A peroxidase catalyzes the oxidation of a substrate with a peroxide. The search for peroxidase-like and other enzyme-like nanomaterials (called nanozymes) mainly relies on trial-and-error strategies, due to the lack of predictive descriptors. To fill this gap, here we investigate the occupancy of \( e_g \) orbitals as a possible descriptor for the peroxidase-like activity of transition metal oxide (including perovskite oxide) nanozymes. Both experimental measurements and density functional theory calculations reveal a volcano relationship between the \( e_g \) occupancy and nanozymes’ activity, with the highest peroxidase-like activities corresponding to \( e_g \) occupancies of ~1.2. \( \text{LaNiO}_3 \) optimized based on the \( e_g \) occupancy, exhibits an activity one to two orders of magnitude higher than that of other representative peroxidase-like nanozymes. This study shows that the \( e_g \) occupancy is a predictive descriptor to guide the design of peroxidase-like nanozymes; in addition, it provides detailed insight into the catalytic mechanism of peroxidase-like nanozymes.
Artificial enzymes aim to imitate the unique catalytic activities of natural enzymes using alternative materials. Recently, functional nanomaterials with enzyme-like catalytic activities, called nanozymes, have emerged as promising alternatives that could overcome the low stability and high cost of natural enzymes\textsuperscript{1-13}. Intriguingly, nanozymes are superior to molecular and polymeric enzyme mimics in several ways, such as the role of oxygen species in these biomimetic catalytic reactions. We focus on the peroxidase-like activity of perovskite TMOs because of the central structural characteristics of the nanomaterials that can be used as empirical approaches is due to the lack of predictive descriptors devoted to developing nanomaterials with peroxidase-like activity\textsuperscript{14}. For example, Yan and colleagues\textsuperscript{1, 2, 19} discovered the unexpected peroxidase-like activity of iron oxide nanoparticles, which were then applied to Ebola detection and tumor immunostaining. We have recently developed Ni oxide-based peroxidase mimics for glucose detection in serum\textsuperscript{20}. However, these peroxidase-like nanozymes are generally developed using trial-and-error strategies\textsuperscript{11}. The prevalence of empirical approaches is due to the lack of predictive descriptors—structural characteristics of the nanomaterials that can be used as proxies for their peroxidase-like activities. This lack of predictive descriptors significantly hampers the identification of more active nanozymes.

Recently, several studies have demonstrated that for electrocatalysis and photocatalysis, the band-center of metals, O 2\textsuperscript{g} antibonding orbitals (\(\sigma^*\)) play a crucial role in the peroxidase-like activity of La\textsubscript{1-x}Sr\textsubscript{x}FeO\textsubscript{3} (Fig. 1b and Supplementary Fig. 7a)\textsuperscript{21}. The dependence of the oxidation state of Fe from +3 in LaFeO\textsubscript{3} to +2.5 in SrFeO\textsubscript{2.5} on the Sr content of La\textsubscript{1-x}Sr\textsubscript{x}FeO\textsubscript{3} was confirmed by matching their PXRD data to the standard pattern of LaFeO\textsubscript{3} (JCPDS card number 75-0541) (Fig. 1d).

