Rational design of photocatalysts for ammonia production from water and nitrogen gas

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Abstract

Photocatalytic N2 reduction has emerged as one of the most attractive routes to produce NH3 as a useful commodity for chemicals used in industries and as a carbon-free energy source. Recently, significant progress has been made in understanding, exploring, and designing efficient photocatalyst. In this review, we outline the important mechanistic and experimental procedures for photocatalytic NH3 production. In addition, we review effective strategies on development of photocatalysts. Finally, our analyses on the characteristics and modifications of photocatalysts have been summarized, based on which we discuss the possible future research directions, particularly on preparing more efficient catalysts. Overall, this review provides insights on improving photocatalytic NH3 production and designing solar-driven chemical conversions.

Keywords: Photocatalyst, Ammonia, Nitrogen

1 Introduction

Recently, there has been an increasing focus on ammonia (NH3) as not only a key commodity for chemicals widely used in industries [1, 2], but also as a liquid energy carrier [3] that enables transport and supply of hydrogen (H2) gas through cracking. Furthermore, NH3 is an alternative carbon-free energy source that can be utilized in energy-conversion devices, for example, direct NH3 fuel cells [4, 5]. Traditionally, NH3 production has mainly relied on the Haber–Bosch process, which is energy intensive and generates considerable volume of CO2 into the atmosphere because of these requirements, along with the needs for H2 and the extreme operation condition [6].

Photochemical NH3 production using N2 and water as a hydrogen source at ambient temperature and pressure can offer a promising alternative route that is less energy intensive and reduces CO2 emission, thereby significantly reducing environmental concerns [7]. NH3 production paired with water oxidation is a thermodynamically uphill reaction; therefore, external energy input is necessary [8]. Photocatalysts can utilize solar energy, which is supplied to Earth with sufficient solar power and abundance and facilitate NH3 production. Since TiO2 photocatalysts applied to N2 reduction, new photocatalysts and their modifications have been intensively suggested to improve photocatalytic NH3 production [9].

Major advances in metal oxides such as TiO2, WO3, and SrTiO3, bismuth oxyhalides, and polymeric carbon nitride photocatalysts have resulted in interests in the development of photocatalysts and their applications for NH3 production [10–14]. This review is composed of mainly two sections: (1) fundamentals for photocatalytic NH3 production, (2) strategies to develop photocatalysts. The first section focuses on the principles and mechanisms involved in the overall photocatalytic reaction. The second section contains recent progresses in the development of catalysts and their major advantages with regard to catalytic performance. The insights and discussions...
provided in this review will serve as useful resources for further development of photocatalysts and provide future research direction for photocatalytic NH₃ production.

2 Fundamentals for photocatalytic NH₃ production
2.1 Principle and mechanism

NH₃ production by N₂ reduction (N₂(g) + 6H⁺ + 6e⁻ → 2NH₃(g), E° = 0.092 V vs. SHE) paired with O₂ production by water oxidation (2H₂O(l) → O₂(g) + 4H⁺ + 4e⁻, E° = 1.229 V vs. SHE) is a thermodynamically uphill reaction that requires a potential of at least 1.137 eV [15] per electron [16]. Moreover, three electrons are required to produce an NH₃ molecule, and four holes are required to produce an O₂ molecule according to eqns. (1) and (2):

Absorption of light:
photocatalyst + hν(> E_{cb}) → e_{cb}^- + h_{vb}^+

Nitrogen reduction (NRR): N₂ → 2NH₃ (1)

Water oxidation (OER): 2H₂O → O₂ + 4H⁺ (2)

A simplified schematic diagram for photocatalytic NH₃ production and challenges in designing photocatalysts are summarized in Fig. 1. For overall NH₃ production, photons with energies > 1.137 eV are required to generate photoexcited electron–hole pairs that carry out the desired redox reactions at the active sites on the surfaces of the photocatalysts. Thus, a photocatalyst must have an energy band gap, (E_g = E_{cbm} - E_{vbm}, where CBM and VBM represent conduction band minimum and valence band maximum), larger than the energy required for the overall NH₃ production. In addition, a photocatalyst must have a suitable conduction and valence band alignment to drive two half-reactions using photoexcited electrons (e⁻) and holes (h⁺) under solar light irradiation.

