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Review

Role of Plasma in Catalyst Preparation and Modification for Oxygen Evolution Reaction

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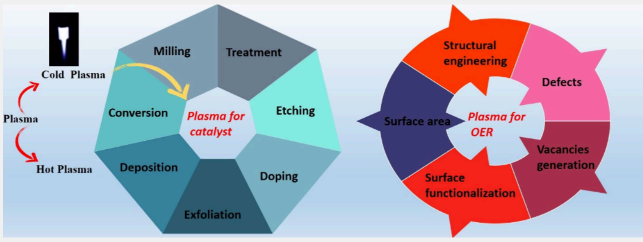
ABSTRACT: Plasma as a promising solution to catalyst synthesis and modification has received great attention in the field of electrochemical water splitting. However, a comprehensive overview detailing how plasma treatments of catalysts enhance oxygen evolution reaction (OER) performance is currently lacking. Here, we review the advances and challenges in cold plasma for catalyst preparation and modification. We discuss the underlying mechanisms responsible for enhanced OER performance on plasma-treated catalysts, where the surface area, active sites, vacancy type/content, heteroatom doping, etching, and surface functionalization could be mediated. This review aims to provide valuable insights into the role of plasma treatments in advancing OER electrocatalysis for sustainable energy applications.



KEYWORDS: *catalyst, cold plasma, plasma synthesis, vacancy generation, surface defects, oxygen evolution reaction*

1. INTRODUCTION

Hydrogen energy is environmentally friendly and highly efficient, and offers a high energy output without generating greenhouse gases or pollution, making it an ideal candidate for future power plants.[1,2] Among the various methods for large-scale hydrogen production, electrochemical water splitting stands out as an effective and environmentally friendly approach.[3] Electrochemical water splitting involves the conversion of electrical energy into chemical energy, utilizing molecular H_2 as a green energy carrier within the water cycle. The overall water-splitting process is based on the catalytic materials used.

Plasma, the fourth state of matter, is increasingly used in catalyst preparation due to its diverse applications (Figure 1) including materials fabrication,[4,5] plasma-assisted combustion[5,6] environmental applications,[5,7] plasma medicine,[4] plasma coating,[8,9] chemical conversion,[5] and plasma agriculture.[10−12] In 2002, Liu et al. provided a comprehensive summary of the use of cold plasma for catalyst preparation.[13] Since then, the treatments of catalytic materials using cold plasma have gained significant attention for their role in enhancing the OER in water splitting.[14−26] The nonthermodynamic equilibrium nature of cold plasma, where electron temperature is much greater than gas temperature, distinguishes it from conventional methods for catalytic material treatments. Cold plasma creates an incredibly active chemical environment, comprising high-energy electrons (and occasionally negative ions), positive ions, ground-state atoms and molecules, excited species, and a strong electric field.[5] This environment accelerates chemical reactions, drastically

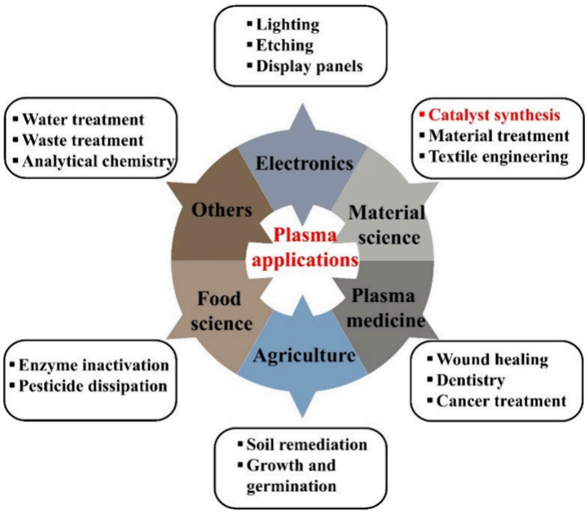


Figure 1. Applications of cold plasma across various fields, including electronics, material science, plasma medicine, agriculture and food science.

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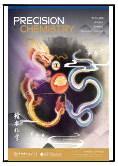

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reducing reaction times from hours to minutes or even seconds. Therefore, the utilization of cold plasma treatment has established itself as a swift, eco-conscious, and effective approach for a wide range of catalytic material processes, including reduction, etching, deposition, doping, exfoliation, milling, conversion, and modification.[27−32]

Currently, researchers in chemistry often view plasma as a black box, with limited attention given to comprehending the controllable synthesis and treatment mechanisms of plasma. In contrast, plasma physicists, lacking a background in chemistry, tend to focus primarily on the plasma discharge mechanism rather than the interaction between plasma and catalytic materials. Therefore, understanding the controllable treatment mechanisms of cold plasma for catalytic material to achieve specific outcomes remains a challenge. Review studies are found in the literature describing the role of plasma treatment in water splitting.[5,33−46] However, most of these review articles describe the positive affect of plasma treatment on catalytic material. Therefore, a detailed exploration of the underlying mechanisms responsible for the improvement in OER performance is needed.

In this review, we seek to provide a comprehensive understanding of the changes in the surface area, active sites, vacancy engineering, heteroatom doping, etching and electronic structure that contribute to the enhanced OER activity. Moreover, we present a detailed overview of both plasma and catalysts, highlighting the devices utilized for plasma treatment and various types of plasma treatments employed for catalytic materials, providing essential insights to individuals from diverse fields for a comprehensive understanding. By addressing these critical knowledge gaps, our review aims to provide valuable insights into the role of plasma treatment in advancing OER electrocatalysis for sustainable energy applications.

2. FUNDAMENTALS OF PLASMA AND CATALYSTS

Exploring plasma and catalysts involves delving into their fundamental principles, which are crucial for understanding their roles in various applications, such as electrochemical water splitting. Plasma possesses unique characteristics, while the catalysts, on the other hand, are key players in accelerating chemical reactions. Besides the basic knowledge of plasma and catalysts, understanding the basic terms and concepts commonly used in plasma and catalysis is of paramount importance when researching the incorporation of plasma treatment and electrochemistry. These fundamental definitions provide researchers and scientists with a common language and conceptual framework necessary to navigate the intricacies of this interdisciplinary field. Clarity in terminology ensures precise communication and interpretation of results, which, in turn, fosters effective collaboration and knowledge sharing among experts in plasma physics and electrochemistry. Therefore, understanding the fundamentals of plasma and catalysts is essential for researchers and scientists working on the development of water-splitting catalysts using cold plasma.

Plasma is a neutral combination of charged and uncharged particles[47] that can be produced in two ways: thermally and electrically. In the former, species obtain energy from thermal sources, while the latter involves charged species gaining energy in an electric field through continuous oscillation and collision.[47] The temperatures of electrons (T_e) and ions (T_i) serve as vital parameters in characterizing plasma. Based on the temperature, the plasma is divided into thermal/hot and nonthermal/cold plasma. In hot plasma, T_i and T_e are equal, while in cold plasma, T_i is significantly lower than T_e, indicating energetic excitation of electrons while the heavy particles retain temperatures close to room temperature. In the context of material synthesis and modification strategies based on plasma, it is crucial to discern and differentiate between the temperature of plasma, surface and bulk material.

The temperature of the plasma is the average temperature at the plasma's core. In nonthermal plasma, although T_e is relatively high, the minimal contribution of electrons, owing to their negligible mass compared to ions and neutrals, results in a plasma temperature similar to T_i but significantly lower than T_e. The temperature of the substrate's surface is referred to as surface temperature. The surface temperature of nonthermal plasma is significantly lower than T_e but slightly higher than T_i, as the energy transferred to the material surface by high-energy electrons is limited by their minimal masses. The bulk temperature is the mean temperature of the bulk material. Due to the heating effect, the bulk temperature is equal to T_i in nonthermal plasma.

The distinguishing kinetic properties of electrons and ions in thermal/hot plasma lead to reactive behavior and intense heating effects, enabling the melting and even vaporization of materials like tungsten. Consequently, thermal plasma is commonly employed in applications involving the melting of metals, ceramics sintering, and material evaporation.[47,48] Conversely, cold plasma exhibits no significant heating effects, but maintains high chemical activity, making it highly desirable for processing materials sensitive to heat or those involving sluggish reactions. Thus, nonthermal plasma has gained extensive interest in the preparation of nanomaterials.

To achieve precise modifications in plasma-induced material surfaces, careful control of processing parameters such as working gas composition, pressure, treatment time, and power is essential. Notably, the interplay between different operating parameters often yields synergistic effects, significantly impacting the final modification outcomes. Here, some important plasma parameters that influence the material modification and electrocatalytic properties are introduced for clarity.[37]

Plasma treatments, utilizing various gaseous feedstock such as Ar, O_2, N_2, H_2, H_2O, and CH_4 are commonly utilized for surface modification and material synthesis.[37,46] The introduction of heteroatom doping on the material surface can be achieved by adjusting the feedstock composition during plasma treatment. For instance, Ar/O_2 plasma has been employed to introduce controlled oxygen doping, leading to the surface restructuring of $FePSe_3$ nanosheets, which improves catalytic activity.[46] The pressure of the gas during plasma processing significantly influences the modification process. The gas pressure, correlating with the electron density, impacts the oscillation during plasma treatment. Changes in pressure have been found to increase the acceleration of gas particles and the electrical field, which can impact how electrons collide with the surface of materials. However, precise control of the gas pressure is crucial to prevent damage to the material surface.[37]

When it comes to plasma modulation, treatment duration and power are related variables. A steady condition of surface modification usually requires higher plasma generator power and shorter treatment periods. Structural damage can be avoided while limiting material surface change by carefully controlling the treatment time and power.[37] This nuanced understanding of plasma parameters and their impact on material modification underscores the importance of precise control in developing advanced catalysts for applications.

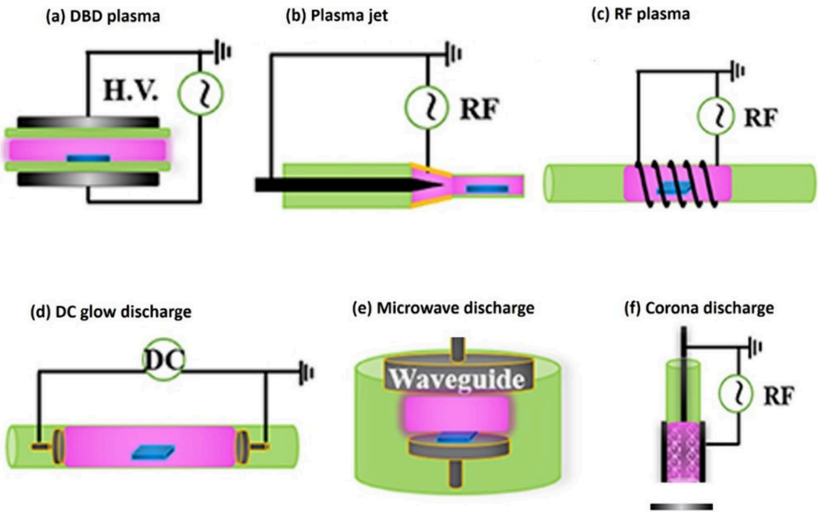

Figure 2. Different types of plasma devices are used for the catalytic materials. (a) Dielectric barrier discharge (DBD), (b) Plasma jet, (c) Radio frequency (RF) plasma, (d) DC glow plasma, (e) Microwave plasma, (f) Corona discharge. Reproduced with permission from ref 5. Copyright 2021, IOP publishing Ltd.

