PREPARATION METHOD AND APPLICATION OF A METAL NANOCLUSTER MODIFIED FENC CATALYST

Field of the Invention

The present invention relates to the field of electroreduction catalyst technology, specifically to a preparation method and application of a metal nanocluster modified FeNC catalyst.

Background to the Invention

Electrocatalytic oxygen reduction reaction (ORR) is an important electrode reaction in various energy devices such as fuel cells and metal air batteries. However, the slow kinetic rate of the reaction seriously affects the energy conversion efficiency. Although Pt based catalysts have the most outstanding ORR activity, their high cost, poor stability, and susceptibility to poisoning significantly affect their commercial applications. This has also inspired researchers to extensively explore highly active and stable non precious metal catalysts. So far, single atom catalysts (SACs), as a new type of catalytic material, have shown excellent performance in various catalytic processes due to their maximum atomic efficiency, tunable electronic structure, and unsaturated coordination. Compared with traditional catalysts, such single atom catalysts, especially carbon based transition metal single atom catalysts (Fe NC) with Fe Nx as the active site, have excellent activity and selectivity, and can be used as ideal materials for studying ORR mechanisms. However, the symmetrical electron distribution of Fe-N_4 can lead to non optimal adsorption of ORR intermediates, ultimately hindering the catalytic process. Therefore, the ORR activity of Fe-N-C catalysts still needs to be improved by adjusting the electronic structure of the active sites reasonably for practical applications.

In order to adjust the binding strength of oxygen-containing intermediates, several strategies have been developed to modify the electronic structure of metal centers to improve their ORR performance. Among them, enhancing the interaction between metal atoms and carriers or heteroatoms can directly regulate the chemical environment near the metal atoms. For example, in Fe-N4, some N atoms are partially replaced by heteroatoms (such as S, P, C), forming asymmetric atomic interfaces that can directly change the catalytic activity of the metal center. However, the close range modification process of metal centers by heteroatoms is difficult to control. In addition, coupling M-N4 sites with other adjacent metal centers or metal nanoclusters has recently been shown to be a feasible strategy for enhancing catalyst activity. Research has shown that due to the synergistic effect between binuclear metal pairs and the asymmetric distribution of electrons around the center of binuclear metals, heteronuclear coordination can modify the d-electron structure of metal atoms, thereby optimizing their adsorption/desorption properties. Therefore, multinuclear sites, especially atomic clusters, are highly effective in regulating the intrinsic catalytic activity of single atoms. Careful control of the quality of nanoclusters (such as spatial distribution, particle size, and composition) can induce electron redistribution of metal single atoms, thereby reducing the energy barrier of the ORR rate determining step and improving catalytic behavior. However, due to fully demonstrated thermodynamic instability, metal nanoclusters are prone to grow into larger crystals during pyrolysis, as surface energy rapidly increases with decreasing particle size.

Currently, He Chuanxin and Wang Lei have synthesized Ru nanoclusters and Cu nanoclusters loaded carbon materials using H_2/Ar mixed gas carbonization method, respectively; Zang Shuangquan et al. prepared Fe nanoparticle modified single atom catalysts using a temperature controlled method; Zhu Chengzhou et al. synthesized graphene encapsulated Fe_3C nanocrystals using $ZnCl_2$ salt templates to enhance the oxygen reduction activity of Fe single atom centers. Although the above method can synthesize metal nanoparticle catalysts, the catalyst particle size is uneven or the overall size is large, the loading is low, and it cannot effectively regulate the electronic structure of single atomic sites. At the same time, the above preparation method involves dangerous, toxic, or costly raw materials such as DMF, H_2, and potassium borohydride, which is not conducive to large-scale promotion and application. In addition, a single regulatory strategy is often insufficient to optimize the electronic and geometric structure of $Fe-N_4$ centers. Combining heteroatoms and metal nanoclusters to synergistically regulate the coordination environment of metal sites is an important way to improve catalytic activity, but controlling the modification of heteroatoms and metal clusters remains a major challenge.

Statement of Invention

The purpose of the present invention is to provide a preparation method and application of a metal nanocluster modified FeNC catalyst, and to provide a universal strategy for effectively regulating the electrocatalytic oxygen reduction activity of metal single atom sites; By coordinating thiosemicarbazide with metal precursor acetylacetonate iron and using in-situ produced $Mg(OH)_2$ as a template, highly dispersed Fe nanoclusters can be prepared by forming metal intermediate Prussian blue nanoclusters, while forming S-atom modified Fe single atom sites. Characterized by speed, simplicity, and high success rate.

To achieve the above technical objectives and achieve the above technical effects, the present invention is implemented through the following technical solutions:

A metal nanocluster modified FeNC catalyst, characterized in that the FeNC catalyst is a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, and the catalyst is Fe-NC-nM, where n=1, 2, 3, and n is the amount of Mg based template.

Furthermore, n=2。

The preparation method and application of a metal nanocluster modified FeNC catalyst, comprises the following steps:

S1: weigh an appropriate amount of thiosemicarbazide and transfer it to a three necked flask filled with water, then place it in an oil bath and heat it to 60-90℃, stirring for 15 minutes, then take an appropriate amount of magnesium chloride hexahydrate, potassium hydroxide, and acetylacetone iron in water or ethanol solution and add it to the three necked flask in a certain time and order, after 30 minutes of reaction, add an appropriate amount of agarose and stir for 2-3 hours, after natural cooling, age the obtained solution for 10 hours and freeze dry it;

S2: place the gel reactant containing $Mg(OH)_2$ and KCl precipitation obtained in step S1 in a N_2 flowing tubular furnace, with a heating rate of 1-5 ℃/min, heat it to 300-400℃, keep it constant for 1-3h, and then heat it to 800-1000℃ at a heating rate of 3-10 ℃/min, keep it constant for 1-3h;

S3: take out the porous carbon product containing $Fe_4[Fe(CN)_6]_3$ obtained in step S2, acid wash it with 0.25-3M H_2SO_4 for 10-14 hours, then rinse it with deionized water until neutral and filter it, dry it to obtain the intermediate; then place the intermediate in a tube furnace with N_2 flow, with a heating rate of 1-5 ℃/min, and heat it to 800-1000℃ for 1-3 hours to obtain FeNC catalyst.

