

# Hydrothermal and solvothermal synthesis of heterojunction nanostructures for photoelectrocatalysis

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**Abstract:** As resource depletion and environmental issues intensify simultaneously, the demand for long-term sustainable energy conversion technologies is growing. Photoelectrochemical (PEC) systems, which convert solar energy into storable chemical energy, have emerged as a promising approach for producing hydrogen and high-value-added chemicals. To overcome the intrinsic limitations of single-component semiconductor photoelectrodes, heterojunction structures which combine semiconductors with different electronic structures have been introduced, enabling a functional separation between light absorption and redox reactions. However, controlling band alignment is insufficient to address the transport pathways and recombination issues of photoexcited charge carriers. Consequently, structural strategies that integrate nanostructure with heterojunctions have recently emerged as a significant alternative. Nanostructured heterojunctions can simultaneously enhance charge separation and transport by shortening charge migration distances and expanding the effective reaction interface. Hydrothermal and solvothermal synthesis methods offer the advantage of precisely controlling nanostructure morphology and interfaces under relatively mild reaction conditions. These methods provide a crucial foundation for exploring the structure-performance correlation in various photoelectrochemical reactions, including water splitting, CO<sub>2</sub> reduction, and organic oxidation reactions. In this review, we systematically summarize the design strategies and structural characteristics of heterojunction nanostructures synthesized primarily via hydrothermal and solvothermal methods, with a focus on charge separation and charge transport in photoelectrochemical reactions.

**Key words:** photoelectrocatalysis; heterojunction; nanostructure; hydrothermal synthesis; solvothermal synthesis

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## 1. Introduction

Fossil fuels emit massive amounts of carbon dioxide (CO<sub>2</sub>), reaching record-high levels by 2025, and thus possess fundamental risks that accelerate climate change and environmental pollution [1,2]. If this trend continues, resource depletion and environmental problems will be inevitable, making a transition to a sustainable energy system essential from a long-term perspective. To address these issues, strategies utilizing solar energy—an abundant and renewable resource—are receiving increasing attention [3–5]. In particular, converting solar energy into chemical energy enables both energy storage and utilization. In this context, photoelectrochemical (PEC) systems, functioning as solar-to-chemical energy conversion systems enabling the production of hydrogen and other high-value chemicals, are emerging as one of the most promising

strategies.

Photoelectrochemical reactions generally follow the sequence: light absorption, generation and separation of electron-hole pairs, charge transport, and surface reactions [6]. Under illumination, the photoelectrode absorbs photons with energies exceeding its bandgap, generating electron-hole pairs. The generated charge carriers are spatially separated before recombination, migrate through the bulk and along the interface, and ultimately participate in oxidation-reduction reactions at the electrode-electrolyte interface [7–9]. During this process, charge recombination occurring in the bulk and at the interface leads to significant carrier losses, thereby reducing the utilization of photoexcited charges and lowering the overall reaction efficiency. Therefore, achieving high photoelectrochemical performance requires electrode designs that enable balanced optimization of light absorption, charge separation and transport, and surface reactions.

Single-component semiconductors exhibit limited photoelectrochemical performance because both light absorption and charge transport occur within the same material, leading to high recombination rates of photoexcited carriers. Furthermore, their intrinsic bandgaps restrict light absorption to specific regions of the solar spectrum, further limiting their practical applicability [10,11]. Generally, semiconductors capable of

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absorbing a broad solar spectrum often suffer from limited charge mobility or redox capabilities. Conversely, semiconductors with strong redox capabilities typically have wide bandgaps, which restrict their solar energy utilization [12,13]. As an alternative, a heterojunction structure formed by coupling two different semiconductors with different bandgaps has been proposed [14]. It offers the advantage of effectively combining the distinct electronic structures and physical properties of each semiconductor [15]. Furthermore, such heterojunctions enable an expanded light absorption range by integrating complementary semiconductors. This approach also enables efficient charge separation and facilitates strong redox reactions. The band structure and band alignment at the heterojunction interface act as key factors determining the driving force for charge separation and transport [16]. Appropriate band alignment facilitates efficient charge transfer without introducing interfacial barriers, thereby enhancing photoelectrochemical efficiency.

In particular, nanostructured heterojunctions maximize charge separation effects at semiconductor interfaces, shorten charge transport distances, and expand active reaction surface [17–19]. To realize such nanostructured heterojunctions, solvothermal and hydrothermal methods are widely employed because they allow precise control over the morphology, size, and composition of nanostructures under low processing temperatures and simple reaction conditions [20]. Through these methods, various nanostructures such as core-shell, nanorods, nanosheets, nanowires, and nanofibers can be synthesized [21–23]. These solution-based processes also facili-

tate intimate interfacial contact between different semiconductors [24]. Due to these advantages, solvothermal and hydrothermal synthesis methods are being utilized as key synthesis strategies for designing nanostructured heterojunctions in photoelectrochemical applications.

This review systematically summarizes the synthesis strategies and structural characteristics of heterojunction nanostructures fabricated via hydrothermal and solvothermal methods, and comprehensively discusses various photoelectrochemical applications, including water electrolysis, CO<sub>2</sub> reduction, alcohol oxidation, and other related reactions. While previous reviews have primarily focused on reaction-specific performance, this review offers a distinct perspective on how hydrothermal and solvothermal synthesis methods control interfacial structure and charge transport behavior. Specifically, beyond simple performance comparisons, this review presents current challenges and suggests future research directions for the development of highly efficient photoelectrocatalysts. Figure 1 schematically illustrates the overall concept of this review, highlighting key design strategies that determine charge separation and charge transport efficiency in heterojunction nanostructures.

## 2. Fundamentals of heterojunctions in photoelectrocatalysis

### 2.1. Definition and advantages of heterojunction nanostructure

As mentioned earlier, a heterojunction between two different

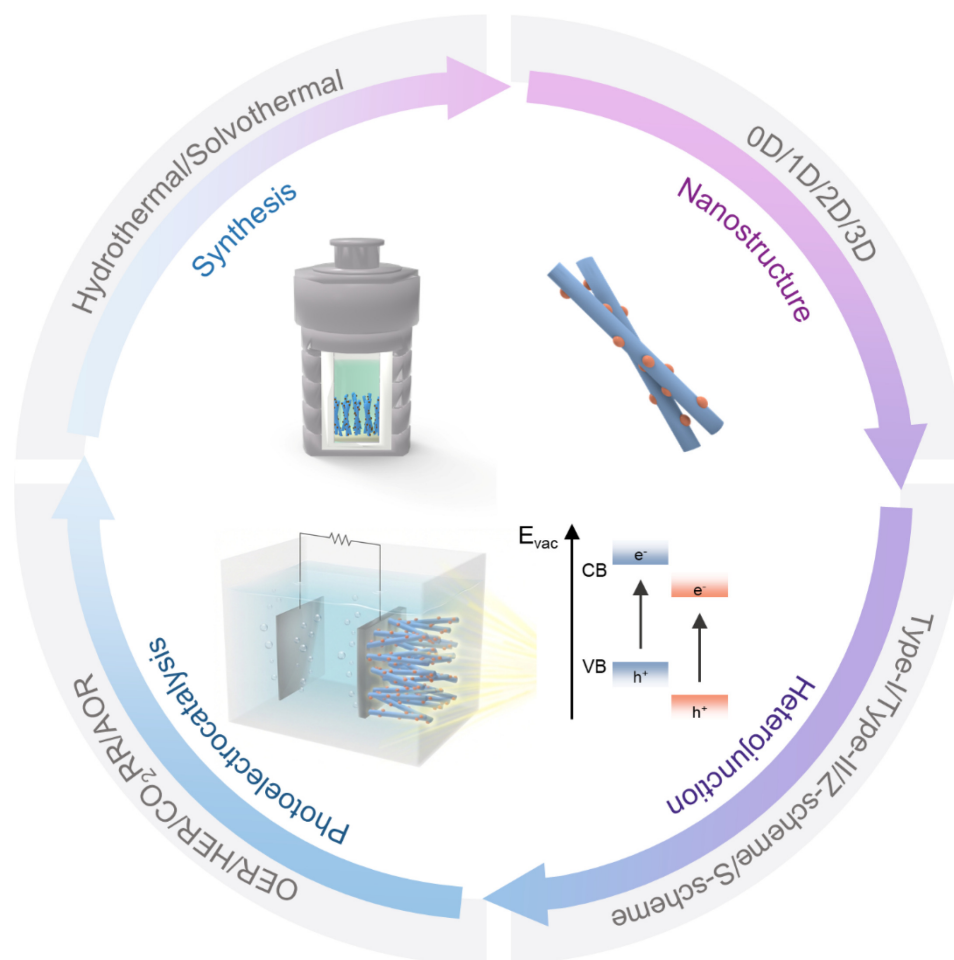


Fig. 1. Schematic overview of hydrothermal and solvothermal synthesis of heterojunction nanostructures for photoelectrocatalytic applications.

semiconductors can regulate the behavior of photoexcited carriers by altering interfacial band alignment and charge distribution [25–27]. The Fermi level mismatch between the two semiconductors drives charge redistribution across the interface, creating a built-in potential and establishing electrochemical equilibrium. These heterojunctions are generally classified by their synthesis methods and resulting band alignments. Figure 2 depicts the band structure and charge-transport characteristics of representative heterojunctions.

In a type-I heterojunction, the conduction band (CB) and valence band (VB) of one semiconductor lie within the bandgap of the other semiconductor (Figure 2a). In this configuration, photogenerated electrons and holes in the wide-bandgap semiconductor tend to migrate and accumulate in the narrow-bandgap semiconductor [28]. This charge accumulation significantly increases charge recombination rates and weakens the overall redox capability [29]. Consequently, type-I heterojunctions are unfavorable for photoelectrocatalytic applications, which require both efficient charge separation and preservation of carrier reactivity.

