Review Insights into the Recent Progress and Advanced Materials for Photocatalytic Nitrogen Fixation for Ammonia (NH₃) Production

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Abstract: Ammonia (NH₃) is one of the key agricultural fertilizers and to date, industries are using the conventional Haber-Bosh process for the synthesis of NH₃ which requires high temperature and energy. To overcome such challenges and to find a sustainable alternative process, researchers are focusing on the photocatalytic nitrogen fixation process. Recently, the effective utilization of sunlight has been proposed via photocatalytic water splitting for producing green energy resource, hydrogen. Inspired by this phenomenon, the production of ammonia via nitrogen, water and sunlight has been attracted many efforts. Photocatalytic N₂ fixation presents a green and sustainable ammonia synthesis pathway. Currently, the strategies for development of efficient photocatalyst for nitrogen fixation is primarily concentrated on creating active sites or loading transition metal to facilitate the charge separation and weaken the N–N triple bond. In this investigation, we review the literature knowledge about the photocatalysis phenomena and the most recent developments on the semiconductor nanocomposites for nitrogen fixation, following by a detailed discussion of each type of mechanism.

Keywords: photocatalysis; ammonia synthesis; N₂ fixation; Haber-Bosch process

1. Introduction

In this current century, the climate changes and energy production are some of the most significant and important challenges that are being faced by the people in the world. In this direction, ammonia (NH₃) and the associated chemicals could provide an alternative energy resource. Similar to molecular hydrogen (H₂), NH₃ is also a carbon-free energy-source for the end-users. Ammonia has a worldwide annual production of around 150 million tons, due to the increasing demand from an increasing world population. However, the depletion of fossil fuels makes the industrial-scale ammonia synthesis processes urges to replace the usages of fossil fuels by a renewable energy source. Currently, NH₃ is being manufactured by the traditional Haber-Bosch (HB) process using pure H₂ and N₂, which requires energy-intensive high temperature (>500 °C) and extremely high pressure (200–300 bar). Nevertheless, the utilization of natural gas as a source of H₂ obtained by steam/gas reforming into the production of ammonia takes up about 1–2% world energy every year and belches out hundreds of millions of tons of CO₂ annually [1,2].

Specifically, in Canada, there are 11 plants manufacturing NH₃ across the country, where they use this HB process to produce ~5 million tons of NH₃ every year. Canada provides approximately 12% of the world’s fertilizer-materials and ~25% of the ammonia produced in Canada is being sent to North America for its direct use the agricultural purposes. The fertilizer industry creates ~$12 billion
in annual economic activity in Canada. Therefore, it is of a considerable significance to develop the low-energy consumption, sustainable and eco-friendly process to manufacture NH\textsubscript{3} through nitrogen fixation in large scale.

This review sheds lights into the recent progress in the development of a variety of routes for the synthesis of advanced materials and emphasizes their application for nitrogen photofixation. This review also concludes with a concise overview of the present status, analyzes potential and future development of photocatalysts with a view towards enhanced performance in different photocatalytic materials.

2. A Brief Insight into the Haber-Bosch Process

The most industrial and practical process for ammonia production is the Haber-Bosch process, where ammonia (NH\textsubscript{3}) is produced directly from its constituent elements, such as hydrogen (H\textsubscript{2}) and nitrogen (N\textsubscript{2}). Conventionally, this synthesis is conducted at 150–250 atm and 400–500 °C, as the gas passes over the reactor with two or four beds of catalyst (Figure 1). Eventually, each time conversion to ammonia is only 15%, by multiple times recycle unreacted gases, an overall conversion of 97% is obtained. The primary source of molecular H\textsubscript{2} is methane from the natural gas. In addition, it is estimated that around 3–5% of the world’s natural-gas production is utilized in the Haber-Bosch (HB) process.

2.1. Equilibrium Considerations and Reaction Rate

In the Haber-Bosch process, the formation reaction of NH\textsubscript{3} is reversible and the forward reaction of NH\textsubscript{3} production is an exothermic: \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \) \((H = -92 \text{ kJmol}^{-1})\). According to Le Chatelier’s principle, this reaction will be supported at the lower temperatures. In this process, the temperature must be as low as possible towards getting as much as ammonia as possible in the equilibrium condition. However, under this condition, the reaction does not proceed at an efficient rate. Therefore, two contrasting considerations are occurring in this synthesis. The viable temperature for this process is 400–450 °C, which bound to produce a reasonably high amount of NH\textsubscript{3} in the equilibrium mixture (15%) in a very short time.

![Figure 1. A flow scheme for the Haber-Bosch process.](image-url)
2.2. Catalyst and Mechanism

The most common catalyst of the Haber-Bosch process based on K$_2$O or Al$_2$O$_3$-promoted iron catalyst. The mechanism that involves the heterogeneous-catalyst is proposed to have the following steps:

\[ \text{N}_2(g) \rightarrow \text{N}_2(\text{adsorbed}) \] (1)
\[ \text{N}_2(\text{adsorbed}) \rightarrow 2\text{N}(\text{adsorbed}) \] (2)
\[ \text{H}_2(g) \rightarrow \text{H}_2(\text{adsorbed}) \] (3)
\[ \text{H}_2(\text{adsorbed}) \rightarrow 2\text{H}(\text{adsorbed}) \] (4)
\[ \text{N}(\text{adsorbed}) + 3\text{H}(\text{adsorbed}) \rightarrow \text{NH}_3(\text{adsorbed}) \] (5)
\[ \text{NH}_3(\text{adsorbed}) \rightarrow \text{NH}_3(g) \] (6)

Reaction (5) occurs in three steps, forming the NH, NH$_2$ and finally NH$_3$. The experimental evidence to Reaction (2) as being the slow, rate-determining step. This is expected since the nitrogen triple bond is the strongest of the bonds that must be broken.

