

ORIGINAL ARTICLE

Synthesis of CeO₂ nanoparticles with different morphologies and their properties as peroxidase mimicBaoliang Zhang  | Yu Huan | Jiqi Wang | Wenbin Wang | Qiuyu Zhang | Hepeng Zhang 

Key Laboratory of Applied Physics and Chemistry in Space, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an, China

Correspondence

Baoliang Zhang and Hepeng Zhang
Northwestern Polytechnical University,
Xi'an, China.
Emails: blzhang@nwpu.edu.cn;
zhanghepeng@nwpu.edu.cn

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Abstract

The overall objective of this work was to identify and determine the controlling factors of catalytic activity of CeO₂ nanoparticles with different properties. Therefore, four kinds of CeO₂ nanoparticles are successfully synthesized and used as peroxidase mimics. The results reveal that the catalytic activity is related to specific surface area and surface oxygen (O_{sur}) content. For different CeO₂ nanoparticles, specific surface area is the leading factor of catalytic activity. The catalytic activity increases with the increasing specific surface area. If the CeO₂ nanoparticles have similar specific surface area, the less O_{sur} contains, the lower catalytic activity will be. Meanwhile, crystallinity is not the influence factor of catalytic activity. Bamboo-like CeO₂ (B-CeO₂) nanoparticles show excellent catalytic activity and the reaction conditions are optimized. Furthermore, the catalytic activity of B-CeO₂ nanoparticles decreases very slightly after 15 cycles of the catalysis experiment. Therefore, B-CeO₂ nanoparticles can serve as effective recyclable peroxidase mimics.

KEYWORDS

catalytic performance, CeO₂ nanoparticles, hydrothermal reaction, mimic enzymes, peroxidase

1 | INTRODUCTION

Catalyst plays an important role in all kinds of catalytic reactions. As the catalyst, natural enzyme is more ideal for its significant advantages including high catalytic efficiency, substrate specificity, and mild catalytic conditions.^{1–3} However, enzymes have the problems of high production and application costs. The main reasons are as follows: (a) The source of natural enzyme is limited; (b) Enzyme is difficult to purify; (c) The enzyme is very sensitive to the environment and easy to inactivate. Thus, the extensive applications of natural enzymes are limited.

With the rapid development of nanotechnology, the variety and application field of nanoparticles have been greatly expanded. In recent years, some nanoparticles have

been found to have catalytic activity as the natural enzyme.^{4–8} Because of the stable structure, simple preparation method and low production cost, nanoparticles have become a hot research hotspot as substitutes of natural enzymes. This application of nanoparticles has important practical value. The nanoparticles with catalytic properties as natural enzymes are named mimic enzymes.

According to the reports, it has confirmed that Fe₃O₄, Co₃O₄, Fe₂O₃, CuO, Au, Ag, Pd, and Cu nanoparticles can exhibit the properties of peroxidase.^{9–14} CdS, Au/Fe₃O₄, Au/V₂O₅, and Au nanoparticles have the same catalytic activity as glucose oxidase.^{15–17} Fe₃O₄, Co₃O₄, Pt, Pd, and Ag/Pt nanoparticles possess the properties of catalase.^{18–21} CeO₂, Pt, Co₃O₄, and Cu nanoparticles show the performance of superoxide dismutase.^{22–24} Pt nanoparticles also

own the capability of uric acid enzyme.²⁵ These nanoparticles, playing the role of natural enzymes, have been widely used in the fields of immunoassay, determination of metal ions, target sensor, degradation of pollutants, hybridization of nucleic acids and organic synthesis.^{5,20,26–31}

Due to the valence of cerium element can be reciprocally transformed in trivalent and tetravalent, CeO₂ nanoparticles can act as catalysts in many reactions, such as photodegradation of organic pollutants, water splitting, oxidation reduction reaction in organic synthesis.^{32–36} Meanwhile, both surface oxygen and lattice oxygen show oxidation in CeO₂ nanoparticles. It has been found that CeO₂ nanoparticles can display the properties of catalase, oxidase, and superoxide dismutase.^{24,36} Based on this, CeO₂ nanoparticles have been used for the determination of glucose and nucleic acid. The oxidizability of CeO₂ nanomaterials is decided by morphology, atomic valence, the existing form and proportion of oxygen atom, specific surface area, etc. The research on the controlling factors for catalytic activity of CeO₂ nanoparticles as peroxidase is rarely seen.

By changing the hydrothermal reaction conditions, four kinds of CeO₂ nanoparticles are prepared in this work. The morphologies of the as-synthesized CeO₂ nanoparticles are sphere (S-CeO₂), octahedron (O-CeO₂), hexahedron (H-CeO₂), and bamboo-like (B-CeO₂). These nanoparticles exhibit different morphologies, surface oxygen content, crystallinity, and specific surface area. More importantly, they have different catalytic activities of peroxidase. Through systematically characterizing, the reason for the difference catalytic performance of the four kinds of CeO₂ nanoparticles is studied. Furthermore, the effects of reaction conditions on the catalytic performance and the reusability of B-CeO₂ nanoparticles are investigated.

2 | EXPERIMENTAL SECTIONS

2.1 | Materials

KCl, NaCl, Na₂HPO₄, KH₂PO₄, KOH, ethanol, H₂O₂ (36 wt%), and Cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) were purchased from Sinopharm Chemical Reagent Co. Ltd. Polyvinyl pyrrolidone (PVP, K29-32) and o-Phenylenediamine (OPD) were purchased from J&K Scientific Ltd (Beijing, China). All the above chemicals were analytical reagent. The water used throughout the work was deionized water produced by apparatus for pharmaceutical purified water (Aquapro Co. Ltd., Asheville, NC).