In a type-II heterojunction, the energy bands are staggered, where both the CB and VB of one semiconductor are higher than those of the other semiconductor (Figure 2b). Under photoexcitation, electrons transfer to the lower-energy CB and holes move to the higher-energy VB, promoting charge separation across the interface [30,31]. Yaw *et al.* reported an orthorhombic  $V_2O_5$ /monoclinic clinobisvanite  $BiVO_4$  photoanode for water oxidation [32]. In this system, the band alignment drives photogenerated electrons in  $BiVO_4$  to transfer to the lower CB of  $V_2O_5$ , while holes generated in  $V_2O_5$  move to the higher VB of  $BiVO_4$ . Such charge transport spa-

tially separates electrons and holes within different semiconductor layers, effectively suppressing bulk and interfacial recombination. This separation reduces interfacial charge transfer resistance and enhances the charge transport rate. However, a key limitation of type-II heterojunctions is that holes and electrons accumulate in semiconductors with relatively weak oxidation and reduction abilities, respectively, leading to an overall reduction in redox potential. In addition, carrier accumulation at the interface can induce electrostatic effects, which may further hinder charge transport efficiency [33,34].

The Z-scheme heterojunction in Figure 2c effectively resolves these issues. Although its band structure is similar to a type-II alignment, the direction of carrier migration is fundamentally different. When the two semiconductors are photoexcited, the lower-energy electrons and holes selectively recombine at the interface, leaving only the highly reducing electrons and highly oxidizing holes to participate in the catalytic reaction [35,36]. This avoids the redox capability reduction problem commonly encountered in type-II heterojunctions. Zhang *et al.* introduced a 2D  $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$  Z-scheme photoanode for photoelectrocatalytic organic pollutant degradation [37]. In situ growth of  $\alpha\text{-Fe}_2\text{O}_3$  on  $\text{g-C}_3\text{N}_4$  enhances interfacial contact and charge redistribution. The difference in Fermi levels between the two components induced an internal electric field and band bending, which selectively promoted recombination between electrons in the CB of  $\alpha\text{-Fe}_2\text{O}_3$  and holes in the VB of  $\text{g-C}_3\text{N}_4$  at the interface. As a result, electrons from  $\text{g-C}_3\text{N}_4$  and holes from  $\alpha\text{-Fe}_2\text{O}_3$  were each conserved, maintaining high redox capability. It is proposed that electrons convert  $\text{O}_2$  to  $\cdot\text{O}_2^-$ , and the generated  $\cdot\text{O}_2^-/\cdot\text{OH}$  radicals drive the decomposition of clofibric acid.

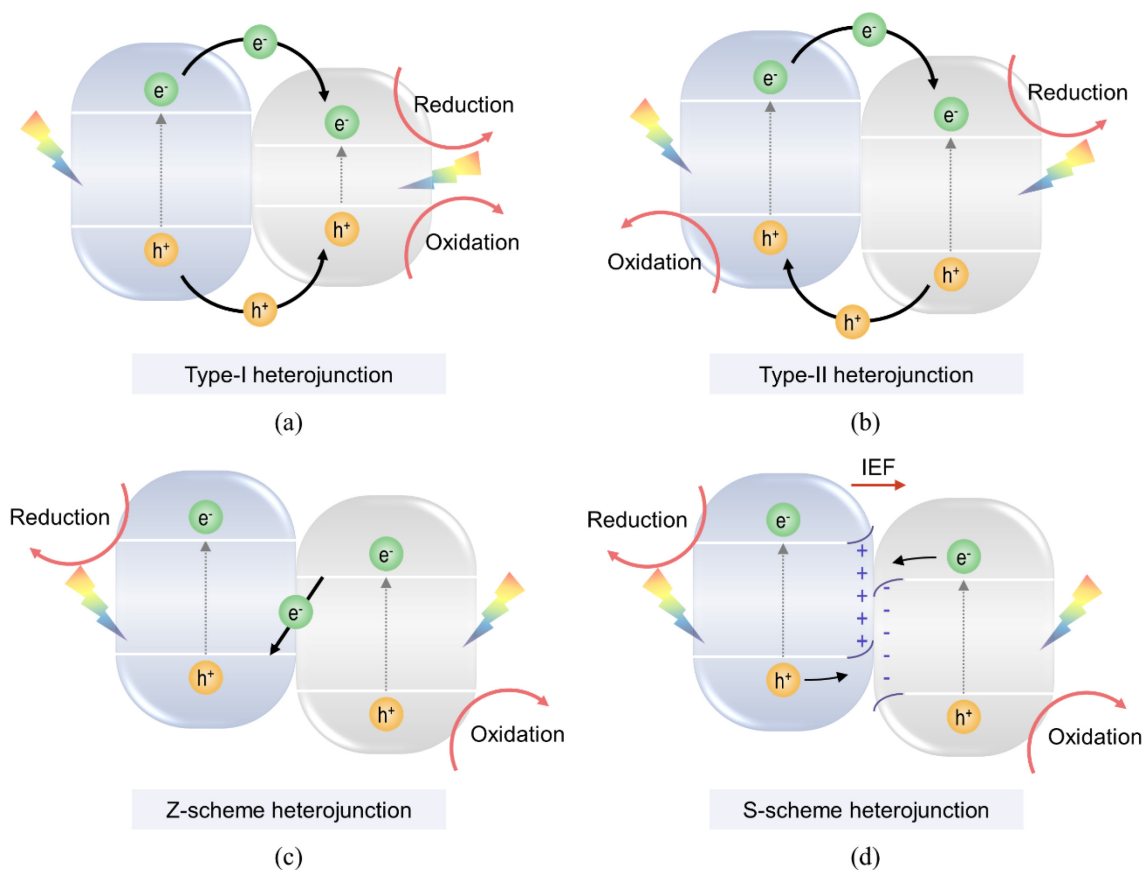


Fig. 2. Schematic illustration of various charge transfer mechanisms in heterojunctions: (a) Type-I; (b) Type-II; (c) Z-scheme; and (d) S-scheme.

The S-scheme illustrated in Figure 2d can be regarded as a redefinition of the Z-scheme from the perspective of interfacial physics. The Fermi level difference between the two semiconductors generates an internal electric field (IEF) and causes band bending [38,39]. When light is irradiated, electron-hole pairs are generated in each semiconductor. The internal IEF then serves as a driving force for selective carrier transfer and separation [40]. This field-driven process induces recombination of electrons and holes at the interface that do not contribute to the reaction. In other words, less favorable carrier combinations are intentionally eliminated. Subsequently, only carriers with high redox potential are utilized in the reaction through this charge transfer mechanism. Yang *et al.* reported a tandem S-scheme  $\text{TiO}_2/\text{SrTiO}_3/\text{BiVO}_4$  photoanode, applying the S-scheme concept to practical PEC photoanode design [41]. In this architecture, the IEF formed at each interface sequentially induces charge transfer and promotes the selective elimination of less favorable carrier combinations. This field-driven mechanism is manifested as a significant reduction in interfacial charge transfer resistance and an increase in photocurrent and photon-to-current efficiency (ABPE). Moreover, radical scavenging results support that the observed active-species generation and reaction pathways are better explained by an S-scheme-based charge screening and selective recombination mechanism than by a simple type-II charge transfer process.

## 2.2. Advantages of coupling nanostructures with heterojunctions

Band alignment control is a key strategy for managing charge transport in heterojunctions, but it alone has limitations in fundamentally resolving the transport and recombination of photoexcited carriers. Consequently, designing heterojunctions with desirable nanostructured architectures has gained attention as an effective strategy to simultaneously improve charge transport and separation [42,43]. Compared to planar films, nanostructures possess a larger surface area, which increases the effective contact region where electrochemical reactions occur at the electrode-electrolyte interface and exposes more active sites within the same geometric area [44,45]. This facilitates charge transfer reactions and potentially leads to increased current density. Indeed, nanostructured photoelectrodes provide favorable transport pathways for charge carriers, reducing recombination losses and promoting charge transport to the electrode-electrolyte interface. Furthermore, controlling the size, arrangement, and morphology of nanostructures can induce desirable energy level alignment, lowering

the transport barriers for charge carriers involved in the photoelectrocatalytic reaction [9,46].

Rationally designed nanostructures can increase the accessible surface area to the electrolyte and enable highly dispersed loading of the upper co-catalyst or light-absorbing layer [47]. In planar thin-film structures, photoexcited charge carriers must travel relatively long distances to reach the electrode-electrolyte interface, during which bulk recombination competes with charge transport. In contrast, nanostructured heterojunctions significantly reduce the distance between the charge generation site and the reaction interfaces, allowing more efficient charge extraction before recombination occurs [48]. Depending on the structural form and dimensionality of the nanostructure, distinct functional advantages can be achieved. Representative SEM images of zero- to three-dimensional nanostructures are summarized in Figure 3 [49–52]. Nanoparticle-based structures, classified as 0D nanostructures, typically exhibit high porosity, providing a large surface area and numerous active sites [53]. This promotes efficient light harvesting and leads to relatively high photoelectrochemical conversion efficiencies. As the dimensionality of nanostructures increases, they can enhance light absorption via scattering and optical path length extension effects, while offering more efficient charge transport pathways that help suppress recombination losses [54]. Vertically aligned 1D nanostructures offer continuous, directional carrier transport pathways, effectively suppressing electron trapping and recombination at particle-particle boundaries [55].  $\text{TiO}_2$  nanotube-based electrodes have been reported to maintain charge transport times comparable to nanoparticle-based electrodes while exhibiting significantly longer charge recombination times. 2D structures exhibit excellent in-plane electrical conductivity, enabling rapid charge transport and enhanced reaction kinetics [56]. Owing to their atomic-scale thickness, the distance that photo-generated charge carriers must travel to reach the surface is significantly reduced, thereby suppressing bulk recombination. Furthermore, their thin and planar morphology allows intimate contact with other materials, making them highly advantageous for heterojunction formation.  $\text{MoS}_2$ , a representative 2D material, exhibits layer-dependent bandgap characteristics, which enhance visible-light absorption and increase the generation efficiency of photoexcited charge carriers [57]. Moreover, modulation of the electronic structure originating from its layered nature clarifies charge transport pathways at the interface, enabling more efficient charge transfer. Consequently, improved interfacial charge separation leads to simultaneously enhanced activity and stability in photoelectrochemical