The inclusion of a catalyst may open up new, lower-energy reaction pathways. From a kinetic perspective, these lowered barriers can accelerate the rate of reaction, resulting in a greater degree of reagent degradation or conversion and the ability to proceed at a lower temperature. Additionally, these alternate reaction pathways can mechanistically boost the yield or selectivity of specific products, and various catalysts can be employed to achieve various outcomes.[43,49] A standard heterogeneous catalyst often comprises a metal oxide or sulfide, utilized either independently or as a backing for an active metal. More complex catalysts could use metal and oxide combinations designed to accomplish particular results or make use of microporous species like zeolites, which enable molecular size-based selectivity. In the gas phase, species continuously collide with the surface, necessitating their binding to the surface for catalysis to occur. The crux of the catalytic process lies in the strength and nature of this bonding.[43,49]

A detailed comprehension of the electronic structures of the surface and adsorbate is necessary to comprehend the bonding. Catalysts frequently use transition metals. The occupation of d-orbitals, which is dictated by the metal's location in the periodic table and the orbital structure of the adsorbate, determines the kind and strength of the bonding between the adsorbate and the metal surface. The formation enthalpies of metal hydrides and oxides are related to the enthalpies of hydrogen and oxygen adsorption on the metal surface. For example, in metals with fewer d electrons, the adsorption of CO is linked to stronger bonding, which can result in stronger chemisorption and dissociative adsorption. Metal oxides are a more widely used class of catalysts. These oxides transmit either an electron or a proton during the adsorbate binding process; hence, depending on their capacity to give or take these charged species, they are commonly referred to as acidic or basic. Metal oxides have a broad variety of work functions, which can be ascribed to many parameters such as the surface roughness of the catalyst, the size of the particles, and the existence of oxygen vacancies in the metal oxide lattice.[43]

Real catalytic surfaces differ greatly from one another, although many elementary theories of catalysis presume that the catalyst surface is homogeneous and uniform, with every site being equal. The local microstructure of the catalyst, which may include impurities, steps, edges, and vacancies of atoms or ions, is frequently responsible for its efficiency. Rates on features like steps and edges are often significantly increased. Furthermore, important are geometric effects, where some adsorbed species have a strong affinity for a specific catalytic surface.[43]

After examining the fundamental characteristics of plasma and catalyst separately, it is important to explore their potential combination and the resulting interactions. Broadly, there are two primary configurations for integrating plasma and catalyst. In the first technique, known as a one-stage plasma-catalytic system, the catalyst or a combination of catalysts is placed directly within the plasma's discharge region. Conversely, in the second arrangement, sometimes referred to as a two-stage setup, the catalytic material is placed downstream of the plasma. A multistage plasma-catalysis processing can be added to the two-stage setup, where each catalyst may target different components of the gas stream and serve different functions.[43] Introducing catalytic materials into the plasma is pivotal in shaping the plasma-catalyst interactions, influencing both the physical and chemical properties of the system.

In both one-stage and two-stage configurations, interactions between the catalyst and plasma can take on several physical and chemical shapes. The intricate and multifaceted nature of plasma-catalysis interactions is highlighted by the dynamic interplay between the catalyst's impact on discharge characteristics and the influence of plasma on the catalyst's performance.[43] The material's surface properties can be changed by interactions between ions, electrons, or photons in addition to generating reactive species above the catalyst surface. The electrical properties of the discharge can be altered by adding catalytic materials, for example, by altering the dielectric effects or changing the type of the discharge from filamentary microdischarges to surface discharges. These various interactions frequently work together to improve processing performance overall, outperforming the impacts of utilizing catalyst or plasma alone.[43] Sometimes there is a synergistic improvement in some characteristics, such as energy efficiency, selectivity or product yields. It is crucial to remember that plasma-catalysis is not always a synergistic process, however, there may be times when it is under certain circumstances.[43] Also, the reactions between active plasma species and catalyst

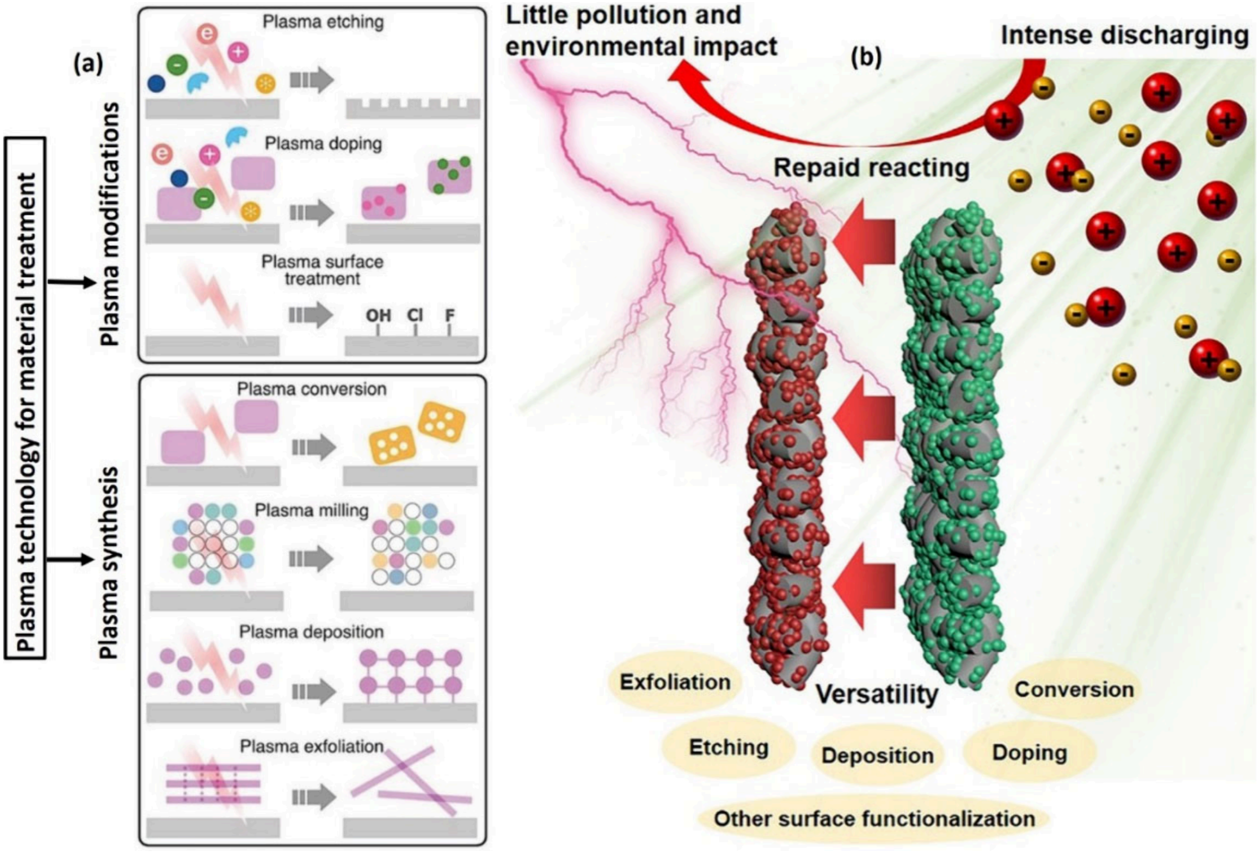

Figure 3. (a) Diagram illustrating various plasma applications in material modification and synthesis. Reproduced with permission from ref 41. Copyright 2018, Wiley. (b) Advantages of plasma surface modification of materials. Reproduced with permission from ref 34. Copyright 2022, Wiley.

precursors occur at significantly accelerated rates compared to thermal catalyst preparation methods. This leads to lightning-fast nucleation of crystals under cold plasma conditions, ensuring swift catalyst formation. Additionally, the operation of cold plasma at relatively low temperatures, such as room temperature with glow discharge, facilitates slow crystal growth. Consequently, this aids in the production of catalysts with smaller particle sizes and higher dispersion.[35]

3. DIFFERENT DEVICES USED FOR PLASMA GENERATION

In previously published review papers, various devices used for plasma generation are discussed in detail, along with their geometry and statistics.[5,33,36] The geometry of those devices varies and can be customized to meet specific needs; however, the working principle of each device remains unchanged and cannot be altered by changing the geometry (Figure 2). A quick summary of the plasma setup used in catalysis is provided below. We do not delve into the specifics of plasma generation devices here, as our primary focus is on understanding the mechanisms of plasma catalysis for OER enhancement.

3.1. Dielectric Barrier Discharge (DBD)

is a well-established atmospheric pressure (AP) plasma generation method involving a dielectric layer that separates a shield electrode from an uncovered electrode. Typically, DBD is powered by an alternating current (AC) high-voltage source operating within a frequency range of 0.05 to 500 kHz. The versatility of DBD lies in its ability to operate at AP without the need for additional gas sources or vacuum equipment, resulting in simple and portable setups. The design flexibility allows for various geometric shapes, such as flat, cylindrical, and capillary, to cater to specific applications. However, the filamentary discharge nature of DBD can sometimes lead to nonuniform surface treatment. DBD setups usually involve a combination of different electrode and dielectric materials, which can influence the discharge diffusion mechanism. Moreover, DBD has been demonstrated to improve the electrocatalytic performance of materials by promoting the formation of active sites, enhancing charge mobility, and boosting electrochemical surface area. This has resulted in advancements in a variety of applications, such as grafting, cleaning, surface modification, and hydrophilic modification of metal films, plates, and polymers.

3.2. Atmospheric Pressure Plasma Jet (APPJ)

is commonly employed to generate AP plasmas. Normally, gases such as He, Ar, O_2, H_2, N and CH_4 are used as working gases.[50] The primary applications of APPJ include material surface modification and polymerization. Notably, the utilization of APPJ enables substantial cost reductions as it eliminates the need for complex vacuum systems, rendering it an environmentally friendly and economical option. APPJ systems are well-suited for operating in open-air environments, they typically deliver relatively low energy levels compared to other plasma systems.