2.2 | Preparation of CeO₂ nanoparticles

We chose four methods to prepare the CeO₂ nanoparticles according to our previous works and literatures. They were used for clearing the controlling factors of catalytic activity

of CeO₂. CeO₂ nanoparticles were prepared through hydrothermal methods.

A typical experimental procedure for the fabrication of S-CeO₂ nanoparticles was as follows.³⁷ Typically, 2 mmol of Ce(NO₃)₃·6H₂O and 4 mmol of PVP were dissolved in 40 mL of purified water. The solution was transferred to a 50 mL teflon-lined stainless-steel autoclave and heated at 200°C for 2.5 hours. The autoclave then slowly cooled at room temperature. The S-CeO₂ nanoparticles were washed with water for three times, and then dried by vacuum freeze-drying.

O-CeO₂ nanoparticles were synthesized by the same method as that of S-CeO₂ nanoparticles. A total of 5 mmol of Ce(NO₃)₃·6H₂O and 10 mmol of PVP were dissolved in 40 mL of solution mixed with purified water and ethanol (volume ratio of was 3:1). After stirring for 30 min, the mixture was transferred to a 50 mL teflon-lined stainless-steel autoclave and heated at 200°C for 24 hours. The O-CeO₂ nanoparticles were obtained after washing with water for three times and vacuum freeze-drying.

H-CeO₂ nanoparticles were prepared as follows. A total of 1 mmol of Ce(NO₃)₃·6H₂O was dissolved in 35 mL of purified water. The solution was mixed by magnetic stirring for 30 min followed by dropwise addition of KOH solution. The concentration of KOH was 0.1 mol/L and the addition quantity was 0.35 mL. Then, the solution was transferred to a 50 mL teflon-lined stainless-steel autoclave and heated at 230°C for 36 hours. The obtained powdery products were H-CeO₂ nanoparticles.

B-CeO₂ nanoparticles were prepared using the same method with H-CeO₂ nanoparticles. The differences between these two preparation methods were reaction temperature and time. For B-CeO₂ nanoparticles, the reaction temperature and time were 100°C and 12 hours, respectively. The calcination conditions of B-CeO₂ nanoparticle was as follows: under the air atmosphere, the heating rate is 10°C/min, the holding time is 3 hours.

2.3 | Determination of catalytic performance

In a typical experiment, 5 mL EP tube was chosen as the reactor. A total of 1 mL of aqueous solution of OPD (80 mg/L) was poured into 1 mL of 0.4 M H₂O₂ plus 1 mL of purified water. A total of 1 mL of CeO₂ nanoparticles (1 mg/mL), which was well dispersed in purified water under ultrasonic treatment, was transferred to the tube. The mixture was incubated at 30°C for a definite time and separated by centrifugation. After centrifugation to isolate the CeO₂ nanoparticles, the supernatant was determined by UV/vis absorption and the absorbance was measured at 428 nm.

The reusability of B-CeO₂ nanoparticles was detected. The same catalytic performance assay was carried out in 15

repeated cycles. For every repetitive cycle, the nanoparticles were removed from the reaction medium by centrifugation and washed with purified water for three times.

2.4 | Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer using Cu Ka

radiation. Specific surface areas and pore size distribution were computed from the results of N₂ physisorption (Tristar 3020, Micromeritics) using the BET (Brunauer-Emmet-Teller). Fourier Transform Infrared (FTIR) spectra were acquired on a TENSOR27 FTIR spectrometer (Bruker). The morphology of the nanoparticles was observed in Scanning Electron Microscope (SEM, JEOL JSM-6700F) and Transmission Electron Microscope (TEM,