The major factors to consider for photocatalyst designs are (1) photon absorption followed by photoexcited carrier generation, (2) their migration and separation, and (3) their consumption by redox reactions on the surfaces of photocatalysts. The dominant photon energy spectrum obtained from the sunlight is in the range of 390–700 nm. Furthermore, because photocatalytic redox reactions require kinetic overpotentials, photocatalysts have a bandgap energy in the range of 1.6–2.4 eV. The generated photoexcited carriers can migrate to active sites on the surface where redox reactions carried out. However, since the kinetics of carrier recombination in the interiors of the photocatalysts is fast, considerable amounts of photoexcited carriers are recombined [17]. Moreover, photoexcited carriers can be trapped in the interior and surface of the photocatalyst, which causes photocorrosion. Thus, a photocatalyst design to improve electron–hole pair migration and separation is important for further development of photocatalytic NH₃ production [18].

Most semiconductors that act as light absorbers in photocatalysts are inactive in the redox reactions with the photoexcited carriers; thus, the active sites on the surface of semiconductor are decorated with cocatalysts [19]. For example, cocatalysts, such as RuO_x, CoO_x, and Co-pi [20–22], combined on the surface of the semiconductor for facile water oxidation by providing active sites. Another critical point to note in NH₃ production via photochemical N₂ reduction is the facile competitive hydrogen evolution reaction by water reduction. NH₃ production is kinetically much more complex than water reduction, although the thermodynamic requirements for those reactions are similar [23]. This indicates that photochemical H₂ production may be predominant, resulting in inactive NH₃ production. Thus, it is critical to modify the surface that provides active sites for the desired redox reaction using suppressing competitive reactions on the semiconductors.

It is also necessary to note the importance of rate balance for photocatalytic reactions on photocatalysts. Since electrons and holes are generated in pairs under illuminations, their consumption must be coupled as well. For instance, if oxidation reactions involving photogenerated holes are sluggish, the total NH₃ production rate should be similar. In this case, scavengers, such as ethanol, methanol, and sulfites, can be employed as sacrificial reagents to facilitate oxidation reaction using photoexcited holes, thereby preventing from photoexcited carrier recombination [24]. However, since scavengers may interfere with counter reactions, here N₂ reduction, or product evaluation methods, the target scavenger should be chosen carefully. It is discussed in detail in the next section.

2.2 Experimental process

The simplest photocatalytic NH₃ production set-up is a particulate PC system where photocatalysts are dispersed in a medium, typically pure water, with N₂ bubbling under simulated solar light illumination, as shown in Fig. 1b. NH₃ and O₂ are generated on a single photocatalyst. The produced NH₃ is technically evaluated by chemical H₂ production may be predominant, resulting in inactive NH₃ production. Thus, it is critical to modify the surface that provides active sites for the desired redox reaction using suppressing competitive reactions on the semiconductors.

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In the presence of $\text{NH}_4^+$, the color of the yellowish indicating solution, which contains the reagents, turns to blue, corresponding to 655 nm. As shown in Fig. 2a and b, thus, the concentration of $\text{NH}_3$ can be quantified by measuring the absorbance change at 655 nm using a UV–Vis spectrophotometer [28]. However, to quantify the concentration of $\text{NH}_3$ generated by photocatalytic $\text{N}_2$ reduction, multiple possible contaminants that interfere with the evaluation should be fully controlled [28]. For example, methanol, a widely used as a hole scavenger, and its derivatives cause incorrect color changes and significantly decrease the accuracy of $\text{NH}_3$ quantification as shown in Fig. 2c and d. Another critical point for $\text{NH}_3$, which is photocatalytically produced, quantification is to eliminate the parts from $\text{NH}_3$ contaminants, unintentionally present introduced through catalyst, components in set-up [26] or even the air. In fact, $\text{NH}_3$ present in human breath, sanitizers, and so can rapidly accumulate in water [29].

