Plasma Preparation and Modification of Multi-Component High Polymer Molecular Nanocomposites

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Abstract. Low-temperature plasma belongs to non-thermal equilibrium plasma, which has higher electron temperature and lower gas temperature, so it is a new method for preparation and modification of nano-catalysts. Low temperature plasma has attracted wide attention in the preparation and modification of nano-catalytic materials because of its high efficiency, environmental friendliness and easy functionalization of materials. It shows outstanding advantages in the unconventional preparation, doping, defect and vacancy manufacture of nano-catalytic materials, so it is widely used in the preparation and modification of all kinds of catalysts. This paper mainly reviews the research progress of low temperature plasma in the preparation and modification of oxygen reduction, oxygen evolution, hydrogen evolution and fuel oxidation catalysts, and expounds the reasons for the performance improvement of these catalysts from different angles. The challenges of low temperature plasma in the preparation and modification of nanocatalysts are summarized, such as relatively high cost, reactor amplification, material controllable preparation and so on. Finally, the development trend of plasma preparation and modification of nanocatalysts is predicted.

Keywords: Plasma preparation, multi-component, molecular nanocomposites, chemical modification.

1. Introduction
In recent years, the continuous consumption of traditional fossil fuels has led to increasing environmental pollution, so it is urgent to develop an environmentally friendly, low-cost and efficient energy conversion and storage system. Electrochemical energy conversion and storage technology is expected to become the next generation of energy storage devices because of its environmental protection, high efficiency and stability, so as to reduce people's dependence on fossil fuels. The new generation of electrochemical devices such as fuel cell and air cell are of great significance in these renewable energy source technologies. However, catalysts play a key role in the rational design and improvement of fuel cells and air cells. Efficient synthesis and surface modification of nanomaterials are important means to prepare high efficiency catalysts. Low-temperature plasma technology has attracted wide attention in the efficient synthesis and modification of nanomaterials because of its high efficiency, unconventional preparation, strong functionalization, environment-friendly and so on.
Plasma is an ionized gaseous substance composed of atoms deprived of electrons and positive and negative ions produced by ionization of atomic groups [1]. When sufficient energy is provided to induce the collision between ions and electrons, plasma can be generated by ionizing gas [2], and the isoionon body must meet several conditions before it can be called plasma. First of all, the plasma as a whole is quasi-electrically neutral, which means that the total charge of electrons and ions in the isoionic body is equal; secondly, the main external effect of plasma is the collective effect. The so-called collective effect means that there is a long-range Coulomb force between charged particles in plasma. The motion of a single charged particle is affected by many other charged particles, and it can produce electromagnetic field and affect the motion of other charged particles. The particles in low temperature plasma mainly include electrons and positive ions. Compared with positive ions, electrons move faster and have less mass, so it is easy to form a strong electric field on the surface of the material. The electric field has three main functions: first, the electrons gather around the nanomaterials to repel each other, avoiding the agglomeration of the nanoparticles, thus improving the dispersion of the particles; secondly, the electrons form a strong electric field on the surface of the catalyst, which can make the nanoparticles exist as a hemispherical on the carrier, thus enhancing the interaction between the metal and the carrier. Finally, electropositive and electronegative carriers can be used in the preparation of the catalyst, which expands the application range of raw materials. In the traditional thermochemical reduction method, due to the influence of surface free energy, metal nanoparticles are easy to agglomerate and distribute on the outer surface of the catalyst at high temperature for a long time. In low temperature plasma, the dispersion of metal nanoparticles on the inner and outer surface of the catalyst is mainly affected by the Coulomb force between electrons and metal precursor ions in the plasma.

Compared with the traditional high temperature calcination / reduction method, low temperature plasma has the advantages of operation at room temperature, non-equilibrium property and low power, which can solve the problems of grain aggregation, sublimation and structure collapse in the preparation process of traditional methods. To realize the unconventional preparation of materials. In addition, low temperature plasmas also show great advantages in modifying nanomaterials: (1) the energy generated by low temperature plasma is low, so the modified nanomaterials only occur on the surface of the materials. Without affecting the inherent characteristics and structure of the material; (2) the action time of low temperature plasma is short and the reaction efficiency is high. (3) the catalytic active sites of the materials can be improved by etching, doping, increasing defects and creating vacancies by low temperature plasma. Therefore, low temperature plasma technology has a strong application potential in the synthesis and modification of nano-catalyst materials. In this paper, the research progress in the preparation and modification of nano-catalyst materials by low-temperature plasma is reviewed.