2.3. Separation of the Ammonia

When the produced NH$_3$ gases depart from the reactor, they are essentially hot and under a very high pressure. However, ammonia will be easily liquefied under such pressure as long as it is not too hot and therefore the temperature of the mixture will be sufficiently lowered for the ammonia gas to turn into a liquid. Notably, the molecular N$_2$ and H$_2$ remain as gaseous states under these high pressures and they can be recycled.

3. Overview: Fundamental of Photocatalytic Nitrogen Fixation

3.1. The Principle of Photocatalysis on Semiconductors

Semiconductors (SCs) are used as photocatalytic materials, thanks to their suitable amalgamation of electronic properties, structure, light-absorption characteristics, charge transport dynamics and favorable lifetime of their excited-state charge carriers. Basically, an SC possesses an energy gap between the top of the filled-valence band (VB) and the bottom of the vacant-conduction band (CB), which is known as the band gap energy of the SC [3–6]. Thus, the separation of charge carrier between these bands only occurs with sufficient energy supply. In semiconductors, the photocatalytic process involves three main steps: Light absorption, charge separation and catalytic reaction. Under light illumination, the electron absorbs a photon with energy higher than or equal to the band gap energy of the semiconductor, excites from VB to CB and releases hole in the VB (Figure 2). This light-induced promoting electron-hole separation is a prerequisite step in all semiconductor photocatalysis. Finally, the photo-generated species transfer to the semiconductor surface and initiate redox reaction of absorbed reagents. However, electrons and holes are to recombine and dissipate the energy in the bulk (volume) or on the surface of the semiconductor, because of the kinetic-barrier for the electron-hole recombination process is relatively low, resulting in a decrease of reaction efficiency [7]. Therefore, prevention of charge recombination is a significant challenge in the photocatalytic field. In the last decades, there has been a considerable amount of effort to increase the lifetime of photogenerated carriers, such as developing photocatalyst with the nanostructure, co-catalyst, surface engineering and junction [8,9].

Moreover, a wide variety of semiconductors, mainly metal oxide and chalcogenides, have been examined with capability for photocatalyst, but only a few of them are considered to be effective photocatalyst, because of the appreciable band gap. In general, wide-band gap semiconductors prove to be better photocatalytic activity compared with low-band gap catalysts. For example, titanium dioxide showed better photocatalysis than cadmium sulfide for hydrogen production, due to the
increased free energy of photo-induced charge species of the TiO$_2$ and the intrinsic low chemical- and photo-chemical stability of the CdS. However, the narrow-band gap materials (such as metal sulfides) absorb solar light better that pave the way to potentially use the effective natural light source, which is the sunlight. Accordingly, a promising strategy with this concern has been attained with the utilization of several methods aiming to improve the electronic state and optical characteristics of semiconductors, including metal deposition, doping, and dye-sensitization. On the other hand, to obtain the effective photocatalytic procedure, the bottom of the CB must be located at a more negative potential than the reduction potential of electron acceptor (A) while the top of CB must beyond the oxidation-potential of electron-donor (D).

![Figure 2. Simulation of semiconductor photocatalysis under light irradiation.](image)

### 3.2. Quantum Yield (QY)

The efficiency of the photocatalytic process is measured by quantum yield (QY), which has been considered to describe the number of molecules converted relative to the total number of incident-photons on the reactor walls for an unknown reactor-geometry and for a polychromatic radiation.

$$\text{QY}(\Phi) = \frac{\# \text{ molecule decomposed}}{\# \text{ photon absorbed}}$$

Additionally, quantum yield could be calculated based on the rate of reaction dividing to the absorbed light intensity ($I_a$),

$$\Phi = \frac{\text{Rate}}{I_a}$$

The measurement of the absorbed light intensity is easy in homogeneous systems; however, it is difficult for heterogeneous reactions, such as thin films or semiconductor suspensions. In this stage, the suspended particle also reflected and scattered incident light instead of total absorption. Thus, it is very exhausted to correct this loss, including 13–76% of the total incident photon flux [10]. Otherwise, light is also absorbed by products or educts of reaction, suggesting QY should be determined at very early reaction time. To conquer such problems in heterogeneous photoreaction, it was proposed replacing the absorbed light intensity by the incident intensity ($I_0$). Therefore, apparent quantum yield (AQY, $\varsigma$) [11,12] has been termed to measure the efficiency of the photocatalytic process:

$$\varsigma = \frac{\text{Rate}}{I_0}.$$
3.3. Materials for Photocatalysis

Based on fundamental chemical composition system, all of the semiconducting materials can be divided into three important categories, mainly metal oxides, metal sulfides and metal free semiconductors.