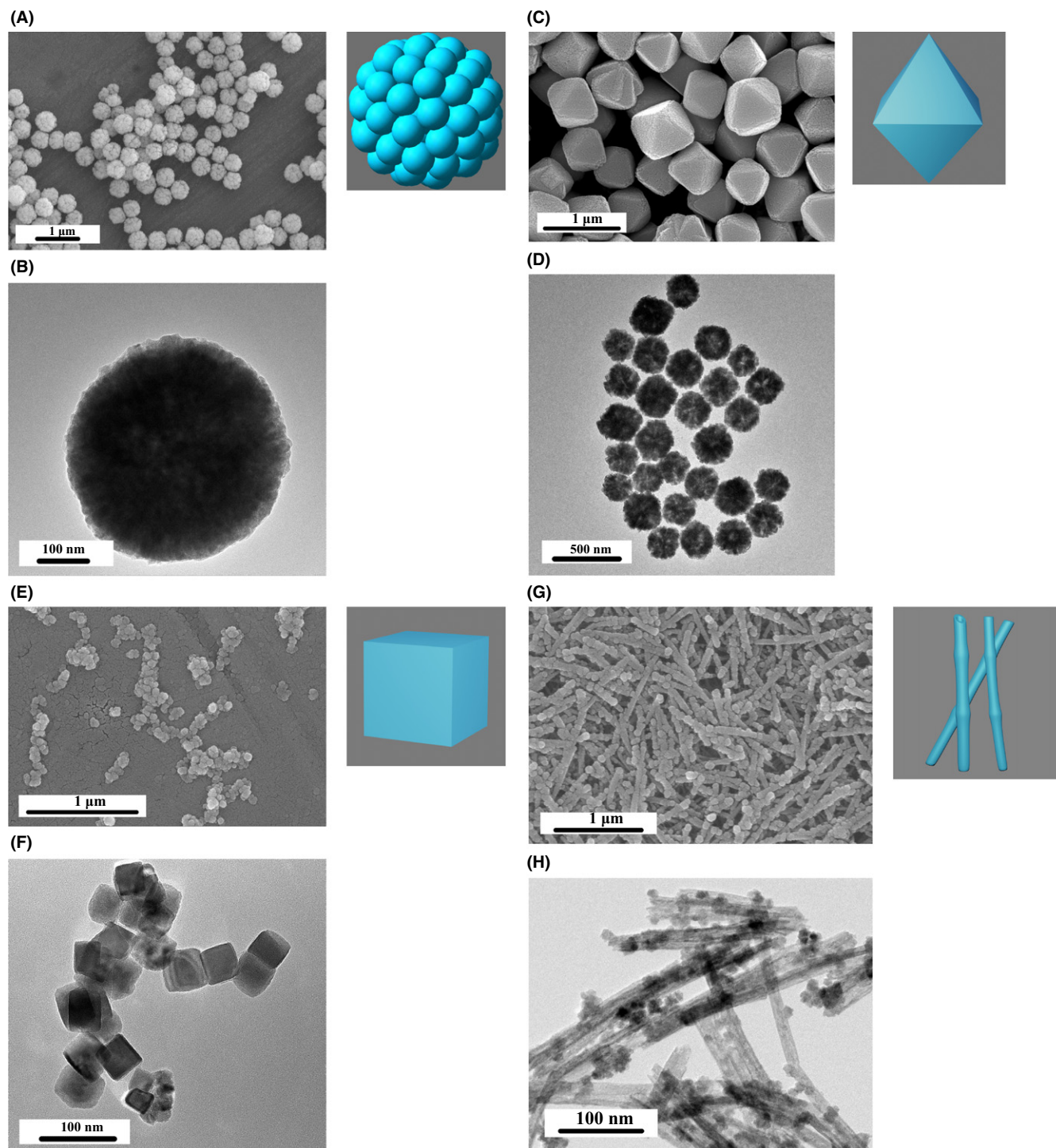


FIGURE 1 SEM and TEM images of CeO₂ nanoparticles: S-CeO₂ (A, B); O-CeO₂ (C, D); H-CeO₂ (E, F); B-CeO₂ (G, H) [Color figure can be viewed at wileyonlinelibrary.com]

JEOL JEM-3020). The concentration of dye was analyzed using a UV-vis spectrophotometer (BlueStar, LabTech). X-ray photoelectron spectroscopy (XPS) data were collected to examine the chemical states of the ceria nanoparticles with an Axis Ultra instrument (Kratos Analytical, Manchester, UK) under ultrahigh vacuum condition ($<10^{-6}$ Pa) and using a monochromatic Al K α X-ray source (1486.6 eV).

3 | RESULTS AND DISCUSSION

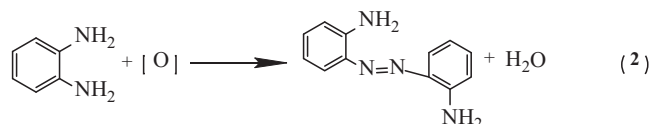
3.1 | Morphology of CeO₂ nanoparticles

Figure 1 shows the TEM and SEM images of the as-obtained CeO₂ nanoparticles. As shown in Figure 1A, S-CeO₂ nanoparticles exhibited narrow particle size distribution and spherical morphology. S-CeO₂ nanoparticles were formed by the stacking of small CeO₂ nanocrystallines, and the bulk density was low. This can be confirmed by the presence of the obvious gap on the surface of S-CeO₂ nanoparticles. The mass thickness contrast of the image was inconsistent and the particle has a granular bulge at the edge (Figure 1B). It proved that S-CeO₂ nanoparticle was not a single crystal but a solid cluster. The hydrodynamic diameter distribution was studied by dynamic light scattering (DLS), the average diameter of S-CeO₂ nanoparticles was 450 nm (Figure S1). The SEM and TEM images of O-CeO₂ nanoparticles were presented in Figure 1C and D. It clearly demonstrated that the particles were octahedron and also formed by nanocrystallines. As shown in Figure S2, the particle size distribution curve displayed that the products had a narrow size distribution and the average particle size was 480 nm. The morphology of H-CeO₂ nanoparticles was shown in Figure 1E and F. It revealed that H-CeO₂ nanoparticles exhibited single crystal structure, which could be approved by the conformable mass thickness contrast in the TEM image. The result of particle size analysis showed that the range of particle size was from 40 to 70 nm, and the average particle size was 63 nm (Figure S3). This observation was in good agreement with the TEM determination. B-CeO₂ nanoparticles with bamboo-like morphology were synthesized, as shown in Figure 1G and H. The length and diameter of the nanotube were measured to be nearly 2 μ m and 100 nm, respectively. The tubular shape contributed to increase the surface area of the nanoparticles.

3.2 | Controlling factors for catalytic activities of CeO₂ nanoparticles

Four kinds of as-obtained CeO₂ nanoparticles were used for catalytic reaction as the mimetic peroxidase. OPD and H₂O₂ were chosen as the substrates for checking the peroxidase mimic property of the catalysts. The catalytic reaction

process was as shown in chemical Equation (1) and (2). The role of CeO₂ was to catalyze the decomposition of H₂O₂ for producing reactive oxygen atom [O], which could oxidize o-Phenylenediamine (OPD).