Furthermore, step S1 specifically comprises:

S1.1: assemble thiosemicarbazide, agarose, $Fe(acac)_3$ mixed hydrogel;

S1.2: formation of $Mg(OH)_2$ and KCl precipitates in situ, followed by freeze-drying.

Furthermore, step S2 specifically comprises:

S2.1: pyrolysis of the dried gel obtained in step S1, decomposition of $Mg(OH)_2$, reconstruction of KCl, and carbonization of the precursor;

S2.2: in the production of MgO and KCl templates FeNC@template generate porous carbon anchored to Prussian blue $Fe_4[Fe(CN)_6]_3$.

Furthermore, step S3 specifically comprises:

S3.1: remove templates and excess Prussian blue particles through acid soaking process.

S3.2: the remaining Prussian blue small particles are redispersed by pyrolysis and stabilized with a large number of N and S atoms from thiosemicarbazide, forming FeNC-nM electrocatalysts decorated with S functional groups and iron nanoclusters, n=1~3；

Furthermore, the initial oil bath step in step S1 is condensation reflux, while the oil bath step after adding agarose is open (requiring evaporation of ethanol).

Furthermore, wherein the mass of hexahydrate magnesium chloride and potassium hydroxide in step S1 is 3.2 g and 1.8 g, thiosemicarbazide is 3 g, acetylacetone iron is 0.84 g, and agarose is 0.8 g.

Furthermore, the iron source in step S1 can be metal sources such as acetylacetonate iron, acetate iron, sulfate iron, etc.

Furthermore, the concentration of sulfuric acid in step S3 is 2 M.

On the other hand, the present invention proposes the application of the above-mentioned catalyst and preparation method in oxygen reduction.

The beneficial effects of the present invention are:

The present invention provides a universal strategy for effectively regulating the electrocatalytic oxygen reduction activity of metal single atom sites. A single atom Fe catalyst enhanced by S atoms and nano metal clusters was synthesized through aggregation redispersion pathway, where Fe directly merges with S bonds adjacent to the metal clusters. Due to close range interactions, the surrounding S atoms and Fe nanoclusters can effectively control the asymmetric interface structure of the central Fe atom, resulting in unique electronic configurations. DFT calculations show that the synergistic effect of heteroatoms and clusters can fully regulate the d-band center of single atom Fe in FeNC-2M, thereby accelerating the desorption of OH * as RDS and reducing the reaction energy barrier, thereby improving ORR kinetics and activity. Thanks to the high activity and accessibility of metal sites, as well as the amazing anti-corrosion ability induced by graphitized carbon supports, the best FeNC catalysts exhibit impressive ORR activity and excellent durability over a wide pH range. In addition, compared with the benchmark Pt/C catalyst, FeNC based zinc air batteries (ZAB) and microbial fuel cells (MFC) exhibit significantly improved catalytic performance, especially in terms of cycle stability, which elucidates the prospects for practical applications. This work delves into the optimization effects of different electron modulation methods on the performance of atomic electrocatalysts, which can stimulate the exploration of efficient SACs. Specifically, it includes:

Improved catalytic activity for oxygen reduction reaction (ORR): Introducing adjacent S atoms and metal nanoclusters can synergistically regulate the electronic state and geometric structure of Fe central sites. Through the aggregation redispersion pathway, S atoms and metal clusters undergo dual modification with FeNC centers, breaking the symmetric electronic interface of Fe-N coordination and altering the 3D orbital configuration of Fe centers. This modulation effect enhances site activity and optimizes the adsorption capacity and desorption rate of ORR intermediates. S atoms and Fe nanoclusters as modulators can effectively control the asymmetric interface configuration of the central Fe atom. At the same time, synergistic induction of electron redistribution between Fe central sites and carbon carriers accelerates the desorption of OH*, thereby enhancing ORR activity; The obtained FeNC catalyst exhibits excellent activity in ORR, with a half wave potential (E1/2) of 0.897V.

Improved durability of the catalyst: The prepared FeNC catalyst has a highly graphitized structure and developed hierarchical porosity. Highly graphitized carbon carriers not only anchor efficient active sites, but also have excellent corrosion resistance, enhancing the durability of active sites. The hierarchical pore structure is conducive to mass transfer, while the graphitized carbon structure is conducive to electron conduction. The prepared FeNC has uniformly dispersed nano cluster loading, highly graphitized carbon skeleton, and developed hierarchical pore structure, which can enhance the durability and mass transfer capacity of the catalyst. This enables FeNC catalysts to maintain excellent activity and durability in applications such as zinc air batteries and microbial fuel cells.

