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Preparation of Chlorella-based Phosphide Catalysts and Their Improvement of HER Performance

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Abstract

Hydrogen evolution reaction (HER) is a core technology for achieving green hydrogen production, and the development of low-cost, highly active catalysts is key to its industrialization. Transition metal phosphides (TMPs) have emerged as an important alternative to precious metal catalysts due to their superior catalytic performance and significantly lower cost. This study uses chlorella, an environmentally friendly biomass, as raw material to prepare phosphide catalysts. chlorella not only provides carbon and phosphorus sources for catalyst synthesis but also regulates the pore structure and morphology of the catalyst surface through its natural spherical structure, optimizing the distribution of active sites. The study systematically analyzed the catalytic mechanism of phosphides in the HER, including electron transfer pathways, the role of active sites, and the influence of surface reconstruction, while also highlighting the advantages of chlorella as a raw material in terms of composition and synthesis process. The results indicate that phosphide catalysts constructed using chlorella significantly enhance HER catalytic activity by improving the adsorption capacity for the reaction intermediate H* and electron conduction efficiency, providing new insights for the design of biomass-based high-efficiency hydrogen evolution catalysts.

Keywords: hydrogenolysis evolution reaction, chlorella-based phosphide catalyst, catalytic activity, biomass-derived catalyst, electron transfer, surface reconstruction

1. Introduction

Hydrogen energy has garnered significant attention and sustained research in recent years. Not only does it offer high energy release efficiency, but it is also clean and harmless, significantly reducing the emission of greenhouse gases and harmful substances compared to fossil fuels. With the increasing demand for low-carbon emissions, the pursuit of sustainable energy has driven the rapid development of water electrolysis technology for hydrogen production. Platinum (Pt), as one of the most widely used metal hydrogen evolution catalysts, has a potential close to zero and can catalyze hydrogen evolution with extremely high efficiency. However, as a precious metal material, it has high development costs and technical challenges, making it unsuitable as a sustainable catalyst material. Therefore, developing a low-cost, abundant hydrogen evolution catalyst holds significant importance.

Traditional fossil fuels are becoming increasingly depleted. Microorganisms in nature serve as a renewable biomass resource, with their surfaces rich in organic functional groups that provide numerous nucleation sites for interacting with metal ions. chlorella, as an autotrophic microorganism, is widely distributed in nature. It can produce oxygen and hydrogen through photosynthesis and convert inorganic substances into organic ones. It is commonly used to improve water quality. Its simple preparation method, low acquisition cost, and ease of cultivation make it a potential catalyst material. Research indicates that chlorella can accumulate phosphorus elements in aquatic environments, providing multiple surface binding sites for metal ions, which can cause corrosion of metal surfaces in aquatic environments. This offers a new approach for transition metal catalyst raw materials applicable to HER.

2. Catalytic Mechanism of Phosphide Materials in HER

2.1 Electron Transfer and Reaction Intermediates in the HER Process

Hydrogen evolution reaction (HER)[1] is an environmentally friendly and efficient method of energy production. Under suitable conditions, it can produce high-purity hydrogen from water or aqueous solutions without emitting

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pollutants. HER is the cathodic half-reaction of the entire water splitting reaction. Its chemical process primarily consists of two steps[2, 3]. The first step is carried out by the Volmer reaction, which is an electrochemical hydrogen ion adsorption process. In this process, depending on the acidity or alkalinity of the reaction solution, protons react with electrons under acidic conditions, while water molecules react with electrons under alkaline conditions. In both cases, electrons are transferred from the electrode to hydrogen ions, resulting in the formation of adsorbed hydrogen atoms H* on the electrode surface.