2. Monomer plasma system

2.1. Brief Introduction of Plasma
The first time that human beings had a systematic understanding of plasma was that Faraday was observing the glow discharge of gas in the 1930s, and then in 1879, the British physicist Crooks proposed the fourth form of matter after studying vacuum discharge. This fourth form is different from the traditional understanding of the three states of matter: solid, liquid and gaseous, but a kind of ionized matter. A plasma is a gas body in an ionized state. Its English name is plasma, which was named by American scientist Langmuir when he studied the discharge phenomenon in mercury vapor at low pressure in 1927. After a period of time, it slowly developed into an independent subject, mainly studying celestial plasma, near-earth ionospheric space plasma and artificial plasma in the laboratory.

The methods of generating plasma usually include flame, microwave, discharge and shock. Low temperature plasma technology is considered to be an efficient tool for preparing and modifying materials based on high electron temperature and low gas temperature [3]. This method is environmentally friendly, can modify the surface of solid materials without changing the original properties of materials [4], and can efficiently prepare nanomaterials with narrow particle size
distribution, and can also lead to thermodynamically impracticable reactions. To achieve unconventional preparation, the process of plasma functionalization on the monomer surface is shown in Figure 1.

2.2. Classification of Plasma
Plasma is divided into high temperature plasma and low temperature plasma. Among them, almost all the components in the high temperature plasma are in thermal equilibrium, which is usually used for thermonuclear fusion power generation. Electrons, ions, atoms and molecules in low-temperature plasmas are not in thermal equilibrium, so they are also called non-thermal plasmas [5,6]. Their electron temperatures can reach 10000 ~ 100000 K (1 ~ 10 eV), so they are mostly used in material synthesis and processing. Low temperature plasma has been widely used in the preparation and modification of various catalysts because of its non-equilibrium properties, low power requirements and its ability to induce physical and chemical reactions at relatively low temperatures. Based on the mechanism of low-temperature plasma generation, the applied pressure and the geometry of the electrode, low-temperature plasma is divided into glow discharge, corona discharge, dielectric barrier discharge (DBD), radio frequency discharge (RF) and microwave discharge. The principles of these plasma discharges and their applications in the field of material preparation and modification are introduced below.

Figure 1. The process of plasma functionalization on the monomer surface

2.3. Surface Modification by Plasma Technology
The poor hydrophilicity of polymer surface and the lack of natural recognition sites limit its application in the field of bone tissue engineering. Surface modification technology can effectively change the surface properties of materials, such as roughness, morphology, charge, chemical composition, surface energy and wettability, and then effectively promote the interaction between polymer and tissue. Active substances in plasma, such as free radicals, ions, excited atoms, molecules and electromagnetic radiation, inactivate microorganisms and viruses without damaging the material itself as shown in Figure 2. And it can activate the material surface without the use of chemical solvents or produce toxic waste to increase its biocompatibility. In addition, when the surface of the modified material is subjected to higher energy, chain breakage will occur, and new chemical configurations and chemical functions will be formed through covalent bonds, which can further promote the interaction between the material and the host, enhance cell adhesion and proliferation, and improve the biological activity of the material.
3. The importance of surface properties of polymers in reactions

3.1. Improving the Biocompatibility of Polymers

There are two main ways to improve the biocompatibility of polymers by plasma modification: one is to improve the surface hydrophilicity of materials by plasma modification, to introduce active groups, to increase the surface roughness of materials, and to change the surface charge. It found that the biomaterials had no adhesion when the surface energy was 20 ~ 30 mJ/m$^2$, but had good adhesion characteristics when the surface energy was 40 ~ 70 mJ/m$^2$. Through the introduction of carboxyl (-COOH), peroxides, hydroxy (-OH), amino (-NH$_3$) groups and polar substances on the polymer surface, plasma causes the rearrangement of polar groups and the surface migration of non-polar groups, increases the surface energy of materials, promotes the contact reaction of body fluid and blood and the adhesion and fixation of cells. After plasma etching, the polymer material forms a micron to nanometer groove-like rough surface, and the cells spread, arrange and migrate along the rough surface after contact. This phenomenon is called "contact guidance", that is, the cellular integrin receptor transfers the change of tension or pressure to the cytoskeleton according to the different surface morphology, and the cellular stretch receptor activates the reconstituted cytoskeleton after bearing the change of force. This leads to a series of biological effects and the change of surface free energy due to the destruction of the surface structure of the material. Synergistic effect on cell adhesion and migration.

