

Progress in TiO₂ nanostructures for photocatalytic H₂ production from water: materials modification, interfacial regulation, and systematic development

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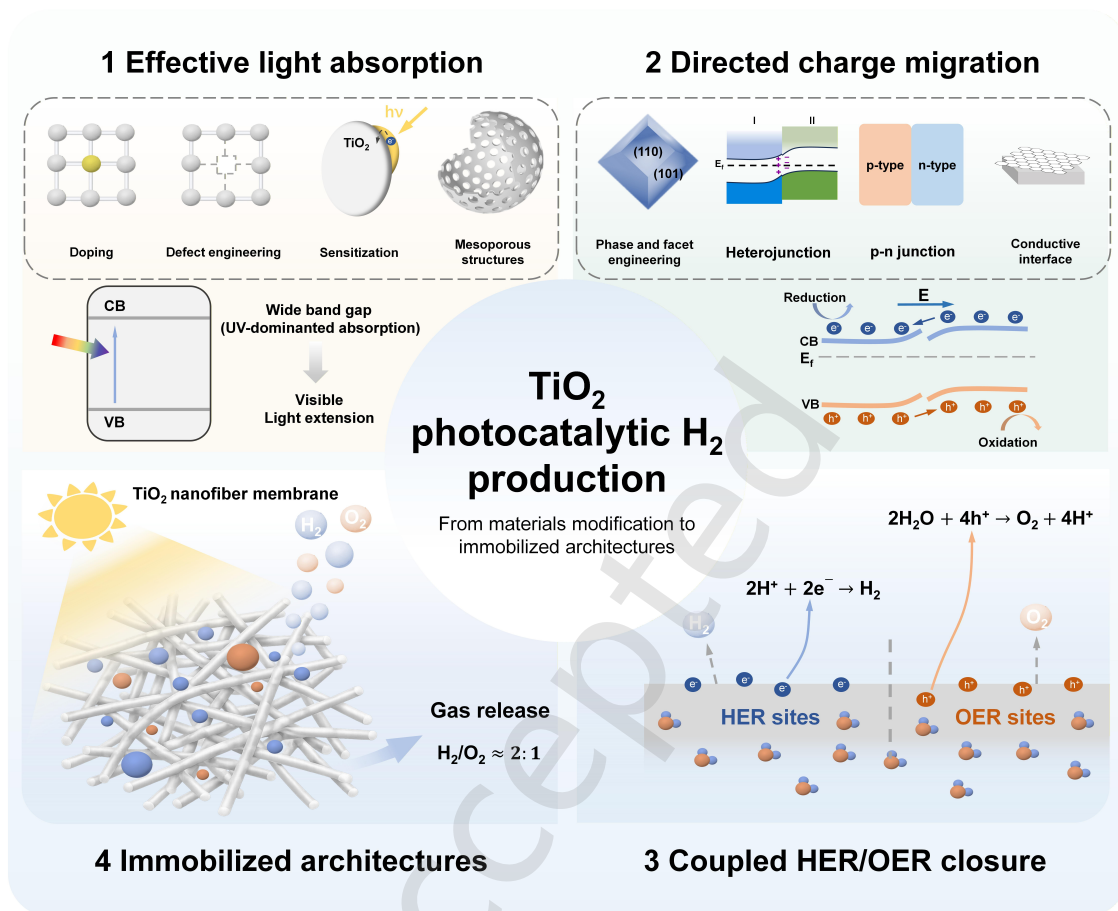
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Using TiO₂ nanostructures as the organizing platform, this review is structured around four connected aspects of photocatalytic H₂ production: effective light absorption, directed charge migration, coupled HER/OER closure, and immobilized architectures. This framework links materials modification and interfacial regulation with TiO₂ nanofiber membranes and related immobilized systems, highlighting how improved absorption, charge transport, and reaction site organization can support stoichiometric H₂/O₂ evolution, gas release, and stable photocatalytic operation.

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ABSTRACT: Titanium dioxide (TiO₂) has long served as both a model photocatalyst and an interfacial scaffold for photocatalytic H₂ production because of its stable oxide lattice, well-defined band structure, and tunable nanoscale morphology. In this review, sacrificial H₂ evolution denotes reduction-side H₂ generation assisted by a hole scavenger; photoreforming couples organic-substrate oxidation with H₂ generation and may derive hydrogen from water, the substrate, or both; and overall water splitting (OWS) uses water as the sole redox substrate and requires simultaneous H₂ and O₂ evolution near a 2:1 molar ratio. TiO₂-based systems now emphasize coupled control of absorption states, directional charge migration, atomic- or nanoscale reaction sites, and immobilized mass-transfer architectures. Their principal losses arise from insufficient light absorption, carrier recombination, HER/OER kinetic mismatch, H₂/O₂ back reaction, bubble retention, and gas management. This review evaluates doping and defect engineering, sensitized absorption, crystal-phase and facet regulation, heterointerfaces, cocatalysts, and nanofiber or immobilized structures through linked criteria: effective absorption, directional migration, HER/OER closure, gas desorption and recovery, long-term stability, and reaction-boundary consistency. The resulting framework uses evidence strength to interpret performance across different reaction regimes.

KEYWORDS: TiO₂ nanostructures; photocatalytic H₂ production; defect engineering; heterointerfaces; cocatalysts; immobilized photocatalytic systems

1 Research background and reaction boundaries of TiO₂ photocatalytic H₂ production

1.1 Advantages and limitations of TiO₂ as a model material for photocatalytic H₂ production

Driven by renewable energy utilization and green hydrogen development, photocatalytic H₂ production from water directly converts solar energy into chemical energy and represents an important direction in solar-fuel research [1, 2]. Among semiconductor materials, TiO₂ has become one of the most representative model systems for photocatalytic H₂ production because of its high stability, well-defined structure, and tunable interfacial chemistry. For nanoscience and nanotechnology, TiO₂ is especially useful because nanotubes, nanosheets, nanofibers, phase-junction particles, and atomic sites provide resolvable platforms for connecting nanostructure, interfacial processes, and photocatalytic function. The central role of TiO₂ can be traced to the classic experiment by Fujishima and Honda, who achieved photoelectrochemical water splitting with a TiO₂ electrode [3]. Its well-defined band structure, stable oxide lattice, and

rich surface hydroxyl chemistry provide benchmarks for analyzing carrier migration, surface water reactions, and interfacial charge transfer [4, 5]. TiO₂ also possesses substantial structural tunability. Ordered nanotube arrays provide axial charge transport pathways [6], whereas anatase nanosheets with a high proportion of {001} facets help regulate reaction sites and spatial charge distribution [7, 8]. TiO₂ is both a model semiconductor for studying light absorption, carrier migration, and interfacial reactions and a stable oxide platform for constructing interfaces in composite systems involving narrow-band-gap semiconductors, metal cocatalysts, MXenes, and carbon materials.

Several reviews provide complementary context for TiO₂ nanostructure design. One-dimensional TiO₂ materials have been surveyed across environmental and energy applications, broader reviews compare 0D–3D TiO₂ architectures and modification routes for light-driven H₂ production, and nanotube-focused work summarizes hydrothermal, solvothermal, template-assisted, and anodic-oxidation routes for solar water splitting [9–11]. The present review extends this literature through an organizing framework centered on reaction boundaries, evidence

strength, and connections from nanostructure to system performance.

Over several decades, TiO_2 has evolved from a single ultraviolet-responsive semiconductor into a stable oxide backbone in nanotubes, facet-controlled particles, and photocatalytic systems with different crystal phases [6–8, 12]. In composite systems, it also functions in electron transport, interfacial support, and cocatalyst anchoring. However, when material-structure regulation is extended toward immobilized systems and sacrificial-agent-free OWS, TiO_2 remains jointly limited by its wide band gap, carrier recombination, HER/OER kinetic mismatch, H_2/O_2 back reaction, and gas management [4, 5]. Although particulate photocatalyst panels and 100 m^2 -scale solar H_2 production systems have provided important references for engineering scale-up of photocatalytic water splitting [13, 14], they do not directly prove that TiO_2 material systems have been applied at the same scale or overcome the intrinsic limitations of OWS.

Rather than providing another catalogue of TiO_2 doping,

defect, and heterojunction strategies, this review reorganizes the literature according to reaction boundaries and the strength of the supporting evidence. Sacrificial H_2 evolution primarily probes reduction-side electron utilization and hydrogen evolution reaction (HER) sites. Photoreforming requires discrimination of the contributions from water and organic substrates to the origin of evolved hydrogen. Sacrificial-agent-free overall water splitting (OWS) requires closure of both the HER and oxygen evolution reaction (OER) half reactions, direct O_2 detection, and H_2/O_2 stoichiometry. On this basis, materials design is discussed at four levels: effective absorption states, directional migration, atomic- or nanoscale reaction sites, and immobilized architectures for mass transfer. The framework clarifies which limiting step is addressed by each nanostructure design.

Figure 1 links materials modification, interface regulation, and system-level evaluation, and summarizes the design logic by which TiO_2 -based photocatalytic H_2 production can progress from a model semiconductor to a verifiable and scalable system.

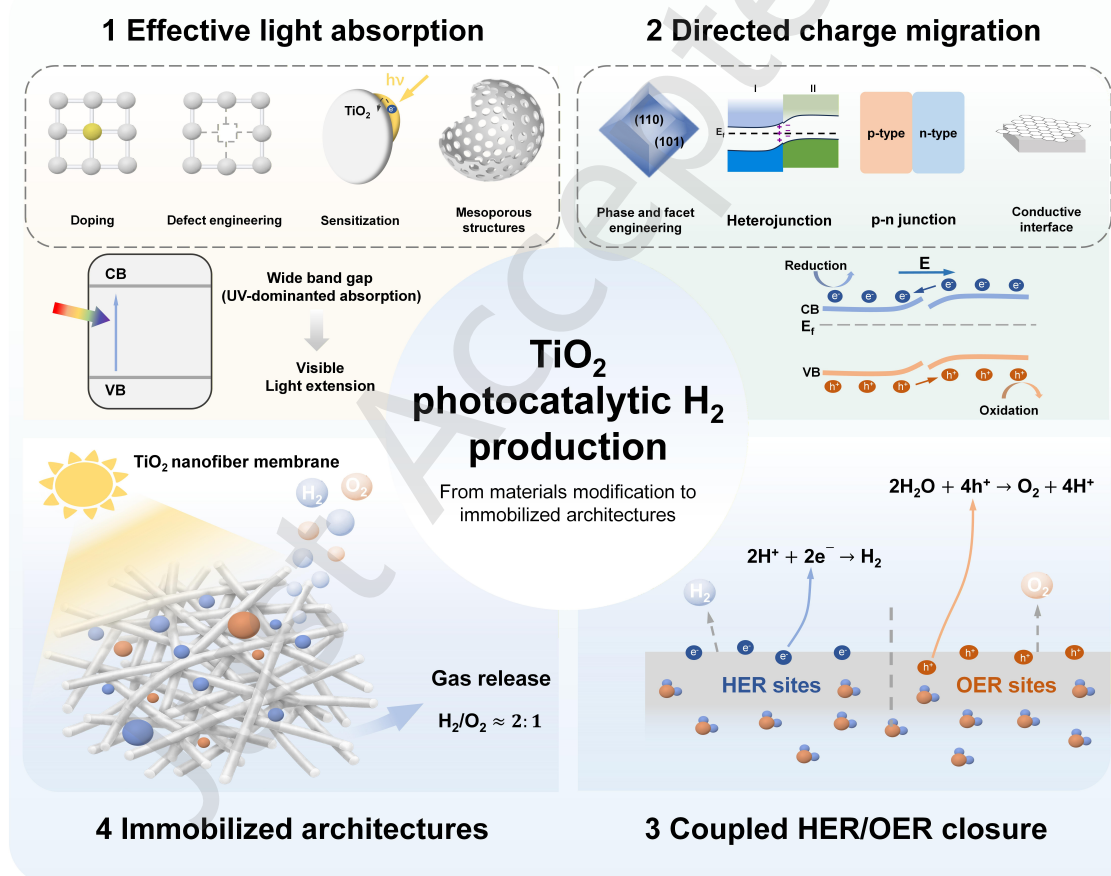


Figure 1 Overall roadmap of TiO_2 -based photocatalytic H_2 production from water. The figure centers on the TiO_2 model platform and summarizes effective light absorption, directional charge migration, HER/OER active sites, immobilized structures, bubble detachment, and gas recovery.

1.2 Distinguishing the boundaries among sacrificial H_2 evolution, photoreforming, and overall water splitting

Research on TiO_2 photocatalytic H_2 production is often based on sacrificial-agent-assisted H_2 evolution. Methanol, ethanol, triethanolamine, lactic acid, sulfide/sulfite, and related sacrificial agents preferentially consume photogenerated holes, allowing electrons to accumulate more readily and enter the $\text{H}^+/\text{H}_2\text{O}$ reduction process. The

high H_2 rates obtained under these conditions mainly reflect reduction-side electron extraction, HER site activity, interfacial transport resistance, and proton reduction kinetics, rather than the efficiency of the complete water-splitting cycle. Hainer et al. clearly distinguished sacrificial H_2 evolution from true water splitting in metal-decorated TiO_2 systems [15]. Costantino and Kamat further noted that H_2 detected in sacrificial systems may be associated with dehydrogenation of organic donors, radical oxidation, or surface reforming, and cannot be assumed to originate

entirely from water splitting [16].

Photoreforming and H_2 production from organic substrates further alter the origin of evolved hydrogen and the hole-consumption pathway. Kawai and Sakata first connected carbohydrate conversion with TiO_2 photocatalytic H_2 production [17]. Mechanistic studies of glucose photoreforming show that substrate oxidation, dehydrogenation, and reforming intermediates affect electron/proton transfer and product distribution [18]. Sacrificial H_2 evolution and photoreforming are most useful for comparing reduction-side electron utilization, HER site construction, and substrate oxidation pathways, but they do not directly establish sacrificial-agent-free OWS capability.

