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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



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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^[1-3]. 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^[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 TiO₂ photoelectrode in 1972, photoelectrochemical (PEC) catalysis based on semiconductor photoelectrodes has attracted extensive attention for solar-to-energy conversion^[7-9]. PEC water splitting combines photocatalysis and electrocatalysis, which can effectively promote charge separation and improve solar energy utilization^[9]. 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-C₃N₄)^[10,11]. 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^[12-14], such as the CO₂ and NH₃ 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^[15,16].

Noble metal oxides, such as RuO₂ and IrO₂, are the most commonly selected materials to modulate photogenerated holes to enhance PEC performance^[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

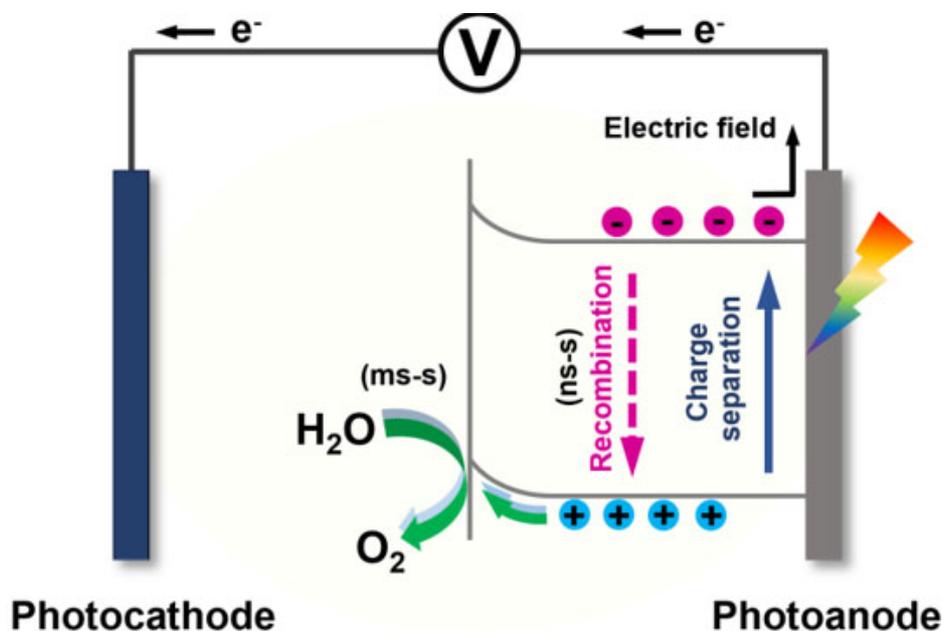


Figure 1. Schematic illustration of the processes of photoinduced charge separation, recombination, transfer and the final catalytic reaction in semiconductor-based photoelectrocatalytic water splitting and the associated reaction timescales.

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^[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^[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

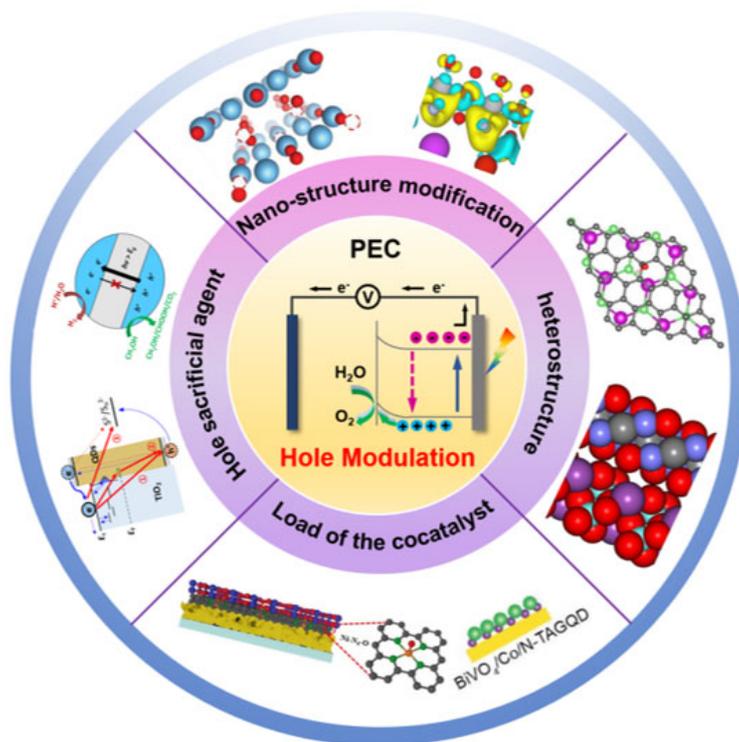


Figure 2. Schematic diagram of photogenerated hole modulation strategies in photoelectrocatalysis.