The relation curves between absorbance of the oxidation of OPD (ox-OPD) and reaction time were shown in

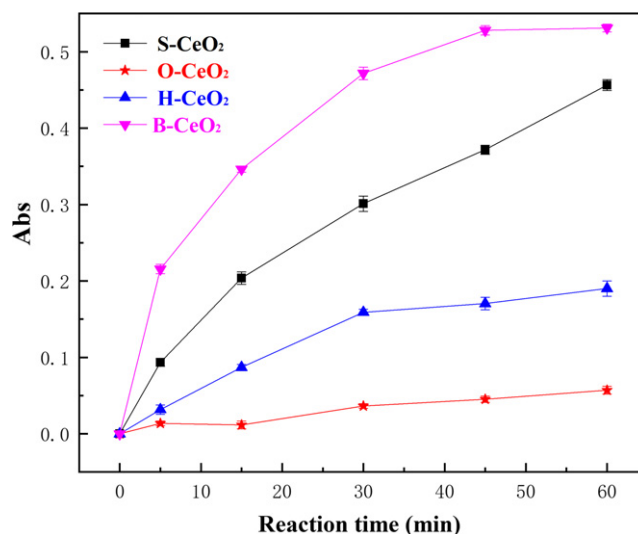


FIGURE 2 The reaction time dependence of absorbance of the products synthesized by different CeO₂ nanoparticles (error bars represent $\pm$ standard deviations, $n = 3$) [Color figure can be viewed at wileyonlinelibrary.com]

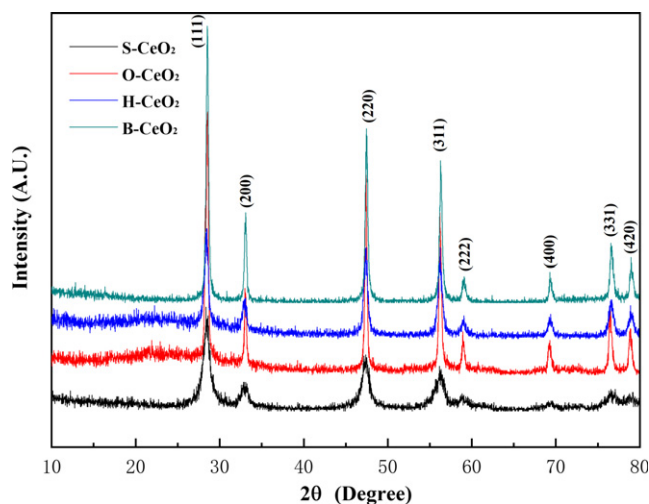


FIGURE 3 XRD pattern of the as-prepared CeO₂ nanoparticles [Color figure can be viewed at wileyonlinelibrary.com]

Figure 2. It can be seen that in descending order the catalytic activity of the mimic enzyme materials was listed as follows: B-CeO₂, S-CeO₂, H-CeO₂, O-CeO₂. Evidently, B-CeO₂ nanoparticles had the fastest catalytic reaction rate. In order to investigate and clarify the reasons for the differences in the catalytic properties, we have carried out a thorough and systematic analysis including crystallinity, the rate of surface oxygen and lattice oxygen, the specific surface area.

The X-ray diffraction (XRD) patterns of CeO₂ nanoparticles were shown in Figure 3. It could be seen that the peaks of the as-prepared four kinds of CeO₂ nanoparticles

TABLE 1 The crystallinity data of CeO₂ nanoparticles

Sample information	S-CeO ₂	O-CeO ₂	H-CeO ₂	B-CeO ₂
Crystallinity ^a	41.01%	87.85%	76.18%	58.97%

^aCrystallinity were calculated by the strongest peak in XRD, which was marked as (111) crystal face.

were almost the same. In the 2θ range of 30–80°, there were eight characteristic peaks corresponded to CeO₂ (2θ = 28.46, 33.02, 47.38, 56.26, 58.98, 69.24, 76.52, 78.96), and the peak positions could be identified as (111), (200), (220), (311), (222), (400), (331), and (420) lattice planes. The typical XRD spectrum can be indexed as that of a standard CeO₂ with fluorite structure. From the figure, the sharpness and half-peak width of the products showed slight differences. The crystallinity was calculated and the data are listed in Table 1. As seen in Table 1, high temperature and pressure condition by solvothermal method were not absolutely beneficial to crystal growth. The significant difference between crystallinity (O-CeO₂ > H-CeO₂ > B-CeO₂ > S-CeO₂) and catalytic activity suggested that the crystallinity might not be the main influence factor of catalytic activity of ceria nanoparticles.

XPS was further performed to determine the surface composition and oxidation states of the products. Figure 4 was the high-resolution spectra of O 1s of the CeO₂ nanoparticles. The peaks appearing at binding energies of