Reliable comparison of TiO_2 -based systems depends on a clear distinction among sacrificial H_2 evolution, photoreforming-based H_2 production, and sacrificial-agent-free OWS. The first two regimes mainly diagnose reduction-side electron utilization and HER site

construction, whereas OWS demands concurrent closure of the reduction and oxidation sides with an H_2/O_2 stoichiometric ratio close to 2:1. Once these reaction boundaries are fixed, H_2 evolution rates, quantum efficiencies, and scale-up potential become comparable in a meaningful way.

Pathway-resolved analysis of transformation products can further strengthen photocatalytic reaction classification. Combining product identification with pathway analysis and toxicity evaluation provides a methodological basis for distinguishing substrate degradation from reaction routes relevant to H_2 production [19]. For TiO_2 -based H_2 systems, such product-resolved analysis should complement gas quantification when distinguishing sacrificial H_2 evolution, photoreforming, and OWS [15–18].

These reaction boundaries can be clarified further by comparing sacrificial half reactions, photoreforming, and OWS systems (Fig. 2).

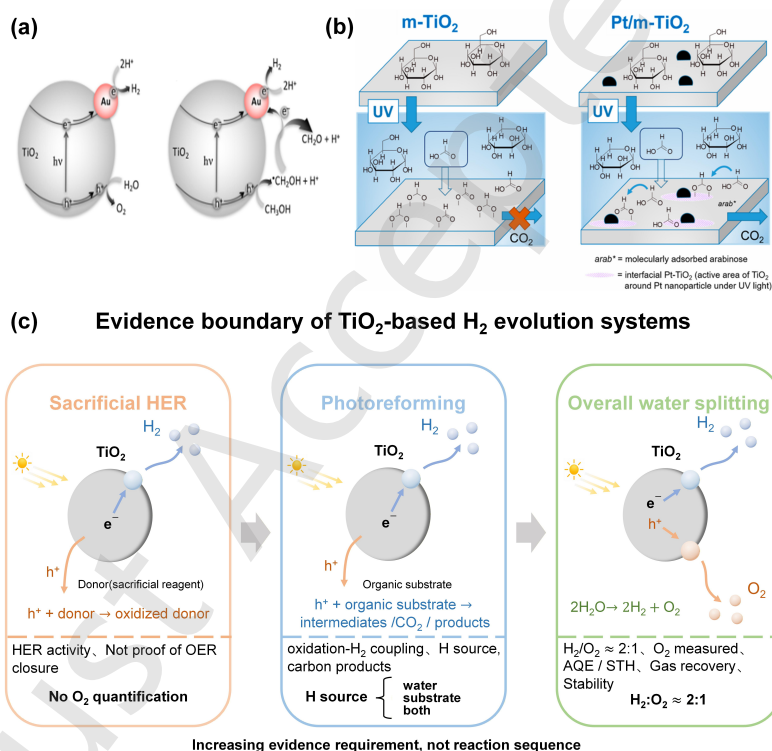


Figure 2 Reaction boundaries among sacrificial H_2 evolution, photoreforming, and overall water splitting. a, Difference between true water splitting and methanol-assisted sacrificial H_2 evolution in metal-decorated TiO_2 , highlighting that half-reaction and OWS conditions correspond to different limiting steps. Reproduced with permission from Ref. [15]. b, Reaction pathways over mesoporous TiO_2 and Pt-modified mesoporous TiO_2 in glucose photoreforming, showing that substrate oxidation, intermediates, and the origin of evolved hydrogen alter system interpretation. Reproduced with permission from Ref. [18]. c, Evidence boundaries of TiO_2 -based H_2 production systems. Sacrificial H_2 evolution mainly supports evaluation of reduction-side electron extraction and HER sites. Photoreforming requires analysis of the origin of evolved H_2 and carbon products. OWS requires reporting H_2/O_2 stoichiometry, direct O_2 signals, apparent quantum yield/efficiency (AQY/AQE), solar-to-hydrogen conversion efficiency (STH), gas recovery, and stability.

2 Intrinsic limitations and interfacial reaction bottlenecks of TiO_2 photocatalytic H_2 production

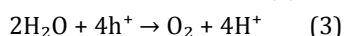
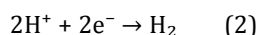
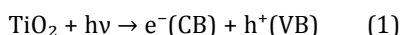
2.1 Wide-band-gap absorption limitation and carrier recombination

TiO_2 photocatalytic H_2 production is limited primarily by weak light absorption associated with the wide band gap and by recombination losses of photogenerated carriers.

Together, these limitations determine light absorption efficiency, carrier utilization efficiency, and interfacial reaction closure in OWS. They also motivate doping regulation, defect engineering, phase-interface construction, and cocatalyst loading.

Absorption limited by the wide band gap is the primary issue affecting photocatalytic water splitting over TiO_2 . When the incident photon energy exceeds the TiO_2 band gap, valence-band (VB) electrons can be excited to the conduction band (CB) while leaving holes in the VB. CB

electrons can participate in $\text{H}^+/\text{H}_2\text{O}$ reduction to generate H_2 , whereas VB holes drive water oxidation. In sacrificial-agent-assisted systems, holes may also be preferentially consumed by the sacrificial agent. The elementary steps are commonly written as Eqs. (1)–(3):



However, anatase and rutile TiO_2 mainly respond to ultraviolet light and can use only a limited fraction of the solar spectrum. Under this constraint, research on TiO_2 -based photocatalytic water splitting has long focused on extending visible-light response through strategies such as nonmetal or metal doping, introduction of defect states, construction of black TiO_2 , and coupling with narrow-band-gap semiconductors. These methods can enhance light absorption to some extent, but whether the newly introduced absorption states truly participate in effective charge separation and surface reactions still requires joint verification by carrier dynamics and product quantification.

Defect-state regulation provides a distinct route to sub-band-gap absorption. Oxygen vacancies and associated Ti^{3+} centers can introduce shallow states approximately 0.1–0.2 eV below the TiO_2 conduction-band edge together with deeper mid-gap states. In hydrogen-treated titanium-oxide nanobelts, the apparent absorption edge moved from about 390 to 440 nm and a longer-wavelength absorption tail appeared, whereas the photocatalytic action spectrum extended to approximately 440 nm [20]. The difference between optical absorption and photoactivity highlights the roles of state dispersion, carrier mobility, and Shockley–Read–Hall recombination. Vacancy-induced absorption should therefore be assessed together with defect-state energy, spatial location, carrier lifetime, and transfer to HER/OER sites. Combined defect-state characterization and interfacial electric-field analysis

provide a methodological framework for evaluating whether defect regulation contributes to directional charge separation [21].

Carrier recombination imposes a second major limitation. Even when TiO_2 generates electron-hole pairs, photogenerated carriers may rapidly recombine at bulk defects, surface states, or heterointerfaces. Studies using transient spectroscopy, time-resolved photoluminescence (PL), surface photovoltage, photocurrent, intensity-modulated photocurrent spectroscopy (IMPS) combined with distribution of relaxation times (DRT), and selective deposition show that carrier behavior in TiO_2 is controlled by bulk migration, surface trapping, interfacial transfer, and reaction consumption [22, 23]. Absorption enhancement or lifetime extension does not by itself guarantee a higher rate; the relevant criterion is whether charges reach effective HER/OER sites before recombination.

On the oxidation side, carrier recombination is coupled with the sluggish kinetics of water oxidation. OER is not an instantaneous oxidation event triggered by a single hole. It involves the accumulation of multiple holes near Ti-OH or adsorbed-water sites and the stepwise completion of O-H bond cleavage, O-O bond formation, and intermediate conversion. Surface oxygen vacancies, hydroxyl groups, facet structures, and local water environments affect hole trapping, interfacial charge transfer, and intermediate stability at the same time. Accordingly, TiO_2 research has shifted from asking whether electron-hole pairs can be generated to asking whether carriers can couple productively with surface water structures and intermediates.

Figure 3 connects surface holes and recombination models resolved by IMPS combined with DRT with bulk, defect-assisted, and surface recombination pathways in TiO_2 , emphasizing that carrier generation is followed by multiple competing loss channels.

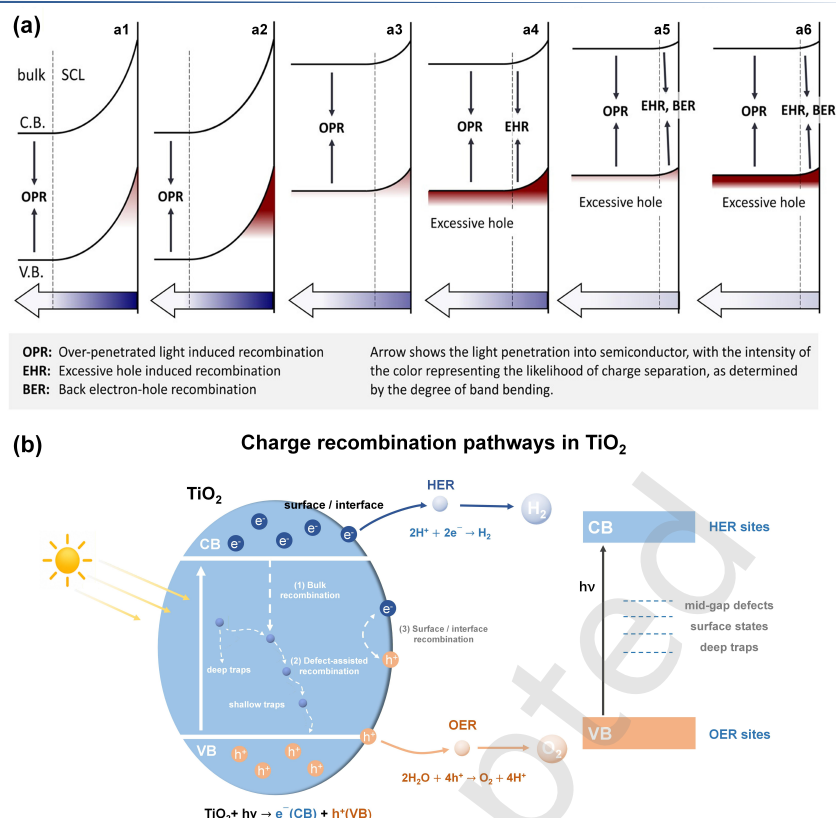


Figure 3 Carrier recombination, surface hole distribution, and effective interfacial transfer in TiO_2 . a, Models of surface hole density, space-charge layer, and recombination pathways under different potentials and light intensities in TiO_2 photoanodes, showing that photogenerated hole accumulation, surface states, and recombination pathways jointly limit interfacial reactions. Reproduced with permission from Ref. [23]. b, Schematic of bulk recombination, defect-assisted recombination, surface or interfacial recombination, and effective transfer to HER/OER sites after photogenerated electrons and holes are produced in TiO_2 .

2.2 HER/OER kinetics at solid-liquid interfaces and back reaction issues

Band-edge positions alone do not determine interfacial reactions in TiO_2 photocatalytic H_2 production. Adsorbed water, surface hydroxyls, oxygen vacancies, cocatalysts, and local electric fields also shape the reaction pathway. HER usually requires electrons to reach reduction sites and proceed through proton transfer, H^* adsorption, H-H coupling, and H_2 desorption. OER requires stepwise hole accumulation to drive O-H bond cleavage, transformation of oxygen-containing intermediates, O-O bond formation, and O_2 release. Thus, H_2 -production efficiency over TiO_2 depends on whether carriers arriving at the interface are matched with the water structure, adsorbed intermediates, and cocatalyst sites, in addition to the conduction-band and valence-band positions.

Mechanistically, photon absorption is followed by carrier thermalization or trapping, bulk-to-surface migration, and competition between recombination and interfacial consumption [22, 23]. At reduction sites, delivered electrons support H^* formation, H-H coupling, and H_2 desorption; at oxidation sites, holes accumulate through multihole chemistry and drive O-H bond cleavage and O-O bond formation [4, 5, 24]. Adsorbed water, surface hydroxyls, and hydrogen-bond networks regulate proton delivery and proton-coupled electron transfer at both reaction sides [25–27]. The two branches must also be kinetically matched: sacrificial H_2 evolution mainly isolates reduction-side utilization, whereas OWS requires direct O_2

detection, H_2/O_2 stoichiometry, and control of the back reaction [12, 15, 16].

Cocatalyst effects on TiO_2 surface reactions cannot be described only as electron accumulation. Conventional Pt, Pd, NiS, MoS_2 , and related cocatalysts are usually used to lower the HER overpotential, promote electron extraction, and facilitate H_2 evolution. Recent studies show that metal-site function also depends on the reaction side, coordination environment, and local electric field. For example, Pt single atoms on TiO_2 photoanodes may participate in water-oxidation kinetics [28]. Studies of reduction-side metal/ TiO_2 interfaces show that proton or hydrogen-intermediate adsorption changes interfacial electron transfer and influences H^* formation and H_2 desorption [24]. HER/OER closure is better judged by analyzing electron delivery, proton supply, adsorbed intermediates, and interfacial water structure within the same reaction network, rather than inference from band-edge positions or PL intensity alone.

The H_2/O_2 back reaction further increases the interfacial complexity of OWS. Highly active metal cocatalysts can accelerate HER, but they may also promote H_2 oxidation or H_2/O_2 recombination when H_2 and O_2 coexist, causing the apparent efficiency and stoichiometry to deviate from true water splitting. A credible evaluation of TiO_2 OWS includes HER/OER closure, H_2/O_2 stoichiometry, quantitative gas recovery, back-reaction suppression, and long-term stability.

These bottlenecks frame the organization of the following

sections: photoresponse extension, charge-separation regulation, surface reaction-site construction, and immobilized-system development. The four levels correspond to effective absorption, directional migration, HER/OER closure, and system mass transfer. Reported performance improvements are therefore interpreted within a common framework that includes product stoichiometry, back-reaction suppression, gas recovery, and long-term stability.

2.3 Multiscale theoretical framework for TiO₂ photocatalytic H₂ production

Density functional theory (DFT) connects dopants, vacancies, facets, and interfaces with defect-formation energies, density of states, band offsets, work functions, charge redistribution, adsorption energies, and elementary reaction barriers [29–36]. These calculations are most informative when a specified structure and charge state are linked to measurable descriptors and when predicted band narrowing or adsorption energetics are paired with experimental photoresponse and H₂-production data.