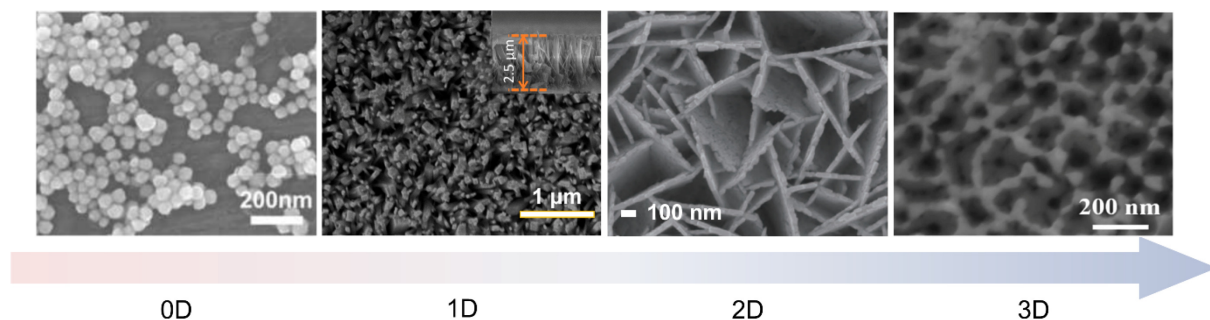


Fig. 3. SEM images of 0D Au nanoparticles, 1D  $\text{TiO}_2$  nanorod arrays, 2D  $\text{Bi}_2\text{MoO}_6$  nanosheet arrays, and 3D porous GaN; Reproduced with permission [49–52].

reactions. 3D structure features an interconnected network with abundant open pores, enabling rapid diffusion of electrolytes, gases, and reactants while effectively suppressing nanoparticle aggregation to maintain structural stability [58]. In addition, it facilitates fast adsorption of reactants and their immediate decomposition, thereby accelerating reaction kinetics. The ZnO nanoflower-based 3D architecture further enhances light absorption efficiency through multiple internal light-scattering effects [59]. Moreover, its continuous framework promotes efficient charge transport and suppresses carrier recombination. Collectively, these structural advantages contribute to achieving both high activity and excellent stability in photoelectrochemical reactions.

When materials with different dimensionalities are combined through a heterojunction, the structural and electronic advantages intrinsic to each dimension can complement one another [32,60,61]. Such multidimensional integration effectively promotes interfacial charge separation and suppresses carrier recombination. As a result, multidimensional heterojunction architectures can simultaneously achieve superior photoelectrochemical activity and long-term stability compared to their single-dimensional counterparts. In this context, Resasco *et al.* fabricated a type-II heterojunction photoanode using a TiO<sub>2</sub> nanowire array as the host for electron transport and highly dispersed BiVO<sub>4</sub> nanoparticles as the guest for light absorption [62]. The nanowire array enables light scattering for enhanced light absorption and provides a one-dimensional electron transport pathway to the back contact. Simultaneously, the type-II band alignment between TiO<sub>2</sub> and BiVO<sub>4</sub> facilitates efficient electron transfer from BiVO<sub>4</sub> to TiO<sub>2</sub>, thereby enabling the effective separation and optimization of light absorption and charge collection. Nanostructured heterojunctions offer the distinct advantage of effectively shortening carrier diffusion lengths [63]. Similarly, to overcome the short charge diffusion length of BiVO<sub>4</sub> (~70 nm), Lee *et al.* constructed BiVO<sub>4</sub> as nanodots on the surface of In<sub>2</sub>O<sub>3</sub> nanorods (NRs) to realize the type-II heterojunction nanostructure. By structurally limiting the charge transport distance, they reduced bulk recombination [64]. The charge separation efficiency ( $\eta_{\text{sep}}$ ) of the nanodot BiVO<sub>4</sub>/In<sub>2</sub>O<sub>3</sub> NRs reached 99%, significantly higher than the 77% achieved by the core-shell BiVO<sub>4</sub>/In<sub>2</sub>O<sub>3</sub> NR photoanode. This indicates that the nanodot-

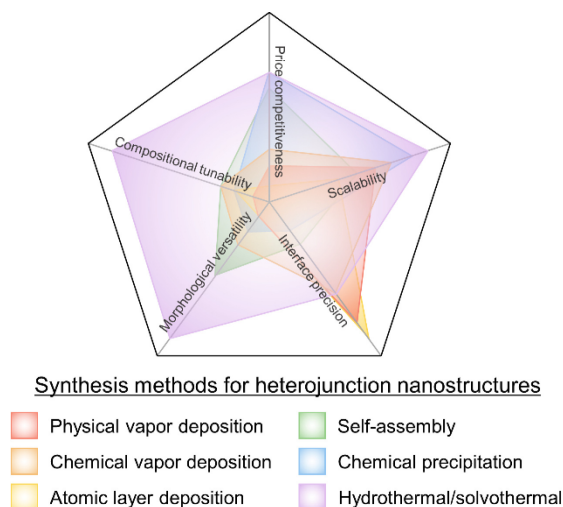
nanorod configuration provides a higher probability for photo-generated charges to participate in transport and reaction without recombination.

### 3. Synthesis of heterojunction nanostructures

#### 3.1. Hydrothermal method

Hydrothermal method is a widely used solution-phase approach for synthesizing heterojunction nanostructures, enabling low-temperature processing, scalable production, and the formation of highly crystalline materials at relatively low cost (Figure 4) [8,65,66]. In a typical hydrothermal process, metal precursors are dissolved in an aqueous solution, sealed in an autoclave, and reacted under elevated temperature and pressure, which promotes nucleation and crystal growth without additional post treatments [8,66]. Such reaction environments facilitate uniform nucleation and controlled crystal growth, providing favorable conditions for forming intimate semiconductor interfaces that are essential for efficient charge separation in heterojunction photoelectrocatalysts [67]. Furthermore, heterojunction architectures can be constructed through sequential or in situ growth by tuning precursor composition and reaction parameters, allowing controlled integration of multiple functional components. Nevertheless, hydrothermal synthesis is constrained by limited precursor and solvent flexibility inherent to aqueous chemistry and by comparatively restricted control over growth kinetics relative to vapor-phase deposition techniques [8,66]. Careful optimization of precursor concentration, temperature, pressure, and reaction duration is thus required to balance crystallinity, morphology, and interfacial quality in hydrothermally synthesized heterojunction nanostructures. Such parameter-dependent control over nucleation and crystal growth also provides a practical strategy for engineering heterojunction interfaces that enable efficient interfacial charge separation in photoelectrocatalytic systems.

Park *et al.* prepared TiO<sub>2</sub> nanorod arrays decorated with In<sub>2</sub>S<sub>3</sub> nanoparticles via a two-step hydrothermal method (Figure 5a) [68]. This hierarchical nanostructure, in which In<sub>2</sub>S<sub>3</sub> nanoparticles are uniformly anchored on 1D TiO<sub>2</sub> nanorod backbones, provides an extended heterointerfacial area and continuous charge transport pathways, promoting efficient light har-



| Hydrothermal |                                                         |
|--------------|---------------------------------------------------------|
| Advantages   | Low-temperature processing                              |
|              | Uniform nucleation and particle growth                  |
|              | Scalable batch synthesis                                |
| Drawbacks    | Limited precursor flexibility                           |
|              | Restricted control over crystal growth kinetics         |
| Solvothermal |                                                         |
| Advantages   | Broad solvent selection                                 |
|              | Controllability over crystal growth and phase formation |
|              | Faster reaction kinetics                                |
| Drawbacks    | Higher temperature and pressure                         |
|              | Increased process complexity                            |

Fig. 4. Comparison of representative synthesis routes for heterojunction nanostructures, highlighting characteristic advantages and limitations of hydrothermal and solvothermal methods.

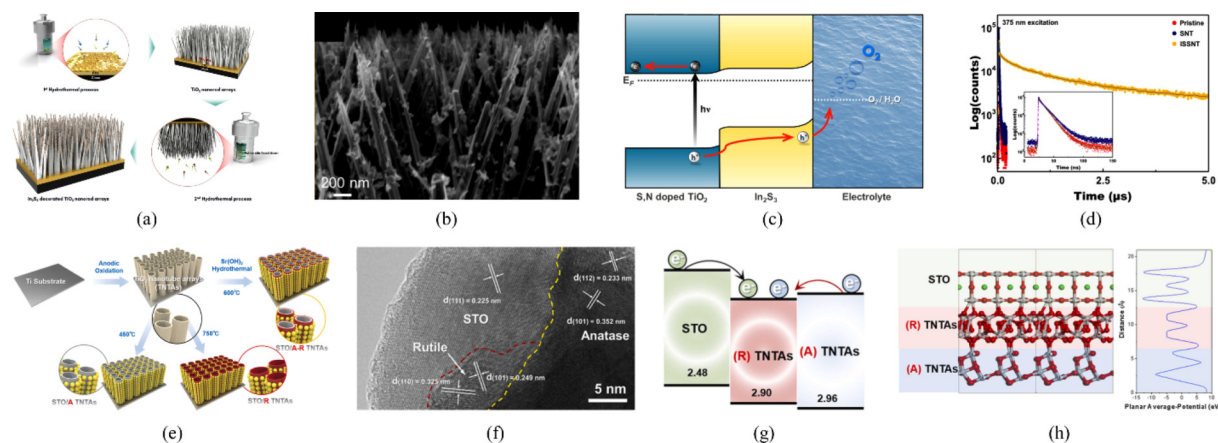


Fig. 5. (a) Schematic illustration showing the hydrothermal synthesis of the  $\text{TiO}_2$  nanorod arrays followed by  $\text{In}_2\text{S}_3$  nanoparticle decoration; (b) SEM image of  $\text{In}_2\text{S}_3/\text{S}$ , N-doped  $\text{TiO}_2$  nanorod arrays; (c) Proposed type-II heterojunction band alignment formed across S, N-doped  $\text{TiO}_2$ ,  $\text{In}_2\text{S}_3$  nanoparticle, and electrolyte after interfacial junction formation; (d) Time-resolved photoluminescence spectra of pristine  $\text{TiO}_2$ , S, N-doped  $\text{TiO}_2$ , and  $\text{In}_2\text{S}_3/\text{S}$ , N-doped  $\text{TiO}_2$  nanorod arrays; Reproduced with permission. [69]. (e) Schematic of the synthetic route of the STO/A-R TNTAs photoanode; (f) HRTEM image of STO/A-R TNTAs; (g) Illustration of the charge transfer mechanism in STO/A-R TNTAs binary junctions; (h) Calculated electrostatic potential distribution across the STO/A-R TNTAs interface; Reproduced with permission. [70].

vesting and directional carrier separation (Figure 5b). The type-II heterojunction is formed between S and N-doped  $\text{TiO}_2$  and  $\text{In}_2\text{S}_3$  without interfacial contact barriers due to the higher Fermi level of the S, N doped  $\text{TiO}_2$  (Figure 5c). This band alignment facilitates efficient photogenerated charge separation while simultaneously suppressing electron-hole recombination. Detailed analysis of the band structure further elucidates the transport behavior of charge carriers. In particular, the substantial valence band offset between  $\text{TiO}_2$  and  $\text{In}_2\text{S}_3$  provides a strong driving force for hole transfer across the interface, leading to accelerated interfacial hole migration and a prolonged carrier lifetime (Figure 5d). In addition, the negatively shifted valence band maximum of  $\text{In}_2\text{S}_3$  provides sufficient driving force to overcome the overpotential of the oxygen evolution reaction.

