Rational Design and Construction of Cocatalysts for Semiconductor-Based Photo-Electrochemical Oxygen Evolution: A Comprehensive Review

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Photo-electrochemical (PEC) water splitting, as an essential and indispensable research branch of solar energy applications, has achieved increasing attention in the past decades. Between the two photoelectrodes, the photoanodes for PEC water oxidation are mostly studied for the facile selection of n-type semiconductors. Initially, the efficiency of the PEC process is rather limited, which mainly results from the existing drawbacks of photoanodes such as instability and serious charge-carrier recombination. To improve PEC performances, researchers gradually focus on exploring many strategies, among which engineering photoelectrodes with suitable cocatalysts is one of the most feasible and promising methods to lower reaction obstacles and boost PEC water splitting ability. Here, the basic principles, modules of the PEC system, evaluation parameters in PEC water oxidation reactions occurring on the surface of photoanodes, and the basic functions of cocatalysts on the promotion of PEC performance are demonstrated. Then, the key progress of cocatalyst design and construction applied to photoanodes for PEC oxygen evolution is emphatically introduced and the influences of different kinds of water oxidation cocatalysts are elucidated in detail. Finally, the outlook of highly active cocatalysts for the photosynthesis process is also included.

1. Introduction

Constant and unhealthy development of modern civilization and industrialization results in worsening a series of environmental problems. The traditional fuel resources are close to be exhausted, the ecosystem is deteriorated, and the environmental pollution is much worse than imagination. Therefore, effective solutions should be proposed to address these issues. It is said that the existence of environmental issues partly attributes to the unreasonable use of traditional fossil fuel, such as excessive exploitation and inefficient utilization. Confronted with this dilemma, it is impending to improve the efficiency of traditional resources or explore new, clean, and sustainable ones if we want to alleviate the environment pressure. Recently, mounting researchers conduct their study based on sustainable energy like solar energy, wind energy, bioenergy, etc. Among them, solar energy is vastly abundant, low cost, and carbon-free, hence becoming dominant and emerging potential application perspectives.

Photo-electrochemical (PEC) water splitting is a facile photosynthesis route and defined as an electrochemical process which occurs when a semiconductor electrode is under light irradiation in order to convert sunlight into oxygen or hydrogen energy. It is cost-competitive, free of collateral contamination, and does not require additional separation process, thus has attracted increasing attention recently. As shown in Figure 1, an exponential growth of related published papers begins from 2004, and the total number of publications and citations in this field reached 4344 and 147 015, respectively (up to 6 October 2018). It indicates the PEC water splitting process becomes more and more important under the current global energy crisis and environmental pollution.

PEC water splitting was first found by Fujishima and Honda, who used TiO2 photoanode to split water into H2 and O2 successfully under ultraviolet (UV) light in 1972. It is considered as the remarkable milestone of solar energy utilization field and caused an explosive impact in this field. Theoretically, the limited efficiency for a single semiconductor photoelectrode with a bandgap around 1.5 eV under 1 sunlight irradiation (100 mW cm−2) is possible to attain ~30%, hence it can reach a high yield of hydrogen and oxygen. Whereas, to the best of our knowledge, the current efficiency of PEC water splitting is still much lower than the ultimate efficiency and far from meeting the demand of industrialization owing to the following shortcomings:

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1) Some of the traditional photoanodes have wide bandgap and can only seize UV light, resulting in low utilization of sunlight and energy conversion efficiency.\[9\] 2) The lifetime of photogenerated carriers is very short. The excited electrons are inclined to recombine with holes in order to maintain a stable state, which has been considered as a major factor of the energy loss. Therefore, after irradiation, only a small portion of the excited electrons and holes can successfully move to the different surface areas of the electrodes and participate in water splitting. 3) Many common photoanodes are electrochemically instable in electrolyte environment or easy to be corroded by photoinduced holes, which will oxidize materials instead of water and reducing the PEC water splitting performance.

Hitherto, these three major problems are still the stumbling blocks for the further development of photoelectrodes. In this case, novel surface engineering strategies have been explored constantly in order to address these problems in terms of optimizing the bandgap of photoelectrodes, restraining recombination, facilitating the immigration of charge carriers for water splitting, as well as improving the stability against photocorrosion and decomposition.\[10\] These strategies mainly include morphology control, heterojunction/homojunction formation, ions doping, cocatalysts engineering, etc. For example, Wu et al.\[11\] and Wang et al.\[12\] demonstrated that by tuning morphology of photoanodes, the efficiency of O$_2$ generation in the PEC water splitting reaction can be optimized. Su et al.\[13\] and Hong et al.\[14\] proposed that the heterojunction formed between interface of WO$_3$ and BiVO$_4$ was conducive to charge transfer and recombination suppression. Pan et al. constructed TiO$_2$ p–n homojunction to realize enhanced PEC H$_2$ evolution performance.\[15\] Yang et al. rationally synthesized nitrogen-doped ZnO nanowire arrays as photoanodes and the obtained photocurrent of ZnO$_x$ increased by an order of magnitude than that of bare ZnO.\[16\]

Alternatively, engineering cocatalysts on the surface of photoelectrodes gradually came to sight recently, as the existence of cocatalysts can bring about the reduced overpotential, accelerated reaction kinetics, enriched active sites, and suppressed corrosion.\[17\] Besides, the methods to incorporate cocatalysts with photoelectrodes such as electrodeposition or photo-electrodeposition are facile and easy to implement. Virtually, it is revealed that most of the excellent PEC water splitting cocatalysts are electrocatalysts,\[18–20\] such as transition metal dichalcogenides (TMDs),\[21–25\] phosphorous metal compounds,\[26–28\] metal oxides,\[29,30\] metal hydroxides,\[29,33\] etc. These electrocatalysts not only play a vital role in electrocatalysis but also have a significant impact on PEC water splitting. Therefore, in a manner of speaking, the discovery of robust
electrocatalysts provides numerous possibilities for cocatalyst engineering strategy and then remarkably promotes the progress of photo-electrocatalysis.

In general, cocatalysts consist of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) cocatalysts. Compared with HER cocatalysts, OER cocatalysts have a more valuable status for PEC water splitting and are explored more extensively. The reasons are as follows: compared with the abundant variety of PEC OER cocatalysts, materials used for PEC HER are limited and most of them are relatively unstable such as TMDs.[25] In addition, water oxidation half reaction is much more demanding than water reduction. Therefore, it is essential to improve the water oxidation capability of photoanodes for better PEC overall water splitting performance. With suitable OER cocatalysts, the photoanodes used for light-induced water oxidation and even the entire PEC process will be highly efficient.

Some reviews related to the rational design and fabrication of photoanodes for PEC water splitting have been published, but few of them are comprehensive with respect to the construction of PEC water oxidation system and especially the functions of cocatalysts deposited onto photoanodes. Hence, there is still a large space for us to further elucidate and discuss from these aspects as well as summarize the progress of the development in a more accessible and detailed way. It needs to be emphasized that this review mainly focuses on the basic information of PEC water oxidation half reaction and the recent advances of OER cocatalysts research applied on the photoanode in order to enhance the efficiency of PEC oxygen production. In the discussion, the modules of a typical PEC cell and the basic mechanism of PEC water splitting will be simply introduced. The benchmark and the diagnostic evaluation parameters commonly used in PEC OER process and the intrinsic function of cocatalysts will be demonstrated. Different categories of water oxidation cocatalysts will be classified and compared. Meanwhile, the typical examples of cocatalysts coupled with photoanodes will be overviewed and the optimization methods to promote catalytic activity of cocatalysts will be described.

2. Basic Principles

2.1. PEC Water Splitting Process

A single PEC water splitting cell is consisted of electrodes (at least one photoelectrode), aqueous electrolyte, as well as electric wire which connects the photoelectrodes (Figure 2). The substrate of photoelectrode is responsible for the generation of semiconductor materials and transfer of electrons in the external circuit. Some common substrates include metal foils and transparent conductive oxide (TCO)-coated glasses. The photoelectrodes work as a sunlight absorber, capturing solar energy to driving water splitting. The electrolyte is also an essential part of the system, as it assists in ionic migration in the internal circuit, and the commonly used electrolytes are Na2SO4, NaOH, K2SO4, etc. When the whole system is under sunlight irradiation, the electron from the photoanode will be excited from valence band (VB) to the unoccupied conduction band (CB) with the hole left on VB after absorbing photons, the energy of which is equal to or higher than the bandgap, as is shown in Equation (1). Then some of the excited electrons transfer over the external circuit to the interface of the cathode and electrolyte and cause the reduction of hydrogen ions, while some of the H+ diffuse to the surface of photoanode and assist oxidation of water. The related half-reaction equations on two electrodes are shown in Equations (2) and (3). In fact, it is impossible for all the electron–hole pairs to transfer to the different electrode surfaces respectively after excitation due to the recombination, thus a bias will be added to the PEC system in order to promote the migration of excited charges and suppress the opportunity of recombination.[14] This bias can be an external voltage provided by a power source, an internal voltage provided by H+ of different concentrations in the electrolyte, or an internal voltage by integrating a photovoltaic cell with this system.[8]

\[ h\gamma \rightarrow e^- + h^+ \]  

(1) where h is the Planck’s constant, γ is the frequency of light, e− is photogenerated-electrons, and h+ is photogenerated-holes.

Photoanode

\[ H_2O + 2h^+ \rightarrow 2H^+ + 1/2O_2 \quad E_{(ox)} = -1.23 \text{ V vs RHE} \]  

(2)

Cathode

\[ 2H^+ + 2e^- \rightarrow H_2 \quad E_{(red)} = 0 \text{ V vs RHE} \]  

(3)

Comparing Equation (2) with (3), it can be seen that water oxidation half reaction is thermodynamically and kinetically demanding. Its energy barrier is much higher and the process is more complex than water reduction. Four holes will be involved to produce one mole of oxygen while only two electrons participate in the reaction for generating one mole hydrogen.  

![Figure 2. A sketch of the PEC cell for water splitting.](Image)
Therefore, the water oxidation half reaction is considered as one of the major challenging steps of the PEC water splitting. It is worth noting that the PEC water splitting takes place at the interface of electrodes and electrolyte. Therefore, it is necessary to understand the conditions of the interface so as to have more insights into the entire reaction processes. However, due to the existence of multiple processes and the unclear reaction mechanisms at the interface, it is very difficult to make the experimental measurements. Thus, researchers turn to modeling and simulation study, which allow for rational computational design of the interface at the atomistic level. Based on these techniques, a common structure model of the semiconductor/electrolyte interface can be set up. As is seen in Figure 3, three layers exist at the interface. In the near surface of the semiconductor, a space charge layer with a thickness of \( \approx 1-0.1 \, \mu m \) is formed because of the nonequilibrium of the Fermi level \( (E_F) \) of the semiconductor and the redox potential of the electrolyte \( (E_{\text{redox}}) \). In most conditions, the space charge layer is a depletion layer full of immobile ionized donors, thus containing positive charges. The interlayer, named as Helmholtz layer, is a negatively charged layer from the solution side and is about 3–5 Å in thickness, consisting of trapped electrons in surface states, adsorbed ions, oriented water molecule dipoles, etc. Next to the Helmholtz layer is the Gouy diffuse layer with the lowest potential among three layers. It is filled with numerous anions and few cations. Due to the different electron densities in these three layers, a potential drop across them exists, causing upward band bending and changing the Fermi level of the semiconductor.

After connecting the semiconductor with the other electrode, an electrochemical chain of a PEC water splitting system can be obtained (Figure 4). From the changes of their band structures, it can be seen that the entire processes can be divided into three main stages: Figure 4a shows that the galvanic contact under dark is formed after connecting the semiconductor and metal with electric wire, which results in the electronic charge transfer from the semiconductor to the electrolyte and the upward band bending due to their difference of energy levels. In this case, the Fermi level of the cathode is lower than the energy level of \( H^+ / H_2 \), hindering the process of PEC water splitting. Once the above system is exposed under light (Figure 4b), the surface potential of the photoanode and the \( H^+ / H_2 \) potential will be reduced. However, at this moment, the \( H^+ / H_2 \) potential is still above the Fermi level of the cathode.
In the end, an external bias is added to the circuit, causing the H⁺/H₂ potential to be lower than Fermi level and then facilitating PEC water splitting proceeding (Figure 4c).

2.2. Primary Components of a PEC Water Oxidation Process

2.2.1. Substrates

A substrate is the essential element of PEC anodes, because it connects the electric wires with the photoelectrode materials. For photoanodes, a conductive material with a smaller work function than that of the semiconductor is qualified to act as a substrate in order to ensure optimal charge carrier transfer at the interface between the semiconductor and the substrate. Furthermore, accessibility, economy, and flexibility are also important parameters when selecting a substrate. The typical substrates including metal substrates, metal-free substrates, and TCO-coated glasses were demonstrated as follows.

Metal substrates, such as Pt,[37] Ti,[37] Ta,[38] copper foils,[39] nickel foams,[40] are usually flexible, heat resisting, and of high conductivity. Particularly, stainless steel,[41,42] which contains common transition metallic elements, like Fe, Ni, can be the source of in situ growth of the PEC catalyst, and thus becomes a suitable substrate alternative. Besides, some metal-free materials like silicon,[41,44] carbon cloth,[45] and ultralong carbon nanotubes (CNTs)[46] can also be applied as substrates due to their good conductivity. Very recently, Kecsenovity et al. revealed the deposition of Cu₂O onto different graphene substrates including 3D graphene foams, CNT networks, and spray-coated graphene films, and found the properties of graphene foams were superior to another two substrates because of its 3D interconnected structure and high conductivity.[47] Generally, the most extensively used substrates currently were TCO-coated glass such as fluorine-doped tin oxide (FTO) and indium tin oxide (ITO). These materials are affordable, corrosion-resistant, versatile, and of excellent transparency. Though they may have a lower intrinsic conductivity in comparison with metal or carbon substrates, it can be offset by adding an ultrathin underlayer of SiOₓ or Nb₂O₅. To date, various photoanodes have been assembled based on these substrates.[48–50] For instance, Yang et al. demonstrated the growth of ZnO:N nanowires onto ITO substrates successfully.[16] Vertically aligned Fe₂O₃ nanorod arrays were also seeded onto FTO substrates uniformly by An et al.[49]

As the semiconductors are usually seeded onto the surface of substrates, the surface chemistry of substrates could significantly influence their growth condition and physico-chemical properties.[51] Gao et al. reported the growth of structure-controlled graphdiyne (GDY) nanowalls on 1D, 2D, and even 3D substrates (stainless steel mesh and graphene foam (GF)), which emerge a great difference in their morphologies, chemical structures, and optical properties.[52] The morphology before and after growing GDY is shown in Figure 5.