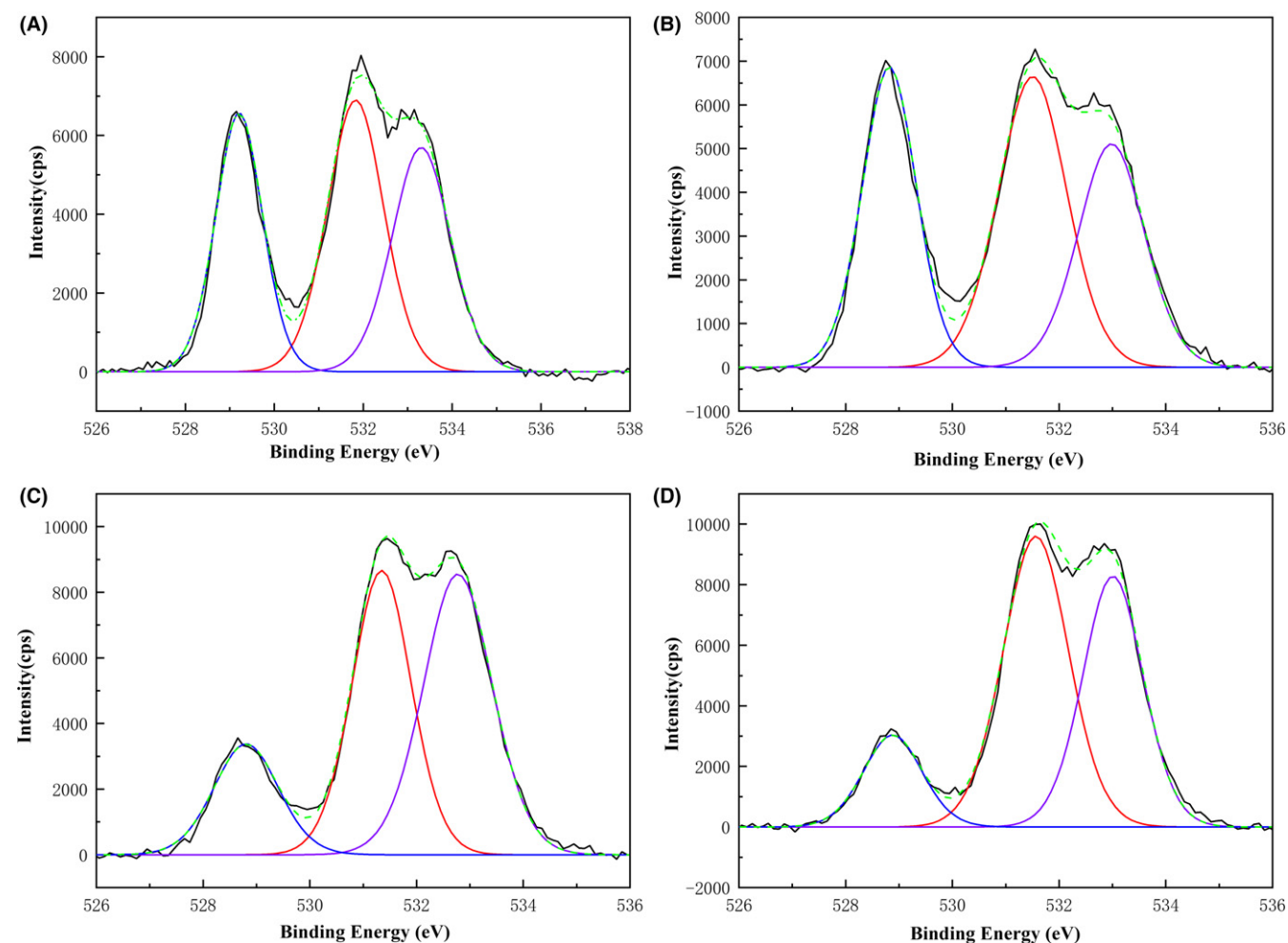


FIGURE 4 High-resolution spectra of O 1s of the as-prepared CeO₂ nanoparticles: S-CeO₂ (A); O-CeO₂ (B); H-CeO₂ (C); B-CeO₂ (D) [Color figure can be viewed at wileyonlinelibrary.com]

529.2, 531.8, and 532.8 eV demonstrated that there were three kinds of oxygen O 1s signals in CeO₂ nanoparticles. According to the references,^{38–40} the lowest binding energy peak at 529.2 eV was attributed to the lattice O (O_{lat}) in CeO₂; the middle binding energy peak at 531.8 eV was ascribed to the surface O (O_{sur}); the 532.8 eV peak was due to the hydroxyl on the surface of CeO₂. Surface oxygen content plays an important role in catalytic performance for CeO₂ materials.^{24,36} O_{sur} ratios of the four kinds of CeO₂ nanoparticles were given in Table 2. In descending order, O_{sur} content was listed as follows: B-CeO₂ > H-CeO₂ > S-CeO₂ ≈ O-CeO₂. Even though the change law of O_{sur} content was not exactly the same as catalytic activity

according to the reported and obtained results, it could be concluded that O_{sur} content should have influence on catalytic activity. The influence was further investigated in this work by fixing other influence factors.

The textural properties of the CeO₂ nanoparticles were studied by nitrogen physical adsorption/desorption measurements. The adsorption/desorption isotherms and the corresponding pore size distribution curves of the samples are shown in Figure 5. The values of BET specific surface area, pore size, and pore volume were summarized in Table 3. From the BET curves, the isotherm profiles of four samples can be categorized as type IV with small hysteresis loops observed at a relative pressure of 0.8–1.0, which indicated these materials had mesoporous and macroporous structure, as shown in Figure 5A,C,E and G. Combining TEM data, the pores were formed by particle stacking. One pore size distribution peak can be observed in the range of 20–100 nm for S-CeO₂, H-CeO₂, O-CeO₂ nanoparticles (Figure 5B,D and F). The extra peak located

TABLE 2 Calculated O_{sur} ratio of as-fabricated samples from the XPS spectrum

Sample information	S-CeO ₂	O-CeO ₂	H-CeO ₂	B-CeO ₂
$\frac{O_{sur}}{O_{sur}+O_{lat}}$	55.84%	55.15%	70.15%	77.93%

