Nanoscale

REVIEW

View Article Online
View Journal | View Issue

Cite this: *Nanoscale*, 2024, **16**, 22099

Advanced strategies for controlling three-phase boundaries in photocatalysis

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Received 6th September 2024,
Accepted 23rd October 2024

DOI: 10.1039/d4nr03651d

rsc.li/nanoscale

This review delves into the latest advancements in controlling three-phase boundaries (TPBs) in photocatalytic systems, with a focus on photo(electro)catalytic processes for nitrogen reduction, oxygen reduction, and water reduction. We critically analyze various strategies and advanced materials designed to enhance TPB performance, evaluating their impact on catalytic efficiency and identifying gaps in the existing literature. By examining sophisticated triphasic systems that integrate superwetting materials, we emphasize their essential role in improving light absorption, charge separation, and mass transfer. Key challenges in TPB optimization are discussed, and future research directions are proposed to advance photocatalytic technologies for sustainable energy applications. This review highlights the crucial importance of TPBs in photo(electro)catalysis, aiming to inspire further innovation for more efficient and scalable solutions.

1. Introduction

In the quest for sustainable energy solutions, photocatalysis has emerged as a promising technology for harnessing solar energy to drive chemical reactions.[1,2] However, the efficiency of photocatalytic systems critically depends on the effective interaction between the three involved phases: the photocatalyst (solid phase), the reactant solution (liquid phase), and

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the generated gases or products (gas phase).[3,4] The interfaces where these phases meet, known as three-phase boundaries (TPBs), are crucial in determining the overall performance of photocatalytic processes. One significant challenge in these multiphase systems is the transport of reactants and products across the interfaces. Interfacial diffusion and mass transfer often become rate-limiting steps that hinder the overall reaction rates and efficiency.[5] The TPB is the region where the gas, liquid, and solid phases converge, and it plays a critical role in photocatalytic reactions by representing a geometrical class of phase boundaries where these phases intersect.[6] A simple analogy is a coastline, where land, air, and sea meet, forming a dynamic zone influenced by solar, wind, and wave energies, supporting diverse ecosystems.

Recently, there has been a groundbreaking shift in materials design with the exploration of three-phase interfacial catalysts. This growing interest is driven by the crucial role of interfacial chemistry in enhancing energy and mass transfer in light-driven multiphase catalytic systems.[7] In photocatalysis, most photo(electro)catalysts are in the solid state, leading to typical configurations involving solid–liquid or solid–gas diphasic systems. These conventional configurations are fundamental to traditional photocatalytic (PC) and photoelectrochemical (PEC) mechanisms.[8] The transition from conventional biphasic systems to advanced triphasic systems, which incorporate superwetting materials, represents a significant advancement in photocatalysis.[9] By improving interactions among the solid, liquid, and gas phases, these advanced systems achieve superior light absorption, charge separation, and reactant/product transfer. Mastering the control of TPBs and utilizing superwetting materials are essential for optimizing photocatalytic efficiency. Continued research and development, inspired by biological phenomena, will lead to innovative solutions for energy and environmental applications, paving the way for more effective and scalable photocatalytic technologies.[10–12]

Controlling the TPBs to maximize photocatalytic efficiency involves optimizing the interactions between the solid, liquid, and gas phases to ensure effective light absorption, charge separation, and the transfer of reactants and products.[13] This requires a thorough understanding of catalyst material properties, the dynamics of reactants in different phases, and the environmental conditions under which the reactions occur. Recent advances in materials science and nanotechnology have introduced new methods for engineering these boundaries, including novel nanostructured photocatalysts with tailored surface properties, innovative reactor designs that enhance phase contact, and the strategic use of co-catalysts and additives.[14] Developing an efficient TPB is crucial for achieving high catalytic performance, but our current understanding of TPB structures is still limited, hindering the rational construction of these systems. Increased focus on TPB studies is essential to gain insights into mass transport, electron conduction, and reaction kinetics, which could guide the design and enhancement of TPB performance, ultimately reducing resource utilization and improving catalytic efficiency.[11]

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Our group has recently published a comprehensive review on the emerging field of superwetting materials and their applications in photocatalytic organic pollutant degradation, highlighting their significant potential for environmental remediation and sustainable energy production.[15] In this review, we will shift our focus to the state of research on controlling TPBs in photocatalytic systems, specifically targeting photo(electro)catalytic processes for nitrogen reduction, oxygen reduction, and water reduction. We will critically examine various strategies and materials designed to enhance TPB performance, assess their impact on overall catalytic efficiency, and address gaps identified in our previous review. Additionally, we will identify key challenges and propose future research directions to advance this crucial aspect of photocatalytic technology, particularly in the energy sector. This review aims to underscore the importance of TPBs in photocatalysis and inspire further innovations for more efficient and scalable applications.

2. Fundamental concepts of three-phase boundaries

The TPB concept (Fig. 1a) is particularly important in heterogeneous catalysis and electrochemical systems because it creates a unique environment that enhances catalytic reactions through the simultaneous interaction of all three phases.[15–19] These effects can lead to enhanced reaction rates, better selectivity, and improved overall performance of the catalytic processes. Hence, the significance of the TPB is as follows:

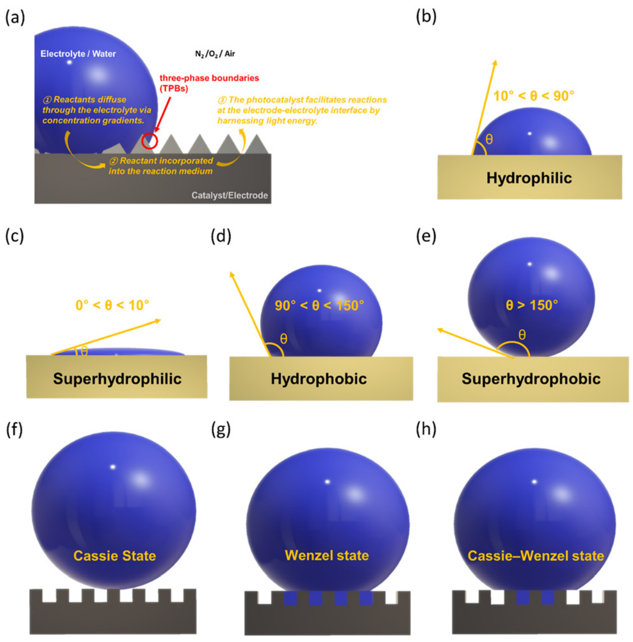

Fig. 1 Schematic of (a) three-phase contact line where the electrolyte–water droplet meets the solid surface and the surrounding gas. Schematic of (b) hydrophilic, (c) superhydrophilic, (d) hydrophobic, and (e) superhydrophobic surfaces with different wetting/non-wetting states. Reprinted (adapted) with permission.[15] Copyright 2024, Elsevier. Schematic of a liquid drop under (f) Cassie state, (g) Wenzel state, and (h) Cassie–Wenzel state.

(i) Enhanced reaction rates: At the TPB, reactants from the gas phase can adsorb onto the solid catalyst surface, while reactants or ions from the liquid phase can also interact at the same site. This simultaneous presence facilitates rapid reaction kinetics, as all necessary reactants are in close proximity to the active sites of the catalyst.

(ii) Increased catalytic efficiency: The efficiency of catalysts can be significantly improved at TPBs due to the higher availability of reactants at the active sites. This leads to more effective utilization of the catalyst material and can reduce the amount of catalyst required for a given reaction.

(iii) Improved selectivity: The controlled environment at the TPB can help in steering the reaction pathways towards the desired products by minimizing side reactions. Specific interactions at the TPB can lead to a higher selectivity for certain products, which is crucial in many industrial processes.

2.1. Surface wettability in triphasic catalytic systems

Wettability plays a crucial role in triphasic catalytic systems in which solid surfaces simultaneously interact with two immiscible phases, typically gases and liquids. Manipulating the surface wettability significantly influences the distribution and interaction of the reactants at the interfaces, thereby affecting the reaction rates and selectivity.[20] Optimizing the wettability properties is essential for enhancing interfacial mass transfer and improving the overall catalytic efficiency.[21] For catalytic reactions involving structured and chemically stable solid substrates, conventional methods for modifying the surface wettability are often limited by the inherent inability to tune the solid surface tension. Therefore, structured surfaces require innovative strategies to achieve tunable surface wettability independent of the solid phase. This approach is essential for optimizing the catalytic efficiency and product selectivity of triphasic catalytic systems.[22,23] Wettability refers to the affinity of a solid substrate for wetting by a fluid and is influenced by the surface polarity or geometric structure.[24] Understanding and categorizing wettability states based on contact angles (θ) help in designing and optimizing surfaces for various applications, including catalysis, where controlling how liquids interact with solid catalysts can profoundly impact reaction efficiency and selectivity.[25,26] The degree of wettability can be categorized into four main states based on the contact angle (θ) formed by a liquid droplet on the solid surface (Fig. 1b–e): (i) superhydrophilic ($0° < \theta < 10°$): on superhydrophilic surfaces, water or other polar liquids spread extensively due to strong adhesive forces, resulting in complete wetting; (ii) hydrophilic ($10° < \theta < 90°$): these surfaces facilitate relatively high spreading and wetting, although not as extensively as superhydrophilic surfaces; (iii) hydrophobic ($90° < \theta < 150$): hydrophobic surfaces repel water and other polar liquids to a significant extent, causing droplets to bead up and minimally wet the surface; and (iv) superhydrophobic ($\theta > 150°$): superhydrophobic surfaces are extremely water-repellent, causing water droplets to bead tightly and roll off the surface easily. These surfaces often exhibit self-cleaning properties because of the minimal contact area between the water droplet and the surface.[15,27–29]

