

Review Article

Progress of Metal Oxide (Sulfide)-Based Photocatalytic Materials for Reducing Nitrogen to Ammonia

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Received 13 July 2018; Revised 1 November 2018; Accepted 5 November 2018; Published 22 November 2018

Academic Editor: Mallikarjuna N. Nadagouda

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The Haber–Bosch process has been an important approach to produce ammonia for meeting the food need of increasing population and the worldwide need of nitrogenous fertilizers since 1913. However, the traditional ammonia production process is a high energy-consumption process, which usually produces 1 metric ton ammonia with releasing around 1.9 metric tons CO₂. Photocatalytic ammonia synthesis under solar light as energy source, an attractive and promising alternative approach, is a very challenging target of reducing fossil energy consumption and environmental pollution. Therefore, photocatalytic ammonia production process would emerge huge opportunities by directly providing nitrogenous fertilizers in a distributed manner as needed in the agricultural fields. In this article, different metal oxide (sulfide)-based photocatalytic materials for reducing nitrogen to ammonia under ambient conditions are reviewed. This review provides insights into the most recent advancements in understanding the photocatalyst materials which are of fundamental significance to photocatalytic nitrogen reduction, including the state-of-the-art, challenges, and prospects in this research field.

1. Introduction

As the important chemicals to our planet, nitrogen (N₂) compounds, such as ammonia (NH₃), nitrates, and urea, have played an essential role in meeting the growing demand for food and the worldwide need of nitrogenous fertilizer since 1913 [1]. It is essential for all living organisms to be provided the N₂ compounds needed for growing tissue [2]. Moreover, the global N₂ cycle, whose small fraction is related to the atmospheric ionization, mainly depends on the biogeochemical cycles [3]. In addition, N₂ photoreduction to nitrogenous compounds (e.g., NH₃) in soils and sands as catalysts also is an important part of global N₂ cycle. Through continuous exploration of nitrogen fixation, the Haber–Bosch process, a thermo-chemical catalytic conversion technology, becomes a primary choice of synthesizing N₂ fixation compounds which were produced from the reaction:



In the past over decades [4], the process has fed the world's growing population and has significantly contributed to the human beings development. The Haber–Bosch process reacted with the pure feed gases at high temperatures and pressures, requiring almost 2% of global energy consumption [5]. On the contrary, there are some negative impacts of the Haber–Bosch process in terms of the overuse of nitrogenous fertilizer that affects the ecosystem balance, human health, climate change, etc. [6]. Then, reducing the fossil energy consumption and environmental pollution would be a very challenging target for this process.

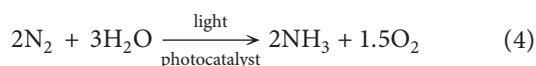
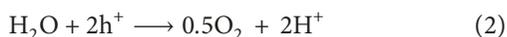
Ambient reduction of N₂ to NH₃ has been a significant research subject of efficiently fixing N₂ under mild conditions. Energy coming from sustainable source as solar, an alternative, sustainable NH₃ synthesis process based on the biological N₂ fixation would be more energy efficient than

the Haber–Bosch process [7]. Additionally, the distribution of nitrogenous fertilizers produced by the Haber–Bosch process requires efficient transportation which may be least easy in the nonindustrialized countries than in the industrialized countries. Then, it would be possible to produce nitrogenous fertilizers close to the farm field as needed and reduce greenhouse gas emission and control the global N₂ cycle. Obviously, due to its energy saving and friendly environmental, photocatalytic reduction of N₂ to NH₃ could be an excellent alternative to the Haber–Bosch process. That is to say, developing efficient photocatalysts for synthesizing NH₃ would emerge huge opportunity to directly provide nitrogenous fertilizers in agricultural fields as needed in a distributed manner. Chemists should discover how to activate the N≡N bond (941 kJ·mol⁻¹) to synthesize ammonia in the presence of novel photocatalysts with less fossil energy consumption and more solar energy [8].