Usually, metal oxides are the most common material, which can be utilized for photocatalysis in various reactions, such as H$_2$ production, CO$_2$ reduction and N$_2$ fixation. This type of materials have a wide range of applications according to their band structure and activities. However, most of them only activate under UV light irradiation due to their large band gap energy. To overcome this difficulty, the substitutions of cations or anions in the lattice of a wide band gap semiconductor has been employed to narrow band gap energy, enhancing the visible light respond. This substitution of cations and anions in the crystal lattice may form intermediate energy levels (due to the energy levels of impurities) within the band gap of photocatalyst that facilitates their absorption in the visible range. For example, titanium dioxide with the properties of stability, non-toxicity and high photocatalytic activity is potentially a suitable catalyst for water splitting reaction. Nevertheless, it only absorbs UV light due to a wide band gap (E$_g$ = 3.2 eV). To deal with this disadvantage, Khan et al. modified n-type TiO$_2$ chemically by doping C on this material. Carbon replaces some of the lattice oxygen atoms, resulting in a decrease in band gap energy to 2.32 eV [13].

Contrary to metal oxides, the metal sulfides normally possess a narrow band gap. Thus, they can absorb visible light to generate electron-hole. Moreover, the conduction reduction potential of water is less negative than their CB and so they can reduce water into molecular hydrogen. Otherwise, these materials also have several disadvantages, such as instability and fast recombination of photexcited charges. The most common example is cadmium sulfide, one of the best semiconductors with high activity for hydrogen production under visible light illumination. With narrow band gap materials, the recombination process of electron and hole is very easy. Reducing particle size of CdS can provide more active sites, decrease the travel path of migration of photexcited electron to the semiconductor surface and prevent charge recombination [14]. In addition, combining CdS nanoparticles with other semiconductors can also enhance their stability and photocatalytic activity [15–18].

Beside these semiconductors, some nitride-based systems also exhibit photocatalytic activities towards water reduction in the visible range of solar light. Recently, graphitic carbon nitride (g-C$_3$N$_4$) has drawn a lot of attention, because of its intrinsic properties, such as narrow band gap and non-toxicity. This metal-free polymeric material shows hydrogen evolution under visible light illumination with high chemical stability. Nevertheless, its photo-conversion efficiency is considerably limited than that of TiO$_2$ or CdS and therefore it requires further efforts to improve its photocatalytic activities.

3.4. Co-Catalyst Loading

A Cocatalyst is an integrated compound to the semiconducting material to promote their photocatalytic activity. In a water decomposition reaction, the cocatalyst can avail enhancing either water reduction or oxidation half reaction. In photocatalysis, cocatalysts are typically tiny metal nanoparticles (NPs), which create a Schottky junction with semiconductor and support for charge-separation in a photocatalyst of a photochemical cell [19,20]. In principle, the interfacial-contact between the semiconductor and metal induces an electric field, which effectively separates the excited electrons and holes more easily [21–23]. Additionally, the metal supplies active sites for H$_2$ generation due to its comparatively low over the water reduction potential.

The most common cocatalysts for photocatalysis are Pt, Rh, Au, NiO, and RuO$_2$. Maeda et al. report that loading both Rh/Cr$_2$O$_3$ and Mn$_2$O$_3$ supported on GaN:ZnO can effectively promote overall water splitting under visible light although the quantum yield of this system was relatively low [24]. Maeda proved that Rh/Cr$_2$O$_3$ acted as electron collectors to host hydrogen evolution while the main function of is the active sites for water oxidation reaction. However,
almost of cocatalyst are noble metals which are rare and expensive, thus prohibiting their wide scale application. Therefore, the development of non-noble and low-cost cocatalyst is extremely important. The physical and chemical characteristics of the co-catalyst, such as particle size and valence states directly affect their activity and are strongly dependent on their loading method onto the surface of host SCs. Although depositing more co-catalyst (concentration) provides more active sites for photocatalytic reactions, it considerably reduces the absorption ability of the semiconductor photocatalyst. Thus, the concentration or the loading amount of co-catalyst should be controlled and optimized to achieve the maximum activity.

3.5. Localized Surface Plasmon Resonance in Photocatalysis

Localized surface plasmon resonance (LSPR) labels the collective charge carrier oscillations in metal nanoparticle created by an incident field that resonant with the periodic movement of the negative charge against the positive nuclei background [25]. In general, the LSPR appears when the size of the metal nanoparticle is considerably smaller than the wavelength of incident light. Upon resonance irradiation, the charge oscillations induce a large electric dipole at the same frequency as that of the incident electric field. Consequently, the electric field intensity in the vicinity of plasmonic metal nanoparticles strengthens up to 1000 times as high as that of the incident field and greatly increases far-field scattering. In a plasmonic-heterostructure, the stored energy in the LSPR can be (i) transferred to the semiconductor or (ii) re-emitted as scattered photons (Figure 3A).

LSPR effect can be effectively applied in photocatalysis by the non-radiative transfer process. Under visible light excitation, LSPR generates hot electrons in the plasmonic nanostructured metal. It should be noted that these electrons possess higher energies than the level of thermal excitation. The injection of the hot electrons into a semiconductor improves the solar photo-voltaic energy conversion. Additionally, the existence of a Schottky barrier at the junction between the metal/semiconductor systems can block electron migration. If the hot electrons absorb sufficient photon energy, they can overcome the barrier and transfer into the conduction band of semiconductor (Figure 3B). Interestingly, the charge carrier injections can occur either from semiconductor or plasmonic metal. It is likely that the excitation state of the semiconductor and plasmonic metal decide where the charge carriers are injected.