3.3. Glow Discharge

a well-recognized form of nonthermal plasma discharge, has found utility in plasma chemistry. This discharge, characterized by its luminous nature, is a continuous and self-sustaining DC discharge featuring a cold cathode. The emission of mostly

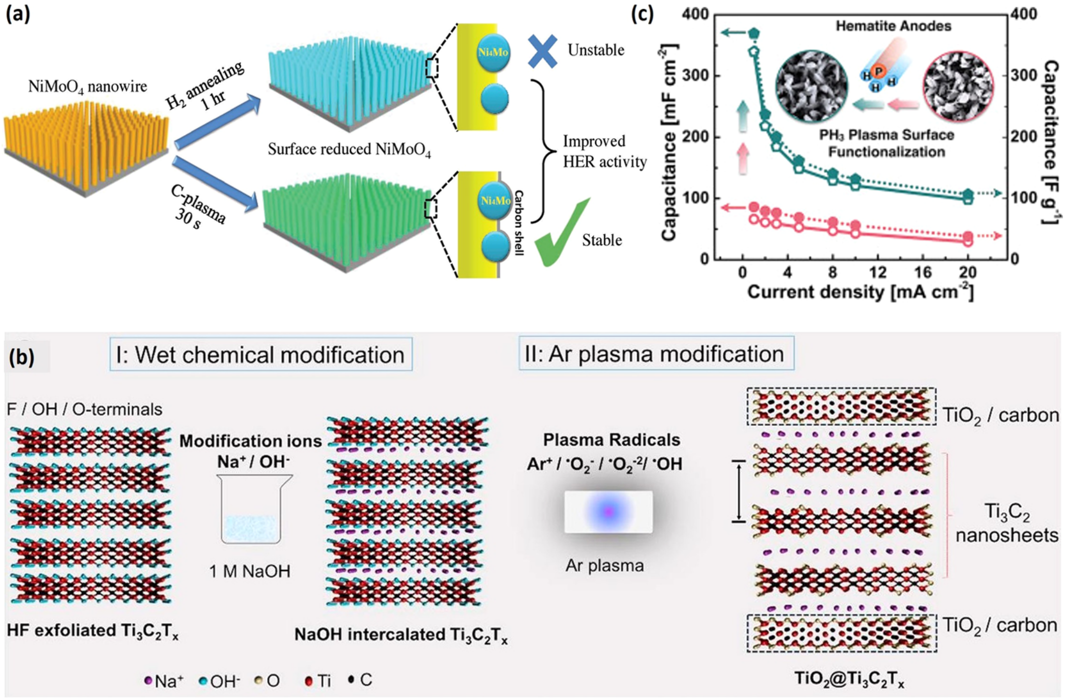

Figure 4. Demonstrates the surface alterations brought about by plasma treatment. (a) NiMoO$_4$ preparation treated with C plasma and annealed in H$_2$. Reproduced with permission from ref 52. Copyright 2018, Wiley. (b) Diagram illustrating wet chemical modification and Ar plasma modification of Ti$_3$C$_2$Tx. Reproduced with permission from ref 29. Copyright 2018, Elsevier. (c) Improved performance for the modified Fe$_2$O$_3$. Reproduced with permission from ref 27. Copyright 2018, Elsevier.

electrons results from secondary emission induced by positive ions. Typically generated in a vacuum, glow discharges occur between two electrodes enclosed in a quartz tube. These electrodes are linked to a DC power source, although an AC power source can be employed if the frequency surpasses 500 Hz to sustain the plasma.

3.4. Radio Frequency (RF)

discharge utilizes RF waves to excite the working gas, with operational frequencies typically ranging between 500 kHz and 300 MHz. RF discharge is further divided into two types (i) capacitively coupled and (ii) inductively coupled reactor. The former cannot be operated at AP due to the potential formation of an arc discharge, while the latter can be operated at AP using an RF power supply. Specific frequencies, such as 13.56 and 27 MHz, are assigned to prevent interference with radio communication systems. The plasma chamber for both setups is often composed of quartz, with the RF coils or electrodes positioned around the chamber. Inductively coupled reactors find applications in chemical synthesis, carbon nanostructure fabrication, and semiconductor growth, whereas capacitively coupled are utilized in atomizers and plasma torches.

3.5. Microwave (MW)

discharges are usually associated with high-pressure systems and are sustained by electromagnetic waves within a centimeter range. At AP, steady-state thermal MW discharges can be sustained by magnetrons operating at power levels of more than 1 kW in the gigahertz frequency range. Constant cooling of the plasma chamber is essential due to the high temperatures that can reach up to 5000 K. MW plasma reactors are used in the synthesis of metal and ceramic-based nanoparticles, waste decomposition, and methane pyrolysis, among other applications.

3.6. Corona Discharges

can produce current with up to a few microamperes of intensity. Arcing can be seen as a conductor approaches the high-voltage electrode. Round tips are chosen over conical tips to avoid voltage leakage. In a corona discharge, the electron temperature rises above 1 eV, but the gas temperature stays at ambient temperature. It finds applications in polymer treatment, precipitators, photocopying, air ionizers, and water treatment.

4. CLASSIFICATION OF PLASMA FOR CATALYTIC MATERIALS

Plasma technology applications for material treatment can be divided into two categories as shown in Figure 3a: (1) Plasma modification, and (2) Plasma synthesis.

The plasma modification method is further divided into three types: (i) plasma treatment (ii) plasma etching, and (iii) plasma doping. On the other hand, plasma synthesis includes methods like (i) plasma deposition, (ii) plasma conversion, (iii) plasma exfoliation, and (iv) plasma milling. Plasma, having high-energy particles, causes powerful chemical and physical reactions when it collides with material surfaces, affecting the local surface structures (Figure 3b). To effectively understand the enhancement of OER resulting from plasma treatment, it is crucial to first comprehend the underlying mechanisms of plasma interaction with materials. Accordingly, the following sections detail various plasma treatment and synthesis techniques.

4.1. Plasma Treatment/Cleaning

In plasma engineering, materials are generally categorized as 'plasma treated' and 'untreated' to distinguish those that have undergone plasma processing from those that have not. Therefore, researchers commonly use the term 'plasma treatment' to refer to plasma-treated materials, regardless of the specific type of plasma used. However, plasma treatment is

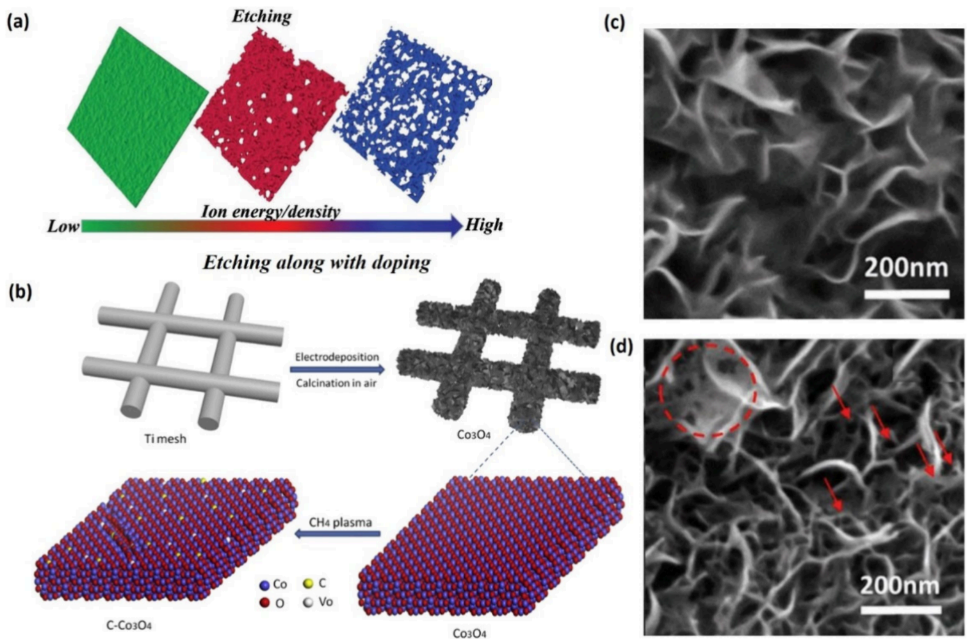

Figure 5. (a) Showing the effects of plasma etching-induced morphological modification of $MoSe_2$ nanosheets. Reproduced with permission from ref 28. Copyright 2020, Wiley. (b) Represents a method having two types of defects etching along with doping. (c) Images of $MoSe_2$ from scanning electron microscopy (SEM) at 0 W. (d) Images of $MoSe_2$ from scanning electron microscopy (SEM) at 20 W. Reproduced with permission from ref 30. Copyright 2019, Elsevier.

basically a short exposure of material to the plasma for cleaning purposes, therefore also termed as plasma cleaning. With the potential to create surface modifications that can be either temporary or permanent, plasma surface treatment/cleaning has become a popular technique to improve the efficiency of materials for energy conversion. One typical use is to apply plasma to temporarily increase the hydrophilicity of the surface, which helps in the infusion of hydrophobic catalysts and promotes the growth of materials. It is crucial to remember that prolonged aging may cause the hydrophilicity of materials treated with plasma to diminish over time. In contrast, when materials need to be oxidized or functionalized, permanent plasma treatment/cleaning becomes necessary.[27,29,51,52] For instance, in the process of reducing CO_2 to ethylene and enhancing the electrocatalytic activity of Cu, an adaptable surface oxidation method has been developed utilizing O_2 plasma.[51] Through detailed analyses, the researchers observed remarkable stability of the surface-layer oxides against reduction, even after prolonged reaction times at relatively high potentials.

Zhang and colleagues also presented that carbon RF plasma is effective in causing $NiMoO_4$ nanowires to partially reduce their surface. This results in increased electrocatalytic performance and better stability (Figure 4a).[52] The author's observation highlights the advantages of C-plasma treatment compared to conventional H_2 annealing. The protective carbon shell plays a vital role in enhancing the physical and chemical stability of the modified metal oxide, enabling exceptional performance during prolonged and intermittent operations for electrocatalytic activity.[52]

Plasma surface treatment is not only a fast but also a powerful method of surface modification, as evidenced by its comparable effectiveness to thermal treatments in increasing catalyst activity. Furthermore, as evidenced by the findings a PH_3/He RF plasma treatment effectively tunes surface properties of Fe_2O_3.[27] The authors demonstrate the complex effects of plasma activation on Fe_2O_3 as a model material. This process enhances conductivity, creates atomic-scale defects or vacancies, and increases the active surface area, resulting in significantly improved performance for modified Fe_2O_3 (Figure 4c).[27] Additionally, plasma serves as a simple and effective approach to surface functionalization. Guo et al. revealed that plasma-induced modification of surface functional groups in Ti_3C_2Tx MXene led to improved capacitive performance, increased hydrophilicity, and enhanced ion transfer at the surface (Figure 4b).[29] These examples underscore the efficacy of plasma treatment in modifying the surface properties, thereby enhancing overall material performance.

4.2. Plasma Etching

Etching occurs when the plasma-induced degradation reaction exceeds the modification effect. The exposed surface materials degrade and are removed when the material is close to the plasma. The bulk material does not change in terms of composition, chemical structure, level of polymerization, or crystallinity. The characteristics of electrocatalysts are significantly changed by plasma-induced defects, which can also affect the catalyst's structure and the movement of charges during catalysis.[28,36] Plasma treatment and etching are quite similar but differ mainly in treatment time. For short treatment durations, we refer to it as plasma treatment, and sometimes as plasma cleaning. In contrast, etching requires a longer exposure to plasma.

