothermal and roasting processes (Scheme 1). First, 1 mmol of $Co(NO_3)_2$ was added into a homogeneous mixture containing glycerin and isopropanol (16 and





60 mL, respectively) and vigorously stirred for 1 h. Second, n mmol of $Fe(NO_3)_3$ (n = 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0) was added and continuously mixed for another 10 h. Third, the mixture was transferred into a 100 mL Teflon container with a stainless-steel autoclave and treated under 180 °C (6 h). The obtained precipitate was purified by alternately washing with water and ethanol (6 times in total) and then dried overnight at 60 °C. The precursor was roasted at 400 °C (2 h) with the protection of N₂ flow. The final samples were recorded as *n*Fe-CoO NCs. Besides, pure CoO NPs were prepared using the similar method without adding Fe³⁺ salt. But without Co²⁺ salt, the Fe³⁺ ions cannot crystallize to be FeO or Fe₃O₄ NPs.

Detailed descriptions for the characterization, activity evaluation, kinetic tests, determination of H_2O_2 and DA, and research mechanism processes are given in the Supporting Information.

RESULTS AND DISCUSSION

Material Characterization. X-ray diffraction (XRD) patterns were determined to analyze the phase composition and purity of the samples. As shown in Figure 1a, the patterns of pure CoO NPs and 0.15Fe-CoO NCs feature five distinct reflections at $2\theta = 36.5$, 42.4, 61.5, 73.7, and 77.6°, corresponding to the cubic CoO (ICDD 43-1004). Note that the characteristic peaks of doped Fe components are not observed in 0.15Fe-CoO NCs, which may be attributed to the low content or very close positions to those of CoO NPs (Figure S1). Fortunately, the XRD patterns of other composites given in Figure S2a confirm the latter hypothesis. The newly emerging peaks correspond to the magnetic γ -Fe₂O₃ (ICDD 43-1004), which endows 0.15Fe-CoO NCs the merit for easily separating from the reaction system. The area ratios of peaks due to γ -Fe₂O₃ and CoO in composites were calculated by peak splitting and fitting (Figure S2b and Table S1). The increasing trend is basically the same as the adding ratio of the Fe^{3+}/Co^{2+} salts. Moreover, no oxidized Co_2O_3 and other impurities were detected in both CoO NPs and 0.15Fe-CoO NCs, implying their high purities.

The porous structures of CoO NPs and 0.15Fe-CoO NCs were investigated by N₂-sorption isotherms. Their isotherms (shown in Figure 1b) are typical type-IV with an H3-type hysteresis loop, indicating the coexistence of a mesoporous/macroporous structure.³³ The determined Brunauer–Emmett–Teller (BET) surface areas of CoO and 0.15Fe-CoO are 216.2 and 205.4 m² g⁻¹, respectively. The BJH pore size distribution of 0.15Fe-CoO is mainly in the range of 2–20 nm,



Figure 1. XRD patterns (a) and N₂-sorption isotherms (b) of CoO NPs and 0.15Fe-CoO NCs.



Figure 2. SEM (a1), TEM (a2, a3) and HRTEM (a4) images of CoO NPs; and SEM (b1), TEM (b2, b3), and HRTEM (b4) images of 0.15Fe-CoO NCs. (c) Element mapping photos of 0.15Fe-CoO NCs.



Figure 3. (a) XPS survey spectra and XPS spectra of (b) Fe 2p, (c) Co 2p, and (d) O 1s for CoO NPs and 0.15Fe-CoO NCs.

while that of CoO centers at about 5 nm and 30 nm (inset). Therefore, 0.15Fe-CoO NCs have a more uniform pore size distribution, which may facilitate the mass transfer for heterogeneous catalysis.³⁴ Although the surface area of CoO NPs is a little higher, 0.15Fe-CoO NCs may have higher

porosity utilization. Notably, the surface area of 0.15Fe-CoO NCs is obviously higher than other composites, implying the key role of Fe^{3+}/Co^{2+} ratio in shaping the porous structure (Figure S3 and Table S2). Besides, 0.15Fe-CoO NCs can be easily separated from the solution using a strong magnet

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(Figure S4). Therefore, the magnetic 0.15Fe-CoO NCs with rich mesoporous structure were successfully fabricated by rationally adjusting the molar ratio of the Fe^{3+}/Co^{2+} salts.