A universal strategy is provided to regulate the electrocatalytic activity of metal single atom sites: a single atom Fe catalyst synergistically enhanced by S atoms and nano metal clusters was synthesized through aggregation redispersion pathway. Iron sources can form cyanide containing complexes with thiosemicarbazide, which can be converted into Prussian blue intermediates through iron carbide salts. Excess Prussian blue is decomposed by sulfuric acid solution to form a highly dispersed carbon based material loaded with Prussian blue nanoparticles. After secondary carbonization, it forms a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms. This strategy fully utilizes the regulatory effect of S atoms and metal clusters on the Fe central site, achieving effective control over the electronic structure of the active site. The catalytic activity of the catalyst was optimized by adjusting the geometric structure, electronic state, and coordination environment of the Fe sites. This method can be used to form different types of metal nanoparticles (such as intermediate states of metal sulfides or metal elements), which provide a universal strategy for the synthesis of atomic level metal sites through strategies such as secondary carbonization or ligand modification. Therefore, this universal strategy can provide reference for the development and application of other single atom catalysts. Significantly improved the performance of zinc air batteries and microbial fuel cells: Zinc air batteries and microbial fuel cells based on FeNC catalysts demonstrated ultra-high power density. FeNC catalyst has high active sites and excellent corrosion resistance, which can effectively drive electron transfer processes involving multiple continuous couplings and improve the energy conversion efficiency of the device. At the same time, FeNC catalyst also exhibits excellent durability and maintains good performance stability during long-term operation, with high practical application potential.

Improved wastewater treatment efficiency: FeNC catalyst demonstrated high chemical oxygen demand (COD) removal rate and high coulombic efficiency in microbial fuel cells. FeNC catalyst has excellent oxygen reduction activity and high conductivity, which can effectively promote the degradation of organic substrates and electron recovery in wastewater. The high COD removal rate and high Coulombic efficiency indicate that the catalyst has excellent substrate oxidation performance and electron transport ability, and has good wastewater treatment effect.

In summary, FeNC catalysts optimize their catalytic activity, durability, and wastewater treatment efficiency by regulating the electronic and geometric structure of metal single atom sites. This provides an effective method and universal strategy for the application of energy materials and electrocatalytic technology.

Of course, implementing any product of the present invention does not necessarily require achieving all of the advantages described above simultaneously.

Brief Description of the Drawings

In order to more clearly illustrate the technical solution of the embodiments of the present invention, a brief introduction will be given to the accompanying drawings required for the description of the embodiments. It is obvious that the accompanying drawings described below are only some embodiments of the present invention. For those skilled in the art, other drawings can be obtained based on these drawings without creative labor.

FIG. 1 is a schematic diagram of the preparation of Fe-NC catalyst prepared in Embodiment 1 of the present invention;

FIG. 2 shows the X-ray diffraction (XRD) pattern of the Fe-NC catalyst intermediate prepared in Embodiment 1 of the present invention;

FIG. 3 shows the XRD patterns of Fe-NC catalysts prepared in Embodiments 1-3 of the present invention;

FIG. 4 shows the XRD patterns of Fe-NC catalysts prepared in Embodiments 1, 4, and 5 of the present invention;

FIG. 5 shows the transmission electron microscope (TEM) image of the Fe-NC catalyst prepared in Embodiment 1 of the present invention;

FIG. 6 shows the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of the Fe-NC catalyst prepared in Embodiment 1 of the present invention;

FIG. 7 is an enlarged HAADF-STEM image of the Fe-NC catalyst prepared in Embodiment 1 of the present invention (corresponding to the red box in Figure 6);

FIG. 8 shows the statistical histogram of the particle size of metal clusters in the Fe-NC catalyst prepared in Embodiment 1 of the present invention;

FIG. 9 shows the *R*-space curve and fitting curve of Fourier Transform Extended X-ray Absorption Fine Structure Spectroscopy (FT-EXAFS) of the Fe-NC catalyst prepared in Embodiment 1 of the present invention. The illustration is a schematic diagram of the Fe-NC atomic model, with C atoms in gray, N atoms in blue, O atoms in red, S atoms in yellow, and Fe atoms in brown;

FIG. 10 shows the linear scan curves of Fe-NC catalysts prepared in Embodiments 1, 4, and 5 of the present invention for oxygen reduction;

FIG. 11 shows the polarization curves and power density curves of Fe NC catalyst and commercial Pt/C catalyst prepared in Embodiment 1 of the present invention for zinc air batteries;

FIG. 12 shows the polarization curves and power density curves of Fe-NC catalyst and commercial Pt/C catalyst prepared in Embodiment 1 of the present invention for microbial fuel cells;

FIG. 13 shows the discharge curves of Fe NC catalyst and Pt/C catalyst prepared in

Embodiment 1 of the present invention for microbial fuel cells. The stability of the microbial fuel cell was evaluated by monitoring the voltage output for approximately 2354 hours under an external resistance of 1000Ω.

Detailed Description

Below, the technical solutions in the embodiments of the present invention will be clearly and completely described in conjunction with the accompanying drawings. Obviously, the described embodiments are only a part of the embodiments of the present invention, not all of them. Based on the embodiments of the present invention, all other embodiments obtained by ordinary skilled persons in the art without creative labor are within the scope of protection of the present invention.

A a metal nanocluster modified FeNC catalyst as described in this embodiment, wherein the FeNC catalyst is a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, and the catalyst is Fe NC nM, where n=1, 2, 3.

In this implementation, n=2.