2.2.2. Electrolytes

The electrolyte of a PEC cell is another essential element affecting the PEC water oxidation. A tiny change in the electrolyte conditions may even result in a momentous variation in the interface catalysis.[53] Good conductivity is an important principle to choose electrolytes in order to smooth charge transfer in the circuit. Employing active cations like K⁺, Na⁺, and anions like SO₄²⁻ or OH⁻ with appropriate concentration (≈0.1 m or above) contributes to minimize solution resistance and facilitates band bending.[54] Hence, selecting highly conductive electrolytes is a critical part of the PEC water oxidation process. Moreover, the pH values of the electrolytes should also be taken into consideration, as the stability of the photoanodes, the redox potential, and the rate of water oxidation reaction are all highly depended on it.[55] A reliable reference for electrolyte selection is Pourbaix diagrams, which indicates the stable phases of materials when varying different pH values.[56] Additionally, as for oxygen evolution (Equation (2)), high concentration of H⁺ will restrain the half reaction from proceeding in the positive direction. From this perspective, low pH is not beneficial for water oxidation which
can be verified by Table 1. Meanwhile, a shift of the band level of a semiconductor material can also occur due to the change in pH value, which will also further affect the efficiency of PEC water oxidation.\(^{[57]}\) Therefore, as a trade-off, it is necessary to find a suitable pH to satisfy above requirements simultaneously.

In addition, the electrolytes need to be compatible with the given photoelectrode. They should not have chemical interactions with photoelectrodes, and their light absorption range cannot overlap with that of photoelectrodes.\(^{[58]}\) Versatile electrolytes that can be compatible with many photoanodes include Na\(_2\)SO\(_4\), K\(_3\)PO\(_4\), NaClO\(_4\), NaOH, etc. Table 1 shows the efficiency of PEC water oxidation on WO\(_3\) with different electrolytes and pH values. It is worth noting that both the electrolyte types and pH values will affect oxidation efficiency. CH\(_3\)COOH, CH\(_3\)COONa, and NaCl are not compatible with WO\(_3\), hence the photoanode cannot converse the photocurrent to oxygen when immersed in these electrolytes. Besides, for different anions, the law of the pH effect varies. For example, when the pH value of NaH\(_2\)PO\(_4\) increases, the conversion efficiency shows an upward trend. By contrast, the conversion efficiency declines as the pH of NaClO\(_4\) rises up. The results are probably influenced by the intrinsic properties of electrolytes. In total, the mechanism of the effects of electrolytes is still an open question remaining to be explored.

Table 1. Summary of the conversion efficiencies of photocurrent to oxygen obtained in electrolytes with varied pH conditions and anions. Reproduced with permission.\(^{[58]}\) Copyright 2012, American Chemical Society.

| Electrolytes  | pH   | Photocurrent to oxygen conversion efficiency [%] |
|--------------|------|-----------------------------------------------|
| CH\(_3\)COOH | 3    | 0                                             |
| CH\(_3\)COONa| 5    | 0                                             |
| NaCl         | 1    | 0                                             |
| NaCl         | 3    | 0                                             |
| NaCl         | 5    | 0                                             |
| NaH\(_2\)PO\(_4\) | 1 | 33                                           |
| NaH\(_2\)PO\(_4\) | 3 | 58                                           |
| NaClO\(_4\) | 5    | 79                                            |
| NaClO\(_4\) | 1    | 32                                            |
| NaClO\(_4\) | 3    | 29                                            |
| NaClO\(_4\) | 5    | 9                                             |
| Na\(_2\)SO\(_4\) | 1 | 35                                           |
| Na\(_2\)SO\(_4\) | 3 | 63                                           |
| Na\(_2\)SO\(_4\) | 5 | 88                                           |

2.2.3. Photoanodes

Photoanodes are the decisive components for a PEC water oxidation system, which is in charge of absorbing solar energy, generating charge carriers, and then producing oxygen by oxidizing water. The oxygen evolving photoanode material should be an n-type semiconductor. The band bending of it will generate an electric field and in turn drive holes to the surface of the materials. The stability under water oxidation conditions and the physicochemical properties like conductivity are also two main factors needed to be considered before selecting photoanodes in order to improve water splitting efficiency and reduce overpotential.\(^{[60]}\) Besides, the level of VB and CB as well as the width of bandgap are also very vital because the position of VB decides whether the water oxidation can proceed and the range of solar light absorption is influenced by the bandgap. Thus, a suitable bandgap (around 2.0–3.2 eV\(^{[61]}\)) and an appropriate position of VB which is positive than the potential of O\(_2\) allow the oxygen production from water.\(^{[60,62]}\) Common photoanodes for water oxidation include hematite, BiVO\(_4\), ZnO, TiO\(_2\), etc. Figure 6 shows the positions of VB and CB as well as the bandgap of representative photoanode materials.

In general, a photoanode consisting of a single semiconductor cannot satisfy the required performance of either photocurrent or conversion efficiency to meet commercial application due to their intrinsic limitations on performance and defects on properties, such as low solar light absorption, poor charge-carrier transportation, and severe photocorrosion under illumination (Table 2). Therefore, effective strategies such as surface modifications\(^{[63]}\) need to be applied to improve these properties of photoanodes. What is noteworthy is that designing functional photoanodes incorporated with cocatalysts to offset the drawbacks of single material is one of the states of art in PEC water splitting.\(^{[57]}\)

Table 3 shows the basic conditions and performances of photoanodes before and after the cocatalysts modification for water oxidation. It is evident that for most single semiconductor photoanodes, there is a significant gap between the practical photocurrent density and the theoretical ones. Whereas, after a photoanode is coupled with the cocatalyst, the current density multiplies and the aforementioned disparity shrinks in varying degrees. Hence, looking for suitable cocatalysts and coupling them with semiconductors are reasonable methods to increase the efficiency of PEC water oxidation.
performance of the obtained photoanodes. The lower the onset potential and higher photocurrent density, the better performance of photoanodes. When the proton energy absorbed by photoelectrodes is equal to or above the bandgap at these operating potentials (that is, \( h\nu \geq E_g \)), the OER at the electrode–electrolyte interface will be driven by a minority of hole carriers in n-type electrodes while the HER will be initiated by a minority of electrons on the cathode surface. The potential at which OER/HER begins to happen under light is defined as the theoretical photocurrent density, which can be calculated by Equation (5)

\[
J_{\text{phmax}} = e \int_{0}^{\lambda_{\text{phmax}}} \frac{1}{E_g} I(\lambda) d\lambda
\]

where \( J_{\text{phmax}} \) is the theoretical photocurrent density, \( E_g \) is the bandgap of the semiconductor, and \( I(\lambda) \) represents the photon flux at the wavelength of \( \lambda \).

The theoretical photocurrent density is mainly determined by the bandgap of the semiconductor. Hence, it implicates the theoretical limit of a semiconductor to employ absorbed protons for water splitting. From Table 3, we can see that there is still a big gap between the practical photocurrent density and the theoretical one for most photoanode materials. Therefore, further research to optimize the performance of the photoelectrodes and approach the theoretical value of current density is quite indispensable.

Both the onset potential and photocurrent density can be demonstrated via linear sweep voltammetry (LSV), which is a voltammetric technique where electric current between working and counter electrode is measured while linearly sweeping the potential of the working electrode in the positive direction. It is also referred to as \( J-V \) measurements (photocurrent density vs voltage). In most cases, the data will be recorded in the dark to minimize complications arising from light exposure. The LSV plot under dark scarcely exhibits any current.\(^{[68]}\) Whereas, all the samples show photoresponse to the radiance after irradiation. Specifically, after the introduction of the semiconductor can be completely absorbed and all of the absorbed protons can be utilized for water splitting, then the photocurrent density will reach a maximum value, also known as the theoretical photocurrent density, which can be calculated by Equation (5)
of Co–Pi onto the BiVO$_4$/ZnO ND photoanode, it emerges as much higher PEC performance than BiVO$_4$/ZnO nanodendrite (ND). The photocurrent density at 1.23 V$_{RHE}$ rises from 2.45 to 3.5 mA cm$^{-2}$, the saturated photocurrent density rises from 3.25 (at 1.35 V) to 3.5 mA cm$^{-2}$ (at 0.8 V), and the onset potential negatively shifts from 0.7 V$_{RHE}$ to 0.3 V$_{RHE}$, indicating that the performance of BiVO$_4$/ZnO ND can be optimized by the cocatalyst Co–Pi significantly.

### 2.3.2. PEC Efficiency

Multiple methods can be used to measure PEC efficiency and help us gain more insight into material performance. Usually these methods can be divided into two main categories: 1) Benchmark efficiency (suitable for mainstream reporting of stand-alone water splitting capability) like solar-to-hydrogen (STH) conversion efficiency and 2) diagnostic efficiencies

### Table 3. Summary of properties of common photoanode materials and PEC performance.

| Photoanodes     | Bandgap [eV] | Bandgap wavelength [nm] | Theoretical STH$^{a}$ efficiency [%]$^{b}$ | Theoretical photocurrent density under 1 Sun irradiation 1.23 V$_{RHE}^{c}$ [mA cm$^{-2}$] | Practical photocurrent density [mA cm$^{-2}$] | Onset potential [mV, RHE] | Experimental conditions |
|-----------------|--------------|-------------------------|---------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------|--------------------------|-------------------------|
| Fe$_2$O$_3$     | 2.20         | 564                     | 12.9                                        | 10.6                                                                           | 0.20                                        | 0.84                     | 1.23 V$_{RHE}$, 0.5 m K-Pi (pH = 7) under AM 1.5G (100 mW cm$^{-2}$) [48] |
| α-Fe$_2$O$_3$/ NiCoAl-LDH$^{d}$ |              |                         |                                              |                                                                                |                                             |                          |                         |
| BiVO$_4$        | 2.40         | 517                     | 9.1                                         | 7.5                                                                            | 1.20                                        | 0.70                     | 1.23 V$_{RHE}$, 0.2 m Na$_2$SO$_4$ (pH = 7), under AM 1.5G (100 mW cm$^{-2}$) [73] |
| β-FeOOH/BiVO$_4$ |              |                         |                                              |                                                                                |                                             |                          |                         |
| TiO$_2$ (Rutile) | 3.00         | 413                     | 2.2                                         | 1.8                                                                            | 0.79                                        | 0.50                     | 1.23 V$_{RHE}$, 0.5 m Na$_2$SO$_4$ (pH = 7), under AM 1.5G (100 mW cm$^{-2}$) [74] |
| TiO$_2$/ZnFe-LDH-PE$^{e}$ NA$^{f}$ |              |                         |                                              |                                                                                |                                             |                          |                         |
| TiO$_2$ (Anatase) | 3.20         | 388                     | 1.3                                         | 1.1                                                                            | 1.30                                        | 0.57                     | 1.23 V$_{RHE}$, 0.1 m Na$_2$SO$_4$, under AM 1.5G (100 mW cm$^{-2}$) [75] |
| TiO$_2$ @CoNi-LDHs NTAs$^{g}$ |              |                         |                                              |                                                                                |                                             |                          |                         |
| WO$_3$          | 2.70         | 459                     | 4.8                                         | 4                                                                              | 0.56                                        | 0.62                     | 1.23 V$_{RHE}$, 0.1 m KNO$_3$ (pH = 1.0), under AM 1.5G (100 mW cm$^{-2}$) [76] |
| WO$_3$/Ir-P0$_3$H$_2$ |              |                         |                                              |                                                                                |                                             |                          |                         |
| CuWO$_4$        | 2.30         | 540                     | 10.8                                        | 9.0                                                                            | 0.58                                        | 0.30                     | 0.8 V$_{RHE}$, 1 m Na$_2$SO$_4$ (pH = 6.8), under AM 1.5G (100 mW cm$^{-2}$) [77] |
| CuWO$_3$/CdS/FeOOH |              |                         |                                              |                                                                                |                                             |                          |                         |
| ZnO             | 3.20         | 388                     | 1.3                                         | 1.1                                                                            | 0.04                                        | 0.76                     | 1.23 V$_{RHE}$, 0.5 m Na$_2$SO$_4$ (pH = 6.62), under AM 1.5G (100 mW cm$^{-2}$) [67] |
| NiO/ZnO         |              |                         |                                              |                                                                                |                                             |                          |                         |
| TaON            | 2.38         | 521                     | 9.9                                         | 7.7                                                                            | 0.80                                        | 0.65                     | 0.6 V$_{Ag/AgCl}$, 0.1 m Na$_2$SO$_4$ (pH = 6), under visible light (λ > 400 nm) [78] |
| IrO$_2$/TaON    |              |                         |                                              |                                                                                |                                             |                          |                         |
| Ta$_3$N$_4$     | 2.07         | 600                     | 15.9                                        | 13.1                                                                           | 0.90                                        | 1.00                     | 1.23 V$_{RHE}$, 1 m NaOH (pH = 13.6), under AM 1.5G (100 mW cm$^{-2}$) [79] |
| Ni(OH)$_2$/Ta$_3$N$_4$ |              |                         |                                              |                                                                                |                                             |                          |                         |

$^{a}$STH: solar to hydrogen; $^{b}$V$_{RHE}$: Volt versus RHE; $^{c}$LDH: layered double hydroxides; $^{d}$PE: photo-assisted electrodeposition (PED); $^{e}$NAS: nanoarrays; $^{f}$NTAs: nanotubes; $^{g}$V$_{Ag/AgCl}$: Volt versus Ag/AgCl.
(to characterize and understand materials system or interface performance), such as incident photon-to-current efficiency (IPCE), absorbed photon-to-current efficiency (APCE), and applied bias photon-to-current efficiency (ABPE). IPCE covers the conversion efficiency of absorbed light and the degree of light absorption while APCE only considered the effects of absorbed light. As shown in Figure 7b, after illumination, only part of the incident photons can be absorbed in photoelectrode. Thus, by definition, the value of IPCE is always lower than that of APCE. Meanwhile, ABPE was measured under bias, so the value is closer to real experiment conditions. Despite that these methods are all used to evaluate the efficiency of a PEC device, they are calculated by different formulas and each have dissimilar emphasis. Hence, they are all unique in PEC research.[36,56]

**STH Efficiency.** STH efficiency is the most essential and practical parameter to characterize the water splitting ability of a PEC cell among all the efficiency metrics. It describes the water splitting efficiency of a PEC cell illuminated by broadband sunlight under zero bias conditions and it is the only device efficiency that can be commonly used to act as a reliable reference to rank a PEC device against others.[85] A STH efficiency higher than 10% can be used for practical application.[86] Table 3 lists the STH efficiency of some typical photoanodes, and it shows the efficiency of photoanodes that can be achieved up to now is still far from being qualified for commercial use.

