

Photoelectrocatalytic Nitrogen Reduction to Ammonia: a Review of Advanced Materials and Interface Engineering

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Abstract

Ammonia is essential for fertilizers, chemicals, and emerging carbon-free energy systems, yet its conventional production relies on an energy-intensive process with substantial carbon dioxide emissions. Photoelectrocatalytic nitrogen reduction has emerged as a promising route for sustainable ammonia synthesis under mild conditions, combining solar light absorption with an electrochemical bias to activate the inert nitrogen molecule. This review examines recent progress in this field, focusing on the design of stable titanium dioxide-based photoanodes and selective photocathodes incorporating copper oxide and two-dimensional transition metal dichalcogenides such as molybdenum disulfide and tungsten disulfide. Synthesis strategies, fabrication methods, cell configurations, reaction mechanisms, and performance parameters are discussed. Key challenges, including the high activation barrier of nitrogen, competing hydrogen evolution, and nitrogen mass-transfer limitations, are analyzed alongside verification protocols and future directions for efficient, carbon-free ammonia production.

Keywords: Photoelectrocatalytic nitrogen reduction; Green ammonia synthesis; Titanium dioxide photoanode; Transition metal dichalcogenide co-catalysts; Solar-to-fuel conversion

1. INTRODUCTION

Ammonia (NH₃) is the second largest commercially produced chemical worldwide, with a production rate of almost 200 million metric tons and a total capacity of almost 240 million tons every year. The role of ammonia in the development of human civilization is of prime importance as 80% of its production is used for fertilizer purposes, which indirectly supports almost 70% of the global population. It is estimated that almost half of the nitrogen present in the human body is due to ammonia present in plants [1]. In addition to fertilizer production, ammonia is used as a vital component for the development of pharmaceutical and other chemicals such as nitric acid, hydrazine, and amino acids. It is also used as a prime refrigerant in various industries. After the Montreal protocol of 1989, which led to the ban on the use of CFC-based ozone-depleting agents (chlorofluorocarbons), the ozone depletion potential (ODP) and global warming potential (GWP) of ammonia remain almost zero, making ammonia an energy-efficient and environmentally friend-

ly refrigerant for various applications [1,2]. Lately, ammonia has been at the center of attention as a prime carrier of hydrogen and as a carbon-free fuel. It is noted that while the storage of pure hydrogen demands extreme conditions of low temperature (–253 °C) or high pressure (70 MPa), it can be liquefied at a moderate –33 °C or 0.8–1.0 MPa at normal temperature [1,3]. More importantly, liquid ammonia is endowed with a volumetric hydrogen density of almost 106 kg·m^{–3} significantly higher than that of liquid hydrogen (70 kg·m^{–3}) and a superior energy density of 3.83 MWh·m^{–3}. These properties allow ammonia to leverage existing fossil fuel infrastructure for global transport and distribution. Moreover, its high-octane rating of 110–130 makes it a promising fuel for internal combustion engines, where it is used in combination with other fuels for optimal combustion and thermal efficiency properties [1,4,5].

However, in spite of these multifaceted advantages, more than 90% of the world's ammonia is currently synthesized by the Haber-Bosch (H-B) process $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$. This is a catalytic reaction carried out

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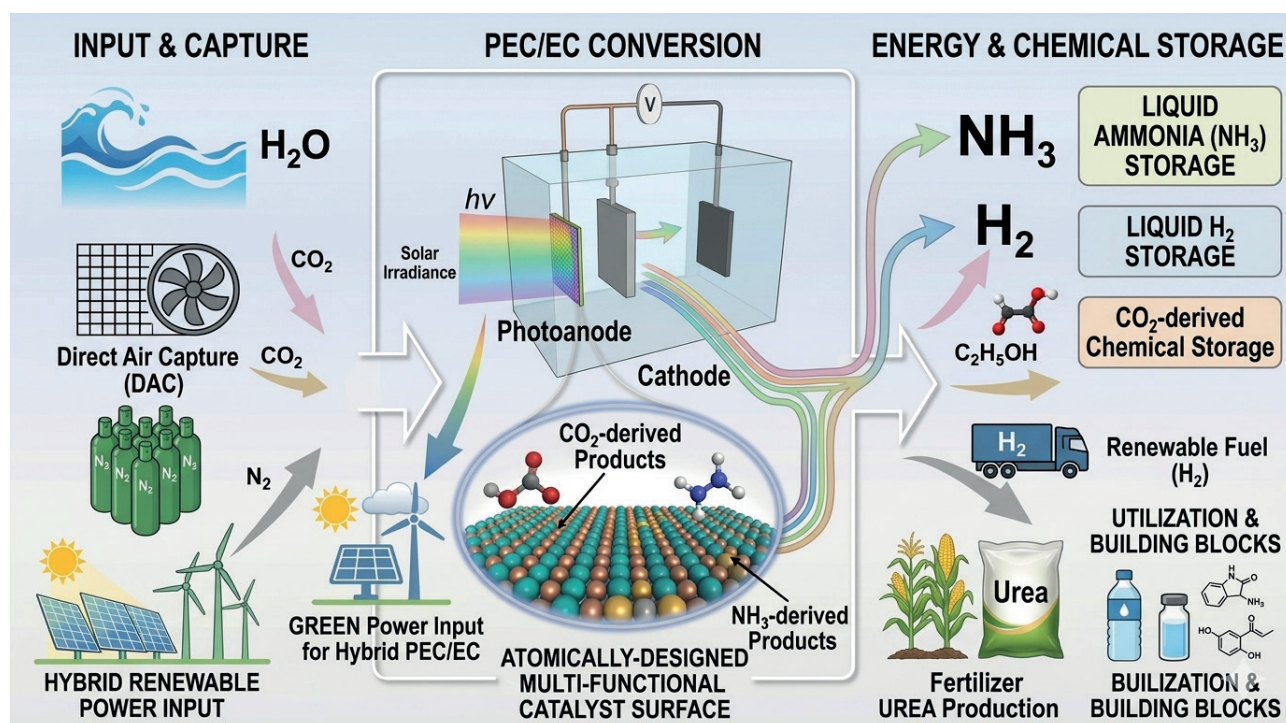


Fig. 1. Schematic represents a photoelectrochemical system for H₂ and NH₃ evolution and CO₂ reduction to value-added chemicals. Adapted from Ref. [11].

in extreme conditions of 300–500 °C and 150–250 bar, consuming approximately 2% of global energy and resulting in significant CO₂ emissions [1]. To address these environmental and energetic challenges, various new technologies have been proposed for the production of “green” ammonia under the mild conditions. In chemical looping, metal hydrides or nitrides can be used as catalysts for the production of ammonia through separated nitrification and hydrogenation loops. This method is promising for the production of ammonia with reduced energy consumption compared to the H-B process. However, the complexity of the reactors and stability of the carrier materials have limited the application of this method for ammonia production [1]. Similarly, while pure electrochemical, photocatalytic, and plasma-assisted methods have been proposed as promising approaches for the production of ammonia, they are currently limited by low Faradaic efficiencies and conversion rates [6,7]. Among the various approaches proposed for the production of ammonia, the perovskite structure (ABX₃) has been commonly observed due to their tunable electronic properties and high catalytic activity under ambient conditions [8].

Building upon these advancements, photoelectrocatalytic (PEC) reduction of nitrogen has been established as the cutting-edge hybrid approach, which exploits the synergistic effects of the combination of sunlight excitation and an electrochemical bias [9]. This method has the potential to overcome the large kinetic barrier of the chemically inert N≡N triple bond in the ambient envi-

ronment [10]; see Fig. 1. The following review assesses the current status in this field, with special emphasis on the development of stable TiO₂-based photoanodes, the design of selective photocathodes/co-catalysts, including CuO and 2D transition metal dichalcogenides (TMDCs) such as MoS₂, WS₂, etc. In this regard, the synthesis options, the fabrication methods for the photoanodes, the contemporary configurations, the reaction mechanisms, and the relevant parameters affecting the synthesis efficiency will be presented.