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_2S - Na_2SO_3 [20,21], triethanolamine (TEOA) [22,23] and H_2O_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_2O_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 [27]. 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 [28]. 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^[29,30]. 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 BiVO₄ photoanode, in which the O sites in NiFeO_x and BiVO₄ were partially replaced by low-electronegativity N atoms, leading to their electronic reconfiguration^[18]. The morphological and structural characterization of the BiVO₄/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 BiVO₄ 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 BiVO₄/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 BiVO₄/N:NiFeO_x photoanode (1.9% at 0.73 V vs. a RHE) was also much higher than that of BiVO₄/NiFeO_x (1.1% at 0.8 V vs. a RHE) and pristine BiVO₄ (0.29% at 0.96 V vs. a RHE), as shown in Figure 3F^[18].

Meng *et al.* synthesized two-dimensional (2D) atomically thin Zn₁₀In₁₆S₃₄ 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 Al₂O₃ 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^[10,34]. 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^[36,37]. Zhang *et al.* fabricated a BiVO₄ catalyst modified with a FeNiOOH cocatalyst rich in oxygen vacancies (BiVO₄/Vo-FeNiOOH) through a simple and economical NaBH₄ reduction method^[38]. 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 BiVO₄/Vo-FeNiOOH catalyst was more than four times that of pure BiVO₄ due to the introduction of oxygen vacancies in the system^[38]. Li *et al.* successfully prepared Bi₇O₉I₃ microspheres rich in oxygen vacancies by a solvothermal method assisted by an ionic liquid^[39]. Compared with Bi₇O₉I₃ with fewer oxygen vacancies after annealing, the valence band maximum position of Bi₇O₉I₃ with rich oxygen vacancies shifted upward, which resulted in better photooxidation ability for the

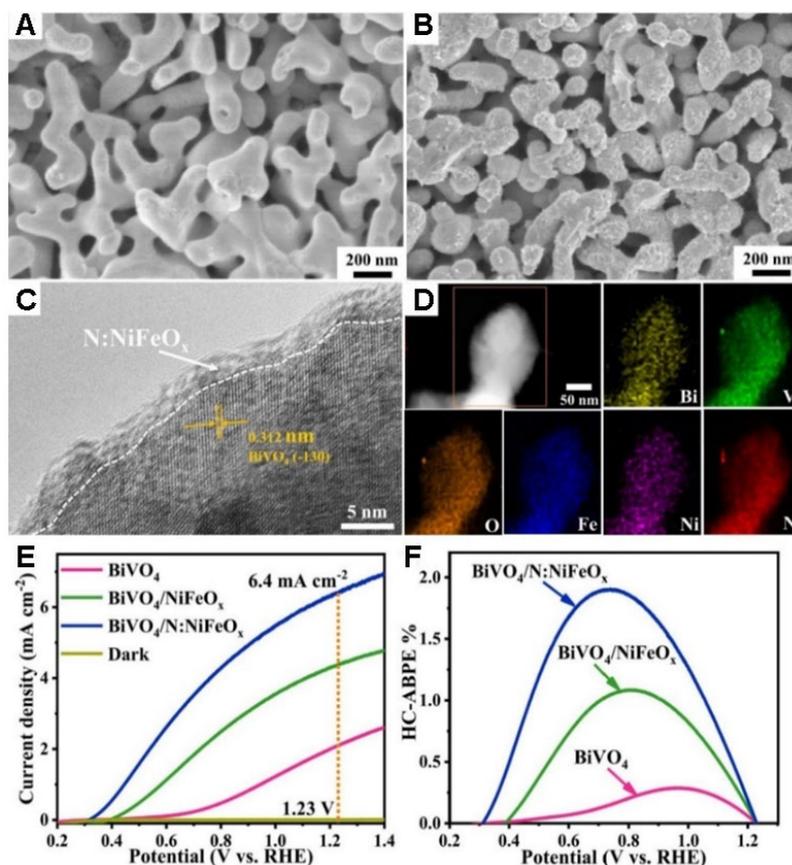


Figure 3. (A-D) Morphological and structural characterization, (E) linear sweep voltammograms and (F) half-cell applied bias photon-to-current efficiency results of $\text{BiVO}_4/\text{N}:\text{NiFeO}_x$ photoanodes^[18].

photogenerated holes and higher separation efficiency for the photogenerated carriers, thus promoting the photocatalytic removal of oxygen and photocatalytic pollutants^[39].