The morphology of pure CoO NPs and 0.15Fe-CoO NCs was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. As shown in Figure 2a1,b1, CoO NPs exhibit a nest-like structure and are cross-linked together, which are difficult to disperse well, while the 0.15Fe-CoO particles are in flower shape with high dispersion. The open hierarchical porous structure can provide effective channels for fast mass transport and charge transfer during catalytic oxidation.^{19,34} However, the excessive use of Fe³⁺ salt would destroy this special morphology and result in larger particles (Figure S5), which is consistent with the results of N₂-sorption. The surface atomic ratio of Fe/Co was also determined by elemental dispersive spectroscopy (EDS) and the results are listed in Table S3. Although the actual Fe/Co ratios in the composite catalysts are mostly higher than the adding ratios of Fe^{3+}/Co^{2+} salts, their increasing trends are basically the same as each other. As shown in Figure 2a2,a3, the CoO NPs consist of a loose core of 400-500 nm and a graphene-like shell of about 100 nm. Certainly, the special morphology endowed CoO with high surface area and developed porous structure. The doping of Fe not only reduced the average particle size of 0.15Fe-CoO NCs but also made the particles dense (Figures 2b2,b3 and S6). Importantly, the flower-like morphology is well maintained, and the petals are composed of tiny nanosheets. The tight adhesion between doped Fe compounds and CoO can effectively promote carrier transfer. The high-resolution TEM (HRTEM) image (Figure 2a4) of CoO identifies the d-spacing values of 0.22 and 0.24 nm, corresponding to the (200) and (111) crystal planes of CoO.14,35 Unfortunately, the lattice spacing of 0.15Fe-CoO NCs shown in Figure 2b4 cannot be distinguished due to the similar XRD peaks of FeO, γ -Fe₂O₃, and CoO. The distributions of Fe, Co, and O elements in 0.15Fe-CoO NCs (Figure 2c) are highly consistent, indicating the uniform doping of Fe onto CoO NPs. Therefore, the open mesoporous-structured Fe-CoO NCs with high dispersion were successfully fabricated.

The valence state of the surface element was examined by the X-ray photoelectron spectroscopy (XPS) technique (Figure 3a). It is clear that no Fe element exists in pure CoO NPs. The Fe 2p spectrum of 0.15Fe-CoO was fitted into five peaks (Figure 3b). The peaks centered at 713.6 and 726.3 eV with a satellite peak at 716.9 eV are assigned to Fe³⁺ ions,³⁶⁻³⁸ while the other two peaks at 710.7 and 720.4 eV correspond to the Fe²⁺ ions.³⁹ The relative contents of Fe³⁺/ Fe²⁺ were calculated to be 59.5 and 40.5% (Table S4), respectively. However, the FeO phase was not observed in the XRD patterns of all composites, which might be due to the characteristic peaks of FeO (Wurstite) being very close to those of CoO. The presence of magnetic FeO can improve the redox cycle of Fe²⁺/Fe³⁺, thus enhancing the electron transfer between the catalyst and the substrates. In Figure 3c, the Co 2p spectra were deconvoluted into six peaks. Among which, the peaks centered at 781.3 and 796.4 eV accompanied by two satellite peaks at 786.2 and 802.9 eV are attributed to the Co²⁺ ions, and the peaks located at 779.6 and 794.7 eV are contributed to the Co³⁺ ions.^{40,41} The presence of Co³⁺ might have originated from the oxidation of surface Co²⁺ by oxygen during preparation. Interestingly, the Co³⁺ content of 0.15Fe-CoO NCs (21.1%) is obviously lower than that of CoO NPs

