Review

Modulation of photogenerated holes for enhanced photoelectrocatalytic performance

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Abstract

Utilizing clean energy derived from photoelectrocatalytic reactions is expected to be an excellent choice to fundamentally solve the problem of the human energy crisis. Photoelectrochemical (PEC) cell can effectively promote charge separation and improve solar energy conversion efficiency since it combines the advantages of photocatalysis and electrocatalysis. However, the hole transfer and subsequent oxidation reaction in the PEC process are slow, resulting in the rapid recombination of photogenerated electron-hole pairs and low PEC performance. The half-oxidation reaction involving photogenerated holes is the bottleneck of PEC water splitting. Therefore, hole modulation has been an important research area in the field of catalysis. However, compared with electron modulation, research on hole modulation is limited and still faces great challenges. It is therefore of great significance to develop effective modulation strategies for photogenerated holes. This review summarizes the hole modulation strategies developed in the last five years, including hole sacrificial agents, nanostructural modification, heterostructure construction and cocatalyst modification. Hole modulation dynamics studies, such as transient absorption spectroscopy, time-resolved photoluminescence spectroscopy, transient photovoltage and scanning electrochemical microscopy, are also summarized. Moreover, relevant conclusions and an outlook are proposed.

Keywords: Photoelectrocatalysis, hole modulation, charge separation, interfacial kinetics
INTRODUCTION

Solar energy is clean, renewable, sustainable and abundant. Currently, solar energy conversion and storage have become important options to solve the global energy shortage and environmental pollution challenges\textsuperscript{[1]–[4]}. Semiconductor-based photocatalysis for splitting water into hydrogen is a renewable and sustainable technology for direct solar-to-chemical energy conversion. However, the relatively low solar energy conversion efficiency limits its practical applications\textsuperscript{[4–6]}. The main semiconductor photocatalytic process can be divided into three steps: (i) the catalyst absorbs photons equal to or greater than the energy of its bandgap width and generates electron-hole pairs by excitation; (ii) photogenerated electron-hole separation and transfer to the semiconductor surface; (iii) transfer to the reactive species to undergo surface reactions (surface complex or effective reactions). The solar energy conversion efficiency is determined by these steps. To improve the efficiency of the photocatalytic process, it is necessary to effectively enhance the separation and transportation of photogenerated charges and simultaneously make the charges migrate to the surface and further initiate the surface reactions of the chemical compounds. During the photocatalytic water splitting process, the hydrogen evolution reaction usually takes place simultaneously with the oxygen evolution reaction (OER). It is noteworthy that the OER becomes the bottleneck of photocatalytic water decomposition because it involves multiple proton- and electron-transfer steps.

The generation rate of holes depends on the illumination light intensity, light absorption and charge separation of the photoelectrode, while the consumption rate of holes depends on the rate of surface charge recombination and hole transfer into solution. However, the water oxidation reaction involving photogenerated holes is much slower than the recombination process. Figure 1 shows a schematic illustration of the processes of semiconductor-based photoelectrocatalytic water splitting and the associated reaction timescales. The accumulated holes not only lead to an increase in the recombination rate of the catalyst, resulting in a reduction in catalytic activity, but also oxidize the catalyst itself, leading to a decrease in catalyst stability and deactivation. Since the discovery of water splitting catalyzed by a single-crystal TiO\textsubscript{2} photoelectrode in 1972,photoelectrochemical (PEC) catalysis based on semiconductor photoelectrodes has attracted extensive attention for solar-to-energy conversion\textsuperscript{[7–9]}. PEC water splitting combines photocatalysis and electrocatalysis, which can effectively promote charge separation and improve solar energy utilization\textsuperscript{[8]}. Furthermore, a series of studies have been carried out on semiconductor materials used as photocatalytic OER photoanodes, including transition metal oxides, hydroxides, nitrides and selenides, metal-organic frameworks (MOFs) and non-metallic polymer semiconductor graphitic carbon nitrides (g-C\textsubscript{3}N\textsubscript{4})\textsuperscript{[10–14]}. However, due to the slow hole transfer and subsequent oxidation reactions, the kinetic mismatch between the bulk charge carrier lifetime and the interfacial catalytic timescale results in high electron-hole recombination rates, thus limiting the PEC performance. Furthermore, the water oxidation reaction is also necessary as a counter reaction for electron-involved half reactions\textsuperscript{[12–14]}, such as the CO\textsubscript{2} and NH\textsubscript{3} reduction reactions. Therefore, intensive efforts need to be focused on the improvement of the half OER regarding materials, systems, and so on. Understanding how to suppress the recombination of electron-hole pairs and improve the subsequent oxidation reaction rate is the main research direction in the PEC catalysis reaction. Hole modulation to accelerate the kinetics of photogenerated hole transfer and the hole-involved surface oxidation reaction has significant potential for addressing these issues\textsuperscript{[15,16]}.

Noble metal oxides, such as RuO\textsubscript{2} and IrO\textsubscript{2}, are the most commonly selected materials to modulate photogenerated holes to enhance PEC performance\textsuperscript{[17]}. However, the high cost of noble metals is not sustainable for practical implementation. Therefore, developing low-cost and efficient photogenerated hole modulation candidates that can rapidly initiate oxidation half-reactions has become an urgent challenge in this field. Regarding hole modulation, by designing and modifying the materials that match the valence band energy level of the photoelectrode semiconductor, the photogenerated holes can be efficiently
extracted and the recombination of photogenerated electron-hole pairs can be suppressed. Catalytic regulation to ensure that the holes in the valence band have sufficient potential to oxidize the target molecule is an alternative method\cite{18,19}. Thus, the effective separation and transport of photogenerated carriers on the surface can be improved and the charges can effectively participate in the surface reaction, which can effectively improve the PEC efficiency. In 2019, Sun et al. reviewed the development of photogenerated hole modulation in PEC catalysis for solar fuel production, with a focus on surface polarization strategies\cite{15}. So far, the recent advancements in PEC catalysts have yet to be reviewed clearly. Compared to electron modulation, limited research work has been contributed to the field of hole modulation.

This review focuses on the hole modulation of semiconductor-based photoelectrocatalysts in the last five years. The studies of modulation strategies and dynamics form two main sections. The PEC performance is sensitive to the electrode surface structure. In this review, the modulation strategies section covers the recent advances in the design strategies of photoelectrocatalysts with excellent PEC performance through hole modulation, including hole sacrificial agents, nanostructural modification, heterostructure construction and cocatalyst modification [Figure 2]. In the cocatalyst modification section, recent progress on low-cost carbon-based materials is highlighted. The analysis of the transport process of photogenerated holes on the surface is helpful for the design and synthesis of efficient photoelectrocatalysts. Therefore, this review also emphasizes various techniques for studying hole modulation dynamics, such as transient absorption spectroscopy, time-resolved photoluminescence spectroscopy, transient photovoltage and scanning electrochemical microscopy. Moreover, relevant conclusions and outlooks are proposed. This review will trigger the design and construction of efficient photoelectrocatalysts.

**HOLE MODULATION STRATEGIES IN PHOTOELECTROCATALYSIS**

To suppress photogenerated electron-hole recombination and accelerate hole-to-solution transfer, methods such as introducing hole sacrificial agents, nanostructural modification, heterostructure construction and
Figure 2. Schematic diagram of photogenerated hole modulation strategies in photoelectrocatalysis.

cocatalyst loading have been developed. The modification of nanostructure regulates the electrostatic field on the surface of the catalyst and promotes the migration of holes. The construction of a heterojunction can realize hole extraction through charge transfer between two semiconductor materials with different energy level positions. The loading of a cocatalyst can effectively extract the photogenerated holes and carry out surface reactions by means of energy level matching with the valence band of the semiconductor.

**Hole sacrificial agents**

In PEC catalysis, the photogenerated holes migrate to the active site and then accumulate, which affects the subsequent hole migration. The consumption of holes can ensure that the subsequent holes continue to migrate and improve the PEC efficiency. Commonly used sacrificial agents in PEC systems include Na$_2$S-Na$_2$SO$_3$ [20,21], triethanolamine (TEOA) [22,23] and H$_2$O$_2$ [24-26] and these have been widely used to evaluate interfacial charge transfer properties. Thorne et al. measured the photocurrent-voltage curves of a hematite photoanode and found that the photoanode with H$_2$O$_2$ as hole scavengers has lower onset potential values [24]. This means that there will be fewer photogenerated holes accumulated on the surface of the photoanode after inducing hole scavengers [24]. Unfortunately, the introduction of excess sacrificial agents not only increases the cost but also results in secondary chemical pollution [25]. Alternatively, it is also an important research direction to transform sacrificial agents into value-added chemicals through selective organic synthesis reactions and to cooperate with electrons in the reduction reaction [26]. However, this process remains a major challenge. According to the current research background, researchers mainly prefer to develop efficient PEC catalysts without the use of sacrificial agents.