2. THE PRINCIPLES AND CHALLENGES OF PEC NITROGEN REDUCTION

Photoelectrocatalytic nitrogen reduction (PEC NRR) has been identified as a highly promising approach that combines the merits of electrocatalysis (EC) and photocatalysis (PC), while circumventing the demerits of the individual processes to provide a “green chemistry-based” alternative to the conventional method of ammonia production [11]. In PEC cells, the mechanism is described to start with light absorption in a semiconductor photoelectrode. As light of energy greater than the band gap energy of the semiconductor material is absorbed, electrons are excited to the conduction band (CB), and holes are left in the valence band (VB); see Fig. 2. The second step of the mechanism is the separation of the generated electrons and holes and their transport to the electrolyte interface and back contact. The last step of the mecha-

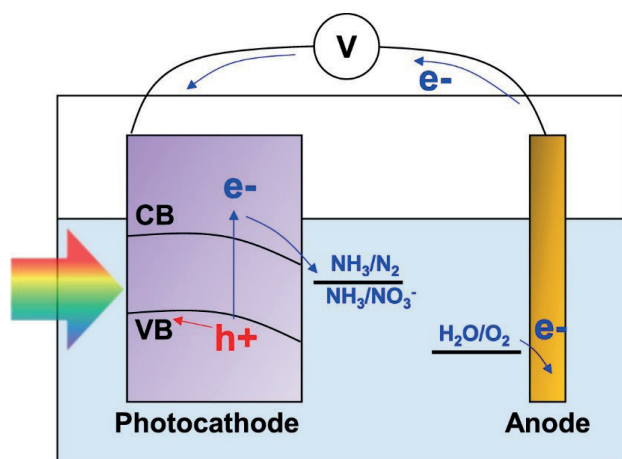


Fig. 2. Schematic illustration of photoelectrochemical ammonia synthetic system using a semiconductor photocathode via N_2 or NO_3^- reduction reactions. Light is irradiated onto the photocathode under electrical bias. Reproduced from Ref. [17] under the terms of the [Creative Commons Attribution 4.0 International \(CC BY\) License](#).

nism is the interfacial charge transfer, which completes the redox reaction necessary for nitrogen fixation [12]. The primary bottlenecks of PEC NRR currently remain the high activation energy barrier for $\text{N}\equiv\text{N}$ bond cleavage (941 kJ/mol) due to the inert property of the symmetric, tightly bound configuration of molecular orbital structure. Moreover, the low solubility of N_2 in aqueous condition due to its low polarity limits the mass transport and reaction flux. In addition, the cathodic NRR usually occurs in the potential range of water dissociation to provide active hydrogen (H^*), where hydrogen evolution reaction (HER) is thermodynamically more favorable ($\Delta G = -16.5 \text{ kJ}\cdot\text{mol}^{-1}$), leading to significant competitive charge utilization. Therefore, improving yield and Faradaic efficiency (FE) remains the central objective of current research and severe HER competition.

One of the major advantages of the new approaches is that protons are extracted from aqueous media (e.g., H_2O), thus obviating the need for gaseous hydrogen [11]. Nevertheless, each of the PC and EC methods has its unique technical challenges [13]. For example, PC NRR is often limited by the low energy content of sunlight and by the fast non-radiative recombination of photoexcited charge carriers, a situation that has been shown to limit the rate of ammonia production, as demonstrated by Zieginbalg et al. [14]. Conversely, although EC NRR has faster production kinetics, its use of high-grade electrical energy, a second energy source, undermines its sustainability, as has been pointed out by Wang et al. [13] and Ismael et al. [15]. Thus, through the integration of the beneficial aspects of these two fields of knowledge, a photoelectrochemical system is designed to harvest incident photons to produce “hot” high-energy electrons to achieve a photovoltage that reduces the required external voltage

and effectively decreases the onset potential for nitrogen fixation. As highlighted by Ren et al. [16] the application of an external voltage in a PE system leads to a band bending at the semiconductor-electrolyte interface and thus creates a strong internal electric field, a so-called depletion layer. This effectively creates a pump for the efficient transfer of holes to the photoanode material (e.g., TiO_2) while at the same time directing a concentrated flow of electrons to the active sites for the fixation of the chemically inert nitrogen molecule [16].

Beyond these mechanistic advantages, PEC-NRR is especially promising because it has the potential to directly convert unlimited clean and green energy to value-added chemicals, thereby contributing to the global energy and environmental sustainability agendas [18,19]. When compared to PC-NRR, it is clear that the external bias used in the PEC system greatly improves the separation efficiency of the photo-generated electron-hole pairs, thus improving the NH_3 yield rate. Moreover, this PEC system has the ability to be integrated with other photo voltaic cells, including other types of solar cells, to further increase the efficiency of the overall system used for the conversion of sunlight into NH_3 . In this context, it is imperative to highlight the need to develop high-efficiency photoelectrodes, particularly n-type semiconductor materials like TiO_2 , which are used as photoanodes. These photoanodes play a critical role in defining the initial efficiency of the entire system, as they are responsible for absorbing light and producing the requisite holes for the oxidation of water, which is responsible for providing the requisite protons (H^+), which are critical for nitrogen fixation. At the same time, the electrons produced in the photoanode are transferred to the cathode, which is responsible for providing the requisite platform for the adsorption, activation, and reduction of N_2 , as proposed in the literature [13]. Therefore, the rational design of the photoanode, along with the cathode, is critical for the future adoption of PEC-NRR, as proposed in the literature [20–22].

However, despite these theoretical advantages, PEC-NRR is still in its infancy compared to other, more established technologies like PEC water splitting, which has already surpassed 30% solar to hydrogen conversion efficiency through the integration of multi-junction solar cells [23,24]. For PEC-NRR to emerge as a viable competitor to conventional technologies, technoeconomic modeling has identified an efficiency threshold of 10% for a viable device [13]. Achieving this goal is extremely challenging since the overall conversion efficiency is the cumulative effect of the efficiencies of photocarrier generation, separation, transport, and the final surface reaction; any loss in these steps affects the performance [25]. The major technical hurdle lies in the very inert nature of the nitrogen molecule, with a bond dissociation energy of $945 \text{ kJ}\cdot\text{mol}^{-1}$, thereby creating a staggering barrier for the

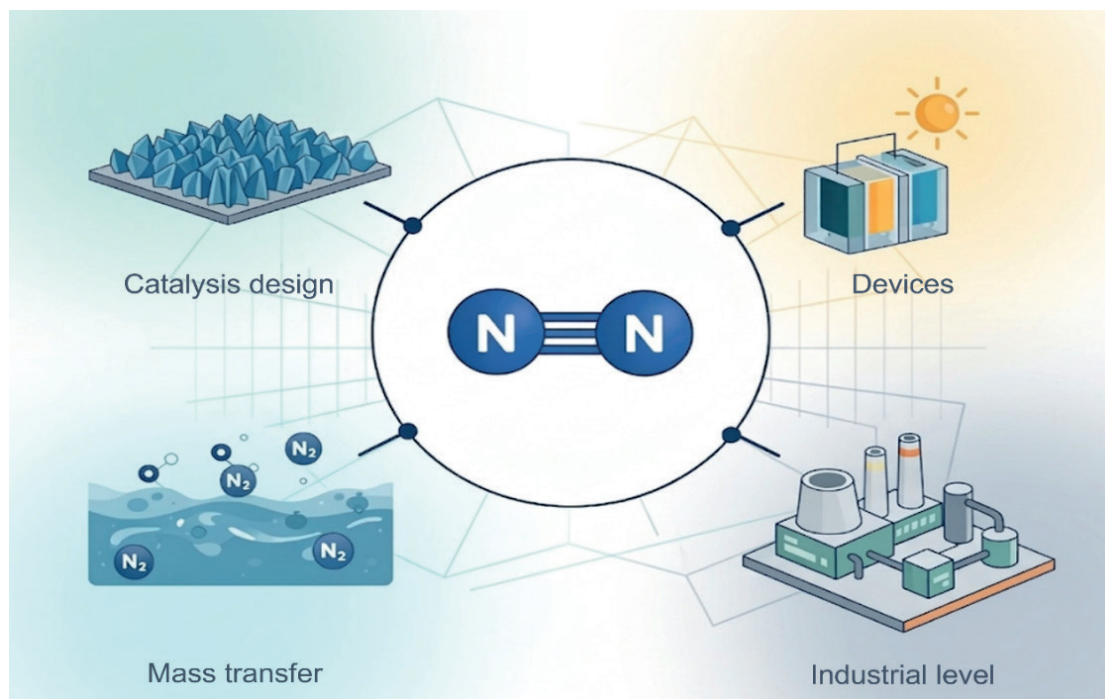


Fig. 3. Key challenges and bottlenecks in PEC-NRR. The major challenge is the thermodynamic stability of the $\text{N}\equiv\text{N}$ triple bond ($945 \text{ kJ}\cdot\text{mol}^{-1}$). To overcome this challenge and make PEC-NRR industrially relevant, the challenges in catalyst design, device fabrication, and scaling up must be overcome to cross the 10% efficiency barrier.

initial electron transfer. In addition, the effectiveness of the process is usually marred by the presence of a hydrogen evolution reaction, which usually overwhelms the catalyst surface due to kinetic advantages, thereby limiting Faradaic efficiency; see Fig. 3 [13,25].