A preparation method of a metal nanocluster modified FeNC catalyst, comprising the following steps:

S1: Weigh an appropriate amount of thiosemicarbazide and transfer it to a three necked flask filled with water. Then place it in an oil bath and heat it to 60-90℃, stirring for 15 minutes. Then take an appropriate amount of magnesium chloride hexahydrate, potassium hydroxide, and acetylacetone iron in water or ethanol solution and add it to the three necked flask in a certain time and order. After 30 minutes of reaction, add an appropriate amount of agarose and stir for 2-3 hours. After natural cooling, age the obtained solution for 10 hours and freeze dry it;

S2: Put the reactant (containing gel precipitated by $Mg(OH)_2$ and KCl) obtained in step S1 in a N_2 flowing tubular furnace, with a heating rate of 1-5 ℃/min, heat it to 300-400 ℃, keep the constant temperature for 1-3h, and then heat it to 800-1000 ℃ at a heating rate of 3-10 ℃/min, keep the constant temperature for 1-3h;

S3: Take out the product obtained in step S2 (porous carbon containing $Fe_4[Fe(CN)_6]_3$, acid wash with 0.25-3MH_2SO_4 for 10-14 hours, then rinse with deionized water until neutral and filter, dry to obtain the intermediate. Then place the intermediate in a tube furnace with N_2 flow, with a heating rate of 1-5 ℃/min, and heat it to 800-1000 ℃ for 1-3 hours to obtain FeNC catalyst.

In this embodiment, step S1 specifically includes:

S1.1: Assemble thiosemicarbazide, agarose, Fe (acac) $_3$ mixed hydrogel;

S1.2: Formation of $Mg(OH)_2$ and KCl precipitates in situ, followed by freeze-drying.

In this embodiment, step S2 specifically includes:

S2.1: Pyrolysis of the dried gel obtained in step S1, decomposition of $Mg(OH)_2$, reconstruction of KCl, and carbonization of the precursor;

S2.2: In the production of MgO and KCl templates（ FeNC@template ）Generate porous carbon anchored with Prussian blue（$Fe_4[Fe(CN)_6]_3$）;

In this embodiment, step S3 specifically includes:

S3.1: Remove templates and excess Prussian blue particles through acid soaking process.

S3.2: The remaining Prussian blue small particles are redispersed by pyrolysis and stabilized by a large number of N and S atoms from thiosemicarbazide, forming FeNC-nM electrocatalysts decorated with S functional groups and iron nanoclusters, n=1~3。

In this embodiment, the early oil bath step in step S1 is condensation reflux, and the oil bath step after adding agarose is open (requiring evaporation of ethanol).

In this embodiment, the mass of hexahydrate magnesium chloride and potassium hydroxide in step S1 is 3.2g and 1.8g. Thiourea is 3g, acetylacetonate iron is 0.84 g, and agarose is 0.8 g.

In this embodiment, the iron source in step S1 can be a metal source such as acetylacetonate iron, acetate iron, sulfate iron, etc.

In this embodiment, the concentration of sulfuric acid in step S3 is 2 M.

On the other hand, the present invention proposes the application of the above-mentioned catalyst and preparation method in oxygen reduction.

Embodiment 1

A preparation method for a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, the catalyst being Fe-NC-2M (Fe-NC-2M-1H), comprising the following steps:

S1: Pour 60ml of water into a three necked flask, then place it in an oil bath and heat it to 80°C. Add 3g of thiosemicarbazide to the three necked flask (condensation reflux), and after 15 minutes, add 3.2g of hexahydrate magnesium chloride (dissolved in 10ml aqueous solution) and 1.8g of potassium hydroxide (dissolved in 7.5ml aqueous solution). After 15 minutes of reaction, add 0.84g of acetylacetonate iron (dissolved in 40 ml of ethanol solution) to a three necked flask. After vigorous stirring for 30 minutes, dissolve 0.8g of agarose into the solution, and then stir continuously at 80°C for 2 hours (open). After natural cooling, the obtained suspension was aged for 10 hours and freeze-dried.

S2: Place the dried gel in a tube furnace flowing with nitrogen, and carbonize it at 350 and 900°C for 1 and 2 hours. Then leach the product in 1 MH_2SO_4 at 80°C for 12 hours to obtain the intermediate. After secondary pyrolysis at 900°C, the final FeNC catalyst was obtained.

Embodiment 2

A preparation method for a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, the catalyst being Fe-NC-2M (Fe-NC-2M-1H), comprising the following steps:

S1: Pour 60ml of water into a three necked flask, then place it in an oil bath and heat it to 80°C. Add 3g of thiosemicarbazide to the three necked flask (condensation reflux), and after 15 minutes, add 3.2g of hexahydrate magnesium chloride (dissolved in 10ml aqueous solution) and 1.8g of potassium hydroxide (dissolved in 7.5ml aqueous solution). After 15 minutes of reaction, add 0.84g of acetylacetonate iron (dissolved in 40 ml of ethanol solution) to a three necked flask. After vigorous stirring for 30 minutes, dissolve 0.8g of agarose into the solution, and then stir continuously at 80°C for 2 hours (open). After natural cooling, the obtained suspension was aged for 10 hours and freeze-dried.

S2: Place the dried gel in a tube furnace flowing with nitrogen, and carbonize it at 350 and 900°C for 1 and 2 hours. Then leach the product in 0.5 MH_2SO_4 at 80°C for 12 hours to obtain the intermediate. After secondary pyrolysis at 900°C, the final FeNC catalyst was obtained.