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_2O_2 etching and adjusted the vacancy concentration by controlling the etching time^[40]. The photocurrent density of the CdS nanorods etched by H_2O_2 for 35 s reached $3.09 \text{ mA}\cdot\text{cm}^{-2}$, 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-C₃N₄/semiconductor composite, the photogenerated electrons of the semiconductor transfer to the valence band of g-C₃N₄ and then recombine with the photogenerated holes derived from g-C₃N₄. Therefore, the photogenerated electrons on g-C₃N₄ 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 π electrons in the linkers [Figure 4]. Wang *et al.* fabricated Z-scheme heterostructures of TiO₂ nanorods (NRs) coated by MOFs and obtained UiO-66@TiO₂ and UiO-67@TiO₂ photoanodes. Compared with pristine TiO₂, UiO-66@TiO₂ and UiO-67@TiO₂ showed enhanced photocurrent density in the PEC water oxidation process^[25].

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 WO₃/BiVO₄, ZnO/BiVO₄, ZnO/Fe₂O₃, TiO₂/ZnO, and so on, have been reported with remarkable PEC performance. Maity *et al.* fabricated a one-dimensional n-ZnO/p-ZnCo₂O₄ nanoheterojunction photoanode^[46]. In this type-II heterojunction photoanode, the ZnCo₂O₄ surface overlayer passivated the surface states of ZnO nanorods, thereby significantly reducing the recombination of photogenerated electron-hole pairs. The generated holes from the ZnO nanorods can migrate rapidly to the surface of ZnCo₂O₄ and initiate the OER. Compared with the pristine ZnO photoanode, the n-ZnO/p-ZnCo₂O₄ 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 Fe₂TiO₅/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 RuO₂ and IrO₂, 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

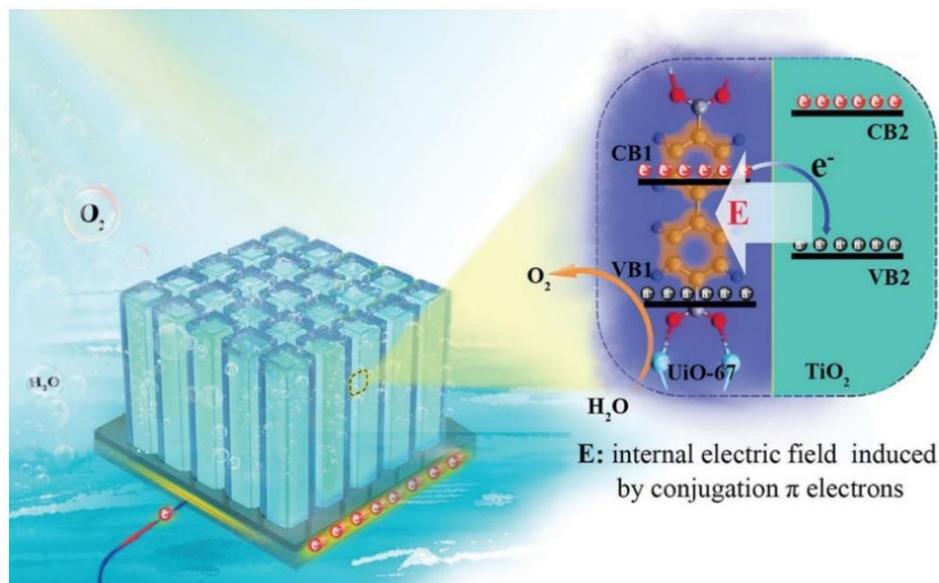


Figure 4. Schematic diagram of conjugated π electrons in a MOF (UiO-67) inducing an internal electric field to promote the charge transfer, followed by the Z-scheme mechanism^[25].