At the solid–liquid interface, *ab initio* molecular dynamics can sample water orientation, hydrogen-bonding, solvation, and surface proton transfer that static slab models do not capture [25–27]. Microkinetic modeling then converts elementary barriers and coverages into rate and sensitivity predictions. For metal-loaded anatase methanol photoreforming, such a model helps distinguish water activation, substrate dehydrogenation, and hydrogen formation within one reaction network [37].

Theoretical assignments therefore require experimental closure. Band alignment and charge-transfer directions should be tested by spectroscopy or potential-sensitive measurements, predicted intermediates by isotope or operando probes, and predicted kinetics by rate, selectivity, and gas-balance data [23, 24, 38–40]. This multiscale framework integrates electronic-structure calculations, molecular dynamics, and microkinetics with direct mechanistic and performance evidence.

3 Progress in extending the photoresponse of TiO₂

Photoresponse extension remains a major theme in TiO₂ photocatalytic H₂ production. Enhanced visible-light absorption, however, does not necessarily lead to higher H₂ production efficiency. The relevant question is whether newly introduced absorption states generate mobile carriers that can reach effective HER/OER interfaces before recombination. This section discusses representative progress, mechanisms, and evaluation boundaries for doping/codoping, defect engineering, sensitized composites, and optical-field regulation.

3.1 Nonmetal/metal doping and codoping

Research on visible-light-response extension in TiO₂ began with nonmetal doping, with N doping being the most representative example. Asahi et al. reported that N-doped titanium oxides show photocatalytic activity under visible light and attributed this behavior to coupling between N 2p-related states and the O 2p valence band. This work

established a basic strategy for extending the TiO₂ photoresponse through valence-band regulation [41]. Subsequently, Esmat, Cui, Wang, and co-workers showed from different perspectives that N-related structures alter the absorption edge and also influence defect distribution, electron extraction, and HER site construction. These perspectives include N-doping-induced oxygen vacancies, coupling between N doping and cocatalysts, and C/N codoping accompanied by Ti³⁺ and oxygen-vacancy formation [42–44]. The focus of N-doped TiO₂ has shifted from the generation of visible-light absorption to the ability of the introduced states to produce carriers that migrate, are consumed at the reduction side, and do not severely weaken oxidation capability.

Visible-light absorption in N-doped TiO₂ can arise from N-derived states, while the intrinsic O 2p valence-band maximum remains an essential reference for oxidation capability. Multi-type N-doped TiO₂ has been associated with substitutional and interstitial N-derived levels approximately 0.14 and 0.73 eV above the valence-band maximum, respectively. Excitation from these higher-lying localized states can extend absorption but leaves holes with less oxidation driving force than holes at the O 2p valence-band maximum. The reported state positions provide quantitative electronic-structure evidence for evaluating this absorption–oxidation trade-off [45].

For N-doped TiO₂ flower-like microspheres (N-TFM), the optical gap decreased from 3.25 to 3.05 eV, absorption extended through 400–500 nm, and the conduction- and valence-band potentials were estimated as –0.36 and +2.69 V versus NHE at pH 0 [43]. Although the valence-band value remains thermodynamically positive enough for water oxidation, OER also requires multihole accumulation and kinetic overpotentials [4, 5, 24]. N doping should therefore be optimized by jointly evaluating state position, carrier lifetime, oxidation-product or O₂ formation, and H₂ kinetics [43]. A rigorous assessment should couple direct redox-product measurements with carrier-dynamic and interfacial electric-field evidence [46].

Debate over N-doped TiO₂ further promoted investigation of the nature of doping states. Livraghi et al. combined electron paramagnetic resonance (EPR) with theoretical analysis to distinguish different N species and their localized electronic structures, showing that not all N-related signals correspond to effective visible-light-active centers [29]. Work on N-doped TiO₂ nanobelts by Wang et al. further showed that visible-light activity originates from the synergy among N states, oxygen vacancies, and nanostructured transport [47]. N doping is better viewed as structural regulation governed by doping position, defect coupling, carrier lifetime, and interfacial charge transfer, rather than as simple elemental incorporation.

In addition to N doping, carbon modification and C/N codoping are frequently used to regulate the photoresponse and surface chemistry of TiO₂. Khan et al. reported that chemically modified n-TiO₂ can extend the response for photochemical water splitting [48], and Sakthivel and Kisch demonstrated enhanced photocatalytic capability of carbon-modified TiO₂ under daylight [49].

These studies reveal that carbon species may exist as substitutional C, interstitial C, surface carbonates, residual carbon layers, or carbon oxide layers, with roles corresponding to valence-band regulation, surface electron transfer, or visible-light sensitization. Recent C/N codoping studies indicate that C/N synergy can translate into practical H₂ production enhancement only when newly introduced absorption, defect passivation, and interfacial electron transfer coexist [30, 50].

Cr substitution promoted adjacent oxygen vacancies, while an N-doped carbon coating enhanced charge separation and water activation in Cr-TiO₂@N-C under visible light. Comparison with Mn-, Co-, Ni-, Cu-, and Zn-modified analogues supports joint consideration of substitutional doping, vacancy formation, and surface-carbon regulation [51].

Metal doping is mechanistically distinct from nonmetal doping. It mainly affects carrier dynamics in TiO₂ through d levels, transient trapping centers, and local lattice distortion. After systematically comparing TiO₂ doped with various metal ions, Choi and Hoffmann noted that low-concentration metal ions can act as transient trapping centers for electrons or holes and delay bulk recombination. However, when dopant levels are too deep, concentrations too high, or spatial distributions inappropriate, these centers become nonradiative recombination channels [52]. Metal doping is best interpreted as kinetic regulation of the competition between carrier trapping and recombination, not simply as a band-gap-narrowing strategy.

Because single doping can readily introduce deep levels or charge-compensation imbalance, codoping has gradually developed. Gai et al. proposed a donor-acceptor passivated codoping strategy, providing a theoretical framework for narrow-band-gap TiO₂ design [31]. Cho et al. combined W/C codoping with one-dimensional TiO₂ nanowires, further showing that codoping effects are influenced by carrier-collection pathways and nanostructured transport features [53]. Codoping can reduce recombination risk from newly introduced states through charge compensation, defect passivation, and structural synergy, rather than by simply adding more elements.

As research has deepened, the criterion for evaluating doping regulation has shifted from absorption-edge redshift to the real charge contribution of newly introduced states. In N-doped, C/N-codoped, and N/TiO₂ systems containing surface oxygen vacancies, EPR, theoretical calculations, and spectroscopy help distinguish N-related localized states, oxygen vacancies, Ti³⁺, and their electronic structures [29, 47, 54]. Studies of W/C and C/N codoping further require that the positions of doping states, defect concentration, carrier lifetime, and interfacial charge transfer be linked to photoelectrochemical or H₂-production outputs [30, 31, 50, 53]. In TiO₂ doping studies, the central issue is not color change or absorption-edge movement, but whether newly introduced absorption states provide carriers that can participate in HER/OER under aqueous illumination and remain stable during operation.

3.2 TiO₂ defect engineering: Oxygen vacancies, Ti³⁺ centers, and black TiO₂

Oxygen vacancies, Ti³⁺ centers, and black TiO₂ are the most representative subjects in TiO₂ defect engineering. Their main function goes beyond changing material color or light absorption; they regulate near-surface electronic structure, defect-state position, and interfacial carrier-transfer pathways. Chen et al. reported hydrogenated black TiO₂ nanocrystals with markedly enhanced solar absorption, making defect engineering an important turning point in visible and near-infrared response studies of TiO₂ [55]. Naldoni et al. further emphasized that the location and nature of defects in black TiO₂ are more important than the total defect amount, because surface and bulk defects have different effects on band-gap narrowing, carrier migration, and photocatalytic activity [56]. Subsequent reports on hydrogen-treated TiO₂ nanowire arrays and black TiO₂ nanotubes further shifted attention from light absorption alone to the participation of defect states in charge separation and interfacial reactions [57, 58].

In addition to hydrogenation, elemental doping, reaction-induced surface reconstruction, and interfacial molecular regulation can affect Ti³⁺ centers and oxygen-vacancy-related structures. Lu et al. observed by liquid-cell transmission electron microscopy (TEM) that TiO₂ forms a self-hydrogenated near-surface layer before photocatalytic H₂ generation, indicating that hydrogen-related Ti³⁺ structures during reaction are not static initial defects but may participate in electron transfer and H₂ nucleation [38]. Foo et al. used variable-temperature X-ray diffraction (XRD) to analyze oxygen defects and nitrogen impurities, suggesting that defect signals need to be interpreted together with lattice response and impurity sources [59]. The appearance of Ti³⁺ or oxygen-vacancy signals in electron paramagnetic resonance (EPR) or X-ray photoelectron spectroscopy (XPS) is insufficient by itself; the formation location, stability, and reaction-induced evolution of defects also require analysis.

An effective treatment of defective TiO₂ requires distinguishing productive defects from deactivating defects. Cushing et al. found that defects introduced into hydrogen-treated titanium oxide nanobelts do not necessarily improve photocatalytic activity. Their effect depends on energy-level depth, spatial location, and interfacial charge-transfer pathways [20]. Zhang et al. compared the effects of surface and bulk defects on H₂ evolution over TiO₂ with exposed {001} facets and further showed that near-surface defects are more likely to participate in interfacial reactions, whereas deep bulk defects more readily become recombination centers [60]. The effectiveness of defect regulation depends on whether defects are located where interfacial transfer can occur and whether trapped charges can continue to move toward HER or OER sites.

Based on this understanding, defect engineering has gradually been coupled with cocatalyst, heterointerface, and conductive-interface design. Interfacial molecular regulation can alter the surface chemical environment around defects and thereby affect electron extraction and proton reduction pathways [61]. Studies of Cu sites, Ru-Cu cocatalytic sites, and MXene/TiO₂ heterointerfaces also

show that defect sites can reduce recombination caused by electron accumulation only when they are effectively connected with reduction-side active centers or conductive channels [62–65]. Defective TiO₂ research has shifted from regulating color and diffuse-reflectance absorption toward optimizing defect location, cocatalyst contact mode, and interfacial charge-extraction pathways, so that newly introduced defect states become usable reaction channels.

Defect engineering is also time dependent. Ti³⁺ and oxygen vacancies may be reoxidized during air storage, illuminated aqueous operation, or exposure to oxygen-containing environments. Sacrificial agents, metal precursors, and photoreduction may induce secondary surface reduction, leading to activity induction periods, structural changes during cycling, or attenuation of post-reaction defect signals. Studies of black TiO₂ and related reduced TiO₂ show that defect states affect initial absorption and charge separation as well as their evolution during storage, illumination, and reaction [38, 55–59]. Performance evaluation of defective TiO₂ should combine pre- and post-reaction EPR and X-ray photoelectron spectroscopy (XPS), long-term activity decay, storage conditions, and structural recovery, instead of relying only on darkened color or enhanced absorption.

Because Ti³⁺ species can evolve during storage and photocatalytic operation, defect stability should be assessed by matched pre-/post-storage and pre-/post-reaction EPR/XPS measurements acquired under controlled atmosphere, transfer, normalization, and fitting procedures [55–61]. A decrease in normalized Ti³⁺ EPR intensity together with a lower Ti³⁺/Ti⁴⁺ XPS ratio is consistent with reoxidation when acquisition and normalization conditions are matched; disagreement between the two may indicate depth-dependent redistribution, surface reconstruction, cocatalyst-induced screening, or sampling artifacts [56, 59, 60]. Operando or quasi-in situ measurements are preferable when transient states are central to the mechanism [59, 62]. Comprehensive stability characterization should integrate cycling, post-reaction XRD, light/dark EPR, irradiation-dependent XPS, isotope tracing, and blank controls [66]. This workflow supports integrated interpretation of activity retention and evolving defect states.

3.3 Sensitized composites and optical-field regulation

Introducing external light-absorbing units is another strategy for compensating for the wide-band-gap limitation of TiO₂. Unlike doping or defect engineering, which directly changes the electronic structure of TiO₂, sensitized composites emphasize a sequential process involving external light absorption, interfacial injection, TiO₂ transport, and surface reduction. After a sensitizer or narrow-band-gap semiconductor absorbs visible light, excited electrons are injected into the TiO₂ conduction band or interfacial states and then migrate along the TiO₂ scaffold to HER sites. The oxidized sensitizing unit then needs prompt regeneration by a sacrificial agent, hole-transport process, or interfacial reaction; otherwise, the system decays through back recombination or photocorrosion. Tachibana et al. provided kinetic insight

into electron injection by studying subpicosecond interfacial charge separation in dye-sensitized TiO₂ [67].

In quantum-dot-sensitized TiO₂ systems, TiO₂ commonly acts as an electron acceptor, transport scaffold, and structural support. Sun et al. constructed CdS quantum-dot-sensitized TiO₂ nanotube arrays, combining visible-light absorption by CdS with ordered electron channels in TiO₂ nanotubes [68]. Subsequent studies of quantum-dot-sensitized TiO₂ nanotube p-n heterojunctions and carbon-dot-sensitized systems moved the research focus from absorption enhancement to electron-injection efficiency, interfacial stability, and environmental compatibility of the light-absorbing component [69, 70]. Sensitized systems therefore need to be evaluated by both visible-light absorption and the stability of electron injection into TiO₂ followed by rapid consumption at HER sites.

Narrow-band-gap semiconductor/TiO₂ composites represent a further development beyond quantum-dot sensitization. Their core is to couple the visible-light-absorbing unit with the electron-accepting and structural-support functions of TiO₂. In TiO₂/CdS/TiN nanorods, CdS provides visible-light excitation, TiO₂ supplies the electron-transport scaffold, and the conductivity and plasmonic effect of TiN help improve photocurrent and H₂ generation [71]. MoS₂/CdS-TiO₂ nanofibers assign roles within one continuous structure, where TiO₂ fibers, the CdS absorbing phase, and MoS₂ edge HER sites work together [72]. g-C₃N₄/TiO₂ systems further illustrate the joint regulation of visible-light absorption, electron acceptance and transport, and competition between interfacial Z-scheme and type-II charge transfer for reduction-side reactions [73, 74].