In initial works, there was a popular perspective that the photocatalytic reduction of N₂ to NH₃ should take place over abundant soil minerals and sand in nature [9]. Since 1977, the TiO₂-based synthetic materials as photocatalysts were firstly applied for N₂ fixation under UV light, and a series of studies [10] have gradually been conducted on photocatalytic N₂ reduction to NH₃ with water and air under light driving force. Although there have been many new photocatalysts and approaches to solve the problems of the Haber–Bosch process, till now, no viable and efficient catalysts could match all requirements of an active, selective, scalable, long-lived catalyst for the sustainable photocatalytic reduction of N₂ to NH₃ [11]. This review tries to make them possible to ascertain a comprehensive understanding of the current knowledge regarding to photocatalytic materials for producing nitrogenous fertilizers from N₂ and to give a solid research perspectives for the next step work in the research field.

2. Photocatalytic Reduction Process of N₂ to NH₃

The photocatalytic reduction of N₂ to NH₃ under ambient conditions is a sustainable NH₃ production process without fossil energy consumption and environmental pollutions. Photocatalysis on semiconductors is a promising method for synthesizing NH₃ from N₂ with water (H₂O) as a reducing reagent. The photocatalytic NH₃ production process mainly consists of the photocatalytic oxidation of H₂O to protons and the photocatalytic reduction of N₂ to NH₃.



The reactions mentioned above imply that the photocatalysts created on the surface of robust semiconductors capable of oxidizing H₂O (Equation (2)) may reduce N₂ by the photoformed conduction band (CB) electrons (Equation (3)). As a result of these behaviours, N₂ is reduced to NH₃ by

the CB electrons (Equation (2)). That is to say, NH₃ could be produced from N₂ and H₂O (Equation (4)) on a metal-free photocatalyst under ambient conditions in these processes. The valence band (VB) should be lower than the oxygen evolution potential, while the position of the CB should be higher than the reduction potential of N₂ hydrogenation. With synthesizing ammonia, the metal oxide-based material as photocatalyst is dynamically converted between its oxidized and reduced states in the process.

Solar light as energy source is a good choice for photocatalytic reduction of N₂ to NH₃ under ambient conditions because it is difficult for the existing power plants to meet the large energy need of producing NH₃ (Figure 1). The CB position of the semiconductor should be more negative than the reduction potential of the N₂ hydrogenation, as well as the VB should be more positive than the oxygen evolution potential (Table 1). Therefore, something must be taken into account that both reduction potential of the adsorbate and position of the energy band are important for the photocatalytic redox reaction occurrence when making a decision on the choice of semiconductor photocatalyst materials.

Normally, the photocatalytic reduction process of N₂ to NH₃ can be divided into several reaction steps [13, 14]. Firstly, the photogenerated electrons (e⁻) are promoted to leave from vacant holes in the VB to the CB. Secondly, some electrons and holes recombine each other in order to improve the solar conversion efficiency and apparent quantum yield of the reduction. Protons could be generated in the endothermic process of H₂O oxidation when solar energy is enough to be absorbed and converted into the chemical energy which can meet the large free energy gain of N₂ to NH₃ ($\Delta G^0 = 339 \text{ kJ}\cdot\text{mol}^{-1}$) [15]. Thirdly, the others transfer onto the surface of the photocatalysts for the redox reaction (Equation (4)) which the photoformed VB holes (h⁺) oxidize H₂O to protons (H⁺) and O₂ under visible light. In the process of photocatalytic ammonia synthesis, the photo-generated holes must also be consumed to satisfy the charge neutrality (CB e⁻ + VB h⁺ = 0) (Equation (2) in Table 1).

By synthesizing NH₃ from atmospheric N₂ and H₂O in the presence of photocatalysts under visible light (Equation (3)) [16], photons as the driving force actually can promote to reduce N₂ to NH₃ after a series of multistep injections of photogenerated electrons and H₂O-derived protons. Therefore, the first electron transfer (-4.16 V vs. NHE) and proton-coupled electron transfer (-3.2 V vs. NHE) (Table 1) must be overcome to reduce N₂ to NH₃. Then, the recombination of charge carriers and a small band gap are important for satisfying semiconductor photocatalysts preferably in the visible light. And it is also necessary for ideal semiconductor materials to have the characteristics of the charge carrier recombination and a small band gap in the visible light region.