2.2. Wetting states and mass transfer processes

The wettability of a catalyst surface plays a crucial role in catalytic processes by influencing the interaction and transfer of reactants across interfaces. The wetting state of the catalyst can be tailored by altering its chemical or physical properties, leading to three distinct states that significantly affect the interfacial mass transfer:[30–32] (i) Wenzel state: in the Wenzel state, the catalyst surface is fully wetted by the liquid phase, with minimal trapped air at the liquid/solid interface. This configuration results in limited three-phase contact and sluggish gas diffusion through the liquid phase, which is slower than that through the gas phase (Fig. 1(f)). The Wenzel state is characterized by reduced efficiency in the mass transfer of gases, potentially limiting catalytic reaction rates;[33] (ii) Cassie state: conversely, the Cassie state describes a surface that is completely non-wetting to the liquid phase, creating a barrier that hinders gas diffusion into the liquid (Fig. 1g). This poor wetting condition limits the interaction between the gas reactants and the liquid phase, thereby restricting the photocatalytic activity and overall catalytic performance;[34] and (iii) Cassie–Wenzel coexistent state: the Cassie–Wenzel coexistent state represents an intermediate condition in which the catalyst surface exhibits mixed wetting characteristics. The liquid partially wets the solid surface, leaving pockets of trapped air at the interface. This configuration maximizes the creation of multiple three-phase contact points, facilitating the efficient mass transfer of reactants in both the liquid and gas phases. The coexistence of the Cassie and Wenzel states enhances interfacial interactions, promoting enhanced catalytic performance by improving the accessibility of reactants to active sites on the catalyst surface (Fig. 1h).[35–37] Understanding and controlling these wetting states are crucial for optimizing catalytic processes, particularly in photocatalysis, where efficient mass transfer between the gas and liquid phases is essential. By manipulating surface wettability, researchers can tailor catalyst designs to maximize interfacial contact and enhance the overall catalytic efficiency.[38]

2.3. Strategies for controlling three-phase boundaries

TPBs are crucial for optimizing catalytic and photocatalytic processes.[25,26,39,40] The effective manipulation of TPBs can enhance the efficiency of these systems by improving the reactant interactions, mass transfer, and overall reaction rates. Strategies for controlling the TPBs in the context of catalysis and photocatalysis are as follows.

2.3.1. Surface modification and functionalization

2.3.1.1. Chemical treatment. Surface modification by chemical treatment can alter the wettability and adsorption properties of the catalyst surface.[41] For instance, introducing hydrophilic or hydrophobic functional groups can help selectively enhance the interactions with liquid or gas phases, respectively.[42–44] In particular, the introduction of hydroxyl groups, oxides, or other polar functional groups onto the catalyst surface can increase its hydrophilicity. Hydrophilic surfaces enhance liquid-phase reactions by promoting the spread and adsorption of the liquid reactants. Moreover, the application of non-polar substances such as silanes, fluorinated compounds, or alkyl chains can make the surface hydrophobic or even superhydrophobic. This is useful for trapping air, thereby promoting gas-phase reactions and inhibiting liquid contact.

2.3.1.2. Application of coating materials. Applying coatings or creating composite layers on the catalyst surface can improve its interactions with different phases. For example, coating photocatalysts with materials that enhance light absorption or charge separation can enhance their efficiency.[28,45,46]

2.3.2. Nanostructuring and texturing. Nanostructuring and texturing significantly influence the superwetting behavior of catalysts and the formation of three-phase boundaries (TPBs). The creation of nanostructures, such as nanorods, nanotubes, or nanopillars, increases the surface area, providing more active sites at the TPBs, which are essential for catalytic reactions. These nanostructures enhance the interaction between the gas, liquid, and solid phases by offering a larger interface for mass transfer and improving the reactant distribution and conversion efficiency.[45,47,48] Moreover, in the context of photocatalysis, these structures can trap light more effectively, increasing the absorption of photons and enhancing the generation of electron–hole pairs. The unique geometries of the nanostructures also help reduce charge recombination by facilitating more efficient charge separation and transport to the active sites. Consequently, nanostructuring and texturing not only optimize the physical and chemical interactions at the TPBs, but also enhance the overall photocatalytic efficiency through improved light harvesting and charge dynamics. Thus, nanostructured catalysts are highly effective for various applications, including environmental remediation and energy conversion.[49–51]

Surface roughness plays a crucial role in defining the three-phase boundaries (TPBs) and significantly affects catalytic performance. Adjusting the surface roughness of materials through mechanical or chemical etching can significantly affect their wettability and phase contact properties. By modifying the surface topology, it is possible to enhance interactions between the gas, liquid, and solid phases, which are crucial for catalysis.[52–54] For example, hydrophobic materials can become superhydrophobic with appropriate roughening, thereby enhancing their ability to trap air and facilitate gas-phase interactions. The combination of micro- and nanoscale features can further enhance the desired wetting properties by promoting liquid spread or air trapping. This multiscale texturing approach allows the fine-tuning of surface characteristics to create optimal three-phase boundaries, thereby improving the mass transfer, reactant distribution, and overall catalytic efficiency.

2.3.3. Wettability control. Wettability and surface energy are crucial factors that influence the formation of TPBs and the superwetting behavior of catalysts, significantly impacting photocatalysis. By adjusting the wettability and surface energy of a catalyst, interactions between the gas, liquid, and solid phases can be optimized, thereby enhancing reactant adsorption and mass transfer. Superhydrophilic surfaces enable extensive wetting by aqueous solutions, which maximizes contact and improves the transfer of liquid-phase reactants. On the other hand, superhydrophobic surfaces trap air, promote gas-phase interactions, and reduce liquid barriers. Achieving the right balance between these properties can create an ideal TPB configuration for the most efficient catalytic reactions. Tailoring surface properties in this way boosts light absorption, charge separation, and overall photocatalytic activity, leading to improved efficiency and selectivity in photocatalytic processes. This customization ensures that the catalyst performs effectively under various environmental conditions, making it more versatile and robust for practical applications.[8] Adjusting a catalyst's wettability by altering its chemical composition or surface texture can control the distribution and interaction of gas and liquid phases. Superhydrophobic surfaces can trap air and promote gas-phase reactions, while hydrophilic surfaces enhance liquid-phase reactions.[27,55]

Additionally, patterning the surface with hydrophobic and hydrophilic regions is a strategic method for creating controlled TPBs that optimize mass transfer and reactant distribution in catalytic systems.[56,57] Selective modification of surface properties, such as wettability and surface energy, allows for tailored interactions with the gas, liquid, and solid phases. Hydrophobic regions repel water, promoting efficient gas-phase interactions and minimizing liquid coverage.[58] Conversely, hydrophilic regions ensure thorough wetting by aqueous solutions, enhancing liquid–solid interactions and facilitating rapid mass transfer of reactants. This spatial control over surface characteristics allows for the creation of well-defined TPBs, directing reactants to active sites and improving catalytic efficiency and selectivity. Such patterning techniques are essential for optimizing catalyst performance in photocatalysis and other catalytic processes.[59]

2.4.4. Catalyst morphology and structure. The morphology and structure of the catalyst play a pivotal role in determining the triphasic superwetting behavior, which significantly affects the catalytic performance. The physical and chemical characteristics of the catalyst surface influence how the gas, liquid, and solid phases interact, thus affecting the overall efficiency of the catalytic and photocatalytic processes.[60–63]

Metal–organic frameworks (MOFs), zeolites, and mesoporous silica are highly porous materials that provide extensive three-phase boundaries (TPBs) and exhibit superwetting behavior, which is crucial for catalytic applications. Their high surface areas and tunable pore structures enhance the interactions between the gas, liquid, and solid phases, facilitating efficient mass transfer and reactant diffusion. MOF catalysts with customizable pore sizes and functional groups can be engineered for specific interactions and wettability properties to optimize the contact with all phases. Zeolites, known for their uniform pore structures and high thermal stability, offer selective adsorption sites that enhance catalytic reactions at TPBs. Owing to its large pore volume and adjustable surface chemistry, mesoporous silica can be modified to achieve superhydrophobic or superhydrophilic surfaces, thereby promoting optimal wetting states for different catalytic processes. These properties can create extensive TPBs, and their adaptable wetting properties make them ideal candidates for enhancing catalytic efficiency and selectivity.[25,61,64–67] Moreover, designing core–shell catalysts, where a reactive core is coated with a shell material, can enhance the stability and activity of the catalyst at TPBs. The shell can be engineered to improve specific interactions with the gas or liquid phase.[68–71]

Dual-phase catalysts, such as Janus catalysts, have distinct surface properties, favoring superwetting behavior that enhances photocatalysis. These catalysts feature one side engineered for hydrophilicity and the other for hydrophobicity, creating a unique interface that promotes efficient interactions among the gas, liquid, and solid phases.[72] This duality ensures optimal light absorption and charge separation, which are crucial for photocatalytic reactions. The hydrophilic side maximizes contact with the aqueous phase, facilitating the transfer of reactants, whereas the hydrophobic side improves gas-phase interactions and reduces the liquid barrier. This strategic design enhances the generation and utilization of reactive species, thereby boosting the overall efficiency and effectiveness of photocatalytic processes. The ability of Janus catalysts to create tailored wetting states and extensive three-phase boundaries makes them highly effective in optimizing photocatalytic reactions.[68,73,74]

The use of bimetallic or trimetallic nanoparticles can create synergistic effects that significantly enhance both catalytic activity and stability. These nanoparticles, composed of two or three different metals, offer unique properties that single-metal catalysts cannot achieve.[75] By carefully selecting and combining metals, these nanoparticles can be designed to optimize the interactions at three-phase boundaries (TPBs).[76,77] One metal may provide high catalytic activity, but there is another issue of stability or resistance to deactivation of the catalyst. Additionally, the combination of different metals can create new active sites and modify electronic properties, leading to improved reaction kinetics.[78] The tailored surface characteristics of bimetallic and trimetallic nanoparticles also facilitate better contact between the gas, liquid, and solid phases, promoting efficient mass transfer and increasing the overall catalytic performance.[79,80] This synergistic approach not only increases the catalytic efficiency, but also extends the durability and operational lifespan of the catalyst, making it highly effective for various catalytic applications, including photocatalysis.