To overcome these complex challenges, from poor light absorption to slow N_2 mass transfer, research is now shifting focus toward the rational design of highly advanced cell and material architectures. In a standard PEC system, the device is comprised of an n-type semiconductor material that functions as a photoanode for oxidation reactions, where the photogenerated electrons are transferred to the cathode or a p-type photocathode to achieve reduction reactions. Due to the inability of the photovoltage from the photoelectrode to provide the necessary overpotential for the reaction, an external DC voltage is often required, or tandem cells consisting of both the photocathode and photoanode are employed to maximize photon absorption and provide the necessary overpotential [13]. Within this paradigm, the design and synthesis of n-type semiconductor materials such as nanostructured TiO_2 , and the introduction of highly advanced and specific 2D co-catalysts such as MoS_2 and WS_2 provide the opportunity to overcome the challenges of N_2 activation by electronic back-donation, along with the suppression of the competing HER reaction [26]. By taking full advantage of the unique electronic properties afforded by the design of heterojunctions with other semiconductor materials such as CuO , highly advanced fabrication techniques are now employed to pro-

vide the optimal charge separation and kinetics required for the synthesis of green ammonia [12].

3. MATERIAL SYNTHESIS & FABRICATION FOR PHOTOELECTRODES

3.1. Fundamental requirements and material selection

The transition from theoretical principles to a functional PEC-NRR device involves the rigorous selection of materials on the basis of thermodynamic and kinetic properties. As mentioned in the previous section, while the fundamental mechanisms of charge transport have been established, their application in practice requires an emphasis on the engineering of the semiconductor-electrolyte interface [27]. For a functioning photoelectrode to be viable in practice, it is required that it satisfies rigorous band-gap conditions far in excess of the theoretical minimum band-gap required to drive an unbiased system, i.e., 1.23 eV. Indeed, in order to satisfy thermodynamic energy losses (0.3–0.4 eV) and overpotentials required to drive surface reaction kinetics (0.4–0.6 eV), an optimized band-gap range of 1.9–3.2 eV is required to drive the necessary voltage required in a functioning system. In system where the intrinsic PV generated is less than the 1.61 V threshold necessary to operate in unbiased mode, it becomes compulsory to incorporate an external bias or a tandem structure. Moreover, the fabrication pro-

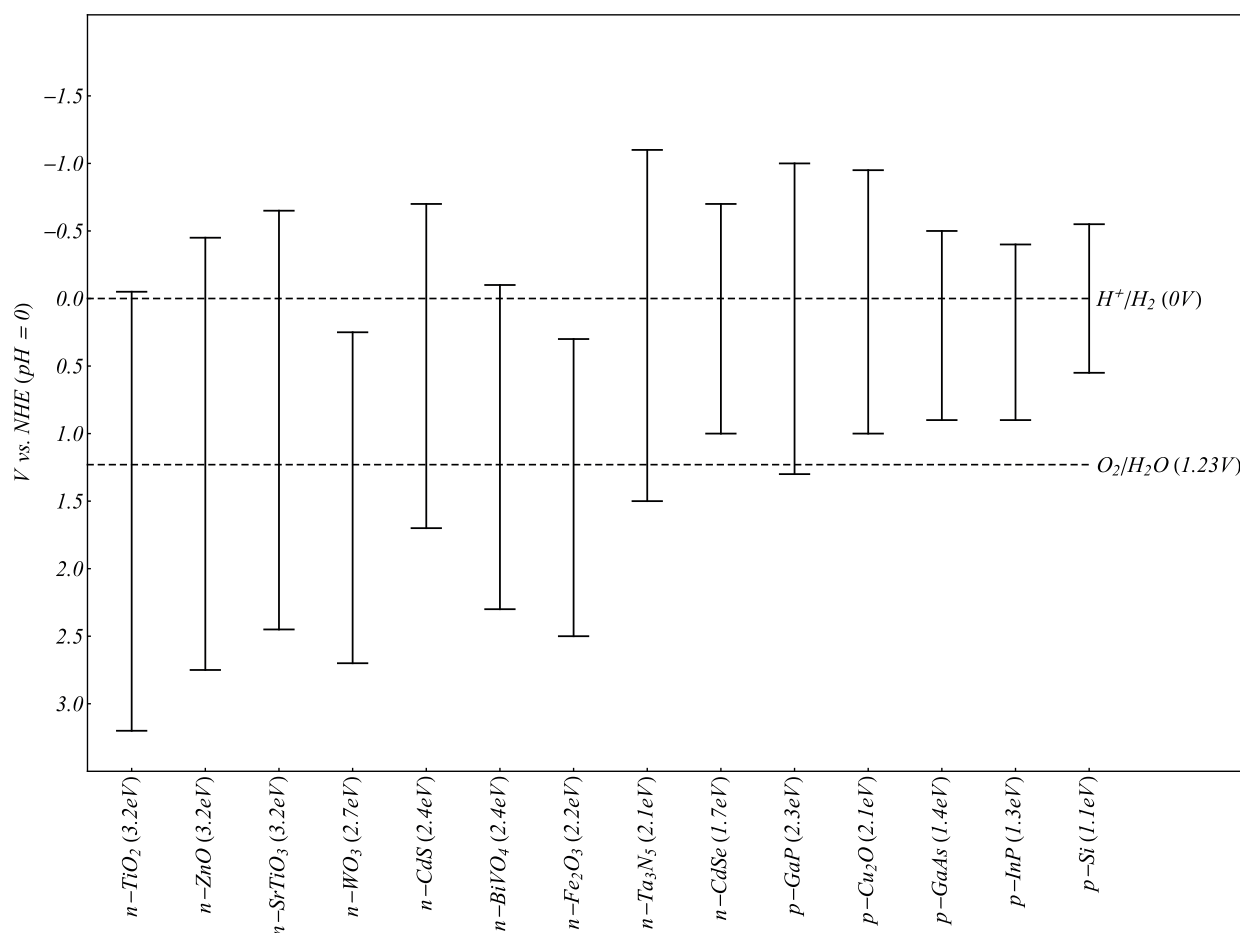


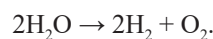
Fig. 4. Energy levels of different semiconductors in relation to the redox potentials for water splitting at pH = 0. Adapted from Ref. [28].

cess must also consider the Nernstian behavior of oxide semiconductors, where the band edges of reference materials such as TiO_2 change by 0.059 V/pH, which is a critical consideration to sustain the potential difference with respect to the redox potentials of water in different chemical environments [27,28]. Aside from thermodynamic stability, the choice of materials is governed by photocorrosion resistance; whereas transition metal dichalcogenides, for example, MoS_2 , are prone to anodic decomposition depending on the pH of the electrolyte, TiO_2 nevertheless remains the standard material for the photoanode due to kinetic stability and abundance of the material on Earth, both of which are crucial for the development of solar-to-fuel devices; see Fig. 4 [27,28].

3.2. Fundamental requirements and performance metrics for photoanodes

Photoanodes are the foundation in the design of PEC systems and are mostly utilized as the primary source in the conversion of solar energy into chemical fuels. The basic principle of a photoanode is the employment of semiconductive materials that are effective in absorbing solar energy. This allows the excitation of the electrons from

the valence band to the conduction band, thereby creating electron-hole pairs that are essential in the initiation of the synthesis of ion radicals that are utilized in the surface redox reactions. The efficacy of the PEC system is strictly dependent upon the effective separation and transportation of the photogenerated carriers, where the electrons are directed toward the cathode and the holes toward the anode interface. The kinetic loss in the transportation of the photogenerated carriers results in the reduction of the solar energy conversion efficiency [28–30]. At the photoanode interface, the photogenerated holes are utilized in the oxidation reaction of water, given by the reaction equation:



This reaction must have an electrode potential that is greater than 1.23 V/NHE to ensure the oxidation reaction of water. Apart from the electronic energy level matching, the photoanode must also demonstrate stability in the application process, particularly in the face of corrosive media in the electrolyte solution. Therefore, the choice of material and the application of modifications are often employed to boost the stability and the kinetics of the photoanode; see Fig. 5 [28,30,31].