The most rigorous procedure to quantify photocatalytically generated $\text{NH}_3$ from $\text{N}_2$ reduction is to use isotope labeled $^{15}\text{N}_2$ gas. The photocatalytic reactions are conducted in a simple particulate system with $^{15}\text{N}_2$.
bubbling. Since the splitting of $^1$H resonance in $^{15}$NH$_4^+$ and $^{14}$NH$_4^+$ resulting from the difference in the scalar interaction between N ($^{15}$ N or $^{14}$ N) and H is differentiated, the $^{15}$NH$_4^+$ produced, which is dissolved in an aqueous reacting solution, can be quantified by $^1$H-NMR [30]. For instance, the $^1$H resonance in $^{15}$NH$_4^+$ can be split into two symmetric signals with a spacing of 73 Hz, whereas the resonance in $^{14}$NH$_4^+$ can be split into three symmetric signals with a spacing of 52 Hz as shown in Fig. 2e. Thus, false positive evaluations for the produced NH$_3$ can be prevented effectively.

3 Strategies to develop photocatalysts
This section is divided into mainly two parts: (1) semiconductors comprising photocatalysts, which have been widely applied as a light absorber in Fig. 3a, and (2)
strategies to modify the catalysts, which have been effectively used to further increase the photocatalytic NH$_3$ production.

3.1 Semiconductors

Titanium(Ti)-based oxides  

Titanium dioxide, TiO$_2$, possesses several advantages that make it attractive for use in photocatalytic NH$_3$ production. TiO$_2$ has a band-gap of ~3.2 eV, which absorbs UV light, and a CBM and VBM that offer sufficient overpotential for the photoexcited electrons to reduce N$_2$ to NH$_3$ and holes to oxidize water to O$_2$, respectively. In addition, the inexpensive, environmentally benign, and stable nature of TiO$_2$ is an additional advantage. Historically, the primary limitation of using TiO$_2$ has been rapid photoexcited electron–hole recombination, which is similar to many other oxide-based photocatalysts. Strontium titanate, SrTiO$_3$ [31], is another candidate showing two major benefits over
TiO₂ for use in the NH₃ production. The CBM of SrTiO₃ is slightly more negative than that of TiO₂, thereby providing a stronger driving force to reduce N₂ using the photoexcited electrons. In addition, intrinsic charge mobility in SrTiO₃ is higher than that in TiO₂, thereby suppressing photoexcited charge recombination [32]. However, despite this thermodynamic advantage, the photocatalytic NH₃ production using TiO₂ or SrTiO₃ is limited because of ineffective light absorption resulting from their wide bandgaps and inactive redox reactions due to the limited active sites on their surface. Recently, many attempts have been made to address these limitations, which include doping, coupling with electrocatalysts (cocatalysts), surface defect engineering, and so on [33–35].

**Bismuth oxyhalide (BiOX)** BiOX (X = Cl, Br, and I) has a layered structure where bismuth and oxygen layers (BiOx) are connected with halide (X) layers alternatingly via Van der Waals forces [36]. Since the VBM is determined by O 2p and X 6p (δ = 3, 4, and 5, corresponding to X = Cl, Br, and I, respectively) and the CBM is mainly evaluated by Bi 6p, their band alignments and bandgap are varied depending on the element comprising the semiconductors [37]. For example, BiOCl, BiOBr, and BiOI have bandgap energies of 2.92, 2.65, and 1.75 eV, respectively [38], and are thermodynamically suitable for NH₃ production, they enable the production of NH₃ and O₂ by the overall photocatalytic N₂ reduction. However, despite these advantages, BiOX semiconductors have severe drawbacks when using them as photocatalysts, mainly due to the insufficient photogenerated charge separation in the bulk and surface. Recently, their fundamental limitations have been investigated, and strategies to improve their photocatalytic performances have been explored.

