Heterogeneous Single-Atom Catalysts: A Novel Artificial Enzyme

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Abstract

Here, we report a high-temperature gas migration strategy for preparing heterogeneous single-atom iron catalysts and demonstrate their excellent natural enzyme-like activities (defined as single-atom enzymes, SAE). The results reveal that the locally well-defined FeN4 sites of Fe SAE are highly analogous to the active metal centers of heme-containing natural enzymes. Fe SAE exhibits exceptionally high peroxidase-, oxidase-, and catalase-like activities, surpassing those of Fe3O4 nanozymes by 40-fold. More importantly, Fe SAE can effectively activate hydrogen peroxide (H2O2) to generate hydroxyl radicals (•OH). This enables it to function as a heterogeneous Fenton-like system for tackling ever-increasing environmental pollution. Our research results open up a new family of artificial materials—mimicking natural

Full Text

Heterogeneous Single Atom Catalyst: A New Type of Artificial Enzyme

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Supporting Information Placeholder

ABSTRACT: Herein, we report a high-temperature gas-migration strategy to fabricate a heterogeneous single iron atom catalyst and demonstrate its excellent natural enzyme-like activity (defined as single atom enzymes, SAEs). The results reveal that the localized well-defined FeN sites of Fe SAEs are highly similar to the active metal centers of natural heme-containing enzymes. The Fe SAEs exhibit exceptional peroxidase, oxidase, and catalase enzyme-like activities, exceeding that of Fe O nanozymes by a factor of 40. Importantly, Fe SAEs can effectively activate hydrogen peroxide (H O) through a hydroxyl free radicals ($\bullet$OH) pathway, making it useful as a heterogeneous Fenton-like system to address increasing environmental pollution. Our findings open up a new family of artificial materials that mimic natural enzymes.

Enzymes are a class of biomolecules that widely participate in various cellular activities to efficiently control the processes of metabolism, nutrition, and energy conversion in organisms. Natural enzymes possess great practical significance in the fields of clinical medicine, biotechnology, and contemporary chemical engineering. Nevertheless, their practical applications are severely restricted due to limited sources, difficult purification methods, and high tendency toward denaturation. Therefore, the development of biomimetic enzymes with similar or even superior performance compared to natural enzymes has become one of the most important topics. Nanozymes are nanomaterials that can exhibit intrinsic natural enzyme-like properties, which has attracted widespread research attention because of their high stability, ease of large-scale production, and economical cost. Since ferromagnetic nanoparticles were first reported in 2007, various nanozymes have achieved intrinsic peroxidase-like activity, finding applications in clinical medicine, environmental protection, and bio-energy fields. Unlike natural enzymes that typically exhibit efficient turnover rates and high substrate specificity, nanozymes usually show relatively low activity and poor specificity due to diverse surface crystallized configurations. To date, the properties of nanozymes can only be adjusted by size control, doping, and surface modification. Meanwhile, unclear active centers of nanozymes also lead to difficulties in gaining insight into the mechanisms of their natural enzyme-like activity. Therefore, developing artificial enzymes with adequate activity, stability, and substrate specificity remains a vital challenge for practical applications.

Single atom catalysts with well-defined electronic and geometric structures have attracted extensive attention in energy conversion and chemical transformation owing to their maximum atom efficiency, unique quantum size effect, and excellent selectivity. Moreover, single atom catalysts could serve as a bridge linking homogeneous catalysis and heterogeneous catalysis. However, the utilization of single atom catalysts in biocatalysis and environmental protection has seldom been reported. In this work, we first demonstrate that single Fe atom catalysts with structures similar to natural heme-containing enzymes perform intrinsic enzyme-mimicking activities, including oxidase, peroxidase, catalase, and others.

Heme-containing enzymes generally contain a ferrous porphyrin structure and play critical roles in hemoglobin, myoglobin, and brain hemoglobin for oxygen storage and transportation. Herein, Fe SAEs exhibit extremely high activity and stability compared to Fe O nanozymes. The calculated specific activity value of Fe SAEs (6.75 U/mg) is greater than that of Fe O (0.17 U/mg) by a factor of 40. With abundant well-defined Fe-N sites, Fe SAEs effectively activate hydrogen peroxide (H O) through a hydroxyl free radicals (• OH) pathway. Meanwhile, Fe SAEs could serve as a heterogeneous Fenton-like system for the degradation of carcinogenic organic pollutants in wastewater. The Fe SAEs exhibit excellent catalytic activities and recyclability during the catalysis process.