Embodiment 3

A preparation method for a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, the catalyst being Fe-NC-2M (Fe-NC-2M-1H), comprising the following steps:

S1: Pour 60ml of water into a three necked flask, then place it in an oil bath and heat it to 80°C. Add 3g of thiosemicarbazide to the three necked flask (condensation reflux), and after 15 minutes, add 3.2g of hexahydrate magnesium chloride (dissolved in 10ml aqueous solution) and 1.8g of potassium hydroxide (dissolved in 7.5ml aqueous solution). After 15 minutes of reaction, add 0.84g of acetylacetonate iron (dissolved in 40 ml of ethanol solution) to a three necked flask. After vigorous stirring for 30 minutes, dissolve 0.8g of agarose into the solution, and then stir continuously at 80°C for 2 hours (open). After natural cooling, the obtained suspension was aged for 10 hours and freeze-dried.

S2: Place the dried gel in a tube furnace flowing with nitrogen, and carbonize it at 350 and 900°C for 1 and 2 hours. Then leach the product in 2 MH_2SO_4 at 80°C for 12 hours to obtain the intermediate. After secondary pyrolysis at 900°C, the final FeNC catalyst was obtained.

Embodiment 4

A preparation method for a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, the catalyst being Fe-NC-2M (Fe-NC-2M-1H), comprising the following steps:

S1: Pour 60ml of water into a three necked flask, then place it in an oil bath and heat it to 80°C. Add 3g of thiosemicarbazide to the three necked flask (condensation reflux), and after 15 minutes, add 3.2g of hexahydrate magnesium chloride (dissolved in 10ml aqueous solution) and 0.9g of potassium hydroxide (dissolved in 7.5ml aqueous solution). After 15 minutes of reaction, add 0.84g of acetylacetonate iron (dissolved in 40 ml of ethanol solution) to a three necked flask. After vigorous stirring for 30 minutes, dissolve 0.8g of agarose into the solution, and then stir continuously at 80°C for 2 hours (open). After natural cooling, the obtained suspension was aged for 10 hours and freeze-dried.

S2: Place the dried gel in a tube furnace flowing with nitrogen, and carbonize it at 350 and 900°C for 1 and 2 hours. Then leach the product in 1 MH_2SO_4 at 80°C for 12 hours to obtain the intermediate. After secondary pyrolysis at 900°C, the final FeNC catalyst was obtained.

Embodiment 5

A preparation method for a Fe single atom catalyst co modified with metal nanoclusters and heteroatoms, the catalyst being Fe-NC-2M (Fe-NC-2M-1H), comprising the following steps:

S1: Pour 60ml of water and 40ml of ethanol into a three necked flask, then place it in an oil bath and heat it to 80 °C. Add 3g of thiourea, 4.8g of hexahydrate magnesium chloride, 2.7g of potassium hydroxide, and 0.84g of acetylacetonate iron into the three necked flask (reflux by condensation). After vigorous stirring for 30 minutes, dissolve 0.8g of agarose into the solution, and then stir continuously at 80 °C for 2 hours (open). After natural cooling, the obtained suspension was aged for 10 hours and freeze-dried.

S2: Place the dried gel in a tube furnace flowing with nitrogen, and carbonize it at 350 and 900°C for 1 and 2 hours. Then leach the product in 1 MH_2SO_4 at 80°C for 12 hours to obtain the intermediate. After secondary pyrolysis at 900°C, the final FeNC catalyst was obtained.

Among them, the naming conditions for each group of catalysts are: changing the concentration of sulfuric acid solution by 0.5 M, 1 M, and 2 M is named Fe-NC-2M-xH, and the template amount here is uniformly 16 mmol.

The changes in $Mg(OH)_2$ and KCl are named Fe NC xM, where x=12 and 3 represent

8mmol, 16 mmol, and 24 mmol of Mg (OH) $_2$ or KCl, respectively. The sulfuric acid concentration here is uniformly 1M.

Embodiment 6

As shown in Figure 1, acetylacetone iron coordinates with thiosemicarbazide and, under the action of templates such as $Mg(OH)_2$, Prussian blue nanoparticles, an intermediate of iron, are obtained through a single carbonization. After acid washing and secondary carbonization, Fe nanoclusters and S atoms co modify the Fe single atom catalyst.

As shown in Figure 2, the Fe-NC catalyst intermediate exhibits a clear diffraction peak of Prussian blue, indicating that Fe mainly exists in the form of Prussian blue in the carbon support. Powder X-ray diffraction (PXRD) was used to study the FeNC-nM catalyst. Sharp diffraction peaks belonging to Prussian blue ($Fe_4[Fe(CN)_6]_3$) were detected in the FeNC-2M intermediate after acid washing (Figure 2), but completely disappeared after subsequent annealing, replaced by two characteristic carbon (002) and (100) diffraction peaks of FeNC-2M (Figure 3), indicating that Prussian blue has successfully transformed into monodisperse iron sites or small clusters. It is worth noting that the XRD pattern (Figure 4) shows that as the amount of Mg $(OH)_2$ and KCl templates increases from 1 to 3, the peak of the graphite phase significantly increases, indicating an increase in the degree of graphitization. The in-situ formation of magnesium oxide templates is crucial for the effective graphitization of precursors and the generation of enriched pore structures. However, in FeNC-3M (Figure 4), some clear diffraction peaks attributed to FeS were observed, which were the result of iron species aggregation at higher template contents.

The transmission electron microscopy (TEM) image of FeNC-2M in Figure 5 clearly shows an interconnected porous framework with numerous mesopores and micropores, indicating the presence of numerous structural defects in the graphite carbon. Meanwhile, the TEM image (Figure 5) also excluded the presence of iron-based large particles. More information comes from aberration corrected high angle annular dark field scanning TEM (AC-HAADF-STEM) measurements. The AC-HAADF-STEM image of FeNC-2M catalyst (Figure 6) shows that many bright spots ranging in size from 1.4 to 3.1 nm are uniformly distributed throughout the carbon skeleton (with an average size of 2.1 nm, Figure 8), without any large particles or nanoclusters clustering. At the same time, in addition to nanoclusters, there are also a large number of well dispersed bright spots (Figure 7), some of which (such as red circles) are closely adjacent to iron nanoclusters (such as yellow circles). This local coordination environment can cause close range interactions between metal single atoms and nanoclusters.