The peroxidase-like activity of the perovskite-based nanozymes was assessed by using absorption spectroscopy to monitor the catalytic oxidation of 3,3′-tetramethylbenzidine (TMB, a typical peroxidase substrate) with H\textsubscript{2}O\textsubscript{2} in the presence of the nanozymes. The oxidation of TMB generates an oxidized product (\(\delta\text{H}_{2}\text{O}_{2}\)) with a characteristic absorption peak at 652 nm. The intensity of this absorption peak (\(\epsilon_{652}\)) increased with increasing Sr content and the highest absorption was obtained for SrFeO\textsubscript{2.5} (Fig. 1e). The time evolution of the \(\epsilon_{652}\) value (Fig. 1f) shows that SrFeO\textsubscript{2.5} also exhibited the fastest reaction kinetics, demonstrating that the Sr substitution effectively enhanced the peroxidase-like activity of La\textsubscript{1-x}Sr\textsubscript{x}FeO\textsubscript{3.5}. The mass-based peroxidase-like activities of nanozymes were measured by steady-state kinetics assays (see Methods section). To separate the effect of surface area from the intrinsic peroxidase-like activity of perovskites (including the Fe-based perovskites discussed in this section), their specific activity (i.e., the mass activity normalized to the surface area) was also calculated, based on the BET surface areas obtained by nitrogen desorption measurements (Supplementary Figs 3 and 6, and Supplementary Table 1). As shown in Fig. 1g, the specific activity of SrFeO\textsubscript{2.5} was 7.76 and 1.79 times higher than that of LaFeO\textsubscript{3} and La\textsubscript{0.5}Sr\textsubscript{0.5}FeO\textsubscript{3.5}, respectively. The dependence of the specific activity on the Sr content of La\textsubscript{1-x}Sr\textsubscript{x}FeO\textsubscript{3.5} and the \(\epsilon_{652}\) occupancy of Fe is plotted in Fig. 1h. A substantial improvement in the peroxidase-like activity of La\textsubscript{1-x}Sr\textsubscript{x}FeO\textsubscript{3.5} was observed as the Sr content increased from 0 to 1 and the \(\epsilon_{652}\) occupancy of Fe decreased from 2 to 1.69.

To study the effect of the \(\epsilon_{652}\) occupancy lower than 1 on the peroxidase-like activity of perovskites, we investigated three Mn-based perovskites with the \(\epsilon_{652}\) occupancy of Mn varying from 0.68 to ~0.08 (i.e., \(\epsilon_{652} = 0.68, 0.53, 0.08\) for LaMnO\textsubscript{3.5}, La\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3.5}, and CaMnO\textsubscript{3.5}, respectively). The TEM and SEM images shown in Supplementary Figs 4 and 5, and the PXRD patterns in Supplementary Fig. 7a demonstrate the successful synthesis of the Mn-based perovskites. As shown in Supplementary Fig. 7c, the specific activity of LaMnO\textsubscript{3.5} was 1.42 and 43.29 times higher than that of La\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3.5} and CaMnO\textsubscript{3.5}, respectively. Supplementary Fig. 7e shows the effect of the \(\epsilon_{652}\) occupancy on the specific peroxidase-like activity of the Mn-based perovskites. Different from the trend observed for the Fe-based perovskites (i.e., the peroxidase-like activity increased as the \(\epsilon_{652}\) occupancy decreased), the catalytic activity of the Mn-based perovskites decreased as the \(\epsilon_{652}\) occupancy further decreased from 0.68 to ~0.08. Taken together, the above
results show a strong but non-monotonic correlation between $e_g$ occupancy and peroxidase-like activity of perovskites, suggesting the $e_g$ occupancy as a potential activity descriptor.

**Evaluation of $e_g$ occupancy as nanzyme activity descriptor.** To further evaluate the correlation between the $e_g$ occupancy and their peroxidase-like activity, overall ten perovskite TMOs covering $e_g$ occupancies of 0–2, six as described above and four others (i.e., LaCrO$_3$, LaCoO$_3$, LaNiO$_3$, and LaMn$_{0.5}$Ni$_{0.5}$O$_3$) were investigated (Supplementary Figs 8–14, Supplementary Table 6, and Supplementary Notes 1–2). As shown in the summary in Fig. 2a, the perovskite TMOs exhibited significantly different specific peroxidase-like activities. Some of them (such as LaNiO$_3$) exhibited a high activity, whereas the activity of others (such as LaCrO$_3$) was negligible. This behavior can be understood by plotting the activities of the ten perovskite TMOs as a function of the corresponding $e_g$ occupancy associated with the B cations: a definitive volcano relationship is obtained (Fig. 2b). The mass-based peroxidase-like activities (i.e., mass activities) of the perovskite TMOs also show a volcano dependence on the corresponding $e_g$ occupancies (Supplementary Fig. 15), confirming that the catalytic activity of the perovskite TMO-based peroxidase mimics is primarily governed by the $e_g$ occupancy of the B cations. In particular, perovskite TMOs with $e_g$ occupancy of ~1.2 exhibit the highest peroxidase-like activity (Fig. 2).