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_3O_4 ^[49], CoO_x ^[50] and NiO ^[51]), transition metal hydroxides (e.g., NiOOH ^[52], CoOOH ^[53] and FeOOH ^[54]) and transition metal phosphates (e.g., Fe-Pi^[55] and Co-Pi^[56]). 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_2O_3 nanowire photoanode [Figure 5A]^[57]. As shown by TEM images [Figure 5B and C], the Fe_2O_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_2O_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_2O_3 photoanode, the turn-on potential had a large cathodic shift of 300 mV^[57]. 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_2 rich in oxygen vacancies ($\text{SnO}_{2-x}/\text{BiVO}_4$)^[58]. In contrast to pure BiVO_4 , the modified BiVO_4 photoanode showed that in the process of water oxidation, the complete reaction of H_2O_2 and O_2 evolution was transformed into H_2O_2 evolution and OH radicals ($\text{OH}\cdot$), accompanied by the inhibition of H_2O_2 decomposition through the hole re-oxidation process. The $\text{SnO}_{2-x}/\text{BiVO}_4$ photoanode achieved an average FE of 86% for the release of H_2O_2 , thereby enabling highly selective water oxidation for producing H_2O_2 ^[58].

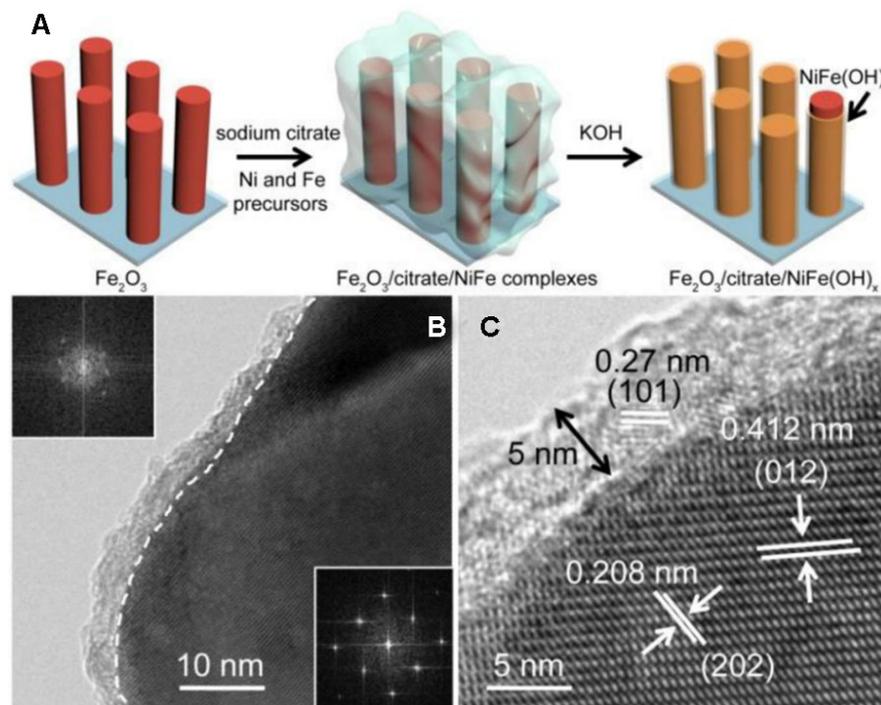


Figure 5. (A) Schematic illustration of depositing NiFe hydroxide overlays on an Fe_2O_3 nanowire photoanode. (B and C) Lattice-resolved TEM images of a NiFe hydroxide-coated Fe_2O_3 nanowire photoanode^[57].

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 *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 ($1.25 \text{ mA}\cdot\text{cm}^{-2}$ at 1.23 V vs. a RHE) can be enhanced by a factor of 1.8 compared to the pristine WO_3 NS ($0.69 \text{ mA}\cdot\text{cm}^{-2}$) 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 *et al.* reported a CD-modified $\text{Co}_3\text{O}_4/\text{In}_2\text{O}_3$ composite photocatalyst for an efficient photo-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