To examine the impact of plasma on the catalytic performance of $MoSe_2$ nanosheets, Xiao et al. performed a study wherein they etched the surfaces using Ar plasma (Figures 5a and 5b).[28] Furthermore, the catalyst's qualities may be improved in concert with the concurrent emergence of two different kinds of defects. Yan et al.[30] created vacancies and doped heteroatoms in Co_3O_4 by concurrently etching the surface of the material with CH_4 plasma and doping it with carbon (Figure 5c and 5d). By creating oxygen vacancies and Co−C bonds in Co_3O_4, these two types of defects worked in concert to boost both OER and HER

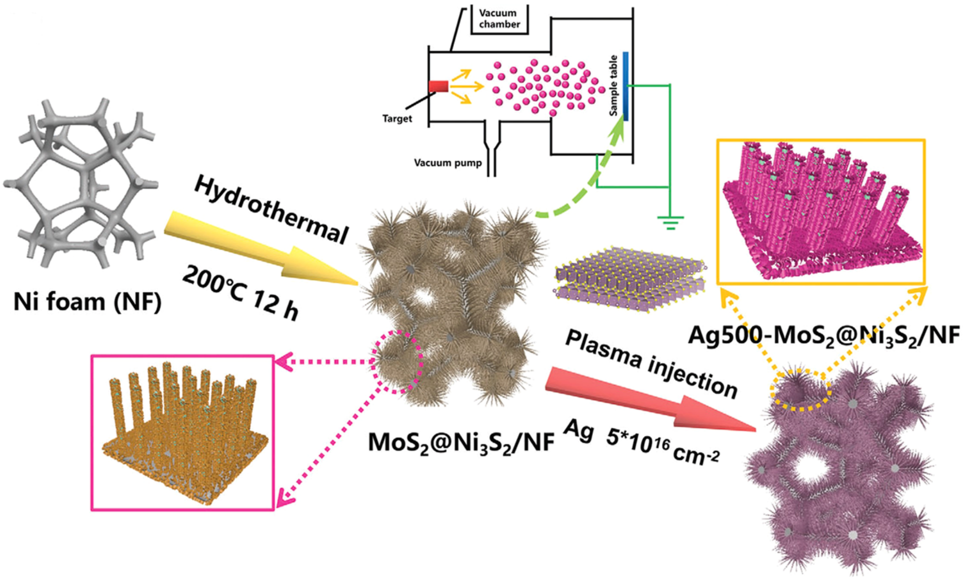

Figure 6. Depicting the plasma doping of Ag-doped $MoS_2@Ni_3S_2$/NF nanorods for improved catalytic properties. Reproduced with permission from ref 56. Copyright 2022, Wiley.

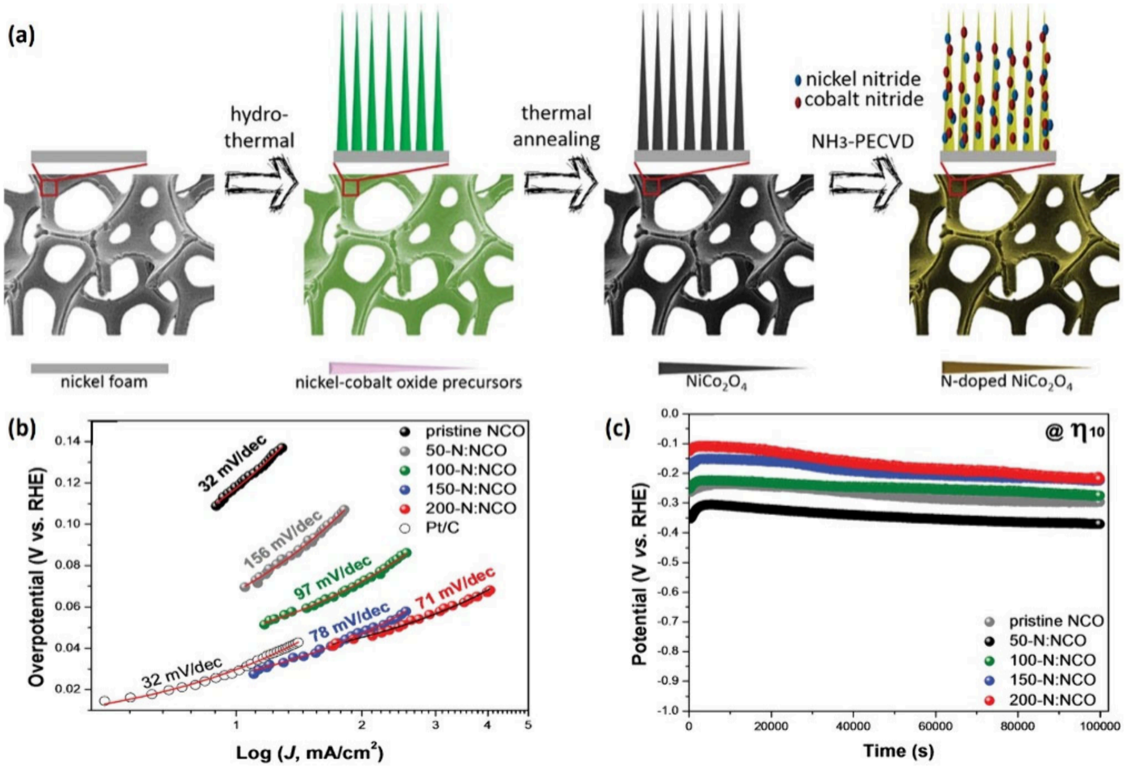

Figure 7. Electrocatalytic performance assessment of N-doped NCO electrodes. (a) The schematic diagram for the Synthesis of N-doped NCO. (b) Represents the Tafel slope of each electrode. (c) Chronoamperometry curves illustrate the long-term stability. Reproduced with permission from ref 31. Copyright 2019, Royal Society of Chemistry.

activity and the modified Co_3O_4 could serve as a bifunctional catalyst. The investigation showed that etching can raise the electrocatalytic material's active sites and electric field, which would improve H^+ adsorption, encourage electron transfer, and boost OER and HER.

4.3. Plasma Doping

Doping is the process of changing a material's or matrix's properties by adding more atoms or chemicals to it. Along with the doped heteroatoms, crystalline vacancies are produced during plasma doping. Through the control of the electrical structure and active sites, these vacancies often combine to promote catalytic activity.[34,53−55]

Elevating catalytic activity involves diminishing the binding energy between intermediates and active sites by introducing defect-rich heterometal doping. Tong et al.[56] utilized plasma to optimally incorporate Ag into $MoS_2@Ni_3S_2$ nanorods (Ag-$MoS_2@Ni_3S_2$/NF) for exceptional alkaline HER performance

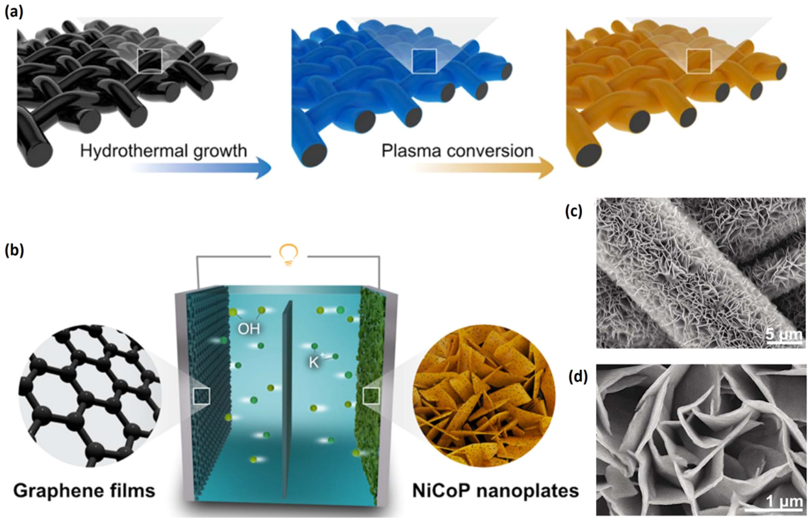

Figure 8. (a) Diagrammatic representation of the metal phosphide nanostructure conversion process. (b) The asymmetric supercapacitors are shown schematically. (c) NiCoP nanoplate images from an SEM on carbon paper substrate (d) NiCoP nanoplate images from a TEM on carbon paper substrate. Reproduced with permission from ref 58. Copyright 2017, Royal Society of Chemistry.

(Figure 6). The reduction in hydrogen adsorption energy, attributed to Ag incorporation with the S sites on the MoS_2 basal plane, preserved the two-dimensional structure while introducing a substantial number of active sites. Furthermore, plasma doping enhances electrical conductivity, increases hole mobility, and promotes ion diffusion. These features are critical to the improved overall performance of catalysts produced through plasma-induced heteroatom doping.

4.4. Plasma Deposition

One method that is frequently used for material production is plasma deposition. The two most common types of plasma deposition techniques are plasma-enhanced atomic layer deposition (PEALD) and plasma-enhanced chemical vapor deposition (PECVD).[42] Since plasma is used to generate activation energy rather than high temperatures, plasma deposition technologies use less energy than techniques like chemical vapor deposition (CVD) and atomic layer deposition (ALD). Elements like As, P, or B are doped into the materials using plasma implantation, and gases like Ar, N_2, and O_2 are typically used as sources for plasma deposition. Unlike conventional chemical synthesis methods, plasma deposition can enhance electrocatalytic performance by precisely controlling the electronic structures during synthesis.[36] For example, the OER catalyst ($NiOx@Co_3O_4/CC$) was effectively synthesized by Yang et al.[57] with strong catalytic activity by growing Co_3O_4 on carbon cloth (CC) treated with RF plasma and then using PEALD to deposit a layer of NiOx film. Moreover, Choi et al.[31] incorporated nitrogen (N) atoms into nanowire arrays of spinel nickel−cobalt oxides (NCO) using Ar gas as the carrier gas in PECVD. The introduction of Ni and Co nitrides occurred during the filling of oxygen gaps on the surface of mesoporous NCO. The results indicate that the NH_3 plasma treatment for N-doping NCO can serve as an effective approach for enhancing the electrochemical performance and stability (Figure 7b and 7c) with a schematic representation in Figure 7a.