The standard definition for STH efficiency under 1 sun condition can be expressed by Equation (6). The numerator is the output energy of H₂ based on the rate of H₂ evolution directly measured by analytical methods, which equals to the rate of hydrogen production (mmol s⁻¹) multiplied by the change in Gibbs energy per mole of H₂ (that is, ΔG₀ = 237 kJ mol⁻¹ at 25 °C). And the denominator is the incident solar energy...
input from sunlight which equals to $P_{\text{total}}$ (solar energy flux, mW cm$^{-2}$) multiplied by the surface area (cm$^2$) of the irradiated electrode.\cite{36,56,68,87} Figure 7c shows the STH efficiency of FeOOH/Mo:BiVO$_4$ versus Ni/Si$\alpha$ as an example. As can be seen, the STH efficiency climbs up from 1.27% to 1.54%, while the $S_{\text{tot}}$ area declines from 1 to 0.2 cm$^2$. As the output power is decided by the thermodynamic water splitting potential (1.23 eV at 25 °C) based on $\Delta G_0$, the short-circuit photocurrent density ($j_{\text{sc}}$), and the Faradaic efficiency ($\eta_F$) for hydrogen evolution, the STH efficiency can also be expressed by Equation (7) as a substitute.\cite{36,56}

$$\text{STH} = \left[ \frac{P_{\text{total}} \left( \text{mW cm}^{-2} \right) \times \text{Area} \left( \text{cm}^2 \right)}{J_{\text{sc}} \left( \text{mA cm}^{-2} \right) \times 1.23(\text{eV}) \times \eta_F} \right]_{\text{AM} 1.5G}$$

(6)

$$\text{STH} = \left[ \frac{j_{\text{sc}} \left( \text{mA cm}^{-2} \right) \times 1.23(\text{eV}) \times \eta_F}{P_{\text{total}} \left( \text{mW cm}^{-2} \right)} \right]_{\text{AM} 1.5G}$$

(7)

It needs to be emphasized that Equations (6) and (7) can be used only if it is confirmed that the water splitting reaction proceeds without any sacrificial electron donor or acceptor. Once they are utilized, water will not be split, and the above equations for STH efficiency become meaningless.\cite{36,56}

IPCE: The IPCE, which is synonymous with the external quantum efficiency (EQE), describes the photocurrent collected per incident photon flux due to the electrons moving through an external circuit as a function of irradiation wavelength. It is independent of the light sources used in the experiment and is one of the most crucial diagnostic tools to understand the inherent performance of a PEC photoanode.\cite{36,56}

The IPCE can be calculated using Equation (8) at a given bias voltage:

$$\text{IPCE} \left( \% \right) = \frac{\text{electrons} \left( \text{cm}^2 \text{s}^{-1} \right)}{\text{photons} \left( \text{cm}^2 \text{s}^{-1} \right)} = \frac{\text{1240}(V \times \text{nm}) \times j_{\text{ph}} \left( \text{mA cm}^{-2} \right)}{\lambda (\text{nm}) \times P_{\text{mono}} \left( \text{mW cm}^{-2} \right) \times (1 - 10^{-10})} \times 100$$

(8)

where 1240 (V × nm) equals to $\hbar$ (Planck’s constant) multiplied by $c$ (the speed of light) and $\epsilon$ (the charge of an electron, 1.6 × 10$^{-19}$ J eV$^{-1}$); $j_{\text{ph}}$ is the measured photocurrent density (mA cm$^{-2}$); $\lambda$ represents the wavelength of incident light (nm); $P_{\text{mono}}$ is the intensity of the incident light (mW cm$^{-2}$); A represents the absorbance of a sample, which can be estimated from Beer’s Law.

ABPE: ABPE is of particular interest because STH cannot reflect a true PEC water splitting process when a bias is applied.\cite{36} It can further elucidate the diagnostic performance of the employed photoelectrodes and also show the net production of current through the extraction of electrons from the electrode by applying a suitable bias voltage. The following formula can be employed to calculate the ABPE in a two-electrode configuration (working electrode and counter electrode)

$$\text{ABPE} \left( \% \right) = \left( \frac{j_{\text{ph}} \left( \text{mA cm}^{-2} \right) \times (1.23 - |V_b|)(V)}{P_{\text{total}} \left( \text{mV cm}^{-2} \right)} \right) \times 100$$

(9)

where $j_{\text{ph}}$ is the obtained photocurrent density under an applied bias $V_b$ (mA cm$^{-2}$); $V_b$ equals applied bias (V); $P_{\text{total}}$ is the illumination intensity of the light source (mW cm$^{-2}$) and $V$ is the open circuit potential recorded from the J–V curve under illumination.\cite{88}

Figure 7c depicts the ABPE performance of the optimized NiFe$_2$O$_4$/Fe$_2$O$_3$ thin films deposited on planar (NF1-P) and 3D-nanostructured substrates (NF1-NSP) relative to pure Fe$_2$O$_3$ deposited on FTO glass under solar irradiation (100 mW cm$^{-2}$). The peak ABPE value of NF1-NSP was 0.206% located at 1.06 V, 1.87 times higher than NF1-P and 4.7 times higher than pure Fe$_2$O$_3$, which means NF1-NSP has better performance than the pure Fe$_2$O$_3$.

2.3.3. Photostability

Photostability is defined as the capability of photocorrosion inhibition. Photostability test is also fundamentally significant to evaluate the durability of a photoanode material. In general, the photostability of a photoanode can be measured by J–t curves (photocurrent density vs time) under illumination with a certain bias between the working electrode and the
counter electrode. A bias that could lead to photocurrent densities corresponding to anticipated PEC operations (typically 1–10 mA cm\(^{-2}\)) will be a suitable bias for testing. For example, Figure 7f describes the \( J-t \) measurement of BiVO\(_4\)/FeOOH/NiOOH photoelectrode in potassium borate buffer (KB) (blue) and KB+V (V\(_2\)O\(_5\)) (red) solution. The photocurrent density of BiVO\(_4\)/FeOOH/NiOOH film in KB solution shows an upward trend for about 20 h and then decreases gradually after about 40 h, indicating that the photoanode is not completely photo-stable over a long time. Correspondingly, the photocurrent density of BiVO\(_4\)/FeOOH/NiOOH film in KB+V solution gradually rises to 3.2 ± 0.2 mA cm\(^{-2}\) during the first 10 h and is maintained for 50 h, suggesting that photocorrosion is suppressed due to the addition of V\(_2\)O\(_5\) to the electrolyte.

2.3.4. Conductivity

The conductivity of the PEC system determines the charge transfer efficiency in the electric circuit. Usually, it can be measured by electrochemical impedance spectroscopy (EIS), which is one of the universal and powerful modulation techniques and is helpful for further understanding the complex reaction at the photoelectrode surface. It allows sample characterization in electrolyte under bias potential, which is one of the major advantages of EIS compared with other spectroscopic techniques.

EIS experiments are composed of applying a small-amplitude sinusoidal signal to the photoanodes at a certain bias and measuring the response of the system to the perturbation. During an EIS experiment, the current density of the electrode is recorded while applying an alternating current signal with different frequencies (usually 0.1 Hz < \( f \) < 10^6 Hz) to the system.\(^{[89]}\) By EIS characterization, Nyquist plot (real vs imaginary impedance) can be obtained. In the spectrum, the X-axis is the real impedance (\( Z' \), in the unit of Ohms), while the Y-axis represents the imaginary impedance (\( Z'' \), in the unit of Ohms).\(^{[90]}\) Theoretically, a typical Nyquist plot can be divided into two parts: high frequency region and low frequency region, as shown in Figure 8a.\(^{[90]}\) High frequency region can be observed close to the original point of the plot. In this region, the photo-electrochemical process is controlled by the rate of charge transfer and the curve exhibits the shape of a semicircle which hints the existence of an interface. In low frequency region (large impedance, far from the origin), the process is determined by the rate of mass transfer. When the applied frequency approaches zero, the \( Z' \) equals to \( Z'' \), and the curve turns into a straight line with a slope of 1.\(^{[30,89,90]}\) Sometimes, there are more than one semicircles on the Nyquist plot. Gomes and Vanmaekelbergh\(^{[91]}\) ascribe these semicircles to a multiple-step electron- or charge-transfer process mediated via surface states or reaction intermediates. In the actual EIS experiments, the curves at the Nyquist plot tend to display a shape of distorted semicircle or a straight line whose slope is not equal to 1, because the shape of the curves could be affected by the intrinsic or electrochemical properties of electrodes, electrolytes, and the conditions of the experiments.\(^{[92]}\)

For the spectrum, the charge-transfer resistance (\( R_{\text{ct}} \)) is in direct proportion to the chord length of the arc. The larger chord length, the larger \( R_{\text{ct}} \) will be, which also indicates its poor charge-transfer ability or conductivity for water splitting.\(^{[30]}\) Furthermore, the capacitance can be determined by fitting the

![Figure 8](https://example.com/figure8.png)

**Figure 8.** a) A typical Nyquist plot of a photoelectrode in the photo-electrochemical process. \( \omega \) is the angular frequency. b) The consists of total impedance. c) A simplified equivalent resistor-capacitor (RC) circuit model. d) Nyquist plots of the sample P and sample D at pH 8. Reproduced with permission.\(^{[88]}\) Copyright 2017, Elsevier.
frequency responses with an equivalent resistor-capacitor (RC) circuit model.\[^{[89]}\] As shown in Figure 8b, at the interface between electrode and electrolyte in a PEC water splitting process, there are inner resistances of electrolyte and photoelectrodes (R\(_o\)), double layer capacitance (C\(_d\), derived from nonreactive ions in the electrolyte which only change the charge distribution), and Faradaic impedance (Z\(_f\), derived from the active ions in the electrolyte, which leads the charge transfer), so an equivalent circuit model can be established based on them to indicate the conductivity of the entire system.\[^{[90]}\] A simplified model is shown in Figure 8c.

Moreover, the light intensity applied to the PEC system will largely influence the impedance spectra. The Nyquist plots of the sample P (pristine Fe\(_2\)O\(_3\)) and sample D (Co-Ac/Ti-Fe\(_2\)O\(_3\) at pH 8 are shown in Figure 8d. The arc of them shows the similar trends but different diameters. It indicates that the internal resistance which determines the rate of charge transfer in the dark is significantly larger than that under light conditions. This resistance is derived from the charge equilibrium, which leads the electrons to accumulate in the electrodes.\[^{[91,94]}\] Whereas, when under illumination, the electrons stored in the conduction band will transfer to the external circuit because of the photoexcitation and then lower the impedance of the system. Furthermore, it is noteworthy that for the same impedance spectrum, more than one equivalent RC circuit models can be used to fit the frequency responses. Hence, it is a subjective approach to speculate a PEC process by an equivalent circuit model.

### 2.4. Cocatalysts

The water oxidation half reaction (Equation (2)) is a fundamental element of water splitting, but it is more complex than water reduction. Therefore, this half reaction is regarded as the most challenging step in the artificial PEC water splitting. To significantly improve the activity of photoanodes, coupling the suitable cocatalysts has been regarded as a very potential and effective approach.

Cocatalyst is a kind of special catalyst which does not have optical absorption property and cannot improve the light harvesting directly but is highly conductive and plays an indirect role in improving the efficiency of PEC water oxidation.\[^{[95]}\] It can be an amorphous structure with enriched reaction sites or a continuous layer with certain crystallinity. Coupling proper cocatalyst with photoanode is an effective method to enhance the PEC water splitting performance. However, the functions of cocatalysts still remain disputed:

1) Cocatalysts are conducive to promoting the separation of electron–hole pairs due to the ability to change the distribution of photogenerated carriers.\[^{[96]}\] After engineering a water oxidation cocatalyst on the photoanode, an intimate junction at the interface will be formed. Then, an enhanced upward band bending occurs due to the difference between the cocatalyst and electrode (Figure 9a), leading electrons to be depleted in the space charge region and excessive holes to occur on the surface of the semiconductor. Then due to the hole capture sites on the cocatalyst, the photogenerated holes of semiconductor will transfer to the cocatalyst through the junction, which provides a shortcut for their transfer for oxidizing water rather than accumulating on the surface. This process could reduce the surface hole concentration of the semiconductor and relieving the pinned quasi-Fermi level to a certain degree which in turn reduces surface recombination.\[^{[96–98]}\]

2) Cocatalysts could increase the stability of photocatalysts physically and suppress the photocorrosion. They can accelerate the reaction process and consume the left photoinduced carriers, especially the holes so as to avoid photocorrosion. For instance, (oxy)sulfides and (oxy)nitrides are easily oxidized by photogenerated holes, resulting in their self-decomposition. Whereas, loading cocatalysts thereon can suppress the decomposition by extracting the photogenerated holes for O\(_2\) evolution, thereby enhancing the robustness of semiconductors.\[^{[97]}\] Furthermore, cocatalysts could also remove the surface trapping states of photoanodes (Figure 9b), which could cause substantial recombination on the surface and pin the Fermi level, and then ensure the stability of the system.\[^{[99,100]}\]

3) In a PEC water oxidation process, cocatalysts possess numerous reaction sites, which can lower the overpotential of O\(_2\) evolution reactions on the surface of semiconductors, give rise to a cathodic shift of onset potential, enhance the kinetics of water oxidation, and then largely improve the PEC water oxidation performance.\[^{[18,97,101]}\]
In total, a multitude of researches have proved that coupling cocatalysts is an effective solution to enhance PEC water oxidation performance and the feasible mechanisms are also explained from different perspectives. Whereas, it is also undeniable that some of the explanations about how cocatalysts work still remain vague, thus it is a must to conduct further research and come up with more clear clarifications to assist us in having insight into the virtual mechanism.