**Nanostructural modification**

As mentioned above, researchers are currently working on developing efficient PEC catalysts that do not use sacrificial agents. PEC performance is sensitive to the electrode surface structure. The valence band
edges of some semiconductors are commonly more positive than the thermodynamic potential for the OER, leading to a high oxidation potential for holes in the valence band. The modulation of holes is a feasible method to enhance photocatalytic performance. Researchers have tuned the electronic structure of the semiconductor by introducing heteroatoms, as well as introducing defect states to adjust the atomic structure to increase the charge separation efficiency and further carry out the surface reaction.

**Heteroatom doping**

The introduction of impurity states through heteroatom doping with, for example, metal cations, S, C, N and O in semiconductors provides the opportunity of trapping photogenerated electrons or holes, so that the photogenerated electrons and holes will be located in different regions, respectively\(^{[25,26]}\). This strategy can reduce the overlap of photogenerated electrons and holes and improve charge transport and separation\(^{[31,32]}\). Zhang et al. introduced non-metallic N atoms into NiFeO\(_x\) catalysts and used them as cocatalysts to modify a BiVO\(_4\) photoanode, in which the O sites in NiFeO\(_x\) and BiVO\(_4\) were partially replaced by low-electronegativity N atoms, leading to their electronic reconfiguration\(^{[18]}\). The morphological and structural characterization of the BiVO\(_4\)/N:NiFeO\(_x\) photoanodes with a rough flocculent structure is shown in Figure 3A-D. The weak electron-attracting capacity of N atoms leads to electron enrichment on Fe and Ni. The electron injection from Ni atoms into the V sites in the BiVO\(_4\) lattice is beneficial for improving the stability of oxygen evolution, while the Fe sites can effectively attract holes to promote the PEC activity. The final obtained BiVO\(_4\)/N:NiFeO\(_x\) exhibited an excellent photocurrent density of 6.4 mA·cm\(^{-2}\) at 1.23 V (vs. a reversible hydrogen electrode (RHE)) under light [Figure 3E]. The half-cell applied bias photon-to-current efficiency of the BiVO\(_4\)/N:NiFeO\(_x\) photoanode (1.9% at 0.73 V vs. a RHE) was also much higher than that of BiVO\(_4\)/NiFeO\(_x\) (1.1% at 0.8 V vs. a RHE) and pristine BiVO\(_4\) (0.29% at 0.96 V vs. a RHE), as shown in Figure 3F\(^{[18]}\).

Meng et al. synthesized two-dimensional (2D) atomically thin Zn\(_{1-x}\)In\(_x\)S\(_2\) nanosheet arrays and achieved oxygen doping and Zn and S vacancies at the surface through low-temperature heat treatment\(^{[33]}\). The excessive surface defect states were then passivated by an ultrathin Al\(_2\)O\(_3\) layer. The obtained photoelectrode showed remarkably enhanced PEC OER performance due to the fast electron-hole pair separation and prolonged lifetime of the carriers\(^{[33]}\). However, improper chemical doping may alter the crystal form of the semiconductor and reduce the lifetime of holes, thereby increasing the kinetic challenge of driving catalysis\(^{[16,14]}\). In addition, the control of the concentration and distribution of heteroatom doping on the surface of the photoanode catalysts remains challenging.

**Defect engineering**

Defect engineering can efficiently modulate the electronic structure and surface properties of a catalyst to reduce the reaction energy barrier for PEC performance. Oxygen vacancies are the most common defects\(^{[35]}\). Any treatment that changes the chemical environment of the catalyst (temperature annealing, treatment under different atmospheres during growth, laser irradiation, and so on) can lead to the formation of these oxygen defect states\(^{[26,27]}\). Zhang et al. fabricated a BiVO\(_4\) catalyst modified with a FeNiOOH cocatalyst rich in oxygen vacancies (BiVO\(_4\)/Vo-FeNiOOH) through a simple and economical NaBH\(_4\) reduction method\(^{[34]}\). The introduced oxygen vacancies accelerate hole transfer and promote efficient electron-hole pair separation, leading to a negative shift in the starting potential and OER acceleration. The achieved photocurrent of the BiVO\(_4\)/Vo-FeNiOOH catalyst was more than four times that of pure BiVO\(_4\) due to the introduction of oxygen vacancies in the system\(^{[36]}\). Li et al. successfully prepared Bi\(_2\)O\(_3\)I\(_x\) microspheres rich in oxygen vacancies by a solvothermal method assisted by an ionic liquid\(^{[39]}\). Compared with Bi\(_2\)O\(_3\)I\(_x\), with fewer oxygen vacancies after annealing, the valence band maximum position of Bi\(_2\)O\(_3\)I\(_x\) with rich oxygen vacancies shifted upward, which resulted in better photooxidation ability for the
Figure 3. (A-D) Morphological and structural characterization, (E) linear sweep voltammograms and (F) half-cell applied bias photon-to-current efficiency results of BiVO$_4$/N:NiFeO$_x$ photoanodes.[18]

In addition to oxygen vacancies, the introduction of other vacancies can also prolong and migrate the photogenerated carriers to the surface to participate in the reactions.[33] Zhao et al. introduced S vacancies to a CdS photoanode surface through H$_2$O$_2$ etching and adjusted the vacancy concentration by controlling the etching time.[40] The photocurrent density of the CdS nanorods etched by H$_2$O$_2$ for 35 s reached 3.09 mA·cm$^{-2}$, which was 6.5 times higher than for CdS.[40] Ma et al. prepared a WO$_3$ overlayer with dual oxygen and tungsten vacancies on a WO$_3$ photoanode by a solution-based process.[41] The obtained mesoporous WO$_3$ achieved a cathodic shift of the onset potential and enhanced photocurrent for the OER.[41] Although significant progress has been made in improving PEC performance by introducing defects, many issues remain unresolved. For example, surface oxygen vacancies favor the final performance of water-splitting photoanodes because they improve charge separation by narrowing the space-charge layer. In general, however, bulk oxygen vacancies are detrimental because they enhance recombination kinetics, thereby reducing the PEC performance. In addition, the concentration of oxygen vacancies also has an effect on the performance. To improve the PEC performance, the optimization of defect density is necessary.[42] However, similar to the heteroatom doping engineering discussed above, control of the defect concentration and distribution in photoanodes remains a challenge.
Construction of heterostructures

In addition to the nanostructural modification of photoanodes, a highly conductive and active semiconductor can also be used directly on the photoanode surface to form a heterojunction photoelectrode. The construction of heterojunctions can effectively separate the photoelectron holes by satisfying the appropriate energy level positions between the two semiconductors \((p-n/n-n)\)^{[43,44].} For low-energy light-induced holes, \(Z\)-type nanocomposites have been successfully constructed by coupling suitable band gap semiconductors \(^{[45]}\). Photoanodes with \(Z\)-type electronic transfer result in enhanced light-harvesting properties and charge separation. For a \(g-C_3N_4/\text{semiconductor}\) composite, the photogenerated electrons of the semiconductor transfer to the valence band of \(g-C_3N_4\) and then recombine with the photogenerated holes derived from \(g-C_3N_4\). Therefore, the photogenerated electrons on \(g-C_3N_4\) and the photogenerated holes on modified oxides have strong reducing and oxidizing properties. This can lead to charge separation and improve the PEC activity of the catalyst. MOFs with a large surface area are also used in PEC systems. The construction of MOF-based heterojunctions can increase the internal electric field by the conjugated \(\pi\) electrons in the linkers [Figure 4]. Wang et al. fabricated \(Z\)-scheme heterostructures of \(\text{TiO}_2\) nanorods (NRs) coated by MOFs and obtained \(\text{UiO}-66@\text{TiO}_2\) and \(\text{UiO}-67@\text{TiO}_2\) photoanodes. Compared with pristine \(\text{TiO}_2\), \(\text{UiO}-66@\text{TiO}_2\) and \(\text{UiO}-67@\text{TiO}_2\) showed enhanced photocurrent density in the PEC water oxidation process \(^{[23]}\).