4.5. Plasma Conversion

Plasma conversion refers to a process in which materials undergo chemical transformations or alterations under the influence of plasma. In contrast to traditional approaches, plasma recently has been used to synthesize a variety of energy-related compounds, such as transition metal nitrides, phosphides, chalcogenides, and oxides, efficiently at lower temperatures.[19,58−60] Plasma can introduce defects and porosity that are conducive to various electrochemical processes, making the use of plasma-assisted conversion routes advantageous. For example, Liang et al.[58] synthesized the metal phosphide ternary NiCoP using PH_3 plasma at significantly lower temperatures 250 °C and in 15 min (Figure 8a and 8b). NiCoP that is produced has rich defects and many porosities, but it still has the nanosheet morphology of NiCo−OH (Figures 8c and 8d). Its metallic conductivity combined with these properties makes NiCoP an extremely effective electrocatalyst for the alkaline electrolyte's OER and HER.

4.6. Plasma Exfoliation

The term "exfoliation" refers to the controlled separation of layers in a material. A developing method called plasma exfoliation is mainly employed in the synthesis of certain materials such as layered double hydroxides (LDHs) and graphene.[41] Zhou et al.[61] developed a room-temperature DBD plasma technique for synthesizing graphene from graphite oxide (GO) (Figure 9a). Plasma formation at low temperatures disrupted polar bonds in GO, releasing H_2O and CO_2, which built up pressure between layers and led to their separation. Surprisingly, after only 120 s of plasma exposure, a considerable expansion of the GO powder was detected, indicating efficient exfoliation of the GO layers. The investigation also demonstrated that the expansion and reduction of GO occurred regardless of the gas utilized, thus altering the electrochemical performance. Plasma exfoliation has several benefits over traditional exfoliation techniques. It is usually less harmful and is more efficient.[41] Moreover, surfactant usage is not necessary for the materials produced by plasma exfoliation, allowing researchers to investigate the intrinsic qualities of these exfoliated materials.

4.7. Plasma Milling

The correct structuring of electrode materials is critical for obtaining maximum performance. To regulate the multiscale structure of materials, many procedures such as hydrothermal/solvothermal treatment, etching, alloying, and ball milling have been developed.[41] Ball milling, in particular, is a popular process

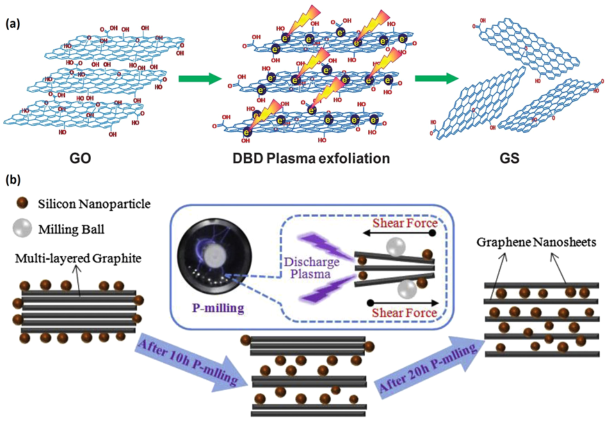

Figure 9. (a) DBD plasma exfoliation of graphite oxide (GO). Reproduced with permission from ref 61. Copyright 2012, Royal Society of Chemistry. (b) DBD plasma milling for Nano-Si/Graphene nanosheets (GNs). Reproduced with permission from ref 62. Copyright 2014, Elsevier.

for reducing particle size, changing characteristics like density and flowability, and inducing the creation of new phases or alloys. Despite its widespread use for large-scale electrode material processing due to its low cost, simplicity, and flexibility, conventional mechanical ball milling has drawbacks such as long milling times (typically tens of hours) and limited control over structure and morphology. Additionally, there is a risk of contamination from milling media and the surrounding atmosphere.[41]

Zhu et al. presented a revolutionary technique called plasma milling, which combines ball milling with DBD plasma, to improve the efficiency of conventional mechanical ball milling.[32] This combination strategy greatly speeds up processing, leading to increased effectiveness. Additionally, the combination of ball milling and DBD plasma allows for the production of unique microstructures that would be difficult to achieve with ball milling alone. Zhu et al. researched fabricating nano-Si/graphene nanosheets (nano-Si/GNs) composites using this method (Figure 9b).[62] The graphite underwent a thermal expansion due to the rapid heating caused by the plasma, which ultimately caused it to peel off and create GNs. The composite material formed by plasma milling had a significantly different morphology compared to traditional milling.

5. PLASMA STRATEGY FOR OER

The OER is essential for processes like water-splitting, yet it typically proceeds at a slow rate. Traditionally, expensive metal-based oxides have been the materials of choice due to their efficiency; however, their widespread use is constrained by high costs, limited availability, and instability under reaction conditions. To mitigate these challenges, researchers have increasingly focused on transition metal-based materials such as Ni and Co. Despite their promise, these materials exhibit low electrical conductivity and a limited number of active sites, which reduces their effectiveness for OER. Various approaches, including creating specific nanostructures and adjusting electronic structures, have been explored to improve bulk electrocatalysts. Recent studies suggest that using plasma technology is a useful approach to modify these electrocatalysts, for improved OER. Plasma treatment enhances OER activity through several mechanisms, such as increasing surface area and active sites, creating vacancies, and introducing surface defects. The details of these parameters are addressed below to properly comprehend the effect of plasma on OER.

5.1. Enhancing Surface Area for Increased Active Sites

Efficient water-splitting electrocatalysts necessitate concurrent strategies for enhancing surface area and generating active sites. Elevating the surface area is crucial, offering more reactive sites for electrochemical reactions and ensuring optimal water molecule interaction. Simultaneously, active site generation

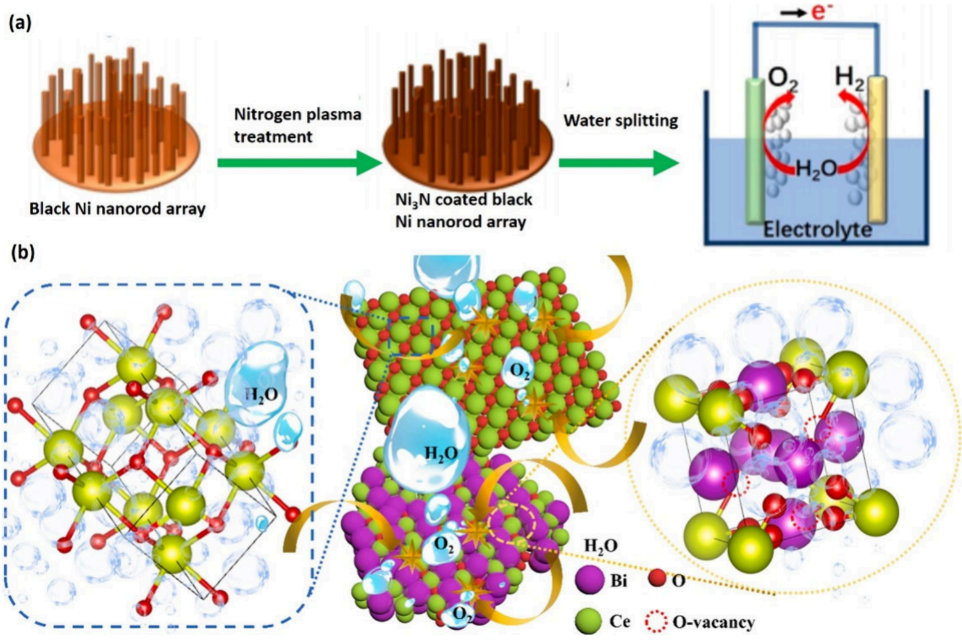

Figure 10. (a) Synthesis process for black Ni sheets. Reproduced with permission from ref 63. Copyright 2020, American Chemical Society. (b) Detailed schematics of the nanostructured oxygen vacancies in CeO_2 and $Bi@CeO_2$. Reproduced with permission from ref 67. Copyright 2022, Elsevier.

plays an important role, creating specific regions for water-splitting reactions with heightened catalytic activity and stability. This synergistic interplay between surface area optimization and active site generation contributes to superior water-splitting performance, enhancing reactivity and mass transport for sustainable electrocatalytic applications. Technique such as plasma treatment is employed to precisely induce active site formation and surface enhancement.

For example, Wang et al.[63] successfully synthesized large-scale black Ni sheets with nanorod arrays, employing an electroplating process and nitrogen plasma treatment on nanostructured silicon, (Figure 10a). This treatment led to substantial enhancements in the electrochemical performance of the resulting black Ni catalysts for OER in alkaline electrolytes. The calculated electrochemical surface area (ECSA) of the black Ni was found to be 10 times higher than that of the pristine Ni sheet, and with a 10 min nitrogen plasma treatment, the ECSA increased to 21 times that of the pristine Ni sheet, resulting in commendable electrochemical stabilities.[63] Dinh et al.[64] proposed an innovative approach combining surface engineering and cation tuning to synthesize a highly efficient two-dimensional Ni_2P electrocatalyst. By introducing vanadium into Ni_2P nanosheets and subjecting them to O_2 plasma, the authors observed enhanced surface area, improved wettability, and reduced charge transfer resistance. This oxygen plasma treatment specifically improved the catalyst's interaction with the KOH solution, leading to a decrease in the contact angle and an increase in the surface area, resulting in low overpotential for OER.[64] Additionally, Wei et al.[65] highlighted the critical importance of designing efficient bifunctional electrocatalysts for sustainable hydrogen fuel production. Leveraging the construction of multiphase interfaces, the researchers transformed Ni−Mo precursor nanosheets into crystalline $Ni_4Mo/MoO_2/C$ through a plasma process, resulting in nanosheets with abundant active sites and exceptional water-splitting activity.[65]

In a different approach Wang et al.[66] transformed Co ions into atomic-scale CoO_x species, utilizing plasma treatment during synthesizing atomic-scale CoO_x catalysts. The formed atomic-scale CoO_x species acted as active sites for OER, while the large surface area ensured excellent mass transport, displaying highly efficient electrocatalytic activity surpassing that of RuO_2. Also, in a recent study Bi, CeO_2, and their composite Bi@CeO_2 electrocatalysts are successfully synthesized to enhance OER activity (Figure 10b).[67] The unique nanostructures and nickel foam substrate of these materials, combined with plasma-induced valence states and oxygen vacancies, led to high electrocatalytic activity (Figure 10b). The resulting catalyst exhibits excellent OER properties.[67]

5.2. Oxygen Vacancies

To achieve optimal OER performance, it is desirable to combine oxygen vacancies with other desirable features, like surface area and active sites, as previously discussed. These oxygen-vacancy strategies, which embody the principle of "less is more," can direct the development of new electrocatalysts with increased oxygen vacancies. Oxygen vacancies, arising from the absence of oxygen atoms in the crystal lattice of metal oxides or other catalyst materials, create active sites for the adsorption and activation of oxygen molecules during the OER. The presence of oxygen vacancies promotes the formation of reactive oxygen species, facilitating the electrochemical processes involved in OER. Additionally, oxygen vacancies influence the electronic structure and charge distribution of the catalyst, leading to improved conductivity and catalytic activity.