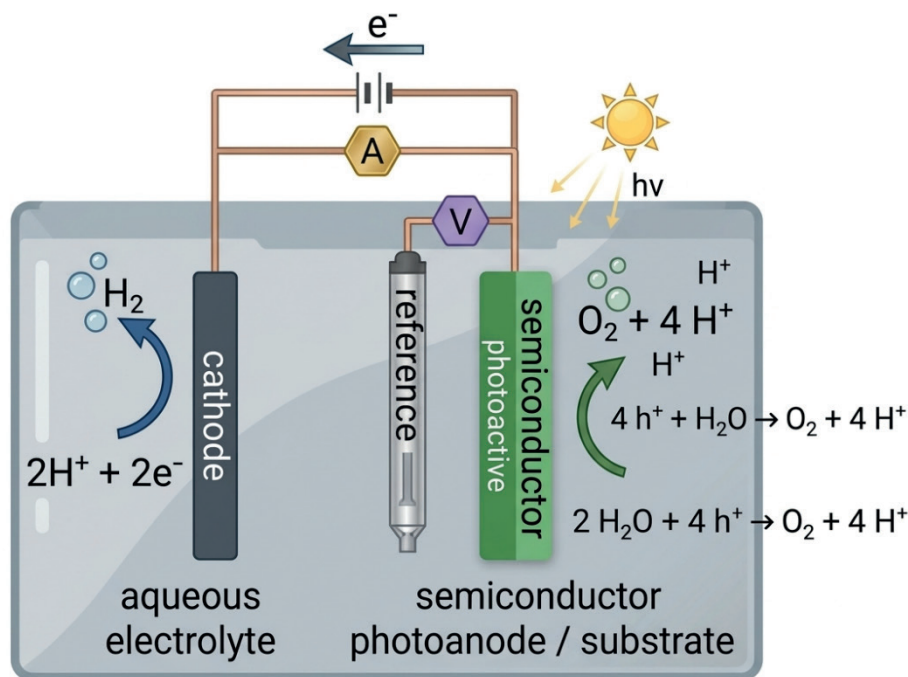


Fig. 5. Schematic representation of the three-electrode photoelectrochemical cell configuration. The figure shows the process of photoexcitation of the semiconductor material of the photoanode, followed by the reaction of water oxidation to yield oxygen and protons, and the flow of electrons from the cathode to the anode via an external circuit to complete the reduction reaction.

Table 1 Performance parameters for PEC NRR

Parameters	Evaluation	Improvement strategy
NH ₃ yield	Catalytic activity	Promoting active site density, mass transfer efficiency
Faradaic efficiency	Selectivity, NRR pathway versus HER	d-band modulation, electrolyte engineering to improve NRR and inhibit HER
AQE/IPCE	Light energy utilization efficiency	Enhancing light absorption and charge separation
STAE/ABPE	Overall energy conversion efficiency	PEC system optimization, covering light, electricity and catalysis
TOF	Intrinsic activity	Electronic structure modulation of active sites

The typical performance parameters for PEC NRR toward ammonia, including NH₃ yield, Faradaic efficiency (FE), apparent quantum efficiency (AQE), incident photon-to-current conversion efficiency (IPCE), solar-to-ammonia efficiency (STAE), applied bias photon-to-current efficiency (ABPE), turnover frequency (TOF) et al. are summarized in Table 1 [32].

To bridge this gap between fundamental operation and real-world application, the efficacy of a photoanode is measured using a set of quantitative parameters. The thermodynamic dissociation of water requires a change in Gibbs free energy (ΔG) of 237 kJ/mol (approximately 2.46 eV per molecule), equivalent to a standard potential (E) of 1.229 V at 25 °C. To measure the efficacy of this thermodynamic process, the following standard parameters are used:

- **Applied Bias Photon-to-Current Efficiency (ABPE):** This determines the efficiency of a PEC cell by

accounting for the externally applied voltage (V_{app}) relative to the measured photocurrent density (J_{ph}):

$$ABPE = \frac{J_{ph} \times (1.23 - V_{app})}{P_{light}},$$

where P_{light} is incident light power density;

- **Incident Photon-to-Current Efficiency (IPCE):** This evaluates the wavelength-specific conversion of light into electrical energy. It is a product of the light-harvesting efficiency, charge separation efficiency, and charge transport efficiency:

$$IPCE(\lambda) = \frac{1240 \times J_{ph}}{\lambda \times P_{light}} \times 100\%.$$

The structural integrity of the photoanode is of utmost importance for the optimization of the above parameters, and the fabrication process must be carried out in a man-

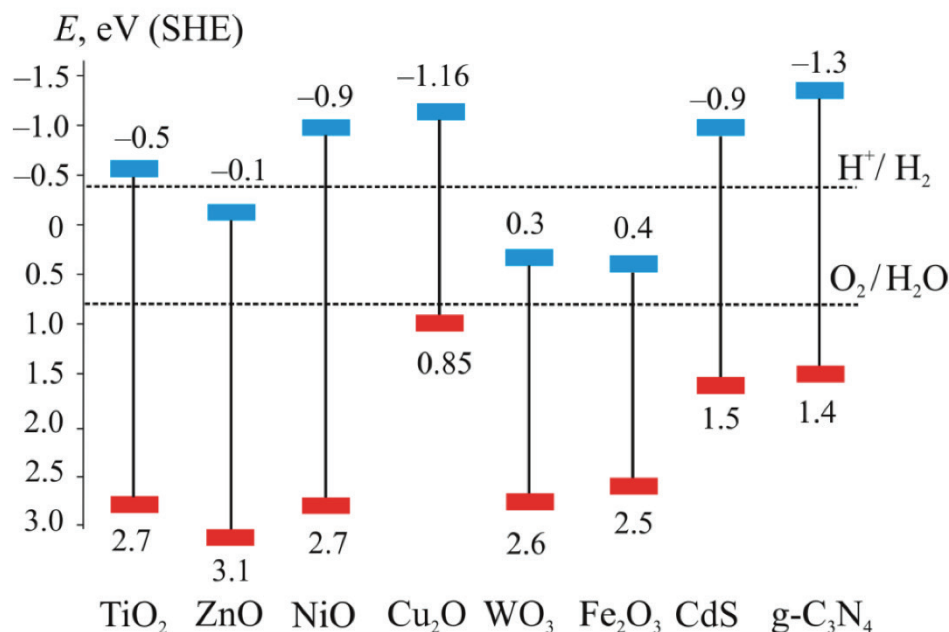


Fig. 6. Schematic illustration of the band gaps of some semiconductors. Reproduced from Ref. [36] under the terms of the [Creative Commons Attribution 4.0 International \(CC BY\) License](#).

ner that minimizes structural defects, as well as reduces the particle size [30].

3.3. Metal oxide photoanodes for PEC

The transition from fundamental metrics to materials-based implementation involves identifying semiconductors that have the ability to drive the oxygen evolution reaction (OER) with high kinetic efficiency. Although thermodynamic bandgap requirements have been established in the previous sections, materials selection for metal oxides is also dictated by the alignment of the valence band maximum below the O₂/H₂O oxidation potential (approximately +1.23 V vs. RHE) and the conduction band minimum above the H⁺/H₂ reduction potential (approximately 0 V vs. RHE). Apart from that, the efficiency of the photoanode is also affected by its carrier dynamics, where it is required that the photoanode must have long minority carrier diffusion lengths or be nanostructured in order that holes have access to OER sites on the surface before being lost due to bulk recombination. At the same time, fast majority carrier (electron) collection at the back contact is also crucial in order that resistive losses do not affect the photocurrent density [33,34].

In addition, operational stability is another factor which is considered to be an issue of concern, considering the fact that some of these materials are highly susceptible to photocorrosion during water oxidation. In this case, strong metal oxides are considered to be of primary importance due to their stability. In addition, in the entire setup of the PEC cell, these photoanodes are used in conjunction with ion exchange membranes which are used for

transporting ions and ensuring that there is no mixing of gases. In light of these requirements, only some of these metal oxides, such as TiO₂, ZnO and NiO have shown adequate properties for PEC-NRR because of they have a band gap greater than 3 eV; see Fig. 6 [33,35].

