

Preparation of Asymmetric Single-Atom Electrocatalysts for High-Performance Oxygen Reduction Reaction

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Abstract: Metal-organic frameworks (MOFs) have been regarded as a kind of supramolecular non-noble metal-organic hybrids via the strong coordination bonds, which have a highly tunable porous structures, high surface area, and fully exposed and uniformly dispersed metal centers, facilitating mass transport and highly-efficient electron transfer. In this study, we explore the synthesis strategy to prepare hierarchical single-atom electrocatalysts with porous and conductive carbon supports based on a serial of MOFs templates. The various MOF templates were prepared by room-temperature self-assembly or hydrothermal processes. The as-synthesized MOFs were well-designed for the construction of hierarchical nanostructures. Subsequently, a facile and controlled high-temperature pyrolysis treatment was applied for the as-synthesized MOF templates, which allowed the organic ligands to reduce metal centers by releasing hydrogen by changing themselves to porous and conductive carbon materials. Finally, the nanostructured morphology and electrical activity of the as-synthesized single-atom catalysts were investigated by the X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectrum, Spherical aberration electron microscopy, and synchrotron radiation characterization, electrochemical impedance, and cyclic voltammetry. Density Functional Theory (DFT) calculations suggest that the designed asymmetric planar four-ligand structure may be the most favorable catalytic sites. Previous studies were restricted by using Cu elements as the metal active centers and S_1N_3 as the ligands, but broadening the catalyst selection areas, e.g., using monoatomic metal centers such as Fe, Mn, and introducing P element in the ligand, may improve the electronic structure properties of the catalyst, which can effectively reduce the energy barrier in the ORR, a key rate-limiting step in fuel cells. Based on this idea, we investigated six asymmetric monoatomic electrocatalysts, namely, Fe- S_1N_3 , Cu- S_1N_3 , Mn- S_1N_3 , Cu- P_1N_3 , Fe- P_1N_3 , and Mn- P_1N_3 , respectively. The synthesized catalysts have abundant and fully exposed active sites, which can be applied in the cathode reaction of fuel cells and help human species to cope with the global energy crisis and the energy transition in fields such as electric vehicles.

1 INTRODUCTION

Metal-organic frameworks (MOFs) combine inorganic and organic chemistry, which is popular in the recent nanostructured materials fields. Metal atoms coordinated by organic ligands can form one-, two- or three-dimensional structures (crystalline materials). MOFs can be used in multiple fields such as adsorption, separation, storage, catalysis, and energy conversion. Common single-atom catalysts using the MOFs as templates are Fe, Co, Ni, Cu, Mn, and W, which have excellent performances in corresponding applications via a well-designed preparation. (Sun, 2019)

Metal-organic framework-derived materials mainly include porous carbon, metal oxides, metal porous carbon composites, metal oxides, and porous carbon composites. The main synthesis strategies are chemical etching, high temperature pyrolysis, oxidation, etc. Considering some disadvantages of metal-organic frameworks in practical applications, such as low crystal stability, poor performance of electrical conductivity, low catalytic site activity, limited mass transfer and diffusion in the microporous structure, etc. There are many synthetic strategies for high-temperature pyrolysis, such as direct pyrolysis of templates, pyrolysis of encapsulated guests. The template of the bulk, the co-pyrolysis of the template carrier, the first solvent

etching and then the pyrolysis, etc. During the pyrolysis process, the heating rate, holding time and gas atmosphere are the key points of pyrolysis strategy research, which directly determine the synthesized metal-organic framework derivatives properties.

Oxygen reduction reaction (ORR) is one of the common energy conversion reactions, and the common products of ORR reactions are H_2O , which is a four-electron reaction product of oxygen reduction reaction, and H_2O_2 , which is a two-electron product of oxygen reduction reaction. At present, the most widely used oxygen reduction catalysts in cathode reaction of fuel cells are precious Pt/C materials, usually 20% or higher content, which are expensive and scarce. (Tang, 2016) Therefore, the three worthwhile goals to design high-performance ORR catalyst are low cost, high activity, and high stability. The biggest advantage of single-atom catalysts is that they can achieve the maximum utilization of atoms. (Sun, 2019)