**Evaluation of other parameters as potential descriptors.** As several other potential descriptors (i.e., oxidation state of transition metal, 3$d$ electron number of B-site ions, O 2$p$-band center, and B–O covalency) have been studied to predict the electrocatalytic and photocatalytic activities of perovskites, we also investigated the relationship between the peroxidase-like activity
and these parameters. As shown in Supplementary Fig. 16, although the oxidation state of B sites affects the peroxidase-like activity of perovskites, there is no apparent relationship between them. These results indicated that the oxidation state of B sites is not an effective descriptor and cannot provide guidance for the rational design of peroxidase-like nanozymes. We then studied the relationship between the peroxidase-like activity and the 3d electron number of B-site ions. As shown in Supplementary Fig. 17, an “M-shaped” relationship with the maximum peroxidase-like activities around $d^4$ and $d^7$ was obtained. Clearly, although the 3d electron number is indicative, it is not a straightforward descriptor, as two maxima are associated with it.

Several recent studies suggested that the $O_2$ dissociation from $O$ K-edge X-ray absorption spectra could be a better activity descriptor than the $e_g$ occupancy to design catalysts for oxygen reduction reaction and oxygen evolution reaction

$$\rightarrow$$

there is no apparent relationship between the B-O covalency and the peroxidase-like activity of the six representative perovskites.

Interestingly, for the perovskites with $e_g$ occupancy close to 1 (i.e., LaMnO$_3$, LaCoO$_3$, and LaNiO$_3$), their peroxidase-like activity increases with the increasing of covalency strength of B-O. These results suggested that the B-O covalency may act as a secondary descriptor for peroxidase-like activity when the $e_g$ occupancy of B-site is close to 1 (Supplementary Note 3).

In short, in contrast to the $e_g$ occupancy, none of the four parameters discussed in this section showed a volcano relationship with the peroxidase-like activity of perovskites. These results further validated that the $e_g$ occupancy as an effective activity descriptor to predict the peroxidase-like activity of perovskites.

**DFT calculations.** To theoretically explain the effect of $e_g$ occupancy on the peroxidase-like activity, we performed DFT calculations for 11 ABO$_3$ perovskites (i.e., LaCrO$_3$, CaMnO$_3$, La$_{0.5}$Sr$_{0.5}$MnO$_3$, LaMnO$_3$, LaCoO$_3$, LaNiO$_3$, SrFeO$_3$, LaMn$_{0.5}$Ni$_{0.5}$O$_3$, La$_{0.5}$Sr$_{0.5}$FeO$_{2.75}$, LaFeO$_3$, and La$_{0.5}$Sr$_{0.5}$FeO$_3$) and proposed molecular mechanisms for the activities. The calculated geometric parameters and $e_g$ occupancy values for these bulk structures generally agreed with the experimental ones (Supplementary Table 9 and Supplementary Figs 20–22).