**Graphitic carbon nitride (g-C₃N₄)** g-C₃N₄ is a polymeric semiconductor with a bandgap energy of 2.7 eV and appropriate positions for the CBM and VBM for the NH₃ and O₂ production, respectively [39]. However, since rapid photoexcited carrier recombination in the bulk results in limited charge separation in the redox reactions and ineffective N₂ adsorption on the surface, as an initial step for N₂ reduction, multiple advancements to develop g-C₃N₄ have been suggested [40].

### 3.2 Strategies to enhance photocatalytic NH₃ production

As described in the introduction section, photocatalysts comprising semiconductors can produce NH₃ using N₂ and water under illumination. However, the typical NH₃ production rate and efficiency of intrinsic semiconductors using solar energy have been far lower than those expected from their bandgap energies. The major limiting factors include (1) limited light absorption because of the intrinsically large bandgaps, (2) significantly fast photoexcited electron–hole pairs recombination, and (3) slow redox reactions including N₂ reduction and water oxidation. Recently, many strategies have been made to address one or more of these challenges, which include engineering defects by extrinsic doping or vacancy introducing, composites forming using multi-light absorbers, and coupling with electrocatalysts. This section will give an overview of each of these attempts and discuss how these strategies affected the photocatalytic NH₃ production.

#### 3.2.1 Defect engineering

Defect engineering has been widely suggested to control bulk and surface properties of catalysts, for example, by heteroatoms doping, vacancies formation, and so on. This defect engineering enhances photocatalytic NH₃ production by changing the light absorption properties, improving charge separation efficiencies, or facilitating surface redox reactions, and it generally influences the multi-mechanistic steps of light harvesting simultaneously [41].

**Heteroatom doping** Heteroatom doping involves intentional introduction of impurity atoms into the lattices of materials to change their optical and electrical properties [42–44]. Depending on the species and degree (concentration) of dopants, changes, in the bandgap energy, band alignment, charge separation efficiency, and N₂ adsorption ability are expected. However, since dopants can provide electron–hole recombination sites or prohibit charge transports, identifying types and concentrations of dopants appropriate for the photocatalytic process is important.

Zaicheng Sun and coworkers prepared a nickel-doped TiO₂ (Ni-x-TiO₂, where x = concentration of the Ni precursor controlled in the preparation step) photocatalyst using the sol–gel method [45] show Their optimized sample (Ni-0.8-TiO₂) exhibited an NH₃ production rate of 46.80 µmol·g⁻¹·h⁻¹ under simulated solar light irradiation, which is seven times higher than the rate using pure reference TiO₂. The Ni-0.8-TiO₂ sample extends the light absorption range to the visible light region with a bandgap energy of 2.92 eV, whereas pure TiO₂ absorbs only UV light with a bandgap energy of 3.2 eV as shown in Fig. 3b. As Ni atoms having 2+ valence that replace the Ti valence that replace the Ti site having 4+ valence, oxygen vacancies (Ov) are created naturally for charge neutrality within the host semiconductors, and they vary the band position of the CBM and VBM in TiO₂, which results in a decrease in the bandgap energy. Besides changes in the optical properties, N₂
adsorption, the initiation step for NH₃ production from N₂, is enhanced by Ni doping on TiO₂, as investigated using a N₂ temperature programmed desorption spectroscopy (N₂-TPD) and a computational analysis.