3.2. Characteristics of Plasma properties

The effect of different rough surfaces on cells also depends on the cell type, material composition and the interaction between the two. Studies have shown that surface grooves (depth 0.5 ~ 1 μm, width 1 ~ 10 μm) can effectively increase alkaline phosphatase activity and accelerate extracellular matrix mineralization in bone marrow cells of powerful rats. In addition, the surface of the material treated by plasma can produce widely distributed anions and cations, functional groups, free radicals and so on. Cations promote protein adhesion through electrostatic interactions, and anions combine with calcium ions to promote extracellular matrix mineralization. In order to further increase the specificity of the reaction, hydroxyl, carboxyl, amino and other reaction groups were introduced as coupling sites on the surface of the material, and covalent ligand was connected by chemical grafting and coating technology. For example, adhesion proteins can promote cell adhesion through ligand-receptor interaction, and growth factors regulate cell proliferation and differentiation. Hydrophilic polymers and biological macromolecules were introduced for non-covalent modification, and electrostatic self-assembly coatings were formed based on the alternating deposition of polyanions and polycations with opposite charges, and cell adhesion was controlled by polyelectrolyte multilayers. In addition, hydroxyapatite, as the main mineral component of bone matrix, plays an important role in bone tissue regeneration in the process of bone repair. After surface modification of polymer with isoionic body, it is infiltrated into
simulated body fluid to induce calcium phosphate deposition. The formed biomimetic apatite coating has been proved to provide good bone conductivity and bone induction.

4. Experimental Results and Analysis

4.1. Vacancy of Atoms Produced by Plasma

Compared with the traditional hydrogen production by steam methane reforming, electrochemical water cracking is more renewable and environment-friendly. However, like other electrochemical reactions, low-cost, stable and durable catalysts are needed to improve reaction efficiency and reduce energy consumption. Therefore, various transition metal compounds such as molybdenum sulfide, molybdenum carbide and cobalt phosphide have been used as substitutes for their catalysts. Both experimental and theoretical studies show that although the edge of monomers is its electrocatalytic active center, its surface is still catalytic laziness. Therefore, more active molecular weight can be increased on the group 2 by modifying its surface as shown in Figure 3.

4.2. Polymerization Effect

Low-temperature plasma is a fast, simple, efficient and environment-friendly new technology for the preparation and modification of nanomaterials, which can not only obtain nano-catalysts with special structure which can not be obtained by traditional methods. High-performance catalysts can also be modified by manufacturing material vacancies and surface defects. This paper briefly introduces the development and classification of low-temperature plasma, and summarizes the applications of low-temperature plasma technology in the synthesis, heteroatom doping, defect and vacancy manufacture of ORR, OER, HER and FOR reaction catalysts in recent years, which provides a new idea for the preparation and performance improvement of nano-catalysts. For different size nano-particles, the degree of polymerization could be different. As shown in Figure 4 (a), when the size is 43nm, the polymerization could be largest.

![Figure 3. Molecular weight changes with reactive time](image-url)
As a new technology, low temperature plasma technology also faces some challenges in material preparation and modification: 1) Plasma energy consumption mainly comes from discharge power and gas cost, which is a relatively expensive technology, which also limits its large-scale application in industry. Therefore, it is necessary to deeply study and develop relatively simple and low energy consumption plasma equipment. 2) At present, the processing capacity of the existing low temperature plasma equipment is generally at the gram level. When the polymerization degree is 5.35, the performance could be the best, as shown in Figure 4 (b). In order to realize industrialization, the problem of equipment amplification needs to be solved urgently. 3) At present, low-temperature plasma still focuses on the expansion of application in material preparation, but the plasma discharge process is more complex, and the mechanism of interaction between plasma and materials is not clear. It is urgent for scholars in the fields of physics, chemistry and materials to work together to study the active species and physical parameters in low-temperature plasma. The controllable preparation of nanomaterials can be realized by adjusting the particle size, dispersion, structure and morphology of the materials.

Figure 4. Effect of polymerization degree
5. Conclusion

For the preparation and modification of nanocatalysts by low temperature plasma technology, it should give full play to its advantages, improve the existing problems and realize technological innovation and development. The future development directions are as follows: 1) monoatomic catalysts are the current research hotspot and the development direction of catalysts in the future. The use of low-temperature plasma-assisted synthesis and improvement of the performance of monoatomic metal catalysts to achieve high loading and high stability of metal monomer catalysts is an important development direction of low-temperature plasma in the future. 2) in recent years, density functional theory ((DFT)), machine learning and other means have made obvious progress in material design, synthesis, simulation and so on. Screening the catalyst system through the above advanced calculation and simulation methods, assisted by low-temperature plasma preparation, will effectively improve the performance of the catalyst. It is believed that with the continuous efforts of researchers, plasma technology will give full play to its unique advantages and continue to expand its application fields.

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