The solar energy conversion efficiency can be improved by plasmonic nanocomposites via the two possible following mechanisms: (1) Direct electron transfer (DET) or by (2) plasmon induced resonant energy transfer (PIRET) [26]. The enhancement of the light absorption in semiconductors by photonic enhancement via (i) increasing the length of the optical path and (ii) concentrating the incident field than that of directly transferring the plasmonic energy from the metal to the semiconductor to induce the charge separation in the semiconductor. The plasmonic charge (hot electron) transfer process is referred to as direct electron transfer, which requires the semiconductor and the plasmonic metal be in direct contact with each other (Figure 3C). However, DET differs in that the plasmonic metal does not have a band gap to determines the charge-transfer kinetics [27]. Rather, the plasmonic carriers have the energy that proportional to the incident photon’s energy besides the Fermi level, therefore they can easily overcome the barriers that are energetically unfavorable at the interface, leading to more choices in the selection of materials. As another mode of non-radiative process, the PIRET is an attractive phenomenon for plasmonic enhancement (Figure 3D).

PIRET describes the non-radiative transfer of energy from the metal LSPR dipole to the semiconductor transition dipole. PIRET depends on the spectral overlap and it does not require any electronic-alignment or even physical-contact to transfer energy as like in DET [29], which essentially provides flexibility in the design of solar energy materials and structures. PIRET can produce electron-hole pairs in the semiconductors, suggesting a strong coupling to the weak band edge states. The plasmon resonance can easily be tuned, which allows for an enhanced solar energy harvesting in the entire visible spectrum. PIRET is also favorable when the charge transfer process creates undesirable effects, such as the degradation of materials or issues in the carrier equilibration.
1.26 V between NH(6 electrons) and thus may be more kinetically challenging. Another limitation is the absorption of N which questions regarding the mechanisms, rates, and thermodynamics still remain. The protonation of any photocatalyst semiconductor possessing a bandgap energy larger than 1.2 eV with proper ammonia formation is favored, with an energy difference of 0.43 V between NH3 and N2H4 and a 1.26 V between NH3 and N2H2. In a thermodynamic aspect, the half-reaction generated NH3 is capable of any photocatalyst semiconductor possessing a bandgap energy larger than 1.2 eV with proper conduction and valence band position. However, this half reaction involves multiple-electron transfer (6 electrons) and thus may be more kinetically challenging. Another limitation is the absorption of N2 molecules over semiconductor photocatalysts and cleavage of highly stable N-N triple bond in order to activate dinitrogen. To overcome these challenges, it is necessary to create appropriate active sites that can effectively absorb nitrogen. This active site also serves as a trapping cage to capture electrons then transfer to absorbed nitrogen as well as suppress charge carrier recombination.

Figure 3. (A) High-energy resonant state decay in two possible form: Re-emission of photons or the generation of energetic charge carriers; (B) excitation electron from occupied energy level to a level above the Fermi energy; (C) hot electron overcoming the Schottky barrier and injected to the conduction band of the neighboring semiconductor; (D) plasmon-induce resonance energy transfer. (Reproduced with permission from MDPI [28]).

3.6. Fundamentals of Photocatalytic Nitrogen Fixation Principle

Since the first work reported by Fujishima and Honda, in the early 1970s, the use of photocatalysts, based on semiconductors, has emerged as the most promising and practical solution to address the challenges of energy and environmental issues [30]. In the last few decades, a renewed interest has been devoted in photocatalytic NH3 production, and several papers have illustrated ammonia [31] and nitrate formation [32] using various kinds of semiconducting photocatalysts, plasmon-enhanced systems, and biomimetic systems.

Basically, the photocatalytic process of N2 fixation is divided into several steps as follows: First, under the sunlight irradiation, photo-generated electrons are excited to the CB, leaving holes in the VB. Afterwards, some of the electrons and holes recombine together, meanwhile, other photo-formed holes (h+) oxidize the water into H+, and O2 (Equation (7)) and N2 reduction by hot-electrons lead to the production of NH3 (Equation (8)). As a result, NH3 is synthesized from water and N2 under ambient conditions using the sunlight as an energy source (Equation (9)). Figure 4 demonstrates the scheme process of photocatalyst materials using for the reduction of nitrogen to ammonia.

\[
\begin{align*}
2\text{H}_2\text{O} + 4h^+ & \rightarrow \text{O}_2 + 4\text{H}^+ \\
\text{N}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow 2\text{NH}_3 \\
\frac{1}{2}\text{N}_2 + 3/2\text{H}_2\text{O} & \rightarrow \text{NH}_3 + \frac{3}{4}\text{O}_2
\end{align*}
\]