Tierui Zhang and coworkers prepared a copper-doped TiO₂ nanosheet (x%-TiO₂, where x=molar ratio of Cu/Ti controlled in the preparation step) photocatalyst using a hydrothermal method [46]. The optimized sample, 6%-TiO₂, exhibited an NH₃ production rate of 78.9 μmol·g⁻¹·h⁻¹, whereas pristine TiO₂ nanosheets exhibited a rate of 0.34 μmol·g⁻¹·h⁻¹. As Cu heteroatoms replaced the sites of Ti in the TiO₂ nanosheets, small amounts of Ti³⁺ valence states in Ti⁴⁺-dominant TiO₂ and Ov sites are created, as observed using X-ray photoelectron spectroscopy and X-ray absorption fine structure spectroscopy. Furthermore, owing to the difference in size between the Cu²⁺ dopants and Ti⁴⁺ hosts, Cu-doped TiO₂ has a compressive strain, which is evaluated by DFT calculations, and it causes changes in the distribution in the electron densities around O and Ti in the materials. The combination of non-stoichiometry and lattice strain in Cu-doped TiO₂ narrows its bandgap energy, corresponding to the extended light absorption range of 600–800 nm, and electrons are accumulated around the sites of O atoms, thereby affecting the changes in the N₂ adsorption affinity.

Jing Zhang and coworkers prepared a Fe-doped SrTiO₃ (FeₓSr₁₋ₓTiO₃, where x=the stoichiometric ratio of Fe precursor and Sr precursor controlled in preparation step) photocatalyst using the hydrothermal method followed by calcination [47]. The Fe₀.₁Sr₀.₉TiO₃ sample exhibited the best NH₃ production rate of 30.1 μmol·g⁻¹·h⁻¹, which is 3.2 times higher than that of pristine SrTiO₃. By replacement of the Fe³⁺ ion, which has a smaller size, on the Sr²⁺ site in SrTiO₃, the size of particles is reduced along with the corresponding increase in the surface area. Furthermore, the Fe₀.₁Sr₀.₉TiO₃ photocatalyst exhibits significantly enhanced N₂ chemisorption and activation ability, which Fe dopants are the major contributor to.

Vacancies Vacancy, one of defect formation strategies, leads to changes in the band structure and chemical adsorption nature on the surface [48]. This section gives an overview of intentionally induced anion vacancies in semiconductor photocatalysts and discusses how they affected the photocatalytic NH₃ production.

Zhong Jin and coworkers compared the NH₃ production activities using BiOBr semiconductors in the presence (Vo-BiOBr) or absence (BiOBr) of oxygen vacancies [49]. The Vo-BiOBr samples were prepared using the hydrothermal method with the addition of polyvinylpyrrolidone surfactants leading to in-situ generation of abundant vacancies, whereas pristine BiOBr samples were synthesized without adding the surfactants. The Vo-BiOBr photocatalysts produced NH₃ at a rate of 54.70 μmol·g⁻¹·h⁻¹ under UV–Vis irradiation, which is 10 times higher than the production rate using BiOBr. The major contribution of this significant improvement is enhanced N₂ adsorption that initiates the intermediate formation for NH₃ production. For example, the amount of adsorbed N₂ was estimated based on N₂ adsorption isotherms, on Vo-BiOBr is considerably higher than that using BiOBr as shown in Fig. 4a. Furthermore, by introduction of the oxygen vacancies, the bandgap energy is reduced with the shifts in the CBM and VBM positions, which leads to increased light absorption as shown in Fig. 4b.

Chuanyi Wang and coworkers prepared metal-free g-C₃N₄ semiconductors by thermal decomposition of melamine and induced nitrogen vacancies (V-g-C₃N₄) within the semiconductors by additional calcination under a N₂ atmosphere [50]. The V-g-C₃N₄ samples produced NH₃ at a rate of 1240 μmol·g⁻¹·h⁻¹ using pure N₂ and water under visible light irradiation, whereas pristine g-C₃N₄ produced negligible amounts of NH₃. Further, morphologies and bandgap energies were not significantly varied depending on the intentional creation of N vacancies; however, two factors changed considerably. Due to the presence of N vacancies on the semiconductor, the signal collected using photoluminescence spectra decreased, indicating the reduction in the carrier recombination and enhancement of their separation. Furthermore, the N vacancies enable selective adsorption and activate N₂, and it was experimentally confirmed that negligible amount of NH₃ produced on g-C₃N₄ selectively blocked the vacancies using Pd particles.