Organic-framework/TiO₂ composites have recently provided clearer interfacial evidence. Black TiO₂/covalent organic framework (COF) and covalent triazine framework (CTF)-TiO₂ systems combine oxygen vacancies, visible-light-absorbing frameworks, and interfacial built-in electric fields, allowing carriers generated by low-energy excitation to separate before recombination and migrate toward reduction-side active sites [75, 76]. Their significance lies in building a continuous pathway from light absorption to reduction-side consumption through functional division among organic-framework absorption, the stable TiO₂ electron scaffold, and the interfacial built-in field, rather than in simply adding another light absorber.

Beyond chemical sensitization, optical-field regulation improves effective light utilization by changing the propagation pathway of incident light in porous or periodic structures, and it can act synergistically with sensitized composites. Work by Ozin and co-workers on TiO₂ inverse opals showed that the slow-photon effect can extend the residence time of specific wavelengths in periodic pore structures, allowing local-field enhancement to match electronic excitation near the TiO₂ absorption edge [77]. After loading Pt nanoclusters, the combination of slow-photon amplification and HER surface sites further demonstrated the synergy between light harvesting and interfacial reactions [78]. Recent work on inverse-opal TiO₂, perovskite-sensitized photonic crystals, and gradient three-dimensionally ordered macroporous (3DOM) TiO₂-

Au-CdS shows that optical-field structures contribute by increasing optical path length and by organizing local absorption, interfacial separation, and pore-channel mass transfer within the same architecture [79–81].

Hierarchical branched TiO_2 and black-phosphorus-sensitized TiO_2 mesocrystals further show that photoresponse expansion does not depend only on absorption-edge movement. It also has to match directional charge transport, mesocrystal channels, and reduction-side electron consumption [82, 83].

Sensitized composites and optical-field regulation affect more than light harvesting. They also influence electron

injection, interfacial transport, reduction-side electron consumption, and mass transfer. Evaluation is better framed around stable injection of excited-state electrons into TiO_2 , regeneration of the oxidized sensitizing unit, suppression of interfacial recombination and photocorrosion, and pore-channel accessibility for reactant renewal and H_2 release.

The doping, codoping, defect, sensitization, and slow-light structures discussed in this section are best understood as distinct routes for controlling effective absorption states and interfacial electron injection, rather than as absorption-enhancement strategies alone (Fig. 4).

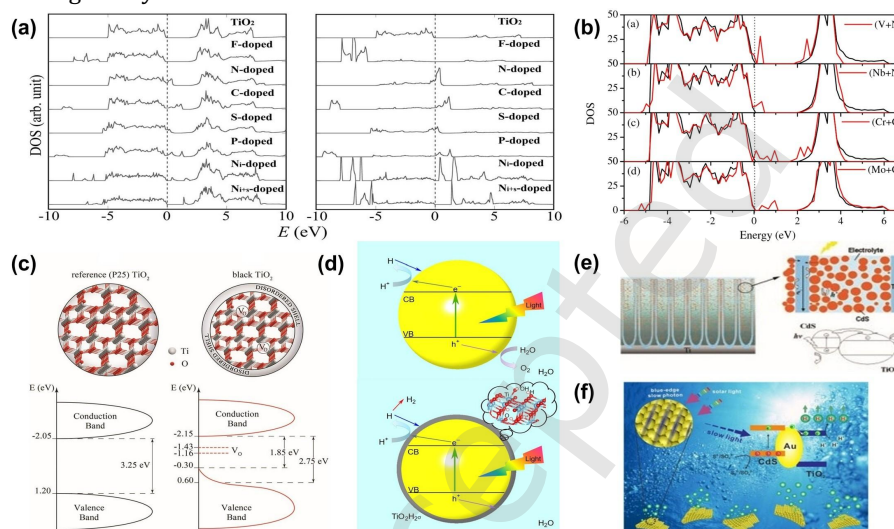


Figure 4 Representative mechanisms for photoresponse expansion in TiO_2 . a, Nonmetal doping states and the electronic structure of N-doped TiO_2 , showing that the position of doping states determines whether they can contribute effective visible-light response. Reproduced with permission from Ref. [41]. b, Density-of-states schematic for donor-acceptor passivated codoping, highlighting the importance of charge compensation and defect passivation in narrow-band-gap design. Reproduced with permission from Ref. [31]. c, Differences in defect location and density of states between P25 and black TiO_2 , showing that surface and bulk defects affect band gap and recombination differently. Reproduced with permission from Ref. [56]. d, Schematic of the photocatalytic process and modification pathway of self-hydrogenated TiO_2 . Reproduced with permission from Ref. [38]. e, Structure and electron-injection pathway of CdS quantum-dot-sensitized TiO_2 nanotubes. Reproduced with permission from Ref. [68]. f, Mechanism by which slow photons promote visible-light H_2 production in gradient 3DOM TiO_2 -Au-CdS. Reproduced with permission from Ref. [81].

The doping, defect, sensitization, and optical-field strategies described above act on key steps including absorption-state formation, defect trapping, interfacial electron injection, and local-field enhancement. To facilitate comparison of mechanistic contributions, representative evidence, and applicable boundaries, Table 1 summarizes the photoresponse expansion pathways of TiO_2 .

Table 1 Comparison of TiO_2 photoresponse expansion strategies, mechanisms, and representative quantitative parameters and performance indicators

Module	Key systems and evidence	Mechanistic keywords	Value and limitations	Representative quantitative parameters and performance indicators
N doping	N- TiO_2 , N-doping-mediated oxygen-vacancy-rich TiO_2 , and N-doped TiO_2 /cocatalyst heterointerfaces [29, 41–44, 47]	N 2p-O 2p coupling, N-induced oxygen vacancies/ Ti^{3+} , and interfacial cocatalyst sites jointly affect visible absorption and electron extraction.	A classic route to visible-light response. Its usefulness depends on matching N species, defect spatial distribution, and reduction-side electron consumption at HER sites, rather than increasing N content or pursuing absorption-edge redshift alone.	N-TFM: band gap, 3.05 eV; $\text{Ni}_2\text{P}/\text{N-TFM}$ H_2 rate, $0.368 \text{ mmol g}^{-1} \text{ h}^{-1}$ versus $0.028 \text{ mmol g}^{-1} \text{ h}^{-1}$ for N-TFM; AQE, 2.13%; 5 cycles [43].
C doping/carbon modification	C-modified TiO_2 and C/N-codoped TiO_2 [30, 44, 48–50, 54]	C species can regulate the valence band, surface sensitization, or electron transfer. C/N synergy is often coupled with Ti^{3+} centers and oxygen vacancies.	Extends surface chemistry. Substitutional C, residual carbon layers, carbonates, and sensitization contributions must be distinguished.	Chemically modified n- TiO_2 : absorption edge, 535 nm; band gap, 2.32 eV; photoconversion efficiency, 8.35%; PEC stability over 6 months; H_2 rate, NR [48].
Metal doping	TiO_2 doped with	Metal d levels can form	Regulates recombination	Fe^{3+} -doped TiO_2 : CHCl_3 -

Module	Key systems and evidence	Mechanistic keywords	Value and limitations	Representative quantitative parameters and performance indicators
	various metal ions [52]	transient trapping centers, but may also become deep-level recombination centers.	kinetics. Effectiveness depends on valence state, concentration, energy level, and spatial distribution.	oxidation/ CCl_4 -reduction quantum yields, 2.38%/1.74% versus 0.16%/0.08% for undoped TiO_2 ; H_2 rate, NR [52].
Codoping	Donor-acceptor codoping and W/C or C/N- TiO_2 systems coupled with Ti^{3+} centers and oxygen vacancies [30, 31, 50, 53, 54]	Charge compensation, defect passivation, and mesoporous/one-dimensional structural synergy reduce recombination risks from newly introduced states.	Favors synergy among absorption, lifetime, and interfacial transfer. Doping sites and spatial distribution remain difficult to control precisely.	C,N- TiO_2 : H_2 rate, $795 \mu\text{mol g}^{-1} \text{h}^{-1}$, versus $300 \mu\text{mol g}^{-1} \text{h}^{-1}$ for C-modified TiO_2 [30].
Oxygen vacancies, Ti^{3+} centers, and black TiO_2	Hydrogenated/reduced black TiO_2 , reaction-induced self-hydrogenation, surface/bulk defects, and defect-coupled transport structures [20, 38, 55–60, 82]	Oxygen vacancies, Ti^{3+} centers, and disordered shells introduce sub-band-gap states and affect trapping, transfer, and interfacial electron consumption.	Substantially extends absorption. Near-surface effective defects must be distinguished from bulk deactivating defects.	H_2 -treated {001}-faceted TiO_2 (TH700): H_2 rate, $15.13 \text{ mmol g}^{-1} \text{h}^{-1}$; 1.7- and 3.7-fold versus TW and TC controls; AQE, 70.3% at 365 nm [60].
Defect-cocatalyst/conductive interface	Defective TiO_2 with Pt-oxygen-vacancy interactions, multivalent Cu, RuCu bimetallic sites, and Ti_3C_2 @ TiO_2 interfaces [61–65]	Surface molecules, metal sites, or conductive components regulate local electron density and accelerate reduction-side electron consumption at HER sites.	Connects absorption/trapping states to reaction sites. Light shielding, interfacial recombination, and oxidation of conductive phases must be controlled.	Ti_3C_2 @ TiO_2 -48 h: H_2 rate, $140.8 \mu\text{mol h}^{-1}$; 2.8-fold versus TiO_2 ; conversion efficiency, 2.2%; 4 cycles [65].
Sensitized composites	Dye/ TiO_2 , CdS/quantum-dot-sensitized TiO_2 , g- C_3N_4 / TiO_2 , COF/CTF- TiO_2 , and black phosphorus/ TiO_2 [67–76, 83]	External light-absorbing units inject electrons into TiO_2 , while TiO_2 acts as the electron acceptor, transport phase, and support.	Extends visible-light utilization. Injection efficiency, photocorrosion suppression, and reaction boundaries must be verified.	TiO_2 -x/TpPa-1-COF (6:4): absorption edge, 630 nm; H_2 rate, $15.33 \text{ mmol g}^{-1} \text{h}^{-1}$; 10.5-fold versus TiO_2 -x; AQE, 6.7% at 420 nm; 5 cycles [75].
Optical-field regulation	Inverse-opal TiO_2 , TiO_2 photonic crystals, and 3DOM TiO_2 -Au-CdS [77–81]	Slow-light effects and photonic band-gap matching extend effective optical paths and increase local absorption probability.	A non-defect light-enhancement pathway. Pore-channel mass transfer and reaction boundaries must be evaluated simultaneously.	3DOM TiO_2 -Au-CdS-250: visible-light H_2 rate, $3.50 \text{ mmol g}^{-1} \text{h}^{-1}$ [81].
Broad-spectrum sensitization	Black phosphorus/ TiO_2 mesocrystal systems with visible to near-infrared response [83]	Narrow-band-gap two-dimensional light-absorbing units are coupled with TiO_2 mesocrystal channels.	Reflects broadband composite design. Aqueous and long-term photostability must be verified.	Black phosphorus/Pt/ TiO_2 mesocrystal: H_2 rates, 1.90 and $0.41 \mu\text{mol h}^{-1}$ at $\lambda > 420$ and 780 nm; AQE, 7.1%/1.2%; 4 cycles [83].

Table note: Values are reproduced as reported in the cited studies and support parameter-level comparison under their respective experimental conditions. Irradiation spectrum and photon flux, catalyst dosage, cocatalyst, sacrificial reagent, reactor geometry, and normalization basis differ among reports. NR, not reported; PEC, photoelectrochemical.

4 Progress in TiO_2 charge separation and interfacial-structure regulation

After photoresponse expansion, TiO_2 -based photocatalytic H_2 production faces the question of whether photogenerated electrons and holes can be directed to the reduction and oxidation sides before recombination and then consumed promptly by HER/OER half reactions [22–24]. This section is organized at four levels. First, it links synthesis variables to phase composition, facet exposure, dimensionality, morphology, defect and surface states, and interface formation. Second, it examines charge separation within crystal phases, phase junctions, and facets. Third, it analyzes migration across heterojunctions, p-n junctions, Schottky or Ohmic contacts, and conductive interfaces. Finally, it considers how nanofibers and immobilized scaffolds translate local charge separation into continuous catalytic layers with controlled mass transfer.

4.1 Synthesis–structure–property relationships in TiO_2 nanostructures

Synthetic variables determine performance through measurable structural descriptors, as summarized in TiO_2 synthesis and nanostructure reviews [9–11]. Precursor chemistry, hydrolysis and condensation rates, solvent composition, pH, temperature, pressure, and residence time determine nucleation, phase composition, crystallite connectivity, facet exposure, dimensionality, defect distribution, and surface termination [7–11]. Calcination atmosphere and temperature subsequently alter crystallinity, anatase/rutile conversion, oxygen-vacancy populations, and carbon or heteroatom residues [20, 55–61].

Hydrothermal and solvothermal routes are well suited to nanotubes, nanosheets, nanorods, and phase-junction particles because supersaturation and surface-selective growth can be tuned [7–11]. Anodization directly forms oriented nanotube arrays on Ti, whereas electrospinning couples precursor conversion with one-dimensional fiber continuity [6, 9–11]. Deposition, ion exchange, hydrogenation, and cocatalyst photodeposition then define interface intimacy and reaction-site accessibility [38, 55, 85]. In one sequential fabrication route, continuous TiO_2

nanofiber films were grown hydrothermally and then functionalized by Ag photodeposition, linking the fabrication sequence with film morphology and accessible functional interfaces [85].

A robust synthesis–structure–property relationship therefore requires matched reporting of synthesis conditions, phase ratio, facet fraction, defect/termination chemistry, interface quality, and pore or film thickness, followed by electronic descriptors such as work function, carrier lifetime, and charge-transfer resistance [9–11]. These descriptors should then be connected to reaction-appropriate H_2/O_2 , quantum-efficiency, selectivity, and stability data [39, 40]. Combining morphology and Brunauer–Emmett–Teller surface area with structural and electronic descriptors and with reaction-specific performance metrics supports identification of the operative performance mechanism.