3. Cocatalysts for Photoanodes: Construction and Regulation

3.1. Metal Phosphates/Phosphides

3.1.1. Metal Phosphates

Metal phosphates, especially cobalt phosphates (Co–Pi), are the pioneer cocatalyst candidates applied in PEC-OER process, as they are earth-abundant, amorphous, ion permeable, easy to form on diverse surfaces of varying semiconductor materials, and self-healing when in the presence of phosphate buffer solution. Besides, they can also be favorable for catalyzing water splitting over a wide pH range of 1–14,[102] making them viable alternatives to noble-metal-based cocatalysts.

In 2008, the formation of amorphous Co–Pi was first reported by Kanan and Nocera.[104] After that, Steimmler and Cho[105] and Zhong et al.[106] also reported the excellent capability of Co–Pi in solar water splitting. Since then, this catalyst has gained numerous interests and become one of the research hotspots. It is reported that Co–Pi can change the reaction pathway to reduce overpotential and promote surface charge transfer kinetics.[107] Co$^{3+}$/Co$^{2+}$ of Co–Pi can be oxidized to a higher valence state of Co$^{3+}$ under the effect of current or holes, and then Co$^{3+}$ can be reverted back to Co$^{2+}$/Co$^{3+}$ rapidly after it oxidized water molecules or sacrificial agents,[108] which is recognized as an entire catalytic reaction cycle. Meanwhile, as the change in valence state of Co ion is invertible, the accumulation of photoinduced holes at the interface of electrode and electrolyte can be relieved timely and effectively and then an improved PEC performance can be achieved.[102]

Recently, in-depth study about Co–Pi for PEC water oxidation has been carried out. Some of the researchers focus on the interaction of Co–Pi and traditional photoanodes, such as α-Fe$_2$O$_3$, BiVO$_4$, TiO$_2$ etc.[96,102,108-112] Some further clarified the mechanism of the Co–Pi applied on semiconductors.[96,109] For example, Carroll and Gamelin[96] reported that water-oxidation kinetics of α-Fe$_2$O$_3$ actually gets slow after the deposition of Co–Pi, but electron–hole recombination slows even more, resulting in a net enhancement of water-oxidation quantum efficiency, which is opposite to previous expectations. Moreover, the methods have also been investigated for optimizing the effects of Co–Pi in terms of experiment conditions such as quantity (i.e., thickness),[102,108] deposition time,[112] pH values of the solution,[106] applied bias potential,[110] or morphology of the semiconductors.[111] For instance, Co–Pi was coated onto BiVO$_4$ photoanode via a PED (photoelectron deposition) technique by Hernández et al.[110] They varied the bias and time for PED to maximize the Co–Pi activity and found that a combination of 1.32 V RHE and 60 s for PED could contribute to an optimum amount of Co–Pi on BiVO$_4$ and an improved photocurrent of up to 3 mA cm$^{-2}$ at 1.23 V RHE at pH 7.

In order to further optimize the PEC performance of catalysts, some ternary composites containing Co–Pi like Fe$_2$O$_3$/CdS/Co–Pi[109] and BiVO$_4$/ZnO/Co–Pi are also proposed.[113-116] These ternary catalysts exhibit much more prominent water oxidation capability due to the intimate contact of three composites and the synergistic effects among them. In most cases, the intermediate material between the photoanode and the Co–Pi works as a charge bridge between them[114-116] (such as what Figure 10a shows) or an electron trap[68] (like Figure 10b) to accelerate the charge separation. For instance, Yang and Wu[68] reported a Co–Pi/BiVO$_4$/ZnO ternary system for water oxidation. As shown in Figure 10b, the photogenerated holes drift to central portions of ZnO trunk and branches and then be depleted while the holes can be collected by Co–Pi on the surface of BiVO$_4$, which significantly promotes the charge separation efficiency and the PEC performance (3.5 mA cm$^{-2}$ at 1.23 V RHE under 1 sun light irradiation).

Except for Co–Pi, other metal phosphates,[117,119-122] such as Ni–Pi[117] and Fe–Pi[121] are also observed to be capable of facilitating PEC water oxidation. For instance, Gao and co-workers[119] employed a deposit-PEC method to incorporate Ni–Pi with Ti doped α-Fe$_2$O$_3$, which showed enhanced PEC water oxidation activity. It also reveals that Ni–Pi could restrain surface states which attribute to Fe$^{3+}$/Fe$^{2+}$ redox couples in oxygen deficient regions and will trap holes or electrons on the surface, causing serious recombination,[121] while Co–Pi could not in this system. Liu et al.[117] described the synthesis of α-Fe$_2$O$_3$ nanoarrays photoanode with ultrasmall NiFe-phosphate (NFP) nanoparticles via a facile dip-coating and annealing method (Figure 10c). The NFP nanoparticles have the combined effects of Ni–Pi and Fe–Pi and show higher catalytic activity due to the synergistic effect on promoting the multiphoton-coupled electron transfer process for the PEC water oxidation (Figure 10d).

3.1.2. Metal Phosphides

Metal phosphides typically have a metallic nature, and the introduction of metal phosphide to the surface of semiconductors could promote the interfacial charge transfer and transportation to the surface. Previously, metal phosphides have been extensively investigated as outstanding OER electrocatalysts, while their application in the PEC-OER process has rarely been reported. Recently, some metal phosphides have been found to work as PEC-OER cocatalysts. For example, Wang et al.[123] reported that GaN:ZnO/ NiCoFeP showed high efficiency for PEC O$_2$ evolution. With NiCoFeP, the surface charge injection is greatly promoted and the photocurrent density at 1.23 V RHE reached up to 3.9 mA cm$^{-2}$.

In spite of the high activity, the demanding preparation conditions in terms of high temperature and the strong reductive ability are still the biggest issues that hinder their extensive application. Confronted with it, researchers have made some efforts to tackle this bottom-neck. Among them, an ideal technique named metal–organic chemical vapor deposition was designed to grow metal phosphide onto semiconductors directly under mild conditions. With this method, Schipper et al.[118] successfully synthesized an efficient TiO$_2$/FeMnP core/shell
photoanode for PEC water oxidation, which reached the theoretical photocurrent density for rutile TiO$_2$ of 1.8 mA cm$^{-2}$ at 1.23 V$_{RHE}$ under 1 sun irradiation (Figure 10d). The structural schematic diagram and photoconversion efficiency can be seen in Figure 10e,f, respectively. Enlightened from the bifunctional effects of metal phosphide in the field of electrochemistry, some researchers also explored their dual function in PEC water splitting. Kim et al.\cite{124} reported a CoP-coupled Mo:BiVO$_4$ photoanode connected with CoP-coupled Ni-foam synthesized by drop casting, exhibiting excellent PEC-OER and PEC-HER activities. And the CoP loading brings ≈90% injection of holes arriving on the surface, which avoided the serious recombination and largely boosted the kinetics of reaction.

3.2. Metal Oxides

Metal oxides such as IrO$_x$, RuO$_x$, NiO$_x$, CoO$_x$, and other hybrid metal oxides are promising materials as cocatalysts for the PEC applications, especially for the water oxidation, due to their easy-established preparation, high stability, and activity facilitating water oxidation.

3.2.1. Noble Metal Oxides

Noble metal oxides such as RuO$_x$ or IrO$_x$ are regarded as one of the most active cocatalysts, and exhibit excellent metallic electronic conductivity.\cite{125} Therefore, they are recognized as very promising candidates for PEC water splitting theoretically. Majumder and Khan\cite{126} revealed an obvious onset potential shift of ≈120 mV using α-Fe$_2$O$_3$ photoanode coupled with RuO$_2$ for PEC water oxidation. Tilley et al.\cite{127} reported the synthesis of IrO$_2$-loaded α-Fe$_2$O$_3$ photoanode via an electrochemical deposition strategy. It is the first time that the photocurrent density of α-Fe$_2$O$_3$ photoanode at 1.23 V$_{RHE}$ could surpass 3 mA cm$^{-2}$. Apart from above, Ag-based catalysts (AgCat) are also very potential for promoting water oxidation due to their high
activity. In 2017, Sordello et al.\cite{128} first reported that when coupling AgCat with TiO₂ and hematite separately, the existence of AgCat can help produce much higher photocurrent density and O₂ production compared with bare semiconductors or Co–Pi modified ones.

However, these noble-metal based materials are not perfect cocatalysts due to some defects. For example, RuO₂ exhibits a weak ability to resist corrosion under alkaline conditions and IrOₓ possesses relatively poor conductivity. Furthermore, the most nonnegligible issue is their high cost, extremely limiting their large-scale application. Thus, it is highly necessary to find highly active cocatalysts with good stability but low cost as alternatives of these precious metal-based cocatalysts, and the earth-abundant transition-metal oxides should be one of the best choices.

### 3.2.2. Earth-Abundant Transition-Metal Oxides

In the recent years, earth-abundant transition-metal oxides gradually emerge with their advantages and become good alternatives due to their low cost and outstanding ability to resist chemical-corrosion or photocorrosion in certain electrolytes. And among these materials, cobalt- and nickel-based oxides are recognized as the promising PEC-OER cocatalysts.

\(\text{CoO}_x\): CoOₓ is very popular as an excellent cocatalyst. It has been confirmed that CoOₓ is capable of reducing reaction activation energy and forming internal built-in electric field which can boost the electrons transfer number at the same time. In addition, other merits of utilizing CoOₓ as the cocatalysts include the selectivity improvement of water oxidation, the large Faradaic efficiency enhancement of the reaction process, and the higher stability.\cite{129} Up to now, CoOₓ has been widely applied in PEC OER water oxidation.\cite{130–141} For example, Ti/Fe₂O₃/CoOₓ was successfully designed for PEC water oxidation\cite{137} and the photocurrent could achieve an obvious enhancement compared with Ti/Fe₂O₃, resulting from the construction of a metallic charge transfer channel between the photoanode and cocatalyst, which could accelerate the flow speed of holes. Apart from inorganic materials, CoOₓ was also reported to be anchored onto organic molecules for oxygen evolution. CoOₓ incorporated perylene diimide was first prepared by Kirner and Finke for PEC water oxidation,\cite{133,140} which made the hypothesis of using organic molecules in water oxidation come true.

Generally, the method to deposit cobalt oxides onto photoanodes was tuned, which realized the modulation of structure and the improvement of PEC performance. Xi et al.\cite{136} revealed an in situ incorporation strategy to couple Co₃O₄ with Fe₂O₃ and the composite exhibited preferable capabilities compared to those prepared by ex situ procedures due to higher surface roughness, larger interfacial area, and smaller particle size. Meanwhile, an atomic layer deposition (ALD) method was also applied to couple hematite with an ultrathin CoOₓ layer at low deposition temperature, the morphology of which after 25 cycles of ALD can be seen in Figure 11a,b.\cite{139} The assembled composite inhibits the recombination and achieves a high IPCE.

![Figure 11](image-url)
increased 66% at 1.23 V_{RHE}. In addition, Zhan et al.\textsuperscript{[130]} reported a WO_3/CoO_x photoanode for water oxidation with a dipping annealing strategy. The result shows the outstanding catalytic performance of WO_3/CoO_x photoanode, with IPCE value reaching 49.1% from 24.9%. Another common technique is impregnation.\textsuperscript{[132,133]} CoO_x fine particles was deposited on Ta,Ni electrode by Niishiro et al.\textsuperscript{[135]} via this way, which conspicuously improved the durability and reaction efficiency of CoO_x/SnNb_2O_6.

A suitable deposition method can modulate CoO_x with improved morphologies and better performance. Besides, other strategies can also boost the capability of cobalt oxides. For example, metal–organic framework (MOFs) technology is used to enhance the activity of CoO_x. MOFs-derived porous CoO_x sheets were employed to modify TiO_2.\textsuperscript{[141]} The prepared photoanode shows fair stability and achieves a photocurrent density of 2.71 mA cm^{-2} at 1.23 V_{RHE} in alkaline electrolyte on account of the large specific surface area and enriched pore structure originated from MOFs.

NiO_x. Nickel oxide (NiO_x) is viewed as one of the best OER cocatalysts as it is earth-abundant, cost-efficient, stable even at high pH, and optically transparent under visible light, which enable the deposited photoanodes possess high durability and excellent water oxidation performance.\textsuperscript{[134]} In 2012, it is found by Sun et al.\textsuperscript{[142]} that when incorporated with n-type silicon (n-Si), the NiO_x thin film can be utilized as the cocatalyst to resist photocorrosion and achieve high oxygen evolution efficiency under neutral pH condition, which brought about some possibilities for nickel oxide to be applied in PEC water oxidation. Subsequently, Sun et al. further investigated the properties of sputtered NiO_x films,\textsuperscript{[143,144]} and found the NiO_x layer is a conductive and chemically stable coating that can stabilize the photoanode and boost the PEC water oxidation efficiency simultaneously. All their work gives a large impetus to the further research of NiO_x serving as a cocatalyst.

Recently, an amorphous NiO_x cocatalyst was induced onto ZnO photoanode by a method of two step electrodeposition and annealing,\textsuperscript{[67]} as shown in Figure 11c. This core/shell hybrid broke the efficiency limit of pristine ZnO and achieved a remarkable 260 mV negative shift of onset potential for photooxidation of water. Another common method named metal–organic chemical vapor deposition strategy was applied to deposit NiO onto GaN. The band alignment between them offered efficient carrier separation and fast hole transport, making its PEC performance significantly outperform that of pure GaN.\textsuperscript{[146]} Besides, an n-silicon photoanode coated by a NiO_x layer was successfully synthesized via a pulsed laser deposition method for efficient PEC oxygen evolution.\textsuperscript{[147]} In addition, Fingerle et al.\textsuperscript{[148]} took a magnetron-sputtering method to deposit nickel oxide on the n-Si/SiO_2 photoanode and described the interaction of NiO_x layer and H_2O at the electrode/electrolyte interface, which was beneficial for the hole transport. All these investigations confirm that nickel oxides can be deposited onto the surface of photoanodes with different methods in order to satisfy various requirements and then gain a better performance.