In this work, we report a high-temperature gas-migration strategy to construct porphyrin-like single Fe sites on N-doped carbon nanomaterials (Fe SAEs). The Fe loading is 1.2%, as determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Figures 1A and 1B show the formation mechanism of Fe SAEs. Volatile Fe atoms produced from iron powder at high temperature successfully migrate to the nitrogen-doped carbon support along with small molecule carbon nitrogen fragments (CN) under nitrogen flow. The well-defined ZIF-8 was synthesized by a modified reported method, exhibiting a narrow and uniform rhombododecahedral shape (Figure 1D and S1). Subsequently, ZIF-8 and iron powder were separately placed in a porcelain boat with nitrogen flow. During the pyrolysis process, the Zn nodes evaporate away under high temperatures (1200 °C), leaving N-rich carbon with abundant defects. Additionally, CN molecules bond with surface Fe atoms of iron powder to form volatile Fe(CN) species. Under nitrogen flow, the volatile Fe(CN) species can be transported and trapped by the defective N-rich carbon, generating isolated Fe SAEs.

The transmission electron microscopy (TEM) image (Figure 1E and S2) indicates the absence of metal nanoparticles in Fe SAEs. The ring-like selected-area electron diffraction (SAED) pattern (Figure 1F inset) demonstrates its poor crystallinity. Both aberration-corrected bright-field scanning transmission electron microscopy (BF-STEM) (Figure 1G) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 1H and S4) were carried out to further elucidate the existence of single Fe atoms rather than nanoparticles. The homogeneously distributed dark dots in BF-STEM images and bright dots in HAADF-STEM images directly confirm the existence of Fe sites due to different Z contrasts among Fe, N, and C. Figure 1I [Figure 1: see original paper] shows the homogeneous elemental distribution of Fe, C, and N throughout Fe SAEs by electron energy-loss spectroscopy (EELS).

Figure 1. (A, B) Schematic illustration for the synthesis of Fe SAEs, (C) Macrostructures and active sites of natural enzymes, nanozymes and Fe SAEs, (D) TEM image of ZIF-8, (E) TEM image of Fe SAEs, (F) HAADF-STEM image of Fe SAEs and corresponding SAED pattern, (G) Magnified BF-STEM image of Fe SAEs, (H) Corresponding HAADF-STEM image of Fe SAEs, showing that

only Fe atoms are present in Fe SAEs, (I) EDS mapping images of Fe, N and C.

Notably, no characteristic peak of Fe crystals was observed in the X-ray diffraction (XRD) pattern for Fe SAEs, further implying its poor crystallinity (Figure 2A). Fe SAEs showed a broad shoulder peak assigned to the (002) plane of graphitic carbon. The Raman spectrum displays a high intensity ratio of D to G (I_D/I_G = 1.03) (Figure S6), confirming the highly graphitic nature of Fe SAEs. As verified by Brunauer-Emmett-Teller (BET) measurement, Fe SAEs possess a large surface area (1249 $m^2g^{\ 1}$) and pore diameter (0.45 nm), benefiting the exposure of more active sites (Figure S9). Furthermore, we investigated the coordination environment and electronic structure by X-ray absorption near-edge structure (XANES). The N 1s spectrum suggests the coexistence of graphitic-N (401.3 eV), pyrrolic-N (400.4 eV), and pyridinic-N (398.7 eV), which facilitates the stabilization of Fe SAEs (Figure 2B). Figure S8 reveals the C K-edge, as measured by XAS. The strong * band and * band indicate Fe SAEs are well graphitized, consistent with the aforementioned XRD and Raman results.

Extended X-ray absorption fine structure (EXAFS) was employed to obtain more detailed structural information of Fe SAEs. As shown in Figure 2C, the intensity of the white-line for Fe SAEs lies between those for Fe foil and Fe O , indicating a positive charge of Fe^ + (0 < < 3). Furthermore, the majority of Fe species is Fe-N with a peak at 1.5 Å, verified by the Fourier transformed (FT) k^3-weighted (k)-function of EXAFS spectra in R space (Figure 2D). The main peak located at 1.5 Å for Fe SAEs further verifies the atomic dispersion of single Fe sites rather than Fe-Fe bonds. According to fitting results shown in Figure 2E and Table S1, the coordination number of Fe-N is 4 for Fe SAEs. Moreover, the XAS result exhibits a single peak at the L -edge for Fe SAEs, indicating delocalized Fe 3d-electrons (Figure 2F).

Figure 2. (A) XRD, (B) XPS spectra for the N 1s region of Fe SAEs, (C) Fe K-edge XANES spectra, (D) The k^3-weighted (k)-function of the EXAFS spectra, (E) The corresponding Fe K-edge EXAFS fitting curves of Fe SAEs, (F) Fe L-edge spectra.