Although the proposed photocatalytic fixing nitrogen pathway is acceptable, many pending questions regarding the mechanisms, rates, and thermodynamics still remain. The protonation reactions versus standard potential are summarized by Lyndley et al. (Table 1). Thermodynamically, ammonia formation is favored, with an energy difference of 0.43 V between NH3 and N2H4 and a 1.26 V between NH3 and N2H2. In a thermodynamic aspect, the half-reaction generated NH3 is capable of any photocatalyst semiconductor possessing a bandgap energy larger than 1.2 eV with proper conduction and valence band position. However, this half reaction involves multiple-electron transfer (6 electrons) and thus may be more kinetically challenging. Another limitation is the absorption of N2 molecules over semiconductor photocatalysts and cleavage of highly stable N-N triple bond in order to activate dinitrogen. To overcome these challenges, it is necessary to create appropriate active sites that can effectively absorb nitrogen. This active site also serves as a trapping cage to capture electrons then transfer to absorbed nitrogen as well as suppress charge carrier recombination.
which was effective in photo-reduction of nitrogen for about 580 h [35]. Interestingly, in the existence which poisoned the catalyst. Therefore, $\text{NH}_3$ after irradiated visible light for 40 min, a maximum ammonia concentration of ca. 4 $\mu\text{mol} \cdot \text{L}^{-1}$ was obtained and continuously decreased due to the decomposition of $\text{NH}_3$ to nitrate in the solution, which poisoned the catalyst. Therefore, $\text{NH}_3$ must be removed immediately from the reaction site to maintain catalytic efficiency. Khader et al. successfully prepared a mixture of $\alpha-$Fe$_2$O$_3$ and Fe$_3$O$_4$, which was effective in photo-reduction of nitrogen for about 580 h [35]. Interestingly, in the existence of 5 at% iron in the form of Fe$^{2+}$ in the partially reduced Fe$_2$O$_3$, $\text{NH}_3$ was detected in an aqueous slurry of the catalyst under UV illumination.

On the other hands, doping Fe into metal oxide, such as TiO$_2$, Al$_2$O$_3$, ZnO, is a practical strategy for utilization of iron active site catalysts. Most of the studies have been focused on metallic Fe modified titanium dioxide photocatalyst. In addition, there has been considerable debate over the role of cation Fe on iron titania photocatalyst. The earlier work suggested that the introduction of Fe$^{3+}$ as an impurity in titania can play an indirect role in decreasing bandgap energy of semiconductor as well as hinders the recombination of photo-generated electron-hole pairs, consequently enhance the absorption ability and the photoactivity. Zhao et al. investigated the photocatalytic activity of Fe-doped TiO$_2$ with highly

Figure 4. Schematic of semiconductor-based photocatalyst used for the $\text{N}_2$ fixation. The redox potentials (Potential (E) vs. Normal Hydrogen Electrode (NHE)) of half reaction water oxidation and dinitrogen protonation are marked on the left.

Table 1. Reduction potentials (vs. Standard Hydrogen Electrode (SHE)) of typical hydrogenation reactions relate to the reduction of $\text{N}_2$ to $\text{NH}_3$.

| Reaction                          | E° (V) vs. SHE |
|----------------------------------|---------------|
| $\text{N}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{N}_2\text{H}_2$ | +0.035        |
| $\text{N}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons \text{N}_2\text{H}_4$ | −0.4          |
| $\text{N}_2 + 6\text{H}^+ + 6e^- \rightleftharpoons 2\text{NH}_3$ | −1.22         |

4. Classification of Photocatalysts for $\text{N}_2$ Fixation Based on Active Sites

4.1. Metal Active Sites

4.1.1. Iron Active Sites

It should be noted that the catalyst of iron is the common catalyst in the Haber-Bosch process due to its good interaction with dinitrogen and weakening N–N bond [33]. In fact, recent studies indicate that ferric photocatalyst is capable of nitrogen reduction to ammonia. However, it is well-known that pure iron oxide had no activity in $\text{N}_2$ photofixation. To overcome this bottleneck, several researchers have employed a various method in the synthesis of defect iron catalyst. Tennakone [34] and his co-worker reported the first system of $\text{N}_2$ reduction using amorphous Fe$_2$O$_3$·nH$_2$O under visible light irradiation. Fe$_2$O$_3$ was prepared by gradual addition of KOH to FeCl$_3$ solution and purged with $\text{N}_2$. After irradiated visible light for 40 min, a maximum ammonia concentration of ca. 4 $\mu\text{mol} \cdot \text{L}^{-1}$ was obtained and continuously decreased due to the decomposition of $\text{NH}_3$ to nitrate in the solution, which poisoned the catalyst. Therefore, $\text{NH}_3$ must be removed immediately from the reaction site to maintain catalytic efficiency. Khader et al. successfully prepared a mixture of $\alpha-$Fe$_2$O$_3$ and Fe$_3$O$_4$, which was effective in photo-reduction of nitrogen for about 580 h [35]. Interestingly, in the existence of 5 at% iron in the form of Fe$^{2+}$ in the partially reduced Fe$_2$O$_3$, $\text{N}_2$ was detected in an aqueous slurry of the catalyst under UV illumination.
exposed (101) facets [36]. The quantum yield of nitrogen photo-reduction using ethanol as scavenger can be reached to $18.27 \times 10^{-2}$ m$^{-2}$. The transmission electron microscopy (TEM) images confirmed that Fe$^{3+}$ ions are successfully incorporated into the anatase crystal and substituted for Ti$^{4+}$ in the TiO$_2$ lattice (Figure 5). Zhao and Soria [37] reported that even doping Fe$^{3+}$ can improve catalytic activity higher than pristine TiO$_2$, but an excess amount of Fe$^{3+}$ doping can limit the continuous growth of TiO$_2$ particles and poisoning the catalyst. In a continuous work of previous studies, further investigations of mechanism on iron titanate photocatalyst were conducted by Rusina [38] and Krich [39] The electron transfer system of photo(electro)catalytic N$_2$ reduction on the Fe$_2$Ti$_2$O$_7$ thin film includes a series of processes of nitrogen-diazene-hydrazine-ammonia-nitrate. Moreover, Lashgari proposed a N$_2$ photofixation mechanism based on H-atom production [40]. In addition to Fe doped metal oxide materials, non-metal oxide semiconductors were modified with iron. Hu et al. adapted graphitic carbon nitride doping with Fe$^{3+}$ for conversion of nitrogen to ammonia [41]. It was found that the N≡N bond is prolonged when N$_2$ molecules interact with Fe$^{3+}$ sites. The delocalization of electron in $\sigma_{g2p}$ orbital (HOMO) of nitrogen when N$_2$ adsorbed on Fe$^{3+}$ doping sites leads to its orbital energy almost overlaps to that of $\pi g^{*2p}$ orbital (LUMO), indicating the direct role of iron in activating the N$_2$ molecule. The highest NH$_4^+$ production rate of 5.4 mgL$^{-1}$h$^{-1}$g$^{-1}$ was achieved with 0.05 wt% Fe doping, which is 13.5 folds compared to pristine g-C$_3$N$_4$. For the comparison of photocatalytic activities of ammonia production based on iron active site photocatalyst, the selected literature report is summarized in Table 2.