3.3.1. Properties and engineering of TiO₂

Titanium dioxide (TiO₂), in particular, has emerged as the most studied semiconductor material in PEC water-splitting devices based on photoanodes, mainly because of its superior chemical and thermal durability, non-toxicity, and abundance in nature. The large refractive index of TiO₂ and its natural preference for water redox reactions make it an excellent material for large-scale solar-driven chemical conversion. Nevertheless, the effective efficiency of pristine TiO₂ is fundamentally limited by several intrinsic bottlenecks. Specifically, its large bandgap (between 3.02 eV and 3.18 eV) limits photoabsorption mainly in the ultraviolet region (wavelength around 380 nm), which makes up only 4–5% of the solar spectrum. Moreover, there is also a high rate of recombination of electron-hole pairs, as well as a high surface kinetic overpotential, which both limit its quantum efficiency and energy-conversion ability [37].

Despite these challenges, TiO₂ still holds a unique competitive advantage over other metal oxides and sulfides, which, although having narrower bandgap values, often lack satisfactory stability in the changing and often extreme pH values that are often required in photocatalytic reactions [30,37]. To overcome these limitations, a broad range of electronic and structural modification approaches has been developed. The sol-gel method, hydrothermal

method, and electrochemical method are used to synthesize unique structures, such as nanotubes, nanorods, and mesoporous materials, to enhance the electrochemically active surface area [30]. Research indicates that morphology is an important parameter for performance, with TiO_2 nanowires showing better efficiencies in converting solar energy to electricity compared to TiO_2 nanorods due to better charge transport characteristics [37]. Besides the control of TiO_2 structure, optical and electronic properties can also be modified by metal or non-metal doping of TiO_2 , as well as the creation of black TiO_2 nanoparticles, which have better photocatalytic activity compared to pure TiO_2 [38].

In this regard, Saïen et al. [39] have reported the optimization of the catalytic activity of TiO_2 materials using a synergistic approach involving both nitrogen doping and surface sensitization. Using a two-step method involving sol-gel and incipient wetness impregnation techniques, HP/N- TiO_2 nanohybrids were synthesized with carboxylic functional groups for surface sensitization. Their research also proved that the amount of incorporated nitrogen plays an important role in affecting the activity of visible light, with an optimized ratio of N/Ti being vital in ensuring that the optical band gap is minimized and surface area is maximized. In addition, the research team used a novel helical flow reactor and response surface methodology (RSM) in optimizing the conditions such as pH and concentration of the catalyst. This ensured that degradation efficiencies of 89.2% were achieved, with the nanohybrid catalyst proving to be highly reusable. Importantly, it was found that the helical flow process is highly efficient in terms of power consumption compared to other conventional processes, with such optimized nanostructures being highly efficient in harnessing solar energy [39]. Beyond nitrogen modification, the incorporation of carbon and its derivatives, such as reduced graphene oxide (rGO) [40], into the TiO_2 lattice represents a high-efficiency strategy for narrowing the optical bandgap and enhancing visible light sensitivity. This is evident in the findings of Shao et al. [41] where the incorporation of carbon into the TiO_2 lattice structure leads to an increase in photocatalytic activity, comparable to that in N- TiO_2 and S- TiO_2 . The mechanism of this phenomenon can be explained by the substitution of oxygen sites with carbon atoms, which leads to the creation of impurity levels between the VB and CB of the semiconductor material [42].

3.3.2. Technical protocols for TiO_2 fabrication

While the conceptual advantages of nanostructuring were discussed in the previous section, the precise control of TiO_2 properties is achieved by a rigorous manipulation of certain experimental parameters. To achieve vertically aligned nanotubes, a titanium foil is subjected to electro-

chemical anodization in a two-electrode electrochemical cell using a DC power supply. The standard protocol involves an electrolyte solution comprising of ethylene glycol with a wt.% composition of 0.3–0.7% ammonium fluoride (NH_4F) and 2–5% volume composition of de-ionized water. The application of a constant potential of 20–60 V for a period of 1–24 hours is also required for the synthesis of nanotubes of diameter ranging from 50–150 nm. The high level of structural order is a direct outcome of the kinetic balance of oxide formation and fluoride dissolution. Alternatively, synthesis of TiO_2 nanorods on FTO substrates is carried out via a hydrothermal synthesis process in a Teflon-lined stainless-steel autoclave. Typically, a recipe for a solution-based synthesis of rutile nanoparticles involves a 1:1 solution of concentrated hydrochloric acid (HCl) and deionized water and a titanium source such as titanium butoxide or TiCl_4 , which is heated to 150–180 °C for 2–10 hours to aid in epitaxial growth of rutile nanoparticles. This method is particularly useful for controlling the aspect ratio and surface density of the nanoparticles by adjusting the temperature and concentration of the solution, according to Robin et al. [43], Quiroz et al. [44], and Prathan et al. [45].

In contrast to these techniques, the solution-phase techniques include the sol-gel process, which involves the hydrolysis of titanium tetraisopropoxide (TTIP) in an acidic alcoholic medium. For the impregnation required in the preparation of high-performance nanohybrids, pre-formed TiO_2 powder is mixed with the volume equivalent to the pore volume of the catalyst to ensure the uniform distribution of the dopants or sensitizers in the lattice. Finally, for all of the aforementioned fabrication techniques, a very important last step is the post-synthetic annealing of the synthesized materials in a muffle furnace. For the synthesis of catalytic TiO_2 in the anatase or rutile crystalline phase from the initially synthesized amorphous state, the electrodes are subjected to annealing in a temperature range of 450 °C to 550 °C. During the annealing procedure, which corresponds to the crystallization of TiO_2 , the temperature increase should take place at a slow rate, i.e., 2 °C/min, in order to avoid the structural failure of the TiO_2 film from the substrate due to the differences in thermal expansion coefficients [46,47].

3.3.3. Synthesis and loading of 2D TMDC co-catalysts (MoS_2 , WS_2)

Although TiO_2 ensures the presence of the essential photovoltage and oxidative stability, the kinetically hindered nature of the $\text{N}\equiv\text{N}$ bond forces the incorporation of co-catalysts to enable nitrogen adsorption and reduction [48]. Two-dimensional transition metal dichalcogenides, i.e., molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), have been identified as the most promis-

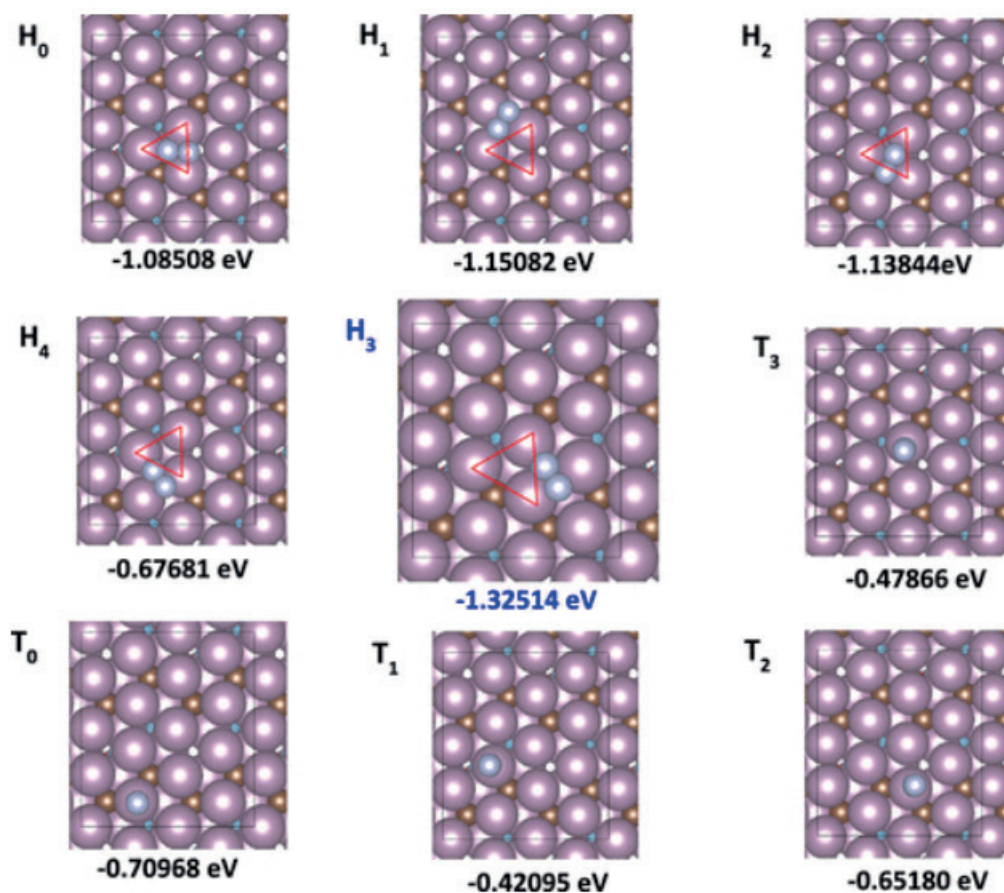


Fig. 7. Adsorption arrangement and adsorption energy at various adsorption locations of the TiO₂-Mo₂C heterostructure. Reproduced from Ref. [63] under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International \(CC BY-NC-ND\) License](#).