Single-atom catalysts has many advantages, such as high efficiency, maximum atomic utilization, efficient and unique electronic structures, and unique geometric construction. To prepare highly active single-atom catalysts, the homo-dispersedly and catalytically active sites are necessary. (Sun, 2019) To improve the transfer of mass and electron as well as the stability of catalytic active sites, and the tight interactions of catalytically active site and carrier are also required and necessary. Many literatures have reported obvious improvements in the single-atom catalysts for ORR. (Shang, 2020; Xie, 2021; Sun, 2019) Typically, Metal- N_x , such as FeN_4 , is usually considered as an ideal catalyst, and the design concept of this configuration has been demonstrated by density functional theory and electrochemical testing with excellent results. (Xie, 2021)

Usually, in addition to metal atoms, single-atom catalysts are N and C elements. In our research, we want to introduce S and P elements, and the key issue is how to design an effective synthesis method. At least one N elements around the metal element needs to be removed and replaced with a sulfur or phosphorus elements. In recent days, a few studies have pointed out that the symmetrical configuration of FeN_4 is not conducive to stable intermediate products. Inspired by this clue, we can try to synthesize single-atom catalysts with asymmetric

coordination. In addition, we would use DFT to explain the underlying catalytic mechanism for the enhanced ORR performances. (Xie, 2021) DFT calculations are a method of quantum chemistry for studying the electronic structures of multi-electron systems. The primary research object of DFT focuses on small molecules or isolated cluster structures, and can calculate transition state energy, bond and reaction energy, molecular orbital, thermodynamic properties, reaction path, etc.

2 EXPERIMENTAL

2.1 Preparation of Materials

2.1.1 Chemicals

The chemicals are usually sourced from Alfa Aesar and Sigma Aldrich, and the purchased reagents were not further purified. The synthesis method uses Cu, Fe, and Mn-ZIF-8 template, the source of S is sulfur powder, and the source of P is phytic acid. (Shang, 2020; Benítez, 2020)

2.1.2 Hydrothermal Synthesis of Metal-Organic Framework Templates

The preparation of MOF templates went through dissolving and recrystallizing the powder. Heating and pressurizing in a sealed pressure vessel, using water as the solvent.

First, mix the solutions of metal ions and organic ligands. Then, transfer the solution to a hydrothermal kettle and heat it in a vacuum oven to keep it warm, allowing the metal ions and organic ligands to coordinate. After that, cooling the solution to room temperature, centrifuged and separated from the MOF, washing several times with methanol solutions, then dried in a vacuum oven.

The key synthesis step is to first hold the temperature at 450 °C for 2 hours in the environment of inert Ar. In this process, the sulfur powder is volatilized into sulfur vapor and embedded in the MOF framework. After incubation at 950 °C for four hours, the template was completely carbonized to synthesize single-atom catalysts with porous and conductive carbon supports. The accurate reaction

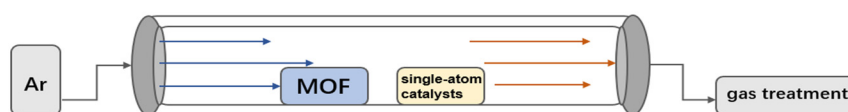


Figure 1: Schematic preparation taking Cu, Fe, and Mn-ZIF-8 as the template.

temperatures of high-temperature pyrolysis can be determined by the thermogravimetric analysis (TGA). (Benítez, 2020) TGA is a method to explore the physical and chemical properties of a substance with an increase in temperature over time. TGA can provide abundant information about phase transitions, such as evaporation, sublimation, absorption, and desorption.

2.2 Electrochemical Measurements

Cyclic voltammetry is the commonly used experimental method in electrochemistry. A three-electrode system was used for electrochemical measurements, with Ag/AgCl in saturated potassium chloride solution as the reference electrode, graphite rod as the counter electrode, glassy carbon as the working electrode, and 0.1 M KOH solution as the electrolyte solution. The catalyst was dispersed in a 5 wt% Nafion solution and dried by a heat lamp before the testing. (Zhou, 2020)

2.2.1 Grind and Disperse Nanomaterials

Grind the nanomaterials into fine particles, and then disperse the nanomaterials in the Nafion solution. Usually, ultrasonic treatments are required for around 0.5 hours to 2 hours. The dispersed solution is usually water and ethanol, the volume ratio is 1:1. (Zhou, 2020)

2.2.2 Preparation of Nanomaterial Working Electrode by the Drop Coating Method

Take 5 microliters of nanomaterial dispersion liquid and drop it on the 3 mm glassy carbon working electrode, and then usually need to volatilize the solvent through an electric heating lamp.