3. Photocatalytic Materials for Reducing N₂ to NH₃

As we all know, photocatalytic NH₃ synthesis from N₂ also needs to overcome the N≡N band energy barrier with the high-energy UV light. Necessarily, the large thermodynamic

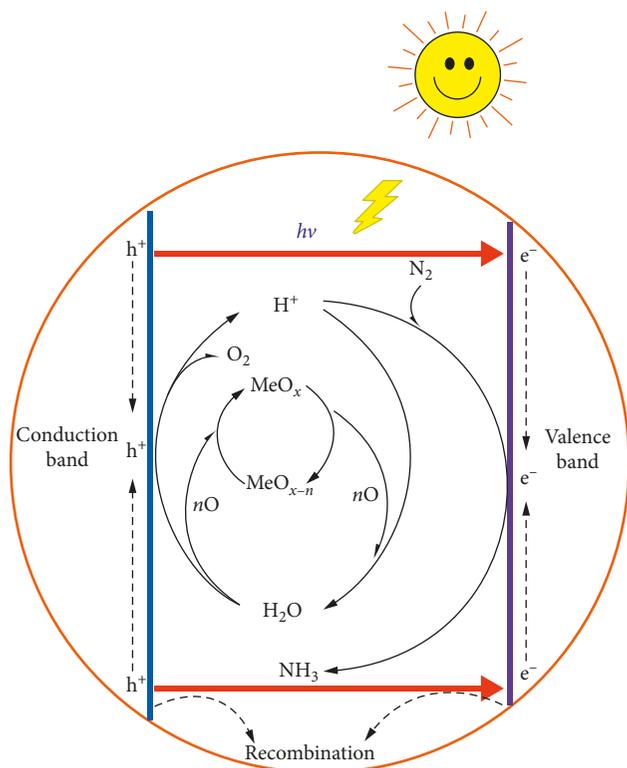


FIGURE 1: Schematic of metal oxide-based photocatalysts for reducing N_2 to NH_3 . MeO_x (MeO_{x-n}): metal oxide-based materials as photocatalysts and Me denotes metals.

TABLE 1: Redox potentials of reducing N_2 to NH_3 [10–12]].

No.	Reaction	E^0 (V)
1	$H_2O + 2h^+ \longrightarrow 0.5O_2 + 2H^+$	1.33 ^b
2	$H^+ + e^- \longrightarrow 0.5H_2$	-0.42 ^a
3	$N_2 + e^- \longrightarrow N_2^-$	-4.16 ^b
4	$N_2 + H^+ + e^- \longrightarrow N_2H$	-3.2 ^b
5	$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3$	0.55 ^b

^a E^0 vs. NHE at pH 7; ^b E^0 vs. NHE at pH 0.

driving force is required for the reduction of N_2 to NH_3 at atmospheric conditions [17]. To solve the problem, developing the efficient photocatalytic materials for the N_2 reduction process maybe are indispensable parts for increasing NH_3 yields significantly.

It is first time that Dhar and his coworkers [18] discovered this photocatalytic reaction in the 1940s. Schrauzer and Guth [13] demonstrated that the photocatalytic NH_3 synthesis on a variety of sterile desert sands until late 1970s. Following this work, some independent results were achieved as gaining synthetic materials for speeding the photocatalytic N_2 reduction rate [19]. However, there are still some differences among these results some of which are in conflict with each other or confused, and no consensus was reached in regard to the photocatalytic materials challenges for the reaction of N_2 and H_2O to NH_3 and oxygen. In this section, the metal oxide-based photocatalytic materials for the reduction of N_2 to NH_3 are classified (Tables 2 and 3) according to their different elemental

compositions and the state-of-the-art research advancements are described, respectively.

3.1. Titanium Oxide-Based Materials. Photocatalytic N_2 fixation has received more and more attentions since synthesizing NH_3 from N_2 was available in the presence of titanium-based catalysts. Dhar and Chowdhry [43] found that titanium oxide (TiO_2) as photocatalytic material could provide the larger NH_3 yields from reducing N_2 than ferric oxide and zinc oxide as photocatalysts. Schrauzer and Guth [13] also discovered this phenomenon of N_2 photoreduction. UV irradiation of TiO_2 with a large number of surface Ti^{3+} species could produce NH_3 from N_2 and H_2O under ambient conditions, which shows the species are actually the active sites for the reduction of N_2 to NH_3 [14].