ing materials to be used in the role of co-catalysts owing to their peculiar band edge structures and large number of active edge sites [49,50]. The main function of these co-catalysts lies in the enhancement of the back-donation of electrons from the catalyst to the anti-bonding orbitals of the N₂ molecule, hence weakening the N≡N bond and lowering the activation energy for ammonia production [51]. The synthesis approaches for both MoS₂ and WS₂ can be grouped into two main categories: “top-down” exfoliation and “bottom-up” chemical growth. Liquid-phase exfoliation (LPE), as a popular “top-down” route, involves the application of high-power ultrasonication or shear mixing to TMDC powders in particular organic solvents (e.g., NMP or IPA), as well as aqueous surfactant solutions [52,53]. Thus, this process overcomes the weak van der Waals forces between the layers and yields a few-layered nanosheet with a high surface area-to-volume ratio. The nanosheets are then integrated onto the TiO₂ photoanode by drop-casting, spin-coating, and electrophoretic deposition methods. Although the LPE method is scalable and cost-effective, the physical interface between the co-catalyst and the photoanode may have a high charge transfer resistance compared to chem-

ically bonded interfaces [54]. Tan group prepared a series of sulfides, selenides, tellurides, carbides, and nitrides featured as atomic-scale thickness 2D metal compounds. The MoS₂, WS₂, MoWS₂ samples were created through a recyclable nanoporous Au assisted chemical vapor deposition process, where the surface Au-Mo/W alloys act as the metal source. Au substrate was removed to form the 3D bicontinuous nanoporous structure [55].

Alternatively, hydrothermal and solvothermal synthesis techniques can be employed to achieve “bottom-up” approaches to the growth of TMDCs directly onto nanostructured TiO₂ scaffolds. Hydrothermal and solvothermal reactions involve the heating of precursors such as ammonium molybdate/thiourea to grow MoS₂ and sodium tungstate/thioacetamide to grow WS₂ in a pressurized autoclave to obtain 3D nano-flowers or vertically aligned sheets [56–58].

This in-situ synthesis ensures robust chemical adhesion and conformal coverage, which are both significant requirements in PEC-NRR stability. Moreover, the process of chemical synthesis enables the engineering of defects, such as the intentional formation of sulfur vacancies. These vacancies are Lewis acid sites that are capable

of specifically binding with the N_2 molecules through the process of chemisorption, thus creating an increased density of active sites beyond what is available on the edges [59,60]. The molecular-level interaction and adsorption energy of nitrogen at these specific atomic sites are critical “methods of study” for predicting the reaction process (see Fig. 7).

However, for precision studies, chemical vapor deposition (CVD) is utilized to form large-area, atomistically thin films of MoS_2 or WS_2 . Although CVD enables higher crystallinity and electronic contact, its stringent temperature and equipment conditions restrict its application to basic studies, not electrode synthesis. Thus, to recap, the rational synthesis and loading of TMDC co-catalysts, optimizing sulfur vacancy density and TiO_2 /TMDC interface quality, is a critical determinant for achieving high Faradaic efficiency and ammonia yield rates for sustainable PEC systems [61,62].

3.4. Photocathodes based on transition metal dichalcogenides

3.4.1. Mechanism and activation

The NRR mechanism toward NH_3 includes associative pathway, dissociative pathway, Mars-van Krevelen (MvK) mechanism et al. [64–66] (see Fig. 8).

Associative pathway. N_2 is gradually hydrogenated to form NH_3 , which is the most supported in catalytic NRR [67,68]. Depending on the hydrogenation sequence, it is widely classified into pathways:

Distal pathway. N atom distal to the catalyst surface is preferentially hydrogenated. One NH_3 molecule is released first, followed by the hydrogenation of the second N atom.

Alternating pathway. Two N atoms are hydrogenated alternately via a hydrazine (N_2H_4) intermediate, ultimately generating two NH_3 molecules after the cleaving of the N–N bond. Notably, this pathway sometimes starts with N_2 -bridge adsorption, and it is named as the enzymatic mechanism [69].

Dissociative pathway. The $N\equiv N$ bond is cleaved first to form the surface nitride, which is progressively hydrogenated to NH_3 . Due to the extremely high energy barrier, this pathway is less observed in photocatalytic systems under mild conditions [70].

Mars-van Krevelen (MvK) mechanism. This reaction mechanism is typically observed on transition-metal nitride catalysts, where lattice N atoms are reduced to NH_3 and as-generated vacancies shall chemically adsorb N_2 for subsequent NRR [71,72]. This pathway could be applicable for the defect-rich catalysts of PEC NRR.

In addition, Chongyi Ling and co-workers proposed the surface-hydrogenation mechanism on noble-metal

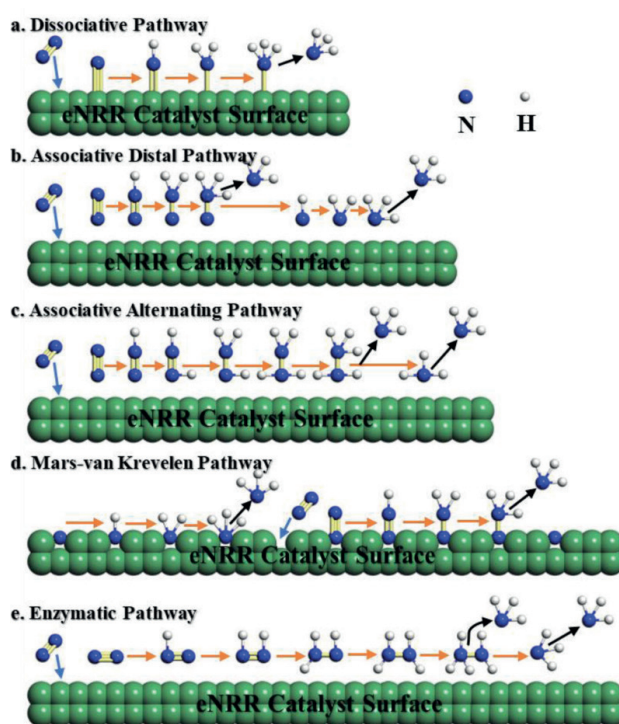


Fig. 8. Schematic diagram of the nitrogen reduction reaction on electrocatalysts. Reproduced with permission from Ref. [66], © 2020 Wiley-VCH GmbH.

based catalysts like Au and Pd with weak N_2 -binding. Adsorbed H^+ is first reduced to surface $*H$, which then reacts with N_2 to form the $*N_2H$ and $*N_2H_2$ intermediate, eventually reducing to NH_3 [73]. This mechanism might be applicable for the noble-metal based photocatalysis system.

In the NRR process, the dissociation of the $N\equiv N$ triple bond and the hydrogenation steps are the potential rate-determining step and remains a core bottleneck in PEC NRR [74,75].

Promoting N_2 activation is essential to achieve a high PEC NRR performance. Typically, transition metal like Ru and Mo sites accept electron donation from the p-orbitals of N_2 via the unoccupied d-orbitals (σ -donation), and back-donate valence electrons from occupied d-orbitals to the π^* antibonding orbitals of N_2 (π -backdonation), which effectively weakens the $N\equiv N$ triple bond. Heterojunction interfaces not only reduce the interfacial charge transfer resistance, but also promote the carriers' migration, synergistically boosting NRR kinetics toward NH_3 . Also, vacancies directly construct electron-rich centers by reducing the coordination number of adjacent non-metallic elements, thus facilitating N_2 adsorption and activation [24,76].

Significantly, the H^* intermediate, which is generated from cathodic water dissociation ($H_2O + e^- = H^* + OH^-$), is important for the activation and hydrogenation of N_2 and N-containing intermediates toward NH_3 . Still, the balance of H^* generation and HER inhibition is a virtual for

selectively NH_3 production. From this aspect, the fine design of active sites is quite important to fulfill the protons and electrons coupled NRR [77,78].