Cao *et al.* prepared a binary junction photoanode by coupling  $\text{SrTiO}_3$  with anatase-rutile  $\text{TiO}_2$  nanotube arrays (STO/A-R TNTAs) through a hydrothermal process followed by thermal crystallization (Figure 5e) [69]. This heterophase configuration exploits the intrinsic band-edge disparity between anatase and rutile  $\text{TiO}_2$  to construct a dam-like electron storage region in rutile domains, enabling sustained electron accumulation and potential elevation that are inaccessible in single-phase TNTAs (Figure 5f). The heterojunction formed between STO and anatase or rutile  $\text{TiO}_2$  enables directional transport of photogenerated electrons from higher to lower energy states (Figure 5g). In the STO/A TNTAs, photoelectrons generated in STO are transferred to the conduction band of anatase  $\text{TiO}_2$  and subsequently collected at the copper foam via an external circuit. Meanwhile, electrons from both STO and anatase  $\text{TiO}_2$  are preferentially accumulated in rutile  $\text{TiO}_2$ , where this effect elevates electron potential, enhancing the potential difference between photoanode and cathode to drive  $\text{CO}_2$  reduction to  $\text{HCOOH}$ . Theoretical calculations reveal that anatase and rutile  $\text{TiO}_2$  possess higher electrostatic potentials than STO, giving rise to an outward built-in electric field at the STO/anatase and anatase/rutile interfaces (Figure 5h). This interfacial electric field directs charge migration and supports the electron storage mechanism, concentrating photogenerated electrons in

rutile  $\text{TiO}_2$  within the STO/A-R TNTAs architecture.

Ryu *et al.* constructed a ternary heterostructure by integrating GaN with ZnO and multi-walled carbon nanotubes (MWCNTs) through a facile hydrothermal approach [70]. The incorporation of the MWCNTs improves electrical conductivity and charge transport within the GaN and ZnO heterostructure, while the interface between GaN and ZnO forms a type-II band alignment that promotes efficient separation of photogenerated charge carriers. In addition, the MWCNTs function as a photosensitizer rather than merely acting as adsorbents or dispersing agents, enabling the wide band gap GaN and ZnO system to exhibit visible light photoactivity through strong interfacial interaction with the semiconductor components. As a result, the ternary heterostructure achieves a photocurrent density of  $3.02 \text{ mA cm}^{-2}$  at 0 V versus a Pt electrode under 1-sun light illumination, corresponding to about 2.58-fold higher than that of pristine GaN photoanodes. Lee *et al.* prepared  $\text{BiVO}_4$  and  $\text{WO}_3$  heterostructures by growing nanoleaves (NLs) of a Bi-containing metal-organic framework (CAU-17) on  $\text{WO}_3$  thin films (TF) followed by reaction with vanadium acetylacetonate [71]. This process enables the uniform formation of a type-II heterojunction between  $\text{BiVO}_4$  and  $\text{WO}_3$  over a large area, improving light absorption and charge separation. Furthermore, the growth of  $\text{BiVO}_4$  NLs on the  $\text{WO}_3$  nanorods (NRs) further enhances the water splitting performance, yielding photocurrent densities of 1.45 and  $2.83 \text{ mA cm}^{-2}$  at 1.23 V versus RHE for  $\text{BiVO}_4\text{-NLs}/\text{WO}_3\text{-TF}$  and  $\text{BiVO}_4\text{-NLs}/\text{WO}_3\text{-NRs}$ , respectively, both of which are significantly higher than those of bare  $\text{WO}_3$  electrodes.

### 3.2. Solvothermal method

Solvothermal method is another important solution phase synthesis strategy for constructing heterojunction nanostructures, in which non-aqueous solvents provide a chemically tunable reaction environment that governs nucleation and crystal growth kinetics (Figure 4) [72,73]. In this approach, metal precursors are dissolved in organic media and reacted in sealed reaction vessels under thermally activated conditions, allowing solvent coordination ability, polarity, and dielectric properties to directly influence crystallization pathways. Such sol-

vent-mediated control enables fine regulation of growth kinetics, which is advantageous for tailoring crystal phase, morphology, and interfacial structures in heterojunction systems [72]. Moreover, high solubility of precursors in organic solvents facilitates progressive component integration during crystal evolution, promoting the formation of hierarchical and compositionally complex nanostructures. However, solvothermal synthesis generally entails increased process complexity relative to aqueous routes, arising from the diversity of solvent chemistries and the strong coupling between thermal input and chemical reactivity [73]. Consequently, the effectiveness of solvothermal synthesis depends on how solvent chemistry and thermal conditions collectively regulate crystallization kinetics and interfacial evolution. This kinetic and chemical tunability provides a versatile platform for directing interfacial assembly and structural integration in complex heterojunction nanostructures.

Zhang *et al.* fabricated a 2D S-scheme heterojunction photocatalyst composed of  $\text{ZnIn}_2\text{S}_4$  nanosheets anchored on  $\text{CeO}_2$  nanosheets through in situ solvothermal method (Figure 6a) [74]. Constructing a 2D/2D heterointerface between  $\text{CeO}_2$  and  $\text{ZnIn}_2\text{S}_4$  maximizes interfacial contact and shortens charge migration pathways, creating a favorable platform for establishing an efficient charge transfer process (Figure 6b and c). As illustrated in Figure 6d,  $\text{CeO}_2$  exhibits a lower Fermi level than  $\text{ZnIn}_2\text{S}_4$ . Upon intimate interfacial contact, electrons spontaneously transfer from  $\text{ZnIn}_2\text{S}_4$  to  $\text{CeO}_2$  to reach Fermi level equilibrium, resulting in electron depletion at the  $\text{ZnIn}_2\text{S}_4$  and electron accumulation at the  $\text{CeO}_2$ . This interfacial charge redistribution generates an internal electric field from  $\text{ZnIn}_2\text{S}_4$  to  $\text{CeO}_2$  and induces band bending at the heterojunction interface.

Under light irradiation, charge carriers are excited from valence bands to conduction bands in both  $\text{ZnIn}_2\text{S}_4$  and  $\text{CeO}_2$ . Driven by the internal electric field and bent band structure, photogenerated electrons in the conduction band of  $\text{CeO}_2$  migrate toward the valence band of  $\text{ZnIn}_2\text{S}_4$ , where they recombine with photogenerated holes. This S-scheme charge transfer pathway not only enhances the spatial separation of photogenerated carriers but also preserves the strong redox capability of the heterojunction system.

Zhu *et al.* synthesized 3D lupinus-like  $\text{TiO}_2$  nanorod@ $\text{Sn}_3\text{O}_4$  nanosheet hierarchical heterostructured arrays ( $\text{TiO}_2$ @ $\text{Sn}_3\text{O}_4$  HHAs) on transparent FTO substrates via a two-step solvothermal method (Figure 6e) [75]. This lupinus-like hierarchical configuration maximizes photon utilization through multidirectional light scattering while preserving efficient carrier extraction via the  $\text{TiO}_2$  nanorod, a structural advantage absent in conventional 1D photoelectrodes (Figure 6f and g). The  $\text{TiO}_2$  nanorod arrays were first grown on FTO, followed by the solvothermal deposition of  $\text{Sn}_3\text{O}_4$  nanosheets to construct the hierarchical heterojunction. Under light irradiation, both  $\text{TiO}_2$  and  $\text{Sn}_3\text{O}_4$  are photoexcited to generate photocarriers at valence band and conduction band. Since  $\text{Sn}_3\text{O}_4$  possesses a more negative conduction band edge than  $\text{TiO}_2$ , photogenerated electrons preferentially transfer from  $\text{Sn}_3\text{O}_4$  to  $\text{TiO}_2$  and are efficiently transported along the aligned  $\text{TiO}_2$  nanorods to the FTO substrate (Figure 6h). Meanwhile, photogenerated holes migrate from the valence band of  $\text{TiO}_2$  to that of  $\text{Sn}_3\text{O}_4$ , whose valence band potential is sufficiently positive to drive water oxidation at the semiconductor-electrolyte interface. Consequently, the synergistic effects of favorable band alignment and hierarchical morphology enable efficient spatial separa-