4.2 Crystal phase, phase junction, and facet regulation

The roles of crystal phase, phase junctions, and facets can be organized using direct evidence for band alignment, surface/bulk carrier trapping, and spatial charge distribution (Fig. 5).

Crystal-phase regulation primarily affects the internal band positions, defect distribution, and interphase contact of TiO_2 , instead of representing mechanical mixing of anatase and rutile. Ruan et al. showed that favorable band alignment and phase interfaces in anatase/rutile heterophase junctions can provide an effective driving force for charge separation and high-quantum-efficiency H_2 evolution [32]. EPR results for mixed-phase P25 TiO_2 and studies on anatase/rutile band alignment further show that the direction of interphase electron migration is not determined by the phase name alone. It is controlled by interface quality, defect state, phase ratio, and preparation route [33, 86]. Mixed-phase TiO_2 research has therefore moved from empirical use of the high activity of P25 toward explicit determination of band alignment, defect distribution, and charge-migration pathways at phase interfaces.

Phase-junction design has moved from nondirectional mixed-phase enhancement to controlled interface construction. Peng et al. regulated anatase/rutile TiO_2 phase junctions in situ on OH-terminated $\text{Ti}_3\text{C}_2\text{T}_x$, coupling the crystal-phase interface with a two-dimensional conductive scaffold to reduce interphase charge-transfer resistance [34]. Qin et al. further constructed a $\text{TiO}_2/\text{Ti}_3\text{C}_2$ Ohmic heterojunction, strengthening electron extraction through low-resistance contact and a built-in electric field [87]. Studies of N-doped in situ phase growth connect

photoresponse expansion with interphase charge migration [35]. These studies describe TiO_2 phase-junction regulation as the simultaneous organization of band differences, built-in fields, and conductive bridging at the phase interface, not as a simple superposition of two crystal phases.

Phase ratio should be evaluated within a specified architecture because interface population, termination, and defect density vary concurrently. In anatase/rutile TiO_2 grown on $\text{Ti}_3\text{C}_2\text{T}_x$, changing the anatase/rutile ratio from 83.5/16.5 to 57.3/42.7 increased the reported H_2 -evolution rate from 2164 to 4672 $\mu\text{mol g}^{-1} \text{h}^{-1}$, and the latter sample showed the smallest Nyquist arc among the compared compositions. In this context, EIS indicates lower interfacial charge-transfer resistance. UPS measurements gave work functions of 4.27 and 3.68 eV for anatase and rutile, whereas the corresponding calculated values were 5.74 and 4.84 eV, supporting electron redistribution across the phase junction [34]. Complementary spectroscopic and computational analyses can be combined to investigate interfacial charge redistribution and charge-transfer pathways in heterostructured photocatalysts [88].

Facet engineering extends charge separation from phase interfaces to the single-particle scale. Anatase single crystals and nanosheets with a high proportion of {001} facets provide controllable models for comparing facet reactivity, adsorption configurations, and surface charge distribution [7, 8]. Liu et al. directly observed charge separation on different facets through selective etching, and Ma et al. compared the relative photooxidation and photoreduction activities of {100}, {101}, and {001} surfaces. These observations indicate that surface energy, adsorption configuration, and spatial charge distribution jointly determine electron- and hole-rich regions [89, 90]. Facet regulation therefore aims to use differences in charge distribution among facets to establish reaction-site division within a single particle, rather than merely expose high-energy facets.

The ultimate goal of crystal-phase, phase-junction, and facet regulation is to establish a stable charge-separation network inside TiO_2 particles. The work of Qin et al. on Sc^{3+} -doped rutile TiO_2 for OWS extends this idea to a stricter coupled HER/OER reaction scenario, showing that defect passivation, facet electric fields, and selective reaction sites can synergistically promote electron/hole separation and spatial charge allocation [91]. This result indicates that crystal-phase/facet engineering needs to be evaluated by the translation of charge separation into HER/OER site matching and H_2/O_2 stoichiometric closure, not by morphology or facet proportion alone.

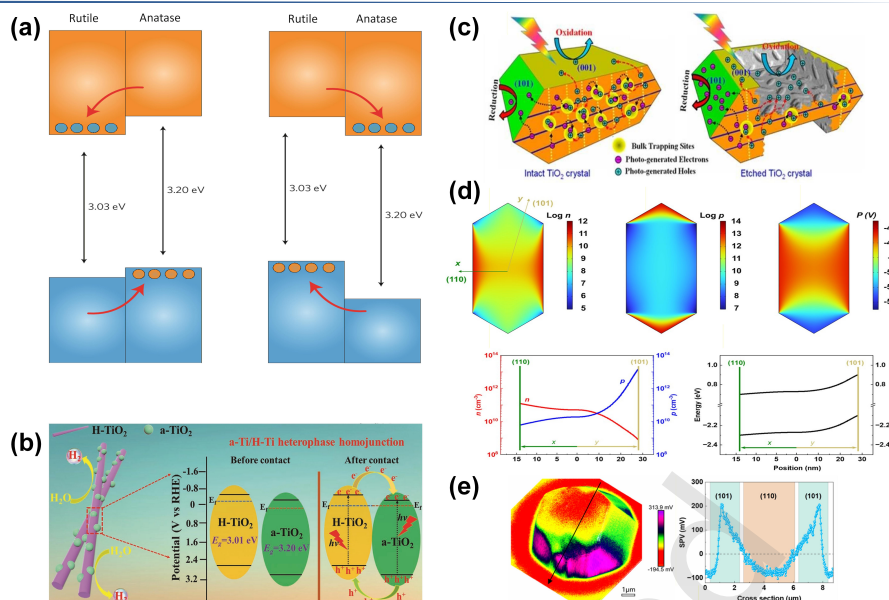


Figure 5 Directional charge separation in TiO_2 regulated by crystal phase, phase junctions, and facets. a, Two band-alignment models for anatase/rutile TiO_2 , showing that interphase electron-migration direction depends on the specific interface and energy-level arrangement. Reproduced with permission from Ref. [33]. b, Band-structure alignment of an $\text{H-TiO}_2/\text{a-TiO}_2$ heterophase homojunction, namely hydrogenated rutile/anatase, illustrating phase-junction-induced charge separation. Reproduced with permission from Ref. [32]. c, Model of surface/bulk carrier trapping in TiO_2 after selective etching of {001} facets. Reproduced with permission from Ref. [89]. d, Schematic of electron/hole spatial distribution and band modulation in Sc-doped rutile TiO_2 . Reproduced with permission from Ref. [91]. e, Surface photovoltage microscopy image and line profile of Sc- TiO_2 as experimental verification of spatial charge separation. Reproduced with permission from Ref. [91].

4.3 TiO_2 -based heterojunctions and conductive interfaces

TiO_2 -based heterojunctions are designed to establish a continuous pathway among external light absorption, interfacial charge migration, and surface reactions. Conventional type-II structures promote spatial separation through energy-level ladders and reduce recombination, which explains the basic role of TiO_2 as an electron-accepting and transport phase. However, such separation is often accompanied by reduced energies of the reduction-side electrons and oxidation-side holes, so it cannot be equated directly with improved OWS efficiency. Later developments involving Z-scheme structures, S-scheme structures, p-n junctions, Schottky interfaces, and MXene conductive interfaces address the same question: how to separate carriers while preserving sufficient redox capability and reducing interfacial consumption resistance.

In visible-light composite systems, TiO_2 usually no longer serves as the main light absorber. Instead, it more often functions as an electron acceptor, transport scaffold, and structural support. In $\text{TiO}_2/\text{CdS}/\text{TiN}$ nanorods, CdS provides visible-light excitation, TiO_2 contributes electron transport and structural support, and the conductivity and plasmonic effect of TiN help improve photocurrent and H_2 generation [71]. Kinetic evidence from g- $\text{C}_3\text{N}_4/\text{TiO}_2$ nanotube systems shows that type-II charge transfer and Z-scheme interactions may coexist at the same interface [74]. Accordingly, TiO_2 heterojunctions need to be evaluated along the sequence of absorption, injection, migration, and interfacial consumption, rather than from static band diagrams alone.

Z-scheme and S-scheme structures further emphasize retention of strongly reducing electrons and strongly oxidizing holes. $\text{TiO}_2/\text{FePS}_3$, $\text{F-TiO}_2/\text{CdS}$, $\text{H-TiO}_2/\text{g-C}_3\text{N}_4/\text{MXene}$, and $\text{Cu}_3\text{P}/\text{TiO}_2$ systems regulate charge migration through interfacial selective recombination, band bending, or built-in electric fields, allowing electrons with stronger reducing ability to be retained and involved in HER

[92–95]. Compared with conventional type-II structures, these structures require stronger evidence of charge-flow direction, such as in situ Kelvin probe force microscopy (KPFM), XPS, EPR, selective deposition, or product response. PL quenching or photocurrent enhancement alone is insufficient for assigning these mechanisms.

Low-dimensional conductive components and defect states can enlarge the contact area of S-scheme or Schottky interfaces, but they may also introduce additional recombination channels. Black TiO_2/COF , CTF- TiO_2 , and $\text{H-TiO}_2/\text{g-C}_3\text{N}_4/\text{MXene}$ structures couple defect trapping, organic semiconductor frameworks, or MXene conductive layers within the same interface [75, 76, 94]. Distinguishing these structures from ordinary multicomponent composites requires mutually consistent evidence for the built-in electric field, intimate contact, selective recombination, and reduction-side electron consumption.

p-n junctions provide another charge-separation pathway through built-in electric fields in depletion regions. Pan et al. constructed $\text{Co}_3\text{O}_4/\text{Ti}^{3+}\text{-TiO}_2/\text{NiO}$ dual p-n junction hollow core-shell structures to enhance photocatalytic H_2 evolution and selective CO_2 photoreduction, showing that p-type oxide interfaces can alter charge separation, hole accumulation, and surface reaction pathways through depletion-layer built-in fields [96]. 0D- $\text{Co}_3\text{O}_4/1\text{D-TiO}_2$ structures further show that coupling one-dimensional TiO_2 scaffolds with Co_3O_4 active sites can improve H_2 generation [97]. The significance of p-n junctions therefore lies in coupling depletion-layer built-in fields, hole accumulation, and surface reaction sites, beyond band matching alone.

Metal/ TiO_2 Schottky interfaces and Ohmic contacts mainly address electron-extraction resistance. Jiménéz-Calvo et al. revisited Pd, Pt, and Au/P25 systems and pointed out that metals are electron sinks and HER sites, but may also promote back reactions when H_2 and O_2 coexist. Their function changes with particle size, loading amount, contact quality, and mass-transport conditions [98]. MXene-derived

Au/C-TiO₂ Ohmic interfaces further show that a two-dimensional conductive component can be transformed at the interface to provide carbon bridges, metal electron sinks, and low-resistance contacts simultaneously, thereby regulating electron-extraction pathways [99]. TiO₂-based interface types are therefore best judged by the consistency among charge-flow direction, redox-capability retention, and

interfacial reaction consumption.

The essential differences among heterointerfaces lie in charge-migration direction, retention of redox capability, and the location of interfacial consumption. Figure 6 summarizes representative mechanisms for type-II/Z-scheme, S-scheme, p-n junction, and Ohmic conductive interfaces.

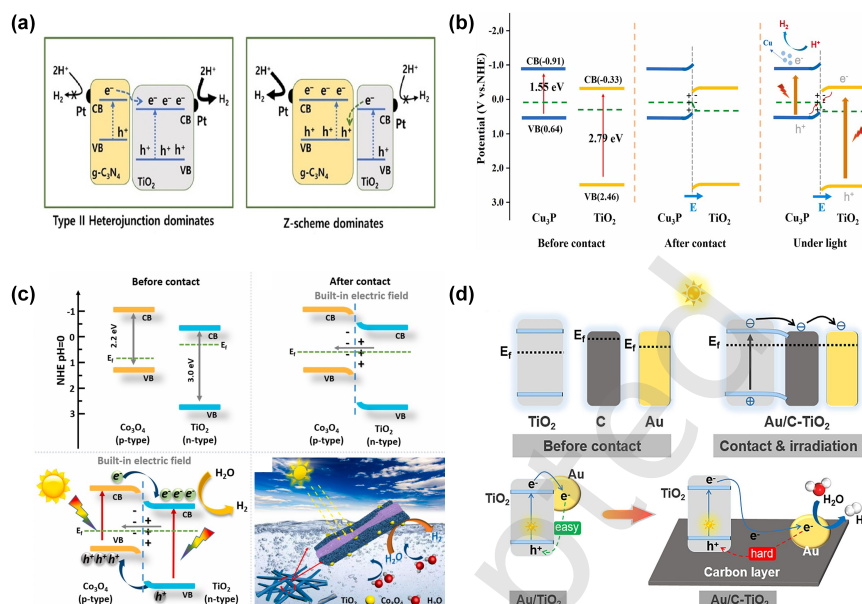


Figure 6 Charge-migration mechanisms in TiO₂-based heterojunctions and conductive interfaces. a, Competition between type-II heterojunction and Z-scheme interaction in g-C₃N₄/TiO₂. Reproduced with permission from Ref. [74]. b, Built-in electric field and charge-migration pathway in a Cu₃P/TiO₂ S-scheme heterojunction. Reproduced with permission from Ref. [95]. c, Band alignment, built-in electric field, and HER site synergy in a zero-dimensional Co₃O₄/one-dimensional TiO₂ p-n junction. Reproduced with permission from Ref. [97]. d, Comparison of electron-transport pathways in C/TiO₂ Ohmic contact and conventional Au/TiO₂. Reproduced with permission from Ref. [99].

4.4 One-dimensional, two-dimensional, and three-dimensional structures and nanofiber systems

Dimensional engineering extends local interfacial charge separation into processable continuous transport scaffolds. One-dimensional TiO₂ nanotube arrays can shorten radial migration distances through the tube walls and provide electron-collection and surface-exposure pathways along the tube axis [6]. The classic work of Chuangchote et al. on electrospun TiO₂ nanofibers showed that electrospinning can produce continuous TiO₂ fiber structures for photocatalytic H₂ generation, providing a basis for later design of immobilized nanofiber catalytic layers [100]. Dimensional engineering addresses more than specific surface area; it also concerns the matching of carrier migration length, reaction-liquid diffusion pathways, and product-release length scales. Compared with particulate TiO₂, electrospun TiO₂ nanofibers provide continuous axial connectivity and membrane-level processability, making them particularly relevant to immobilized photocatalytic layers.