For example, recent research by Huang et al.[21] employed an innovative approach involving Ar-plasma to enhance the catalytic performance of Co_3O_4 Nano needle arrays grown on CC (denoted as P−Mo−Co_3O_4@CC) for the OER (Figure 11a). The Ar-plasma technology was leveraged to create surface vacancies on hydroxide, which facilitated the binding of Mo anion salts through electrostatic interactions. This, in turn, led to the substitution of Mo atoms and the generation of oxygen vacancies on the Co_3O_4 surface. The resulting P−Mo−Co_3O_4@CC catalyst exhibited impressive OER performance, with a low overpotential, robust stability and high selectivity. Theoretical studies also showed that the incorporation of Mo with varying valence states effectively adjusted the atomic ratio of Co^{3+}/Co^{2+} and increased the oxygen vacancies. This, in turn, led to charge redistribution and the tuning of the d-band center of Co_3O_4, improving the adsorption energy of *OOH (oxygen intermediates), on P−Mo−Co_3O_4@CC during the OER.[21] The plasma-engraving technique was also utilized to synthesize Fe MOF nanosheets with abundant oxygen vacancies.[68] The generated oxygen vacancies, are promoted under coordinated Fe sites, facilitating the adsorption of oxygen-containing intermediates and improving OER electrocatalytic properties (Figure 11b).

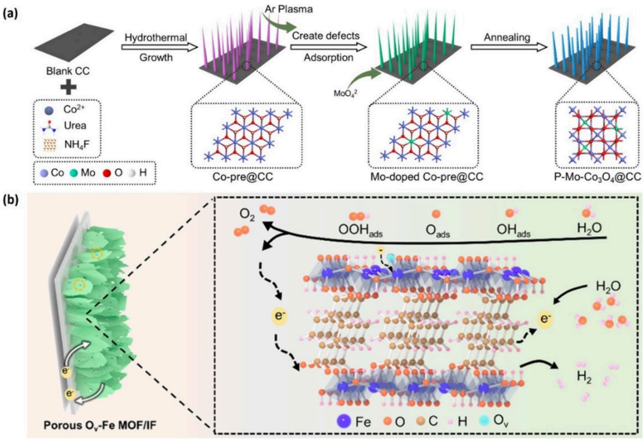

Figure 11. (a) Represents the schematic diagram of the synthesis process of P−Mo−Co_3O_4@CC. Reproduced with permission from ref 21. Copyright 2023, Wiley. (b) Diagrammatic illustration of the improved alkaline water electrolysis process on the porous Ov-Fe MOF/IF. Reproduced with permission from ref 68. Copyright 2022, Royal Society of Chemistry.

Recent studies have focused on enhancing the electrocatalytic properties of layered double hydroxides (LDHs). One notable approach involved exfoliating bulk CoFe LDHs into ultrathin nanosheets using Ar plasma etching. This process not only thinned the material to a 2D structure but also created multiple vacancies, including oxygen, cobalt, and iron vacancies. These vacancies, combined with the increased surface area of the nanosheets, significantly boosted the intrinsic catalytic activity by exposing more active sites.[22,69−72] Similarly, other studies have shown that the catalytic performance of materials like P−Co_3O_4 is influenced by specific sites, such as the Co^{2+} (Td) site, further highlighting the importance of structural engineering in enhancing OER efficiency.[16,73,74]

Spinel-type metal oxides have emerged as promising electrocatalysts for the OER owing to their distinctive electronic structure and cost-effectiveness. Meng et al.[75] facilitated the generation of oxygen vacancies in $CoFe_2O_4$ ($CoFe_2O_4$−VO) by phosphorus doping using plasma. The findings indicated the creation of oxygen vacancies on the surface of $CoFe_2O_4$−VO, alongside substantial adsorption of *OH, indicating favorable hydrophilicity.[75] In alkaline solutions, $CoFe_2O_4$−P exhibited superior OER activity, evidenced by its highest current density, lowest onset potential, and smaller Tafel slope. Density functional theory (DFT) calculations further validated that phosphorus doping can optimize the charge distribution near the Fermi level and fine-tune the d-band center position.[75] Also in a study by Wang et al.[22] the significance of oxygen vacancies was highlighted through the plasma strategy employed to synthesize Co_3O_4 nanosheets. The electrocatalytic performance of Co_3O_4 in the OER is strongly influenced by both surface area and the presence of oxygen vacancies. The expanded surface area facilitated a greater number of active sites, while the generated oxygen vacancies enhanced the material's electronic conductivity and fostered the formation of more active defects for the enhancement of the OER process.[22]

Co_3O_4, known for its efficient OER catalysis but limited HER activity, faces challenges in stabilizing oxygen vacancies (VO) crucial for enhanced OER. To address this, a novel approach introduced by Xiao et al.[73] involves filling VO in Co_3O_4 with phosphorus (P) via Ar plasma treatment resulting in P−Co_3O_4. Structural analysis using X-ray absorption spectroscopy confirms the creation of oxygen vacancies in VO-Co_3O_4 and efficient P filling in P−Co_3O_4. The catalytic ability of P−Co_3O_4, surpasses other nonprecious metal-based electrocatalysts, exhibiting superior performance for OER.[73] Similarly, He et al.[14] use the RF plasma treatment to generate sulfur and oxygen vacancies in electrocatalysts supported on graphene for the OER. Different plasma systems, including H_2, Ar/H_2, and Ar, were employed to create vacancy defects and reduce Co^{3+} to Co^{2+} on the surface of cobalt compounds and graphene. Among these systems, H_2 plasma proved the most effective in creating vacancy defects. The resulting electrocatalyst, H_2−VS/rGO, exhibited excellent OER performance.[14] Furthermore, etching Co_3O_4 nanosheets with NH_3 plasma revealed the creation of porous Co_xO_y nanosheets with N-doping and oxygen vacancies for improved OER.[16] The introduced Co^{2+} played a crucial role in forming active sites (CoOOH), and the combined effects of N-doping and oxygen vacancies contributed to the improved OER performance.[16] Additionally, recent research by Huang et al.[76] and colleagues utilized soft X-ray absorption spectroscopy (SXAS) to scrutinize the electronic structure of Co_3O_4 during OER (Figures 12a and 12b). Their findings unveiled that under elevated voltage, Co^{2+} in D-Co_3O_4 shifted to low-spin Co^{3+}, with a portion of it further transitioning to low-spin Co^{4+}. Most Co^{2+} in Co_3O_4 underwent conversion to Co^{3+} but infrequently to Co^{4+} however, by turning off the voltage the Co^{4+} intermediates disappeared.[76]

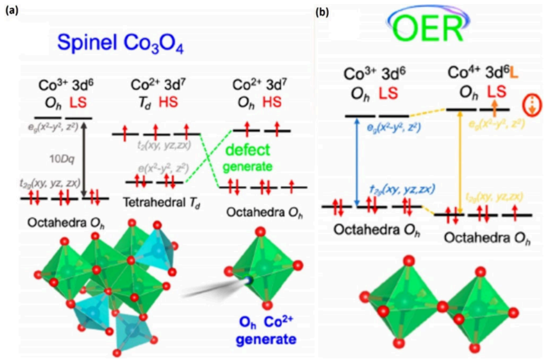

Figure 12. (a) Co_3O_4 with the Co^{3+} ion in octahedral coordination (b) D-Co_3O_4 under OER conditions with Co^{3+} and Co^{4+} ions in octahedral coordination. Reproduced with permission from ref 76. Copyright 2023, American Chemical Society.

5.3. Surface Functionalization

Plasma-based surface functionalization plays an essential role in enhancing the OER by introducing tailored modifications to electrode materials. The energetic and reactive nature of plasma enables the creation of oxygen-containing functional groups on the material's surface. For example, the work by Huang et al.[77] presents an innovative approach to activating CC for the OER by introducing oxygen-containing functional groups on its surface using peroxovanadium complexes, a rather unconventional choice for oxidizing carbon-based materials. The study reveals that surface functionalization with the ketone group C = O played an important role in OER as an active site (Figure 13a).[77] This activation process results in an activated CC characterized by an increased surface area and enhanced electron transfer rates. Notably, activated CC exhibits a significantly lower overpotential, positioning it as one of the most promising nonmetal catalysts for OER reported to date. In addition, Wang et al.[78] addressed the lack of active sites by directly creating active sites on CC through in situ exfoliation. Ar plasma treatment induced the formation of pores and rich edges/defects in the exfoliated graphene on the CC surface (Figure 13b and 13c), enhancing electrolyte affinity and improving mass transport. The enhanced catalytic activities were attributed to the synergetic effect of defects and oxygen doping induced by Ar plasma treatment. The higher electronegativity of oxygen in the adsorbed functional groups led to electron attraction from surrounding carbon atoms, resulting in charge redistribution on those carbon atoms. Carbon atoms with positive charges were identified as active sites, enhancing the adsorption of intermediate species in OER and consequently improving the electrochemical properties.[78] Also, Che et al.[79] modified commercial CC's surface using plasma treatment for OER enhancement (Figure 13d). The process resulted in the generation of several oxygen-containing functional groups on the surface of CC, leading to significant enhancement in OER activity. The suggested mechanism for the improved OER activity of the modified CC involves the surface carboxyl groups that facilitate proton-transfer kinetics, thereby expediting the deprotonation from AOOH to AOO* during the OER.[79] This shows that plasma-based surface functionalization proves instrumental in enhancing the OER by introducing tailored modifications, such as oxygen-containing functional groups.

5.4. Structural Engineering

Utilizing plasma-based structural engineering presents a cutting-edge approach to enhance the OER. Through controlled plasma treatments, tailored structural modifications can be induced in catalyst materials, optimizing active sites and electronic configurations. This innovative strategy holds promise for advancing electrocatalysts, contributing to more efficient and sustainable OER processes in various applications. For example, Yang et al.,[57] synthesized a catalyst by combining two transition metal oxides, cobalt, and nickel. O_2 plasma treatment was initially employed on CC to enhance hydrophilicity and introduce surface defects. Subsequently, Co_3O_4 nanowire arrays were grown on the plasma-treated CC to facilitate effective

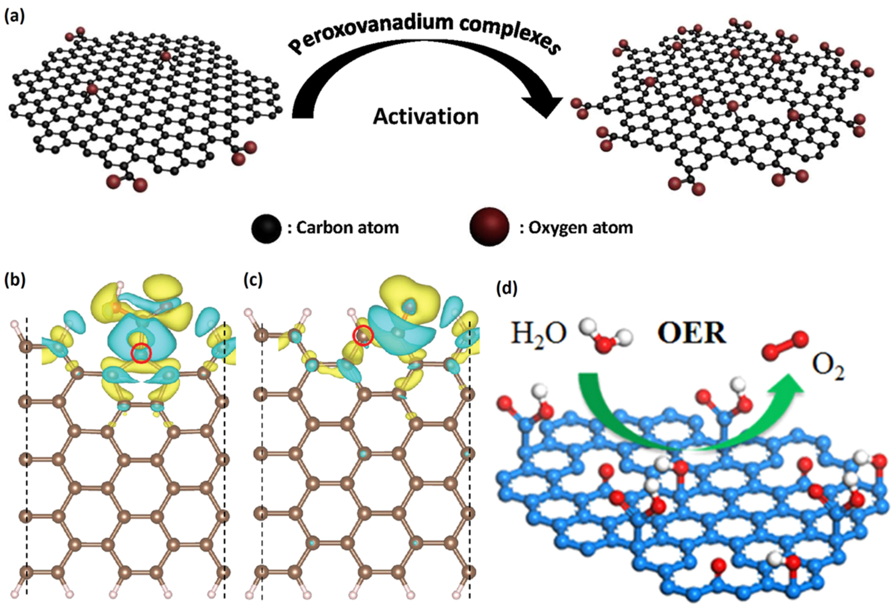

Figure 13. (a) Diagram for the development of oxygen-containing functional groups on the surface of CC. Reproduced with permission from ref 77. Copyright 2018, Elsevier. (b, c) Charge transfer analysis of defective and nondefective graphene, respectively. Red circles in (b) and (c) represent the most active sites. Reproduced with permission from ref 78. Copyright 2017, Wiley. (d) Diagram for OER process on CC. Reproduced with permission from ref 79. Copyright 2020, Elsevier.