We proposed that these perovskites mimicked peroxidases via mechanisms of Fig. 3a: (1) the adsorption (I) and dissociation (II) of $H_2O_2$ molecules on ABO$_3$ surfaces to generate the OH adsorption
species; (2) the conversion of these OH adsorption species to O adsorption species, which subsequently oxidize TMB substrates (IIa and IV); (3) or alternatively, the direct oxidation of TMB by the OH adsorption species (IIib). Perovskite ABO$_3$ (001) surfaces with the BO$_2$ termination were selected as the surfaces of reactions, because transition metal B in these surfaces are all five coordinated and each has one open coordination site. The five coordinated BO$_2$ termination is analogous to metalloporphyrins, the active centers of many natural enzymes. The adsorption of H$_2$O$_2$ on perovskite (001) surfaces has no energy barriers (Supplementary Fig. 23), suggesting step 1 does not determine the overall reaction rate. The variations of adsorption energies (E$_{ads}$) for O (E$_{ads,O}$) and OH (E$_{ads,OH}$) with respect to $e_g$ occupancy are shown in Fig. 3b, c, and that for H$_2$O$_2$ (E$_{ads, H_2O_2}$) in Supplementary Fig. 24. Volcano-like relationships were found for E$_{ads,O}$ and E$_{ads,OH}$ with $e_g$ occupancy (Fig. 3b and c and Supplementary Fig. 24). Further analysis shows that the five perovskites with $e_g$ occupancy < 1.2 (i.e., LaCrO$_3$, CaMnO$_3$, La$_{0.5}$Sr$_{0.5}$Mn$_2$O$_{4.5}$, La$_{0.5}$Sr$_{0.5}$FeO$_{3.5}$, and LaNiO$_3$) have strong OH$^*$ and O$^*$ adsorption energies. The other five perovskites with $e_g$ occupancy > 1.2 (i.e., LaMn$_{0.5}$Ni$_{0.5}$O$_3$, SrFeO$_3$, La$_{0.5}$Sr$_{0.5}$Fe$_{2.5}$O$_6$, La$_{0.5}$Sr$_{0.5}$Fe$_{2.5}$O$_6$, and Fe$_2$O$_3$) as well as LaNiO$_3$ have weak OH$^*$ and O$^*$ adsorption energies. Perovskites with $e_g$ occupancy of ≈ 1.2 have the weakest O and OH adsorption, in which the transfer of these oxygen species to TMB substrates is the easiest, in agreement with their highest peroxidase-mimicking activities. However, LaFeO$_3$ with negligible peroxidase-like activity also possesses weak O and OH adsorption. Therefore, we reasoned that the oxidation of the substrate (i.e., IIb and IV of Fig. 3a) is not the only rate-determining step. Reportedly, when a kinetic profile goes through a maximum as a function of a given parameter, it means that there is a change of the rate-determining step governing the reaction mechanism$^{32}$. To identify all the rate-determining steps and to validate the mechanisms of Fig. 3a, we further calculated the energies for species involved in the proposed reaction pathways (Supplementary Figs 23–25). Supplementary Fig. 25 plots the energies of species involved in the proposed reaction pathways. It reveals that for the five perovskites with $e_g$ occupancy < 1.2, which are all located on the left side of Fig. 2b’s volcano-like plots, the rate-determining step should be the oxidation of the substrate (i.e., IIb and IV of Fig. 3a); for the other five with $e_g$ occupancy > 1.2, which are all located on the right side of the volcano-like plots, the rate-determining step should be the O–O bond splitting of the adsorbed H$_2$O$_2^*$ (II of Fig. 3a); LaNiO$_3$ is the maximum point where the rate-determining step changes. Taking these results together, $e_g$ occupancy influences the peroxidase-mimicking activities of perovskites by altering the E$_{ads}$ of reaction intermediates and the rate-determining step governing the catalytic reactions. Perovskites with $e_g$ occupancy of ≈ 1.2 possess optimal E$_{ads}$ and can facilitate these rate-determining steps efficiently, which further lead to the high peroxidase-like activity.