Three-dimensional networks and composite scaffolds can translate local charge separation into continuous electron transport. TiO₂/RuO₂ hybrid nanofibers couple a continuous oxide fiber scaffold with surface RuO₂ sites, organizing light absorption, electron transport, and aqueous mass transfer within the same fiber network [101]. MXene-derived Au/C-TiO₂ Ohmic interfaces further show that a two-dimensional conductive phase can be converted on the TiO₂ surface into carbon bridges and metal electron sinks, reducing cross-interface transport resistance [99]. Compared with simple particle mixtures, these structures reorganize electron-

transport channels, interfacial contacts, and reaction sites within a continuous scaffold instead of merely superimposing multiple materials.

Nanofibers are distinctive because they span microscopic, mesoscopic, and macroscopic scales. At the microscopic level, grain connectivity within fibers determines whether electrons can migrate continuously along the axial direction. At the mesoscopic level, inter-fiber pores control water renewal, ion diffusion, and bubble release. At the macroscopic level, fiber membranes facilitate recovery, immobilized assembly, and modular integration. The work of Li et al. on TiO₂/RuO₂ hybrid nanofibers shows that a continuous fiber scaffold, surface cocatalyst sites, and aqueous mass-transport adaptability can jointly influence H₂ generation [101]. Electrospun TiO₂ nanofibers are therefore cross-scale structural units that connect photocatalytic materials with immobilized reactors, rather than simple powder substitutes.

Tests in saline-water or seawater models further extend the application boundary of fiber engineering. Hierarchical branched TiO₂ constructs continuous charge channels through defective nanostems and Ti-defective nanobranches, maintaining open pores and stable charge transport in complex interfaces involving high ionic strength and bubble evolution [82]. This work indicates that fiber or branched structures need to integrate light-field distribution, pore connectivity, interfacial reactions, and product release to maintain continuous catalytic-layer operation in simulated seawater or complex aqueous environments, in addition to improving the activity of a single material.

Studies of electrospun TiO₂ nanofibers, TiO₂/RuO₂ hybrid nanofibers, fixed-bed reactions, and bubble detachment

indicate that nanofibers and dimensional engineering should be evaluated beyond scanning electron microscopy (SEM) morphology and mass-normalized rates. Fiber diameter, grain connectivity, porosity, membrane thickness, wettability, spatial distribution of cocatalysts, and mechanical stability should also be considered [100–103]. Together, these parameters determine whether charge transport, interfacial contact, liquid renewal, and product release can be coupled within the same structure.

Cross-scale interface design cannot equate structural advantages directly with OWS capability. Red-phosphorus-grafted high-index-faceted TiO₂ heterostructures show that high-index facets, interfacial light-absorbing components, and spatial separation of reaction sites can act synergistically in pure water splitting, but the effect cannot be attributed simply to TiO₂ facets themselves [104]. CoO/h-

TiO₂ and F-TiO₂/Mn_{0.2}Cd_{0.8}S systems more often reflect band alignment, built-in fields, and H₂ production behavior under sacrificial or cocatalyst-containing HER conditions [105, 106]. Mesoporous TiO₂/Co₃O₄ nanosheets can serve as mechanistic references for coupling pore structures, p-n interfaces, and oxidation/reduction sites, but they should not be described directly as evidence for sacrificial-agent-free OWS before synchronous H₂/O₂ stoichiometry, direct O₂ detection, and blank controls are confirmed [107].

At the charge-separation level, crystal-phase/facet regulation, heterointerfaces, p-n junctions, Schottky/Ohmic contacts, and conductive scaffolds address migration problems at different spatial scales and interface types. Table 2 summarizes these strategies according to structural unit, representative systems, mechanistic features, and evaluation boundaries.

Table 2 Comparison of TiO₂ charge-separation and interfacial-structure regulation strategies

Module	Key systems and evidence	Mechanistic keywords	Value and limitations
Crystal-phase/phase-junction regulation	Anatase/rutile TiO ₂ , anatase/rutile heterophase homojunctions, and TiO ₂ /Ti ₃ C ₂ phase junctions [32–35, 86, 87]	Crystal-phase differences, defect states, band alignment, and built-in electric fields jointly determine interphase migration.	Builds separation pathways inside TiO ₂ . Controlled by phase ratio, interface quality, and conductive bridging.
Facet regulation	High-proportion {001} facets, selectively etched facets, and facet-cocatalyst spatial effects [7, 8, 89–91]	Different facets possess different surface energies, adsorption configurations, and charge distributions, enabling division of reaction sites.	Helps charge separation within individual particles. High-energy facets are not necessarily highly active.
Type-II heterojunction	TiO ₂ /CdS/TiN and g-C ₃ N ₄ /TiO ₂ [71, 74]	Electrons and holes migrate along energy-level ladders to different components, reducing recombination.	Mechanistically clear, but redox capability may decrease after separation.
Z-scheme/S-scheme heterojunction	TiO ₂ /FePS ₃ , F-TiO ₂ /CdS, H-TiO ₂ /g-C ₃ N ₄ /MXene, Cu ₃ P/TiO ₂ , and related systems [92–95, 105, 106]	Selective recombination and built-in fields retain strongly reducing electrons and strongly oxidizing holes.	Requires in situ potential, spectroscopic, and product-response evidence. It should not be assigned solely from PL quenching.
p-n junction	Co ₃ O ₄ /Ti ³⁺ -TiO ₂ /NiO, OD-Co ₃ O ₄ /1D-TiO ₂ , and mesoporous TiO ₂ /Co ₃ O ₄ [96, 97, 107]	p-type components and n-type TiO ₂ form a depletion-layer built-in field that drives charge separation.	Can serve as a reference for built-in-field and site synergy. If OWS is claimed, H ₂ /O ₂ ratio, direct O ₂ detection, blank controls, and use of sacrificial agents or added cocatalysts must still be checked item by item.
Schottky interface	Pd, Pt, and Au/P25-TiO ₂ [98]	Metal/TiO ₂ contacts form electron sinks and barriers, promoting reduction-side electron extraction.	Reduces reduction-side recombination. Noble metals may also promote H ₂ oxidation or back reactions.
MXene/conductive interface	Ti ₃ C ₂ @TiO ₂ and MXene-derived Au/C-TiO ₂ Ohmic interfaces [65, 99]	Two-dimensional conductive phases or carbon bridges lower interfacial transport resistance and tune barriers.	Improves electron transport. Oxidation, termination groups, light shielding, and derived carbon-layer structures require attention.

5 TiO₂ surface reaction sites and H₂ production system design

Photoresponse expansion and interfacial-structure regulation determine whether TiO₂-based systems can generate, separate, and transport effective carriers. Surface reactions determine whether electrons and holes are converted into H₂ and O₂, respectively. Evaluation of TiO₂ photocatalytic H₂ production systems therefore goes beyond enhanced absorption or improved charge separation and examines carrier-consumption pathways, reaction selectivity, and long-term stability at surface sites. Sacrificial-agent-assisted HER can amplify reduction-side differences and clarify HER kinetics, whereas Pt-TiO₂, MXene/TiO₂, and single-atom/TiO₂ systems mainly reveal electron extraction and H* formation at metal/TiO₂ or conductive-interface/TiO₂ junctions. These results should not be directly equated with sacrificial-agent-free OWS.

5.1 HER cocatalysts

Pristine TiO₂ has limited ability to adsorb H* and promote H–H coupling. The primary function of HER cocatalysts is to

capture and relay conduction-band or defect-trapped electrons to surface sites that mediate proton reduction. Early work by Kawai and Sakata on H₂ production from photoreforming over Pt/TiO₂ established the basis of noble-metal/TiO₂ interfaces in the H₂-evolution half reaction [17]. Studies on the size and coverage of Ni/Pt cocatalysts, coupling between Pt and surface oxygen vacancies, stabilization of Pt single atoms by Ti-deficient TiO₂, and hydrogen injection on Pt₁-TiO₂ surfaces further show that Pt particle size, oxidation state, surface coordination, and metal-support contact jointly regulate electron extraction, H* adsorption, and H₂ desorption [108–111]. These results establish reduction-side half-reaction kinetics; evaluation of OWS additionally requires paired O₂ evolution, H₂/O₂ stoichiometry, and evidence for sustained oxidation-side activity.

Evaluation of noble-metal/TiO₂ interfaces cannot stop at HER rates. Pt, Pd, Au, and related metals can act as electron sinks and HER sites, promoting photogenerated-electron transfer to the reduction side and lowering the kinetic barrier for proton reduction. However, the study by Li et al. on the unidirectional suppression of hydrogen oxidation by

oxidized Pt clusters shows that the Pt surface state changes the competition among H₂ generation, H₂ oxidation, and O₂ reduction [112]. Wang and Gong further proposed that robust metal cocatalysts should be designed by considering the HER barrier, light-shielding effect, particle aggregation, oxidative deactivation, and back-reaction suppression simultaneously [36]. Noble-metal cocatalyst design therefore needs to optimize electron extraction, H* adsorption, H₂ desorption, back-reaction suppression, and site stability, rather than only increasing the H₂ evolution rate.

Non-noble-metal, low-noble-metal, and conductive interfaces expand the design space for reduction-side sites. Multivalent Cu sites, Ru-Cu synergistic cocatalytic sites, and MXene conductive interfaces such as Ti₃C₂@TiO₂ can improve HER kinetics by regulating interfacial electronic structures, providing low-resistance transport channels, or introducing reduction-side active sites [62–65]. These studies reduce noble-metal loading while also tuning H* adsorption strength, electron-transfer pathways, and aqueous stability through interfacial composition and electronic structure. However, most non-noble-metal or conductive-interface systems are still evaluated under sacrificial HER or half-reaction conditions, so their performance gains cannot be directly extrapolated to OWS.

Earth-abundant cocatalysts offer alternatives to noble metals, with each metric interpreted under its reported reaction conditions. In sacrificial photocatalysis, Ni₂P/N-TFM reached 0.368 mmol g⁻¹ h⁻¹ and retained activity over five cycles [43], while isolated Ni atoms on anatase TiO₂ reached 2.90 mmol g⁻¹ h⁻¹ [113]. In a MoS₂/CdS-TiO₂ nanofiber system, the optimized sample was 3.0 and 4.0 times as active as matched MoS₂/CdS-P25 and Pt/CdS-TiO₂ controls, respectively [72]. These measurements quantify reduction-side electron extraction and HER-site design under specified sacrificial conditions; assessment of OWS additionally requires paired O₂ evolution and H₂/O₂ stoichiometry [12, 15, 16].

Electrocatalytic HER data provide complementary descriptors of interfacial kinetics. Co/TiO₂ required 229 mV at 10 mA cm⁻² in 1.0 M KOH; after 2000 potential cycles the overpotential increased by 39 mV, and it changed negligibly during a 10 h chronopotentiometric test [114]. TiO₂/MoS₂ nanotubes required approximately 210 mV at 10 mA cm⁻² and retained their polarization response after 2000 cycles and 24 h operation [115]. These electrode results are presented through overpotential, current density, and durability metrics, alongside the photocatalytic rates reported under illumination.

Single-atom and cluster cocatalysts further advance HER active centers toward atomic-scale coordination environments. Studies of Pd single atoms on TiO₂, Ni/Co single atoms, Pt-TCPP planar coordination, Ru single atoms, and Co single-atom/RuO_x cluster co-modified TiO₂ show that metal sites, support defects, coordination environments, and oxide clusters can synergistically regulate electron extraction, H* adsorption, and H₂ desorption [113, 116–119]. These studies indicate that TiO₂ cocatalyst research has shifted from nanoparticle loading to the identification and design of atomic-level HER sites.

HER is intrinsically a coupled process involving protons, electrons, and adsorbed H* intermediates. Proton-promoted electron transfer at metal/TiO₂ interfaces is regarded as an important HER step [24]. Studies on ultrasonic-induced surface disordering and Pt single-atom stabilization also

show that the local coordination, electron density, and interfacial water structure of HER sites affect H* formation, H-H coupling, and H₂ desorption [120–122]. Cocatalyst evaluation therefore needs to include electron-extraction pathways, H* adsorption strength, H₂ desorption kinetics, back-reaction suppression, and site stability.

The stability and working state of single-atom sites also determine HER sustainability. Studies of Grätzel-type TiO₂ loaded with Pt single atoms, fluorine-aided stabilization of Pt single atoms, Cu atomic subnanoclusters, and Pt single atoms on thin-layer TiO₂ electrodes show that accessibility, coordination state, and operating-state stability of active sites need to be tracked together [121–124]. Defect-anchored Pt clusters, the distribution of Pt single-atom coordination environments, and scanning transmission electron microscopy (STEM) atomic-resolution imaging provide bases for establishing structure-reactivity correlations [125–127]. Single-atom cocatalysts therefore cannot be assessed only by high metal utilization; structural identifiability and long-term stability of active sites during reaction also need to be demonstrated.

Overall, HER cocatalysts should be evaluated by electron extraction, H* adsorption, H₂ desorption, back-reaction suppression, and site stability. In TiO₂-based OWS, HER enhancement becomes meaningful only when OER closure, H₂/O₂ stoichiometry, and long-term structural stability are verified together.

5.2 OER sites, proton-coupled reactions, and overall water-splitting closure

HER cocatalysts can markedly amplify the reduction half reaction of TiO₂, but the bottleneck of OWS often shifts to the oxidation side and to the matching of the two half-reaction rates. TiO₂ valence-band holes are thermodynamically capable of oxidizing water, but practical OER involves the sustained accumulation of multiple holes on the surface, followed by O-H bond cleavage, transformation of oxygen-containing intermediates, O-O bond formation, and O₂ desorption. Tang et al. linked water-oxidation activity over TiO₂ with hole lifetime and multihole accumulation through transient spectroscopy, showing that OER is not an instantaneous event triggered by a single hole [4]. Zhao and Liu theoretically analyzed how active sites and surface charge states on TiO₂ in aqueous surroundings affect water-splitting pathways [5]. Therefore, TiO₂ OWS requires simultaneous assessment of whether holes reach effective OER sites and whether the oxidation and reduction sides are closed.