2.4.5. Innovative fabrication techniques. Innovative fabrication techniques such as electrodeposition and electrospinning play a pivotal role in tailoring catalysts with controlled surface properties and morphologies, thereby enhancing their superwetting behavior and creating three-phase boundaries (TPBs).[81] Electrodeposition allows for the precise deposition of metallic nanoparticles onto catalyst surfaces, influencing their wettability and interaction with both the liquid and gas phases.[82] This technique can be used to create catalysts with tailored surface roughness and composition, and to optimize TPBs for efficient mass transfer and catalytic activity. The growing issue of oily wastewater and organic pollutants necessitates efficient oil–water separation. A superwetting, visible-light catalytic Cu@C_2O film was developed *via* one-step electrodeposition, and it displayed underwater superoleophobicity and underoil superhydrophobicity after prewetting. Its unique wettability and small pore size enable the effective separation of water-in-oil and oil-in-water emulsions under gravity. Performance was optimized at the TPB, which enhanced the mass transfer and separation efficiency. In addition, the visible light catalytic properties of the film enabled pollutant degradation during the separation process, thus enabling both oil and contaminant removal.[83]

Chemical vapor deposition (CVD) is typically performed in a sealed chamber under controlled conditions to deposit specific chemicals onto substrates. CVD has been widely used to increase surface roughness and thereby aid in the development of hydrophobic or superhydrophobic materials for oily wastewater separation. Graphene-based porous materials fabricated *via* CVD have garnered significant attention because of their high chemical stability, large surface area, and three-dimensional (3D) networks that exhibit extreme water repellence. These properties make them highly effective for oil–water separation.[84] Moreover, the formation of TPBs in these materials further enhances the mass transfer and separation efficiency by optimizing the interactions between the solid surface, oil, and water.[85–87]

On the other hand, electrospinning enables the fabrication of nanofibrous structures with large surface areas and high porosity, ideal for promoting superhydrophilic or superhydrophobic properties depending on the application. Hydrophobic materials, such as polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), and fluorinated silane compounds, and hydrophilic materials, such as poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), and poly(vinylpyrrolidone) (PVP), have been widely used in the development of electrospun membranes for oil–water separation. These membranes effectively leverage surface wettability to achieve efficient separation by repelling or attracting water and oil, depending on their composition.[88–90] By leveraging these advanced fabrication methods, catalysts can be engineered to exhibit enhanced superwetting behavior, facilitating superior performance in photocatalytic applications through improved reactant accessibility and reaction kinetics at the TPBs.[91–93]

Self-assembly methods provide a powerful approach for creating structured surfaces or composite materials that optimize three-phase boundaries (TPBs) to enhance catalytic performance.[8,94] These methods utilize natural molecular interactions or external stimuli to spontaneously organize molecules into ordered structures at various scales. Many superwetting particle coatings have been developed for efficient oil–water separation using this technique. For example, 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (POTS) has been employed to increase both the water contact angle (WCA) and oil contact angle (OCA) by forming larger particles, resulting in a superhydrophobic surface. This modification enabled a treated stainless steel mesh to achieve effective oil/water separation. Additionally, superhydrophobic and superoleophilic polytetrafluoroethylene (PTFE)-coated porous metal fiber sintered felt (PMFSF) was fabricated *via* a layer-by-layer (LBL) assembly method that utilized electrostatic interactions to enhance separation performance.[95,96] Moreover, this technique enables precise control of the surface morphology, porosity, and chemical composition, all of which are critical for catalytic activity. By directing the assembly process, catalysts can be engineered with tailored TPBs, in which the gas, liquid, and solid phases interact efficiently. For example, self-assembled monolayers (SAMs) on surfaces can modify the surface chemistry to promote specific interactions with reactants, whereas self-assembled nanomaterials can create hierarchical structures that maximize the surface area and expose catalytically active sites. Such approaches not only improve mass transfer and reactant distribution, but also enhance stability and durability, making self-assembly a promising strategy for advancing catalytic technologies across various industrial and environmental applications.[97]

In addition to the common fabrication methods discussed above, several other techniques, such as spray coating, phase separation, electroplating, and grafting, have been employed to construct novel superwetting materials with exceptional properties to optimize wettability and improve performance in various applications.[98,99]

3. Importance of TPBs in photocatalysis

Three-phase boundary interfaces (TPBs) play a crucial role in photocatalysis by involving the convergence of the solid, liquid, and gas phases.[4] Typically, these boundaries include a photocatalyst in the solid phase, an aqueous solution in the liquid phase, and gases such as oxygen or hydrogen in the gas phase.[8,100] TPBs are essential for facilitating key processes such as light absorption, charge separation, and redox reactions, which are fundamental to the efficiency of photocatalytic systems. The characteristics of TPBs, including their surface areas, structural properties, and chemical compositions, critically influence the effectiveness of these processes.[101] Optimal TPBs promote enhanced contact between phases, facilitating efficient transfer of reactants and products and thereby improving overall reaction rates.

In engineering designs focused on three-phase systems, efforts are concentrated on optimizing the interfaces between the gas, solid, and liquid phases to enhance the interfacial mass-transfer processes essential for catalytic efficiency.[8,102] Manipulating the wettability of the surfaces within these configurations can significantly impact reaction kinetics, further enhancing the performance of photocatalytic systems.

3.1. Role of three-phase boundaries (TPBs) in photocatalysis mechanism

Three-phase boundaries (TPBs) play a crucial role in the photocatalytic mechanism, where the solid, liquid, and gas phases converge to facilitate key processes. The TPBs can enhance the efficiency of photocatalytic systems by offering several advantages.

(i) Enhanced surface interaction: Enhanced reactant contact facilitated by TPBs is crucial for photocatalysis, in which these boundaries create a specialized interface. TPBs enable direct interactions between reactants from the solid, liquid, and gas phases and the photocatalyst surface, thereby enhancing the availability of reactants and promoting efficient catalytic reactions. Moreover, TPBs increase the number of active adsorption sites, which are essential for processes such as hydrogen evolution, oxygen reduction, and the degradation of organic pollutants. This dual role of TPBs in promoting surface interactions and providing abundant adsorption sites underscores their significance in optimizing the photocatalytic efficiency and performance.[15,103]

(ii) Optimizing light absorption and charge separation: To facilitate key processes in photocatalysis, three-phase boundaries (TPBs) play a critical role in enhancing light absorption and charge separation mechanisms. In TPBs, photocatalysts can absorb light more effectively, initiating the generation of electron–hole pairs, which are crucial for subsequent redox reactions. This efficient light absorption is pivotal for the activation of photocatalytic processes. Additionally, TPBs enhance the separation and migration of photogenerated electrons and holes, thereby minimizing recombination losses and significantly increasing the overall photocatalytic activity. By optimizing both the light absorption and charge separation, TPBs contribute substantially to improving the efficiency and effectiveness of photocatalytic systems.[15,104]

(iii) Optimized mass transfer: TPBs optimize the diffusion pathways for reactants and products across solid–liquid–gas interfaces, significantly enhancing the dissolution of gas-phase reactants into the liquid phase and the desorption of liquid-phase products into the gas phase. Additionally, TPBs minimize diffusion resistance by promoting improved contact between phases, thereby enabling faster and more efficient mass-transfer processes. The dual capabilities of TPBs to facilitate reactant diffusion and minimize resistance underscore their pivotal role in enhancing the overall efficiency of catalytic systems.[105]

(iv) Redox reaction sites facilitate redox reactions; TPBs serve as active sites where oxidation and reduction reactions can occur simultaneously.[106,107] For example, in processes such as water splitting, TPBs facilitate the reduction of protons to hydrogen gas and the oxidation of water to oxygen gas. Moreover, TPBs enhance the transfer of electrons to the adsorbed reactants, thereby accelerating redox reactions and significantly improving the overall photocatalytic performance. TPBs play a crucial role in enhancing the effectiveness and efficiency of photocatalytic systems.[108]

(v) Chemical composition: The chemical composition of the TPBs plays a critical role in determining the binding strength of the reactants and intermediates, which in turn affects the reaction pathways and product selectivity. By influencing the interaction of reactants with the catalytic surface, the chemical nature of TPBs directly affects the efficiency and specificity of the catalytic processes. Understanding and manipulating the chemical composition of TPBs are essential for optimizing the reaction pathways and enhancing the selectivity of the desired products in various catalytic applications.[109]

Therefore, understanding and optimizing TPBs are crucial for designing highly efficient photocatalytic systems that enhance reactant contact, facilitate key processes, optimize mass transfer, and provide efficient redox reaction sites.

4. Recent advances and case studies

4.1. Photo/photoelectrocatalytic N_2 reduction

Green ammonia is increasingly emerging as a key future energy carrier in the drive toward a net-zero carbon landscape. The nitrogen reduction reaction (NRR) is a multifaceted catalytic process involving several proton-coupled electron transfer steps.[110] As a result, the efficiency of NRR pathways is often hindered by slow N_2 adsorption and activation kinetics, competing reductions with hydrogen and ammonia, and the limited capabilities of current photo(electro)catalysts. These challenges collectively limit the overall effectiveness of NRR strategies, highlighting the complexity and intricacy involved in enhancing nitrogen fixation technologies.

Recent advancements in catalyst engineering have focused on the rational control of interfacial chemistry in light-driven multiphase systems, emphasizing the development of three-phase interface catalysts as a promising approach. These catalysts can mitigate mass transfer limitations observed in conventional two-phase systems by enhancing the efficiency of the interface between the gas, liquid, and solid phases. This enhancement leads to improved N_2 adsorption and activation, facilitates better separation and migration of photogenerated charge carriers, and ultimately boosts the overall efficiency of the nitrogen reduction reaction (NRR). The unique structure of three-phase interface catalysts promotes the diffusion of reactants and products across the gas–liquid–solid interfaces, reducing diffusion resistance and accelerating reaction kinetics. Furthermore, the interface design optimizes the separation of photogenerated electrons and holes, thereby minimizing recombination losses and enhancing photocatalytic activity.