**General applicability of the $e_g$ occupancy.** To test whether $e_g$ occupancy could also predict the activity of non-perovskite TMOs with the same metal-oxygen octahedral coordination geometry as the perovskites described above, we investigated the peroxidase-like activity of five binary metal oxide nanoparticles (Supplementary Figs 26–28, Supplementary Table 7, and Supplementary Note 4). First, to determine the predictive power of the descriptor, CoO and Mn$_2$O$_3$-$\delta$ nanoparticles with unit $e_g$ occupancy were tested, as their peroxidase-like activities are unknown. If the $e_g$ occupancy descriptor was also applicable to the binary metal oxides, these nanoparticles would be expected to exhibit high peroxidase-like activities. As shown in Supplementary Figs 29, 30a and Fig. 4a, both nanoparticles exhibited excellent activities, in agreement with the prediction based on the $e_g$ occupancy descriptor. By contrast, the measured peroxidase-like activities of MnO$_2$ ($e_g$ = 0), Fe$_2$O$_3$ ($e_g$ = 2), and NiO ($e_g$ = 2) nanoparticles were nearly negligible (Supplementary Fig. 29 and Fig. 4a), again in agreement with the prediction. These results clearly demonstrate that the peroxidase-like activity of binary metal oxides with octahedral coordination geometry is similarly associated with the $e_g$ occupancy, with a similar volcano dependence to that obtained for the perovskite TMO-based peroxidase mimics (Supplementary Fig. 30b and Fig. 4b).

**Comparison with other peroxidase mimics.** Among the 16 TMOs studied in this work (Figs 2, 4 and Supplementary Fig. 10), LaNiO$_{1.8}$ was identified as the most active peroxidase mimic, in terms of both specific and mass activities (Supplementary Note 5). Over the last decade, dozens of nanomaterials have been proposed as peroxidase mimics$^{41}$. A comparison between the nanozymes developed in this work and those reported in the literature may be useful for searching for new nanozymes. However, a direct comparison between data produced by different studies is difficult, because the applied protocols or even the specific test conditions, such as temperature and H$_2$O$_2$ concentration, could significantly influence the peroxidase-like activity of the nanomaterials. To allow for a reliable and rigorous comparison, we synthesized several peroxidase mimics reported in previous studies (Fig. 5, Supplementary Methods, Supplementary Figs 26–28, 31–32, and Supplementary Table 5).

![Figure 4](https://example.com/fig4.png)  
**Fig. 4** Binary TMOs as peroxidase mimics. **a** Specific peroxidase-like activities of MnO$_2$, CoO, Mn$_2$O$_3$-$\delta$, NiO, and Fe$_2$O$_3$. **b** Specific peroxidase-like activities of the binary metal oxides as a function of $e_g$ occupancy. The two lines are shown for eye-guiding only. Source data are provided as a Source Data file.
and compared their peroxidase-like activities with that of LaNiO$_{3-\delta}$ under the same conditions. Fe$_3$O$_4$ nanoparticles and Cu(OH)$_2$ supercages were chosen as representative peroxidase mimics for comparison: Fe$_3$O$_4$ nanoparticles were the first reported peroxidase mimics, whereas Cu(OH)$_2$ supercages are the state-of-the-art representatives of these systems, with $K_{cat}$ (catalytic constant) values comparable to those of natural peroxidase$^{1, 42}$. Fig. 5a,b confirm the successful preparation of Fe$_3$O$_4$ nanoparticles and Cu(OH)$_2$ supercages. The time evolution of the $A_{652}$ parameter (Supplementary Fig. 33 and Fig. 5c) shows that the mass activity of LaNiO$_{3-\delta}$ is 28.9 and 13.6 times higher than that of the Fe$_3$O$_4$ nanoparticles and Cu(OH)$_2$ supercages, respectively. Moreover, Fig. 5d shows that the specific activity of LaNiO$_{3-\delta}$ was 91.4 and 49.0 times higher than that of the Fe$_3$O$_4$ nanoparticles and Cu(OH)$_2$ supercages, respectively, because of the smaller surface area of the LaNiO$_{3-\delta}$ nanoparticles prepared by the sol-gel method. Other representative nanozymes (such as CeO$_2$, CuO, single-walled carbon nanotubes, and graphene oxide (GO-COOH)) were also investigated. The results in Fig. 5c,d confirm the superior performance of LaNiO$_{3-\delta}$ in terms of both specific and mass activity, further demonstrating the power of the $\varepsilon_g$ occupancy descriptor for identifying nanozymes of particularly high activity.