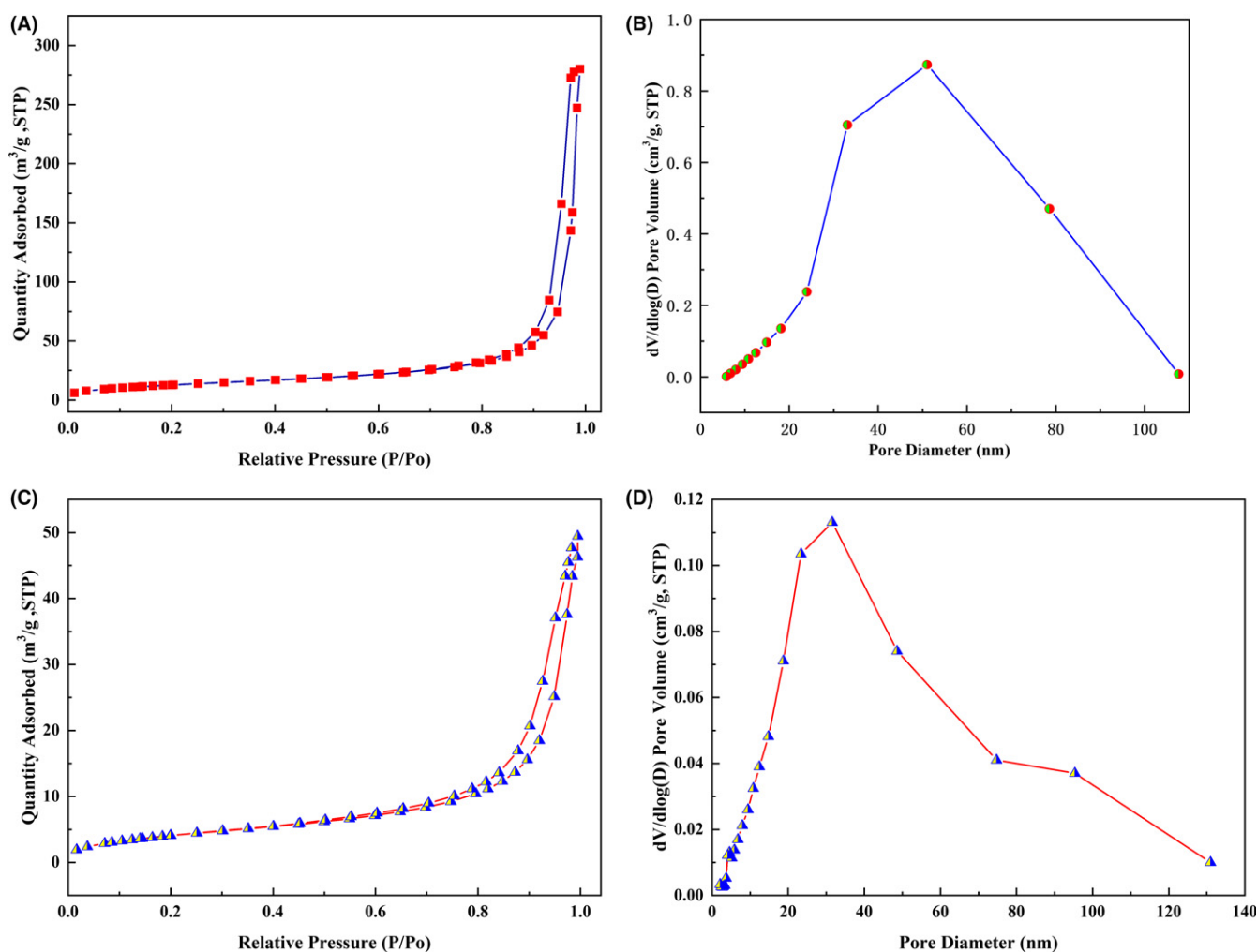


FIGURE 5 N₂ adsorption/desorption isotherms (A, C, E, G) and pore size distribution (B, D, F, H) of samples: S-CeO₂ (A, B); O-CeO₂ (C, D); H-CeO₂ (E, F); B-CeO₂ (G, H)

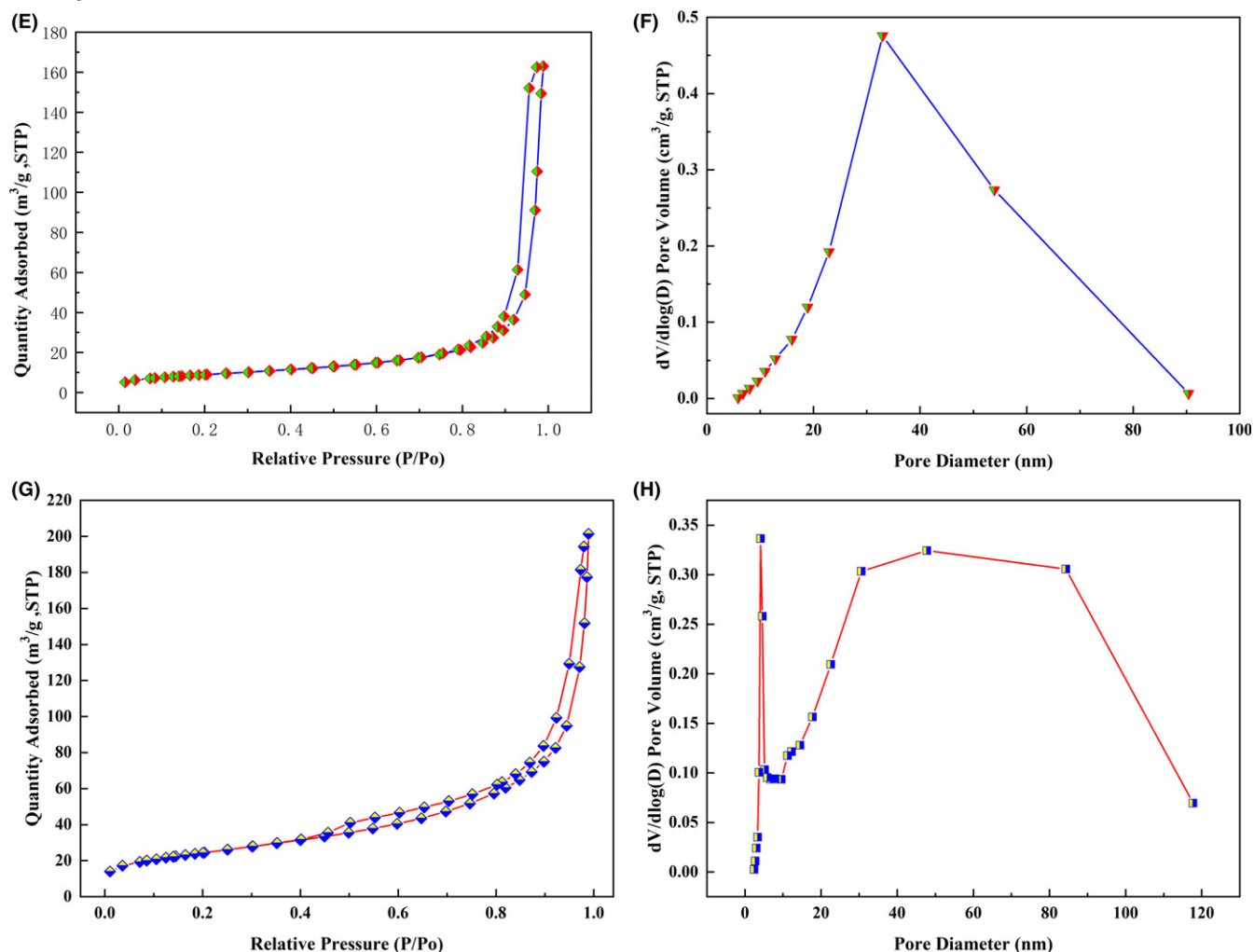


FIGURE 5 (Continued)