Figure 5. (a,b) TEM images of titanate nanotubes prepared by hydrothermal reaction. © transmission electron microscopy (TEM) images and (d) high resolution transmission electron microscopy (HRTEM) image of 100 $\times$ 10$^{-6}$ Fe$^{3+}$ doped TiO$_2$. (Reproduced with permission from Elsevier [36]).
4.1.2. Titanium Active Sites

Among all the well-known photocatalysts, TiO$_2$ is the most prominent material and has applied in a variety of photocatalytic applications, because of its abundance, efficient charge separation, and stability. In earlier publications, the metal doped titanium dioxide or titanate was used for photocatalytic fixing nitrogen. In later studies, trivalent titanium complex has been employed to via electron donation. These reduction reactions create Ti$^{4+}$-amine complexes which finally release NH$_3$ is necessary.

Table 2. Summary of iron active site photocatalysts for the reduction of N$_2$ to NH$_3$.

| Catalyst                          | Light Source | Sacrificial Reagent | NH$_3$ Rate          | Ref.   |
|----------------------------------|--------------|---------------------|----------------------|--------|
| 0.2% Fe-doped TiO$_2$            | 390–420 nm   | -                   | 10 $\mu$molg$^{-1}$h$^{-1}$ | [42]   |
| 0.5% Fe-doped TiO$_2$            | UV           | -                   | 6 $\mu$molg$^{-1}$h$^{-1}$  | [37]   |
| Fe-doped TiO$_2$                 | 254 nm       | Ethanol             | 400 $\mu$M.h$^{-1}$    | [36]   |
| Partially reduce Fe$_2$O$_3$     | UV-vis       | Ethanol             | 10 $\mu$molg$^{-1}$h$^{-1}$ | [34]   |
| Fe$_2$O$_3$                      | UV-vis       | Ethanol             | 1362.5 $\mu$M.h$^{-1}$  | [40]   |
| FeO$_2$·nH$_2$O                   | Visible      | Ethanol             | 6 $\mu$M.h$^{-1}$      | [34]   |
| Fe(O)OH                          | Vis          | -                   | 9.25 $\mu$M.h$^{-1}$   | [43]   |
| Fe doped C$_3$N$_4$              | Vis          | Ethanol             | 120 $\mu$M.h$^{-1}$    | [41]   |
| Fe-load 3D Graphene              | UV           | -                   | 24 $\mu$molg$^{-1}$h$^{-1}$ | [44]   |
| Hydrous oxide of Fe and Ti       | Vis          | -                   | 22 $\mu$M.h$^{-1}$     | [45]   |
| Iron loaded bentonite            | UV           | -                   | 1.33 $\mu$M.h$^{-1}$   | [46]   |
| Iron titanate thin film           | $>$320 nm    | Ethanol             | 0.57 $\mu$M.h$^{-1}$cm$^{-2}$ | [38]   |

4.1.3. Molybdenum Active Sites

Owing to excellent electrical, optical, and photovoltaic properties, ultrathin transition metal dichalcogenides (TMDs) have been considered as promising materials. Among them, MoS$_2$ semiconductor is known as an efficient photocatalyst for hydrogen evolution and CO$_2$ conversion reaction. Recently, its application in N$_2$ reduction has been unveiled since the first report of Sun’s group [50]. In this research, the photocatalytic activity of MoS$_2$ photocatalysts under different preparation conditions was investigated. The results show that the sonicated ultrathin MoS$_2$ induced charged excitons (trions) when applying visible light (Figure 7a). These trions carried multiple
electrons in one bound state, which located around Mo sites. Naturally, three Mo atoms surround adsorbed dinitrogen on the S vacancy and facilitate the six-electron transfer process. Consequently, the rate of ammonia production of 325 $\mu$mol.g$^{-1}$h$^{-1}$ was achieved, which is much higher than the rate of hydrothermal MoS$_2$ and bulk MoS$_2$ samples. Particularly, it can be concluded that a multiple electrons reduction process was responsible for the enhancement of photocatalytic dinitrogen reduction to ammonia.