**Discussion**

Using experimental measurements and DFT calculations, we have identified the $\varepsilon_g$ occupancy as a predictive and effective descriptor for the peroxidase-like activity of TMO (including perovskite TMO) nanomaterials. The catalytic activity of peroxidase-like nanozymes with metal-oxygen octahedral coordination geometry shows a volcano dependence on the $\varepsilon_g$ occupancy. Namely, nanozymes with $\varepsilon_g$ occupancies of $\sim$1.2 had the highest catalytic activity, whereas $\varepsilon_g$ occupancies of 0 or 2 corresponded to negligible activities. The systematic comparison of more than 20 representative peroxidase-like nanozymes revealed that LaNiO$_{3-\delta}$ had the highest catalytic activity. Besides supporting an approach to the design of highly active peroxidase mimics based on the $\varepsilon_g$ occupancy, the present study also provided deep insight into the catalytic mechanism of the peroxidase-like activity of the nanozymes. Taking into account the adaptable structures and catalytic activities of TMO-based nanozymes, the current study has prompted us to further explore the application of the $\varepsilon_g$ occupancy descriptor to predict the enzyme-like activities of other metal oxides.

**Methods**

**Synthesis of perovskite TMOs.** The perovskite TMOs were synthesized via a sol-gel method$^{36}$. Briefly, the respective metal nitrate salts in appropriate stoichiometric ratios (3 mmol in total) and citric acid (12 mmol) were dissolved in 100 mL of H$_2$O, followed by the addition of 1.5 mL of ethylene glycol. The resulting transparent solutions were treated at 90 °C under stirring to condense them into gel, which were then decomposed at 180 °C for 5 h to form the solid precursors. The latter were decomposed at 400 °C for 2 h to remove the organic components and obtain foam precursors, which were further annealed at 700 °C (850 °C in the case of CaMnO$_3$) for 5 h with a ramp rate of 5 °C min$^{-1}$ to obtain the final perovskite TMOs.

**Structure characterization.** PXRD data were collected at room temperature using a Rigaku Ultima diffractometer using Cu Ka radiation. The diffractometer was operated at 40 kV and 40 mA, with a scan rate of 5° min$^{-1}$ and a step size of 0.02°. TEM images were recorded on a JEOL JEM-2100 or FEI Tecnai F20 microscope at an acceleration voltage of 200 kV. SEM measurements were performed on a Hitachi S-4800 microscope operated at 5 kV. UV-visible absorption spectra were collected using a spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co. Ltd, China). Nitrogen adsorption–desorption isotherms were measured at 77 K using a Quantachrome Autosorb-IQ-2C-TCD-VP analyzer and were used to calculate the surface areas of the nanozymes with the BET method. The temperature-dependent magnetization was measured on a MPMS SQUID magnetometer (MPMS-3, Quantum Design) with a magnetic field of $H = 1$ kOe under field-cooling procedures. O K-edge X-ray absorption spectroscopy (XAS) measurements were performed at the beamline BL12B-a (CMD) in Hefei Synchrotron Radiation Facility, National Synchrotron Radiation Laboratory.