2.2.3 Assembling the Three-Electrode System

The nanomaterial-modified electrode is the working electrode and usually uses the Ag/AgCl electrode or saturated calomel electrode (SCE) as the reference electrode. (Shang, 2020)

2.3 Materials Characterizations

Material characterizations were divided into three parts: (1) Crystal Structure Analysis; (2) Morphology analysis by electron microscope; and (3) Material surface element and valence analysis. The performance characterization of ORR materials is mainly performed by voltammetry.

3 RESULTS AND DISCUSSION

3.1 Novelities

Our study provides a general approach for synthesizing and tuning the activity of single-atom catalysts and applying in the fields of energy conversion. The synthesis of Cu and S₁N₃-coordinated single-atom catalysts based on metal-organic framework templates has been reported, which is a Cu-S₁N₃ coordination form, namely, asymmetrically Cu-S₁N₃. (Shang, 2020) Inspired by this report, we explored high-performance ORR catalysts using Fe, Cu, and Mn as single-atom metal centers coordinated with S₁N₃, and P₁N₃, namely, Fe-S₁N₃, Cu-S₁N₃, Mn-S₁N₃, Cu-P₁N₃, Fe-P₁N₃ and Mn-P₁N₃, respectively. We hope the oxygen reduction activity is higher than that of Cu-S₁N₃ while introducing multiple metal atoms and phosphorus.

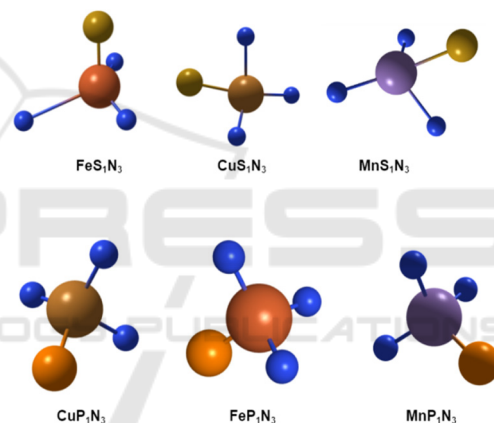


Figure 2: Schematic atomic interface model of Fe-S₁N₃, Cu-S₁N₃, Mn-S₁N₃, Cu-P₁N₃, Fe-P₁N₃ and Mn-P₁N₃.

3.2 Materials Characterizations

Tuning atomic interfaces is an important method to tune the activity of single-atom catalysts. Two strategies to improve catalyst activity are to improve the number of active sites and improve the activity of a single catalytic active site, while the metal single-atom is the catalytic center.

Mesoporous metal-organic framework materials are good templates to increase the number of exposed active sites and improve catalytic performance. Pyrolysis of metal-organic framework materials is an effective way to increase the number of catalysts, the key lies in the formation of mesoporous structure, which is beneficial to improve electron transfer and material structure.

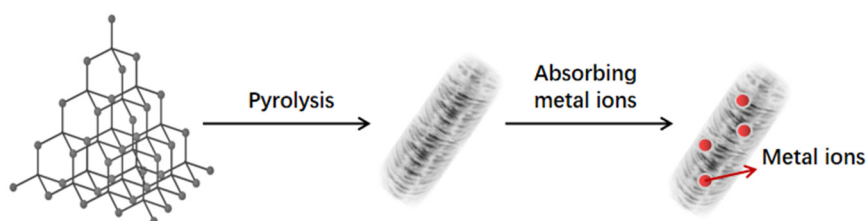


Figure 3: Schematic illustration of the preparation of mesoporous metal-organic framework materials.