To characterize the heme-containing enzyme-like activity of Fe SAEs, we conducted experiments using natural heme-containing enzyme substrates under physiological conditions. By studying the oxidation of 3,3,5,5-tetramethylbenzidine (TMB) and o-phenylenediamine (OPD) in the presence of H O or O to produce blue and yellow coloration, Fe SAEs exhibited Michaelis-Menten kinetics in the TMB and OPD colorimetric reactions, proving that Fe SAEs possess peroxidase (POD)-like (Figure 3A, S13-S15 and Table S2) and oxidase (OXD)-like activity (Figure 3B and S11-S12). Electron paramagnetic resonance (EPR) results provided insight into the heme-containing enzyme-like activity mechanism for Fe SAEs. As shown in Figure 3D, Fe SAEs produced a 5,5-dimethyl-1-pyrroline N-oxide (DMPO) trapped EPR spectrum with an intense set of four peaks, matching perfectly with hydroxyl radicals (•OH) species.

Based on the EPR results, we further applied Fe SAEs in a Fenton-like catalysis system for the degradation of stubborn organic pollutants. Phenol was selected as a representative pollutant to evaluate the performance of Fe SAEs. As expected, Fe SAEs can effectively degrade phenol in aqueous solutions, with over 83% of phenol removed within 30 minutes (Figure 3E [Figure 3: see original paper]). In contrast, Fe O , N-C, and H O alone give removal efficiencies of only 24.4%, 8.5%, and 3%, respectively. More importantly, the performance of Fe SAEs was maintained over more than ten cycles without significant loss of activity (Figure 3F), implying that the Fe-N structure possesses robust stability under rigorous conditions.

Figure 3. (A, B) POD-like and OXD-like activity of Fe SAEs (time-dependent absorption spectra of TMB oxidation), (C) Comparison of the activity of Fe SAEs, N-C, Fe O MNPs and N-C, (D) EPR spectrum detected in peroxidase-like activity of Fe SAEs, (E) Fenton-like catalytic performance, phenol degradation curves, (F) Reusability of the Fe SAEs in phenol degradation.

To gain insight into the origin of the superior activity of Fe SAEs toward peroxide-mimicking reactions, we carried out density functional theory calculations to investigate the catalytic reaction mechanisms of the peroxidase process. We used an FeN structure embedded in graphene as the experimental model to examine the peroxide-mimicking activity of Fe SAEs. The energy profile and reaction pathway of peroxidase-mimicking on the confined Fe atom are depicted in Figure 4.

First, the H O molecule can spontaneously dissociate into an H O molecule and a Fe=O intermediate with a favorable energy of -2.35 eV. Then, dissociation of another H O molecule on the other side of the central Fe atom is identified to be exothermic by 0.74 eV, forming an O=Fe=O intermediate. The extra O species of the O=Fe=O intermediate facilitates adsorption of the first TMB molecule via formation of an O-H bond with an energy of -0.01 eV, which agrees well with previous studies. However, adsorption of a second TMB molecule is the rate-determining step (RDS) with an energy uphill of 0.86 eV, since the O species has been saturated with the former H atom. The twice deprotonation process of oxTMB forming • OH radicals is exothermic with energies of -0.31 and -0.34 eV, which has been detected by EPR experiments (Figure 3D). In Figure 4, we can see the overall change in energy (E_Total) is -2.80 eV, and the largest E_RDS is 0.86 eV. The negative E_Total and small E_RDS values indicate that Fe SAEs oxidation of TMB by H O is thermodynamically favorable, which is consistent with the experimentally observed peroxidase-mimicking performance. It should be noted that the RDS will become thermodynamically favored as the temperature increases, especially when the contribution of entropy is considered.

The reaction pathway of catalase-mimicking activity is also considered and shown in Figure S16. The overall change in energy of catalase-mimicking is (E_Total) -3.67 eV, and the largest E_RDS is 0.67 eV. Therefore, the decomposition of H O to form O is also thermodynamically favorable.

In summary, we have demonstrated that Fe SAEs successfully perform intrinsic enzyme-mimicking activity similar to natural heme-containing enzymes. The Fe SAEs exhibit exceptional peroxidase, oxidase, catalase enzyme-like, and Fenton-like activities, making them useful in bio-detection and environmental protection. This work opens up a new family of artificial materials that mimic natural enzymes.

ASSOCIATED CONTENT

Supporting Information: Detailed experimental procedures; SEM and TEM images; BET data, XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes: The authors declare no competing financial interests.

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