3.2.2 Coupling with multi-light absorbers Coupling with multi-light absorbers to form heterojunctions has been widely investigated to improve light absorption capacity under single illumination and separation of photoexcited electron–hole carriers through their designed band alignments. This strategy for catalyst design is effective in improving the photocatalytic NH₃ production.

Zhong Jin and coworkers prepared Bi₂MoO₆/Ov-BiOBr composites, where Ov denotes the oxygen vacancies using two-step methods, and synthesized Bi₂MoO₆ by solution-phase reflux process followed by the hydrothermal process to couple Ov-BiOBr on as-prepared Bi₂MoO₆ [51]. Despite minimal difference in light absorption before and after coupling, the Bi₂MoO₆/Ov-BiOBr composites showed a significantly enhanced NH₃
production rate (90.7 μmol·g⁻¹·h⁻¹), which is almost 30 and 3 times higher than the rates evaluated using Bi₂MoO₆ and Ov-BiOBr, respectively as shown in Fig. 5a. The major role of coupling is the formation of cascaded band alignments at the interface between two semiconductors. The photoexcited holes are transported and oxidize the electron donor on Bi₂MoO₆ where the VBM is located relatively higher, whereas the photoexcited electrons are transported and reduce N₂ on Ov-BiOBr where the CBM located relatively lower. Furthermore, oxygen vacancies on BiOBr show synergistic effects on the NH₃ production by providing N₂ adsorption and activation sites as shown in Fig. 5b.

Jimmy Yu and coworkers prepared Ov-TiO₂ using the hydrothermal method followed by loading Au nanoparticles. The Au nanoparticles generate hot electrons under visible light illumination [51], which is known as plasmonic phenomena. The hot electrons are injected into the CBM of TiO₂ and then trapped in vacant sites where N₂ is reduced into NH₃. The generated holes remain on Au and oxidize the electron donors, methanol, in solution as shown in Fig. 5c and d. The optimized Au/TiO₂-Ov samples produced NH₃ with a rate of 78.6 μmol·g⁻¹·h⁻¹ under visible light irradiation, which is at least 98 and 35 times higher those using Au/TiO₂ and TiO₂-Ov photocatalysts, respectively.

3.2.3 Surface modification and reaction engineering

As discussed above, photocatalytic activities have been developed significantly by modifying photocatalysts, for example, defects engineering and composite formation. However, although photogenerated charge generation and separation are advanced by multiple possible strategies, if the surfaces of the semiconductors exhibit slow charge injection and are poorly catalytic for N₂ reduction, the NH₃ production rate may not be enhanced directly. The surface modification on the semiconductors using a robust electrocatalyst (cocatalyst) for N₂ to NH₃ conversion is the simplest way to improve the limiting factor at the interface between the semiconductors and liquid where reactants are present. Therefore, the modification of the semiconductor surface with various NH₃ production catalysts, such as Ru, Cu, and Au, has been investigated [20, 34, 53].
In contrast, since the rates of reduction and oxidation reactions always correspond to one another, the sluggish photo-oxidation using holes may become a limiting factor for the photocatalytic NH$_3$ production. To overcome the possible limitation, it has been widely suggested to load appropriate electrocatalysts (cocatalysts) for water oxidation on the semiconductor or provide a more facile hole acceptor (electron donors) than water, such as methanol or ethanol (Table 1).

4 Summary and outlook

In summary, we reviewed the mechanistic and experimental steps for photocatalytic NH$_3$ production and examined various strategies to modify photocatalysts employed to enhance the production activities. This review clearly shows that although significant development of photocatalysts has been reported thus far, further advances for practical NH$_3$ production are required. First, the efficiency for charge generation via solar light absorption should be enhanced. Considering that the majority of incident photons are in the range of visible light, development of absorbers, can harvest the incident solar light, is required by determining appropriate materials and engineering semiconductors.