The currently reported strategy is to select suitable MOFs. The organic ligand of the template contains amino groups and the metal center is Al^{3+} . After high-temperature pyrolysis, the carbon support of the MOFs can be obtained. The aluminum catalyst carrier should be pyrolyzed into a carbon skeleton at high temperature, immersed in Fe (II)-phenanthroline solution, then removed and dried after adsorbing iron atoms, and then pyrolyzed again to obtain zero-valent iron atoms.

3.3 Electrochemical Properties

First, we used cyclic voltammetry to evaluate the electrochemical performances of $Fe-S_1N_3$, $Cu-S_1N_3$, $Mn-S_1N_3$, $Cu-P_1N_3$, $Fe-P_1N_3$ and $Mn-P_1N_3$. The onset potential, half-wave potential, and maximum limited current are three important indicators for ORR. We expect that we could select the best electrochemical performances of ORR catalysts from the small library of $Fe-S_1N_3$, $Cu-S_1N_3$, $Mn-S_1N_3$, $Cu-P_1N_3$, $Fe-P_1N_3$ and $Mn-P_1N_3$ single-atom solid catalysts based on the indicators of onset potential, half-wave potential, and maximum limited current. We would pay much attention to the overpotential of ORR. This indicator is highly related with the voltage efficiency of fuel cells. To overcome the potential differences of ORR thermodynamically controlled values and experimentally measured values, the single-atom solid electrocatalysts were decorated on the cathode electrode. The as-synthesized novel $Fe-S_1N_3$, $Cu-S_1N_3$, $Mn-S_1N_3$, $Cu-P_1N_3$, $Fe-P_1N_3$ and $Mn-P_1N_3$ single-atom solid catalysts could reduce the Gibbs free energy greatly. As a result, the onset potential and half-wave potential would be reduced as well as maximum limited current would be increased. More heat loss would be avoided due to the excellent ORR performance in the fuel cells.

To explore the electrical properties of $Fe-S_1N_3$, $Cu-S_1N_3$, $Mn-S_1N_3$, $Cu-P_1N_3$, $Fe-P_1N_3$ and $Mn-P_1N_3$ single-atom solid catalysts, we also plan to use electrochemical impedance measurements. The proposed equivalent circuits would support the analysis of nanostructured materials and be expected to be in line with a series of materials charac-

terizations. (Small, 2017) We would pay much attention to the value of charge-transfer resistance. If the $Fe-S_1N_3$, $Cu-S_1N_3$, $Mn-S_1N_3$, $Cu-P_1N_3$, $Fe-P_1N_3$ and $Mn-P_1N_3$ single-atom solid catalysts have an excellent electrochemical performance, the value of charge-transfer resistance fitting from a proposed equivalent circuit would be reduced greatly. Since the oxygen has a faster diffusion rate, the diffusion-related parameters would be analyzed in our research.

The schematic Zinc air fuel cells are exhibited in the Fig. 4. The zinc-air fuel cells get the energy via zinc oxidation of oxygen in the air. The oxygen reduction reaction is the rate-limiting step. The as-synthesized asymmetric single-atom electrocatalysts would boost this reaction rate, as a result, the zinc-air battery based on asymmetric single-atom electrocatalysts is expected to get better performances. (Chen, 2018) Many advanced studies have been explored in the Zinc-air fuel cells. For example, in recent Science paper, non-alkaline rechargeable zinc air Batteries was reported. The stable circulation in air could persist for 1600 hours amazingly. (Sun, 2021) For the first time, a new non-alkaline rechargeable zinc-air battery was reported, and the reaction mechanism of reversible generation and degradation based on zinc peroxide (ZnO_2) was successfully analyzed.