Under acidic conditions: $H^+ + e^- \rightarrow H^*$

Under alkaline conditions: $H2O + e^- \rightarrow H^* + OH^-$

The second step is carried out by the Heyrovsky reaction or the Tafel reaction, which is the process of molecular hydrogen formation, and both reaction pathways generally occur simultaneously. If the Heyrovsky reaction is used, depending on the acidity or alkalinity of the reaction solution, under acidic conditions, hydrogen ions in the electrolyte combine with adsorbed hydrogen atoms H* on the electrode to form hydrogen molecules, while under alkaline conditions, water molecules in the electrolyte combine with adsorbed hydrogen atoms H* on the electrode to form hydrogen molecules. In this process, electrons are carried by H* and transferred to hydrogen molecules after the reaction.

Under acidic conditions: $H^* + H^+ + e^- \rightarrow H2$

Under alkaline conditions: $H^* + H2O+e^- \rightarrow H2 + OH^-$

If the Tafel reaction occurs, two adsorbed hydrogen atoms H* directly combine to form hydrogen molecules.

$H^* + H^* \rightarrow H_2$

Throughout the HER process, H* is an indispensable reaction intermediate and serves as the electron transfer carrier. Electrons flow out from the electrode, and hydrogen ions or water molecules react with electrons to form H*, which then reacts with hydrogen ions or water molecules to produce hydrogen gas or directly forms hydrogen gas from two H* molecules.

2.2 Influence of Interface Activation Sites

The active sites on the catalyst surface are highly active regions where catalytic reactions occur, capable of adsorbing intermediates. Therefore, the number and stability of active sites directly affect the reaction rate of catalytic reactions [4, 5]. On the active sites of phosphide [6] catalysts, phosphorus atoms can easily cleave H_2 molecules and capture the reaction intermediate H* [7–9]. From a microscopic atomic structural perspective, the atomic radius of phosphorus atoms is larger than that of other atoms in the material, so phosphorus atoms typically occupy the internal space of structural units to form a triangular prism structure [10]. This unique structure not only exposes more unsaturated active sites in different phosphide combinations or types but also exhibits higher mechanical strength and stability. Additionally, phosphide materials contain not only a large number of P–M (metal) bonds but also numerous P–P bonds and M–M bonds, giving them alloy-like properties with enhanced conductivity and improved efficiency in electronic transfer [11]. In summary, the active sites on the surface of phosphide materials exhibit greater quantity, better stability, and higher electron transfer efficiency due to the trigonal prismatic structure formed by phosphorus atoms. This unique structure and properties form the foundation for the excellent stability and catalytic performance of phosphide catalysts [12].

2.3 Surface Reconstruction of Phosphide Catalysts

Surface reconstruction refers to the mechanical structural changes in the surface lattice of a catalyst during a catalytic reaction, caused by the transfer or alteration of surface atoms or molecules. Such changes may result in alterations to the number and properties of active sites on the catalyst surface, thereby affecting the progression of the catalytic reaction. On one hand, the changes in active sites caused by surface reconstruction can lead to a decrease in catalytic activity [13]. Therefore, enhancing the stability of active sites and resistance to surface reconstruction is a method to improve catalyst performance. Surface reconstruction in metal phosphide catalysts typically involves the transfer or loss of metal elements. The loss of metal elements may reduce electron transfer efficiency [14]. The presence of phosphorus (P) can enhance electron transfer, compensate for the loss of electron pathways caused by metal element loss, and strengthen the control of reconstructed surface activity to minimize catalytic activity loss due to reconstruction.

On the other hand, surface reconstruction can be utilized as a method to improve active sites and enhance the catalytic activity of catalysts [15]. Introducing electrochemical principles into the catalytic system, such as depositing a carbon coating layer on the surface of phosphide catalysts, represents an efficient catalyst optimization strategy. This method allows for precise control over the thickness of the carbon layer on the catalyst surface through electrochemical cycling, while simultaneously removing non-active carbon layers accumulated on the catalyst surface. The catalyst [16] provides electrons to the carbon layer on the surface, enabling the catalyst to tightly bond with multi-layered graphene [17]. The negatively charged carbon layer then serves as the active surface of the catalyst [15], facilitating catalytic reactions in the active site regions of the catalyst [18, 19]. The electrochemical restructuring strategy for carbon layer coating through electrochemical cycling optimizes the electronic structure of the catalyst surface interface by utilizing surface reconstruction, thereby significantly promoting the catalytic reaction.