TABLE 3 The pore performance of the as-prepared CeO₂ nanoparticles

Sample information	S-CeO ₂	O-CeO ₂	H-CeO ₂	B-CeO ₂
Surface area (m ² /g)	48.45	15.67	32.78	88.20
Average pore size (nm)	32.44	18.73	27.27	14.50
pore volume (cm ³ /g)	0.45	0.08	0.26	0.32

at about 4.11 nm in Figure 5H was due to the tubular structure of B-CeO₂ nanoparticles, thus reflecting a large specific surface area (88.20 m²/g). In descending order, specific surface area was listed as follows: B-CeO₂ > S-CeO₂ > H-CeO₂ > O-CeO₂. As shown in the above characterization results, the specific surface area and catalytic activity of the four kinds of CeO₂ nanoparticles displayed the same change rule. Therefore, it could be concluded that specific surface area was the leading factor of catalytic activity for different CeO₂ nanoparticles. The catalytic activity increased with the increasing specific surface area.

In order to further clarify the synergistic effect of crystallinity, O_{sur} content and the specific surface area, the

following experiments were carried out. B-CeO₂ nanoparticles were calcined under oxygen atmosphere. The intrinsic properties and catalytic performances of the calcined products were studied systematically. The characterization data were listed in Table 4. With the increasing calcination temperature, the crystallinity gradually became better, but the O_{sur} content decreased, the specific surface area, average pore size, and pore volume had no significant change. Compared with the XRD spectrum of uncalcined B-CeO₂ nanoparticles (Figure 3), the peaks of the product calcined at 700°C did not show obvious change (Figure S4), which illustrated the product was still cerium oxide with fluorite structure. Figure S5 showed the high-resolution spectra of O 1s of the B-CeO₂ nanoparticles calcined at different temperature. It can be found that the peak intensity at 532.8 eV became weaker with the increasing calcination temperature, indicating that the oxygen in the form of hydroxyl decreased. The pore performance of B-CeO₂ nanoparticles were not affected by calcination, which can be confirmed by the results of nitrogen adsorption analysis of the products calcined at 300 and 700°C, which are shown in

TABLE 4 Calculated O_{sur} content and pore performance of B-CeO₂ nanoparticles calcined at different temperature^a

Calcination temperature (°C)	Uncalcined sample	300	400	500	600	700
Crystallinity ^b	58.97%	59.62%	60.01%	63.35%	64.71%	65.58%
$\frac{O_{\text{sur}}}{O_{\text{sur}}+O_{\text{lat}}}$	77.93%	72.74%	64.00%	63.25%	61.19%	58.84%
Surface area (m ² /g)	88.20	86.33	89.08	87.59	85.62	87.38
Average pore size (nm)	14.50	15.63	13.98	14.22	14.87	15.16
Pore volume (cm ³ /g)	0.32	0.33	0.31	0.32	0.31	0.32

^aThe heating rate of calcination was 10°C/min and the holding time was 3 hours.

^bCrystallinity were calculated by the strongest peak in XRD, which was marked as (1111) crystal face.

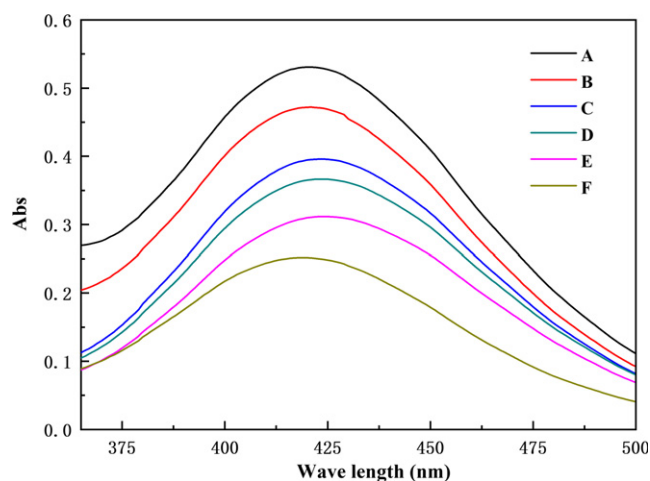
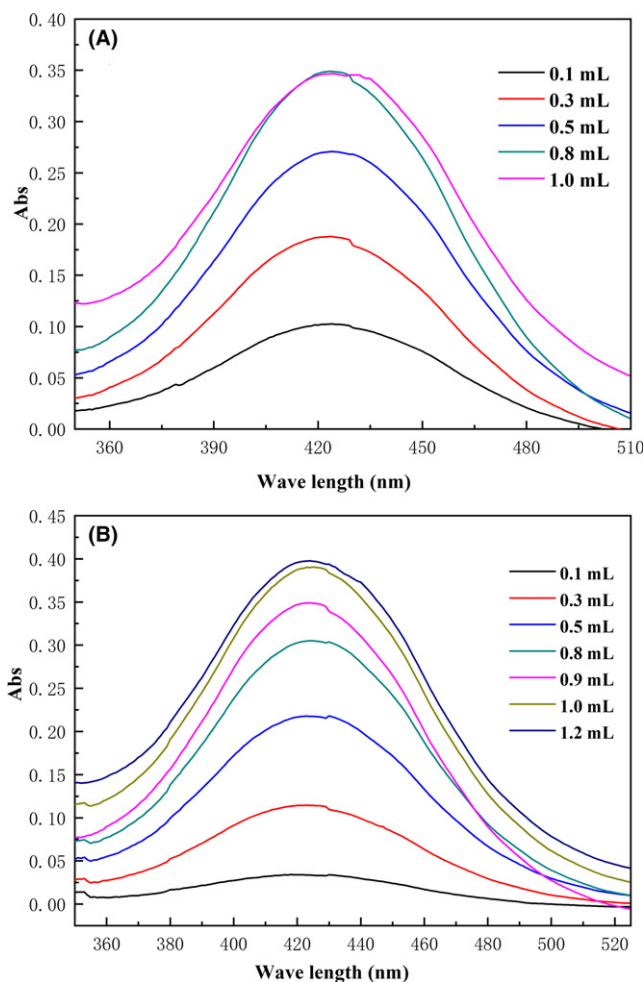
**FIGURE 6** The influence of calcination temperature on the catalyst performance: Uncalcined (A); 300°C (B); 400°C (C); 500°C (D); 600°C (E); 700°C (F). (The reaction time was 45 minutes)