(24.9%), suggesting that the Fe doping inhibited the oxidation of surface Co²⁺. Also, a proper ratio of Co²⁺/Co³⁺ can promote the electron transfer between 0.15Fe-CoO and the reactants. The O 1s spectra (Figure 3d) were split into three peaks at 529.8, 531.2, and 532.6 eV, corresponding to the lattice oxygen (O_a) in Fe-O and/or Co-O, surface oxygen (O_β) associated with the OVs, and the oxygen functional groups (O_γ).⁴² Notably, compared with CoO, the O_a and O_β contents on 0.15Fe-CoO improved by 9.8 and 8.3%, respectively. Therefore, the doping of Fe compounds endowed CoO NPs excellent magnetic separation property and higher density of surface reactive sites, thus exhibiting a better catalytic performance.

Dual Enzyme-like Activities. As shown in Figure 4a,b, the peroxidase-mimicking activity of the composite catalysts



Figure 4. (a) Evaluation of the peroxidase-mimicking activity of Fe-CoO NCs: (1) CoO, (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, (6) 0.30, (7) 0.40, (8) 0.60, (9) 0.80, and (10) 1.00; (c) control experiments for confirming the dual enzyme-like activities of 0.15Fe-CoO: (1) TMB, (2) $H_2O_2 + TMB$, (3) CoO + TMB, (4) CoO + $H_2O_2 + TMB$, (5) 0.15Fe-CoO + TMB, and (6) 0.15Fe-CoO + $H_2O_2 + TMB$; (b) and (d) are the corresponding color images.

increases with the Fe³⁺/Co²⁺ ratio increasing from 0 to 0.15 (lines 1–4), which can be attributed to the Fe doping. Nevertheless, the activity would be reduced when the ratio exceeds 0.20 (lines 5–7), and even lower than that of CoO (ratios of 0.60–1.00, line 8–10), due to the excessive doping of Fe compounds that destroyed the porous structure of the CoO NPs. Thus, 0.15Fe-CoO NCs show the highest catalytic activity and the optimal molar ratio of Fe³⁺/Co²⁺ salts is 0.15.

The TMB alone cannot be oxidized by dissolved oxygen and H_2O_2 (Figure 4c,d, lines 1 and 2). In the absence of H_2O_2 , CoO NPs still slightly catalyze the oxidation of TMB, indicating their mild oxidase-like activity (line 3). The specific absorbance is further improved with H_2O_2 (line 4); thus, CoO NPs also possess peroxidase-mimicking activity. Notably, the doping of Fe hardly affected the oxidase-like activity of CoO (line 5) but significantly improved its peroxidase-like activity (line 6). Meanwhile, the 0.15Fe-CoO + H_2O_2 + TMB system generated the deepest color at the same time intervals. When high-purity N₂ was purged for 30 min before reaction, the obvious decrease in the activity of CoO and 0.15Fe-CoO could be observed as shown in Figure S7a,b, revealing that the dissolved oxygen was also involved in the catalytic reaction. The results suggest that the oxidase- and peroxidase-like activities of 0.15Fe-CoO NCs are mainly derived from CoO and the doped Fe compounds, respectively.⁴³ The remarkable dual enzyme-like activities of 0.15Fe-CoO NCs may be



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Figure 5. Influences of pH (a) and temperature (b) on the catalytic activity of 0.15Fe-CoO NCs; and (c) change of TMB under different pH values and temperatures.



Figure 6. Steady-state kinetics for 0.15Fe-CoO as peroxidase mimics: (a) varying H_2O_2 from 2 to 20 mM and keeping TMB of 0.1 mM; (c) varying TMB from 10 to 100 μ M and keeping H_2O_2 of 20 mM. (b) and (d) are the corresponding linear double reciprocal curves of (a) and (c).

ascribed to the highly dispersed flower-like structure and the synergistic effect between Fe compounds and CoO. For convenience, subsequent experiments were performed on the basis of their peroxidase-mimicking activity.