3.1.1. Iron-Doped Materials. As key factors underlying photocatalytic performance, the influence of the crystalline phase and iron dopants on the catalytic activity of TiO_2 photocatalytic material for the N_2 reduction was focused. Under UV light, NH_3 yields reached a maximum value when over 0.2% Fe_2O_3 was doped into TiO_2 material. However, Hirakawa et al. [14] demonstrated that Ru, Pt, or Pd particles loaded in the TiO_2 materials were unhelpful to increase the NH_3 yields due to their particles covering the catalytic active site Ti^{3+} of TiO_2 photocatalytic material and changing surface defects. Interestingly, Augugliaro et al. [44] supported Fe_2O_3 -hybridized TiO_2 on Al_2O_3 as photocatalyst which was applied in gas-solid fluidized bed reactors to improve NH_3 yields because of the influence of iron ions on the TiO_2 crystalline [45]. Lashgari and Zeinalkhani [21] photosynthesized NH_3 in a H_2O photosplitting setup in the presence of some synthetic Fe_2O_3 and TiO_2 -based uniform nanoparticles and obtained the maximum NH_3 yield. Bourgeois et al. [26] suggested that thermal pretreatments could generate surface defects or impurity states on the surface of unmodified TiO_2 that showed the photocatalytic activity of reducing N_2 after annealing in air. As a highly efficient method, high pretreatment temperatures ($\sim 1000^\circ C$) inducing surface defects in TiO_2 material and the small amounts ($< 1\%$) of iron impurities are necessary to enhance the NH_3 yields [46].

Observing no reduction of N_2 to NH_3 in the presence of pure TiO_2 material, Augugliaro et al. [47] put forward a hypothesis that Fe^{3+} of photoassisted organ iron compound could temporarily trap photons and promote the separation of charge carriers, which has played an important role in the NH_3 production processes. Exposing the facets of Fe-doped TiO_2 with ethanol as the scavenger enhanced the photocatalytic reduction of N_2 to NH_3 [22]. No nitrite was formed in the ethanol solution that could prevent the oxidation of NH_3 . Keeping a low doping concentration on the surface of TiO_2 material was very important to inhibit charge recombination for forming Fe^{2+} and Fe^{4+} and to transfer electrons and holes to Ti^{4+} and OH^- for generating Ti^{3+} and OH^- [18]. Similarly, Ranjit and Viswanathan [48] observed that the $FeTi_2O_5$ phase in Fe-doped titanium materials could

TABLE 2: Summary of metal oxide-based materials for photocatalytic reduction of N_2 to NH_3 .

Catalytic materials	Catalysts	T (K)	Light source	Organic scavenger	Average NH_3 production rate	Year	Ref.
Titanium oxide-based materials	$TiO_2@g-C_3N_4$	ACs	Visible light	CH_3OH	$250.6 \mu mol g^{-1} h^{-1}$	2018	[20]
	$Pb/Fe_2O_3-TiO_2$	298	Xenon light	Distilled water	$1150 \mu M \cdot h^{-1}$	2017	[21]
	Fe-doped TiO_2	—	UV	Ethanol	$400 \mu M \cdot h^{-1}$	2014	[22]
	$RuCl_3-TiO_2$	RT	UV-Vis	Humic acid	$4 \mu M \cdot h^{-1} \cdot cm^{-2}$	2008	[23]
	P_3MeT/TiO_2	293	UV	None	$8.3 \mu mol \cdot h^{-1} \cdot m^{-2}$	2001	[24]
	Fe-doped TiO_2	313	UV-Vis	None	$10 \mu mol \cdot g^{-1} \cdot h^{-1}$	1997	[13]
	Ru-doped TiO_2	—	UV-Vis	None	$22.7 \mu mol \cdot g^{-1} \cdot h^{-1}$	1996	[19]
	Fe^{3+} -doped TiO_2	353	UV	None	$6 \mu mol \cdot g^{-1} \cdot h^{-1}$	1991	[25]
	TiO_2	RT	UV	Wet nitrogen flux	$0.83 \mu mol g^{-1} h^{-1}$	1988	[26]
Other metal oxide-based materials	$BaTiO_3$	313	UV	None	$0.87 \mu mol \cdot g^{-1} \cdot h^{-1}$	1983	[27]
	$g-C_3N_4/Mg_{1.1}Al_{0.3}Fe_{0.2}O_{1.7}$	303	Visible light	Ethanol	$166.8 \mu M \cdot h^{-1}$	2017	[28]
	BiO	ACs	Solar light	Deionized water	$50.5 \mu M \cdot h^{-1}$	2017	[29]
	Fe_2O_3	298	UV-Vis	Ethanol	$1362.5 \mu M \cdot h^{-1}$	2017	[21]
	H- Bi_2MoO_6	RT	Solar light	None	$1300 \mu mol g^{-1} h^{-1}$	2016	[30]
	$BiOBr$	RT	Visible light	None	$1042 \mu M \cdot h^{-1}$	2015	[31]
	$\beta-Ga_2O_3$	298	UV	Tert-butanol	36.1%	2015	[32]
	Pt-loaded ZnO	—	UV	Na-EDTA	$860 \mu mol \cdot g^{-1} \cdot h^{-1}$	2010	[33]
	$Cu_2O \cdot xH_2O \cdot CuCl$	ACs	UV	None	$70 \mu M \cdot h^{-1}$	1989	[34]
	$Fe_2O_3 + Fe_3O_4$	303	Xenon light	None	$10 \mu mol \cdot g^{-1} \cdot h^{-1}$	1987	[35]