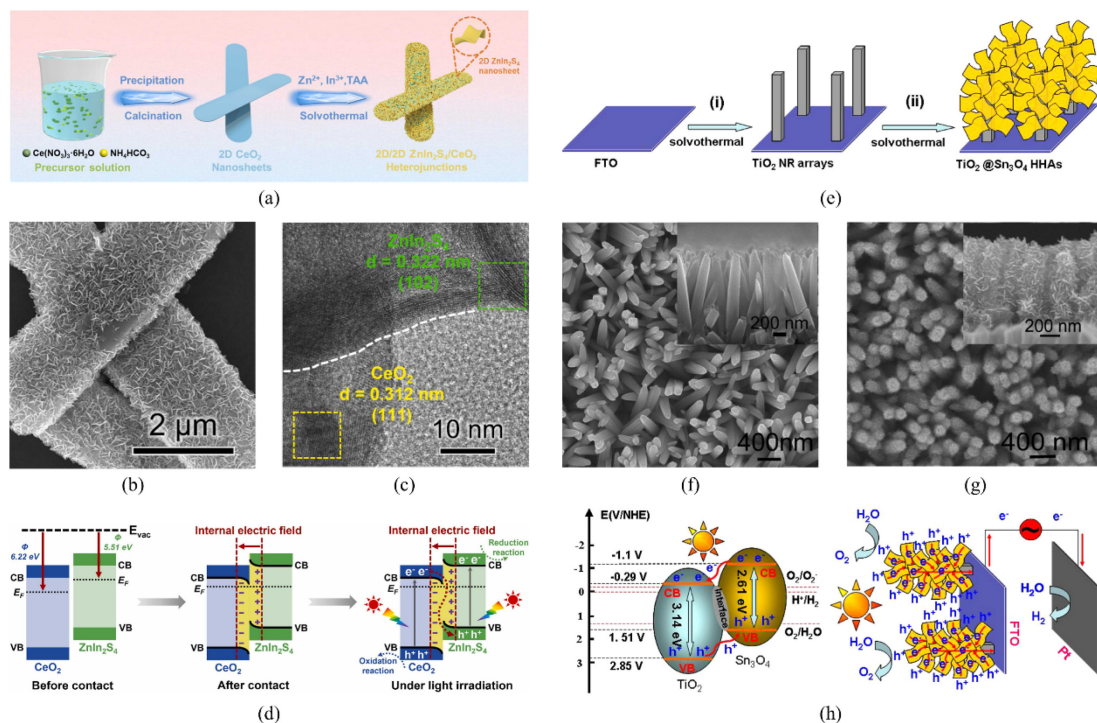


Fig. 6. (a) Schematic illustration of the fabrication procedure of 2D/2D  $\text{ZnIn}_2\text{S}_4/\text{CeO}_2$  heterojunction photocatalyst; (b) SEM image of  $\text{ZnIn}_2\text{S}_4/\text{CeO}_2$ ; (c) HRTEM image of  $\text{ZnIn}_2\text{S}_4/\text{CeO}_2$ ; (d) Formation pathway of the S-scheme  $\text{ZnIn}_2\text{S}_4/\text{CeO}_2$  heterojunction photocatalyst with the corresponding interfacial charge transfer mechanism; Reproduced with permission. [75]. (e) Schematic representation of the synthesis process of the 3D lupinus-like  $\text{TiO}_2$ @ $\text{Sn}_3\text{O}_4$  HHAs; (f) SEM images of  $\text{TiO}_2$  NRs on FTO; (g) SEM images of 3D lupinus-like  $\text{TiO}_2$ @ $\text{Sn}_3\text{O}_4$  HHAs; (h) Scheme of the electron-hole pair separation and charge transfer process in the 3D lupinus-like  $\text{TiO}_2$ @ $\text{Sn}_3\text{O}_4$  HHA electrode; Reproduced with permission. [76].

tion of photogenerated electrons and holes. In addition, the heterojunction architecture promotes interfacial charge migration, while the enlarged surface area enhances light harvesting through increased photon-matter interactions from multiple reflection and scattering.

Chen *et al.* constructed a type-I high-low heterojunction by integrating Bi@O<sub>V</sub>-BiOBr with Cu<sub>3</sub>P via a solvothermal process [76]. During the reaction, Cu<sub>3</sub>P nucleates and grows directly on the Bi@O<sub>V</sub>-BiOBr surface, resulting in an intimately contacted interface. In this configuration, Cu<sub>3</sub>P functions as an efficient hole acceptor, extracting photogenerated holes from Bi@O<sub>V</sub>-BiOBr. Meanwhile, metallic Bi species formed in situ provide conductive pathways that facilitate rapid electron transport toward the electrode. The coexistence of spatially separated electron and hole transport channels effectively suppresses charge recombination and enhances interfacial charge transfer. As a result, the Bi@O<sub>V</sub>-BiOBr/Cu<sub>3</sub>P composite exhibits a hydrogen evolution rate of 723.85  $\mu\text{mol cm}^{-2} \text{ h}^{-1}$ . Li *et al.* developed a hybrid photocatalytic system by anchoring the S-scheme ZIS-NiSe<sub>2</sub> heterostructure onto Ti<sub>3</sub>C<sub>2</sub> MXene using a two-step solvothermal approach [77]. The work function mismatch between ZIS and NiSe<sub>2</sub> establishes an internal electric field, which drives directional charge redistribution following the S-scheme pathway. Specifically, photoexcited electrons in the conduction band of NiSe<sub>2</sub> recombine with holes in the valence band of ZIS, preserving the strong redox carriers. Furthermore, Schottky junctions formed at the MXene-ZIS interface enable efficient electron extraction from ZIS to the conductive MXene substrate. These synergistic effects accelerate charge separation and transport kinetics. Consequently, the optimized system achieves a hydrogen evolution rate of 23.51  $\text{mmol g}^{-1} \text{ h}^{-1}$  and an apparent quantum yield of 10.9% under 450 nm illumination, representing a 23.51-fold enhancement compared to pristine ZnIn<sub>2</sub>S<sub>4</sub>.

#### 4. Photoelectrochemical applications of heterojunction nanostructures

Heterojunction nanostructures synthesized by hydrothermal and solvothermal methods provide a versatile platform for photoelectrochemical energy conversion [78,79]. The synthetic flexibility inherent to these solution phase methods allows precise control over composition, morphology, and interfacial electronic structure. This level of control enables intimate integration of dissimilar semiconductors, which is essential for engineering band alignment, generating internal electric fields, and optimizing charge transfer pathways. Importantly, the realization of heterojunction functionality relies on the design of appropriate nanostructures that maximize interfacial contact while simultaneously optimizing light absorption and carrier transport. As a result, hydrothermally and solvothermally derived heterojunction nanostructures have been extensively explored in a wide range of photoelectrochemical reactions, where efficient separation and directional transport of photogenerated carriers require reaction-specific nanostructure design for interfacial redox processes [80,81]. In the following sections, recent advances in the application of such heterojunction nanostructures to representative photoelectrochemical reactions, including water electrolysis, carbon dioxide reduction, alcohol oxidation, and other emerging reactions, are discussed.

##### 4.1. Water electrolysis

Photoelectrochemical water electrolysis represents the most extensively investigated application of heterojunction nanostructures, as overall efficiency is strongly limited by interfacial reaction kinetics and charge utilization at photoelectrode surfaces. In this context, heterojunctions have been explored to regulate hole extraction, transport, and interfacial energetics, directly influencing catalytic activity and operational stability. These interfacial charge transfer processes ultimately determine how efficiently photogenerated carriers participate in water splitting reactions. Fareza *et al.* developed a vertically aligned ZnO/ZnS/MoS<sub>2</sub> (ZSM) photoanode by introducing ZnS nanoparticles and few-layer MoS<sub>2</sub> nanosheets onto directly grown ZnO nanorods on an FTO substrate via a single-step hydrothermal process [82]. This vertically aligned and binder-free nanoarchitecture uniquely ensures direct electrical coupling between the multicomponent heterojunctions and the conductive substrate through the ZnO nanorod, a structural advantage that overcomes the charge transfer limitations inherent to randomly stacked or binder-assisted ternary heterostructures. The in situ formation of ZnO/ZnS and ZnS/MoS<sub>2</sub> interfaces also extends visible light absorption, increases surface active sites, and enhances interfacial charge separation, leading to improved photoelectrochemical activity and stability. The photoelectrochemical performance was evaluated by linear sweep voltammetry under simulated solar illumination in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte (Figure 7a). The ZSM heterostructure delivers a nearly sixfold enhancement to 0.72  $\text{mA cm}^{-2}$  compared with pristine ZnO, which exhibits a low photocurrent density of 0.12  $\text{mA cm}^{-2}$  at 1.23 V versus RHE due to limited light absorption and severe recombination. This improvement arises from the favorable band alignment within the heterojunction, which accelerates charge separation and transport. Band structure analysis indicates a type-II alignment at the ZnS/MoS<sub>2</sub> interface and a type-I alignment at the ZnO/ZnS interface, directing electrons toward the ZnO backbone for hydrogen evolution, while holes participate in oxygen evolution (Figure 7b). As a result, spatial separation of charge carriers is effectively achieved, suppressing recombination within the hierarchical heterostructure.

Chen *et al.* fabricated a BiVO<sub>4</sub>/BiO<sub>x</sub> asymmetric heterojunction photoanode on FTO substrates through sequential spin-coating of precursor solutions, calcination, and subsequent hydrothermal treatment [83]. This asymmetric heterojunction benefits from an in situ-generated BiO<sub>x</sub> phase derived from the BiVO<sub>4</sub> substrate itself, which ensures strong interfacial coupling and facet-selective junction formation, overcoming the inefficient charge transfer associated with post-deposited secondary semiconductors. Compared with pristine BiVO<sub>4</sub>, the BiVO<sub>4</sub>/BiO<sub>x</sub> exhibits more than a threefold enhancement in short-circuit photocurrent density with an approximately 75 mV cathodic shift in photocurrent onset potential. The photovoltage reaches 170 mV, which is notably higher than that of BiVO<sub>4</sub> (110 mV), consistent with the observed onset potential shift and confirming the role of BiO<sub>x</sub> in enhancing photovoltage (Figure 7c). Based on the relative positions of the Fermi levels and band edges, a type-II band alignment is formed between BiVO<sub>4</sub> and BiO<sub>x</sub> (Figure 7d). As BiO<sub>x</sub> is a p-type semiconductor with a more positive Fermi level, the resulting p-n heterojunction generates a built-in electric field across the interface,