Figure S6. When the calcination temperature increased to 700°C, B-CeO₂ nanoparticles still maintained their excellent pore performance. Figure S7 shows SEM images of B-CeO₂ nanoparticles calcined at different temperature, and TEM image of B-CeO₂ nanoparticles calcined at 700°C. The nanoparticles remained their bamboo-like morphology. The catalytic property of the calcined B-CeO₂ nanoparticles was investigated, results are shown in Figure 6. It was clear to see that the catalytic activity of the nanoparticles decreased with the increase in calcination temperature. These findings indicated that for the same material with similar specific surface area, the less O_{sur} of the ceria nanoparticles contained, the lower catalytic activity would be. Meanwhile, crystallinity was not the influence factor of catalytic activity.

3.3 | Catalytic performance of B-CeO₂ nanoparticles

As the more efficient catalyst, the catalytic performance of B-CeO₂ nanoparticles was further investigated. The main factors influencing the catalytic efficiency including the dosage of H₂O₂ and B-CeO₂ nanoparticles were studied

**FIGURE 7** The influence of additional amount of H₂O₂ (A) and B-CeO₂ nanoparticles (B) on the catalyst performance (The reaction time was 15 minutes)

and optimized, the results are shown in Figure 7. It can be seen that the absorbance value kept invariant as the dosage of H₂O₂ was more than 0.8 mL (Figure 7A). Before reaching this amount, the quantity of the products increased with the increasing addition amount of H₂O₂. As shown in Figure 7B, the absorbance of ox-OPD increased drastically as the dosage of B-CeO₂ nanoparticles was less than 0.8 mg, then a slow and gradual increase was observed until the

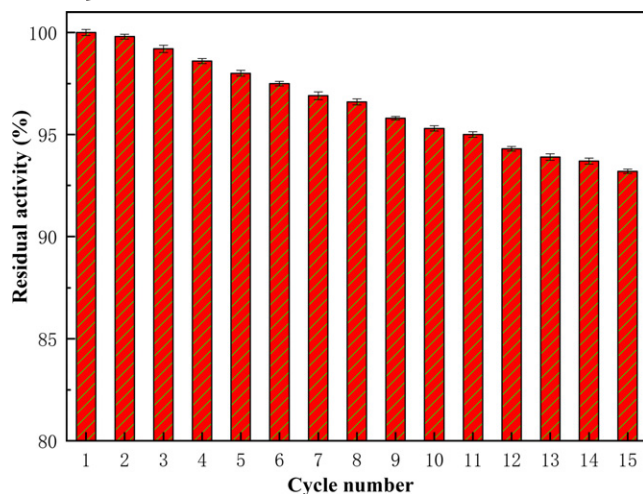


FIGURE 8 Reusability of B-CeO₂ nanoparticles as catalase mimic (error bars represent standard deviations, $n = 3$)

dosage reached 1.0 mg. Therefore, the optimal addition amount of H₂O₂ and B-CeO₂ nanoparticles were confirmed to be 0.8 mL and 1.0 mg, respectively.

The reusability of B-CeO₂ nanoparticles was investigated after fifteen cycles. As shown in Figure 8, the residual activity after the fifteenth cycle changed slightly. The activity retention rate was 93.2%. This result indicated that the B-CeO₂ nanoparticles, which were used as mimetic peroxidase, could be used repeatedly many times with high catalytic activity.

4 | CONCLUSION

In conclusion, four shaped CeO₂ nanoparticles are prepared by hydrothermal methods. The nanoparticles with different nanostructures such as sphere, octahedron, hexahedron, and bamboo-like have been demonstrated as enzyme mimics that possess peroxidase-like activity. Particularly, the reaction conditions of B-CeO₂ nanoparticles as the best catalyst are investigated. On the basis of the characterization and comparison of as-obtained CeO₂ nanoparticles, it is found that the main influencing factors on the catalytic activity are specific surface area and O_{sur} content. At the same time, the influence rules have been clarified. B-CeO₂ nanoparticle exhibits excellent catalytic activity and reusability, indicating its potential application in industry. Similar studies on other enzyme mimicking nanomaterials will be expected, just like Fe₃O₄ and Co₃O₄ nanoparticles. It is helpful to confirm the universality of the conclusion and develop high effective nanoparticle-based enzyme mimetics.

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ORCID

Baoliang Zhang  <http://orcid.org/0000-0002-0290-4949>

Hepeng Zhang  <http://orcid.org/0000-0003-0919-1221>

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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