Through meticulous optimization of the catalyst's surface area and structure, more active sites for N_2 adsorption and activation are made available, resulting in heightened catalytic performance. In conclusion, the strategic engineering of three-phase interface catalysts holds great promise for advancing solar-driven NRR technology. This approach addresses inherent process challenges and advances more efficient and sustainable ammonia synthesis, thereby significantly contributing to the future landscape of green energy.[111,112]

The low solubility and slow diffusion of nitrogen (N_2) in water significantly hinder the efficiency of nitrogen fixation into ammonia (NH_3). Sun *et al.* developed a bio-inspired hierarchical assembly, carbonized loofah sponge@BiOBr–OV/Au (CL@BiOBr–OV/Au), to enhance nitrogen diffusion by immobilizing hydrophilic BiOBr–OV/Au onto a hydrophobic CL sponge. In this case, the AuNPs generated high-energy electrons that were injected into the conduction band of BiOBr–OV, leaving holes in the valence band. The electrons reduce adsorbed N_2, whereas the holes oxidize H_2O. CL@BiOBr–OV/Au formed a triphase interface, enhancing the N_2 supply, light absorption, and nitrogen fixation efficiency through synergistic effects. This hydrophobic CL sponge established an optimized directional pathway for N_2 diffusion to the triphase interface (N_2 gas, H_2O liquid, and BiOBr–OV/Au solid), thereby providing ample N_2 for the photocatalytic reaction and mitigating the slow diffusion of N_2 through the liquid phase. The continuous supply of N_2 effectively captured the generated electrons, preventing electron–hole recombination and facilitating N_2 activation. Incorporating Au nanoparticles broadened the photoresponse range of BiOBr–OV, increased the oxygen vacancy concentration, and improved N_2 adsorption and activation. As a result, CL@BiOBr–OV/Au exhibits outstanding nitrogen fixation performance with high selectivity and recyclability, achieving 2.64 mmol $gcat^{-1}$ h^{-1}, which is 10.2 and 8.0 times greater than that of CL@BiOBr–OV and BiOBr–OV/Au, respectively. This study introduces a practical method for developing bio-inspired triphase catalysts with a directed N_2 transport channel to enhance the nitrogen fixation efficiency and demonstrates significant potential for other reactions involving gas consumption (Fig. 2a–e).[113]

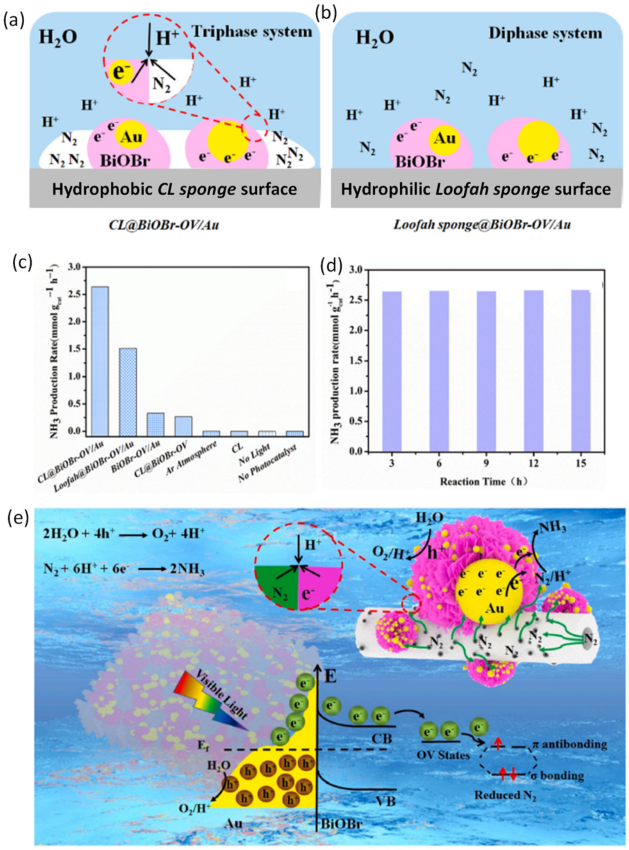

Fig. 2 Schematic illustration of photocatalytic nitrogen fixation in (a) a triphase system of CL@BiOBr–OV/Au and (b) a diphase system of Loofah@BiOBr–OV/Au. (c) Photocatalytic nitrogen fixation activities of CL@BiOBr–OV/Au, loofah@BiOBr–OV/Au, BiOBr–OV/Au, CL@BiOBr–OV, CL and control experiments with loofah@BiOBr–OV/Au. (d) The recycling runs of the photocatalytic nitrogen fixation over CL@BiOBr–OV/Au. (e) Schematic illustration of the N_2 transport and triphase interface, as well as plasmonic hot electron generation, injection, and N_2 reduction processes in the photocatalytic nitrogen fixation with CL@BiOBr–OV/Au under visible light irradiation. Reprinted (adapted) with permission.[113] Copyright 2022, Elsevier.

Photocatalytic NH_3 production from N_2 and H_2O at room temperature and atmospheric pressure offers a safe, clean, and sustainable method for ammonia synthesis. However, the poor solubility and slow diffusion rate of N_2 in water significantly hinder nitrogen activation efficiency. To address this issue, Fan *et al.* (2019) developed a photocatalyst with a hydrophilic–hydrophobic structure, creating a gas–liquid–solid triphase reaction interface. They deposited hydrophilic $Bi_4O_5Br_2$ onto the surface of hydrophobic ZIF-8, forming a novel $Bi_4O_5Br_2$/ZIF-8 composite photocatalyst. In conventional diphase systems, the photocatalyst's surface is fully wetted by the reaction solution, preventing direct contact between the catalyst and air. As a result, only dissolved N_2 is available, which is limited by its poor solubility and slow diffusion rate in water. In contrast, the triphase system supplies N_2 directly from the air phase. The hydrophilic–hydrophobic structure of $Bi_4O_5Br_2$/ZIF-8 creates triphase interfaces, enabling direct N_2 delivery from air to the photocatalytic reaction site, thereby improving electron–hole pair separation and nitrogen fixation performance (Fig. 3a–c). This architecture bypasses the need for N_2 to diffuse through the liquid phase, significantly enhancing the nitrogen fixation rate and the overall efficiency of the photocatalytic process.[114] Chen *et al.* conducted experiments demonstrating that doping MIL-88A with transition metals enhances its responsiveness to visible light by reducing the band gap from 1.93 eV to 1.85 eV for Mn-MIL-88A and 1.78 eV for Zn-MIL-88A. Additionally, the conduction band positions of the synthesized catalysts were favorable for CO_2 reduction and N_2 fixation. The experimental results revealed efficient electron transfer in the doped catalysts, improving charge-separation efficacy and consequently enhancing photoactivity. The poor solubility and slow diffusivity of gases in the aqueous surface layer of the hydrophilic catalyst in the triphase photocatalyst system controlled the product formation rate. Detailed *in situ* studies identified the active reaction intermediates, helping to elucidate a plausible mechanism for the photocatalytic reactions. A systematic comparative study using manganese (Mn) and zinc (Zn) as dopants in an iron-based MOF, MIL-88A, was conducted to address the role of d-orbitals and the poor electron conductivity of MOFs. MIL-88A, a three-

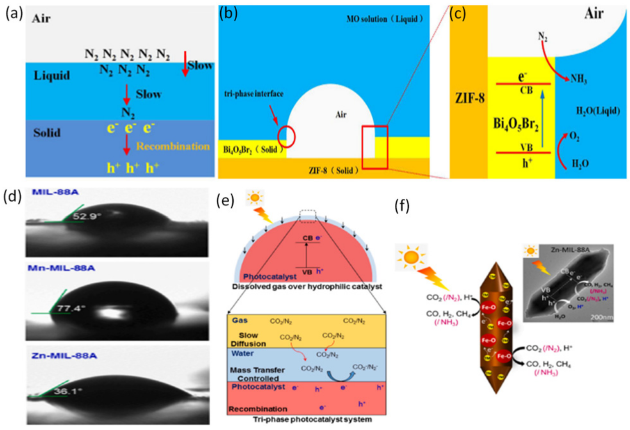

Fig. 3 (a) Schematic illustration of the tri-phase. (b) and (c) Photocatalytic mechanism of $Bi_4O_5Br_2$/ZIF-8 (30%). Reprinted (adapted) with permission.[114] Copyright 2019, Elsevier. (d) Contact angle measurement of water on the tested catalysts. All tested catalysts are hydrophilic and can readily form an aqueous surface layer. (e) Tri-phase photocatalyst system: the schematic displays slow diffusion and poor solubility of CO_2/N_2 in water, which makes the process essentially controlled by mass-transfer, and (f) schematic illustration of charge migration mechanism in Zn-MIL-88A. Here, TM stands for transition metals (*i.e.*, Mn and Zn) doped in MIL-88A. Under illumination, electrons transfer from O^{2-} to Fe^{3+} of pristine MIL-88A. As shown in the schematic, TM acts as the electron donor for Fe–O clusters that substantially facilitates the charge separation efficacy. Reprinted (adapted) with permission.[115] Copyright 2021, Elsevier.