A comprehensive evaluation of the ORR performance of the designed catalyst was conducted across a wide range of pH values using various techniques. Table 1 summarizes the ORR activity parameters obtained from ring disk electrode (RDE) testing. Under alkaline conditions, FeNC-2M exhibits excellent electrocatalytic activity at high half wave potential and kinetic current density (E1/2, 0.897V; Jk, 8.37mA cm-2) (Figure 10), surpassing FeNC-1M (0.873, 4.60) and FeNC-3M (0.840, 2.54), and even surpassing commercial Pt/C (0.852, 3.41). The Fe NC catalyst prepared in Embodiment 1 exhibits excellent electrocatalytic oxygen reduction activity, with a half wave potential of 0.897 V vs RHE.

Table 1 Comparison of ORR performance of all catalysts

Catalyst	RDE vs. RHE (0.1M KOH)			(0.05 M PBS)		(0.5M H2SO4)	
	Eonset	JK (0.85V)	E1/2	Eonset	E1/2	Eonset	E1/2
FeNC-1M	0.974	4.60	0.873	-	-	-	-
FeNC-2M	0.986	8.37	0.897	0.882	0.683	0.873	0.794
FeNC-3M	0.946	2.54	0.840	-	-	-	-
FeNC-2M-0.25H	0.975	4.79	0.873	-	-	-	-
FeNC-2M-0.5H	0.985	7.70	0.890	-	-	-	-
FeNC-2M-2H	0.979	6.62	0.882	-	-	-	-

Pt/C (20wt%)	0.982	3.41	0.852	0.851	0.637	0.930 [a]	0.819[a]

[a]For Pt/C catalyst, the acidic electrolyte is 0.1 M $HClO_4$

As shown in Figure 11, FeNC-2M-ZAB achieved an impressive peak power density of 326 mW cm^{-2} at a current density of 410 mA cm^{-2}, significantly exceeding Pt/C-ZAB (243 mW cm^{-2}) and most other ZABs previously reported. As shown in Figure 12. FeNC-2M MFC achieved a maximum power density of 2790 mW cm^{-2}, which validates the significant advantage of MFC driven by Pt/C (2036 mW cm^{-2}) and other non precious metal ORR catalysts previously reported (Table 2).

Table 2 Comparison of ORR activity and power density between FeNC catalyst and other non precious metal catalysts previously reported

	$E_{1/2}$ [V vs. RHE]			Power density		
Catalyst	KOH	PBS	H_2SO_4	ZAB	MFC	Reference
$FeMn_{ac}/Mn\text{-}N_4C$	0.90	-	0.79	207 [mW cm^{-2}]	- [mW m^{-2}]	Angew. Chem. Int. Ed. 2022, e202214988
Fe_5-Cu-N-mC	0.92	-	0.80	214.8	-	Angew. Chem. Int. Ed. 2023, e202308344
Fe_x/Cu–N@CF	0.944	-	0.815	156	-	Energy Environ. Sci. 2023, 16, 3576
Fe/Meso-NC-1000	0.885	-	-	-	-	Adv. Mater. 2022, 34, 2107291
Fe/NC-3	0.898	-	-	-	-	Small Methods 2021, 5, 2001165
N-HPCNSs-800	0.887	0.79	0.75	240	1122.13	Nano Energy 2018, 49, 393

β-FeOOH/PNGNs	0.883	0.697	0.680	164.5	-	Adv. Funct. Mater. 2018, 28, 1803330
Ni/CoNC	-0.049 V vs. Hg/HgO	0.108 V vs. SCE	-	-	4335.6 (Escherichia coli cell)	Adv. Sci. 2016, 3, 1500265
GO-Zn/Co (1:1)-800	0.81	0.59	-	-	773	Nano Energy 2019, 57, 811
Fe/Fe3C/NHCS	0.84	0.71	0.67 (HClO4)	-	-	Chem. Eur. J. 2019, 25, 9650
Fe,N/PGC-30	0.82	0.61	0.64	-	-	J. Mater. Chem. A 2016, 4, 14364
NP-Fe-NHPC	0.93	-	0.76	266.4	-	Adv. Mater. 2020, 1907399
Fe-N/P-C-700	0.867	-	0.72	133.2	-	J. Am. Chem. Soc. 2020, 142, 2404
Fe-N/CNT-2	0.922	-	0.77 (HClO4)	-	-	Adv. Funct. Mater. 2019, 1906174
FeCo-N-HCN	0.86	-	0.75	-	-	Adv. Funct. Mater. 2021, 2011289
CoFe20@CC	0.86	-	-	190.3	-	Adv. Mater. 2019, 1904689
FeSA-N-C	0.90	-	0.80 (HClO4)	-	-	Nat. Commun. 2020, 11, 2831
Fe/Ni-Nx/OC	0.938	-	0.840	148	-	Adv. Mater.