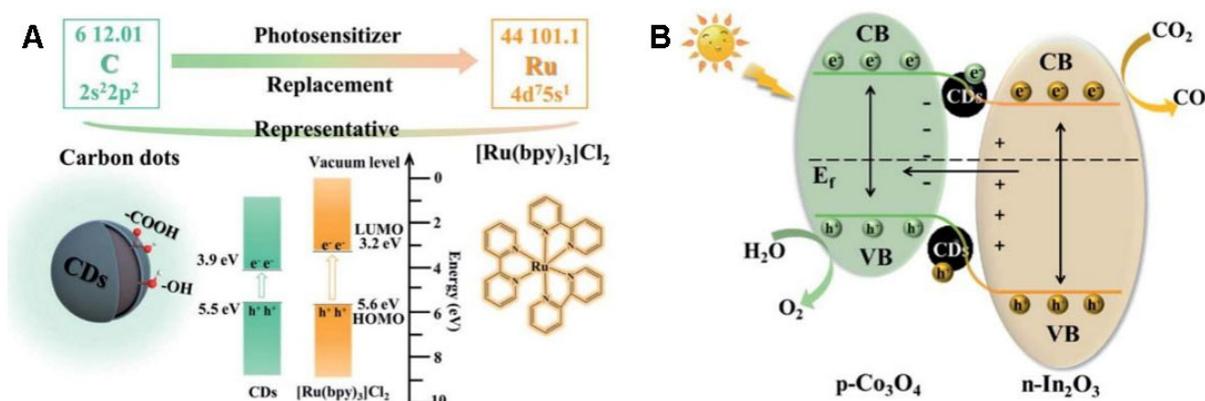


Figure 6. (A) Schematic comparison of carbon and noble metal Ru regarding resource consumption and economic cost. (B) Proposed mechanism of CD/Co₃O₄/In₂O₃ composite for water oxidation and CO₂ reduction reaction^[67].

[Figure 6B]^[67,68]. The current density of the obtained CDs/Co₃O₄/In₂O₃ composite was increased compared with that of the Co₃O₄/In₂O₃ heterostructure. Ye *et al.* loaded CDs between a BiVO₄ core and a NiOOH/FeOOH shell^[69]. Through the analysis of the transfer efficiency of BiVO₄, CD/BiVO₄, NiOOH/FeOOH/BiVO₄ and NiOOH/FeOOH/CD/BiVO₄ 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 BiVO₄ core to the NiOOH/FeOOH shell, thus accelerating the OER kinetics^[69]. Wang *et al.* obtained FAT through formic acid-treated dicyandiamide and modified it with CDs to achieve CD/FAT catalysts^[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^[70]. The CD/FAT catalysts exhibited the efficient selective reduction of CO₂ to methanol under neutral conditions^[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^[71]. Zhou *et al.* designed a FeOOH/BiVO₄ photoanode and then co-modified CDs to obtain a CD/FeOOH/BiVO₄ composite^[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 BiVO₄ and FeOOH/BiVO₄ 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 BiVO₄ suppresses the bulk charge recombination effectively; (iii) CDs effectively promote the harvesting of ultraviolet and visible light^[72]. Wang *et al.* synthesized nitrogen-doped CDs with a phenolic group (N-TACDs) from tannic acid^[73]. The N-TACDs were then deposited on a BiVO₄ photoanode via metal-ligand complexation^[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])^[74]. 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 BiVO₄ 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/BiVO₄ was increased by ~2.5 times compared to a pristine BiVO₄ 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/TiO₂ 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 BiVO₄/CdS photoanode. The photogenerated holes from the photoanode can be extracted rapidly by these molecules. Among these different hole transport molecules, the obtained BiVO₄/CdS-TPA/CoBi exhibited an ultralow onset potential of 0.15 V vs. a RHE and the highest photocurrent density of 5.2 mA/cm²^[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 H₂ 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.