For a type-II heterojunction, the semiconductor photoanode will be combined with a semiconductor that has a relatively low valence band position. The photogenerated electrons in the conduction band of the modified semiconductor will be transferred to the photoanode. The photogenerated holes in the semiconductor anode will be transferred to the modified semiconductor and further induce the transfer of holes. Different type-II heterojunction photoanodes, such as \(\text{WO}_3/\text{BiVO}_4\), \(\text{ZnO/BiVO}_4\), \(\text{ZnO/Fe}_2\text{O}_3\), \(\text{TiO}_2/\text{ZnO}\), and so on, have been reported with remarkable PEC performance. Maity et al. fabricated a one-dimensional \(n-\text{ZnO/p-ZnCo}_2\text{O}_4\) nanoheterojunction photoanode \(^{[46]}\). In this type-II heterojunction photoanode, the \(\text{ZnCo}_2\text{O}_4\) surface overlayer passivated the surface states of \(\text{ZnO}\) nanorods, thereby significantly reducing the recombination of photogenerated electron-hole pairs. The generated holes from the \(\text{ZnO}\) nanorods can migrate rapidly to the surface of \(\text{ZnCo}_2\text{O}_4\) and initiate the OER. Compared with the pristine \(\text{ZnO}\) photoanode, the \(n-\text{ZnO/p-ZnCo}_2\text{O}_4\) nanoheterojunction photoanode achieved a significant increase in photocurrent density \(^{[46]}\). \(N\)-type semiconductors with suitable band edges for water oxidation have also been coupled with photoanodes to improve the PEC water splitting performance. Ho et al. constructed an epitaxial \(\text{Fe}_2\text{TiO}_4/\text{ZnO}\) nanodendrite heterojunction array photoanode. Due to the decoupled light harvesting and hole transport paths, the photocurrent density was greatly improved \(^{[47]}\).

Type-II heterojunctions are widely used for hole modulation. The construction of the heterojunction reduces the chance of photogenerated carrier recombination, thereby improving the energy conversion efficiency of PEC catalysts. In addition to these, in order to fully reveal and exploit the advantages of heterostructures, more in-depth fundamental research, especially on the understanding of interfacial properties, is required.

Loading of cocatalysts

Coupling semiconductor photoanodes with good electrocatalytic OER cocatalysts is a common strategy to enhance the charge transfer efficiency from the semiconductor to the electrolyte and improve the oxidation kinetics \(^{[48]}\). The addition of OER catalysts can significantly inhibit the surface recombination of photogenerated charge carriers and reduce the accumulation of holes on the electrode surface. Moreover, some OER cocatalysts have been reported to passivate the photoanode surface to prevent corrosion of the photoanode, thereby improving its stability under operating conditions. Noble metal oxides, such as \(\text{RuO}_2\) and \(\text{IrO}_2\), are the most commonly used hole transfer cocatalysts, which can effectively reduce the overpotential of oxidation reactions \(^{[17]}\). However, due to the high cost of these catalysts, the development of
abundant and low-cost cocatalysts is indispensable.

*Transition metal-based catalysts*

To replace high-cost precious metals and their oxides for OER cocatalysts, many transition metal-based catalysts have been investigated extensively for improving PEC kinetics, including transition metal oxides (e.g., Co$_3$O$_4$[59], CoO$_x$[60] and NiO[61]), transition metal hydroxides (e.g., NiOOH[62], CoOOH[63] and FeOOH[64]) and transition metal phosphates (e.g., Fe-Pi[65] and Co-Pi[66]). However, despite these impressive achievements, the role of the cocatalysts in photoanodes is still under debate. Traditional cocatalysts as OER electrocatalysts increase the oxidation rate of water by reducing the activation energy of the four-electron oxidation process, which is the rate-determining step in the water splitting process. Some researchers have reported that the role of the cocatalyst is to rapidly trap the hole, thereby reducing recombination at the semiconductor surface. Li *et al.* demonstrated a citrate-assisted deposition method, in which Ni-Fe hydroxide was overlaid on a Fe$_2$O$_3$ nanowire photoanode [*Figure 5A*][67]. As shown by TEM images [*Figure 5B* and *C*], the Fe$_2$O$_3$ sample was coated with a Ni-Fe hydroxide layer (~5 nm thick). In the photoanode, Ni-Fe hydroxide as the OER catalyst is beneficial for hole migration and surface passivation and reduces electron-hole recombination on the Fe$_2$O$_3$ surface. Therefore, the obtained composite photoanode exhibited a turn-on potential as low as 0.53 V vs. a RHE. Compared to that of the pristine Fe$_2$O$_3$ photoanode, the turn-on potential had a large cathodic shift of 300 mV[67]. In addition, by loading a cocatalyst, the water oxidation kinetics can also be regulated to tune the product. Zhang *et al.* tuned the surface hole oxidation reaction kinetics of BiVO$_4$ by modifying it with SnO$_x$ rich in oxygen vacancies (SnO$_{x-x}$/BiVO$_4$)[68]. In contrast to pure BiVO$_4$, the modified BiVO$_4$ photoanode showed that in the process of water oxidation, the complete reaction of H$_2$O$_2$ and O$_2$ evolution was transformed into H$_2$O$_2$ evolution and OH radicals (OH·), accompanied by the inhibition of H$_2$O$_2$ decomposition through the hole re-oxidation process. The SnO$_{x-x}$/BiVO$_4$ photoanode achieved an average FE of 86% for the release of H$_2$O$_2$, thereby enabling highly selective water oxidation for producing H$_2$O$_2$[68].

*Figure 4.* Schematic diagram of conjugated π electrons in a MOF (UiO-67) inducing an internal electric field to promote the charge transfer, followed by the Z-scheme mechanism[25].
Carbon-based materials

Carbon-based materials have been widely investigated as cocatalysts for PEC catalysis due to their abundance, low cost and variety\(^{(59)}\). Carbon-based nanomaterials, such as graphene\(^{(60)}\), carbon nanotubes (CNTs)\(^{(61)}\) and carbon dots (CDs)\(^{(62)}\), offer multiple benefits in PEC systems. For example, they not only facilitate light harvesting but also act as channels for charge transport, thereby facilitating enhanced PEC activity due to synergistic effects and electrical coupling\(^{(63)}\). The high charge-carrier mobility of graphene and CNTs makes them promising candidates for high-mobility charge. However, the reports on those materials are mainly for electron modulation and rarely for hole modulation. Zhao \textit{et al.} fabricated a WO\(_3\) nanosheet array/silane/graphene oxide (WO\(_3\) NS/silane/GO)-based photoanode\(^{(64)}\). On the photoanode, the silane molecules act as hole collection sites and drive the fast transfer of the collected holes to the GO. As a hole transfer channel, GO can immediately promote holes to participate in chemical reactions at the electrode-electrolyte interface, resulting in stable and continuous charge carrier separation and transfer. The results showed that the photocurrent of the WO\(_3\) NS/silane/GO electrode (1.25 mA·cm\(^{-2}\) at 1.23 V vs. a RHE) can be enhanced by a factor of 1.8 compared to the pristine WO\(_3\) NS (0.69 mA·cm\(^{-2}\)) electrode\(^{(64)}\).

Compared to the above-mentioned carbon materials, CDs exhibit unique PEC properties, including photoluminescence and photoinduced electron transport and storage, and have been widely used as photoelectrocatalytic cocatalysts\(^{(65,66)}\). A large number of studies have reported CDs as cocatalysts for electron regulation. In recent years, some works have also reported the application of CDs in hole regulation. Liang \textit{et al.} reported a CD-modified Co\(_3\)O\(_4\)/In\(_2\)O\(_3\) composite photocatalyst for an efficient photon-driven CO\(_2\) reduction reaction\(^{(67)}\). CDs can be obtained by the electrolysis of graphite rods. The preparation process of CDs is simple and compared with the noble metal Ru, the economic cost of CDs is negligible [Figure 6A]. Through analysis by transient photoelectric technology, it was found that the CDs in the composite not only participated in the electron transfer process but also in the hole transfer process.
Figure 6. (A) Schematic comparison of carbon and noble metal Ru regarding resource consumption and economic cost. (B) Proposed mechanism of CD/Co$_3$O$_4$/In$_2$O$_3$ composite for water oxidation and CO$_2$ reduction reaction\(^\text{[67]}\).