The oxidation side is one of the main limitations determining whether OWS can be closed, and it is more than a hole-scavenging channel. Photoelectrochemical (PEC) experiments on TiO₂ photoanodes bearing Pt single atoms show that isolated Pt sites may also regulate water-oxidation kinetics [28]. Sc³⁺-doped rutile TiO₂ further shows that facet built-in electric fields and spatial separation of reaction sites can promote coupled HER/OER synergy [91]. Mesoporous TiO₂/Co₃O₄ nanosheets can serve as a reference for coordinated pore structure, oxidation-side sites, reduction-side sites, and charge separation [107]. High H₂ rates in sacrificial systems are relevant to OWS only when O₂ generation, H₂/O₂ stoichiometry, and back-reaction suppression are also demonstrated.

The surface water structure connects lattice holes in TiO₂ with chemical-bond cleavage. Calculations by Vittadini et al.

on water adsorption on anatase $\text{TiO}_2(101)$ and (001) surfaces showed that different facets have different tendencies to stabilize molecular water, dissociated water, and surface hydroxyls [25]. Ma et al. and Verduci et al. further showed that the first-layer water structure, hydrogen-bond network, and local electric field change water orientation, proton migration, and hydroxyl coverage, thereby affecting OER pathways [26, 27]. Band-edge positions alone are therefore insufficient for judging TiO_2 OWS. Surface hydroxyl coverage, local electric fields, proton-coupled electron transfer (PCET) channels, and OER intermediate stability need to be integrated into the same evidence chain.

Surface hydroxyls exert coverage- and configuration-dependent effects on OER. Molecular and dissociative water adsorption differ between anatase $\text{TiO}_2(101)$ and (001) . Terminal and bridging hydroxyls regulate exposed Ti sites, hydrogen-bond connectivity, local electric fields, and the formation and interconversion of surface OH, O, and OOH intermediates, thereby modulating proton-coupled electron-transfer (PCET) kinetics. Connected, labile hydrogen-bond networks can facilitate interfacial proton transfer, whereas less labile adsorption configurations can restrict site accessibility. Accordingly, the total O 1s surface-OH area should be interpreted together with operando vibrational or isotope-sensitive probes, kinetic isotope effects, direct O_2 quantification, and reaction-appropriate controls [25–28]. Combined scavenger tests, EPR, and electronic-structure calculations provide a methodological framework for relating reactive-intermediate evolution to surface and defect regulation [128].

Proton-coupled electron transfer makes the HER and OER ends no longer isolated half reactions. Proton-promoted

electron transfer at metal/ TiO_2 interfaces reveals the feedback effect of reduction-side proton adsorption on electron injection [24]. The self-hydrogenated near-surface shell observed by liquid-cell TEM indicates that proton reduction, subsurface hydrogen diffusion, and Ti^{3+} structural reconstruction may jointly affect electron transfer and H_2 nucleation [38]. Ultrasonic-induced surface disordering further shows that the distribution of shallow and deep traps changes carrier separation and reduction-side reaction kinetics in water-methanol sacrificial HER systems [120]. These results indicate that electrons, holes, protons, and interfacial water networks require organization cooperatively at the same solid-liquid interface, while different evidence types still require separate interpretation for HER half reactions, PEC, and OWS.

Sacrificial-agent-free OWS requires both spatial separation and matching of the two reaction rates. Li et al. achieved OWS using TiO_2 -based photocatalysts of different phases, showing that TiO_2 has the thermodynamic basis to drive water reduction and oxidation. However, phase-dependent carrier migration and surface reaction pathways determine the extent of H_2/O_2 closure [12]. Sc^{3+} -doped rutile TiO_2 further moves the evaluation scale from single-ended HER enhancement to synchronous HER/OER verification, H_2/O_2 stoichiometric generation, and long-term operational stability [91]. Therefore, OWS-related claims should be reserved for systems where gas stoichiometry, direct O_2 detection, blank controls, back-reaction suppression, and operational stability are reported together.

Placing the reduction side, oxidation side, back reaction, and interfacial water structure within the same figure clarifies why the design of TiO_2 surface reaction sites must go beyond comparison of a single HER rate (Fig. 7).

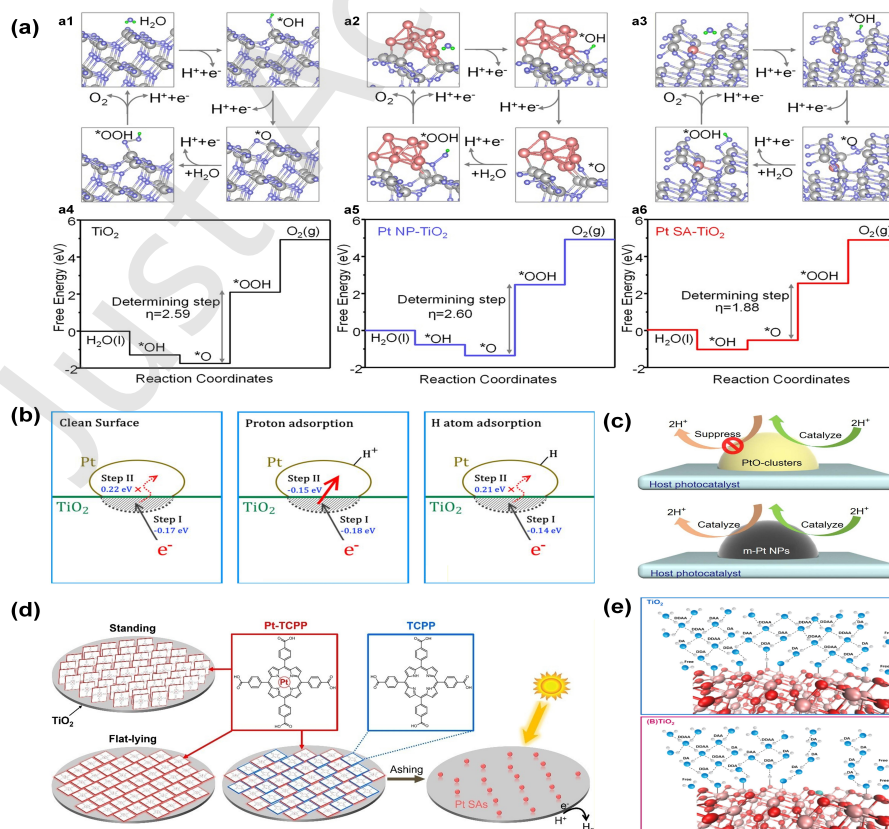


Figure 7 TiO_2 surface HER/OER sites, back reaction control, and interfacial water structure. a, OER adsorption models and free-energy pathways for TiO_2 , Pt nanoparticle- TiO_2 , and Pt single atom- TiO_2 , showing regulation of water-oxidation kinetics by isolated Pt sites. Reproduced with permission from Ref. [28]. b, Two-step mechanism of proton-promoted electron transfer at metal/ TiO_2 interfaces. Reproduced with permission from Ref. [24]. c, Different effects of oxidized Pt clusters and metallic Pt nanoparticles on HER and the H_2/O_2 back reaction. Reproduced with permission from Ref. [24].

[112]. d, Self-assembled single-atom construction mechanism of Pt-TCPP/TCPP on TiO₂ surfaces. Reproduced with permission from Ref. [117]. e, Hydrogen-bond network of water molecules near the TiO₂ surface. Reproduced with permission from Ref. [27].

5.3 Coupled H₂ evolution and organic oxidation reactions

Coupling H₂ evolution with organic oxidation uses photogenerated electrons and holes in complementary half-reactions, and the reaction category is determined by the fate of the organic substrate. Selective, acceptorless alcohol dehydrogenation targets a carbonyl product and H₂, whereas photoreforming proceeds through multiple oxidation intermediates and may approach carbon mineralization [17, 18, 37, 129]. OWS constitutes a separate regime in which water is the sole redox substrate and H₂ and O₂ are generated together [12, 15, 16].

A Pt/N-TiO₂ system activated through ligand-to-metal charge transfer converted alcohols under visible light while coproducing H₂ and aldehydes. Correlating H₂ formation with substrate conversion, carbonyl yield, expected stoichiometry, and controls for solvent or adventitious donors establishes selective dehydrogenation [129]. Glucose photoreforming over TiO₂ and Pt-loaded mesoporous TiO₂ [18], together with microkinetic analysis of methanol photoreforming on metal-loaded anatase [37], shows how substrate-derived intermediates, water activation, and proton transfer jointly influence H₂ production. Accordingly, coupled systems should report substrate conversion, product selectivity and yield, H₂/product stoichiometry, and carbon balance or total organic carbon where relevant. Isotope and blank controls, photon-normalized efficiency, and catalyst stability should also be reported. Together, these data identify selective chemical synthesis, sacrificial hole scavenging, photoreforming, and complete redox closure through their respective product and stoichiometric signatures.

5.4 TiO₂-based immobilized photocatalytic systems, bubble detachment, and reactor scale-up

When TiO₂ moves from powder-suspension systems into nanofiber membranes, immobilized catalytic layers, or photocatalyst panels, the evaluation object expands from single-particle activity to light-field distribution, liquid renewal, bubble detachment, and gas separation. The work of Wei et al. on fixed-bed reactions shows that electron transport and semiconductor-cocatalyst contact within continuous catalytic layers change the efficiency of reactions such as organic dehydrogenation, providing a reference for transport design in immobilized TiO₂ systems [102]. Once particulate photocatalyst panels and large-area solar H₂ production systems are considered, materials factors become coupled with gas collection, flow-field management, and safe separation [13, 14].

Wettability influences TiO₂ photocatalytic H₂ production across molecular and reactor scales. At the molecular scale, surface termination, hydroxylation, and interfacial water structure govern molecular and dissociative water adsorption and proton-transfer networks, as discussed in Section 5.2 [25–27]. At the reactor scale, wettability affects liquid spreading and renewal as well as bubble adhesion, contact-line pinning, growth, coalescence, and release [103]. Together with roughness, pore geometry, gas supersaturation, and flow shear, these effects can influence H₂ productivity through liquid access, bubble residence,

local mass transfer, and optical shielding [103, 130]. Contact angle should therefore be interpreted with surface termination and hydroxylation and with bubble size, residence time, surface roughness, and hydrodynamic conditions.

Bubble-induced loss should be quantified using synchronized imaging and H₂-production measurements. For an illuminated area A_i observed for time T, the time-averaged projected bubble coverage is:

$$\bar{\theta}_b = \frac{1}{A_{\text{ill}} T} \int_0^T A_b(t) dt \quad (4)$$

For approximately circular, non-overlapping bubbles of diameter d_i and surface residence time t_i, the same descriptor can be estimated as:

$$\bar{\theta}_b \approx \frac{\pi}{4A_{\text{ill}} T} \sum_i d_i^2 t_i \quad (5)$$

An operational loss factor should be measured against a matched reference in which attached bubbles are actively removed or their residence time is minimized:

$$L_b = 1 - \frac{r_b}{r_{\text{ref}}} \quad (6)$$

Projected coverage and the operational loss factor should be measured separately because refraction, scattering, total internal reflection, local mass-transfer resistance, and bubble overlap can produce nonlinear optical and kinetic penalties. Periodic light chopping reduced bubble growth time and detachment diameter on a TiO₂ photoelectrode and enhanced near-surface convective transport [103]. Single-bubble measurements on a Si-based model photoelectrode resolved increasing optical losses for attached H₂ bubbles with radii above 100 μm using scanning photocurrent microscopy and optical modeling [130]. A complementary multi-parameter validation strategy supports reporting bubble imaging together with gas balance, cycling, and post-reaction characterization [66].

Immobilized TiO₂ membranes differ from powder-suspension systems because the reaction interface changes from dispersed particles to continuous catalytic layers with thickness, pore channels, and electrical connections. Pore connectivity determines liquid renewal and gas release. Layer thickness determines light attenuation and the effective catalytic fraction. Contact resistance and mechanical stability affect inter-particle or inter-fiber transport. Powder systems have high external surface area and short mass-transport pathways, but they suffer from aggregation, sedimentation, light shielding, post-treatment difficulty, and gas-entrainment risks. Immobilized systems facilitate recovery and continuous operation, but they need to overcome internal low-light regions, mass-transport resistance, and mechanical-stability limitations [102–104].

Performance indicators for immobilized TiO₂ systems expand from mass-normalized rates to area-normalized productivity, thickness- or volume-normalized efficiency, gas-recovery efficiency, and long-term stability. For nanofiber membranes and immobilized catalytic layers, fiber structure, membrane thickness, and pore connectivity

are related to charge transport and liquid renewal [100–102], whereas wettability and bubble-detachment behavior affect product release and local light shielding [103]. Systems evaluated for solar-fuel conversion should also report apparent quantum yield/efficiency (AQY/AQE), solar-to-hydrogen conversion efficiency (STH), gas recovery, and necessary blank controls according to unified protocols [39, 40].

Saline water, seawater models, and wastewater/pollutant-coupled systems further require that competitive salt-ion adsorption, substrate oxidation pathways, and safe gas collection be included in a unified evaluation. Hierarchical branched TiO_2 emphasizes the importance of open pores and charge channels in H_2 production tests using saline-water/seawater models [82]. Metal-organic framework (MOF)-derived TiO_2 coupling herbicide degradation with H_2 generation, simultaneous value-added utilization over Pd/TiO_2 , and microkinetic models for methanol reforming show that pollutant/substrate oxidation, H_2O_2 generation, selective organic oxidation, and methanol-reforming

pathways change hole consumption, the origin of evolved hydrogen, and product distributions [37, 131, 132]. These systems are better evaluated through electron/hole utilization, product selectivity, gas recovery, and long-term operating conditions than through a single H_2 evolution rate.