Mixed Metal Oxides: The previous research mainly focused on the functions of monometallic oxide on the photoanodes, while the utilization of mixed metal oxides in PEC-OER is still under exploration though they usually possess higher conductivity and augmented active surface sites compared with monometallic catalysts. The reasons for that include: 1) mixed metal oxides are hard to grow uniformly onto the surface of semiconductors; 2) the chemical and crystal properties of most mixed metal oxides cannot be compatible with the semiconductors, resulting in the increment of interfacial recombination sites; 3) band alignment between semiconductors/catalysts/electrolytes must be suitable to reduce charge transfer resistance across interfaces; 4) partly due to the lack of predictive models used for the guidance of selecting precursor materials.\textsuperscript{[149]} Thus, the integration of mixed metal oxides with semiconductors to achieve high efficiency of solar water oxidation is still full of challenge.

In recent years, some researchers have broken this bottleneck and successfully synthesized the mixed metal oxides coated photoanodes with excellent PEC activity. Wu et al. reported the successful incorporation of NiMoO_4 nanosheet with TiO_2/Si nanowire arrays by a facile hydrothermal method for the first time.\textsuperscript{[149]} This photoanode could achieve a photocurrent value of 8.7 mA cm^{-2} at 2.5 V_{RHE}, remarkably higher than TiO_2/Si nanowire arrays. Han et al.\textsuperscript{[150]} also demonstrated that the CoWO_4 has very excellent catalytic activity even under mild conditions and can have a nonnegligible effect on the PEC performance of FeO_x photoanode. The existence of CoWO_4 can cause a significant reduction of charge transfer resistance at the photoanode/electrolyte interface. Thus, the CoWO_4/FeO_x system exhibits a competitive current density of 1.36 mA cm^{-2}, around threefold higher than bare hematite electrode. Furthermore, Xu et al.\textsuperscript{[151]} and Hajibabaei et al.\textsuperscript{[152]} reported the binary nickel and iron oxide modified hematite with enhanced efficiency. The performance of Fe-rich catalyst (Ni_{0.25}Fe_{0.75}O_x) coated hematite photoelectrode is optimized compared to the bare electrode. While the PEC activity of the Ni-rich (Ni_{0.75}Fe_{0.25}O_x) catalyst is lower than the former owing to the presence of interface trap states on the Ni_{0.75}Fe_{0.25}O_x that serves as the photocarrier recombination centers (Figure 12a,b). These results all indicate that the introduction of bimetallic oxide cocatalysts is capable of remarkably promoting the PEC performances of photoanodes.

Except for bimetallic oxide catalysts, polymeric oxides like FeNiCoO_x\textsuperscript{[153]} also show great potential for PEC oxygen evolution. Guevarra et al. discovered the BiVO_4 photoanodes evenly coated with combinatorial integration of Ni–La–Co–Ce oxides,\textsuperscript{[154]} and studied the properties of 858 mixed metal oxides covering a series of metal oxide loadings and then established a full Ni–La–Co–Ce oxide quaternary composition space. Figure 12c presents the composition maps of electrochemical power generation (P_{max}) for all three discrete composition libraries (L1, L2, L3), and each library contains 286 compositions of Ni–La–Co–Ce oxides. They found that around one third of the coatings would reduce the reaction efficiency, while selecting suitable combinations of metal oxide composition and loading can realize a topmost increment (14-fold) for PEC water oxidation in pH 13 electrolytes. Specifically, the antirefection effect of Ce-rich coatings is beneficial to augment the activity of photoanode, yielding a 20-fold enhancement in conversion efficiency compared to bare BiVO_4. Subsequently, they also explored the effects of Ni–Fe–Co–Ce oxides onto BiVO_4...
The result demonstrates that a specific combination of metal oxide composition and loading facilitates the yield of oxygen achieving a 13-fold increment in alkaline conditions. Their work provides a valuable reference for the research of pertinent interfaces and engineering mixed metal oxides anchored photoanodes with high performance for PEC water oxidation.

3.3. Metal (Oxy)hydroxides

It is well known that metal (oxy)hydroxides and their derivatives are among the well-established catalysts for PEC-OER process due to their low price, natural abundance, and abilities to lead to a large potential drop of Helmholtz layer at the photoanode/electrolyte junction. Most recently, some researches uncovered that metal (oxy)hydroxides have the potential to serve as the active cocatalysts integrated with suitable photoelectrodes for PEC water oxidation. Among these materials, nickel-based, iron-based, cobalt-based (oxy)hydroxides, as well as layered double hydroxides (LDHs) exhibit the superior performance and gained extensive interest.

3.3.1. Nickel-Based (Oxy)hydroxides

Numerous researches have confirmed that nickel (oxy)hydroxide cocatalysts can bring about an obvious negative shift of onset potential and a higher PEC water oxidation performance on various semiconductor photoanodes like hematite, vanadate, silicon, and vice versa. Quiñonero and Gómez coupled a small amount of Ni(OH)₂ on α-Fe₂O₃ films for improved PEC water oxidation activity. Liu et al. also reported the Ni(OH)₂-modified H-ZnO/CdS photoanode, which could achieve an enhanced photocurrent density of 4.65 mA cm⁻² at 0.4 VAg/AgCl.

In 2013, Wang et al. elucidated a detailed mechanism study about the role of Ni(OH)₂ in PEC water splitting. As
shown in Figure 13a, the effects of Ni(OH)₂ include two steps: first, the Ni²⁺ ions are oxidized to Ni³⁺ ions rapidly; then the Ni³⁺ ions are oxidized to Ni⁴⁺ ions at a low speed. The achieved Ni⁴⁺ ions are recognized as the actual active centers for water oxidation. However, the accumulated Ni³⁺ ions slowly formed Ni⁴⁺ ions and their instability significantly limited the application of Ni(OH)₂, although the introduction of Ni(OH)₂ can indeed enhance current density (Figure 13b). Since then, strategies have been adopted to promote the activity and stability of Ni(OH)₂. For example, Wang et al. [168] coupled Ni(OH)₂ with more active IrO₂ to realize its full catalytic activity (Figure 13c). As Figure 13d describes, with the introduction of IrO₂, another channel to transfer holes is formed. Through this channel, holes can be transformed to IrO₂ rapidly and then consumed for the water oxidation rather than oxidizing Ni³⁺ species to higher oxidation state, which largely enhanced the rate of water oxidation. However, with further investigations, some inherent limitations such as large thickness, poor electrical conductivity, and low hole transfer kinetics, which greatly restrict their further application, have been gradually discovered. Recently, NiOOH also possesses good stability and impressive PEC water splitting catalytic performance compared with Ni(OH)₂. For instance, the NiOOH coated (Sn, Zr) codoped Fe₂O₃ photoanode demonstrated by Tamirat et al. gives rise to a reduced onset potential of 0.58 V and an improved photocurrent density of 1.64 mA cm⁻² at 1.23 V_RHE [169]. And a Si/SiOₓ/ITO/NiOOH hybrid photoanode [170] was also revealed to provide plentiful active sites, facilitating the water oxidation efficiency to a large extent. All these works indicate practical applications of NiOOH for solar driven water oxidation. However, one of the defects restricting the application of NiOOH is that up to now the only valid synthesis route to synthesize NiOOH is the photoassisted electrodeposition [161]. Therefore, an alternate deposition method of NiOOH is still highly desired.

3.3.2. Iron-Based Oxyhydroxide

Iron-based oxyhydroxide has also been extensively investigated for efficient PEC oxygen production [33, 73, 101, 171–176]. It has potential advantages such as feasible synthesis, well stability, and resource abundancy [173, 176]. Yu et al. [176] reported the synthesis Fe₂O₃/FeOOH photoanode for better PEC water oxidation. Gong and co-workers [171] reported a FeOOH-loaded TiO₂/TiFe₂O₃ photoanode. With the introduction of FeOOH, the charge separation efficiency on the surface is significantly increased to 90% at 1.23 V_RHE.

However, with further investigations, some inherent limitations such as large thickness, poor electrical conductivity, and low hole transfer kinetics, which greatly restrict their further application, have been gradually discovered.
some innovative strategies have been taken to address these issues.\cite{33,73,101,173,175} A novel method of solution impregnation was utilized by Zhang et al.\cite{73} to synthesize oxygen vacancies enriched $\beta$-FeOOH ultrathin nanolayers on BiVO$_4$. The morphology differences of bulk FeOOH and this $\beta$-FeOOH can be seen in Figure 14a,b separately. Finally, the designed complex photoanode achieved a high photocurrent density of 4.3 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$, around twofold of the amorphous FeOOH nanofilms fabricated by electrodeposition (Figure 14c). Cho et al.\cite{33} innovatively added an extra oxalic acid etching step before depositing FeOOH onto Fe$_2$O$_3$, as Figure 14d presents, which could get rid of the surface disorder layer of hematite nanorods (NRs), enhance charge transfer efficiency, and largely improve the interface quality between the OER cocatalyst and photoanode.

3.3.3. Co-Based (Oxy)hydroxides

Moreover, Co-based (oxy)hydroxides were also recognized as the robust and promising cocatalysts to lower onset potential and favor injection of charge carriers.\cite{177} Many groups have been working on it.\cite{103,177–182} A Co(OH)$_x$ cocatalyst could help Ta$_3$N$_5$ photoanode have a significantly improved photocurrent.
of 5.5 mA cm\(^{-2}\) at 1.23 \(V_{\text{RHE}}\), which is one of the highest values among all currently available Ta\(_3\)N\(_5\) photoanodes.\(^{[182]}\) And Tang et al.\(^{[183]}\) demonstrated that the coating of CoOOH onto BiVO\(_4\) could form oxobridge bonding which can remove the surface trapping states and enhance photocurrent.

Lately, some researchers have explored the intrinsic factors that affect catalytic activity of Co-based (oxy)hydroxides. For example, Xu et al.\(^{[178]}\) described a successful synthesis of Ti-doped Fe\(_2\)O\(_3\) photoanode coated with CoOOH of three different crystallinities for water oxidation. They found that the moderate crystalline CoOOH can partially screen electrolyte, thus leading to an ideal band bending for charge separation and the most highly activity for water oxidation among these three kinds of CoOOH with various crystallinity. The interfacial energies and photocurrent when coated with CoOOH of different crystallinity are presented in Figure 14e,f. Wang et al.\(^{[180]}\) utilized a two-step impregnation method to load untrasmall Co(OH)\(_x\) nanoparticles onto TiO\(_2\) and polyheptazine (TiO\(_2–\)PH) hybrid photoanodes for water oxidation, the photocurrent of which remarkably outperforms that of conventional cocatalyst Co–Pi. They emphasized that the structural and optical properties will both have an impact on the activity of cocatalysts.

### 3.3.4. LDHs

LDHs, usually represented by the chemical formula \([\text{M}^{2+}\text{M}^{3+}(\text{OH})_2]\text{[A}^{x/n}\text{]}\cdot n\text{H}_2\text{O}\),\(^{[183–185]}\) belong to a large family of anionic clay materials and can be characterized by hydrotalcite-like layered structure, tunable composition, as well as flexible ion exchangeability. The lamellar framework (Figure 15a) consists of evenly distributed divalent and trivalent metal hydroxide octahedra stacked along the crystallographic c-axis. Water and anions are present between the interlayers. Reproduced with permission.\(^{[186]}\) Copyright 2014, Royal Society of Chemistry. b) The morphology model of TiO\(_2/r\text{GO/NiFe-LDH}\) system. Reproduced with permission.\(^{[195]}\) Copyright 2016, Royal Society of Chemistry. c) Cross-sectional schematic and energy band structure of \(n^+\text{p-Si/SiO}_2/\text{Ni/NiO}_x/\text{NiFe-LDH}\) photoanode for water oxidation. Reproduced with permission.\(^{[196]}\) Copyright 2018, American Chemical Society. d) \(J–V\) curves of Ti-TiO\(_2\)@LDH deposited for 40 s with three kinds of LDH (CoAl-LDH, CoCr-LDH, and CoFe-LDH) under illumination. Reproduced with permission.\(^{[201]}\) Copyright 2017, Royal Society of Chemistry. e) The proposed mechanism of water splitting on NiCoAl-LDH coated \(\alpha\text{-Fe}_2\text{O}_3\) photoanode and Pt cathode. f) LSV curves of \(\alpha\text{-Fe}_2\text{O}_3, \text{CoAl-LDH/\alpha}\text{-Fe}_2\text{O}_3, \text{NiAl-LDH/}\alpha\text{-Fe}_2\text{O}_3, \text{and NiCoAl-LDH/}\alpha\text{-Fe}_2\text{O}_3\) under AM 1.5G radiation in the 0.5 M K-Pi solution (pH 7) with a scan rate of 20 mV s\(^{-1}\). Reproduced with permission.\(^{[48]}\) Copyright 2018, Elsevier.