The current density of the obtained CDs/Co$_3$O$_4$/In$_2$O$_3$ composite was increased compared with that of the Co$_3$O$_4$/In$_2$O$_3$ heterostructure. Ye et al. loaded CDs between a BiVO$_4$ core and a NiOOH/FeOOH shell\(^\text{[69]}\). Through the analysis of the transfer efficiency of BiVO$_4$, CD/BiVO$_4$, NiOOH/FeOOH/BiVO$_4$ and NiOOH/FeOOH/CD/BiVO$_4$ samples, the kinetic facility of transfer of the surface reached holes into the solution can be compared. The results showed that the CDs in the catalyst not only broadened the light absorption range but also facilitated the transfer of holes from the BiVO$_4$ core to the NiOOH/FeOOH shell, thus accelerating the OER kinetics\(^\text{[69]}\). Wang et al. obtained FAT through formic acid-treated dicyandiamide and modified it with CDs to achieve CD/FAT catalysts\(^\text{[70]}\). Wang et al. observed that CDs could extract holes in FAT with an efficiency of nearly 75% on a sub-microsecond timescale, leading to the reduction of the electron-hole recombination rate and a larger photoelectron density\(^\text{[70]}\). The CD/FAT catalysts exhibited the efficient selective reduction of CO$_2$ to methanol under neutral conditions\(^\text{[70]}\).

In addition to accelerating the extraction of holes and inhibiting the recombination of photogenerated carriers, CDs also appear to accelerate the kinetics of the oxidation reaction\(^\text{[71]}\). Zhou et al. designed a FeOOH/BiVO$_4$ photoanode and then co-modified CDs to obtain a CD/FeOOH/BiVO$_4$ composite\(^\text{[72]}\). The modified photoanode had a lower overpotential and higher photocurrent. The maximum incident photon-to-current conversion efficiency of the composite catalyst was 6.70 and 1.86 times higher than that of the BiVO$_4$ and FeOOH/BiVO$_4$ electrodes, respectively. Zhou et al. reported that these results were due to the joint influence of three effects: (i) the coordinated catalysis of CDs and FeOOH significantly improves the OER kinetics due to the introduction of oxygen vacancies; (ii) the heterojunction between CDs and BiVO$_4$ suppresses the bulk charge recombination effectively; (iii) CDs effectively promote the harvesting of ultraviolet and visible light\(^\text{[72]}\). Wang et al. synthesized nitrogen-doped CDs with a phenolic group (N-TACDs) from tannic acid\(^\text{[73]}\). The N-TACDs were then deposited on a BiVO$_4$ photoanode via metal-ligand complexation\(^\text{[73]}\). The N-TACDs can act as hole-storage layers to improve the charge separation efficiency and also improve the catalytic activity with a suitable band position.

CDs have many unique advantages as cocatalysts, as they can facilitate light harvesting and act as agents for photogenerated charge transfer. Furthermore, CDs can also serve as active centers, providing more electrochemically active sites through inherent structural defects, abundant surface/edge functional groups and heteroatom doping. The physical and chemical properties of CDs, such as size, defects, dopants and functional groups, strongly influence their PEC performance. Therefore, in order to realize the wide application of CDs, the controlled synthesis of CDs with specific structures is necessary. Furthermore, to
understand the origin and decay of activity, more control experiments are required to investigate the effect of CD structure on PEC performance.

**Organic hole transfer materials**

Currently, because of the tunable electrical properties of organic semiconductors or organic molecular materials, the construction of inorganic/organic composite photoanode has attracted increasing attention. Organic long-chain polymer hole transport materials are widely used in solar cells, such as spiro-OMeTAD (2,2',7,7'-tetrakis(N,N-p-dimethoxyphenylamino)-9,9'-spirobifluorene) and PTAA (poly-[bis(4-phenyl)(2,4,6-trimethylphenyl)amine])\(^{[24]}\). In addition, some research has shown that polyimide polymers have high thermal and chemical stability. Polyimide film electrodes with the semiconductor characteristics of a narrow band gap and suitable band structure have good catalytic ability and stability for the OER in strongly alkaline electrolytes. Thus, the integration of semiconductors with functional polymer layers can be used to achieve efficient and stable photoelectrodes under alkaline conditions. Gao et al. coated a metal-free poly(p-phenylene pyromellitimide) (PI) film on a BiVO\(_4\) photoanode by in-situ polymerization\(^{[75]}\). The PI film not only acts as a good OER catalytic layer but also promotes the transfer of photogenerated holes on the surface of the photoanode. The photocurrent density of the obtained PI/BiVO\(_4\) was increased by ~2.5 times compared to a pristine BiVO\(_4\) photoanode\(^{[75]}\). Gu et al. reported a metal-free bifunctional polyaniline (PANI)/CD electrocatalyst capable of producing hydrogen under light, in which PANI as a p-type semiconductor was used to solve the problem of insufficient protons\(^{[76]}\).

Small molecular materials that are soluble in water or polar solvents are more suitable for photoelectric catalytic systems. Currently, many research works have reported that organic hole-transporting molecular materials can be used to modify photoanodes as cocatalysts for hole modulation to improve charge separation efficiencies, such as ferrocene ligands, phenothiazine (PTZ) and trifluoroacetic acid\(^{[77-80]}\). A suitable hole-accepting ligand should satisfy the energy requirement for continuous hole transfer and interact closely with the photoelectrode to enable ultrafast hole transfer. Niu et al. systematically studied the role of carbazole-derived hole transport molecules anchoring on the surface of a CdS QD/TiO\(_2\) film\(^{[80]}\). As shown in Figure 7, dithiol-functionalized carbazole and a ruthenium coordination compound (RubdaS) were used as a hole transfer molecule and OER catalyst, respectively. These results demonstrated the importance of hole transport molecules for rapid hole transfer. A series of hole transport molecules, including carbazole, triphenylamine (TPA) and PTZ, were further anchored on the surface of a BiVO\(_4\)/CdS photoanode. The photogenerated holes from the photoanode can be extracted rapidly by these molecules. Among these different hole transport molecules, the obtained BiVO\(_4\)/CdS-TPA/CoBi exhibited an ultralow onset potential of 0.15 V vs. a RHE and the highest photocurrent density of 5.2 mA/cm\(^2\)\(^{[81]}\). Wu et al. reported the transfer kinetics of photogenerated holes in CdS nanorods (NRs) by PTZ molecules adsorbed on the surface\(^{[82]}\). In the presence of PTZ, the trapped holes are transferred to the PTZ to form PTZ' radical cations and this hole transfer rate is found to be much faster than the slow electron-trapping hole recombination in CdS NRs. This proved that the adsorbed PTZ can effectively extract trapped holes in CdS NRs\(^{[82]}\). In addition, Li et al. fabricated CdSe QDs modified with PTZ hole-accepting ligands and found that the PTZ modification of the CdSe QDs could significantly enhance the PEC H\(_2\) evolution efficiency\(^{[83]}\).

**RESEARCH METHODS FOR KINETICS OF HOLE TRANSFER**

In the semiconductor photocatalytic process, the lifetimes of the kinetic processes, such as migration, transport and recombination, generally range from a few nanoseconds to a few microseconds, whereas the timescales of photocatalytic reaction process are microseconds to seconds. Therefore, to effectively study the transport and transfer of charges in photoelectrodes, time-resolved analytical testing techniques are necessary.
Figure 7. Simplified interfacial hole hopping scheme for integrated photoanode[80].

**Transient absorption spectroscopy (TAS)**

Time-resolved spectroscopy is a new field developed by pulse technology combined with weak and transient signal detection methods, focusing on the investigation of the interaction between light and the sample. TAS is a pump-probe time-resolved technique that has been widely used to investigate dynamic processes. TAS can directly obtain information on the molecular ground, excited, oxidation and reduction states at different relaxation times and is therefore an effective means to explore the kinetics of charge transfer[84]. Tamaki et al. studied the intrinsic dynamics of electron-hole pairs in the range from femtoseconds to picoseconds and found that the holes could be trapped on the nanoparticle surfaces rapidly while the electrons were slowly trapped in the bulk phase with long lifetimes[85]. Wang et al. used TAS to fundamentally understand the charge carrier dynamics of hole-accepting CDs as cocatalysts[71]. The transient absorption spectra of g-C$_3$N$_4$ measured with and without Ag$^+$ electron scavengers showed that the signal observed at 510 nm was mainly attributed to photogenerated holes, while the wide signal at 700 nm was attributed to photogenerated electrons. The amplitude of *m*CDs/CN at 700 nm was higher than that of pure CN, indicating that the holes were transferred to *m*CDs efficiently and the number of long-lived electrons in CN was increased.