**Peroxidase-like activity measurements.** Steady-state kinetics assays were conducted at 37 °C in 1.0 mL cuvettes with a path length of 0.2 cm. A 0.2 M NaOAc buffer (pH 7.0) was used as the reaction solution. The reaction was initiated by the addition of 0.1 mL of H$_2$O$_2$. The reaction was monitored at 210 nm using a UV-visible spectrophotometer at an interval of 10 s. The kinetic data were fitted to a single first-order reaction model $\frac{d[A]}{dt} = -k[A]$, and the specific activity $k_{cat}$ was determined as the slope of the linear curve. The catalytic constant $K_{cat}$ was calculated using the equation $k_{cat} = \frac{V}{[S]}$, where $V$ is the initial rate of the reaction and $[S]$ is the substrate concentration.
buffer solution (pH 4.5) was used as the reaction buffer and 10 µg mL⁻¹ of nanozymes were used for their kinetics assays. The kinetics data were obtained by varying the concentration of H₂O₂ while keeping the TMB’s concentration constant (Supplementary Table 8). The kinetics constants (i.e., vₘₐₓ and Kₘₑₐₙ) were calculated by fitting the reaction velocity values and the substrate concentrations to the Michaelis–Menten equation as follows:

\[
v = \frac{v_{\text{max}} \times [S]}{K_m + [S]} \tag{1}
\]

where \(v\) is the initial reaction velocity and \(v_{\text{max}}\), is maximal reaction velocity; \([S]\) is obtained under saturating substrate conditions. \(K_m\) is the substrate concentration. \(K_m\) is the Michaelis constant, equal to the concentration of substrate when the initial reaction velocity reaches half of its maximal reaction rate. As for TMOs with negligible activity (i.e., LaCrO₃, LaFeO₃, CaMnO₃-δ, NiO, MnO₂, and Mn₃O₄) we assumed the initial reaction velocity in the presence of 10 µmol L⁻¹ of nanozymes, 1 mM TMB, and 100 mM H₂O₂ as the \(v_{\text{max}}\), because the kinetics measurements for them were difficult and not reliable.

The mass activities of the nanozymes were defined as follows:

\[
\text{Mass activity} = \frac{v_{\text{max}}}{\text{BET area}} \tag{2}
\]

The specific activities of the nanozymes were calculated from Eqs (3) and (4):

\[
\text{Specific activity} = \frac{\text{Mass activity}}{\text{Normalized BET area}} \tag{3}
\]

\[
\text{Normalized BET area} = \frac{\text{BET area of nanozyme}}{\text{BET area of LaNiO₃-d}} \tag{4}
\]

**DFT calculations.**

The bulk structure of each defect-free perovskite was modeled using the \(A_{2}B_{2}O_{7}\) unit cell, which was sufficiently large to contain all possible G-type antiferromagnetic (G- AFM), A-type antiferromagnetic (A-AFM), and paramagnetic (PM) magnetic orderings previously reported for perovskites (Supplementary Fig. 20). Geometrically relaxed ground-state bulk structures were then used to build the \((001)\) slabs, each of which contained six layers: three AO and three BO₂ (Supplementary Fig. 21). For geometry optimizations of the bottom two layers (i.e., one AO and one BO₂) were frozen and those in the above layers were allowed to move; lattice parameters were frozen for calculations with slab models. The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional was used for geometry optimizations and energy calculations, in a plane-wave basis set with an energy cut-off of 500 eV and 5 eV for core–valence and valence–valence interactions, respectively. All calculations were performed using the VASP code. More details of the computations can be found in Supplementary Note 6.

**Data availability**

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

H.W. and X.W. designed the experiments. X.W. prepared the catalysts, performed the structural characterization, steady-state kinetics measurements, and analyzed the data. X.I.G. and X.G. conducted the DFT calculations and analyzed the DFT data. L.Q. assisted with catalysts preparation, structural characterization, and peroxidase-like activity measurements. C.W. and L.S. carried out XAS measurements. G.Z. and Z.J. performed the characterization of N2 adsorption-desorption. Y.-N.Z., W.C., S.L., L.Z., K.W., H.Z. and P.W. assisted with the structural characterization. X.W., X.I.G., X.G., and H.W. wrote the manuscript with inputs from all the authors.

Additional information

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