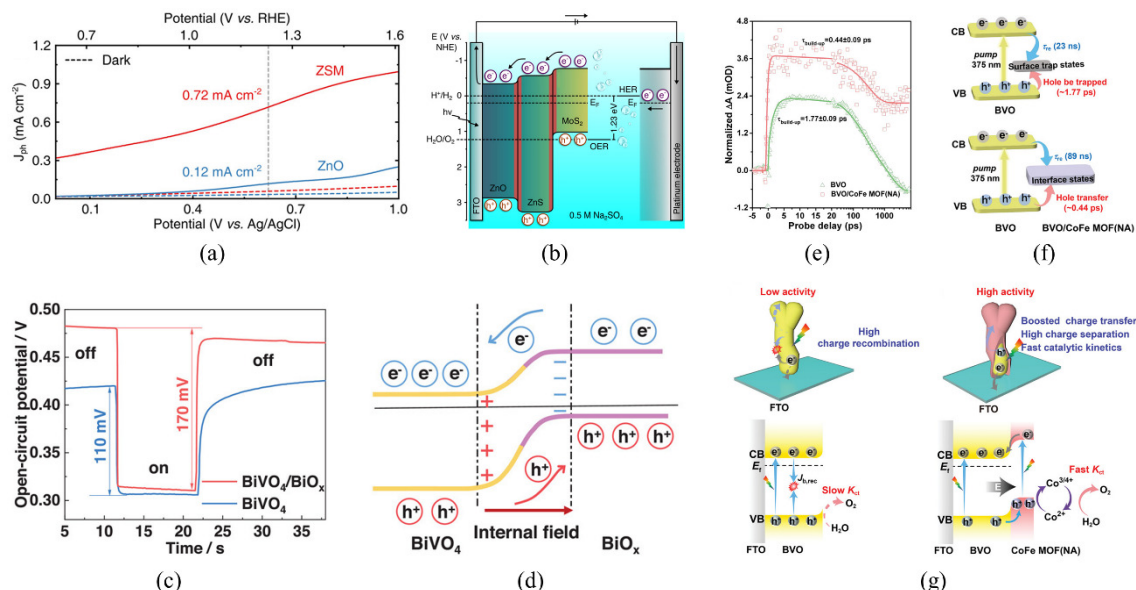


Fig. 7. (a) LSV curves measured under 75 mW cm<sup>-2</sup> illumination in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte; (b) Proposed charge transfer mechanism of the ZSM heterostructure, highlighting type-II band alignment at the ZnS/MoS<sub>2</sub> interface and type-I band alignment at the ZnO/ZnS interface; Reproduced with permission. [83]. (c) Open-circuit potentials (OCPs) of the BiVO<sub>4</sub> and BiVO<sub>4</sub>/BiO<sub>x</sub> photoanodes under dark and illuminated conditions; (d) Mechanism for the enhanced PEC performance of the BiVO<sub>4</sub>/BiO<sub>x</sub> photoanode; Reproduced with permission. [84]. (e) Normalized fs-TA spectra probed at 620 nm for the BVO and BVO/CoFe MOF(NA) under 375 nm excitation; (f) Electron transfer pathways involved in BVO and BVO/CoFe MOF(NA) heterostructure systems; (g) Conceptual illustration of the charge generation, separation, and transfer processes, along with corresponding energy level diagrams for PEC water oxidation on pristine BVO and BVO/CoFe MOF(NA) photoanodes; Reproduced with permission. [85].

which facilitates charge separation and increases the photovoltage. Consequently, the improved photoelectrochemical water splitting performance of the BiVO<sub>4</sub>/BiO<sub>x</sub> photoanode is primarily attributed to the formation of an interfacial p-n junction that enhances carrier separation and photovoltage under illumination.

Yang *et al.* reported a BiVO<sub>4</sub>/CoFe MOF(NA) heterostructured photoanode, in which an ultrathin CoFe metal organic framework (MOF) layer, constructed using nicotinic acid (NA) as the organic linker, was conformally deposited onto BiVO<sub>4</sub> via a solvothermal process [84]. This ultrathin coating suppresses the aggregation and insulating effects often observed in surfactant-mediated MOF growth, while maintaining intimate interfacial contact with the underlying BiVO<sub>4</sub>. Such structural features enable efficient hole extraction and reduce interfacial charge transfer resistance. Femtosecond-transient absorption (fs-TA) measurements provide further insight into the charge carrier dynamics. The BiVO<sub>4</sub>/CoFe MOF(NA) exhibits a positive photoinduced absorption signal with a build-up time of 0.44 ± 0.04 ps, followed by a rapid decay within 300 ps and stabilization at a positive offset, significantly faster than pristine BiVO<sub>4</sub> (Figure 7e). Notably, the absence of pronounced negative photoinduced bleach (PB) features indicates that hole trapping from the valence band of BiVO<sub>4</sub> to surface trap states is effectively suppressed upon MOF integration. These results suggest rapid hole extraction across the interface, consistent with the prolonged carrier lifetime observed in photoluminescence measurements (Figure 7f). Under AM 1.5G illumination, pristine BiVO<sub>4</sub> suffers from severe bulk recombination and sluggish surface kinetics, resulting in limited photoelectrochemical water oxidation activity. Integration with CoFe MOF(NA) forms a type-II heterojunction that establishes an interfacial

electric field (Figure 7g), driving holes toward the MOF layer while promoting electron transport within BiVO<sub>4</sub>. Together with the reduced interfacial resistance and the catalytic function of the MOF layer, these effects lead to enhanced charge utilization and improved photoelectrochemical performance.

## 4.2. CO<sub>2</sub> reduction reaction

Photoelectrochemical reduction of CO<sub>2</sub> introduces additional complexity from multielectron and proton-coupled transfer pathways, as well as competition with hydrogen evolution. The heterojunction nanostructures have been investigated as platforms to control electron accumulation, band alignment, and interfacial charge distribution, which are closely linked to reaction selectivity and efficiency. The spatial distribution and availability of photogenerated electrons at the interface become critical determinants of selectivity between CO<sub>2</sub> reduction and the competing hydrogen evolution. Wei *et al.* reported surface-state (SS) modulation of ZnTe photocathodes by in situ forming an ultrathin ZnO overlayer (ZnTe@ZnO) by a one-step hydrothermal method [85]. The SS-induced band tail, originating from energetic disorder ( $\sigma$ ) within the ZnTe band gap, broadens the distribution of localized states and promotes interfacial recombination rather than productive electron transfer, making energetic disorder a critical limiting factor for PEC CO<sub>2</sub> reduction. The donor-like SS on pristine ZnTe act as recombination centers, inducing band bending and carrier loss as photogenerated holes occupy states above the Fermi level (Figure 8a). Under illumination, quasi-Fermi level splitting occurs, but excess electrons are partially trapped and recombined through these SS. The ZnO layer redistributes the surface-state density and reduces the energetic disorder, narrowing the localized state band tail and increasing the fraction of electrons participating in the CO<sub>2</sub>

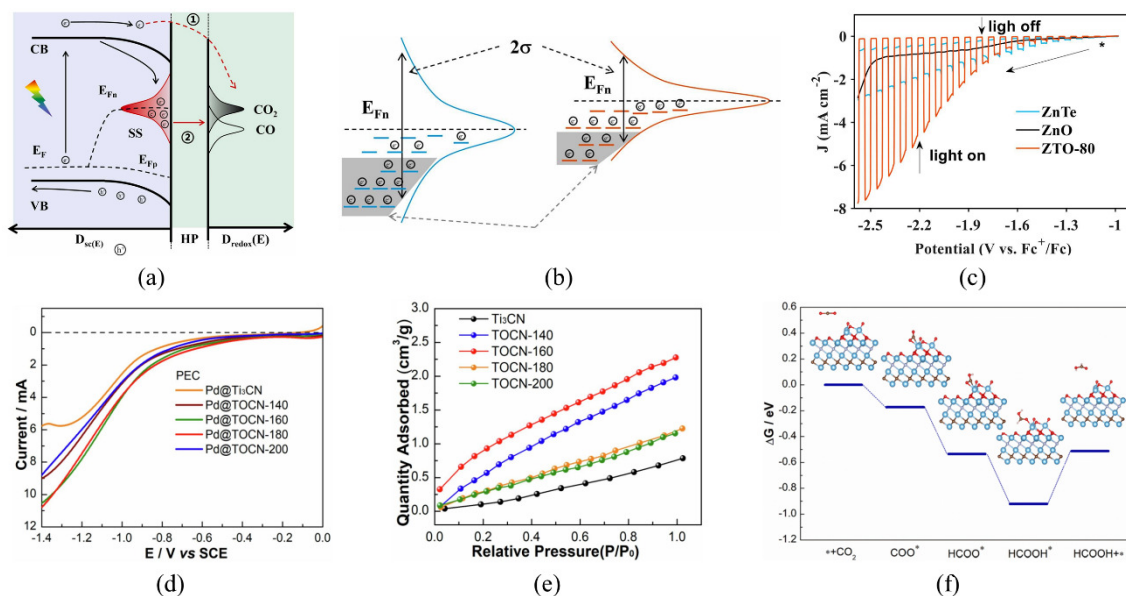


Fig. 8. (a) Energy band diagram of a photoelectrode for  $\text{CO}_2$  reduction to CO; (b) Modulation of surface states by reducing the disorder; (c) LSV curves of the ZTO-80, ZnTe, and ZnO photocathodes; Reproduced with permission. [86]. (d) LSV curves for Pd@Ti<sub>3</sub>CN and Pd@TOCN electrodes; (e)  $\text{CO}_2$  adsorption isotherms for Ti<sub>3</sub>CN and TOCN electrodes; (f) Gibbs free energy diagrams and structural models for the reduction pathway of  $\text{CO}_2$  into HCOOH; Reproduced with permission. [87].

reduction pathway rather than recombination (Figure 8b). This enhancement originates from suppressed energetic disorder rather than increased photocarrier generation. Consistent with this mechanism, the ZnTe@ZnO (ZTO-80) photocathode exhibits a photocurrent density of  $-7.7 \text{ mA cm}^{-2}$  at  $-2.58 \text{ V}$  versus  $\text{Fc}^+/\text{Fc}$  in  $\text{CO}_2$ -saturated acetonitrile under chopped AM 1.5G illumination, corresponding to a 2.75-fold enhancement compared with bare ZnTe, while ZnO alone shows negligible activity (Figure 8c). This performance improvement is attributed to reduced energetic disorder at the interface, which enhances the electron transfer coefficient and increases overall electron utilization.