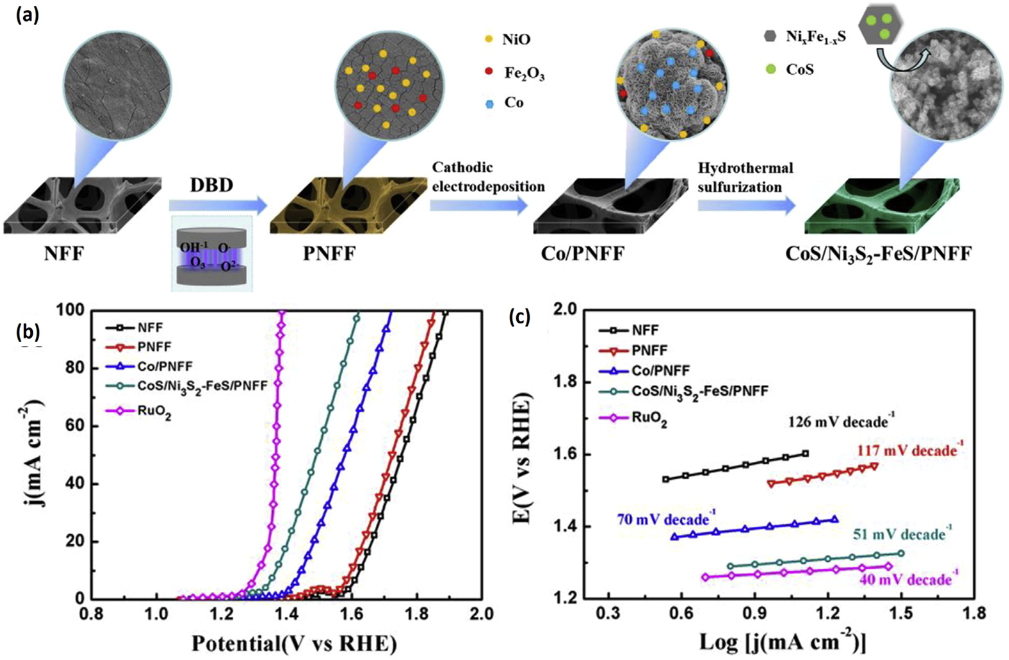

Figure 14. (a) Schematic diagram of the synthetic route for CoS/Ni_3S_2−FeS on the Ni−Fe foam. (b) LSV curves and (c) Tafel slopes for CoS/Ni_3S_2−FeS on the Ni−Fe foam. Reproduced with permission from ref 81. Copyright 2018, Elsevier.

electrolyte-catalyst contact. An ultrathin layer of nickel oxide, approximately 1.2 nm, was deposited on the Co_3O_4 nanowire arrays. The resulting $NiO_x@Co_3O_4$/CC electrocatalyst demonstrated excellent OER performance. Liang et al.[59] utilized PH_3 plasma to convert NiCo hydroxides into ternary NiCoP. The resulting NiCoP exhibited exceptional catalytic activity for the OER with a low overpotential of 280 mV, representing one of the best-reported values for non-noble metal catalysts.

Transition-metal nitrides have garnered significant attention due to their remarkable chemical stability and electrical conductivity. The incorporation of nitrogen atoms has a profound impact on the electronic structure of the host metals, influencing charge-transfer processes and potentially inducing structural modifications.[19] This unique electronic structure positions transition metal nitrides as excellent catalysts across various domains. Capitalizing on these advantages, Zhang et al.[19] utilized N_2 plasma to convert cobalt oxide into cobalt nitride nanowires, significantly reducing reaction times to approximately 1 min at room temperature, as opposed to the few hours required for conventional high-temperature NH_3 annealing. The plasma-prepared catalyst exhibits exceptional catalytic activity.

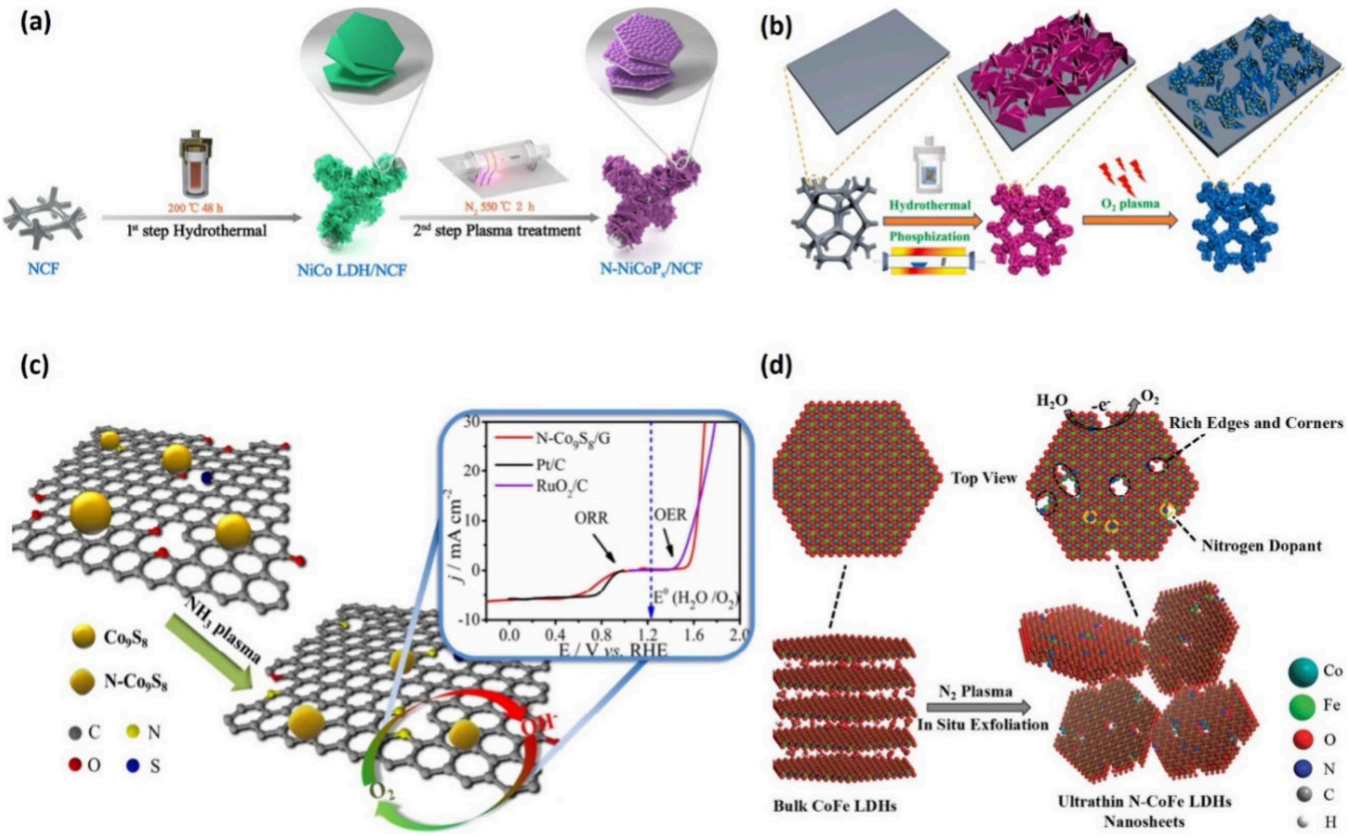

Figure 15. (a) Synthesis of N-NiCoP$_x$ catalyst on Ni−Co foam. Reproduced with permission from ref 82. Copyright 2020, Elsevier. (b) Synthesis of the Fe−Ni_2P catalyst. Reproduced with permission from ref 83. Copyright 2022, Elsevier. (c) Simultaneously etched and doped Cobalt sulfides-graphene hybrids with NH_3 plasma to improve the OER. Reproduced with permission from ref 54. Copyright 2016, Royal Society of Chemistry. (d) Diagram showing how N_2 plasma exfoliates bulk CoFe LDHs into ultrathin CoFe LDH nanosheets. Reproduced with permission from ref 55. Copyright 2018, Wiley.

Besides transition metal oxide and nitride, transition metal phosphides have been discovered as effective bifunctional electrocatalysts for water splitting, offering enhanced conductivity and stability. Monometallic cobalt phosphides exhibit good performance in the HER; however, they face limitations in the OER. While the intrinsic activity of nickel phosphides is constrained by surface atom types for HER. Synergistic modulation, exemplified by binary NiCo phosphides, enhances conductivity and stability. To further optimize performance, quaternary MnNiCoP nanoflowers-like electrocatalysts were synthesized recently through electrodeposition and PH_3 plasma treatment on NF, demonstrating improved water electrolysis efficiency and stability.[80] Optimal ratios of trimetallic components and phosphorus doping facilitate charge transfer kinetics, leading to superior OER performances. The hybrid $Mn_1Ni_1Co_1$−P/NF electrode displays superb electrochemical activity with an ultralow η_{10} of 1.48 V vs RHE and excellent chronoamperometric stability for 50 h.[80]

In a separate study by Qu et al.,[81] a 3D nanostructured catalyst was synthesized by treating Ni−Fe foam (NFF) with DBD plasma under ambient conditions (Figure 14a). Concurrently, exposure to hot filaments generated in DBD plasmas in air resulted in NiO and Fe_2O_3 spots on the NFF foam. Subsequently, 3D CoS/Ni_3S_2−FeS nanopetals with a cross-linked structure emerged on the plasma-treated NFF surface (PNFF) through the sulfurization of Co nanosheets electrodeposited on PNFF. The resulting CoS/Ni_3S_2−FeS/PNFF nanocomposite exhibited remarkable electrocatalytic activity and stability for overall water splitting (Figure 14b and 14c).[81] Nevertheless, further investigation is essential to elucidate the specific contribution of PNFF to achieving this ultralow overpotential. Previous studies have highlighted the effectiveness of plasma-treated CC as a good electrocatalyst. However, in the present work, the authors demonstrate comparable electrocatalytic activity between NFF and PNFF (Figures 14b and 14c). Hence, a more in-depth study is warranted to uncover the distinct role played by PNFF in the observed electrocatalytic performance.