2.4 Chemical Composition and Stoichiometric Ratio

There are numerous types of metal phosphides, with over 100 types of bimetallic phosphides already identified. [20] Different compositions yield a variety of structural, electronic, magnetic, and physicochemical properties, while varying chemical compositions and stoichiometric ratios confer significant potential for exploring the performance of metal phosphide catalysts. [21] By altering the chemical composition and stoichiometric ratios of metal phosphides, we can adjust and optimize the structure and physicochemical properties of catalysts, [22] thereby enhancing catalytic efficiency. Previous studies have extensively explored the doping of phosphide catalysts, such as single-metal doping with Fe, [23] Cu, [24] Al, [25] etc., [26] Ni and Co, [27] Ni and M, [28] Ni and Ru [29], and other multi-metal dopants, [30] Mn, [31] V, [32] W [33], and other transition metal dopants, as well as S and Mn, [34] N and Co [35], and other metal-nonmetal mixed dopants, among others. After determining the chemical composition of the phosphide, the stoichiometric ratio of different components in the catalyst is a key variable affecting catalytic performance. For example, iron phosphide has at least six possible stoichiometric ratios: Fe_4P, Fe_3P, Fe_2P, FeP, FeP_2, and FeP_4. [36] The structural and compositional differences among various iron phosphides result in variations in the surface electronic and physicochemical properties of iron phosphide-based catalysts. [37] Elemental doping has been widely demonstrated as an effective strategy to enhance the intrinsic activity of TMPs. Exogenous atoms with different electronegativities can alter the electronic structure, thereby facilitating intermediate adsorption or improving conductivity, which in turn enhances HER activity.

3. Advantages of Using Chlorella as a Raw Material for Catalyst Preparation

3.1 Advantages of Biomass Raw Material Composition

chlorella can be used as a catalyst raw material to convert unfavorable nutrient-rich biomass into useful catalyst materials, which fully demonstrates the advantages of chlorella biomass as a raw material. Eutrophication of water bodies is not uncommon, and phosphorus-enriched water bodies can cause chlorella to proliferate extensively, leading to algal blooms that pollute the water. Therefore, we can utilize the phosphorus elements enriched in chlorella biomass [38] as a phosphorus source for catalyst preparation. From this perspective, chlorella are abundant, easily accessible, highly usable, and do not occupy arable land [39, 40], ensuring a sufficient and low-cost supply of raw materials. Compared to expensive precious metal catalysts [41, 42], chlorella offer multiple advantages in terms of raw material sourcing. From another perspective, chlorella biomass has a rich composition, including proteins, lipids, inorganic salts, carbohydrates, and vitamins. Therefore, it is not merely a phosphorus source but can also serve as a source of multiple elements, providing components such as carbon sources for carbon-based structures and phosphorus sources for metal phosphide particles in catalyst preparation. Additionally, chlorella has been studied in the synthesis of other metal compound catalysts and non-metal compounds.