Xu *et al.* prepared  $\text{TiO}_2/\text{Ti}_3\text{CN}$  (TOCN) heterojunction photoelectrodes via a facile hydrothermal oxidation process, followed by the deposition of Pd nanoparticles onto TOCN-FTO substrates using a pulsed electrodeposition method [86]. This 2D TOCN nanostructure combines the high conductivity and rich surface terminations of MXene with intimate interfacial contact, providing efficient charge transport pathways and abundant accessible active sites for  $\text{CO}_2$  adsorption and activation. Under photoelectrochemical conditions, the Pd@TOCN electrode exhibits higher photocurrent densities than Pd@Ti<sub>3</sub>CN, indicating that the heterojunction effectively enhances light absorption, charge separation, and transport. In addition, all TOCN heterojunctions display superior  $\text{CO}_2$  adsorption capacity compared with Ti<sub>3</sub>CN (Figure 8d), suggesting a favorable surface environment for  $\text{CO}_2$  activation. The in situ-formed TOCN heterojunctions exhibit markedly enhanced  $\text{CO}_2$  adsorption relative to Ti<sub>3</sub>CN, with TOCN-160 showing the highest uptake, providing a more favorable surface environment for subsequent  $\text{CO}_2$  activation and reduction (Figure 8e). Density functional theory calculations further elucidate the  $\text{CO}_2$  reduction pathway on the  $\text{TiO}_2/\text{Ti}_3\text{CN}$  heterojunction, where adsorbed  $\text{CO}_2$  is sequentially converted into  $\text{CO}_2^*$ ,  $\text{HCOO}^*$ , and  $\text{HCOOH}^*$  intermediates before desorption of HCOOH as the potential-determining step (Figure 8f). The calculated free energy profile indi-

cates that the heterojunction can spontaneously activate  $\text{CO}_2$  and stabilize key intermediates, favoring HCOOH formation. These insights are consistent with photoelectrochemical  $\text{CO}_2$  reduction performance, confirming the preferential production of HCOOH on  $\text{TiO}_2/\text{Ti}_3\text{CN}$  heterojunction surfaces.

Li *et al.* developed a  $\text{Cu}_2\text{O}$ -BiOBr nanohybrid catalyst with strong visible light responsiveness by combining energy band alignment with morphology engineering [87].  $\text{Cu}_2\text{O}$  nanowires (NWs) were first obtained through high temperature annealing of  $\text{Cu}(\text{OH})_2$  in  $\text{N}_2$  atmosphere, after which two-dimensional BiOBr nanosheets were introduced between the nanowire arrays via a hydrothermal process to form a bridged architecture. The resulting architecture consists of interwoven one-dimensional nanorods and two-dimensional nanosheets that create a three-dimensional bridge-like network. With this nanostructure,  $\text{Cu}_2\text{O}$  serves as an electron-rich active center, while BiOBr functions as both a co-catalyst and an electron reservoir for photogenerated carriers, enabling efficient photoelectrochemical  $\text{CO}_2$  reduction under visible light irradiation. The optimized  $\text{Cu}_2\text{O}$ -BiOBr photocathode delivers a Faradaic efficiency of 51% for  $\text{C}_{2+}$  products at  $-0.6 \text{ V}$  versus RHE, corresponding to a 2.55-fold improvement compared with pristine  $\text{Cu}_2\text{O}$ . The enhanced  $\text{C}_{2+}$  selectivity and production rate originate from improved  $\text{CO}_2$  activation, reduced reaction energy barriers, and stronger  $\text{CO}_2$  adsorption. In addition, the incorporation of BiOBr enhances catalyst stability by mitigating photocorrosion of  $\text{Cu}_2\text{O}$ , indicating that heterojunction engineering offers an effective strategy for achieving efficient and stable photoelectrochemical  $\text{CO}_2$  conversion to multicarbon products.

### 4.3. Alcohol oxidation reaction

Photoelectrochemical alcohol oxidation is increasingly explored as an alternative anodic process to water oxidation, offering the dual benefit of lowering the anodic energy requirement while generating value-added chemicals. In such sys-

tems, heterojunction nanostructures are essential for directing photogenerated holes toward organic substrates and modulating interfacial oxidation pathways, which govern the selectivity of alcohol conversion. Niu *et al.* prepared a Co-LDH/Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> photoanode by sequential electrodeposition of Bi<sub>2</sub>O<sub>3</sub> onto TiO<sub>2</sub> nanorod arrays followed by hydrothermal growth of a Co-LDH overlayer [88]. The resulting architecture extends visible light absorption and establishes dual type-II charge separation pathways, effectively suppressing photogenerated charge recombination. All modified photoelectrodes exhibit enhanced photocurrent densities compared to pristine TiO<sub>2</sub>, with Co-LDH/Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> delivering the highest activity (Figure 9a). In particular, the glycerol conversion rate reaches 1304.54 mmol m<sup>-2</sup> h<sup>-1</sup>, corresponding to a 4.7-fold increase relative to bare TiO<sub>2</sub> (Figure 9b). Product analysis further reveals a distinct shift in oxidation pathways. Pristine TiO<sub>2</sub> predominantly produces glyceraldehyde with a low dihydroxyacetone (DHA) selectivity of 12%, whereas the heterostructured photoanodes favor alternative oxidation routes. This behavior originates from interfacial electronic interactions among TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Co-LDH. The differences in Fermi levels drive electron transfer from Bi<sub>2</sub>O<sub>3</sub> and Co-LDH to TiO<sub>2</sub>, generating internal electric fields (Figure 9c). Upon illumination, photogenerated electrons accumulate in TiO<sub>2</sub> while holes migrate to Bi<sub>2</sub>O<sub>3</sub> and Co-LDH, confirming the formation of dual type-II heterojunctions that facilitate efficient charge separation and utilization.

Li *et al.* synthesized AgVO<sub>3</sub>/LaVO<sub>4</sub> heterojunctions via a one-step hydrothermal method and evaluated their photoelectrocatalytic methanol oxidation performance [89]. This hierarchical particle-nanorod configuration integrates spherical LaVO<sub>4</sub> nanoparticles with 1D AgVO<sub>3</sub> nanorods, reducing particle agglomeration while increasing exposed active sites and interfacial contact area, providing a structurally favorable platform. Linear sweep voltammetry demonstrates that the 2% AgVO<sub>3</sub>/LaVO<sub>4</sub> photoanode delivers a higher current density than pris-

tine AgVO<sub>3</sub> or LaVO<sub>4</sub>, indicating its superior photoelectrocatalytic activity (Figure 9d). Electronic structure analysis shows that the valence band edge of AgVO<sub>3</sub> and the conduction band edge of LaVO<sub>4</sub> are dominated by Ag and V states, respectively, leading to strong interfacial hybridization upon heterojunction formation. As a result, the AgVO<sub>3</sub>/LaVO<sub>4</sub> heterostructure exhibits a significantly reduced bandgap of 0.31 eV compared with the individual components, which expands visible light absorption and facilitates carrier excitation (Figure 9e). Furthermore, charge density difference analysis reveals pronounced electron redistribution at the interface, with electrons preferentially transferring from AgVO<sub>3</sub> and LaVO<sub>4</sub> (Figure 9f). This charge transfer establishes a built-in electric field across the interface, which effectively suppresses electron-hole recombination and promotes carrier separation, accounting for the enhanced photocatalytic and electrocatalytic performance of the AgVO<sub>3</sub>/LaVO<sub>4</sub> heterojunction.

#### 4.4. Other reactions

Beyond water electrolysis, CO<sub>2</sub> reduction, and alcohol oxidation, heterojunction nanostructures have been extended to a broader range of photoelectrochemical reactions, including pollutant degradation and nitrogen conversion. In these systems, reaction-specific charge transfer behavior and surface chemistry define the functional role of the heterojunction, requiring distinct interfacial configurations depending on the targeted reaction pathway. Yu *et al.* reported a MoS<sub>2</sub>@LZO heterostructure, consisting of 2D MoS<sub>2</sub> nanoflakes assembled on mixed-phase La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (LZO) nanofibers through a hydrothermal process [23]. The resulting architecture integrates MoS<sub>2</sub> with oxygen vacancy-rich LZO, enabling directional electron transfer from MoS<sub>2</sub> to vacancy sites while providing a robust and high surface area support. Transient photocurrent measurements show stable and reproducible responses for all samples, with the 60 wt% MoS<sub>2</sub>@LZO exhibiting a markedly higher photocurrent compared with bare LZO and MoS<sub>2</sub>, indicating more

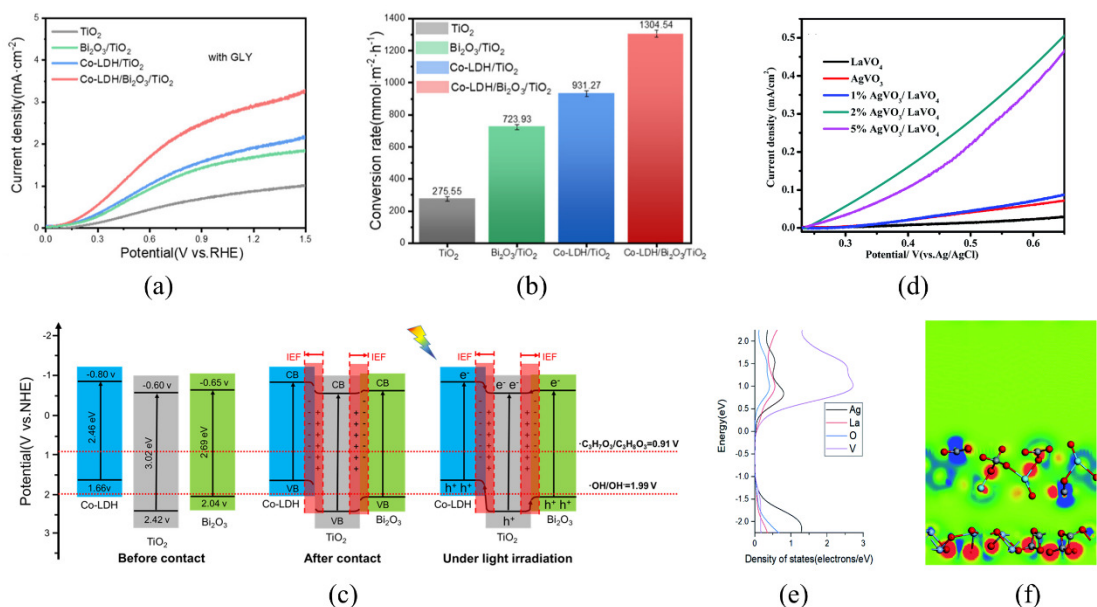


Fig. 9. (a) LSV curves of various photoanodes in the presence of glycerol; (b) Glycerol conversion rates of different photoanodes; (c) Schematic illustration of the charge transfer mechanism between TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and Co-LDH before and after contact, as well as that of Co-LDH/Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> under light irradiation; Reproduced with permission. [89]. (d) LSV curves of AgVO<sub>3</sub>, LaVO<sub>4</sub>, and AgVO<sub>3</sub>/LaVO<sub>4</sub> photocatalysts; (e) Density of states of AgVO<sub>3</sub>/LaVO<sub>4</sub> heterostructure; (f) Charge density difference map for the AgVO<sub>3</sub>/LaVO<sub>4</sub> heterostructures; Reproduced with permission. [90].