dimensional framework composed of iron(III) octahedral trimers linked to fumarate dianions, is known for being non-toxic, inexpensive, chemically stable, and responsive to visible light. Efficient charge transfer at the interface between the transition metals and semiconductors significantly enhances photocatalyst efficiency. The study investigated the photoactivity of Mn- and Zn-doped MIL-88A for CO_2 reduction and N_2 fixation using water under UV–vis irradiation and ambient conditions. The apparent quantum yield of Zn-MIL-88A was found to be 2.16 times higher than that of pristine MIL-88A. Furthermore, Zn-MIL-88A exhibited the highest NH_4^+ generation rate. Analysis revealed that electrons were efficiently transferred from the doped transition metals to the Fe–O cluster of MIL-88A (Fig. 3d–f). The hydrophilic surfaces of the tested catalysts in the tri-phase photocatalyst system indicated that the process was controlled by mass transport, influencing product distribution and reaction kinetics. Experimental results also demonstrated that incorporating transition metals enhances the stability, charge separation, and overall efficiency of the photocatalysts.[115]

The direct plasmonic photocatalytic nitrogen fixation (P2NRR) method reported by Chen *et al.* converts inert N_2 into NH_3 using solar energy, in which Au nanoparticles (AuNPs) are encapsulated within porous (MOFs) membranes. Upon visible light irradiation, hot electrons generated on AuNPs are injected into N_2 molecules adsorbed on Au surfaces and activated by the localized surface plasmon resonance (LSPR) field, resulting in a supralinear intensity dependence of ammonia evolution with a higher apparent quantum efficiency and lower activation energy under stronger irradiation. The gas-permeable Au@MOF membranes with numerous interconnected nanoreactors ensured AuNP dispersion and stability, facilitated the mass transfer of N_2 molecules and (hydrated) protons, and enhanced plasmonic photocatalytic reactions at the gas–membrane–solution interface. Consequently, an ammonia evolution rate of 18.9 mmol g_{Au}^{-1} h^{-1} was achieved under visible light (>400 nm, 100 mW cm^{-2}) with an apparent quantum efficiency of 1.54% at 520 nm. Unlike previous systems using plasmonic nanoparticles solely as antennas, each AuNP in the MOF matrix acts as both a photosensitizer and a cocatalyst, harvesting light and generating electrons to catalyze dinitrogen reduction. Synergistic LSPR effects, including electron transfer, energy transfer, and localized electric field polarization, activate the surface-adsorbed N_2 molecules and reaction intermediates. Porous MOF substrates such as UiO-66 stabilize and disperse AuNPs while ensuring their accessibility to N_2 molecules and (hydrated) protons. The specially designed gas–membrane–solution interface increases N_2 availability near the AuNPs, enabling efficient ammonia production under ambient conditions with high efficiency.[116]

Photocatalytic N_2 fixation provides a low-cost route to generate ammonia, although poor photon-to-ammonia conversion efficiency due to the low N_2 concentration hinders its progress. Herein, we demonstrate a photocatalyst with surface oxygen vacancies (Vo) and F-modified surfaces that facilitate N_2 adsorption and activation on the catalyst surface. The Vo sites promoted the chemical adsorption of N_2 and electron transfer from the catalyst to N_2, whereas F modification altered the TiO_2 surface properties from hydrophilic to aerophilic, enhancing N_2 adsorption (Fig. 4a). This modification suppresses the hydrogen evolution reaction (HER), as protons struggle to adsorb onto the F-capped surfaces. Consequently, the optimal NH_3 production rate reaches 206 μmol h^{-1} g^{-1}, approximately 9 times higher than that of pure TiO_2 nanoparticles (~23 μmol h^{-1} g^{-1}) (Fig. 4b and c). Introducing oxygen vacancies onto the

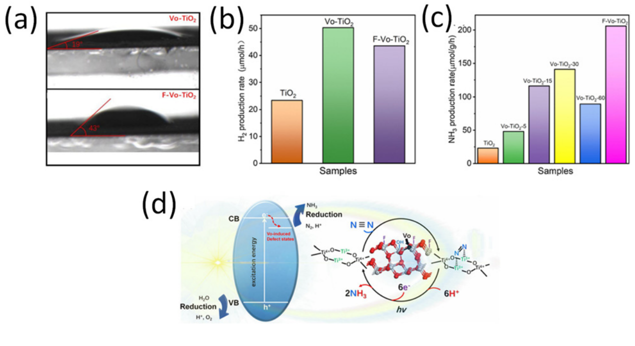

Fig. 4 (a) Contact angle measurement of water on Vo–TiO_2 and F–Vo–TiO_2. (b) H_2 production rate of pristine TiO_2, Vo–TiO_2 and F–Vo–TiO_2; (c) NH_3 production rate of pristine TiO_2, Vo–TiO_2-*n* (*n* = $NaBH_4$ treatment time) and F–Vo–TiO_2; (d) photocatalytic N_2 fixation mechanism on the surface of hydrophobic treated defective TiO_2 NPs with F and Vo. Reprinted (adapted) with permission.[117] Copyright 2021, Elsevier.

TiO_2 surface *via* $NaBH_4$ treatment creates active sites for high N_2 adsorption and activation. The modification of F changed the surface wettability to form an aerophilic surface, enriching N_2 molecules on the catalyst surface and limiting proton adsorption, thereby slowing the HER. Both experimental and theoretical calculations confirmed that oxygen vacancies enhance N_2 chemical adsorption and electron transfer, whereas F modification facilitates N_2 physical adsorption, leading to an NH_3 production rate approximately 10 times higher than that reported for TiO_2 samples. This strategy effectively overcomes mass-transfer limitations and achieves high conversion efficiency, as shown in Fig. 4(c). The detailed mechanism for photocatalytic N_2 fixation on the hydrophobic surface of treating defective TiO_2 NPs with F and Vo is shown in Fig. 4(d).[117]

Lee *et al*. designed an advanced three-phase boundary (TPB) engineered PNRR system using oxygen-vacant TiO_2 photocatalysts embedded in poly(*N*-isopropyl acrylamide) (PNIPAm). The oxygen vacancies in the TiO_2 lattice generate Ti^{3+} species that function as active sites. The physicochemical properties of PNIPAm, including its porosity and hydrophilic–hydrophobic nature, change with the environmental temperature, thus adjusting the relative concentrations of N_2 and H_2O around the oxygen-vacant TiO_2 photocatalysts for an efficient TPB. TiO_2 with PNIPAm exhibited a significantly high NH_3 production rate (11.12 μmol g^{-1} h^{-1}) at the lower critical solution temperature (LCST; 32 °C). This study is the first to combine the defect engineering of TiO_2 photocatalysts and TPB engineering using a thermoresponsive polymeric hydrogel for effective PNRRs. Experimental results indicated that the Sollen-collapsed transition of PNIPAm controls the mass transfer of reactants (N_2 and H_2O) around the photocatalyst, with TiO_2 Vo@PNIPAm showing reversible switching of its surface characteristic from hydrophilic to hydrophobic depending on the temperature. This transition changed the pore size of the PNIPAm network, thereby enhancing NH_3 production. At the LCST, TiO_2 Vo@PNIPAm exhibited a hydrophobic contact angle (CA) of 110°, compared to a hydrophilic CA of 66° below the LCST and a predominantly hydrophobic CA of 130° above the LCST. These temperature-dependent changes in PNIPAm's physicochemical properties increase the relative concentration of N_2 around the photocatalyst, forming abundant TPBs for enhanced NH_3 production.[55]

Sun *et al*. suggested modifying defective TiO_2 surfaces with alkyl acids with different carbon chain lengths (C2, C5, C8, C11, and C14) to adjust the surface properties of the catalyst. The presence of defect sites notably boosts N_2 adsorption and activation, whereas the wettability of the catalyst can shift from hydrophilic to hydrophobic depending on the length of the alkyl chain. A hydrophobic surface enhances N_2 adsorption and local concentration owing to its aerophilic characteristics, and simultaneously decreases proton adsorption, thereby reducing the HER. This combined effect significantly advanced the nitrogen reduction reaction (NRR). Among the modified samples, *n*-octanoic acid-defective TiO_2 (C8–Vo–TiO_2; Vo = oxygen vacancy) demonstrated the best NRR performance, with an ammonia production rate reaching up to 392 μmol g^{-1} h^{-1}. This paper presents a novel approach for efficient ammonia synthesis at a three-phase interface using photocatalyst technology.[118]

Photoelectrochemical nitrogen reduction reaction (PEC NRR) is a gas-consuming reaction in which the diffusion rate of N_2 molecules significantly affects the reaction efficiency. Traditional two-phase NRR catalytic systems reduce N_2 molecules dissolved in the electrolyte to NH_3. However, owing to the low solubility of N_2 and slow diffusion in the electrolyte, there is an insufficient supply of N_2 on the catalyst surface. Additionally, a high concentration of H^+ in the liquid phase enhances the hydrogen evolution reaction (HER), thereby limiting the NRR efficiency. A feasible strategy for enhancing the NRR is to transfer gaseous N_2 directly to the photoelectrochemical reaction interface *via* a hydrophobic surface, thereby increasing the N_2 concentration and reducing the H^+ concentration at the reaction center. The hydrophobic interface provides an efficient three-phase reaction interface for N_2 (gas), the electrolyte (liquid), and the catalyst (solid). Nanocomposites (SNP/MSO) were prepared by loading hydrophilic SnO_2 nanoparticles (SNP) onto hydrophobic MoS_2 (MSO) surface-modified with silicomolybdic acid. This hydrophobic interface eliminates the N_2 transport barrier in the liquid phase to the reaction center, inhibits the HER by lowering the contact area with liquid protons, and accelerates effective electron transfer through the heterojunction structure formed between MSO and SNP. This synergistic effect results in a high NH_3 yield (19.6 μg h^{-1} mg^{-1}) and a faradaic efficiency (FE) of 40.34% for SNP/10MSO in the PEC system. Compared with the nanocomposites (SNP/MSI) prepared using hydrophilic MoS_2, the FE increased by 10 percentage points, demonstrating the effectiveness of the hydrophobic interface and heterojunction structure in enhancing the PEC NRR efficiency, as shown in Fig. 5(a–c).[119]