RT denotes room temperature. ACs denote ambient conditions.

TABLE 3: Summary of metal sulfide-based materials for photocatalytic reduction of N_2 to NH_3 .

Catalytic materials	Catalysts	T (K)	Light source	Organic scavenger	Average NH_3 production rate	Year	Ref.
Metals sulfide-based materials	MoS_2	298	Xenon light	None	$325 \mu mol \cdot g^{-1} \cdot h^{-1}$	2017	[12]
	$[Mo_2Fe_6S_8(SPh)_3]-[Fe_4S_4]$	ACs	Xenon light	None	$18.82 \mu M \cdot h^{-1}$	2016	[36]
	$Mo_{0.1}Ni_{0.1}Cd_{0.8}S$	303	Visible light	Ethanol	$71.2 \mu M \cdot h^{-1}$	2016	[37]
	$Zn_{0.1}Sn_{0.1}Cd_{0.8}S$	303	Visible light	Ethanol	$105.2 \mu M \cdot h^{-1}$	2016	[38]
	$[Mo_2Fe_6S_8(SPh)_3]^{3+}$ and $[Sn_2S_6]^{4-}$	RT	Solar light	—	$18.82 \mu M \cdot h^{-1}$	2015	[39]
	Pt/ $CdS \cdot Ag_2S/RuO_2$	303	Visible light	$K[Ru(EDTA-H)Cl]_2H_2O$	$1260 \mu M \cdot h^{-1}$	1991	[40]
	$CdS/Pt/RuO_2$	303	Visible light	None	$620 \mu M \cdot h^{-1}$	1988	[41]
	CdS/Pt	311	UV	None	$3.26 \mu mol \cdot g^{-1} \cdot h^{-1}$	1980	[42]

RT denotes room temperature. ACs denotes ambient conditions.

enhance the separation of charge carriers and also demonstrated this hypothesis. However, Soria et al. [25] suggested that excess Fe dopants might lead TiO_2 materials to lose themselves all photocatalytic activities. Therefore, the low bulk Fe^{3+} concentrations significantly assist in charge separation. TiO_2 nanoparticles codoped with N_2 and Fe^{3+} were prepared using the homogeneous precipitation-hydrothermal method. The cooperation of N_2 and Fe^{3+} leads to narrow the band gap, improve the photocatalytic activity in the visible light region, and promote the separation of the photogenerated electrons and holes to accelerate the transmission of the photocurrent carrier [49].

Generally, titanium oxide-based photocatalytic materials for the N_2 reduction have made much progress in several aspects, such as the importance of iron dopants. However, some atomic-scale behaviours of TiO_2 photocatalytic N_2 reduction to NH_3 are chaos, such as the $N \equiv N$ dissociation transition-states and active sites of TiO_2 photocatalytic materials. Future research works should mainly discover the secrets on how to reduce N_2 to NH_3 in the presence of titanium-based materials from a molecular-level viewpoint.