						2020, 2004670
FeN-HMCTs	0.841	-	-	-	-	Adv. Funct. Mater. 2020, 2009197
Fe/Ni-N-C	0.861	-	-	-	-	Appl. Catal. B-Environ. 2021, 285, 119778
SA-Fe-Nx-MPCS	0.88	-	-	-	-	Appl. Catal. B-Environ. 2021, 293, 120176
MNDCS-0.3	0.814	-	-	-	-	Energy Environ. Mater. 2021, 4, 81
meso-Fe-N-C	0.846	-	-	-	-	ACS Catal. 2021, 11, 74
Fe-N-C HNSs	0.87	-	-	-	-	Adv. Mater. 2018, 31, 1806312
FeCo-N-C-700	0.896	-	-	150a	-	J. Mater. Chem. A 2020, 8, 9355
NPMC-1000	0.85	-	-	55a	-	Nat. Nanotechnol. 2015, 10, 444
C-MOF-C2-900	0.82	-	-	105a	-	Adv. Mater. 2018, 1705431
S,N-Fe/N/C-CNT	0.85	-	-	102.7	-	Angew. Chem. Int. Ed. 2017, 56, 610
Fe/N-CNRs	0.90	-	-	181.8	-	Adv. Funct. Mater. 2020, 2008085
OLC/Co-N-C	0.855	-	-	238a	-	Angew. Chem. Int. Ed. 2021,

						60, 1
Fe,Mn/N–C	0.928	-	0.804 (HClO4)	160.8b	-	Nat. Commun. 2021, 12, 1734
Mn-SAS/CN	0.910	-	-	220b	-	Adv. Energy Mater. 2021, 11, 2002753
S/N_Fe-27	0.87	-	-	-	-	J. Am. Chem. Soc. 2014, 136, 14486
Fe-ISA/SNC	0.896	-	-	-	-	Adv. Mater. 2018, 1800588
CuSA@HNCNx	0.91	-	-	212b	-	Nat. Commun. 2020, 11, 3049
FeSA@HNCNx	0.84	-	-	-	-	
CoSA@HNCNx	0.82	-	-	-	-	
Fe3C@C-Fe SAS	-	0.91	-	74.8	-	Nano Energy 2021, 84, 105840
Fe/SNC	0.86	0.77	-	-	-	Angew. Chem., Int. Ed. 2017, 56, 13800
Ni-Co/C-N	-	0.58 (KNO3)	-	65	-	Nano 2019, 14, 1950028
NG/CB-10	-	0.6	-	-	936	Nanomaterials 2019, 9, 836
N/S-G	-	-0.35 V vs. Ag/AgCl	-	-	1368	New J. Chem. 2019, 43, 9389
Ag/FeS/PGC-0.6	-	0.15 V vs.	-	-	1361	Carbon 2017, 119, 394

		Ag/AgCl				
CN-800	-	-0.096 V vs. Ag/AgCl	-	-	371	Environ. Res. 2020, 182, 109011
3D Fe-N-C	-	-0.08 V vs. SCE	-	-	3118.9 (Escherichia coli.)	Appl. Catal. B-Environ. 2017, 202 550
FeN4/HOPC-c-1000	-	-	0.80	-	-	Angew. Chem. Int. Ed. 2020, 59, 2688
Fe–N/C	0.823	~0.08 V vs. SCE	0.719	-	1232.9	J Power Sources 2020, 469, 228184
IR/CN-50%	0.89	0.59	-	-	1402.8	J Power Sources 2020, 450, 227681
Mn–Fe@g-C3N4	0.172	-0.042 V vs. Ag/AgCl	-	-	413	J Power Sources 2020, 467, 228313
NiFe-LDH@Co3O4	-	-	-	-	467.35	J. of Power Sources 2020, 453, 227877
N-CNTs/rGO (700)	0.859	-	-	-	1329	Nano Energy 2019, 61, 533
N/S-Fe-HPC	0.86	-	0.73(HClO4)	-	-	Appl. Energy 2016, 175, 468
FeSAs/PTF-600	0.87	-	~0.74	-	-	ACS Energy Lett. 2018, 3, 883
FeNC-D0.5	0.866	0.692	0.750	356a	1041.3	Small 2021, 17,

						2006178
FeNC-SN-2	0.890	0.723	0.792	260a	1785	Adv. Funct. Mater. 2021, 31, 2100833.
FeNC-2M	0.897	0.683	0.794	326a	2790	This work

Evaluate the stability of MFC by monitoring the voltage output for approximately 2354 hours under an external resistance of 1000Ω. In the early stage of MFC operation, all MFC devices had unstable voltage and no voltage plateau appeared. This can be explained as the inoculated bacteria requiring sufficient time to adapt and reproduce. After the second cycle, the output voltage of MFC shows a stable plateau state and periodically changes with the consumption and replacement of organic matrix. As shown in Figure 13, during the 16 cycles, all voltage plateaus of FeNC-2M MFC were significantly higher than those of Pt/C-MFC. FeNC-2M-MFC achieved a maximum output voltage of 594 mV in the second cycle, and then slowly decreased to 529 mV in the 16th cycle, with a corresponding voltage decay of only 10.9%. In contrast, the maximum voltage of Pt/C-MFC was 471 mV in the second cycle and sharply decreased to 108 mV in the 16th cycle, with a decay rate of 77%, attributed to chloride or sulfide poisoning. The reproducible voltage platform indicates that the FeNC-2M cathode has high resistance to poisoning and exhibits unparalleled stability during MFC operation.