![Figure 7](image)

**Figure 7.** (a) Schematic illustration of the trion induced multi-electron N$_2$ reduction process [50]; (b) Schematic representation of Mo$_2$Fe$_6$S$_8$—Sn$_2$S$_6$ biomimetic chalcogel (FeMoS chalcogel), building block scheme (Mo, blue; Fe, red; S, yellow; Sn, black), and a complete chalcogel shown at right [51]; and (c) Nitrogenase-inspired biomimetic chalcogels [52]. (All the figures are reproduced with permission from the respective publishers).

In addition, enzyme nitrogenase has also been widely studied for application of catalytic nitrogen fixation [53]. A nitrogenase is a two-component system comprising a MoFe protein and an associated Fe protein. Based on this inspiration, in 2015, Banergee and Kanatzidis supposed that solid chalcogels consisting of FeMoS inorganic clusters is able to reduce dinitrogen to amonia by utilizing white light [51]. The double-cubane Fe$_2$Mo$_6$S$_8$ units were associated by Sn$_2$S$_6$ ligands (Figure 7b) to form a stable amorphous complex in aqueous solution. The FeMoS cluster (FeMoS cofactor, a synthetic clusters bearing Mo−Fe linkages) of the biomimetic chalcogel system is a structural and functional analogue of the MoFe active site in the enzyme nitrogenase. This work showed that the high density of FeMoS active sites can boost multi-electron transformation as well as mimic the function of biological nitrogenases in N$_2$ fixation. In order to gain insights into the performance of the FeMo cofactor in nitrogenases. Brown and coworkers fabricated a biohybrid system of nitrogenase coupled with CdS semiconductor. The MoFe protein coated CdS nano rods produced 315 nmol of NH$_3$ per min over one
mg MoFe-protein, which is estimated for 3.3% of Quantum Yield. In MoFe Protein, FeMo cofactor plays a role as an active site, receiving photogenerated electrons from CdS nanocrystals. By changing condition reactions, Liu found that lack of FeMo cofactor did not produce amonia. Furthermore, the role of Mo and Fe in the MoFe protein are revealed in another study. Liu et al. discussed the photocatalytic activity of nitrogen reduction by the nitrogenase-inspired biometric chalcogel [52]. In this system, $\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SPh})_3$, $\text{Fe}_4\text{S}_4$ and redox-inert ions are assembled with $\text{Sn}_2\text{S}_8$ (Figure 7c). However, iron was expected to be more active than molybdenum for the solar reduction of $\text{N}_2$, due to the fact that a weak bonding orbital between nitrogen and iron emerged via the localized orbital analysis. Moreover, their conclusion that the Fe is a better active site for $\text{N}_2$ binding than Mo has been demonstrated by recent biochemical and spectroscopic data.

4.1.4. Nickel Active Sites

The study of Schrauzer and Guth examined the effect of various metal dopant over titania for photocatalytic $\text{NH}_3$ formation. In addition to doping Mo and Fe, only Co and Ni dopant performed the contribution to the enhancement of $\text{NH}_3$ production efficiency [42]. The other metal doped, such as Pd, V, Cu, showed no improvement in catalytic activity. It can be explained by the influence of Ni, Co accelerates the phase transformation while this phenomenon is unobtainable for other dopants. This explanation is consistent with the conclusion of Ranjit. In his work, Ranjit also compared 12 elements doped TiO$_2$ photocatalyst and found the order of photoactivity was Fe > Co > Mo > Ni. Ye et al. loaded Ni$_2$P on a binary metal sulfide solid solution for photocatalytic $\text{N}_2$ fixation under visible light [54]. The deposited transition metal phosphide affects both the VB and CB of metal sulfide, resulting in higher photocatalytic reduction ability. Moreover, the transition metal phosphide of Ni$_2$P supports the photo-induced charge carrier separation process, which is confirmed by photoluminescence spectra (PL) and electrochemical impedance spectroscopy (EIS). For Ni$_2$P/Cd$_{0.5}$Zn$_{0.5}$S, the $\text{NH}_3$ production rate achieved 101.5 $\mu$mol L$^{-1}$ h$^{-1}$ (35.7 times than that of unloaded metal phosphine cocatalyst), corresponding to 4.23% of apparent quantum efficiency at 420 nm.

4.2. Non-Metal Vacancies

4.2.1. Oxygen Vacancies

In the earlier studies, the synthesis of ammonia by $\text{N}_2$ photoreduction has been far from acceptable, because of the impoverished binding of $\text{N}_2$ to catalytic active sites and the high energy of the intermediates required in the reactions. It has been concerned a significant challenge of activation and cleavage of the highly stable $\text{N}=\text{N}$ triple bond relying only on light-induced electrons from semiconductor materials in solar-driven $\text{N}_2$ fixation. To conquer this challenge, the electron-transfer supportive centers should be introduced as the primary-step active sites to absorb the molecular $\text{N}_2$ and weaken the $\text{N}=\text{N}$ bond, which could allow the photo-induced electrons to inject for the subsequent reduction reactions. Oxygen vacancies (OVs), with their rich localized-electrons, have been proved to serve as electron trapping centers that can effectively capture and activate the inert gases, such as $\text{O}_2$, $\text{CO}_2$, and $\text{N}_2$ in particular. Table 3 summarizes the most recent advanced oxide materials containing OVs for nitrogen photo-fixation.