3.1.2. Transition Metal-Doped Materials. Transition metals as dopants in photocatalytic materials have some advantages for the higher NH_3 yields, such as less charge carrier recombination, stronger photocatalyst absorbance, and lower overpotential for the N_2 reduction. In the process of preparing titanium-based photocatalytic materials for NH_3 synthesis, preprocessing titanium-based materials with high temperatures ($\approx 1000^\circ C$) and adding transition metal impurities ($< 1\%$) were necessary and benefit to obtain efficient titanium dioxide-based photocatalytic materials [46]. Since then, $CuCl$, WO_3 , and $FeOx$ as photocatalysts for NH_3 synthesis from N_2 have been investigated [34, 50]. Those surface oxygen defects of titanium metal could play an important role in the atmospheric N_2 photoreduction.

Some transition metals taking place of iron as dopants in TiO_2 materials were investigated [13], such as Co, Mo, Ni, Pd, V, Cr, Cu, Pt, Ag, Au, and Pb. Only did Co, Mo, and Ni dopants among these metals enhance the NH_3 yields, and the other metals not. Differently, Palmisano found that chromium-doped TiO_2 material was effective in the photocatalytic N_2 reduction to NH_3 [51]. Besides their dopant

role, transition metals on the surface of TiO_2 materials could be effective in NH_3 synthesis as cofactors of photocatalysts. For example, Ru-doped TiO_2 could photocatalyze the reduction of N_2 to NH_3 [42]. As cocatalysts of TiO_2 materials, the photocatalytic activities of transition metals are associated with the strength of the M–H bonds (M: transition metal), such as $\text{Ru} > \text{Rh} > \text{Pd} > \text{Pt}$ [19].

Due to lower Fermi level than the others, transition-metal dopants as electron sinks in titanium photocatalysts could minimize the probability of carrier recombination to promote greater NH_3 yields, which is a critical factor for designing photocatalytic systems. To increase N_2 reduction driving force to NH_3 synthesis, Co, Mo, Ni, Ru, and Pt dopants have been added into the titanium-based materials, respectively, which resulted in increasing the NH_3 yields [9, 19]. Anatase TiO_2 was prepared by the sol-gel method through the hydrolysis of titanium tetrachloride and doped with transition metal ions like V^{5+} and Zn^{2+} . Although both doped samples showed similar red shift in the band gap, Zn^{2+} (0.06 at.%) doped TiO_2 materials showed enhanced activity which was attributed to smaller crystallite size and larger surface area for accelerating the interfacial charge transfer [52]. Under ambient temperature and atmosphere, the photocatalytic activity of the Ag- TiO_2 multiphase nanocrystal composite thin films prepared by the liquid phase deposition method exceeded that of pure TiO_2 thin films when the AgNO_3 concentration was kept in the range of 0.03–0.05 [53]. The presence of dopants in the band gap could effectively improve photocatalytic performance through inducing defect states which assist in charge separation of photogenerated electrons and holes [26]. However, all transition metal dopants did not show more perfect photocatalytic activities than iron dopant in the TiO_2 photocatalytic NH_3 synthesis process [54]. Due to their lower Fermi level, transition metals act as electron sinks which creates a Schottky barrier, trapping photogenerated electrons and minimizing the probability for carrier recombination [20]. Therefore, reducing carrier recombination is a significant issue to design photocatalytic materials for the NH_3 synthesis from N_2 .

3.1.3. Other Metal Oxide-Based Materials. In addition to titanium oxide-based materials, other metal oxide-based materials as photocatalyst have also obtained more and more attentions on their behaviours of reducing N_2 to NH_3 in the past several decades. All of these metal oxide-based materials reported have different degrees of photocatalytic activities for NH_3 synthesis from N_2 under ambient conditions.