The influences of pH and temperature were systematically investigated. As shown in Figure 5a, the 0.15Fe-CoO catalyst exhibits higher catalytic activity under a wider pH range of 4– 5. However, at strong acidic conditions (pH<4), TMB would be directly oxidized to the yellow benzidine.^{44,45} Under the pH range of 6–8, the activity of the 0.15Fe-CoO NCs is significantly inhibited owing to the direct decomposition of most H₂O₂ into H₂O and O₂.⁴³ The 0.15Fe-CoO NCs can retain larger than 80% of the highest activity at higher temperatures (30–50 °C), revealing their excellent temperature resistance (Figure 5b). Especially, they display the highest activity around body temperature (37 °C), which is essential for their practical application in medical diagnosis. Similarly, too high temperature (>50 °C) would also cause excessive oxidation of TMB. Figure 5c clearly shows the change of TMB under different pH values and temperatures. Therefore, pH of 5 and temperature of 37 °C were selected for the following reactions. Besides, the 0.15Fe-CoO catalyst also exhibits excellent durability and reusability (Figure S8a,b), which are essential for its practical applications.

Steady-State Kinetics of 0.15Fe-CoO NCs. As shown in Figure 6a,c, the steady-state kinetics of H_2O_2 and TMB as substrate conform to the typical Michaelis—Menten (M–M) curves. From the corresponding double reciprocal curves (Figure 6b,d), the M–M constants (K_m) of the 0.15Fe-CoO NCs toward H_2O_2 and TMB were calculated to be 11.2 and 0.170 mM, respectively. They are comparable to or lower than those of horseradish peroxidase (HRP) (3.7 and 0.434 mM)¹ and many nanozymes such as Fe₃O₄ MNPs (154 and 0.098 mM),¹ WS₂ nanosheets (15.2 and 0.805 mM),⁴⁶ and so on



Figure 7. (a) H_2O_2 detection limit tests: varying H_2O_2 concentration in 1–100 μ M; (b) selectivity of 0.15Fe-CoO to H_2O_2 (100 μ M) and interferences (500 μ M). (c) ΔA responses of the sensor toward DA in 1–50 μ M; and (d) selectivity of the sensor to DA (50 μ M) and interferences (500 μ M). Conditions: nanozymes 30 μ g mL⁻¹, TMB 0.1 mM, H_2O_2 20 mM, pH of 5, *T* of 37 °C, and 60 s.

(Table S5), indicating the high affinity of 0.15Fe-CoO toward H_2O_2 and TMB. The Fe²⁺/Fe³⁺ and Co²⁺/Co³⁺ balances as well as the special mesoporous structure may contribute to a high binding affinity to the substrates.⁴⁷ Besides, the maximum reaction rates (V_m) with H_2O_2 and TMB as substrate are 24.1 × 10⁻⁸ and 50.9 × 10⁻⁸ M s⁻¹, respectively, much higher than those of the contrast catalysts except WS₂ NSs, well explaining the fast reaction rate of the 0.15Fe-CoO + H_2O_2 + TMB system in just 60 s.