Scale-up from materials to reactors is not achieved by increasing catalyst mass or illuminated area alone. It requires mutual matching among light-absorption depth, carrier-diffusion length, pore-channel scale, bubble-detachment scale, and gas-separation pathway. TiO_2 -based photocatalytic systems become comparable and verifiable solar H_2 platforms when materials-scale charge-separation advantages are translated into stable gas evolution, reliable recovery, and scalable operation in immobilized structures.

For immobilized TiO_2 systems, the central task is to organize charge transport within fibers or membranes, liquid renewal, bubble detachment, and gas-recovery evaluation procedures in one structure, rather than only fixing powders on a support (Fig. 8).

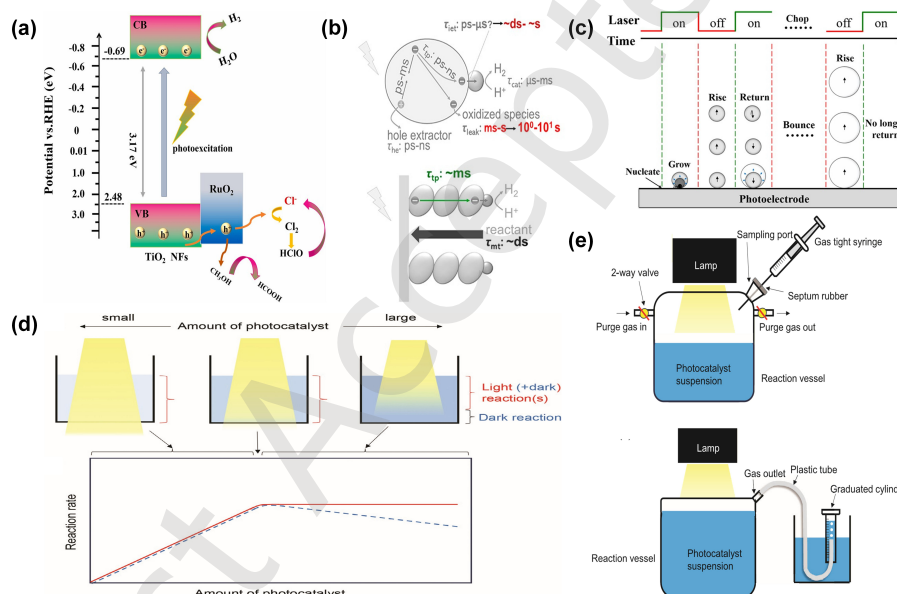


Figure 8 TiO_2 -based immobilized structures, bubble detachment, and evaluation protocols. a, Charge-migration and H_2 production mechanism of $\text{TiO}_2/\text{RuO}_2$ hybrid nanofibers in saline-water and seawater-model systems under sacrificial-agent conditions. Reproduced with permission from Ref. [101]. b, Differences in reaction time scales and electron-transport processes between slurry systems and fixed-bed reactors. Reproduced with permission from Ref. [102]. c, Bubble bouncing and detachment mechanism on a TiO_2 photoelectrode surface. Reproduced with permission from Ref. [103]. d, Schematic of light penetration depth under different photocatalyst loadings, showing that mass-normalized rates may be affected by light penetration. e, Gas sampling and upward water-displacement gas collection, supporting gas-recovery and testing protocols. Reproduced with permission from Ref. [40].

Because different reaction systems support different conclusions, evaluation of TiO_2 -based H_2 production needs to align reactant sources, product pathways, and gas stoichiometry [15–18, 129], together with system-scale performance metrics [39, 40]. Table 3 distinguishes

sacrificial H_2 evolution, selective organic oxidation/dehydrogenation coupled with H_2 production, photoreforming, pollutant-coupled systems, simultaneous value-added utilization, sacrificial-agent-free OWS, and immobilized systems.

Table 3 Reaction boundaries and required reporting indicators for TiO_2 -based photocatalytic H_2 production

Reaction/system	Conclusions supported	Conclusions not supported	Required reporting and checks
Sacrificial-agent-assisted H_2 evolution [15, 16]	Reduction-side electron extraction, HER cocatalyst activity, and differences in interfacial transport resistance.	Does not prove sacrificial-agent-free OWS and does not directly demonstrate closure of the OER side.	Sacrificial-agent type and concentration, light source conditions, AQE, hydrogen-origin controls, blank experiments, and cycling stability.
Selective organic oxidation/dehydrogenation coupled with H_2 production [129]	Coupled use of reduction and oxidation equivalents with simultaneous H_2 formation and a quantified selective organic product.	Classified as coupled selective conversion because the organic substrate participates in the oxidation half-reaction; OWS requires water as the sole redox substrate.	Substrate conversion; product selectivity/yield; H_2 /product stoichiometry; carbon balance; isotope/blank controls; AQY/AQE; stability.

Reaction/system	Conclusions supported	Conclusions not supported	Required reporting and checks
Organic-substrate reforming [17, 18, 37]	Coupled pathways of substrate oxidation and H ₂ generation, hole utilization, and reduction-side kinetics.	Cannot be equated with pure water splitting. H ₂ may originate from water, substrate, or both.	Carbon oxidation products, intermediates, total organic carbon or selectivity, isotope/blank controls, and catalyst reconstruction.
Pollutant-coupled H ₂ production [131]	Possibility of coupling pollutant oxidation as a hole consumption pathway with HER.	Cannot serve as evidence for clean-water H ₂ production or OWS.	Degradation pathway, mineralization degree, toxic intermediates, H ₂ origin, and long-term antifouling stability.
Simultaneous value-added utilization [132]	Photogenerated electrons and holes enter value-added product channels, such as H ₂ O ₂ formation or selective oxidation.	If H ₂ is not generated, it cannot be described as H ₂ production evidence. Without closure of the OER side, it cannot be described as OWS.	Quantification of electron-side and hole-side products, selectivity, Faradaic or carbon balance, competing reactions, and stability.
Sacrificial-agent-free OWS [12, 39, 40, 91]	Coupled HER/OER closure, H ₂ /O ₂ stoichiometry, and solar H ₂ production evaluation.	Cannot be extrapolated from HER half reactions, PEC half cells, or sacrificial systems.	H ₂ /O ₂ ≈ 2:1, AQY/AQE and STH efficiency, gas-recovery rate, isotope/blank controls, back reaction suppression, and long-term stability.
Immobilized systems [13, 14, 39, 40, 101–103]	Feasibility of translating material activity into continuous catalytic layers, bubble release, and gas-recovery processes.	Mass-normalized rates do not directly represent reactor performance. Engineering references do not automatically prove TiO ₂ scale-up.	Areal rate, catalyst loading/membrane thickness, light penetration, pore-channel mass transfer, bubble detachment, mechanical stability, and safe separation.

6 Conclusions and outlook: From TiO₂ model systems to verifiable and scalable solar H₂ production systems

The development of TiO₂ photocatalytic H₂ production reflects a transition from model-semiconductor studies to verifiable reaction systems. The TiO₂ electrode work by Fujishima and Honda established the starting point for photoelectrochemical splitting at semiconductor/water interfaces [3]. Studies by Tang, Zhao, Liu, and others on hole dynamics, surface water structure, and active sites further show that TiO₂ serves as a light absorber, a resolvable oxide lattice, a band-structure platform, and a solid-water interfacial model [4, 5]. As work has confronted the wide band gap, recombination loss, sluggish HER/OER kinetics, and H₂/O₂ back reaction, the field has moved from single-parameter activity enhancement toward coordinated optimization of effective absorption, directional migration, coupled HER/OER reaction closure, and system-scale mass transfer.

6.1 From single-point modification to coupled structures: Effective states, directional migration, and reaction closure

Photoresponse expansion is best evaluated through effective carriers. N-doped TiO₂ established the basic concept of extending visible-light response through valence-band regulation, but subsequent studies of N/C doping, codoping, black TiO₂, oxygen vacancies, and Ti³⁺ centers show that newly introduced states can still become recombination centers if they are too deep, too dense, or mainly located in the bulk. Doping and defect strategies are better judged by absorption-state positions, carrier lifetimes, spatial defect distribution, pre- and post-reaction stability, and product consistency, rather than by color change or absorption-edge shift alone. Sensitized composites and broadband absorbing units form sustainable H₂ production pathways when electron injection, sensitizer regeneration, photocorrosion suppression, and HER site consumption operate together.

Charge separation, surface reactions, and system-level mass transfer also need to be designed cooperatively within the same structure. Crystal-phase/facet/phase-junction regulation, heterojunctions, p-n junctions, Schottky/Ohmic interfaces, and conductive scaffolds address directional migration. Metal or bimetal sites, single-atom sites, RuO_x,

and surface water networks extend the discussion to interfacial processes such as H⁺ adsorption, PCET, OER hole accumulation, H₂/O₂ back reaction, and bubble detachment. These strategies constitute meaningful OWS improvements when product generation, H₂/O₂ stoichiometry, long-term stability, and necessary controls mutually support one another.

6.2 Future research priorities: From reaction boundaries to scalable systems

Future research on TiO₂-based photocatalytic H₂ production begins with tighter alignment between reaction boundaries and performance evaluation. Sacrificial H₂ evolution is suitable for diagnosing reduction-side electron utilization and HER site activity. Photoreforming requires clear assignment of substrate contributions and the origin of evolved hydrogen. OWS requires reporting of H₂/O₂ stoichiometry, direct O₂ signals, AQY/AQE, STH, gas recovery, blank controls, back-reaction suppression, and long-term stability. Clear reaction boundaries are needed before H₂ generation rates, quantum efficiencies, and system scale-up potential can be compared meaningfully.

Mechanistic assignment of heterojunctions and conductive interfaces should move from static band diagrams toward in situ evidence. Type-II, Z-scheme, and S-scheme structures cannot be assigned solely on the basis of absorption enhancement, PL quenching, or photocurrent increase. They require support from in situ KPFM, XPS, EPR, transient absorption, selective deposition, radical and product responses, and interfacial-contact evidence to confirm whether charge-flow direction, retention of strongly reducing electrons and strongly oxidizing holes, and reaction-site consumption are consistent. For TiO₂, an effective interfacial structure does more than add components. It addresses electron/hole separation, preservation of redox capability, and interfacial reaction closure within the same system.

Cocatalyst design is moving from HER-only enhancement toward coupled HER/OER closure. Noble metals, non-noble metals, single atoms, and cluster sites can regulate electron extraction, H⁺ adsorption, H₂ desorption, and reduction-side kinetics. OWS, however, also requires attention to OER hole accumulation, PCET, surface water networks, H₂/O₂ back reaction, and long-term site stability. For highly active metals such as Pt, Pd, and Au, their HER activity can be exploited while minimizing the risk of back reactions or

product recombination under coexisting H_2/O_2 conditions.

For lab-to-industry translation, optically thin immobilized layers and continuous-flow configurations should preserve controllable photon penetration, residence-time distribution, liquid renewal, and pressure drop during scale-up. Bubble disengagement and gas separation should be evaluated as independent reactor-level variables. Areal H_2 productivity, catalyst loading, illuminated-area-to-volume ratio, single-pass conversion, gas-recovery efficiency, and energy consumption should be reported together.

Modular numbering-up can limit dark zones and nonuniform flow when each module preserves irradiance, hydrodynamics, bubble-removal paths, and safe H_2/O_2 handling. Continuous operation should track catalyst loss, delamination, fouling, and activity retention together with surface corrosion and elemental leaching.

Durability encompasses both physical failure—including cracking, delamination, fiber or film breakage, pore collapse, and catalyst loss—and chemical deactivation through cocatalyst dissolution, defect reoxidation, phase or interface reconstruction, elemental leaching, or surface contamination. TiO_2 -based systems should therefore evaluate bulk-phase and surface/interface evolution together with catalyst retention and leaching.

During prolonged UV-driven operation, accumulated photoholes can promote surface corrosion of TiO_2 photoanodes, whereas rapid hole consumption and formation of an amorphous titanium-hydroxide surface layer were reported to suppress photocurrent decay [133]. These observations motivate tracking charge accumulation and surface reconstruction during prolonged photocatalytic testing. Durability enhancement should therefore combine rapid hole consumption and surface-state stabilization with robust catalyst anchoring and recoverable immobilized architectures.

For application-oriented immobilized systems, non-targeted molecular-networking and mass-spectrometric workflows can complement elemental analysis by screening previously unidentified migrants or leachables [134].

A minimum durability protocol should combine long-duration irradiation, light-dark cycling, gas balance, and activity normalization. Immobilized systems should additionally quantify catalyst recovery and dissolved elements. Matched pre-/post-reaction structural characterization and surface or defect analysis by XPS or EPR should be selected according to the expected degradation mode.

Data-driven approaches can accelerate TiO_2 optimization when input and target definitions explicitly encode reaction boundaries. A Gaussian-process model has linked lattice parameters and surface area to the band gaps of doped anatase TiO_2 [135], while a separate model trained on 971 literature entries predicted cocatalyst-deposited TiO_2 H_2 -evolution rates using active photon flux, cocatalyst work function and loading, and alcohol identity and concentration as input features [136]. These examples connect electronic-property prediction and reaction-rate prediction to their respective input descriptors.

Future screening of dopants and heterojunctions should include defect formation energy, band-edge position, work-function difference, interface compatibility, redox retention, water/intermediate adsorption, and stability. These

descriptors can then be combined with data-driven screening and experimental validation. Because light spectrum, photon flux, catalyst loading, sacrificial reagent, reactor geometry, and normalization basis strongly affect reported rates, harmonized metadata, uncertainty estimates, negative results, and external validation are prerequisites for transferable models.

Verifiable and scalable TiO_2 H_2 -production systems require nanoscale evidence to be connected with photon-delivery and gas-recovery metrics and with durability and gas-management criteria for immobilized operation.

Data availability

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

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Q. D. L.: Writing – original draft, Investigation, Data curation, Visualization. Y. H. Y.: Validation. Y. X.: Validation, Visualization. X. T. C.: Validation, Visualization, Resources. X. Y.: Writing – review & editing. Y. T. L.: Writing – review & editing. B. D.: Writing – review & editing, Supervision, Funding acquisition.

Use of AI statement

During the preparation of this work, the authors used Gemini to polish language and check grammar. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the final manuscript.

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