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**Figure 15.** a) The structure model of carbonate-intercalated LDHs with different \(M^{2+}/M^{3+}\) molar ratios showing the metal hydroxide octahedra stacked along the crystallographic c-axis. Water and anions are present between the interlayers. Reproduced with permission.\(^{[186]}\) Copyright 2014, Royal Society of Chemistry. b) The morphology model of TiO\(_2/r\text{GO/NiFe-LDH}\) system. Reproduced with permission.\(^{[195]}\) Copyright 2016, Royal Society of Chemistry. c) Cross-sectional schematic and energy band structure of \(n^+\text{p-Si/SiO}_2/\text{Ni/NiO}_x/\text{NiFe-LDH}\) photoanode for water oxidation. Reproduced with permission.\(^{[196]}\) Copyright 2018, American Chemical Society. d) \(J–V\) curves of Ti-TiO\(_2\)@LDH deposited for 40 s with three kinds of LDH (CoAl-LDH, CoCr-LDH, and CoFe-LDH) under illumination. Reproduced with permission.\(^{[201]}\) Copyright 2017, Royal Society of Chemistry. e) The proposed mechanism of water splitting on NiCoAl-LDH coated \(\alpha\text{-Fe}_2\text{O}_3\) photoanode and Pt cathode. f) LSV curves of \(\alpha\text{-Fe}_2\text{O}_3, \text{CoAl-LDH/\alpha}\text{-Fe}_2\text{O}_3, \text{NiAl-LDH/}\alpha\text{-Fe}_2\text{O}_3, \text{and NiCoAl-LDH/}\alpha\text{-Fe}_2\text{O}_3\) under AM 1.5G radiation in the 0.5 M K-Pi solution (pH 7) with a scan rate of 20 mV s\(^{-1}\). Reproduced with permission.\(^{[48]}\) Copyright 2018, Elsevier.
metal cations, with anions intercalated. This structure avails fast diffusion of reagents and products and efficient proton-coupled electron transfer process, making them become excellent catalyst candidates for PEC-OER.[187,188]

Lately, some 3D earth-abundant metal-based LDHs have been successfully synthesized. It is proved that they are outstanding cocatalysts of PEC water oxidation and can significantly enhance the yield of oxygen. Nowadays, the most commonly used LDH is NiFe-LDH, as Ni and Fe are both earth-abundant and it shows the best catalytic activity among the Ni-based LDH, which was reported by Diaz-Morales et al.[189] They have been applied to some potential metal-based photoanodes including TAO,[190] BiVO₄,[191,192] WO₃,[193] α-Fe₂O₃,[194] and have shown promoted performance in onset potentials, photocurrent densities, as well as photostability. Other researchers incorporated nonmetal compounds like graphene[188,195] or carbon dots[187] with NiFe-LDH, and found their synergetic effect could further propel the PEC water oxidation process. Taking the TiO₂/rGO/NiFe-LDH system[195] (Figure 15b), for example, the high work function and superior electron mobility of rGO contribute to the fast electron transportation and the introduction of NiFe-LDH enables faster surface water oxidation reaction kinetics. In this system, a high photocurrent density of 1.74 mA cm⁻² at 0.6 V_RHE is achieved, which outdistanced the TiO₂-based photoanodes once reported in benign and neutral media. Besides, Guo et al.[196] reported a special bridging layer strategy to overcome the bottleneck that LDHs are difficult to be coupled with Si-based photoelectrodes. Figure 15c depicts the Ni/NiOₓ interlayer simultaneously contacting photoabsorber Si and NiFe-LDH nanosheet array. The result showed that this system could afford a very low onset potential (~0.78 V_RHE) and a high photocurrent density (~0.37 mA cm⁻²) at 1.23 V_RHE maintaining for 68 h in alkaline conditions under AM 1.5G. It is the highest OER activity reported to date for the crystalline Si-based photoanodes.

Except for NiFe-LDHs, other metal-based LDHs like CoNi-LDH,[175,176,178] CoAl-LDH,[199–201] ZnFe-LDH,[74] etc., also emerge high PEC-OER performance. For example, α-Fe₂O₃ photoelectrode coupled with CoAl-LDH was fabricated by Chong et al.[197] It assisted the α-Fe₂O₃ photoanode to remain remarkably stable in near neutral electrolyte and simultaneously showed outstanding activity due to the synergistic effect between Co²⁺, providing active catalytic sites for OER, and Al¹⁹, giving support for the layered skeleton. The result helps further investigations of PEC water oxidation in neutral pH environments. Based on the previous research, Guo et al.[201] compared the different catalytic activities between three common LDH materials, including CoAl-LDH, CoCr-LDH, and CoFe-LDH. They employed them to incorporate with reduced titania for solar water oxidation and found that the reduced titania@CoCr-LDH exhibited the highest efficiency for PEC oxygen evolution, as Figure 15d shows. The result reveals that a good match of the band structure helps boost driving force and the migration of holes from reduced titania to LDH, followed by the LDH catalyzing water oxidation.

Whereas, though Co- or Ni-based binary-component LDHs have shown enhanced PEC water oxidation performance, they still suffered from low electrical conductivity because of the fully occupied bonding t₂g orbitals of Mo₆ center.[202] Recent researches revealed that ternary-component LDHs containing three kinds of transition metals could realize faster migration of photocarriers and higher conductivity.[203–205] Therefore, engineering photoanodes with ternary-component LDHs is probably a good choice to further boost PEC water oxidation efficiency. For example, a α-Fe₂O₃ photoanode modified by ultrathin NiCoAl-LDH via in situ growth was reported to show superior efficiency and stability in neutral pH electrolytes (Figure 15e).[188] The onset potential shown in Figure 15f is 0.55 V_RHE and the photocurrent density is 2.56 mA cm⁻² at 1.23 V_RHE, which is 13, 2, and 1.4 times higher than that of pure α-Fe₂O₃, NiAl-LDH/α-Fe₂O₃, and CoAl-LDH/α-Fe₂O₃, respectively.

3.4. Metal-Based Boron Compounds

To date, some studies have shown the tremendous promotion of PEC-OER performance catalyzed by nickel-borate (Ni–Bi)[206,207] and cobalt-borate (Co–Bi).[208] As the derivatives of Co–Pi, they share the similar catalytic mechanisms for facilitating PEC water oxidation process.[209] Besides, these nonprecious catalysts in alkaline environments exhibit competitive activity and stability with IrO₂ and Co–Pi.[210] Hence, it can be speculated that these metal-borate catalysts can also be used as very promising cocatalysts for higher PEC water oxidation efficiency. Hong et al.[211] reported the introduction of Ni–Bi onto the Fe₂O₃, which is the first time that Ni–Bi was deposited onto a photoanode for water oxidation to the best of our knowledge. The obtained photoanode brought about a large cathodic shift of the onset potential and enhanced photocurrent, providing a large inspiration for deeper research. After that, Choi et al.[209] integrated NiBi with BiVO₄ via photodeposition and electrodeposition, and they revealed the catalytic activity of Ni–Bi largely depended on the deposition methods and time. Gan et al.[212] reported that the Ni–Bi layer on the BiVO₄ photoanode enables a 350 mV cathodic shift of onset potential for PEC water oxidation at pH 9. Though the study on Ni–Bi had made some progress, the role of Ni–Bi as a cocatalyst is still not completely explicit in PEC water oxidation process. However very recently, Dang et al.[210] reported the Ni–Bi/Fe₂O₃ photoanode with enhanced PEC capability (Figure 16a) and demonstrated two functions of Ni–Bi in this system: Ni–Bi can unpin the Fermi level and lead to an enhanced upward band bending. Specifically, The Bi in the Ni–Bi facilitates releasing protons and then prompts the PEC performance. The schematic diagram of mechanism is shown in Figure 16b. His elaboration may shed more lights on our understanding of the mechanism of Ni–Bi.

Cobalt borate (Co–Bi) is another robust cocatalyst which has been reported to be applied in PEC-OER.[213,214] A recent research has also reported that the performance of Co–Bi cocatalysts photodeposited on SrTiO₃ photoelectrodes for water oxidation is superior to Co–Pi under the same conditions due to that the concentration of Co–Bi on SrTiO₃ is higher than that of Co–Pi. This indicates there are much more reaction sites on the Co–Bi/ SrTiO₃ compared with Co–Pi/ SrTiO₃.[215] In addition, transition-metal borides such as NiB alloy which possess the metallic nature and the significant electron interaction between metal and B also belong to the family of boron
compounds, but the activity is quite distinguished from the transition-metal borate cocatalyst. For instance, Dang et al.\[216\] demonstrated the difference between NiB cocatalyst and Ni–Bi cocatalyst coupled with BiVO₄. It is found that the loading of the NiB can lead to a lower onset potential and a higher photocurrent (Figure 16c) due to a more conspicuous upward band bending compared with the loading of the Ni–Bi cocatalyst. They explained that the higher work function of NiB can be responsible for this phenomenon (Figure 16d). In fact, much attention has been paid to transition-metal borate catalyst, while transition-metal borides applied in water splitting are rarely investigated though they are very common in electrocatalysis. Hence, it is still necessary for us to explore more potential of these transition-metal borides for PEC water oxidation process.

## 3.5. Metal-Free Cocatalysts

It can never be ignored that usually the materials containing metallic ions tend to be toxic, which could limit their further applications. Besides, the large thicknesses or dimensions of these materials probably hinder sunlight absorption and prolong the transfer distances of photogenerated holes.\[217\] Hence, it would be an alternative choice for researchers to work on the investigation of novel metal-free cocatalysts for favoring the solar water oxidation.\[218\]

Graphene is a very promising metal-free material which contains 2D sp² carbon atoms aligned in a honeycomb structure and has been widely incorporated with semiconductors owing to its intrinsic physicochemical properties and large specific surface area.\[219\] Lately, graphene has been introduced in some PEC system in order to facilitate water oxidation. For example, Ahmed et al.\[220\] fabricated TiO₂ photoanodes coupled with graphene for solar fuel generation. In this process, graphene works as an electron transfer channel and accelerates the kinetics of electron transportation, leading water oxidation reaction to be much more efficient.

One of the derivatives of graphene, denoted as reduced graphene oxide (rGO), has the similar properties with graphene but higher conductivity, thus also used as a PEC-OER cocatalyst. Zhang et al.\[221\] reported that the rGO integrated on ITO/hematite nanowires could remarkably boost the water oxidation. The complex photoanode could yield a photocurrent of 5.38 mA cm⁻² at 0.6 V versus saturated calomel electrode (V SCE), a 3.5-fold and tenfold of ITO/Fe₂O₃ and pure Fe₂O₃ photoanode respectively under same circumstances. Phuan et al.\[222\] designed an e-rGO (electrochemical reduced graphene oxide)/hematite photoanode via a two-step electrodeposition method with high PEC performance. The existence of e-rGO brings about an eightfold increment of photocurrent density compared with bare hematite (Figure 17a), which can be ascribed to the enhanced light absorption, added active reaction sites, and accelerated electron transfer. The schematic diagram explaining how the cocatalyst works is presented in Figure 17b. Other studies\[223,224\] also imply that rGO can improve the conductivity of the surface and eventually give rise to an enhanced PEC performance. In order to further promote the catalytic activity and durability of rGO, heteroatom doping strategy has been taken. Common heterodopants include nitrogen, phosphorous, and sulfur.\[225–227\] Part of the carbon sites in the...
framework structure of rGO can be replaced with these hetero-
dopants and the introduction of defects also arises from them. Elbakkay et al.\[219\] successfully synthesized the S-TiO$_2$/S-rGO photoanodes. They found that the doping of S could make the thickness of rGO cut down to 0.51 nm and the roughness risen up to 1.328 mm, resulting in a higher photocurrent density of 3.36 mA cm$^{-2}$ at 1 V Ag/AgCl than the pure TiO$_2$ photoanode.

On top of abovementioned materials, graphitic carbon nitride (g-C$_3$N$_4$) with a structure of tri-s-triazine/heptazine also gives rise to a new research upsurge among researchers due to its high performance in the field of energy conversion recently.\[228\] Feng et al.\[217\] elucidated a simple ethylene glycol dispersion and impregnation method to fabricate ultrathin graphitic C$_3$N$_4$ nanosheets (g-C$_3$N$_4$-NS) coated BiVO$_4$ photoanodes, as can be seen in Figure 17c. These ultrathin g-C$_3$N$_4$ nanolayers can not only restrain the interfacial charge recombination of BiVO$_4$, but also promote the transformation and storage of photogenerated holes for water oxidation. In addition, Huang et al.\[229\] reported the N-Doped carbon dots acting as the cocatalyst on Fe$_2$O$_3$. Under simulated solar irradiation, the photocurrent density of N-CDs@α-Fe$_2$O$_3$/Ti photoanode shows a 3.4-fold increment with a 280 mV negative shift of the onset potential and better durability compared with that of pristine α-Fe$_2$O$_3$/Ti. Other common carbonaceous materials that can be employed as cocatalysts also include CNT, fullerene, etc. Very recently, a novel ternary hematite photoanode with fullerene and 2D-electrochemical rGO was designed by Phuan et al.\[234\] as shown in Figure 17d, the introduction of C60 and rGO contributes to a 16.8-fold enhancement in photocurrent density and a 0.8-fold reduction in charge transfer resistance in comparison with the pure hematite photoanode.

Generally, all the above results confirm that metal-free materials are the competitive cocatalysts for further application and play a pivotal role in boosting the PEC performance. Hence, it can be expected that metal-free cocatalysts can provide a different route to develop more photoanodes with higher performance for oxygen evolution.

3.6. Non-Noble Metal Atoms

Selecting non-noble metals such as Ni, Fe, Bi, etc., to be substitutes of precious metal-based cocatalysts to improve solar water oxidation is also a good choice, as they are earth-abundant, low-cost, and recently reported to be the excellent electrocatalysts,\[235–237\] with decent OER performance in basic conditions. Ueda et al.\[238\] reported the Co modified BaTaO$_2$N photoanode. It achieved a photocurrent of 4.2 mA cm$^{-2}$ at 1.2 V$_{RHE}$ under AM 1.5G and a STH efficiency of 0.7% at 1.0 V$_{RHE}$. Wang et al.\[239\] deposited Bi film onto BiVO$_4$ via photoassisted reduction. They adopted the large work function of Bi particles and its ability to capture electrons to generate a broader
visible light absorption edge and enhanced charge separation. Furthermore, nickel,[240–244] as a member of non-noble metal family, is capable of resisting photocorrosion and providing high OER activity. Its modification is considered as a facile and efficient route to enhance water oxidation, thus it has also been widely investigated. Lately, Oh et al.[245] have introduced a novel photo-electrochemical system with Si-based photoanode in alkaline solutions. They integrated the photoanode with an orderly 3D porous nanostructure, defined as Ni inverse opal (IO) (Figure 18a), in order to tackle the limited water oxidation efficiency arising from the curved surface area of conventional cocatalysts coated onto photoanodes (Figure 18b). By using the Ni IOs to enlarge surface area of cocatalyst and hence offering more active sites, the overpotential is reduced by 120 mV compared with planer Ni coupled Si photoanode (Figure 18c). After that, they synthesized the NiFe alloy IOs for solar water oxidation. The top and cross-section of scanning electron microscope (SEM) images of NiFe IO structures and the IO structures with 2.5, 5, and 10 thickness layers as well as NiFe planar film can be seen in Figure 18d,e. The onset potential is reduced to 0.94 V_RHE and the photocurrent density rises up to 31.2 mA cm^{-2} at 1.23 V_RHE in alkaline environment under 1 sun irradiation.