For heterostructured systems, Lian et al. synthesized CdS/ZnS core/mesoporous-shell (CdS@mZnS) heterostructures with superior photocatalytic activity[86]. TAS and the time-resolved microwave conductivity revealed efficient photoinduced hole transfer from the CdS core to the ZnS shell. The long-lived photoinduced charge separation (> 2.4 ms) via defect-mediated hole transfer resulted in good catalytic activity and stability for CdS@mZnS[86]. Andrews et al. also demonstrated sub-picosecond hole-transfer kinetics in β-Sn$_{0.23}$V$_2$O$_5$/CdSe heterostructures by TAS measurements[87]. The three-dimensional TA color maps of β-Sn$_{0.23}$V$_2$O$_5$ nanowires and β-Sn$_{0.23}$V$_2$O$_5$/CdSe heterostructures were acquired. The bare β-Sn$_{0.23}$V$_2$O$_5$ nanowires have two broad induced absorption bands at 500-600 and 650-750 nm, assigned to excited holes in the mid-gap state and β-Sn$_{0.23}$V$_2$O$_5$ electrons in the conduction band, respectively. The results demonstrated that the β-Sn$_{0.23}$V$_2$O$_5$/CdSe heterostructures have rapid excited-state charge transfer kinetics[87].

**Time-resolved photoluminescence (TRPL) spectroscopy**

In addition to TAS, TRPL spectroscopy is another effective means to probe electron transfer kinetics[88]. With the development of science and technology, the temporal resolution of fluorescence spectroscopy has reached the femtosecond scale (< 100 fs). Direct hole transfer rate tests can be carried out by adding a small amount of hole sacrificial agent to the catalyst with the corresponding carrier lifetime achieved by TRPL spectroscopy. Yu et al. tested the lifetime of photogenerated carriers of InP/ZnS-S QDs using TRPL...
A range of carrier lifetimes can be obtained by the stepwise addition of electron and hole sacrificial agents (N\textsuperscript{2+}/H\textsubscript{2}A) [Figure 8A and B]. The final electron and hole transfer rates were obtained by fitting the obtained data, indicating a calculated electron transfer rate from InP/ZnS-S QDs to Ni\textsuperscript{2+} of \(7.64 \times 10^{7} \text{ s}^{-1} \text{mM}^{-1}\) and a hole transfer rate from InP/ZnS-S QDs to H\textsubscript{2}A of \(1.25 \times 10^{8} \text{ s}^{-1} \text{mM}^{-1}\) [Figure 8C and D]\textsuperscript{[93]}. Fan et al. tested the static photoluminescence quenching and trap-state photoluminescence decay curves of CdSe and CdSe with surface S\textsuperscript{2-} (CdSe-nS) QDs with the sacrificial agent isopropyl alcohol\textsuperscript{[90]}. After the TRPL measurements of CdSe QDs with different molar ratios of S\textsuperscript{2-} ions, it was found that the corresponding hole transfer rate increased with increasing molar ratios of S\textsuperscript{2-} ions and was saturated at \(n = 75\). The TRPL measurements showed that the S\textsuperscript{2-} ligands were beneficial for hole transfer\textsuperscript{[90]}.

**Transient photoelectric technology (TPV)**

TPV is also an effective technique for determining interfacial charge transfer kinetics and photoelectron extraction in composites. In contrast to TAS and TRPL, TPV is a characterization technology that excites the catalysts in a photoelectrode by an optical signal and measures the dynamic process of the electrical signal inside the composite materials. Zhang et al. reported SnO\textsubscript{2-x} overlay-coated BiVO\textsubscript{4} (SnO\textsubscript{2-x}/BiVO\textsubscript{4}) and investigated its hole migration via TPV\textsuperscript{[94]}. The photoanode provided positive TPV signals, meaning that the surface migration behavior of photogenerated holes occurred. Compared with pure BiVO\textsubscript{4}, the SnO\textsubscript{2-x}/BiVO\textsubscript{4} photoanode had the highest TPV signal intensity, indicating that the coated SnO\textsubscript{2-x} overlay facilitated the photoinduced holes to reach the photoanode surface. In addition, the prolonged delay time of the photovoltage signal for both the SnO\textsubscript{2-x}/BiVO\textsubscript{4} and SnO\textsubscript{2-x}/BiVO\textsubscript{4} photoanodes indicated the existence of long-lived holes as a result of the reduction in surface recombination\textsuperscript{[95]}. Kang et al. reported a metal-free dual-function photo-assisted catalyst of PANI/CDs for overall water splitting\textsuperscript{[96]}. It was found that the addition of CDs reduced the recombination rate of photogenerated carriers. The number of photogenerated electrons consumed in the catalytic reaction could be calculated by integrating the tested TPV curves. It was found that the photocurrent intensity of PANI/CDs in 5 vol.% KOH (pH = 8.5)/ACN (v/v) was much higher than that in ACN solution, which may be due to the participation of photogenerated holes in the OER, resulting in increasing photocurrent intensity\textsuperscript{[76]}.

**Electrochemical impedance spectroscopy (EIS)**

Different from the above photophysical methods, electrochemical methods can directly record information, such as the photocurrent and photocurrent-potential (i-V) curves of PEC reactions. Photocurrent responses can reveal the separation efficiency of photogenerated electron-hole pairs. Among the electrochemical methods, EIS, through transient measurements, can be employed to investigate interfacial processes, such as redox reactions at the interfaces and the migration of electroactive species\textsuperscript{[89,92]}. EIS measurements are based on the perturbation signals with a set of sine voltages or current signals at different frequencies. Currently, EIS analysis is a relatively well-established method for investigating PEC systems\textsuperscript{[92]}.

Abbas et al. studied the hole transfer pathway in a TiO\textsubscript{2} photoanode sensitized by Au nanoclusters using EIS\textsuperscript{[98]}. Through the analysis of the Nyquist plots obtained as a function of applied potentials under light, the possible charge transfer mechanism in the photoelectrode can be achieved. From the low-frequency semicircle in the Nyquist plots at low bias potentials, the hole transfer process can be analyzed. The EIS studies confirmed that when Au\textsubscript{15}(SG)\textsubscript{13} and Au\textsubscript{16}(SG)\textsubscript{14} were employed, hole transfer occurred through the HOMO level of the nanoclusters and when Au\textsubscript{15}(SG)\textsubscript{13} was used, the hole transfer proceeded with the surface traps in TiO\textsubscript{2} \textsuperscript{[94]}. In EIS, the charge transfer resistance (R\textsubscript{ct}) of the photoanode is sensitive to surface processes and can be used to analyze the transfer of photogenerated holes. Kolay et al. investigated the charge recombination rate in a CdS-sensitized TiO\textsubscript{2} photoanode by modifying CDs through EIS and found that the R\textsubscript{ct} has a strong dependence on illumination but a low dependence on voltage\textsuperscript{[96]}. This implies that
Figure 8. Steady state and time-resolved photoluminescence quenching experiment of InP/ZnS-S QDs (525 nm, 15 min). Static photoluminescence quenching for InP/ZnS-S QDs in water after addition of different amounts of Ni$^{2+}$ (A) and H$_2$A (B). PL decay curves of InP/ZnS-S QDs after addition of different amounts of Ni$^{2+}$ (C) and H$_2$A (D), respectively.

charge transfer is influenced by photogenerated holes$^{[95]}$. 