There is no doubt that this breakthrough work not only provides new understanding and research ideas for the subsequent development of highly reversible secondary metal-air batteries. However, in addition to the excitement, there is a question worth wondering: Has the problem of zinc-air batteries really been solved? The answer is negative. In addition to problems such as electrolyte evaporation and dendrite growth, another issue that requires the most attention is the charge-discharge rate. This work takes up to 20 hours for a charge-discharge cycle. So, we would select our as-synthesized $Fe-S_1N_3$, $Cu-S_1N_3$, $Mn-S_1N_3$, $Cu-P_1N_3$, $Fe-P_1N_3$ and $Mn-P_1N_3$ single-atom solid catalysts based on the time of the stable circulation in air. Since the interaction of single atoms and carbon support is coordination bond. This kind of chemical bond has a much better stability than the metal bond that traditional nanoparticles have. In

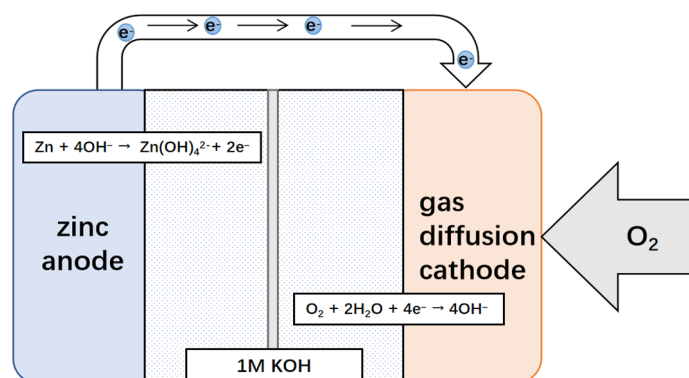


Figure 4: Zinc–air fuel cells.

the addition, the as-synthesized carbon support based on MOF templates has the porous and conductive nanostructures. The reliable stability of carbon supports is also expected in the stability testing of Zinc air fuel cells.

3.4 Applications and Comparisons

The search for high-performance ORR reaction catalysts is the "Holy Grail" catalyst for electrochemical energy conversion devices. (Mohamed Fathi Sanad, 2021) In catalytic reactions, it is generally believed that the electronic properties of the catalyst determine how the reactants and intermediates bind to the catalyst surface. Density functional theory (DFT) calculations show that the single-atom catalyst can effectively activate and dissociate the O-O bond, reducing the energy barrier of O-O bond breaking and improving the ORR activity. In addition, the DFT calculations would provide plenty of information about the energy of adsorption and desorption. DFT calculations would give us scientific guidance about the ORR catalysts design and preparation. (Shang, 2020) Since the Fe-S₁N₃, Cu-S₁N₃, Mn-S₁N₃, Cu-P₁N₃, Fe-P₁N₃ and Mn-P₁N₃ single-atom solid catalysts have different metal centers and ligands, make quantitative analysis of oxygen adsorption and desorption would inspire us the design of more variety of asymmetric single-atom catalysts.

Single atom catalysts (SACs) have a high utilization rate of metal active center and adjustable coordination structure. However, because of the lack of group sites connected by multiple atoms, single atom sites are difficult to be used in complex and multi-step catalytic reactions. (Xie, 2021) For example, monatomic Pt catalyst in THE ORR catalytic process, isolated Pt atom cannot destroy the O-O bond through lateral adsorption, so it is difficult

for monatomic Pt catalyst to effectively catalyze ORR by four-electron mechanism.

There are literature reports on the synthesis of Cu-Co bimetallic ORR catalysts via Cu-Co MOFs. (Mohamed Fathi Sanad, 2021) Through XPS analysis and DFT calculations, we demonstrate the forceful electronic coupling between Cu-Co, which triggers an efficient electron transfer process, and it is the key to achieving high-performance ORR-active catalysis.

The synthesis process of Co-Cu bimetallic metal-organic framework is based on a low-temperature hydrothermal method. (Mohamed Fathi Sanad, 2021) The catalytic activity is superior to that of the noble metal Pt in alkaline environments because of the specific electronic collaboration existing in the Co-Cu bimetallic center in the MOF. (Mohamed Fathi Sanad, 2021)

In addition, the common products of ORR reactions are H₂O, which is a four-electron reaction product of oxygen reduction reaction, and H₂O₂, which is a two-electron product of oxygen reduction reaction. So, we need to analyze the products of ORR carefully. We should avoid the generation of H₂O₂ in the ORR based on the design and selection of Fe-S₁N₃, Cu-S₁N₃, Mn-S₁N₃, Cu-P₁N₃, Fe-P₁N₃ and Mn-P₁N₃ single-atom solid catalysts. Because the H₂O₂ product would make the maximum limiting current become much smaller and H₂O₂ product has the oxidative activity that would damage the fuel cells devices if we want to pursue an actual application with a long time duration.