3.4.2. Role of photons and applied bias

In photoelectrocatalytic systems, the role of photons and applied bias cooperatively boost the NRR process. Upon absorbing photons with energy equal to or greater than the bandgap of p-type semiconductor photocathodes, the electrons are excited from the valence band to the conduction band, generating the electron-hole pairs. As-generated electrons would migrate to the electrode surface to directly participate in N_2 reduction. Meanwhile, the holes transport to the counter electrode in the external circuit for the anodic oxidation reactions, which is separated from NRR to avoid side reactions and to enhance reaction selectivity. Illumination enriches the conduction band of the photocathode with photogenerated electrons, activating surface catalysts through the charge accumulation effect to facilitate the proton coupled multi-electron process toward ammonia.

During the reaction, applied bias would directionally separate photogenerated carriers and suppress electron-hole recombination, and provide additional driving force for NRR. The conduction band edge potential must be more negative than the N_2 reduction potential so as to ensure the sufficient energy of photogenerated electrons to drive the reaction. Meanwhile, the applied bias should be conserved to avoid excessive HER side reaction [79].

3.4.3. TMDCs for PEC NRR

Among various catalytic platforms, transition metal dichalcogenides (TMDCs, MX_2 , where $\text{M} = \text{Mo}, \text{W}, \text{Ni}, \text{Co}, \text{Cu}, \text{In}, \text{Sn}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$) have attracted considerable attention as photocathode materials due to their tunable electronic structures, large specific surface areas, and rich defects. But they require further modulation toward efficient PEC NRR because of the limited ability to activate N_2 molecules, photogenerated carrier recombination, competitive HER et al. [80,81]. They could be facially prepared via chemical vapor deposition, colloidal synthesis, high-pressure method, metal transfer method, atomic plane gliding method et al. [82,83]. Strategies for the efficient active sites in TMDCs-based photocathodes including doping, defect engineering, heterojunction and interface engineering, et al, have been reported in recent reports. In addition, integrated strategies are also developed to maximize N_2 adsorption and inhibit HER competition [84].

Doping and defect engineering are effective strategies for modulating the electronic structure and surface chemistry of TMDCs. Introducing dopants and vacancies could break the stoichiometry of TMDCs. As generated new

states within the band gap serve as the active sites for N_2 adsorption and activation while simultaneously promotes the separation of photogenerated charge carriers. For instance, Sc-doped MoS_2 with S vacancies for PEC NRR achieved an NH_3 yield of $124.26 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, which is 6.16, 2.23, and 2.69 times higher than those of pristine MoS_2 , MoS_2 with S vacancies, and Sc-doped MoS_2 , respectively. Theoretical calculations revealed that the combination of S vacancies and Sc doping significantly enhances N_2 adsorption and reduces the free energy barrier for hydrogenation [85].

Meanwhile, the construction of heterojunctions formed by TMDCs and another semiconductor is a cornerstone strategy to enhance charge separation efficiency. An internal electric field is established at the interface which would drive the spatial separation of photogenerated charge carriers and extend their lifetimes. The $\text{MoS}_2/\text{TiO}_2$ nanojunction prepared via a facile hydrothermal synthesis exhibited the interfacial electronic coupling and the synergistic effects of both components, contributing to an NH_3 yield rate of $1.42 \text{ mmol} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ and a remarkable FE of 65.5%. The $\text{MoS}_2/\text{TiO}_2$ photocathode exhibited excellent stability and the robustness of the heterojunction structure [86].

Dispersing $\text{UiO-66}(-\text{NH}_2)$ nanoparticles onto hierarchical CuInS_2 nanosheets formed an S-scheme n-p heterojunction, which achieved an NH_3 yield of $398 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ for N_2 fixation under visible light illumination. The synergistic effect is originated from the sulfur-deficient CuInS_2 component with abundant surface active sites and effective

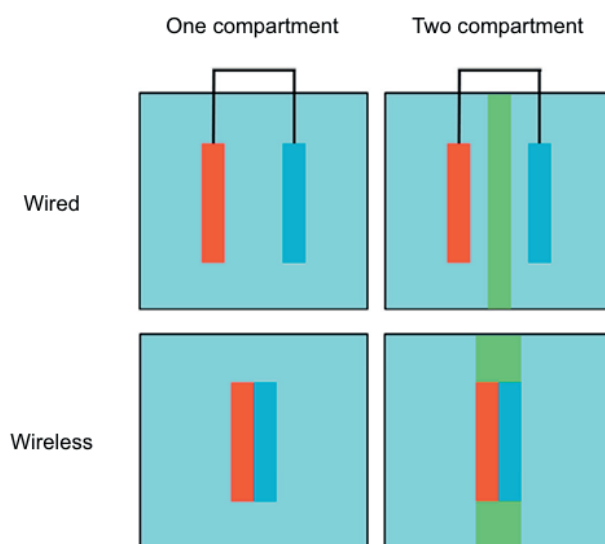


Fig. 9. Schematic diagram of the main configurations for an experimental PEC cell, showing how matrix is linked to wired/wireless systems and one- or two-compartment systems. Red, blue, and green represent anode, cathode, and molecular separator, respectively. Reproduced from Ref. [88] under the terms of the [Creative Commons Attribution 4.0 International \(CC BY\) License](#).

visible-light absorption, and the charge migration pathway in the S-scheme for efficient spatial separation of redox-active carriers [87].

4. CELL CONFIGURATION, SYSTEM DESIGN AND PERFORMANCE

The transition from the synthesis of the material to the performance evaluation necessitates a critical understanding of the architecture of the photoelectrochemical cell. As established in the study of Bosserez et al. [88], experimental PEC cells (exPEC) are mainly categorized depending on their electrode assembly configurations and their degree of compartmentalization, as shown in Fig. 9. The major difference between PEC cells involves whether they use a wired or a wireless assembly, which influences how PECs collect charge carriers. The wired PECs have their electrodes connected externally, allowing detailed electrochemical characterization using potentiostats and voltmeters. Although this takes advantage of the high electrical conductivity of wires, there is an increased electron pathlength. On the contrary, PECs with a wireless or monolithic assembly involve a monolithic integration of photoactive materials, which reduces electron pathlengths but increases ionic transport resistance in the electrolyte [88,89].

Thus, the efficiency of such systems is fundamentally determined by the nature of electrical junctions between the semiconductor light absorber and its environment. These electrical junctions fall into two categories: semiconductor-liquid junctions (SLJ) in which charge carriers are involved in redox reactions, and solid-solid junctions (SSJ) that allow carriers to be extracted to an external circuit (Fig. 10) [90,91].

In the realm of PEC-NRR, these are additionally classified as SLJ-A for anodic processes and SLJ-C for cathodic processes. To improve durability, the addition of intentionally applied protective layers results in SLJ-PA or SLJ-PC configurations. Concerning carrier extraction, SSJs are categorized as transparent (SSJ-T) for front-side illumination, opaque (SSJ-O) for backside contacts, or as recombination layers (SSJ-R) used in the monolithic integration of tandem semiconductors [89–91]. One of the main aims of a PEC design is the development of these systems to allow the required bias-free operation with the required overpotential. Wired tandems are relatively simple to measure with the required external circuitry, although they are disadvantaged by the longer transport paths. Wireless monolithic tandems are the theoretical perfect system with minimized electrical ohmic losses due to the absence of lateral transport paths. This, however, is not a trivial task, as performance has to be measured through gaseous product collection using chromatography rather than direct electrical measurement. Apart from cell

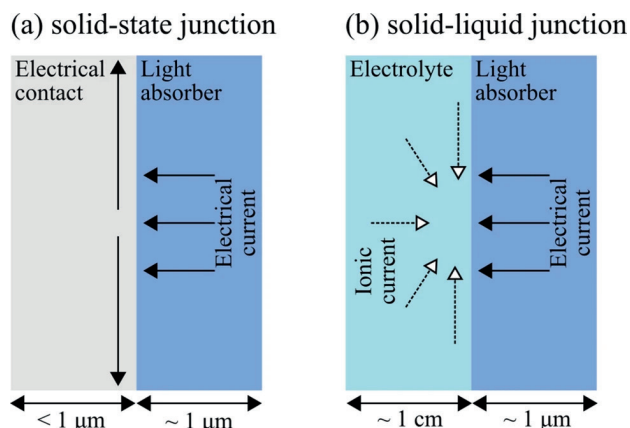


Fig. 10. Visual comparison of charge carrier extraction routes: (a) via a solid-solid junction (SSJ) necessitating lateral movement across an extensive surface area, and (b) via a semiconductor-liquid junction (SLJ) where carriers traverse solely the thickness of the absorber layer, reducing ohmic losses. Reproduced from Ref. [90] under the terms of the [Creative Commons Attribution 4.0 International \(CC BY\) License](#).

type, PEC cells are classified depending on their degree of compartmentalization. Though single-compartment PEC cells are adequate for screening purposes, they have been shown to be limited because gases tend to mix. As such, dual-compartment H-type PEC cells, which use ion exchange materials such as Nafion that ensure molecularly separate volumes, are critical. This is an important “method of study” factor, which ensures that there is no back oxidation of ammonia and thus enables the measurement of Faradaic and quantum efficiencies [88,92].