3.2 Advantages of Synthetic Step Design

In the traditional preparation steps for phosphide catalysts, the synthesis process of chemical phosphorus sources involves the widespread use of many toxic reagents, such as sodium hypophosphite, which has long posed high operational risks for laboratory personnel and strong pollution risks from experimental waste liquids [43]. This has also led to issues such as high synthesis costs and complex synthesis processes for chemical phosphorus sources. Using chlorella as a phosphorus source can avoid these issues. Its raw material acquisition methods are simple, and there are various processing methods available. For example, microwave-assisted pyrolysis under a carbon dioxide atmosphere [44, 45] is a rapid, clean, and efficient heating method. Furthermore, chlorella can be concentrated for processing through methods such as flocculation and sedimentation [46] before combining with the catalyst, or processed after adsorption and dispersion steps during catalyst preparation, offering high flexibility in experimental design. The spherical structure of chlorella facilitates their dispersion and arrangement during catalyst preparation and also influences the structure of metal phosphide nanoparticles [43, 47]. Furthermore, due to the presence of oxygen-containing groups on the surface of their cell walls, chlorella readily adsorb metal elements [48], making adsorption a convenient method for combining chlorella with catalysts. As shown in Figure 1, subsequent processing typically involves high-temperature calcination, which involves calcining in an inert atmosphere using equipment such as a calcination furnace to prepare porous carbon matrices [49] and phosphide metal nanoparticles on their surfaces [49, 50]. During the calcination and carbonization of microalgal biomass, the properties, pores, and shape of the catalyst surface exhibit highly controllable flexibility due to the prior arrangement of the microalgal biomass. This allows for the pre-design of active sites on the catalyst surface to achieve higher catalytic activity [43], and even enhances control over catalyst surface reconstruction.

In summary, chlorella itself can be calcined into an ideal carbon matrix, and highly dispersed metal phosphide nanoparticles can be loaded onto the carbon matrix formed, which can greatly improve the activity of the catalyst [51]. Therefore, chlorella has excellent compatibility as a raw material for phosphide catalysts. chlorella offers distinct advantages as a catalyst raw material in terms of raw material supply, component diversity, raw material processing methods, experimental procedure design, and catalyst preparation techniques. It can meet the design requirements for many low-cost, high-efficiency catalysts and is a raw material with high potential.

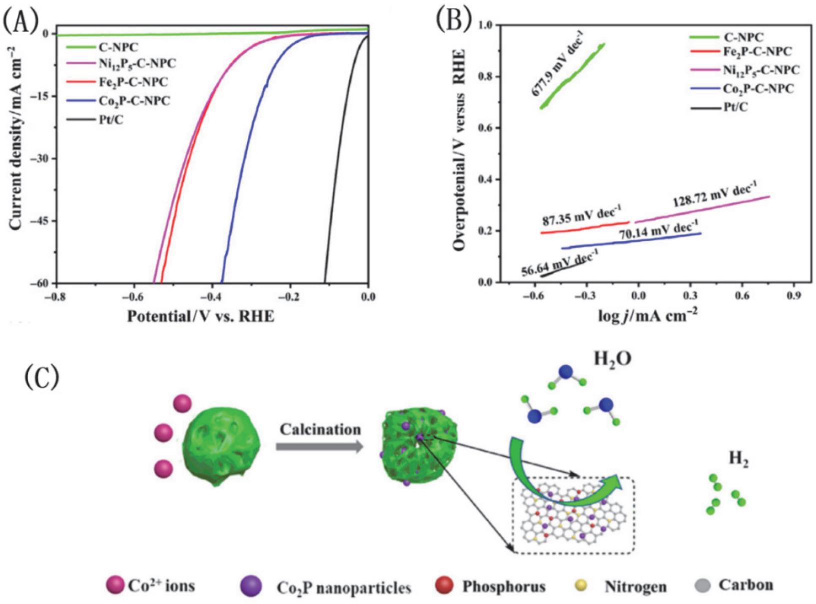

Figure 1. (A) Overpotential data table of chlorella catalyst prepared by calcination under alkaline conditions and (B) corresponding Tafel plot. [43] (C) Process flow diagram of metal phosphide prepared by calcination. [43]