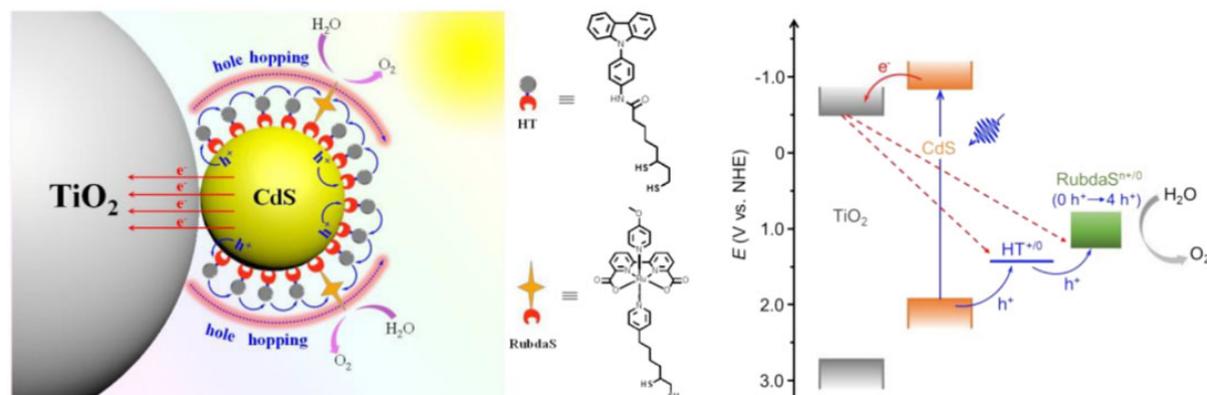


Figure 7. Simplified interfacial hole hopping scheme for integrated photoanode^[80].

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-C₃N₄ 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 ^mCDs/CN at 700 nm was higher than that of pure CN, indicating that the holes were transferred to ^mCDs 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}V₂O₅/CdSe heterostructures by TAS measurements^[87]. The three-dimensional TA color maps of β -Sn_{0.23}V₂O₅ nanowires and β -Sn_{0.23}V₂O₅/CdSe heterostructures were acquired. The bare β -Sn_{0.23}V₂O₅ 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}V₂O₅ electrons in the conduction band, respectively. The results demonstrated that the β -Sn_{0.23}V₂O₅/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

spectroscopy^[89]. A range of carrier lifetimes can be obtained by the stepwise addition of electron and hole sacrificial agents ($\text{Ni}^{2+}/\text{H}_2\text{A}$) [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^{2+} of $7.64 \times 10^8 \text{ s}^{-1} \cdot \text{mM}^{-1}$ and a hole transfer rate from InP/ZnS-S QDs to H_2A of $1.25 \times 10^8 \text{ s}^{-1} \cdot \text{mM}^{-1}$ [Figure 8C and D]^[89]. Fan *et al.* tested the static photoluminescence quenching and trap-state photoluminescence decay curves of CdSe and CdSe with surface S^{2-} (CdSe-nS) QDs with the sacrificial agent isopropyl alcohol^[90]. After the TRPL measurements of CdSe QDs with different molar ratios of S^{2-} ions, it was found that the corresponding hole transfer rate increased with increasing molar ratios of S^{2-} ions and was saturated at $n = 75$. The TRPL measurements showed that the S^{2-} ligands were beneficial for hole transfer^[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_{2-x} overlay-coated BiVO_4 ($\text{SnO}_{2-x}/\text{BiVO}_4$) and investigated its hole migration via TPV^[58]. The photoanode provided positive TPV signals, meaning that the surface migration behavior of photoinduced holes occurred. Compared with pure BiVO_4 , the $\text{SnO}_{2-x}/\text{BiVO}_4$ photoanode had the highest TPV signal intensity, indicating that the coated SnO_{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 $\text{SnO}_2/\text{BiVO}_4$ and $\text{SnO}_{2-x}/\text{BiVO}_4$ photoanodes indicated the existence of long-lived holes as a result of the reduction in surface recombination^[58]. Kang *et al.* reported a metal-free dual-function photo-assisted catalyst of PANI/CDs for overall water splitting^[62]. 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^[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^[91,92]. 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^[93].

Abbas *et al.* studied the hole transfer pathway in a TiO_2 photoanode sensitized by Au nanoclusters using EIS^[94]. 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 $\text{Au}_{15}(\text{SG})_{13}$ and $\text{Au}_{18}(\text{SG})_{14}$ were employed, hole transfer occurred through the HOMO level of the nanoclusters and when $\text{Au}_{25}(\text{SG})_{18}$ was used, the hole transfer proceeded with the surface traps in TiO_2 ^[94]. In EIS, the charge transfer resistance (R_{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_2 photoanode by modifying CDs through EIS and found that the R_{ct} has a strong dependence on illumination but a low dependence on voltage^[95]. This implies that