The charge separation effect is also required for photocatalytic NH$_3$ production through suppression of their recombination. For example, strategies for doping and composite formation will exhibit advances in the future and may increase the photon absorption efficiency simultaneously. In addition, morphology engineering [72–76] for photocatalysts will be promising and can be achieved by controlling the distances for carrier transportation and lifetime duration between the photo-induced generation and recombination. Furthermore, this may change facets and surface area, thereby providing active sites for the redox reactions using transported carriers. Moreover, if the facets are optimized with increasing surface area, morphology engineering can be significantly beneficial for NH$_3$ production.

With improvements in photon absorption and charge separation, surface engineering will be able to provide active sites where N$_2$ reduction using electrons and oxidation using holes is important. Thus, defect engineering, for example, formation of vacancies, cocatalyst coupling, and applying sacrificial reagents have been suggested. It is noteworthy that N$_2$ diffusivity control close to photocatalysts make an important contribution to practical photocatalytic NH$_3$ production. For instance,
The importance of three-phase interfaces, where a catalyst and two phases reactants such as water and active gas faced, has been demonstrated [7778]. This indicates that even if highly robust catalysts are prepared, if the supply of N\textsubscript{2} gas and water is insufficient at the region close to the catalyst, the NH\textsubscript{3} production is limited. Thus, environmental engineering, for example, via hydrophobicity control on the catalysts, will be significantly effective. The mechanism, experimental methods, discussion, insights, and suggestions contained in this review provide a good fundamental and foundation for further improvement of photocatalytic NH\textsubscript{3} production.

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### Authors' contributions

SC, SMK, YL, JS, JJ, and Prof. YJJ contributed to prepare this review. Prof. JJJ and Prof. JSL supervised this work and Prof. YJJ, Prof. JSL, and SC are major contributors in writing the manuscript. All authors read and approved the final manuscript.

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**Table 1** The summary of photocatalytic nitrogen reduction performances and its operating conditions: photocatalysts