efficient photogenerated carrier generation (Figure 10a). Photoelectrochemical nitrogen reduction measurements performed in 0.1 M KOH reveal a higher current density of MoS<sub>2</sub>@LZO under N<sub>2</sub> relative to Ar, confirming that electrons are effectively utilized for ammonia production. Among the series, the 60 wt% MoS<sub>2</sub>@LZO photocathode shows the lowest onset potential and the highest ammonia yield (Figure 10b). Band structure analysis indicates that interfacial contact between MoS<sub>2</sub> and LZO induces band bending and forms a type-II heterojunction (Figure 10c). Under illumination and applied bias, photogenerated electrons are transferred across the interface and preferentially trapped at oxygen vacancy sites, while holes are extracted to maintain charge balance. The uniform nanoflake morphology of MoS<sub>2</sub> on LZO nanofibers further increases the density of accessible active sites, collectively contributing to the enhanced nitrogen reduction performance.

Mushtaq *et al.* reported the synthesis of hierarchical flower-like MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> micro/nanostructures via a scalable in situ hydrothermal method [90]. The resulting architecture couples 2D MoSe<sub>2</sub> with g-C<sub>3</sub>N<sub>4</sub> within a multilevel heterojunction, where the hierarchical morphology promotes light harvesting through internal scattering while providing abundant nitrogen-coordinated active sites. The MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> hybrid with an optimized loading of 7 wt% exhibits a higher photovoltage than pristine g-C<sub>3</sub>N<sub>4</sub> and MoSe<sub>2</sub>, indicating more efficient separation of photoinduced charge carriers within the heterojunction (Figure 10d). Time-resolved measurements show a prolonged carrier lifetime relative to pure MoSe<sub>2</sub>, consistent with suppressed recombination enabled by rapid interfacial charge transfer to g-C<sub>3</sub>N<sub>4</sub>. In contrast, pristine g-C<sub>3</sub>N<sub>4</sub> and MoSe<sub>2</sub> suffer from fast recombination and limited photocurrent genera-

tion. Optical characterization reveals a bandgap reduction from 2.69 eV for g-C<sub>3</sub>N<sub>4</sub> to 2.45 eV for MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> (7 wt%), accompanied by a red shifted absorption edge that enhances visible light utilization. The optimized MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> hybrids deliver an ammonia yield rate of 7.72 μmol h<sup>-1</sup> cm<sup>-2</sup> with a Faradaic efficiency of 28.91% at -0.3 V versus RHE under ambient conditions. The enhanced activity can be attributed to the combined effects of the 2D heterojunction and the hierarchical architecture, which together facilitate charge separation and increase the density of accessible nitrogen-related active sites (Figure 10e).

## 5. Challenge and prospects

Despite substantial advances in hydrothermal and solvothermal synthesis of heterojunction nanostructures for photoelectrocatalysis, several fundamental challenges remain that hinder their practical implementation [91,92]. One of the most critical issues is the limited ability to precisely control heterojunction interfaces. Although solution-based synthesis enables low temperature processing and flexible morphological control, variations in precursor chemistry and growth kinetics frequently result in interfacial disorder, unintended defect formation, or nonuniform junction coverage [93,94]. Since carrier separation and transport are highly sensitive to local band alignment and interfacial electronic states, such variability can cause large discrepancies in photoelectrochemical performance. In parallel, rational heterojunction design requires balancing light absorption, carrier transport, and surface catalytic activity, which are often interdependent yet competing factors. This balance is strongly dictated by nanostructure geometry, which governs optical path length, carrier diffusion distance, and surface reaction kinetics. While hierarchical micro

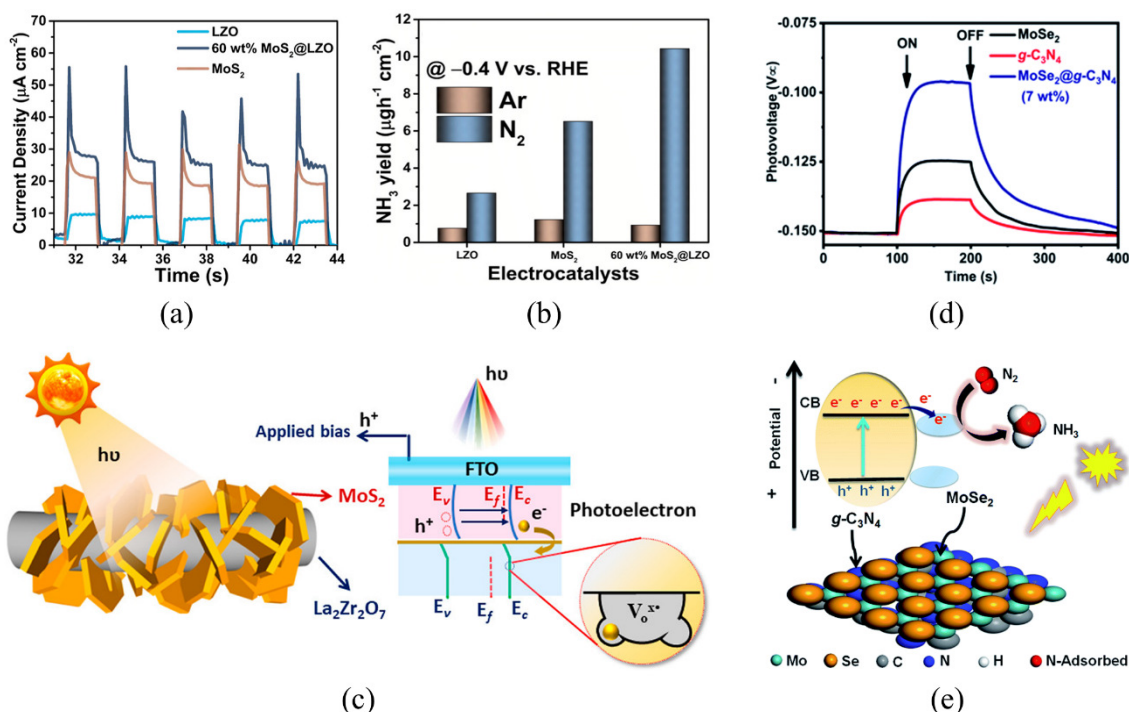


Fig. 10. (a) Transient photocurrent response of MoS<sub>2</sub>, LZO, and 60 wt% MoS<sub>2</sub>@LZO under light irradiation; (b) Comparison of ammonia yields for pristine LZO, pristine MoS<sub>2</sub>, and 60 wt% MoS<sub>2</sub>@LZO samples at -0.4 V vs. RHE; (c) Schematic band structure illustrating the type-II heterojunction in MoS<sub>2</sub>@LZO, showing a reduced Fermi level under applied bias and solar illumination; Reproduced with permission. [23]. (d) Transient open-circuit voltage decay (OCVD) measurements of MoSe<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, and MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> (7 wt%); (e) PEC performance of hierarchical micro- and nanoflower MoSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> heterojunctions; Reproduced with permission. [91].

and nanostructures enhance light harvesting and shorten diffusion lengths, excessive structural complexity may introduce trap states and recombination centers, thereby limiting performance gains. Stability under operating conditions remains another critical bottleneck. Many heterojunction photoelectrodes suffer from photocorrosion, interfacial delamination, or phase reconstruction during prolonged illumination and applied bias [95,96]. Although hydrothermal and solvothermal routes can access metastable, defect-rich structures with high intrinsic activity, preserving interfacial integrity and electronic functionality over long-term operation remains challenging.

Another important challenge concerns the scalable synthesis of heterojunction nanostructures. Although hydrothermal and solvothermal methods are inherently compatible with solution-based processing and offer potential advantages for large scale production, translating laboratory scale autoclave reactions into industrially viable synthesis routes remains challenging. Maintaining uniform temperature and pressure distribution in large reaction volumes, controlling nucleation and growth kinetics over extended spatial scales, and ensuring homogeneous precursor mixing are critical factors that often lead to batch to batch variability in product morphology and heterojunction quality. Recent efforts have explored strategies such as continuous flow hydrothermal systems, improved reactor engineering, and precursor chemistry optimization to address these issues [65,97]. Nevertheless, achieving reproducible interface formation, efficient precursor utilization, and scalable electrode fabrication remains a key technological barrier. Further development of scalable reactor platforms and process control strategies will therefore be essential to bridge the gap between laboratory synthesis and practical photoelectrochemical device applications.

Beyond these challenges, the future development of heterojunction photoelectrodes will increasingly depend on establishing clear and quantitative links between interfacial electronic structure and macroscopic photoelectrochemical performance [92]. While current design concepts are largely guided by static band alignment models and ex situ characterization, emerging operando and time-resolved techniques provide new opportunities to directly capture transient carrier dynamics, interfacial reconstruction, and reaction induced electronic redistribution under operating conditions [98,99]. Such approaches are expected to refine existing heterojunction models and enable more predictive interface engineering. From a design perspective, rather than relying on empirical optimization, correlating electronic structure descriptors such as band bending and interfacial states with carrier transport parameters including diffusion length and lifetime provides a physically grounded basis for mechanism-driven material selection [100]. This shift will also promote synthesis by design, where precursor chemistry, growth kinetics, and defect landscapes are deliberately tuned to realize targeted band bending and built-in electric fields. Coupled with device relevant testing conditions and scalable electrode architectures, these advances will facilitate the rational translation of hydrothermally and solvothermally synthesized heterojunction nanostructures into robust and efficient photoelectrochemical platforms [101].

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## Conflicts of Interest

The authors declare that there are no conflicts of interest in this work.

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