Peter et al. characterized the competition between photogenerated carrier transfer and the recombination of an α-Fe$_2$O$_3$ electrode using photoelectrochemical impedance spectroscopy (PEIS)$^{[96,97]}$. The variation of EIS with electrodes for different layered α-Fe$_2$O$_3$ films was also recorded. The PEIS response of the α-Fe$_2$O$_3$ electrode exhibits characteristic transmission line behavior in the high-frequency part. Peter et al. speculated that this may be due to the slow hole transport, probably between adjacent surface iron species$^{[96,97]}$. Moreover, Peter et al. studied the effects of introducing Mn on the surface carrier dynamics of the hematite nanorods through intensity-modulated photocurrent spectroscopy (IMPS)$^{[98]}$. In contrast to EIS, IMPS measurements control the intensity of light on the electrode. In IMPS, the upper quadrant semicircle corresponds to the competition between charge transfer and recombination and the lower quadrant semicircle corresponds to the RC attenuation of the system [Figure 9]. Compared to the pristine hematite, the radius of the low-frequency semicircle (upper quadrant) of the Mn-doped hematite decreased and the hole transfer efficiency improved. The IMPS result revealed that the introduction of Mn not only increased the hole transfer rate constant but also reduced the surface recombination rate constant$^{[98]}$.

In addition, for the development of the PEC performance, understanding the interactions between ions in the electric double layer and charge carriers is critical. EIS measurements can also be used to study the surface ion adsorption. Zheng et al. showed that the capacitance at the interface of an InSe/graphene photoanode and the solution under illumination was ~2.3 times greater than that in the dark$^{[99]}$. The result showed an interaction between the photogenerated holes and OH$^-$ species, which further enhanced the concentration of OH$^-$ surface adsorption and improved the PEC performance$^{[99]}$. 


Figure 9. (A) Schematic of competition between hole transfer ($k_{tr}$) and recombination ($k_{rec}$). (B) A typical photocurrent of a photoanode in an electrolyte. (C) A typical example of a complex photocurrent or IMPS spectrum[98].

Scanning electrochemical microscopy (SECM)

Furthermore, it is of great significance to measure the interfacial processes of photoanodes at the microscopic scale. SECM is a scanning probe technique for electrical analysis, which can obtain information on substrate topography and localized electrochemical activity[100]. The concept of SECM is to place the ultramicroelectrode (diameter of < 25 μm) near the surface of the photoanode (or substrate) and to probe the changes in the concentration of active molecules in the electrolyte to investigate its chemical properties. Therefore, it is a powerful tool for imaging microelectrochemical activity and studying the kinetic behavior of reactive species under in-situ liquid-phase reaction conditions. In addition, the ultramicroelectrode can be scanned locally in the x, y or z direction through a piezoelectric actuator or stepper motor, so SECM can also be used to investigate spatial electrochemical information. SECM has also been used to explore the OER interfacial hole migration kinetics of composite photocatalytic systems [Figure 10A]. Zhang et al. studied the effect of oxygen vacancies on the hole transfer behavior of a BiVO$_4$/V$_2$O$_5$-FeNiOOH catalyst through SECM. SECM was employed at a UV-vis/SECM platform by the feedback mode[38]. Under visible-light irradiation, the current at the UME increases, which is mainly caused by photogenerated holes participating in the oxidation process of the active species [Figure 10B]. The results show that the kinetics of hole transfer in different photoanodes was in the order of: BiVO$_4$/V$_2$O$_5$-FeNiOOH BiVO$_4$/FeNiOOH BiVO$_4$ [Figure 10C and D], confirming that the strategy of introducing oxygen vacancies on the cocatalyst can improve the photogenerated charge transfer ability and further suppress the interfacial recombination[38].

The interfacial kinetic data of photogenerated holes can be further achieved through theoretical model simulations after obtaining different approaching curves. Liu et al. fabricated a CD-modified TiO$_2$ (CD/TiO$_2$) anode and investigated the regeneration kinetics of the CD sensitizer, i.e., the rate constant of the hole transfer from the oxidized CDs to the solution[101]. In this work, SECM measurements were performed by examining the ultramicroelectrode (UME) feedback current related to the change in the active species concentration under short-circuit conditions. The active species was chosen as I$_3^-$ /I$^-$ in acetonitrile. Under illumination (475 nm), the photoexcited state of the CDs injected electrons into the conduction band of...
TiO$_2$. As the UME approaches the substrate, the oxidation state (CD$_{+}^{+}$) generated is regenerated by reacting with I$^{-}$ in the electrolyte. Furthermore, the regeneration rate constant of CD$_{+}^{+}$ was achieved by fitting and analyzing the approaching curves obtained by testing different concentrations of active species and light intensities. SECM can also be used to further study the back-transfer behavior (electron participation process) and dye regeneration (hole participation process) at the interface between the photoanode and electrolyte for the effect of cocatalysts on the separation of electron-hole pairs. Yu et al. used SECM to study the surface kinetics of a BiVO$_4$/NiFe-LDH composite photocatalyst. It was found that the rate constant ratio of photogenerated surface holes and electrons reacting with the active species (k$_{h+}$/k$_{e-}$) was five times higher than that of BiVO$_4$. The results indicate that the NiFe-LDH cocatalyst can significantly inhibit electron back transfer and ultimately reduce surface recombination.

CONCLUSIONS

In this review, the strategies of hole modulation to improve solar-to-energy conversion efficiency are outlined. The modulation of holes facilitates the efficient separation of photogenerated carriers and accelerates the subsequent oxidation reactions. The catalysts in photoanodes with different compositions and structures show different reactivity. Hole modulation strategies, including hole sacrificial agents, nanostructural modification, heterostructure construction and cocatalyst modification, are effective methods to suppress electron-hole pair recombination and enhance PEC performance. The design of catalysts to modulate holes is summarized and the application of low-cost carbon materials as cocatalysts in hole modulation is highlighted. In addition, some kinetic techniques have also been summarized to analyze the transport and transfer kinetics of photogenerated holes. Although some achievements have been made, understanding how to acquire highly active PEC photoanodes via the rational design and regulation of fine structures and interfaces remains a significant challenge. The effects of the compositions and structures of the photoanode on the photogenerated charge migration and PEC properties need to be studied more thoroughly.
In these discussions, we have focused on designing and developing PEC catalysts for efficient solar-to-energy conversion. However, there are still many significant challenges that need to be addressed in order to make catalysts economically competitive. First, the PEC process involves the transport of charges and the coupling of subsequent reactions. The rate at which the photogenerated holes transfer to the semiconductor surface is effectively matched with the rate of transferring into the solution, enabling the efficient utilization of the photogenerated charges. Therefore, it is important to develop research methods to effectively distinguish the kinetic processes for the achievement of rate matching. Second, if the spatially separated photogenerated charges cannot be overlapped and synergized with the catalytic sites, it will lead to the recombination of the photogenerated charges, thereby reducing the PEC efficiency. The development of high-resolution characterization instruments can effectively promote the design of efficient PEC catalysts.

DECLARATIONS

Authors’ contributions
Conceptualization, investigation, writing - original draft: Liu N
Writing - review & editing: Liu Y (Yixin Liu), Liu Y (Yunliang Liu), Li Y, Cheng Y
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Conflicts of interest
All authors declared that there are no conflicts of interest.

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REFERENCES
1. Fang Y, Hou Y, Fu X, Wang X. Semiconducting polymers for oxygen evolution reaction under light illumination. Chem Rev 2022;122:4204-56. DOI PubMed
2. Kranz C, Wächtler M. Characterizing photocatalysts for water splitting: from atoms to bulk and from slow to ultrafast processes. Chem Soc Rev 2021;50:1407-37. DOI PubMed
3. Morikawa T, Sato S, Sekizawa K, Suzuki TM, Arai T. Solar-driven CO₂ reduction using a semiconductor/molecule hybrid photosystem: from photocatalysts to a monolithic artificial leaf. Acc Chem Res 2022;55:933-43. DOI PubMed
4. Pan J, Shen S, Chen L, Au C, Yin S. Core-shell photoanodes for photoelectrochemical water oxidation. Adv Funct Mater 2021;31:2104269. DOI PubMed
5. Thalluri SM, Bai L, Lv C, Huang Z, Hu X, Liu L. Strategies for semiconductor/electrocatalyst coupling toward solar-driven water splitting. Adv Sci 2020;7:1902102. DOI PubMed PMC
6. Niu F, Wang D, Li F, Liu Y, Shen S, Meyer TJ. Hybrid photoelectrochemical water splitting systems: from interface design to system assembly. Adv Energy Mater 2020;10:1900399. DOI
Meng L, Rao D, Tian W, Cao F, Yan X, Li L. Simultaneous manipulation of O-doping and metal vacancy in atomically thin 2D materials. *Microstructures* 2022;3:2022022. DOI PubMed