Indeed, plasma-based structural engineering represents a powerful and versatile approach for the enhancement of OER electrocatalysts. By tailoring the surface characteristics and electronic structures of various materials, plasma treatments have demonstrated significant improvements in catalytic activity, stability, and efficiency. The examples discussed highlight the potential of this technique to drive advancements in water-splitting technologies, paving the way for more sustainable and efficient energy conversion processes. Continued research in this area will likely yield further innovations, contributing to the development of next-generation electrocatalysts.

5.5. Dual Defects (Heteroatom Doping and Defects/Vacancies Generation)

Heteroatom doping and the intended introduction of defects represent key strategies in the design of advanced materials for electrocatalytic applications. Heteroatom doping involves the incorporation of external atoms into a material's crystal lattice, altering its electronic structure and chemical reactivity. Simultaneously, the introduction of defects creates active sites, influencing the material's surface reactivity and facilitating catalytic processes. Together, heteroatom doping and defects generation serve as powerful tools in tailoring the properties of materials, particularly in the development of high-performance catalysts. For example, in a study conducted by Yan et al.,[30] a bifunctional electrocatalyst was developed by efficiently introducing carbon atoms into oxygen vacancy-rich Co_3O_4 using CH_4 plasma treatment at room temperature. The resulting product exhibited a unique combination of two types of point defects: (i) doped heteroatoms and (ii) vacancies. On one hand, the plasma process etched the surface of Co_3O_4, creating oxygen vacancies with modified Co valence distribution, significantly enhancing the OER activity. On the other hand, the CH_4 plasma discharge introduced active carbon species, which filled the oxygen vacancies to form Co−C bonds (C doping), thus enabling an excellent performance in the HER. The author also explained that the configuration of surface atoms on electrocatalysts plays a crucial role in determining their activity. Precious metal catalysts studied through single-crystal electrochemistry have revealed that surfaces with high indices and open atom structures exhibit heightened activity due to their relatively low coordination numbers. Consequently, defect engineering becomes imperative in the modulation of surface atom arrangements. Defects can effectively adjust the electronic structure and surface properties of catalysts, significantly impacting their electrochemical performance.[30] Another bifunctional catalyst is synthesized through a hydrothermal reaction followed by N_2 and P plasmas (Figure 15a).[82] This method not only effectively regulates the incorporation of nitrogen and phosphorus elements but also significantly enhances the stability and activity of the resulting electrocatalysts.[82]

Furthermore, the utilization of O_2 plasma to synthesize Fe-doped Ni_2P (Fe−Ni_2P) nanosheets, remarkably achieved defect engineering introducing P vacancies, and the formation of new species, namely phosphate grown on the conductive NiFe foam (Figure 15b).[83] The presence of P vacancies was found to modulate the electrocatalyst's electronic structure during the OER process, while the newly formed phosphate species facilitated water adsorption and enhanced charge transfer.

Recently, the combined etching and nitrogen-doping processes were also applied to hybrid Co_9S_8/graphene electrocatalysts, resulting in notable enhancements in their electrocatalytic performance for the OER. The utilization of an NH_3 plasma process proved to be an effective method for introducing heteroatoms and generating additional edge-active sites on the surface of the hybrid electrocatalysts. As a result, the prepared N−Co_9S_8/G material exhibited highly efficient activity for OER. The NH_3 plasma treatment of Co_9S_8/G not only facilitated nitrogen doping in both the Co_9S_8 and graphene components but also partially etched the surface of these materials. The introduction of heteroatom doping effectively adjusted the electronic properties of Co_9S_8 and graphene, while the surface etching led to the exposure of more active sites for electrocatalysis (Figure 15c). These improvements significantly contributed to the augmented electrocatalytic performance for OER observed in the N−Co_9S_8/G material.[54]

LDHs have recently raised considerable interest in the context of the OER. Enhancing the number of reactive sites by exfoliating LDHs has proven to be effective. However, conventional liquid-phase exfoliation methods are known to be labor-intensive and time-consuming. Conversely, incorporating appropriate heteroelement doping and implementing edge engineering techniques offer valuable strategies to fine-tune the intrinsic reactivity of these sites. In a recent study, Wang et al.[55] successfully exfoliated bulk CoFe LDHs into ultrathin CoFe LDHs nanosheets using nitrogen plasma. This process introduced nitrogen doping and defects into the nanosheets, effectively increasing the number of reactive sites and altering the electronic arrangement around these sites, thereby facilitating the adsorption of OER intermediates (Figure 15d). The electrocatalytic activity was further enhanced by the introduction of defects, which increased the number of dangling bonds neighboring reactive sites and reduced the coordination number of these sites, as a result, these electrocatalysts exhibited impressive OER activity.[55]

As a result, the strategic incorporation of heteroatom doping and defect engineering has proven to be a powerful approach to optimizing the electrocatalytic properties of materials. These advancements not only enhance the performance of catalysts but also pave the way for innovative applications in energy conversion technologies. Continued research in this area holds significant promise for the development of next-generation electrocatalysts.

In summary, the application of plasma-based techniques emerges as a versatile and effective strategy for enhancing the OER in electrocatalytic materials. Through precise control of plasma treatments, various structural modifications, surface functionalization, and the generation of defects or vacancies can be achieved, contributing to the optimization of catalyst properties. The pivotal role of plasma in tailoring materials for OER enhancement is evident across diverse studies. Plasma-induced surface area augmentation, active site generation, and the introduction of oxygen vacancies collectively result in superior electrocatalytic performance. Additionally, the incorporation of heteroatoms through plasma-based methods, further enriches the catalysts, contributing to increased active sites and improved electronic structures. Furthermore, the combination of surface functionalization and structural engineering, facilitated by plasma treatments, allows for the creation of tailored catalysts with exceptional OER performance. The synergistic effects of defects, heteroatom doping, and increased surface area induced by plasma treatments lead to advanced electrocatalysts. Noteworthy advancements have also been made in dual-defect engineering, where heteroatom doping and defects are deliberately introduced to optimize electrocatalyst functionality. To summarize, strategies utilizing plasmas present a viable path toward the logical development and production of extremely effective electrocatalysts for OER. The enhanced OER is due to the combination of various factors discussed above, however, the exact mechanism depends upon three factors (material, method, and plasma type). Therefore, exact mechanism cannot be elaborated in a review, however, the main factors playing a role in the OER enhancement mechanism are presented. Further understanding of the mechanistic aspects behind these enhancements will be an interesting topic of research.

6. CHALLENGES AND RECOMMENDATIONS

Despite of favorable outcomes discussed above plasma catalysis faces various challenges in understanding complex interactions, necessitating improved in situ characterization. Some challenges and future recommendations are given below.

6.1. Challenges

Unfortunately, current knowledge of plasma physics and chemistry, material-plasma interaction, and reaction kinetics in plasma environments is insufficient. Additional challenges for in situ characterization of target materials, identification of roles of particular plasma species, monitoring of reaction pathways during plasma treatment processes, and computational modeling arise from the complex and extremely dynamic plasma environment. Though they have not yet received much attention, these fundamental questions are anticipated to become significant areas of study shortly.

The selection of an optimum catalyst requires appropriate process conditions, considering parameters such as temperature and activation energy. Understanding the fundamental attributes necessary for catalyst activation in plasma environments is vital, yet defining the appealing properties for effective plasma catalysts remains a challenge due to the complexities of plasma-catalyst interactions and the localized, temporal nature of observed effects. An efficient experimentation-modeling loop can potentially address this challenge by incorporating the nonhomogeneity of properties resulting from the presence of plasma and catalysts.

Transitioning from laboratory-scale achievements to large-scale industrial prototypes is a pivotal challenge in plasma catalysis. This requires a profound understanding of fundamental principles and efforts to minimize energy costs, enhancing the competitiveness of plasma catalysis for industrial applications.

A major challenge in plasma catalysis is the lack of comprehensive in situ characterization tools. Understanding surface phenomena at the catalyst's surface, including adsorption, diffusion, and recombination, remains vital for grasping plasma-catalyst synergy.

6.2. Recommendations

Although there is evidence of a synergistic relationship between plasma and many materials used as catalysts, relatively little is known about the chemistry of the plasma surface. In-situ characterization approaches can help overcome this lack of data by providing a more accurate image of the events occurring within the reactor chamber. To fully realize the promise of plasma catalysis, a good collaboration combining theory and experiments is essential. This collaboration will create a productive cycle of simulations and experiments, leading to a better understanding and enhanced efficiency of the process.

Due to the simultaneous occurrence of various reactions in plasma, carefully controlling the plasma parameters (like electron density, electron temperature, and exposure time) will help to protect the structural damage to materials and enhances control over reaction kinetics.

Adopt various diagnostic methods like optical emission spectroscopy and mass spectroscopy to determine plasma parameters and active species. Tuning these parameters is vital for the controlled processing of catalytic materials by plasma.

Cold plasma holds considerable potential for advancing electrocatalytic and photocatalytic applications by enabling surface modifications, introducing active sites, and optimizing electronic structures. In electrocatalysis, plasma treatment can increase surface area and defect density, enhancing reaction efficiency and stability, while in photocatalysis, it offers pathways to improve light absorption and charge separation, thereby boosting energy conversion processes. Future research should extend plasma techniques to materials using in situ tools to fine-tune interactions, positioning cold plasma as a key tool for catalytic performance and sustainable energy advancements.

7. CONCLUSION

The global search for clean and sustainable energy solutions has propelled hydrogen energy, particularly through electrochemical water splitting, to the forefront of scientific exploration. Amidst challenges associated with the conventional use of noble metal catalysts like Pt and Pd, the innovative application of cold plasma for catalyst preparation has emerged as a transformative avenue. This review underscores the significant strides made in understanding the impact of plasma treatments on catalytic materials, specifically focusing on their role in enhancing the OER. By elucidating the mechanisms through which plasma induces changes in catalyst behavior, such as increased surface area, active site generation, and heteroatom doping, the review contributes to a comprehensive understanding of plasma-based techniques. The versatility of plasma treatments in tailoring electrocatalysts, as demonstrated through techniques like plasma treatment, atomic layer deposition, and plasma engraving, holds promise for scalable and efficient hydrogen production. The synergistic effects of defects, heteroatom doping, and increased surface area, orchestrated by plasma, underscore the transformative potential of these techniques. As the world navigates the complexities of the energy crisis, the exploration of plasma-based strategies not only addresses the limitations of traditional catalysts but also opens new avenues for the rational design and production of highly effective electrocatalysts, paving the way for a sustainable energy future.

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Notes

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