4.2. Photo/photoelectrocatalytic O_2 reduction

H_2O_2 is widely used as a clean oxidant in various industries such as organic synthesis, water treatment, and pulp bleaching. Photocatalysis offers an eco-friendly method for H_2O_2 production, in which photogenerated electrons reduce O_2 to form H_2O_2 and the holes oxidize water or other hole scavengers, such as ethanol or formic acid. Traditionally, this reaction occurs at the solid–liquid interface, where O_2 must diffuse from the liquid phase, which has a low concentration and diffusion coefficient. This limited interfacial O_2 concentration often leads to significant recombination of photogenerated electron–hole pairs, resulting in low electron utilization efficiency and hindering of the efficiency of the reaction under high light intensity. To address this issue, conducting photocatalytic reactions at a gas–liquid–solid interface is a rational solution. The O_2 concentration in the gas phase at this triphase interface is much higher than that in water, and O_2 can be delivered to the catalyst surface at a diffusion rate significantly higher than that in water. This setup facilitates rapid O_2 reduction, overcomes the sluggish O_2 supply in the aqueous

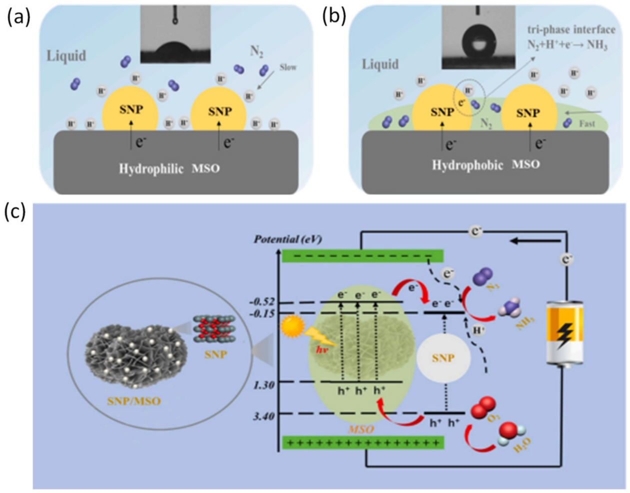

Fig. 5 Schematic diagram of the three-phase reaction interface of N_2, electrolyte and catalyst (a) hydrophilic interface and (b) hydrophobic interface. (c) Schematic diagram of the SNP/MSO heterostructure PEC NRR mechanism. Reprinted (adapted) with permission.[119] Copyright 2022, Elsevier.

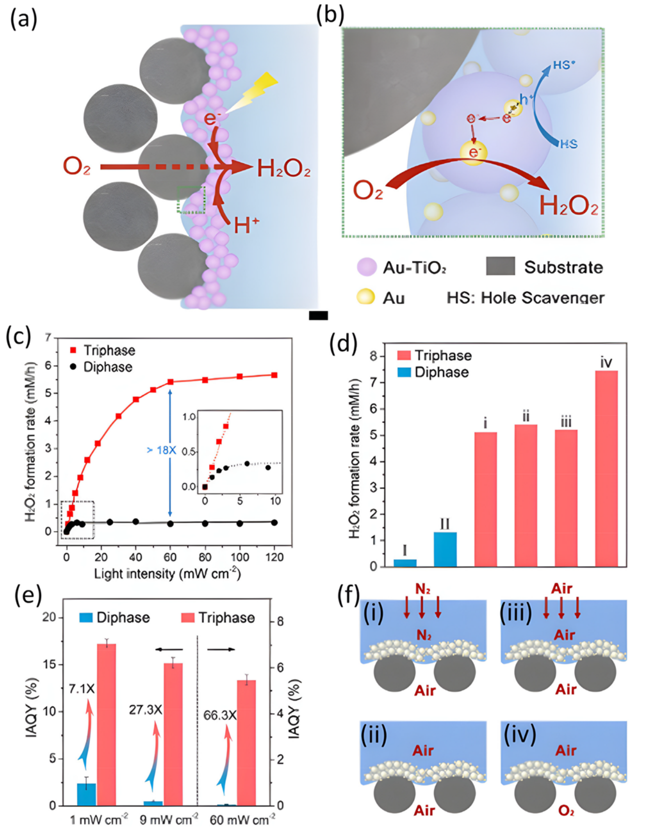

Fig. 6 (a) Schematic representation of the triphase system for plasmonic photocatalytic synthesis of H_2O_2. (b) Enlarged view of the reaction zone with an air–liquid–solid triphase interfacial microenvironment where reactant O_2 is available directly from the air phase. Based on such a triphasic system, the enhanced accessibility of electron acceptor O_2 to the catalysts can effectively suppress the recombination of photo-generated charge carriers and boost the photocatalytic reaction. Reprinted (adapted) with permission.[121] Copyright 2021, Elsevier. (c) Rate of H_2O_2 formation under different light intensities using triphase (red line) and diphase (dark line) systems. (d) H_2O_2 formation rates based on different operational conditions using these two systems under illumination of 60 mW cm^{-2}. (e) IAQYs for the two systems under 1 mW cm^{-2}, 9 mW cm^{-2}, and 60 mW cm^{-2} illumination. Data of IAQYs for 1, 9, and 60 mW cm^{-2} illumination are 17.29 ± 0.44, 15.23 ± 0.57, and 5.49 ± 0.21, respectively, in the triphase system and 2.45 ± 0.64, 0.55 ± 0.08, and 0.08 ± 0.009, respectively, in the diphase system. (f) Schematic illustration of the H_2O_2 formation rates based on different operational conditions (i, ii, iii, and iv). Reprinted (adapted) with permission.[100] Copyright 2019, Elsevier.

phase, and promotes the separation of electron–hole pairs by forming reactive oxygen species, thus enhancing the photocatalytic kinetics. Additionally, O_2 from air can reach the reaction interface through an atmosphere-connected porous substrate without the need for aeration support. Therefore, photocatalysts with porous structures, chemical stabilities, and hydrophobic properties are ideal candidates for the formation of stable triphase boundaries and efficient air-diffusion channels.[120]

Au nanoparticle-decorated TiO_2 (Au–TiO_2) has garnered attention as a visible-light-active photocatalyst, although its efficiency has been constrained, particularly under visible-light irradiation. Feng *et al.* introduced an effective triphasic photocatalytic system for visible-light-driven H_2O_2 synthesis using Au–TiO_2.[121] This system operates at an air–liquid–solid triphasic interface, allowing for a direct and ample supply of O_2 from the ambient atmosphere, which significantly increases its concentration at the reaction site. This triphasic photocatalytic system enhances reaction kinetics and results in a higher steady-state H_2O_2 concentration. Remarkably, only one-tenth of the light intensity is required to achieve a comparable H_2O_2 formation rate to that of conventional diphasic systems (Fig. 6a and b). This triphasic approach provides a novel platform for exploring intrinsic photocatalyst kinetics and plasmonic mechanisms. The triphase system allows O_2 to diffuse directly from the air phase to the reaction interface, rather than through slow diffusion in the liquid phase. This interface architecture significantly increases the photocatalyst's accessibility to O_2, enhancing the reaction rate between O_2 and photogenerated electrons, suppressing electron–hole recombination, increasing charge utilization efficiency, and reducing degradation reactions between H_2O_2 and photogenerated electrons, thereby greatly enhancing H_2O_2 production rates. Inspired by nature, the same group fabricated superhydrophobic substrates by utilizing the cooperative effect of low surface energy and rough surface structure. They constructed a triphase photocatalytic interface architecture by immobilizing Au-decorated TiO_2 nanoparticles onto a polytetrafluoroethylene-treated superhydrophobic porous membrane composed of carbon fiber. The interface environment generally governs the performance of interfacial catalytic reactions. The interfacial environment plays a critical role in the performance of interfacial catalytic reactions. In this study, the authors overcome these limitations by introducing a reaction system that utilizes an air–liquid–solid triphase interface to optimize the conditions and thereby significantly enhance the catalytic activity (Fig. 6c–f).[100]

The triphenylbenzene–dimethoxyterephthaldehyde covalent organic framework (TPB–DMTP-COF) demonstrated high activity for H_2O_2 generation by reducing O_2 in pure water under visible light irradiation. Importantly, a triphase reaction interface was created by exploiting the hydrophobic nature of this polymeric semiconductor, which was achieved by immobilizing TPB–DMTP-COF onto porous carbon fiber paper. Owing to the hydrophobic nature of the TPB–DMTP-COF immobilized on the porous carbon fiber paper, a triphase reaction interface was created. This configuration achieved a record H_2O_2 generation rate of 2882 μmol gcat^{-1} h^{-1}, surpassing diphasic systems by 15 times. Enhanced mass transfer of O_2 through the porous carbon support elevated O_2 levels at the triphase interface, facilitating improved separation of charge carriers (holes and electrons) and enhancing photocatalytic kinetics. TPB–DMTP-COF operates effectively across a wide pH range without sacrificial agents and maintains long-term photochemical stability. Density functional theory calculations identified the triphenylbenzene moiety as the primary site for O_2 activation and electron transfer. This COF-based photocatalyst achieved a solar-to-chemical conversion efficiency of 0.76% for H_2O_2 generation. Its hydrophobic and mesoporous properties enable the formation of a gas–liquid–solid triphase interface, boosting H_2O_2 production to approximately 2.9 mmol gcat^{-1} h^{-1} by mitigating O_2 mass-transfer limitations in water. Theoretical and photoelectrochemical analyses confirmed that the increased yield stems from enhanced mass transfer and higher interfacial O_2 concentration, validating the triphenylbenzene component as the reactive site (Fig. 7a–g).[122]