Pan JB, Wang BH, Wang JB, et al. Activity and stability boosting of an oxygen-vacancy-rich BiVO₄ photoanode by NiFe-MOFs thin film. *Microstructures* 2022;3:17989-8009. DOI PubMed
layer for water oxidation. Angew Chem Int Ed Engl 2021;60:1433-40. DOI PubMed
38. Zhang R, Ning X, Wang Z, et al. Significantly promoting the photogenerated charge separation by introducing an oxygen vacancy regulation strategy on the FeNiO\textsubscript{2}/n-ZnO Co-catalyst. Small 2022;18:e2107938. DOI PubMed
39. Ji M, Chen R, Di J, et al. Oxygen vacancies modulated Bi-rich bismuth oxyiodide microspheres with tunable valence band position to boost the photocatalytic activity. J Colloid Interface Sci 2019;533:612-20. DOI PubMed
40. Zhao Q, Liu Z, Guo Z, Ruan M, Yan W. The collaborative mechanism of surface S-vacancies and piezoelectric polarization for boosting CdS photoelectrochemical performance. Chem Eng J 2022;433:133226. DOI
41. Ma M, Zhang K, Li P, Jung MS, Jeong MJ, Park JH. Dual Oxygen and tungsten vacancies on a WO\textsubscript{3} Photoanode for enhanced water oxidation. Angew Chem Int Ed Engl 2016;55:11819-23. DOI PubMed
42. Fernández-climent R, Giménez A, García-tecedor M. The role of oxygen vacancies in water splitting photoanodes. Sustain Energy Fuels 2020;4:5916-26. DOI
43. Xu W, Tian W, Meng L, Cao F, Li L. Interfacial chemical bond-modulated z-scheme charge transfer for efficient photoelectrochemical water splitting. Adv Energy Mater 2021;11:2003500. DOI
44. Li J, Yuan H, Zhang W, et al. Advances in Z-scheme semiconductor photocatalysts for the photoelectrochemical applications: A review. Carbon Energy 2022;4:294-331. DOI
45. Mane P, Bae H, Burungale V, et al. Interface-engineered Z-scheme of BiVO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} photoanode for boosted photoelectrochemical water splitting and organic contaminant elimination under solar light. Chemosphere 2022;308:136166. DOI PubMed
46. Maity D, Karmakar K, Pal D, Saha S, Khan GG, Mandal K. One-dimensional p-ZnCo\textsubscript{2}O\textsubscript{4}/α-ZnO nanoheterojunction photoanode enabling photoelectrochemical water splitting. ACS Appl Mater Energy 2021;4:11599-608. DOI
47. Ho W, Chen J, Wu J. Epitaxial, energetic, and morphological synergy on photocatalyst collection of the Fe\textsubscript{2}TiO\textsubscript{4}/ZnO nanodendrimer heterojunction array photoelectrode for photoelectrochemical water oxidation. ACS Sustain Chem Eng 2021;9:8868-78. DOI
48. Hao J, Zhang Z, Cao K, et al. Unraveling the electronegativity-dominated intermediate desorption on high-entropy alloy electrocatalysts. Nat Commun 2012;3:2662. DOI PubMed PMC
49. Dong G, Hu H, Huang X, Zhang Y, Bi Y. Rapid activation of Co\textsubscript{3}O\textsubscript{4} co-catalysts with oxygen vacancies on TiO\textsubscript{2} photoanodes for efficient water splitting. J Mater Chem A 2018;6:21003-9. DOI
50. Cao X, Wang Y, Lin J, Ding Y. Ultrathin Co\textsubscript{3}O\textsubscript{4} nanolayers derived from polyoxometalate for enhanced photoelectrochemical performance of hematite photoanodes. J Mater Chem A 2019;7:6294-303. DOI
51. Li H, Yin M, Li X, Mo R. Enhanced photoelectrochemical water oxidation performance in bilayer TiO\textsubscript{2}/α-Fe\textsubscript{2}O\textsubscript{3} Nanorods Array Photoanode with Cu\textsubscript{3}NiO\textsubscript{4} as hole transport layer and Co-Pi as Cocatalyst. ChemSusChem 2021;14:2331-40. DOI
52. Wei J, Zhou C, Xin Y, Li X, Zhao L, Liu Z. Cooperation effect of heterojunction and co-catalyst in Bi\textsubscript{2}O\textsubscript{3}/Bi\textsubscript{2}S\textsubscript{3}/NiOOH photoanode for improving photoelectrochemical performances. New J Chem 2018;42:19415-22. DOI
53. Zhang B, Huang X, Hu H, Chou L, Bi Y. Defect-rich and ultrathin CoOOH nanolayers as highly efficient oxygen evolution catalysts for photoelectrochemical water splitting. J Mater Chem A 2019;7:4415-9. DOI
54. Wang T, Long X, Wei S, et al. Boosting hole transfer in the fluoride-doped hematite photoanode by depositing ultrathin amorphous FeOOH/CoOOH Cocatalysts. ACS Appl Mater Interfaces 2020;12:49705-12. DOI PubMed
55. Vo T, Tai Y, Chiang C. Novel hierarchical ferric phosphate/bismuth vanadate nanocactus for highly efficient and stable solar water splitting. Appl Catalysis B: Environ 2019;243:657-66. DOI
56. Klahir B, Gimenez S, Fabregat-Santiago F, Bisquert J, Hamann TW. Photoelectrochemical and impedance spectroscopic investigation of water oxidation with “Co-Pi”-coated hematite electrodes. J Am Chem Soc 2012;134:16693-700. DOI PubMed
57. Li M, Liu T, Yang Y, et al. Zipping Up Ni(Fe)(OH)\textsubscript{x}-encapsulated hematite to achieve an ultralow turn-on potential for water oxidation. ACS Energy Lett 2019;4:1983-90. DOI
58. Zhang K, Liu J, Wang L, et al. Near-complete suppression of oxygen evolution for photoelectrochemical H\textsubscript{2}O oxidative H\textsubscript{2}O\textsubscript{2} synthesis. J Am Chem Soc 2020;142:8641-8. DOI PubMed
59. Liu Z, Du Y, Zhang P, Zhuang Z, Wang D. Bringing catalytic order out of chaos with nitrogen-doped ordered mesoporous carbon. Matter 2021;4:3161-94. DOI
60. Kaplan A, Yuan Z, Benck JD, et al. Current and future directions in electron transfer chemistry of graphene. Chem Soc Rev 2017;46:4530-71. DOI PubMed
61. Rai S, Kram A, Sahai S, Dass S, Shrivastav R, Satsangi VR. CNB based photoelectrodes for PEC generation of hydrogen: a review. Inter J Hydrog Energy 2017;42:3994-4006. DOI
62. Kang Z, Lee ST. Carbon dots: advances in nanocarbon applications. Nanoscale 2019;11:19214-24. DOI PubMed
63. Ali M, Pervaez E, Sikandar U, Khan Y. A review on the recent developments in zirconium and carbon-based catalysts for photoelectrocatalytic water-splitting. Inter J Hydrog Energy 2021;46:18257-83. DOI
64. Zhao Z, Zheng L, Hu W, Zheng H. Synergistic effect of silane and graphene oxide for enhancing the photoelectrocatalytic water oxidation performance of WO\textsubscript{3}NS arrays. Electrochimica Acta 2018;292:322-30. DOI
65. Dordiiev L, Arcudi F, Cacioppo M, Prato M. A multifunctional chemical toolbox to engineer carbon dots for biomedical and energy applications. Nat Nanotechnol 2022;17:112-30. DOI PubMed
66. Zhai Y, Zhang B, Shi R, et al. Carbon dots as new building blocks for electrochemical energy storage and electrocatalysis. Advan Energy Mater 2022;12:2103426. DOI
67. Liang Q, Yan X, Li Z, et al. Replacing Ru complex with carbon dots over MOF-derived Co\textsubscript{3}O\textsubscript{4}/In\textsubscript{2}O\textsubscript{3} catalyst for efficient solar-
driven CO₂ reduction. J Mater Chem A 2022;10:4279-87. DOI
68. Li F, Liu Y, Chen Q, et al. Transient photovoltage study of the kinetics and synergy of electron/hole co-extraction in MoS₂/Ag-In-Zn-S/carbon dot photocatalysts for promoted hydrogen production. Chem Eng J 2022;439:135759. DOI