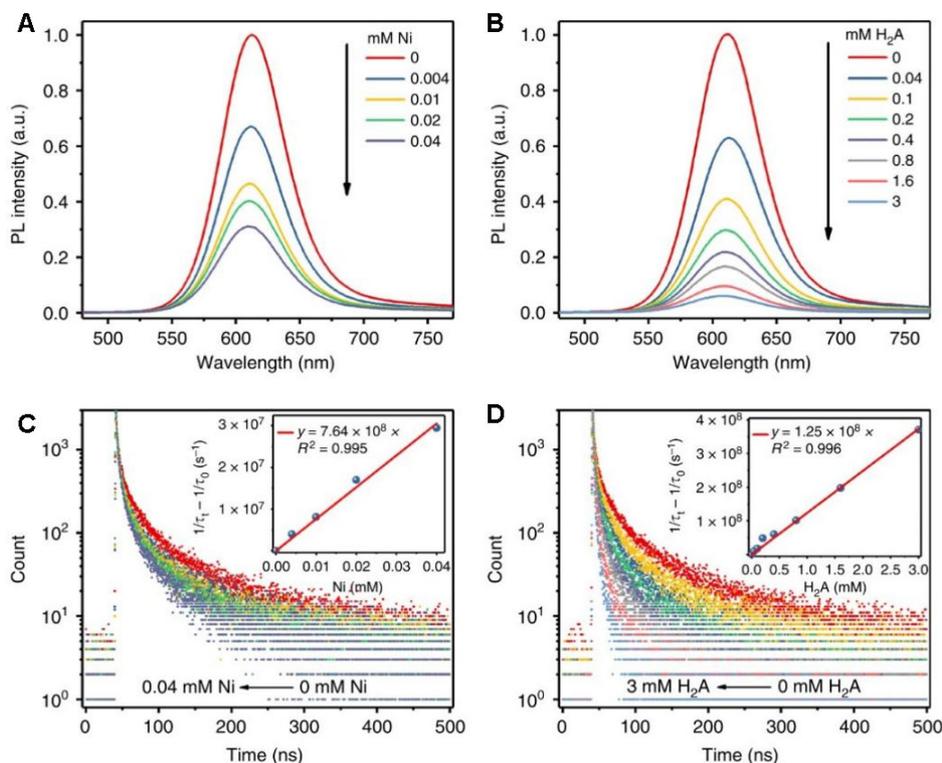


Figure 8. Steady state and time-resolved photoluminescence quenching experiment of InP/ZnS-S QDs (525 nm, 15 min). Static photoluminescence quenching for InP/ZnS-S QDs in water after addition of different amounts of Ni^{2+} (A) and H_2A (B). PL decay curves of InP/ZnS-S QDs after addition of different amounts of Ni^{2+} (C) and H_2A (D), respectively^[89].

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

Peter *et al.* characterized the competition between photogenerated carrier transfer and the recombination of an $\alpha\text{-Fe}_2\text{O}_3$ electrode using photoelectrochemical impedance spectroscopy (PEIS)^[96,97]. The variation of EIS with electrodes for different layered $\alpha\text{-Fe}_2\text{O}_3$ films was also recorded. The PEIS response of the $\alpha\text{-Fe}_2\text{O}_3$ 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].