Recently, Lou *et al*. designed a two-layered (2L) Janus fiber membrane photocatalyst with asymmetric hydrophobicity for efficient H_2O_2 production. The top layer consists of superhydrophobic PTFE fibers with dispersed modified carbon nitride (mCN) photocatalyst, onto which an amphiphilic Nafion (Naf) ionomer was sprayed to achieve moderate hydrophobicity, featuring both hydrophobic –CF2 and hydrophilic $-SO_3^-$ groups (Fig. 8a). The bottom layer consists of highly hydrophobic PTFE fibers, while the top layer modulates its hydrophobicity. This configuration ensured that most of the mCN was exposed at the gas–liquid–solid interfaces, enhancing the mass transfer of gaseous O_2 within the membrane and increasing the local O_2 concentration near the mCN photocatalyst (Fig. 8b and c). Consequently, the optimized 2 L-mCN/F-Naf membrane achieved a remarkable H_2O_2 production rate of 5.38 mmol g^{-1} h^{-1} under visible light irradiation.[123]

Developing high-performance bio-photoelectrochemical (bio-PEC) assay systems requires bio-photoelectrodes with rapid charge- and gas-phase mass-transport capabilities. Chen *et al*. demonstrated a solid–liquid–air triphase bio-photoelectrode (TBP-electrode) by immobilizing glucose oxidase (GOx), a model enzyme, onto one-dimensional single-crystalline TiO_2 nanowire arrays grown on a superhydrophobic carbon textile substrate. This triphase configuration allows continuous oxygen supply from the air phase to enhance enzymatic reactions, thereby improving oxidase kinetics. In addition, the photogenerated electrons are rapidly transported and efficiently collected along the TiO_2 nanowire arrays. Our TBP electrode system showed a detection range 100 times greater than that of conventional diphase bio-photoelectrodes, with sensitivity over 10 times higher and detection limits 30 times lower than those of nanoparticle-based TBP-electrodes. The bio-PEC assay operates at a low potential (+0.1 V *vs.* Ag/AgCl), approximately 0.5 V lower than traditional electrochemical systems, making it resistant to many easily oxidizable interferences. This triphase

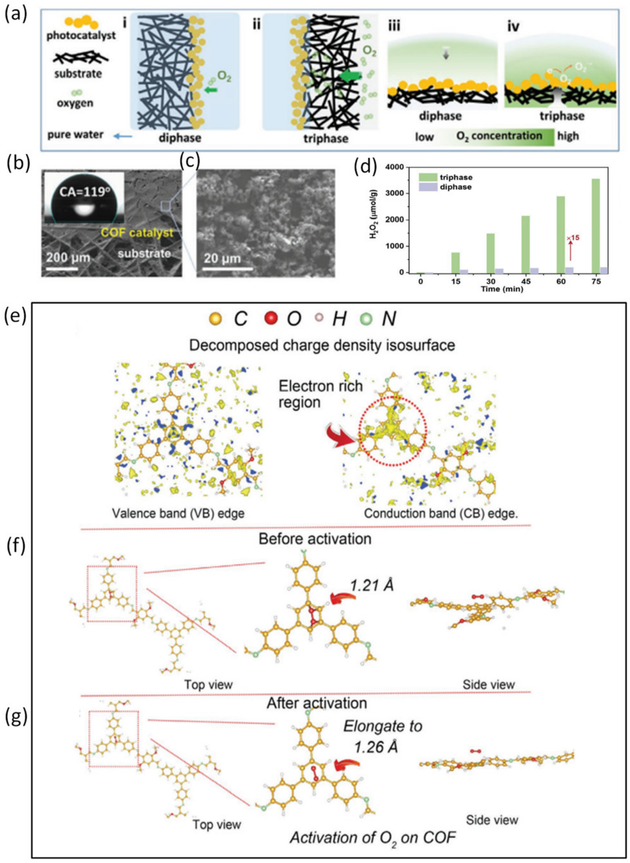

Fig. 7 Photocatalytic O_2 reduction in a triphase system. (a) Schematic illustration of the diphase and triphase photocatalytic conditions. Photocatalytic H_2O_2 generation in a (i) diphase system (pure water pre-saturated with oxygen) and in a (ii) triphase system. The local oxygen concentration at the catalyst surface for the (iii) diphase and (iv) triphase reaction systems. The scale bar indicates the oxygen concentration in the reaction system. (b) The SEM image of polytetrafluoroethylene (PTFE)-treated superhydrophobic carbon paper substrate loaded with TPB–DMTP-COF catalyst. (c) The inset of (b) is the photograph of water droplets placed on CFP loaded with COF catalyst. (d) Time course of H_2O_2 production under different reaction conditions under visible light irradiation in pure water. Theoretical calculations. (e) Decomposed charge density isosurface for the valence band (VB) edge and conduction band (CB) edges. (f) Structure of O_2-COF before activation. (g) Structure of O_2-COF after activation. Carbon atoms are yellow, oxygen atoms are red, hydrogen atoms are white, and nitrogen atoms are green. Reprinted (adapted) with permission.[122] Copyright 2021, John Wiley and Sons.

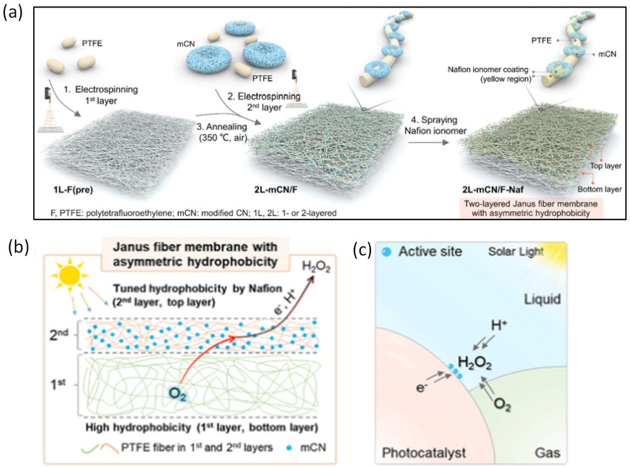

Fig. 8 (a) Schematic illustration of the synthesis route for the Janus 2L-mCN/F-Naf fiber membrane. Note that the aluminum (Al) foil substrate supporting the membrane is omitted for clarity. (b) Schematic illustration of the two-layered structure of the 2L-mCN/F-Naf fiber membrane and its advantageous features. (c) Schematic illustration of TPI in the 2L-mCN/F-Naf fiber membrane for photocatalytic O_2 reduction to H_2O_2. Reprinted (adapted) with permission.[123] Copyright 2024, American Chemical Society.

bio-PEC assay system presents a powerful platform for environmental analysis and clinical applications, with its design principles broadly applicable for fabricating other high-performance triphase bio-photoelectrodes.[124]

4.3. Photo/photoelectrocatalytic water reduction

Solar water splitting provides a sustainable and environmentally benign route for the production of a storable chemical fuel in the form of clean hydrogen from sunlight, and has attracted tremendous research interest since the report by Fujishima and Honda in 1972.[125] Superhydrophilic materials significantly enhance photocatalytic water reduction by promoting efficient water interactions and improving the establishment of the TPB between the solid catalyst, liquid water, and gaseous products. This optimized TPB facilitated enhanced charge separation and transfer, leading to improved reaction kinetics and overall photocatalytic performance. Padmanabhan *et al.* reported the morphology-dependent spatial separation of charge carriers in TiO_2 and graphene hybrids were synthesized using a tailor-made hydrothermally modified sol–gel method. TiO_2/graphene hybrids were created at various weight percentages of graphene oxide (GO), with TiO_2 growing *in situ* while GO was simultaneously reduced to reduced graphene oxide (rGO). The hybrids were analyzed for photocatalytic H_2 generation, photodegradation under UV and visible-light irradiation, and photoinduced superhydrophilicity. The spatial charge separation of photogenerated electron–hole pairs in TiO_2 was achieved through exposed crystal facets with different surface potentials, which play a critical role in the TPB between the solid, liquid, and gas phases. The high-energy {010}/{100} and {001} facets of TiO_2 endowed the hybrids with self-cleaning properties, whereas an optimal mix of these high-energy and low-energy {101} facets enhanced H_2 production.[126]

Remarkably, a mere 0.1% w/w graphene loading significantly boosted the photoactivity of the hybrids by establishing a chemical linkage between the {010} facet of TiO_2 and the graphene layers, thus further enhancing the TPB and promoting effective charge separation and hydrogen evolution.[125]

A 2D/2D S-scheme $NiTe_2$/g-C_3N_4 heterojunction was successfully synthesized using an *in situ* deposition strategy with g-C_3N_4 nanosheets as the substrate. In this case, the TPB plays a crucial role in enhancing catalytic performance, particularly in photocatalytic hydrogen evolution reactions. The 2D contact interface between $NiTe_2$ and g-C_3N_4 provides an ideal platform for TPB formation. TPBs facilitate the migration of photogenerated carriers and subsequent redox reactions. Pristine g-C_3N_4 and $NiTe_2$ exhibit WCAs of 8.5° and 121.1°, respectively, highlighting the excellent hydrophilicity of g-C_3N_4. However, the WCA of the $NiTe_2$/g-C_3N_4 composite increases to 149.6°, approaching superhydrophobicity, likely owing to the influence of organic solvents during the *in situ* $NiTe_2$ growth. After mercaptopropionic acid treatment, the WCA of the composite decreases to approximately 0°, indicating the superior superhydrophilicity of $NiTe_2$/g-C_3N_4. Improved hydrophilicity increases the contact area between the liquid phase (water) and solid catalyst surface, thereby optimizing the surface proton reduction reactions occurring at the TPB. This enhanced hydrophilicity promotes selective contact between reactant molecules and catalytic active sites, thereby boosting hydrogen evolution reaction (HER) activity. Moreover, S-scheme charge transfer minimized carrier recombination while maximizing redox potential. Enhanced hydrophilicity further improves H_2O adsorption on the catalyst surface, optimizes surface redox kinetics, and boosts the photocatalytic water-splitting performance. Therefore, this study presents a novel strategy for advancing surface redox kinetics and developing efficient and stable 2D/2D semiconductor heterojunction photocatalysts.[127]