Iron was early used as catalysts in the catalytic ammonia production processes by Dhar and Chowdhry [43]. As we know, iron plays an important role in the Haber–Bosch process, but it is ferric oxide (Fe_2O_3) not iron as the alternative to titanium that could photocatalytic the reduction of N_2 to NH_3 . However, pure Fe_2O_3 is not capable of photocatalytic NH_3 synthesis from N_2 unless partially reduced [20] and hydrous [23] Fe_2O_3 . To solve the problem, Khader et al. [35] partially reduced a- Fe_2O_3 to Fe_3O_4 for

photoactivating N_2 , which resulted in detecting NH_3 in aqueous slurry of the catalyst. Furthermore, the photoactivity of mesoporous $\beta\text{-Ga}_2\text{O}_3$ nanorods in N_2 photoreduction was ameliorated in the presence of different alcohols, such as ethanol and tert-butanol [32]. Besides ZnO prepared by means of wet etching or precipitation methods, it was reported that the NH_3 yield of unmodified ZnO was higher than that of Pt-loaded ZnO materials [33].

As-synthesized bismuth monoxide (BiO) materials were applied in the photocatalytic reduction of N_2 to NH_3 under solar light. Research results [28] showed that the NH_3 synthesis rate is up to $1226 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ which is about 1000 times higher than that of the Fe- TiO_2 photocatalyst (Table 2). Obviously, deactivation of this photocatalyst did not occur even after being used more than 120 hours. Bismuth oxyhalides, BiOX ($X = \text{Cl}, \text{Br}, \text{and I}$), have recently become popular due to their excellent applications in photocatalytic NH_3 synthesis from N_2 . BiOBr has also been focused on their material defects. Li et al. [29] employed BiOBr nanosheets with oxygen vacancies (OVs) to reduce N_2 under visible light, and the N_2 reduction rate was estimated to be $104.2 \text{ mmol}\cdot\text{h}^{-1}$. The structure of BiOBr provides enough space to polarize atoms, and the efficient separation and transformation of charge carriers must depend on the as-formed internal electric field [30]. Moreover, the large number of OVs on the surface of BiOBr hampered the recombination of electron-hole pairs.

Interestingly, except the N-type semiconductors above, there are some P-type semiconductors which should be also suitable for the photocatalytic N_2 reductions, such as CrO, MnO, FeO, NiO, Cu_2O , VO_2 , Cr_2O_3 , and Ag_2O . In addition, being added into some impurity atoms such as boron atoms, aluminum atoms, indium atoms, and gallium atoms, the others would turn into P-type semiconductors whose conductivity (i.e., charge carriers) mainly depends on positive vacant holes.

So far, hydrated P-type semiconductors as photocatalysts have been mainly used to reduce N_2 to NH_3 . Early in 1987, hydrous FeO photocatalysts were discovered by Tennakone et al. [55] and were superior to TiO_2 in the case of reducing N_2 to NH_3 under visible light [56]. Hydrous Cu_2O after impregnation with CuCl was able to photoreduce N_2 to NH_3 . Presumably, the high NH_3 yield resulted from the reduction sites $\text{Cu}_2\text{O}\cdot x\text{H}_2\text{O}$ [34]. In 1992, vanadium-doped hydrous FeO could enhance reducing N_2 to NH_3 and the average NH_3 production rate was $200 \text{ mM}\cdot\text{h}^{-1}$ or so, which benefited from the V impurities increasing vacant holes [57] whose concentration is much larger than the free electrons concentration. Therefore, the more the impurity is added, the higher the concentration of multivalent holes, the stronger the conductivity of the semiconductor.

3.1.4. Metal Sulfide-Based Materials. Similar to the metal oxide-based photocatalysts, metal sulfides have recently become a hot research topic in the field of photocatalytic NH_3 synthesis due to their strong absorption of visible light (Table 3). The NH_3 synthesis rate is up to $325 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ in the presence of ultrathin MoS_2 as photocatalysts, but without

charged excitons, the bulk MoS₂ did not have the ability of reduction of N₂ under the same conditions [32]. Miyama et al. [42] suggested that NH₃ yield of CdS/Pt binary photocatalysts was drastically higher than that of pristine CdS under UV irradiation. CdS/Pt/RuO₂ [33] and Pt/CdS-Ag₂S/RuO₂ [31] photocatalysts were successively applied to reduce N₂ to NH₃ under visible light. The holes in the valence band trapped the electrons that released from RuO₂. To keep the high photocatalytic activity of CdS for a longer time, maybe some measures must be taken to stop the degradation of CdS to S and Cd²⁺.