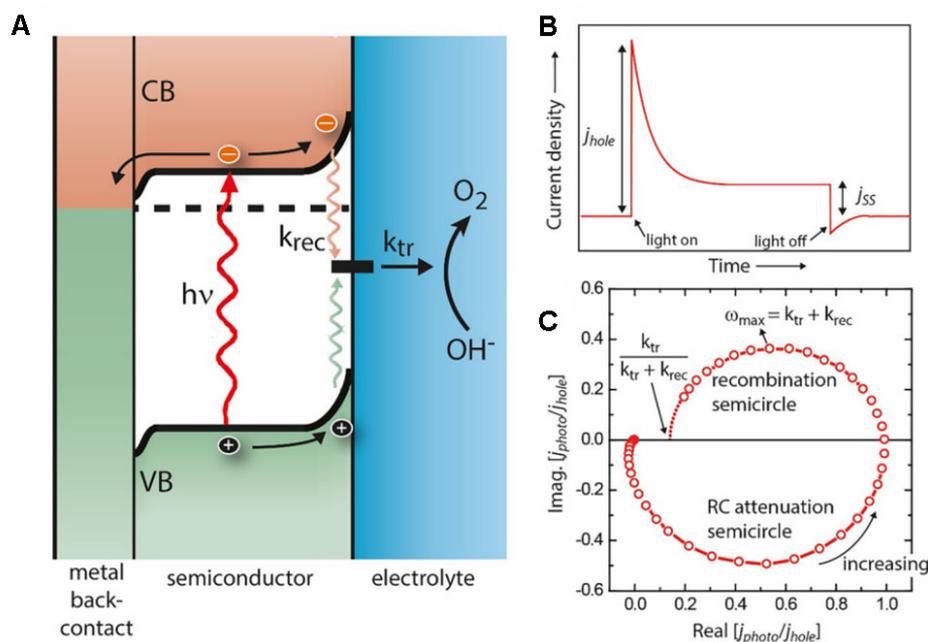


Figure 9. (A) Schematic of competition between hole transfer (k_{tr}) and recombination (k_{rec}). (B) A typical photocurrent of a photoanode in an electrolyte. (C) A typical example of a complex photocurrent or IMPS spectrum^[98].

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 $< 25 \mu\text{m}$) 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 $\text{BiVO}_4/\text{V}_\text{O}-\text{FeNiOOH}$ 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: $\text{BiVO}_4/\text{V}_\text{O}-\text{FeNiOOH} > \text{BiVO}_4/\text{FeNiOOH} > \text{BiVO}_4$ [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

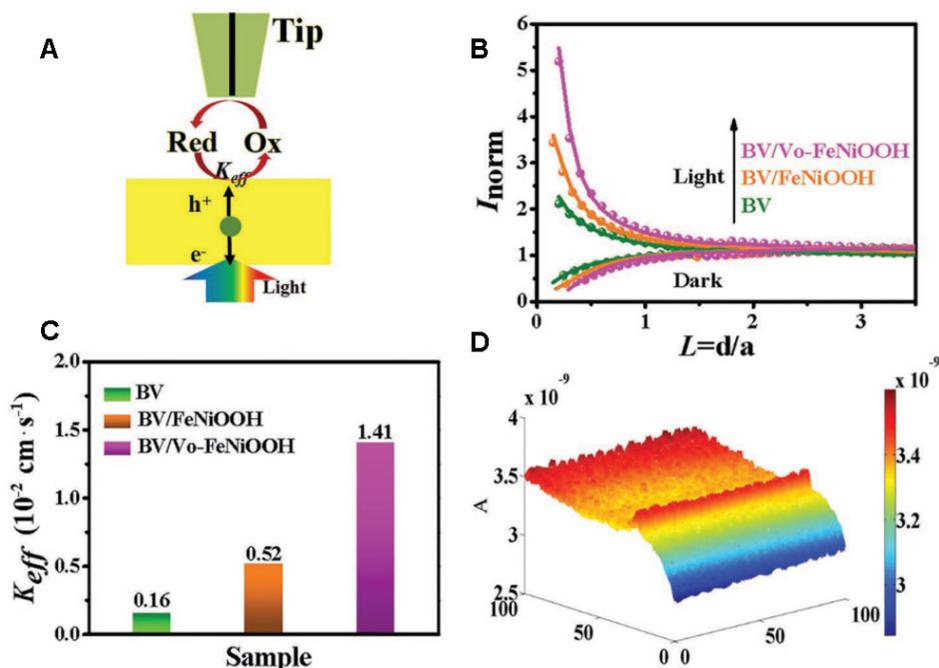


Figure 10. (A) Principle of SECM setup. (B) Probe approach curves and (C) rate constants (K_{eff}) of BiVO₄-based photoanodes. (D) SECM image ($100 \times 100 \mu\text{m}^2$) of BiVO₄/Vo-FeNiOOH photoanode surface under light^[38].

TiO₂. As the UME approaches the substrate, the oxidation state (CDs⁺) generated is regenerated by reacting with I⁻ in the electrolyte. Furthermore, the regeneration rate constant of CDs was achieved by fitting and analyzing the approaching curves obtained by testing different concentrations of active species and light intensities^[101]. 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 BiVO₄/NiFe-LDH composite photocatalyst^[102]. 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 BiVO₄. The results indicate that the NiFe-LDH cocatalyst can significantly inhibit electron back transfer and ultimately reduce surface recombination^[102].

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 (Yixian Liu), Liu Y (Yunliang Liu), Li Y, Cheng Y

Writing - review & editing, supervision, funding acquisition: Li H

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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