4 CONCLUSIONS AND PERSPECTIVES

There are main challenges in the synthesis of single-atom catalysts and their application in energy: (1) There are many kinds of MOFs, but only a few (ZIF-

8, ZIF-67, MIL-101-NH₂, and UiO-66-NH₂) can synthesize SAC, and the catalytic active sites are limited to Fe, Co, Ni, Cu, Mn, W, so looking forward to exploring more types of MOFs with metal active sites. (Shang, 2020) (2) Usually, the metal content of SAC is very low because to prevent the formation of metal agglomerates, it is necessary to increase the metal content under the premise of preventing metal agglomeration. (3) There is still a lack of methods for regulating the shape of catalyst nanometers. (4) The in-depth analysis based on DFT calculations for asymmetrical single-atom catalysts still need to be explored and provide more specific information for asymmetrical single-atom catalysts design. (5) There are many works should be explored about the evaluation of fuel cells in real applications.

It's worth noting that in situ X-ray absorption spectroscopy and situ electron microscopy provide powerful tools for studying the catalytic mechanism behind SAC in recent years. In one aspect, we expect the commercial applications of fuel cells in the near future if the low-cost, abundant, high active ORR catalysts can be acquired easily. This would boost the transitions of global energy structures from fossil energy domination. Many key climate issues would also be solved due to this advancement. In the other aspect, exploration of many advanced instruments for ORR catalysts analysis is highly desirable in the next few years. This would help us know the underlying scientific mechanism and ensure the sustainability of technology developments.

REFERENCES

- Benítez, A., Amaro-Gahete, J., Esquivel, D, et al. MIL-88A Metal-organic Framework as a Stable Sulfur-host Cathode for Long-cycle Li-s Batteries. *Nanomaterials* 2020, 10, 424.
- Huishan Shang, Xiangyi Zhou, Juncai Dong, et al. Engineering unsymmetrically coordinated Cu-S1N3 single atom sites with enhanced oxygen reduction activity. *Nature Communications* 2020, 11, 1-11.
- Haolin Tang, Shichang Cai, Shilei Xie, et al. Metal-organic-framework-derived Dual Metal- and Nitrogen-doped Carbon as Efficient and Robust Oxygen Reduction Reaction Catalysts for Microbial Fuel Cells. *Advanced Science* 2016, 3 1500265
- Mohamed Fathi Sanad, Alain R. Puente Santiago, Sarah A. Tolba, et al. Co-Cu bimetallic metal organic framework catalyst outperforms the Pt/C benchmark for oxygen reduction. *Journal of the American Chemical Society*, 2021, 143, 4064-4073.
- Small, Leo J, Tina M. Nenoff. Direct Electrical Detection of Iodine Gas by a Novel Metal-Organic-Framework-

- Based Sensor. *ACS applied materials & interfaces*, 2017, 9, 44649-44655.
- Sun Wei, Fei Wang, Bao Zhang, et al. A rechargeable zinc-air battery based on zinc peroxide chemistry. *Science* 2021, 371, 46-51.
- Tingting Sun, Lianbin Xu, Dingsheng Wang, et al. Metal organic frameworks derived single atom catalysts for electrocatalytic energy conversion. *Nano Research*, 2019, 12, 2067-2080.
- Xiaoying Xie, Lishan Peng, Hongzhou Yang, et al. MIL-101-derived mesoporous carbon supporting highly exposed Fe single-atom sites as efficient oxygen reduction reaction catalysts. *Advanced Materials*, 2021, 33, 2101038.
- Yuanjun Chen, Shufang Ji, Shu Zhao, et al. Enhanced oxygen reduction with single-atomic-site iron catalysts for a zinc-air battery and hydrogen-air fuel cell. *Nature Communications* 2018, 9, 5422.
- Yazhou Zhou, Xiafang Tao, Guangbo Chen, et al. Multilayer Stabilization for Fabricating High-loading Single-atom Catalysts. *Nature Communications* 2020, 11.