4. Improvement Of HER Performance by Chlorella-Built Phosphide Catalysts

4.1 Optimization Of Catalyst Performance Through Control of Calcination Arrangement Structure

Due to the slow reaction kinetics, the HER process always requires a high overpotential [52, 53]. A low Tafel slope is one of the indicators of efficient catalytic performance. To maintain a low Tafel slope in catalytic experiments where chlorella is used to construct phosphides for HER, thereby ensuring efficient catalytic performance, it is necessary to analyze the catalyst itself. In addition to the inherent properties of phosphorus, the active structures formed by the surface arrangement of chlorella during catalyst preparation also play a significant role. As mentioned in the second major point, the phosphorus doping process in algae exhibits high flexibility, allowing for either pre-extraction or dispersion of algae on a porous carbon matrix followed by calcination. The latter approach not only utilizes the cellular mechanical structure of algae to form a carbon layer using the algae's own carbon to protect metal phosphide nanoparticles [50], thereby enhancing catalyst stability, but also allows for the arrangement of phosphorus sites on the catalyst surface, enabling structural regulation of the catalyst—particularly its active sites—to achieve the highest catalytic efficiency through the most optimal arrangement. This enables the HER to achieve the desired current density with a lower overpotential, thereby optimizing catalyst performance while reducing HER energy consumption and carbon emissions.

4.2 Performance Characteristics of the Chlorella Phosphide Catalyst System

Previous studies have explored synthetic routes using chlorella as a synthetic platform [54]. In this study, phosphorus was introduced into the system to analyze the performance of chlorella-based phosphide catalysts. chlorella's own hydrogen evolution reaction is photosynthetic hydrogen evolution. Under light conditions where phosphorus is depleted, the electron transport chain for oxygen release is hindered due to intracellular phosphorus deficiency, thereby limiting oxygen release and extending the hydrogen production stage of photosynthesis. The phosphorus element within chlorella can also serve as raw material for phosphide catalysts to catalyze the HER. Whether it is chlorella's photosynthetic hydrogen production or phosphide catalyst-catalyzed hydrogen production, phosphorus, due to its excellent electron transfer capability, bridges the gap between chlorella and hydrogen production, providing a raw material-rich, inexpensive, and efficient catalyst option for HER catalytic research. chlorella also provides a platform for efficient HER catalysis using phosphorus. On the surface of phosphide catalysts, the formation of active sites containing phosphorus requires the carbon matrix formed by chlorella calcination and metal phosphide nanoparticles to be jointly constructed, and the arrangement of active sites can be controlled by the arrangement of chlorella. Inspired by the optimization of the HER catalytic environment in chlorella, the efficiency of electron transfer determines the catalytic performance of the catalyst. Therefore, the inherent activity of the catalytic center and its high sensitivity [55, 56], as well as the influence of the catalytic environment on electron transfer in the catalytic reaction [57], are critical considerations in catalyst design. Additionally, the uniform dispersion and rational arrangement of the chlorella, combined with their high C, P, and N content, high surface area, and high porosity, have collectively led to the construction of an efficient and environmentally friendly phosphide catalyst. This catalyst enhances HER performance through improved adsorption capacity for the reaction intermediate H* and enhanced electron conduction efficiency.

5. Conclusion

This study uses chlorella as a biomass feedstock to prepare a phosphide catalyst, leveraging its natural advantages as a source of carbon and phosphorus. By regulating the spherical structure to control the pore distribution and active site distribution of the catalyst, the HER performance is significantly enhanced. Systematic studies indicate that chlorella-based phosphides, with their unique trigonal prismatic structure, abundant active sites, and surface reconstruction optimization through electrochemical regulation, enhance H* adsorption capacity and electron transfer efficiency, thereby improving HER catalytic activity.

Although research has confirmed that biomass-derived catalysts can serve as sustainable alternatives to precious metals, future efforts should focus on optimizing synthesis processes to precisely control the stoichiometric ratio and morphology of phosphide nanoparticles. Additionally, it is crucial to employ in situ characterization techniques to thoroughly investigate the dynamic surface reconstruction mechanisms during the HER process. Extending their application to neutral or seawater electrolyte systems and advancing scalable production processes will further enhance the practical application value of these environmentally friendly catalytic systems.

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