| Photocatalysts | Light source | Hole scavenger | Ammonia production rate | Ammonia detection methods | Refs |
|---------------|--------------|----------------|-------------------------|---------------------------|------|
| PCN/GO(0.2)   | 250 W Xe lamp 400 nm < λ < 800 nm | 1 mM EDTA-2Na | 544.6 µmol·L\textsuperscript{-1}·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent\textsuperscript{b} | [14] |
| Ru/TiO\textsubscript{2} | 300 W Xe lamp | 20% C\textsubscript{2}H\textsubscript{2}OH | 3.31 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Indophenol blue | [20] |
| Cu/g-C\textsubscript{3}N\textsubscript{4} | 300 W Xe lamp 400 nm < λ < 800 nm | 20% C\textsubscript{2}H\textsubscript{2}OH | 186 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [34] |
| Ni-0.8-TiO\textsubscript{2} | 300 W Xe lamp | None | 46.80 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [45] |
| 6%-TiO\textsubscript{2} | 300 W Xe lamp | None | 78.9 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [46] |
| Fe\textsubscript{2}O\textsubscript{4}·Si\textsubscript{2}O\textsubscript{5}·TiO\textsubscript{4} | 300 W Xe lamp | None | 30.1 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [47] |
| TiO\textsubscript{2}/Au/a-TiO\textsubscript{2} | 300 W Xe lamp | None | 54.70 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [49] |
| V-g-C\textsubscript{3}N\textsubscript{4}\textsuperscript{a} | 300 W Xe lamp 420 nm > λ | 20% C\textsubscript{2}H\textsubscript{2}OH | 1240 µmol | Nessler’s reagent | [50] |
| Bi\textsubscript{2}MoO\textsubscript{6}/O\textsubscript{2}BiOBr | 300 W Xe lamp None | None | 1226 µmol | Nessler’s reagent | [51] |
| 5% Ru@n-GaN NWs | 300 W Xe lamp None | None | 180 µmol | Nessler’s reagent | [52] |
| Fe-doped g-C\textsubscript{3}N\textsubscript{4} | 250 W Na lamp 400 nm < λ | 10% C\textsubscript{2}H\textsubscript{2}OH | 78.6 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Indophenol blue | [53] |
| Au/Bi\textsubscript{2}O\textsubscript{3}O\textsubscript{V} | 300 W Xe lamp | None | 38.2 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Indophenol blue | [54] |
| BiOCl | 500 W Xe lamp | 25% CH\textsubscript{2}OH | 92.4 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [55] |
| Bi\textsubscript{2}O\textsubscript{3} | 300 W Xe lamp | 20% CH\textsubscript{2}OH | 111.5 µmol·L\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [56] |
| Bi\textsubscript{2}O\textsubscript{3}Br | 300 W Xe lamp 400 nm > λ | None | 1380 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [57] |
| 20Fe-2Al@3D Graphene | 500 W Hg lamp | None | 430 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Indophenol blue | [58] |
| Ultrathin Mo\textsubscript{2}O\textsubscript{3} | 500 W Xe lamp 420 nm > λ | None | 325 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Isotopic labeling | [59] |
| CuCr-NSs | 300 W Xe lamp 400 nm > λ | None | 184.8 µmol·L\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [60] |
| Mo-doped W\textsubscript{18}O\textsubscript{49} | 300 W Xe lamp | 1 mM Na\textsubscript{2}SO\textsubscript{4} | 195.5 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent, Ion chromatography | [61] |
| BiO quantum dots | 500 W Xe lamp | None | 1226 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Indophenol blue | [62] |
| C-W\textsubscript{O}\textsubscript{2}H\textsubscript{2}O | 500 W Xe lamp | None | 205 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [63] |
| Fe-doped g-C\textsubscript{3}N\textsubscript{4} | 250 W Na lamp 400 nm < λ < 800 nm | 0.1% C\textsubscript{2}H\textsubscript{2}OH | 317.1 µmol·L\textsuperscript{-1}·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [64] |
| 5% Ru@n-GaN NWs | 300 W Xe lamp | None | 120 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Indophenol blue | [65] |
| Ga\textsubscript{2}O\textsubscript{3}·DBD/g-C\textsubscript{3}N\textsubscript{4} | 300 W Xe lamp | 0.04 mM CH\textsubscript{2}OH | 122.5 µmol·L\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [66] |
| TiO\textsubscript{2}·g-C\textsubscript{3}N\textsubscript{4} | 300 W Xe lamp 420 nm > λ | 20% CH\textsubscript{2}OH | 250.6 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [67] |
| g-C\textsubscript{3}N\textsubscript{4}·MgAlFeO | 250 W Na lamp 400 nm < λ < 800 nm | 0.1% C\textsubscript{2}H\textsubscript{2}OH | 440.4 µmol·L\textsuperscript{-1}·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [68] |
| TiO\textsubscript{2}/Au/a-TiO\textsubscript{2} | 300 W Xe lamp | None | 0.0134 µmol·cm\textsuperscript{-2}·h\textsuperscript{-1} | Indophenol blue | [69] |
| Fe\textsubscript{3}O\textsubscript{4} | 500 W Xe lamp | 0.1% C\textsubscript{2}H\textsubscript{2}OH | 1362.5 µmol·L\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [70] |
| H-Bi\textsubscript{2}MoO\textsubscript{6} | 300 W Xe lamp with a 420 nm cutoff filter | None | 1300 µmol·g\textsuperscript{-1}·h\textsuperscript{-1} | Nessler’s reagent | [71] |

\textsuperscript{a} Where V denoted nitrogen vacancies

\textsuperscript{b} Nessler’s reagent, K\textsubscript{2}HgI\textsubscript{4}, is one of photometric indicators for NH\textsubscript{3} detection and quantification [71]
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**Availability of data and materials**

The datasets used and analyzed during the current study are available from the corresponding references listed.

**Declarations**

**Competing interests**
The authors declare that they have no competing interests.

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