In the same year, Song et al.[246] also reported the NiFe IOs which can serve as bifunctional cocatalysts incorporated to Si-based photoanode (Figure 18f). Ultimately, this system realized the overall water splitting and resulted in a 9.54% STH efficiency after 24 h without bias, very close to the requirement of commercial utilization. In a word, this special 3D nanostructure brings significant benefit in PEC water oxidation and it is believable that these investigations can undoubtedly inspire researchers to design more distinguished bifunctional cocatalysts for solar energy conversion.

3.7. Molecular Cocatalysts

Molecular materials have also been assembled onto photoanode as cocatalysts for PEC-OER due to their large surface area and porous structure. Enlightened by the role of enzyme Photosystem II (PSII) for water oxidation in natural photosynthesis, researchers attempt to design PSII coated photoanodes for artificial PEC water oxidation.[247] For example, Kato et al.[248] reported a complex photoanode consisting of PSII and a mesoporous indium-tin oxide (meso-ITO) electrode which is 3D and biocompatible for solar water oxidation (Figure 19a). This employed PSII-meso-ITO photoanode allows for a direct electron transfer from meso-ITO to PSII. Others also reported the formation of entire solar-driven water splitting devices consisted of PSII anchored photoanodes and photocathodes[249–251] and these cells also achieved a desired STH efficiency. Except PSII, other metal-based molecular catalysts also come into sight. It is reported that a Co-based molecular catalyst was coated onto an amorphous silicon photoanode which carried out a water splitting reaction efficiency of 4.7% for a wired configuration and 2.5% for a wireless configuration.
under 1 sun. Kamire et al. also demonstrated that the organic dye-sensitized nano-TiO$_2$ photoanode coated with IrSil molecular catalyst could enhance photocurrent and reduce charges recombination. Figure 19b,c shows the promoted photocurrent density after introducing IrSil cocatalyst and its schematic diagram, respectively. However, many metal-based molecular catalysts will gradually become unstable over time due to the photodegradation. Therefore, tackling this shortcoming is indispensable if we want to further investigate their functions as OER cocatalysts.

3.8. Dual Cocatalysts

Thus far, most related studies concentrate on the roles of single cocatalysts for PEC water oxidation, while few about dual cocatalysts have been reported. However, compared with single cocatalysts, dual cocatalysts tend to possess different functions, hence they usually emerge superiorities of higher PEC water oxidation performance due to synergetic effects caused by their interactions. For example, it is reported that a FeOOH and Au dual cocatalytic system helps α-Fe$_2$O$_3$ become one of the photoanodes with highest PEC performance ever reported for water oxidation. In this system, FeOOH is responsible for trapping holes and then carrying them to the interface efficiently, while the Au NPs give electrons to neutralize holes, allowing water oxidation reaction to proceed sustainably at the interface of α-Fe$_2$O$_3$/electrolyte. In addition, novel Co$_3$O$_4$/Co–Pi nanosheets with mesoporous and networked structure were synthesized in a simple and scalable way. This kind of hybrid cocatalyst hosts enriched active sites and enlarged surface area, facilitating BiVO$_4$ photoanode to achieve an excellent PEC OER performance.

Except the combination of metal-based cocatalysts, some researchers also synthesized the dual cocatalysts consisting of metal-based and metal-free materials. For example, Zhang et al. conjugated Co$_3$O$_4$ cocatalyst with graphitic carbon nanodots (CDots) to form a synergetic system and applied this system onto hematite photoanode. They reported that this system could achieve a 60 mV negatively shifted onset potential, an obvious increment in terms of IPCE values and a photocurrent density of 1.48 mA cm$^{-2}$ at 1.23 $V_{RHE}$, which is 78% higher than bare hematite photoanode. Besides, rGO/phosphate and rGO/Ni:FeOOH reported by Sun et al. and Zhang et al. respectively also show desirable stability and prominently promotive PEC water oxidation capability.

As the molecular materials are gradually applied into PEC process, a few dual cocatalysts composed by organic and inorganic materials have also been successfully designed. Kato et al. deposited PSII/Ferricyanide-intercalated LDHs onto the ITO substrates (Figure 20e) and concluded that the photoanode could exhibit a 0.5 ± 0.1 s$^{-1}$ of TOF (turnover frequency) and a 920 ± 40 of TO (turnover numbers) for 1 h, implying it will be a potential material to boost PEC water oxidation. Certainly, all of these studies prove that constructing effective dual cocatalytic systems will be a feasible method to help initiate a new route for developing more outstanding water-splitting photoanodes with high performance.

3.9. Others

On top of above common and deeply investigated cocatalysts, other newly developed cocatalysts such as iron titanate, MOFs, metal carbonate hydroxide, etc., are also recognized as potential cocatalysts but received less attention in prior work. MOFs, which have characteristics of large porosity and high surface area, are usually applied in electrocatalysis, while they are hardly utilized as PEC water oxidation cocatalysts before. Very lately, Tang et al. fabricated the Co$_3$O$_4$ cocatalyst derived from MOFs and incorporated it with TiO$_2$/Si heterojunction. They reported that the MOF-derived Co$_3$O$_4$ could improve higher reaction activity by broadening light absorption range and enriching reaction sites. Jiao et al. also described a Fe/W Co-doped BiVO$_4$ photoanode loaded with MOF MIL-100 (Fe) with good activity (Figure 21a). This composite photoanode could lead to a 14-fold increment of photocurrent density compared with bare BiVO$_4$ (Figure 21b), indicating the introduction of MOF will be beneficial for PEC oxygen production.

Besides, Hegner et al. deposited CoFe prussian blue-type cocatalysts (CoFe-PB) onto BiVO$_4$ photoelectrode (Figure 21c), resulting in a 6 times increment of IPCE at the same wavelength and a decrease of ≈15% of stability over 50 h irradiation.
3.10. Factors Affecting Catalytic Activities of Cocatalysts

Cocatalysts can be divided into isolated patches or overlayers. The catalytic activities of these cocatalysts largely depend on their optically transparent property, thickness, size, morphology, footprint area on the surface of semiconductors, etc. As for cocatalyst overlayers, the catalytic activities can be determined by their thickness. Eftekharinia et al.\cite{108} reported the deposition of Co–Pi layer onto hematite and found the overlayer had an optimized thickness at a deposition time of 5 min, and when the layer became much thicker, a negative effect will occur due to the difficult mass transfer inside it. It is noteworthy that the intrinsic properties of different materials will affect the correlation between the thickness of cocatalysts and the PEC-OER performance. Chemelewski et al.\cite{101} reported that for very thin films, α-FeOOH has nearly the same activity as Co–Bi, while for thicker films Co–Bi performs better than α-FeOOH (Figure 22a) because of the solution penetration of Co–Bi which α-FeOOH does not possess. This ion permeation...
property of Co–Bi produces more active sites in Co–Bi films with thickness increasing which is beneficial for better PEC performance, though it also brings about corrosion and reduces the stability of photoanodes simultaneously. By contrast, despite that thicker film of \( \alpha \)-FeOOH means less activity, it also hints that it can better protect unstable photoanodes and ensure the photoanode to maintain a good performance in a large range of pH conditions, as can be seen in Figure 22b. Another dimension that contributes to the difference of catalytic performance of cocatalysts is crystallinity. Xu et al.\[178\] reported the Ti-Fe\(_2\)O\(_3\) photoanodes modified with CoOOH of different crystallinity (Co-L, Co-M, Co-H) for PEC water oxidation. CoOOH with low crystallinity is highly ion-permeable, leading to an intimate interaction between semiconductor and electrolyte rather than CoOOH and semiconductor; CoOOH with high crystallinity is close to ion-impermeable, showing a low catalytic activity because of the sluggish charge transfer; While CoOOH with moderate crystallinity is partially electrolyte-screened which is beneficial to form an ideal band bending and lower overpotentials of water oxidation. Actually, the size of cocatalytic particles is also a critical factor affecting cocatalyst activity in PEC. For metal particles, larger cocatalyst particles are more effective for performance enhancement, since larger particles can assist them in extracting holes more efficiently and providing less charge recombination centers at the cocatalyst/particle interface if they are in the size range of the depletion width, which has already been verified by the solid-state theory.\[138\] In addition, Oh et al.\[245\] also revealed that the catalytic activities of 2D planes (Figure 22c) differ significantly with that of 3D nanostructures (Figure 22d). And Figure 22e presents that in terms of 2D planar cocatalyst, the current density declines with footprint area increasing. They explained that although increasing footprints could provide more reaction sites, reduce overpotential, and enhance PEC-OER rate, the worse optical shading effect due to the increasing cocatalyst footprint decreases the photocurrent and limits its performance. With regard to the structured cocatalysts, with increased reaction sites, as can be seen in Figure 22f, the electrochemical overpotential can be significantly reduced as the footprint increases though a limited current density maintains. Besides, as the surface area increases, the PEC efficiency also increases along with it. They attributed the result to the large surface area and the lower light absorption from the surface area of the cocatalysts.

In total, the catalytic performance of cocatalysts is complex and synergistically affected by many dimensions such as the aforementioned ones rather than just linearly related with a certain parameter. Therefore, to optimize the capability of cocatalysts for better facilitating solar water oxidation, many influences need to be taken into consideration and some trade-offs are necessary to be made.
4. Conclusions and Perspective

The work of Fujishima and Honda on semiconductor electrodes in 1972 is a historical turning point in the energy field, which opened up a new gateway of solar applications and laid the foundation of photo-electrochemical water splitting technology. The PEC water splitting system can not only eliminate expensive investment of electrolyzers, but also has the potential to further reduce cost through enhancing the solar-energy-conversion efficiency. And up till now, many advances have been achieved due to the unrelenting endeavor of researchers. With the development of PEC water splitting, the researchers are no longer satisfied with the PEC water splitting study itself. In the recent years, the integration of PEC systems with photovoltaic (PV) cells and the study of bifunctional PEC systems have become the new favorites of some researchers. In a PEC–PV integration system, PV cells can play a role of bias supplier, which is conducive to reducing initial capital and operation cost. A WO$_3$/BiVO$_4$ photoanode with a GaAs/InGaAsP PV cell as the bias provider is constructed by Pihosh et al. for water splitting, reaching a total STH efficiency of up to 8.1%.[269]

PEC cells can not only convert solar energy to chemical fuels, some of them can also degrade pollutants simultaneously. Park et al. demonstrated the design of multilayered BiO$_x$-TiO$_2$ electrodes, which were utilized for phenol degradation as well as H$_2$ production simultaneously.[270]

Figure 22. a) Overpotential versus thickness at 1 mA cm$^{-2}$ (hollow circles) and 10 mA cm$^{-2}$ (filled circles) for α-FeOOH and Co-Bi in 1 M Na$_2$CO$_3$. b) Overpotential versus pH at 1 mA cm$^{-2}$ (black circles) and 10 mA cm$^{-2}$ (red circles) for α-FeOOH and Co-Bi in 1 M Na$_2$CO$_3$. Reproduced with permission.[101] Copyright 2014, American Chemical Society. Schematics of the c) planar and d) 3D nanostructured cocatalysts deposited onto a photoelectrode. The PEC J–V curves of a photoelectrode with e) planar and f) 3D-structured cocatalysts. $A_{\text{cat}}$ indicates the proportion of the metal cocatalysts on the whole surface of a photoelectrode. $A_{3D}$ is the increased surface area of the 3D catalyst structure with the given $A_{\text{cat}}$. $\eta_{\text{half-STH}}$ is the half cell solar-to-hydrogen efficiency. As for traditional planar cocatalysts, an optimum $A_{\text{cat}}$ exists for the maximum PEC performance. By contrast, a photoelectrode with the 3D structured cocatalysts can achieve the ultimate PEC performance of the semiconductor and cocatalyst materials. Reproduced with permission.[245] Copyright 2017, American Chemical Society.
However, all these efforts still cannot support the PEC water splitting systems for further commercialization currently. US Department of Energy once set a benchmark conversion efficiency of 10% for commercialization application. However, the efficiency for most of the PEC water splitting systems at present is still stuck below this benchmark. Even though a tiny minority of them can reach this benchmark, either the stability cannot meet the demand of practical usage or the cost is still significantly higher than the target of $2–4 per kg for H₂ production yet. Except that, other considerations such as accessibility, environmental friendliness, renewability, and simplification still remain to be realized. In total, the realization of the commercial application of PEC water splitting in the future will be a long-term course full of challenges and difficulties. However, for now, the most imperative mission is to significantly boost the performance and stability of PEC water splitting, especially PEC water oxidation via effective strategies.

With an initial purpose of introducing the concept of PEC water splitting, especially the PEC water oxidation half reaction, demonstrating the important status of the water oxidation cocatalysts in the PEC water splitting system, and providing tutorial guidance for researchers to conduct relative researches, this review systematically and detailedly provides a basic framework of PEC water oxidation half reaction, including the basic principles of water splitting, the major modules to establish a PEC water oxidation system, essential parameters extensively used to evaluate their performance of PEC cells. Besides, this review also intensively introduces the mechanisms and the categories of promising cocatalyst materials (Table 4) that have been widely used and newly developed in recent years such as metal oxides or (oxy)hydroxides, LDHs, transition metal phosphides (TMPs), metal-free materials, molecular materials, etc. These cocatalysts all emerge their own advantages such as earth-abundance, stability, as well as high catalytic activity when loading onto the surface of photoanodes. It is also concluded that these cocatalysts help PEC water oxidation by increasing band bending, serving as the hole trap to collect holes from semiconductors, or even acting as the protecting layer to prevent from photocorrosion. However, from another facet, some cocatalysts cannot match the bandgap position of specific photoanodes. Except that, cocatalyst application may also induce optical shield effect and added recombination sites, neither of which are favorable for PEC water oxidation. Hence, these intractable problems of cocatalysts still need to be coped with in the future.