69. Ye K, Wang Z, Gu J, et al. Carbon quantum dots as a visible light sensitizer to significantly increase the solar water splitting performance of bismuth vanadate photoanodes. Energy Environ Sci 2017;10:772-9. DOI
70. Wang Y, Godin R, Durrant JR, Tang J. Efficient Hole trapping in carbon dot/oxygen-modified carbon nitride heterojunction photocatalysts for enhanced melanhol production from CO₂ under neutral conditions. Angew Chem Int Ed Engl 2021;60:20811-6. DOI PubMed PMC
71. Wang Y, Liu X, Han X, et al. Unique hole-accepting carbon-dots promoting selective carbon dioxide reduction nearly 100% to methanol by pure water. Nat Commun 2020;11:2531. DOI PubMed PMC
72. Zhou T, Chen S, Wang J, et al. Dramatically enhanced solar-driven water splitting of BiVO₄ photoanode via strengthening hole transfer and light harvesting by co-modification of CQDs and ultrathin β-FeOOH layers. Chem Eng J 2021;403:126350. DOI
73. Choi Y, Bae S, Kim B, Ryu J. Atomically-dispersed cobalt ions on polyphenol-derived nanocarbon layers to improve charge separation, hole storage, and catalytic activity of water-oxidation photoanodes. J Mater Chem A 2021;9:13874-82. DOI
74. Rombach FM, Haque SA, Macdonald TJ. Lessons learned from spiro-OMeTAD and PTAA in perovskite solar cells. Energy Environ Sci 2021;14:5161-90. DOI
75. Gao B, Wang T, Li Y, et al. Boosting the stability and photoelectrochemical activity of a BiVO₄ photoanode through a bifunctional polymer coating. J Mater Chem A 2021;9:3309-13. DOI
76. Gu X, Chen Z, Li Y, et al. Polyol/line/carbon dots composite as a highly efficient metal-free dual-functional photoassisted electocatalyst for overall water splitting. ACS Appl Mater Interfaces 2021;13:24814-23. DOI PubMed
77. Li F, Liu Y, Mao B, et al. Carbon-dots-mediated highly efficient hole transfer in I-III-VI quantum dots for photocatalytic hydrogen production. Appl Catalysis B Environ 2021;292:120154. DOI
78. Liu Y, Zhou X, Shen C, et al. Hydrogen-bonding-assisted charge transfer: significantly enhanced photocatalytic H₂ evolution over g-C₃N₄ anchored with ferrocene-based hole relay. Catal Sci Technol 2018;8:2853-9. DOI
79. Olshansky JH, Balan AD, Ding TX, Fu X, Lee YY, Alivisatos AP. Temperature-dependent hole transfer from photoexcited quantum dots to molecular species: evidence for trap-mediated transfer. ACS Nano 2017;11:8346-55. DOI PubMed
80. Niu F, Zhou Q, Liu R, Hu K. Photoinduced hole hopping across CdS quantum dot surfaces for photoelectrochemical water oxidation. ACS Appl Energy Mater 2022;5:1244-51. DOI
81. Niu F, Zhou Q, Han Y, et al. Rapid hole extraction based on cascade band alignment boosts photoelectrochemical water oxidation efficiency. ACS Catal 2022;12:10028-38. DOI
82. Wu K, Du Y, Tang H, Chen Z, Liu T. Efficient extraction of trapped holes from colloidal CdS nanorods. J Am Chem Soc 2015;137:10224-30. DOI PubMed
83. Li XB, Liu B, Wen M, et al. Hole-accepting-ligand-modified CdSe QDs for dramatic enhancement of photocatalytic and photoelectrochemical hydrogen evolution by solar energy. Adv Sci 2016;3:1500282. DOI PubMed PMC
84. Forster M, Cheung DWF, Gardner AM, Cowan AJ. Potential and pitfalls: on the use of transient absorption spectroscopy for in situ and operando studies of photoelectrodes. J Chem Phys 2020;153:150901. DOI PubMed
85. Tamaki Y, Furube A, Murai M, Hara K, Katao R, Tachiya M. Dynamics of efficient electron-hole separation in TiO₂ nanoparticles revealed by femtosecond transient absorption spectroscopy under the weak-excitation condition. J Phys Chem C 2007;11:1453-60. DOI PubMed
86. Lian Z, Sakamoto M, Kobayashi Y, et al. Anomalous photoinduced hole transport in type I core/mesoporous-shell nanocrystals for efficient photocatalytic H₂ evolution. ACS Nano 2019;13:8356-63. DOI PubMed
87. Andrews JL, Cho J, Wangh L, et al. Hole extraction by design in photocatalytic architectures interfacing CdSe quantum dots with topochromically stabilized tin vanadium oxide. J Am Chem Soc 2018;140:17163-74. DOI PubMed
88. Taheri MM, Elbert KC, Yang S, et al. Distinguishing electron and hole dynamics in functionalized CdSe/CdS core/shell quantum dots using complementary ultrafast spectroscopies and kinetic modeling. J Phys Chem C 2021;125:31-41. DOI
89. Yu S, Fan XB, Wang X, et al. Efficient photocatalytic hydrogen evolution with ligand engineered all-inorganic InP and InP/ZnS colloidal quantum dots. Nat Commun 2018;9:4009. DOI PubMed PMC
90. Fan XB, Yu S, Wang X, et al. Susceptible surface sulfide regulates catalytic activity of CdSe quantum dots for hydrogen photogeneration. Adv Mater 2019;31:e1804872. DOI PubMed
91. Bredar ARC, Chown AL, Burton AR, Farnum BH. Electrochemical impedance spectroscopy of metal oxide electrodes for energy applications. ACS Appl Energy Mater 2020;3:66-98. DOI
92. Gimenez S, Dunn HK, Rodenas P, et al. Carrier density and interfacial kinetics of mesoporous TiO₂ in aqueous electrolyte determined by impedance spectroscopy. J Electroanal Chem 2012;668:119-25. DOI
93. Cui J, Daboczi M, Regue M, et al. 2D bismuthene as a functional interlayer between BiVO₄ and NiFeOOH for enhanced oxygen-evolution photoanodes. Adv Funct Mater 2022;2207136-48. DOI
94. Abbas MA, Bang JH. Anomalous transition of hole transfer pathways in gold nanocluster-sensitized TiO₂ photoelectrodes. ACS Energy Lett 2020;5:3718-24. DOI PubMed PMC
95. Kolay A, Kokal RK, Kalluri A, et al. New antimony selenide/nickel oxide photocathode boosts the efficiency of graphene quantum-dot co-sensitized solar cells. ACS Appl Mater Interfaces 2017;9:34915-26. DOI PubMed
96. Wijayantha KG, Saremi-Yarahmadi S, Peter LM. Kinetics of oxygen evolution at α-Fe2O3 photoanodes: a study by photoelectrochemical impedance spectroscopy. Phys Chem Chem Phys 2011;13:5264-70. DOI PubMed
97. Cummings CY, Marken F, Peter LM, Wijayantha KG, Tahir AA. New insights into water splitting at mesoporous α-Fe2O3 films: a study by modulated transmittance and impedance spectroscopies. J Am Chem Soc 2012;134:1228-34. DOI PubMed
98. Peter LM, Wong LH, Abdi FF. Revealing the influence of doping and surface treatment on the surface carrier dynamics in hematite nanorod photoanodes. ACS Appl Mater Interfaces 2017;9:41265-72. DOI PubMed
99. Zheng H, Lu Y, Ye KH, et al. Atomically thin photoanode of InSe/graphene heterostructure. Nat Commun 2021;12:91. DOI PubMed
100. Bard AJ, Faulkner LR. Scanning electrochemical microscopy, 2nd ed.; New York: Marcel Dekker. 2001.
101. Liu N, Qin Y, Han M, et al. Investigation of regeneration kinetics of a carbon-dot-sensitized metal oxide semiconductor with scanning electrochemical microscopy. ACS Appl Energy Mater 2018;1:1483-8. DOI
102. Yu Z, Huang Q, Jiang X, et al. Effect of a cocatalyst on a photoanode in water splitting: a study of scanning electrochemical microscopy. Anal Chem 2021;93:12221-9. DOI PubMed