Determination of H₂O₂ and DA. A colorimetric sensor (0.15Fe-CoO + H_2O_2 + TMB) was constructed based on the 0.15Fe-CoO NCs for the determination of H₂O₂. As depicted in Figure 7a, the feature absorbance first rapidly increases and then slightly increases over a broad H₂O₂ concentration range of 1–100 μ M. The absorption maxima show a linear relationship with H_2O_2 concentration in the range 6–20 μM (inset, $R^2 = 0.9910$). As a result, the limits of detection (LOD) of this sensor toward H₂O₂ was calculated to be 4.40 μ M (3 σ / k), where σ represents the standard deviation of night blank groups without adding H₂O₂, and k is the slope of the linear fitting curve. The LOD is comparable to or lower than that of many reported works (Table S6). Although fluorescence and electrochemical methods are more sensitive, the colorimetric strategy exhibits unique merits including simple operation and the much shortened reaction time. Besides, the selectivity of the sensor toward H₂O₂ was studied in comparison with metal ions (K⁺, Na⁺, Ca²⁺, Mg²⁺), sugars (Fru, Mal), and amino acids (Arg, His, Ser). As can be seen from Figure 7b, 0.15Fe-CoO exhibits a strong response only to H2O2, even though the concentrations of interferences are 5 times higher than that of H₂O₂. These results demonstrate the good sensitivity and selectivity of 0.15Fe-CoO NCs for H₂O₂ sensing.

Furthermore, the proposed sensor was applied for DA sensing by determining the absorbance difference (ΔA) at 652 nm before and after adding DA (Figure 7c). The ΔA values are linearly related to the DA concentrations in the range of 2–10 μ M (inset, $R^2 = 0.9912$). As a result, the LOD was determined as 1.99 μ M, which is comparable to that of many previous reports (Table S7). Importantly, as shown in Figure 7d, the

sensor shows strong response only to DA (50 μ M), compared to various interferences (500 μ M). Therefore, the developed colorimetric sensor also shows excellent sensitivity and selectivity for the determination of DA.

To evaluate the practical performance of the colorimetric sensor, the H_2O_2 and DA in human urine samples were determined by the standard addition method. As shown in Table 1, for H_2O_2 detection, the recovery values are between

Table 1. Results of H_2O_2 and DA Detection in Human Urine Samples

samples	spiked (μM)	found (μM)	recovery (%)	RSD (%)
H_2O_2	6	5.89	98.2	13.3
	10	10.06	100.6	9.24
	14	14.89	106.4	2.99
	18	17.57	97.6	5.54
	20	19.73	98.6	2.85
DA	2	1.89	94.6	0.17
	4	4.29	107.2	0.14
	6	5.89	98.2	0.05
	8	8.08	102.0	0.08
	10	10.33	103.3	0.06

97.6 and 106.4% with the relative standard deviations (RSDs) of 2.85–13.3%. As for the determination of DA, the recovery values are 94.6–107.2% with RSDs ranging from 0.06 to 0.17%. Therefore, the sensing platform based on 0.15Fe-CoO NCs is highly accurate and has great potential for H_2O_2 and DA detection in real samples.

Possible Mechanism. After reacting for 30 min, the 0.15Fe-CoO + PTA + H_2O_2 system produces bright blue fluorescence, which has the maximum emission (λ_m) at around 433 nm (Figure 8a). No obvious fluorescence can be observed in the pure PTA system (line 1). Interestingly, the λ_m of the PTA+0.15Fe-CoO (30 μ g mL⁻¹) system appears at about 387 nm (line 2). This may be because, in the absence of H_2O_2 , 0.15Fe-CoO NCs act as oxidase mimics to react with dissolved oxygen, producing ${}^{\circ}O_2^{-}$ to combine with PTA. Note that the λ_m intensity increases with the catalyst concentration

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Figure 8. (a) Fluorescence probe tests: (1) PTA, (2) PTA+0.15Fe-CoO (30 μ g mL⁻¹), (3–9) PTA + H₂O₂ + 0.15Fe-CoO (0, 5, 10, 15, 20, 25, and 30 μ g mL⁻¹); (b) radical trapping experiments using IPA, PBQ, and EDTA-2Na to scavenge [•]OH, [•]O₂⁻, and h⁺, respectively. Each experiment was repeated three times.

increasing from 0 to 30 μ g mL⁻¹ (lines 3–9), implying that the higher catalyst concentration creates more °OH radicals. Besides, radical trapping experiments were performed using IPA, PBQ, and EDTA-2Na to scavenge °OH, °O₂⁻, and hole (h⁺), respectively. As shown in Figure 8b, the addition of IPA and PBQ significantly reduced the absorbance but not for EDTA-2Na. Therefore, it can be concluded that both °OH and °O₂⁻ species participated in the oxidation of TMB catalyzed by 0.15Fe-CoO with H₂O₂ as an additive.