Despite its potential as a photocatalyst, pristine graphitic carbon nitride (g-C_3N_4) suffers from limited light absorption, insolubility, small specific surface area, and rapid electron–hole pair recombination. This study addresses these issues by developing a hydroxyl-grafted oxygen-linked tri-s-triazine-based polymer (HGONTP) through the polycondensation of hydrothermally pretreated dicyandiamide (DCDA) by the Luo group. By adjusting the degree of cyclization and hydrolysis of DCDA, the content of C–O–C linkers and terminal OH groups in the HGONTP could be controlled by replacing the pendant NH_2 groups with OH groups. The resulting oxygen species of the HGONTP photocatalyst affected the hydrophilicity and facilitated the photoexcited separation of charge carriers. Moreover, HGONTP exhibits exceptional light absorption from UV to near-IR, a narrow band gap of 2.18 eV, a large specific surface area of 96.1 m^2 g^{-1}, and reduced charge recombination. Consequently, HGONTP demonstrates a hydrogen evolution rate 27.7 times higher than that of pristine g-C_3N_4 (6.54

versus 0.236 mmol g^{-1} h^{-1}), with apparent quantum yields of 12.6% at 420 nm and 4.1% at 500 nm. This innovative approach opens new avenues for the development of a HGONTP, enhances hydrophilicity, and facilitates the formation of a three-phase boundary (TPB) that significantly improves the separation of photoexcited charge carriers and promotes hydrogen evolution reaction (HER) efficiency.[128] An optimal reaction environment at the water–catalyst interface is essential for high-efficiency semiconductor-based water splitting. Traditionally, the hydrophilic surface of a semiconductor catalyst has been considered crucial for effective mass transfer and proper water contact. Recently, Jiang *et al.* developed a superhydrophobic PDMS–Ti^{3+}/TiO_2 (P–TTO) interface with nanochannels formed by nonpolar silane chains that significantly enhanced the TPB interactions. Remarkably, the P–TTO interface achieved a tenfold increase in water-splitting efficiency under both white light and simulated AM1.5G solar irradiation compared with the hydrophilic Ti^{3+}/TiO_2 (TTO) interface. Additionally, the electrochemical water splitting potential on the P–TTO electrode decreased from 1.62 V to 1.27 V, approaching the thermodynamic limit of 1.23 V. *In situ* diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) detected a nanochannel-induced water configuration transition, and density functional theory (DFT) calculations confirmed the lower reaction energy at the water/PDMS–TiO_2 interface. This work demonstrates that efficient overall water splitting can be achieved through nanochannel-induced water configurations without altering the bulk properties of the semiconductor catalyst, highlighting the significant impact of the interfacial water status on the water-splitting reaction efficiency. The P–TTO catalyst, with its superhydrophobic surface, showed over 13.5 times improvement under white light and 8.7 times under AM1.5G simulated solar irradiation, with reduced reaction potentials for both the oxygen evolution reaction (OER) and overall water splitting, compared to untreated TTO.[129]

A novel high-performance photoelectrochemical (PEC) water oxidation photoanode material, a Co-nanoparticle-modified Ti_3C_2 MQD (Co-MQD) Schottky catalyst, was rationally designed, demonstrating significantly enhanced PEC water oxidation performance.[130] The Co content in the Co-MQD product could be efficiently controlled by optimizing the ion thermal anchoring temperature of the initial cobalt precursor. The surface plasmon effect introduced by the cobalt terminals broadened the optical response properties of the Co-MQDs. Acting as water oxidation reaction centers, the cobalt terminals effectively accelerated the surface water oxidation kinetics of the pristine MQD. Moreover, the Schottky junction introduced by the Janus Co-MQDs enhances the photogenerated carrier separation and injection efficiency. Consequently, the Co-MQD-48 Schottky-catalyst exhibits a boosted photocurrent density of 2.99 mA cm^{-2} and a carrier migration efficiency of 87.56%, representing improvements of 194% and 236%, respectively, compared to the pristine MQD. After 10 hours of cycling, a photocurrent density of 2.79 mA cm^{-2} is maintained, confirming the good photostability of Co-MQD. This outstanding PEC performance is among those of the state-of-the-art photoanode materials. The Janus structure photocatalysts, characterized by their dual-sided morphology with distinct chemical or physical properties, play pivotal roles in optimizing TPBs during photocatalytic reactions as well as improving mass transfer and charge separation for photoenergy conversion applications.

5. Challenges and future perspectives

Controlling TPBs in photocatalytic systems presents several challenges that directly affect catalytic efficiency. One of the primary difficulties lies in the precise engineering of the TPB interfaces to ensure optimal contact among the solid catalyst, liquid reactant, and gaseous reactant. Achieving a uniform distribution and stable maintenance of these interfaces is crucial for maximizing the active surface area and facilitating efficient charge transfer. The inherent complexity of multi-phase interactions often leads to issues such as poor wettability, agglomeration of catalysts, and formation of non-uniform active sites, all of which can significantly reduce catalytic performance.

Another challenge is the stability of the TPBs under operational conditions. Photocatalytic processes, particularly those involving nitrogen reduction, oxygen reduction, and water splitting, often require harsh environments such as high temperatures, extreme pH values, and intense illumination. These conditions can degrade the catalyst and disrupt the integrity of the TPB, leading to decreased efficiency and shorter operational lifetimes. Moreover, the dynamic nature of photocatalytic reactions can cause continuous changes in the TPB configuration, which complicates the control and optimization of these systems.

Several future research directions can be explored to address the challenges in enhancing TPB performance. One promising avenue is the development of advanced materials with tailored surface properties to promote stable and uniform TPBs. For instance, the incorporation of superwetting materials, which we previously reviewed in the context of organic pollutant degradation, could be extended to TPB applications. Potential innovations include superwettability-patterned, superwettability-responsive, Janus (super)wettable, slippery wettable, and superamphiphobic photocatalysts. These advanced materials offer promising capabilities for TPB-related applications and can significantly enhance catalytic performance through improved surface interactions.[131–136] These materials significantly improve wettability and ensure better contact between different phases, which enhances overall photocatalytic efficiency. Another important research avenue is the use of nanostructured catalysts. Nanostructures offer high surface-area-to-volume ratios and can be engineered to possess specific surface properties conducive to stable TPB formation. For example, the design of catalysts with hierarchical structures can facilitate the simultaneous presence and interaction of all three phases at the nanoscale, leading to more efficient charge separation and transfer.

Integrating advanced characterization techniques and computational modeling can provide deeper insights into the TPB dynamics and guide the rational design of more effective photocatalytic systems. *In situ* characterization methods can be used to monitor the real-time behavior of TPBs under operational conditions, revealing critical information about phase interactions and catalyst stability. Coupled with computational models, these insights can help predict optimal TPB configurations and identify key parameters for enhancing the catalytic performance.

Moreover, the integration of advanced reaction devices that optimize the interactions between the solid, liquid, and gas phases is essential to maximizing the potential of TPBs in photocatalysis. Innovative designs, such as structured photoreactors and flow reactors, facilitate enhanced mass transfer and improved light penetration, which increases the effectiveness of TPBs. For example, microfluidic devices can create controlled environments that enable the precise manipulation of dynamics at the TPB, resulting in significantly improved reaction rates and selectivities.[137–139] Additionally, the incorporation of novel materials, such as nanostructured photocatalysts with maximized surface areas, can further increase the availability of TPBs.[140] This strategy not only addresses current challenges in photocatalytic efficiency but also lays the groundwork for future advancements in sustainable energy and environmental remediation technologies. The development of such reaction devices is critical for overcoming the existing limitations and optimizing the roles of TPBs in photocatalytic processes.

Finally, exploring hybrid systems that combine photocatalysis with other catalytic processes, such as electrocatalysis or biocatalysis, could offer synergistic effects and new pathways for improving the TPB efficiency. Such hybrid approaches can leverage the strengths of different catalytic mechanisms, leading to more robust and versatile systems capable of operating under a wider range of conditions.

By addressing the current challenges and pursuing future research directions, significant advancements can be made in controlling TPBs, ultimately leading to more efficient and scalable photocatalytic applications. This will not only enhance our understanding of photocatalytic processes but also contribute to the development of sustainable energy solutions and environmental remediation technologies.

6. Conclusions

This review emphasizes the critical roles of TPBs in enhancing the photo/photoelectron catalytic efficiencies of processes such as nitrogen reduction, oxygen reduction, and water splitting. The key strategies for optimizing TPBs include the use of advanced materials with tailored surface properties, nanostructured catalysts, and hybrid catalytic systems. *In situ* characterization techniques and computational modeling provide valuable insights into the dynamic behavior of TPBs, and guide the design of more effective photocatalytic systems.

Despite the challenges of maintaining stable and uniform TPBs under operational conditions, these advancements present promising pathways for improving the catalytic performance. Understanding and controlling TPBs are critical for advancing photo/photoelectrocatalytic processes, particularly nitrogen reduction, oxygen reduction, and water splitting. Control of TPB dynamics can significantly enhance the catalytic efficiency by optimizing the interactions between the solid catalyst, liquid reactant, and gaseous reactant. Despite the challenges posed by the complexity and stability of TPBs under operational conditions, innovative material designs, nanostructuring, and advanced characterization techniques offer promising pathways to overcome these obstacles. Future research focused on these strategies could lead to substantial improvements in photocatalytic performance, paving the way for more efficient and scalable applications in sustainable energy production and environmental remediation. Understanding and controlling TPBs not only advance the fundamental science of photocatalysis but also drive technological innovations essential for addressing global energy and environmental challenges.

Author contributions

Lagnamayee Mohapatra: conceptualization and writing – original draft preparation; Lekha Paramanik: review and editing. Subhashree Sabnam: review and editing; Seung Hwa Yoo: conceptualization, review & editing, project administration, and funding acquisition.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) (NRF-2022R1I1A3064533, RS-2023-00221529) and Commercialization Promotion Agency for R&D Outcomes (COMPA) grant funded by the Korean Government (Ministry of Science and ICT) (RS-2023-00304743).

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