Multicomponent metal sulfides with sulphur vacancies, such as Zn_{0.1}Sn_{0.1}Cd_{0.8}S [34] and Mo_{0.1}Ni_{0.1}Cd_{0.8}S [27], could reduce N₂ as photocatalysts under visible light, and the concentration of sulphur vacancies trapping electrons were linear related to the NH₃ yields. In addition, G-C₃N₄/ZnSnCdS [42] and g-C₃N₄/ZnMoCdS [35] were, respectively, employed for the fixation of N₂. A tight junction coupling between g-C₃N₄ and ZnMoCdS was the key for efficient charge transfer.

Only nitrogenases can catalyze reduction of N₂ to NH₃ at room temperature and atmospheric pressure [55]. The nitrogenase complex consists of two proteins: Fe-protein which is responsible for the supply of electrons and MoFe-protein which uses the provided electrons to reduce N₂ to NH₃ [57]. Mimicking the catalytic activity sites FeMo-cofactor of MoFe-protein, a synthetic complex of Fe, Mo, and S should be taken into account, and organic-sulfide catalysts have also been designed for enhanced N₂ fixation activity. Banergee et al. [39] demonstrated that synthetic FeMoS inorganic clusters could reduce N₂ to NH₃ in aqueous media under light, which showed that structural analogues of nitrogenase can be functional to photocatalytic N₂ fixation. Katherine et al. [31] reported that cadmium sulfide (CdS) nanocrystals can be used to drive the enzymatic reduction of N₂ to NH₃ by photosensitizing the MoFe-protein of nitrogenase not ATP hydrolysis. Under optimal conditions, the turnover rate was 75 per minute, 63% of the ATP-coupled reaction rate for the nitrogenase complex. Both [Mo₂Fe₆S₈(SPh)₃] and [Fe₄S₄] clusters comprised in nitrogenase could do so at ambient temperature and pressure, and results suggest [58] that the nitrogenase could keep its photocatalytic activity when the [Fe₄S₄] clusters were replaced with other inert ions such as Sb³⁺, Sn⁴⁺, and Zn²⁺. In this process, Fe is necessary but Mo is not; however it does not mean that Mo is not playing a role in N₂ binding. In addition, the biohybrids of CdS and MoFe-protein provide a photochemical model for achieving the photocatalytic NH₃ production process. Therefore, redox-active iron sulfide containing clusters with high-energy photoexcited states could photocatalyze the reduction of N₂ to NH₃.

4. Conclusions

Although the Haber–Bosch process is an important chemical industrial approach to the worldwide population, this traditional NH₃ production process is a high energy-consumption and environmental pollution process. Therefore, there have been more and more research interests in

photocatalytic reduction of N₂ to NH₃ in the past decades. Difficultly, photocatalytic NH₃ synthesis from N₂ also needs to overcome the energy barrier of N≡N triple band under the spin-polarized plane-wave pseudopotential method. The Density-functional theory has been used to calculate the electronic band structures and the optical absorption spectra of nitrogen-doped and oxygen-deficient anatase TiO₂. The calculated results are in good agreement with our experimental measurements. These calculations reveal that the optical absorption of nitrogen-doped TiO₂ in the visible light region is primarily located between 400 and 500 nm, while that of oxygen-deficient TiO₂ is mainly above 500 nm. These results have important implications for the understanding and further development of photocatalytic materials that are active under visible light. However, synthesis of photocatalytic NH₃ is still kept in a laboratory-scale level.

This work would like to assist in understanding state-of-the-art in the photocatalytic NH₃ synthesis field for promoting the research field of N₂ fixation. Past reports on photocatalytic NH₃ synthesis focused primarily on titanium oxide-based materials. However, recent studies demonstrated that the N₂ reduction could occur in different photocatalytic reaction systems composed of transition metal-doped materials, metal sulfide-based materials, and other metal oxide-based materials (e.g., P-type semiconductors) as photocatalysts, respectively. Unfortunately, up to our knowledge, no viable and efficient photocatalysts for sustainable NH₃ synthesis could meet all requirements of an active, selective, scalable, long-lived catalyst. With the application of modern computational and experimental techniques, developing efficient photocatalysts should be encouraged to discover the mechanism on how N₂ reduction happens with the photocatalysts in the molecular level.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this manuscript.

Acknowledgments

This work was supported by the China Scholarship Council (No. 201706565033).

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