Based on the results and discussion of the whole work, the feasible catalytic mechanism of 0.15Fe-CoO NCs was preliminarily investigated (Scheme 2). First, the catalytic

Scheme 2. Possible Catalytic Mechanism of 0.15Fe-CoO NCs with Dual Enzyme-Like Activities



reactions mainly occurred on the doped Fe compounds (FeO and γ -Fe₂O₃). Fe²⁺ ions with excellent Fenton reactivity catalyzed the decomposition of H₂O₂, generating °OH radicals to oxidize the TMB. The oxidized Fe³⁺ ions would be restored back to Fe²⁺ by H₂O₂, meanwhile, producing a molecule of O₂. So, in the presence of H₂O₂, the composite catalyst exhibited peroxidase-mimicking activity. Then, the reactions moved to the support CoO NPs. Co²⁺ ions first reacted with dissolved O₂ and the O₂ from the decomposition of H₂O₂ to create $^{\circ}O_2^{-}$ radicals. Then, TMB would be oxidized by $^{\circ}O_2^{-}$ under weakly acidic conditions. However, the oxidation capacity of $^{\circ}O_2^{-}$ is significantly lower than that of $^{\circ}OH$. Thus, 0.15Fe-CoO NCs showed weak oxidase-like activity. At last, Co³⁺ ions could immediately oxidize TMB, indicating that CoO NPs also possess a certain degree of oxidation.

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \to \mathrm{Fe}^{3+} + \mathrm{OH}^- + {}^{\bullet}\mathrm{OH}$$
(1)

$$^{\circ}\text{OH} + \text{TMB} \rightarrow \text{ox} - \text{TMB}$$
 (2)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2 + 2H^+$$
 (3)

$$Co^{2+} + O_2 \to Co^{3+} + {}^{\bullet}O_2^{-}$$
 (4)

$$TMB + O_2^- + 2H^+ \rightarrow ox - TMB + H_2O$$
(5)

$$Co^{3+} + TMB \rightarrow ox - TMB + Co^{2+}$$
 (6)

CONCLUSIONS

In summary, a series of magnetic Fe-CoO NCs were successfully synthesized and were found to possess dual enzyme-like activities (oxidase and peroxidase). Control of the Fe^{3+}/Co^{2+} ratio in hydrothermal process determined not only the morphology but also the catalytic activity of the composite catalysts. Especially, the flower-shaped 0.15Fe-CoO NCs with open mesoporous structure were highly dispersed, due to the Fe doping effectively inhibiting the agglomeration of CoO NPs. The superior catalytic activity could be attributed to the high specific surface area, special flower-like structure, and increased surface active species. The TMB oxidation was achieved by catalyzing the generation of •OH and •O2radicals. A colorimetric sensor was developed based on 0.15Fe-CoO NCs for rapid and sensitive determination of H₂O₂ and DA. The good magnetic separation characteristic and the accurate real-sample detection ability prove that this catalyst has a strong practical performance. This work provides a general strategy for synthesizing high-efficiency nanozymes through functional doping.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03355.

Detailed descriptions for the characterizations, activity evaluation, kinetic tests, determination of H_2O_2 and DA, and mechanism research processes; XRD patterns; N_2 adsorption/desorption isotherms; magnetic separation photos; N_2 bubbling experiments; tables of the parameters of N_2 adsorption/desorption and XPS analysis; and tables of the kinetic parameters; and H_2O_2 and DA sensing parameters compared with previous reports (PDF)

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Notes

The authors declare no competing financial interest.

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