Figure 3 shows Fe NC catalysts treated with different concentrations of sulfuric acid solutions, namely 0.5 M, 1 M, and 2 M sulfuric acid solutions. When the concentration of sulfuric acid solution is 1 M and 2 M, the XRD pattern of the catalyst only shows the diffraction peaks of the carbon support (i.e., 100 and 002 crystal planes), without obvious metal particle derived peaks, indicating that Fe exists in the form of single atoms or clusters in the catalyst and no serious agglomeration phenomenon has occurred. When the concentration of sulfuric acid solution is 0.5 M, the XRD pattern of the catalyst not only shows diffraction peaks of the carbon support, but also obvious peaks derived from metal particles, corresponding to the crystal planes of elemental Fe and FeC_3, indicating a significant agglomeration phenomenon of metals in the catalyst, forming metal particles.
Based on the results shown in Figure 1, Prussian blue decomposes more in concentrated

sulfuric acid solutions, which can remove a large amount of excess iron intermediates. The resulting Prussian blue nanoclusters can form Fe single atom sites and metal clusters after secondary carbonization. In addition, all three catalysts exhibit distinct graphitized carbon (100) crystal diffraction peaks, indicating that this type of material has a high degree of graphitization and can enhance the stability of catalytic sites.

Figure 4 presents Fe-NC catalysts synthesized using different template amounts, namely 16 mmol, 8 mmol, and 24 mmol $Mg(OH)_2$ and KCl templates, respectively. When the plate amount was 8 mmol and 16 mmol, the XRD pattern of the catalyst only showed diffraction peaks of the carbon support, without obvious metal particle derived peaks. When the plate amount is 24 mmol, the XRD pattern of the catalyst shows sharp FeS diffraction peaks. In addition, the degree of graphitization of the catalyst significantly increases with the increase of template amount. In summary, the carbon skeleton of Fe-NC catalyst decomposes significantly with the increase of template amount, and the bonding between metal Fe and S atoms also increases accordingly. Therefore, by controlling the amount of templates, the aggregation degree and bonding mode of metals can be controlled.

As shown in Figure 5, there are no obvious particles or lattices on the porous carbon support, indicating that metal species exist in the form of atomic scale or nanoclusters.

As shown in Figure 6, a large number of white bright spots are uniformly dispersed on the porous carbon carrier, indicating that the metal forms a large number of uniformly dispersed nanoclusters without serious agglomeration.

As shown in Figure 7, there are a large number of single atom sites (marked by red circles) distributed around each metal cluster, indicating that a large number of single atom metal sites interact closely with the nanoclusters.

As shown in Figure 8, the size range of metal clusters in Fe-NC catalyst is 1.4~3.1 nm, with an average size of 2.1 nm belonging to the range of nanoclusters, indicating the successful preparation of Fe-NC catalyst with a large number of Fe nanoclusters loaded.

As shown in Figure 9, there is a significant main peak at approximately 1.4 Å, which is mainly attributed to the Fe-N/O first coordination shell. Small shoulder peaks and distinct secondary peaks appear at 1.92 Å and 2.3 Å, respectively, corresponding to the Fe-S and

Fe Fe scattering paths, indicating the coexistence of Fe-N (O/S) and metallic Fe. Combining the fitting results, it is shown that Fe atoms coordinate with 3 N atoms and 1 S atom to form Fe-N3S coordination centers, and there are also some Fe Fe derived peaks corresponding to the formation of metal clusters. The FT-EXAFS and HAADF-STEM results indicate that metal Fe is mainly formed by Fe-N_3S species, which are anchored in porous carbon containing a large number of Fe metal clusters.

As shown in Figure 10, the Fe NC catalyst prepared in Embodiment 1 exhibits excellent electrocatalytic oxygen reduction activity, with a half wave potential of 0.897 V vs RHE.

As shown in Figure 11, the Fe NC catalyst prepared in Embodiment 1 reached a peak power density of 326 mW cm^{-2} at a current density of 410 mA cm^{-2} when used in zinc air batteries, significantly exceeding Pt/C (243 mW cm^{-2}).

As shown in Figure 12, the maximum power density of the Fe-NC cathode prepared in Embodiment 1 for microbial fuel cells is 2790 mW m^{-2}, which is significantly higher than that of the Pt/C catalyst (2036 mW cm^{-2}).

As shown in Figure 13, within 16 cycles, all voltage platforms of the Fe-NC cathode prepared in Embodiment 1 were significantly higher than those of the commercial Pt/C cathode. The maximum output voltage appeared in the second cycle at 594 mV, and then slowly decreased to 529 mV in the 16th cycle, with a corresponding voltage decay of only 10.9%. In contrast, the maximum voltage of Pt/C-based fuel cells in the second cycle was 471 mV, which sharply decreased to 108 mV in the 16th cycle, with a decay rate of 77%, due to chloride or sulfide poisoning. The experimental results show that Fe-NC cathode has high anti toxicity performance and excellent stability in the operation of microbial fuel cells.

In summary, the present invention proposes a preparation method and application of a metal nanocluster modified FeNC catalyst, which synthesizes a single atom Fe catalyst synergistically enhanced by continuous S atoms and nano metal clusters through aggregation redispersion pathway.

This strategy fully utilizes the regulatory effect of S atoms and metal clusters on the Fe central site, achieving effective control over the electronic structure of the active site. The catalytic activity of the catalyst was optimized by adjusting the geometric structure, electronic state, and coordination environment of the Fe sites. This universal strategy can provide reference for the development and application of other single atom catalysts.

The preferred embodiments of the present invention disclosed above are only intended to assist in illustrating the present invention. The preferred embodiment does not provide a detailed description of all the details, nor does it limit the invention to only the specific embodiments described. Obviously, many modifications and changes can be made based on the content of this manual. This manual selects and specifically describes these embodiments in order to better explain the principles and practical applications of the present invention, so that those skilled in the art can understand and utilize the present invention well. The present invention is limited only by the claims and their full scope and equivalents.