Recent cutting-edge reviews by Moon and his group [90,91] highlight that for nitrogen reduction, cell designs must tackle the significant mass-transfer constraints resulting from the low solubility of N_2 in water. An essential measure in evaluating synthesis efficiency is examining ohmic losses when scaling up the device. In systems utilizing SSJ-T, charge carriers are required to move horizontally along the device surface; studies show that resizing a photoanode from a laboratory-scale 0.24 cm^2 to a usable 50 cm^2 can lead to a photocurrent decrease of up to 65% because of the lateral resistance in the TCO layer. In theory, a lateral measurement of 8 cm may cause a voltage drop of roughly 350 mV. Conversely, SLJ configurations have advantages in scaling due to charge transport only over the thickness of the device, which is on the order of a micrometer. In order to reduce losses due to ionic transport, high levels of acidity or alkalinity in the electrolyte, flowing electrolyte to prevent depletion of ions, and louvered or perforated cell configurations to reduce transport path lengths must be incorporated in more advanced configurations. In terms of practical application, monolithic configurations with an SSJ-O connected to an electrocatalyst (SLJ-A/SSJ-R/SSJ-O) offer advantages in hermetically sealing high-pressure reactors, effectively

eliminating crossover of products while maintaining stability [90,91].

Thorough assessment of PEC NRR is crucial to differentiate between genuine catalytic performance and possible nitrogen contamination, a difficulty intensified by the strong thermodynamic stability of the $\text{N}\equiv\text{N}$ triple bond. In this regard, Wilder et al. [93] highlight the need for standardized verification protocols, promoting the comprehensive application of $^{15}\text{N}_2$ isotopic labeling. This labeling acts as the conclusive “study method” to confirm that the synthesis adheres to the isotopic reduction pathway [93]:



By examining the resulting $^{15}\text{NH}_4^+$, proton nuclear magnetic resonance spectroscopy (^1H NMR) will allow the researchers to distinguish the characteristic doublet peak of ^{15}N from the triplet peak of ^{14}N due to environmental impurities. With regard to the basic “reaction process,” Liu et al. [94], emphasized the importance of synergistic interfaces and defects. The PEC process involves the redox reaction occurring at the photoanode and photocathode interfaces. At the TiO_2 photoanode interface, the redox reaction for the oxidation of water to provide the necessary protons and electrons [94] is:



To define the synthesis efficiency, the system's performance is characterized using the ammonia yield rate and the FE, parameters that are critically dependent on the applied potential and the reaction's ability to consume active sites. The major technological challenge in reaching high values of FE is the HER ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow$), as the reaction tends to dominate the catalyst's surface because of its kinetic rate and overpotential [95,96]. According to the explanation given by Nash and his team [97], the selectivity of the PEC-NRR process is very potential-dependent, and hence, the precise control of the electrochemical conditions is required to inhibit the HER while maintaining the driving force for the fixation of nitrogen [97]. In this direction, Ma et al. [98] have shown that the development of heterostructures consisting of MoS_2 and TiO_2 can enhance the efficiency by minimizing the interfacial charge transfer resistance (R_{ct}), thus facilitating the selective transport of carriers to the NRR active sites [98]. Detection of the produced ammonia is generally done using the Indophenol Blue method or ion chromatography (IC), the latter being particularly crucial in the case of electrodes involving materials such as CuO , in order to avoid interference from the leached metal ions [99]. However, as emphasized through the strict guidelines followed in the literature mentioned above, a good study goes beyond the simple argon (Ar) control experiments. It also includes exhaustive blank experiments such as the open circuit and catalyst only experiments to account for any possible nitrogenous impurities

present in the cell components or environment, which may give a false positive signal for catalytic activity [100,101]. Finally, the long-term sustainability of the PEC system is evaluated through a stability analysis, whereby the morphological and electrochemical stability of the TiO_2 and CuO interfaces are continuously maintained under steady-state conditions and during prolonged cycles of reactions under illumination and biasing conditions [102,103].

5. CONCLUSION

The development of PEC-NRR represents a transformative shift toward the sustainable production of “green” ammonia, offering a decentralized and low-energy alternative to the carbon-intensive Haber-Bosch process. This review has established that the overall efficiency of the PEC system is fundamentally dictated by the synergistic integration of advanced material architectures and optimized cell designs. TiO_2 remains the cornerstone for photoanode fabrication due to its robust oxidative stability and the versatility of its nanostructured forms, such as nanotube arrays and nanowires. However, to overcome its intrinsic electronic limitations, the rational application of synthesis options including nitrogen and carbon doping, as well as the formation of p–n heterojunctions with CuO is essential for broadening the optical photoresponse and accelerating charge carrier separation.

Furthermore, the kinetic barrier of the chemically inert $\text{N}\equiv\text{N}$ bond is effectively addressed through the strategic loading of 2D TMDCs such as MoS_2 and WS_2 . As demonstrated in the literature, the engineering of sulfur vacancies and active edge sites within these co-catalysts facilitates the critical “back-donation” of electrons, thereby enhancing N_2 adsorption and selectivity. Transitioning from laboratory-scale H-cells to high-performance configurations, such as GDE (gas diffusion electrode) and wireless monolithic tandems, is a decisive factor in overcoming the mass-transfer limitations of dissolved nitrogen and minimizing ohmic losses.

Despite these advancements, the field must still overcome the “10% efficiency barrier” to emerge as a viable industrial competitor. Achieving this goal requires a shift toward rigorous standardization in methods of study, particularly the universal adoption of $^{15}\text{N}_2$ isotopic labeling and exhaustive blank control experiments to eliminate the risk of false-positive results. Future research should prioritize the exploration of atomic-level interface engineering and the development of cost-effective, earth-abundant catalysts that can effectively suppress the competing HER. By combining these rigorous verification protocols with the innovative cell and material designs discussed herein, the vision of a carbon-free, solar-driven ammonia economy can be realized, contributing significantly to global energy and environmental sustainability agendas.

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AI DISCLOSURE STATEMENT

Figures 1, 3 and 5 as well as Graphical Abstract in this article were created using AI generation tools — Cloud + Google Gemini (Nano Banana Pro); accessed March and September 2026. All details were cross-checked by the authors.

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Фотоэлектрокаталитическое восстановление азота до аммиака: обзор перспективных материалов и дизайна поверхности

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Аннотация. Аммиак необходим для производства удобрений, химикатов и перспективных безуглеродных энергетических систем, однако его традиционное производство основано на энергоёмком процессе со значительными выбросами углекислого газа. Фотоэлектрокаталитическое восстановление азота стало перспективным методом устойчивого синтеза аммиака в мягких условиях, сочетающим поглощение солнечного света с электрохимическим воздействием для активации инертной молекулы азота. В данном обзоре рассматриваются последние достижения в этой области, с акцентом на разработку стабильных фотоанодов на основе диоксида титана и селективных фотокатодов, включающих оксид меди и двумерные дихалькогениды переходных металлов, такие как дисульфид молибдена и дисульфид вольфрама. Обсуждаются стратегии синтеза, методы изготовления, конфигурации ячеек, механизмы реакций и параметры производительности. Анализируются ключевые проблемы, включая высокий активационный барьер азота, конкурирующее выделение водорода и ограничения массопереноса азота, а также протоколы проверки и будущие направления для эффективного безуглеродного производства аммиака.

Ключевые слова: фотоэлектрокаталитическое восстановление азота; зелёный синтез аммиака; фотоанод из диоксида титана; сокатализаторы на основе дихалькогенидов переходных металлов; преобразование солнечной энергии в топливо