In fact, despite that the research of cocatalysts has continued for many decades and some tolerable progress has been made, few significant breakthroughs are achieved to assist the study of cocatalyst in making a giant leap currently. Accordingly, there is a long way to go forward in order to gain cocatalysts with much higher performance and ultimately achieve commercial water splitting. It is anticipated that in the near future, many works based on the cocatalysts applied in PEC water oxidation will focus on the following aspects:

4.1. In-Depth Interpretation of Mechanisms

The mechanisms how cocatalysts work have not yet been stated clearly. Some of the explanations are based on hypothesis and the results of characterization, which actually do not have enough persuasion. Besides, some paradoxes still exist and in certain papers which focus on the synergies of cocatalysts, the clarifications of their effects are still superficial. Thus, further rationally designed experiment verifications, through characterizations, maintain to be conducted in order to provide much more powerful evidences and specific explanations. In addition, theoretical calculations, especially density functional theory study, are of equal importance. It can make up the defects of experimental measurements and plays an important role in validation and prediction. Hence, these strategies are recognized as a rather powerful ancillary tool to better understand the results of experiments, investigate the underlying mechanism how cocatalysts work, and provide practical guidance for designing high-performance cocatalyst-assisted PEC water oxidation system.

4.2. The Exploration of New Efficient and Sustainable Catalyst Materials

Novel materials like metal-free materials, molecular materials, or MOFs are all worthy to be explored for expanding the family of cocatalysts and offering more options. As mentioned in introduction, most electrocatalysts can be used as PEC cocatalysts. Thus, the state-of-art electrocatalysts can probably provide some inspirations for us in exploring novel PEC cocatalysts.

4.3. The Further Regulation and Optimization of Cocatalysts

Hitherto, the properties of cocatalysts are still far from satisfying the requirement of practical usage. There is a large space for us to further improve the performance of cocatalysts. Feasible methods include manufacturing defects or vacancies, nanostructuring, rational selection of conductive substrates, improved deposition method, morphology regulation, interfacial modulation, structure control, size adjustment, cocatalyst synergies, etc.

4.4. Coupling the Means of Cocatalyst Introduction with Others to Synergistically Promote the PEC-OER Performance

For example, heterojunctions, dye sensitization, ion doping, surface defects, plasmon resonance technology, and piezoelectric technology, etc., can all be considered. As the PEC water oxidation process is relatively complex, evolving multielectron transfer and multiple reaction steps, it is hard to reach a more outstanding catalytic efficiency and higher stability far beyond current average level and realize industrialization via depositing cocatalyst alone. Hence, it is indispensable to combine cocatalysts loading and other methods for much higher performance.

4.5. The Design of Multifunctional Catalysts

Fabricating cocatalysts to act as both OER and HER excellent cocatalysts so as to realize ultimate overall water splitting with
### Table 4. The summary of common cocatalysts and their PEC OER performance.

| Cocatalysts | Photoanodes | Deposition method | Morphology | Photocurrent density (mA cm$^{-2}$) | Onset potential | Conditions | Ref. |
|-------------|-------------|-------------------|------------|----------------------------------|----------------|------------|------|
| Metal phosphates | Co–Pi | Fe$_2$O$_3$/Co–Pi | Electron beam evaporation | Thin films | 1.5 at 1.5 V$_{RHE}$ | 0.9 V$_{RHE}$ | 1 M NaOH (pH = 13); under AM 1.5G (100 mW cm$^{-2}$) | [108] |
| | Co–Pi | Fe$_2$O$_3$/CdS/Co–Pi | Photo-assisted deposition | Nanoparticles | 3.29 at 0.7 V$_{RHE}$ | 0.4 V$_{RHE}$ | 1.0 M NaOH + 0.1 M Na$_2$S (pH = 13.3); under AM 1.5G (100 mW cm$^{-2}$) | [50] |
| | Co–Pi | BiVO$_4$/Co–Pi | Photo-electrodeposition | Films | 3 at 1.23 V$_{RHE}$ | 0.4 V$_{RHE}$ | 0.1 M NaPi buffer (pH = 7); under AM 1.5G (100 mW cm$^{-2}$) | [110] |
| NiFe–Pi | NiFe–Pi/α–Fe$_2$O$_3$ | Facile dip-coating and annealing | Nanoparticles | 1.2 at 1.23 V$_{RHE}$ | 0.74 V$_{RHE}$ | 0.1 M KOH (pH = 12.6); under AM 1.5G (100 mW cm$^{-2}$) | [117] |
| Metal phosphides | CoP | Mo$_3$BiVO$_4$/CoP | Drop casting | Nanoparticles | 3.0 at 1.23 V$_{RHE}$ | 0.3 V$_{RHE}$ | 0.5 M KPi buffer (pH = 7); under AM 1.5G (100 mW cm$^{-2}$) | [124] |
| | FeMnP | TiO$_2$/FeMnP | Metal–organic chemical vapor deposition | Film | 1.8 at 1.23 V$_{RHE}$ | =0 V$_{RHE}$ | 0.5 M NaOH under AM 1.5G (100 mW cm$^{-2}$) | [118] |
| Metal (oxy) | Ni(OH)$_2$ | BiVO$_4$/Ni(OH)$_2$ | Chemical bath deposition | Ultrathin layer | <0.75 at 1.23 V$_{RHE}$ | =0 V$_{RHE}$ | NaBi (pH = 10) buffer; under AM 1.5G (100 mW cm$^{-2}$) | [163] |
| | Ni$_2$O$_5$ | (Sn, Zr) α–Fe$_2$O$_3$/ Ni$_2$O$_5$ | Photo-assisted electrodeposition | Rough films | 1.64 at 1.23 V$_{RHE}$ | 0.58 V$_{RHE}$ | 1 M NaOH (pH = 13.6); under AM 1.5G (100 mW cm$^{-2}$) | [169] |
| | FeOOH | FeOOH/BiVO$_4$ | Facile solution impregnation | Nanolayer (2 nm) | 4.3 at 1.23 V$_{RHE}$ | 0.5 V$_{RHE}$ | 0.2 M Na$_2$SO$_4$ under AM 1.5G (100 mW cm$^{-2}$) | [73] |
| | Ni:FeOOH | Ni:FeOOH/BiVO$_4$ | Hydrothermal process | Films | 1.6 at 0.4 V$_{Ag/AgCl}$ | =−0.2 V$_{Ag/AgCl}$ | 0.1 M Tris-PBS 5.0; under AM 1.5G (100 mW cm$^{-2}$) | [159] |
| Metal oxides | CoOOH | Co(OH)$_2$/Ti–Fe$_2$O$_3$ | Electrochemical deposition | Crystalline layers | 1.8 at 1.23 V$_{RHE}$ | 0.7 V$_{RHE}$ | 1 M NaOH (pH = 13.6); under AM 1.5G (100 mW cm$^{-2}$) | [178] |
| | MOFs$^{(4)}$ | MOFs-derived Co$_3$O$_4$/TiO$_2$/Si | Electrodeposition/hydrothermal method | Hierarchical structure | 2.71 at 1.23 V$_{RHE}$ | 0.4 V$_{RHE}$ | 1 M NaOH; under AM 1.5G (100 mW cm$^{-2}$) | [141] |
| | NiO$_x$ | p–n+ InP/NiO$_x$ | Sputter deposition | Films | 17.1–17.9 at 1.23 V$_{RHE}$ | 0.85–0.87 V$_{RHE}$ | 1 M KOH; under AM 1.5G (100 mW cm$^{-2}$) | [143] |
| | NiMnO$_4$ | TiO$_2$/Si/NiMnO$_4$ | Hydrothermal method | Nanosheets | 1.4 × 10$^{-2}$ at 1.23 V$_{RHE}$ | 0.85 V$_{RHE}$ | 0.25 M KOH; under AM 1.5G (100 mW cm$^{-2}$) | [149] |
| | FeN$_{2}$O$_{4}$ | Fe$_3$TiO$_4$/FeN$_{2}$O$_{4}$ | Photo-electrochemical deposition | Films | 0.93 at 1.23 V$_{RHE}$ | =−0.6 V$_{RHE}$ | 1 M NaOH; under AM 1.5G (100 mW cm$^{-2}$) | [265] |
| Layered double | ZnFe–LDH | TiO$_2$/ZnFe–LDH | Photo-electrochemical deposition | Nanoplates | 1.51 at 1.23 V$_{RHE}$ | 0.4 V$_{RHE}$ | 0.5 M Na$_2$SO$_4$ under AM 1.5G (100 mW cm$^{-2}$) | [74] |
| | NiCo–LDH | α–Fe$_2$O$_3$/ NiCoAl–LDH | In situ growth | Films | 2.56 at 1.23 V$_{RHE}$ | 0.55 V$_{RHE}$ | 0.5 M KPi, (pH = 7); under AM 1.5G (100 mW cm$^{-2}$) | [48] |
| Metal-based boron | Ni–Bi | H–BiVO$_4$/Ni–Bi | Photodeposition | Films | 3.34 at 1.23 V$_{RHE}$ | 0.02–0.1 V$_{RHE}$ | 0.1 M KPi (pH = 9); under AM 1.5G (100 mW cm$^{-2}$) | [212] |
| compounds | NiB | BiVO$_4$/NiB | Drop-casting | Nanoparticles | 3.47 at 1.23 V$_{RHE}$ | 0.25 V$_{RHE}$ | 0.5 M KPi (pH = 9.20); under AM 1.5G (100 mW cm$^{-2}$) | [216] |
| Metal-free | N–CDs$^{(5)}$ | α–Fe$_2$O$_3$/Ti/N–CDs | Facile “top down” method | Nano dots | 0.41 at 1.23 V$_{RHE}$ | 0.79 V$_{RHE}$ | 1 M KOH (pH = 13.6); under AM 1.5G (100 mW cm$^{-2}$) | [229] |
| materials | C$_3$N$_4$ | BiVO$_4$/g–C$_3$N$_4$ | Ethylene glycol dispersion and impregnation | Ultrathin nanosheets | 3.12 at 1.23 V$_{RHE}$ | 0.4 V$_{RHE}$ | 0.1 M Na$_2$SO$_4$ visible-light (λ > 420 nm) | [217] |
| Metal atoms | NiFe alloy | p–n+Si/SiO$_2$/NiFe I Os | Electrodeposition | 3D nanoporous network | 31.5 at 1.23 V$_{RHE}$ | 0.94 V$_{RHE}$ | 1 M KOH; under AM 1.5G (100 mW cm$^{-2}$) | [245] |
| | | | | | | | | |
| Molecules | Ir WOC$^{(6)}$ | Fe$_2$O$_3$/Ir WOC | Anodic photo-electrodeposition | Amorphous monolayer | ≈0.9 at 1.23 V$_{RHE}$ | 0.6 V$_{RHE}$ | 0.1 M KNO$_3$+HNO$_3$ (pH = 1.01); under AM 1.5G (100 mW cm$^{-2}$) | [266] |
| Dual cocatalysts | Ir$_2$O$_3$/Ru$_2$O$_3$ | Ir$_2$O$_3$/Ru$_2$O$_3$/hematite | Electrodeposition | Films | ≈1.52 at 1.23 V$_{RHE}$ | 0.5 V$_{RHE}$ | 1 M KOH (pH = 13.6); under AM 1.5G (100 mW cm$^{-2}$) | [267] |
Table 4. Continued.

| Cocatalysts | Photoanodes | Deposition method | Morphology | Photocurrent density [mA cm⁻²] | Onset potential | Conditions | Ref. |
|-------------|-------------|------------------|------------|--------------------------------|----------------|-----------|-----|
| FeOOH/Au    | Fe₂O₃/FeOOH/Au | Facile “top down” method | FeOOH: Films/ Au: nanoparticles | 3.2 at 1.23 V_RHE | 0.6 V_RHE | 1 M KOH; under AM 1.5G (100 mW cm⁻²) | [173] |
| CoCubate/tr complex | Ni(OH)/CoCubate/tr complex/ FV¹/Ⅱ/Ta₂N₆ | Facile “top down” method | Particles | 12.1 at 1.23 V_RHE | 0.65 V_RHE | 1 M NaOH; under AM 1.5G (100 mW cm⁻²) | [79] |
| CdTe QDs² | CdTe QDs/LDH/ BiVO₄ | | 2.23 at 1.23 V_RHE | 0.3 V_RHE | 0.1 M phosphate buffer (pH = 7); under AM 1.5G (100 mW cm⁻²) | [268] |
| Others (MOF) | Fe/W codoped BiVO₄/(MOF) MIL-100(Fe) | Spin-coating | Nanoparticles | 2.76 at 0.8 V_SCE | 0 V_SCE | 0.1 M Na₂SO₄; under AM 1.5G (100 mW cm⁻²) | [262] |
| CoFe-PBG | CoFe-PB/BiVO₄ | Sequebtially dipping | Amorphous particles | ≈1.17 at 1.23 V_RHE | 0.3 V_RHE | 0.1 M KPi buffer (pH = 7); under AM 1.5G (100 mW cm⁻²) | [263] |

*MOF: metal–organic framework; N-CDs: N-Doped carbon dots; IOs: inverse opals; WOC: water oxygen catalysts; Fh: ferrhydrite; QDs: quantum dots; CoFe-PB: CoFe Prussian blue-type electrocatalysts*

the same cocatalyst is one of the ideals of PEC application. Due to the incompatible pH conditions of traditional HER cocatalysts (normally work under pH < 7) and OER cocatalysts (usually conducted under pH > 7), it becomes difficult to assemble an overall water splitting system with anode and cathode coupled with HER and OER cocatalysts respectively at the same time, and the performance is often below our expectation. Thus, looking for some bifunctional cocatalysts to facilitate overall water splitting is of great importance in the future investigation of PEC overall water splitting system.[277]

All in all, the PEC water oxidation plays an indispensable role in sufficient solar light utilization and oxygen evolution. Therefore, the research of PEC water oxidation cocatalysts is of great value and deserves to be further investigated. It is expected that this review could not only deepen the comprehension of PEC water splitting and the role of water oxidation cocatalysts for artificial PEC synthesis but also open up new inspirations and feasibilities for cocatalyst applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cocatalysts, oxygen evolution reaction, photoanodes, solar energy, water splitting

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