| Catalyst               | Light Source | Sacrificial Reagent | $\text{NH}_3$ Rate | Ref.  |
|------------------------|--------------|---------------------|--------------------|-------|
| BiOBr nanosheets       | UV-Vis/Vis   | -                   | 104.2 $\mu$mol g$^{-1}$ h$^{-1}$ | [31]  |
| Bi$_5$O$_7$Br nanotubes| Vis          | -                   | 1.38 mmol g$^{-1}$ h$^{-1}$ | [55]  |
| TiO$_2$/Au/a-TiO$_2$   | Vis          | -                   | 13.4 mmol cm$^{-2}$ h$^{-1}$ | [56]  |
| BiO quantum dots       | UV-Vis       | -                   | 1226 $\mu$mol g$^{-1}$ h$^{-1}$ | [57]  |
| Reduced TiO$_2$        | Infrared light| -                   | 3.33 $\mu$mol g$^{-1}$ h$^{-1}$ | [58]  |
Oxygen Vacancies Based on Titanium Dioxide

Recently, Zhang et al. created solid-state sources of solvated electron based on reduced titanium dioxide for nitrogen photofixation [55] (Figure 8). Since oxygen vacancies were introduced in TiO₂, electrons are trapped at the vacancy sites and released by infrared (IR)-light excitation, consequently reducing N₂ to NH₃. The number of trapped electrons can be enriched by tuning the concentration of oxygen defects. However, the amount of generated ammonia nearly ceased after 24 h, due to the consumption of releasable trapped electron. For recharging of electrons, the reacted TiO₂ could be treated with chemical reduction method.

Another group, Li, and his partner conducted the photo-electrochemical reduction of N₂ to NH₃ on the surface oxygen vacancies of plasmon-induced TiO₂ [56] (Figure 9). Li suggested that only superficial oxygen vacancies can act as active sites, the other internal vacancies in crystal structure play a role as undesired defects. By using the atomic layer deposition method, oxygen vacancies are successfully introduced onto the surface of TiO₂ without creating bulk defects (introduction of oxygen vacancies to bulk structure to form defects). It is worthy to note that surface oxygen vacancies not only serve as N₂ absorption sites, but also promote charge-carrier transportation to the adsorbed nitrogen while bulk-vacancies act as recombination centers to trap the photo-excited electrons and holes. The optimized ammonia production rate of 13.4 nmol cm⁻² h⁻¹ was obtained by the sample of surface oxygen vacancies modified TiO₂/Au/amorphous TiO₂ electrode, which is 2.6-folds higher than pristine TiO₂. Moreover, Hirai and his group have studied systematically the role of oxygen vacancy and Ti³⁺ active site [49]. He concluded that oxygen vacancy can facilitate the dissociation of the N≡N triple bond. This conclusion is consistent with Zhang and Li’s group.
In contrast with the above research, Medford and Comer employed density functional theory (DFT) analysis to discuss the role of oxygen vacancy [63]. The defected surface (110) titania possessing an oxygen vacancy was compared to pristine TiO$_2$ by examining nitrogen reduction. The DFT calculations rejected the traditional mechanism of nitrogen photofixation that the breaking of N–N bond is conducted directly by oxygen vacancy. Otherwise, his hypothesis is that a considerable stabilization of the unstable NH$_x$ intermediates by the oxygen vacancy makes NH$_x$ binding close to exo-thermic, indicating that it can enhance nitrogen reduction and ammonia generation after the N–N bond has been dissociated.

**Figure 9.** (a–d) Illustration of the experimental procedures for preparation of bare TiO$_2$, TiO$_2$/Au, TiO$_2$/a-TiO$_2$, and TiO$_2$/Au/a-TiO$_2$ photo-electrodes. (e–h) Scanning electron microscopy (SEM) and (i–l) HRTEM images of photo-electrodes. Key: TiO$_2$/a-TiO$_2$ (a,e,i), bare TiO$_2$ (b,f,j) (inset:selected area electron diffraction (SAED) pattern of the bare TiO$_2$ NR), TiO$_2$/Au (c,g,k), TiO$_2$/Au/a-TiO$_2$ (d,h,l). (Reproduced with permission from Wiley [56]).

**Oxygen Vacancies Based on Bismuth Oxyhalide**

Bismuth oxyhalides, BiOX (X = Cl, Br, and I), have recently gained considerable interests for their intrinsic optical properties; they are also practical for industrial applications, such as the photodecomposition of organic pollutants and CO$_2$ reduction. The structural layer of BiOX provides sufficient space for the polarization of atoms and the as-formed internal electric field will play an effective role in their efficient charge separation and transfer process.

Due to containing interior oxygen vacancy, bismuth oxyhalides has been considered as a promising catalyst for nitrogen fixation, particularly in photofixation [64,65]. Most recently, Bi$_2$O$_2$Br nanotubes were investigated its photoactivity of ammonia evolution by Wang et al. [55]. Owing to the excessive number of oxygen vacancies as active centers, the highest NH$_3$ production rate is obtained at 1.38 mmol·g$^{-1}$·h$^{-1}$, corresponding to an apparent quantum yield of 2.3% at 420 nm. However, bismuth oxybromide photocatalysts are susceptible to photocorrosion. During the reduction reaction, the oxygen vacancies is filled by O atoms form the water, reducing the number of active sites and lose its activity. Interestingly, the reacted oxygen vacancies can be regenerated by applying visible light
illumination, which continuously provides the reversible light-switchable surface oxygen vacancies for N\textsubscript{2} fixation. Figure 10A demonstrates repeated circulation of oxygen vacancies over TiO\textsubscript{2} for ammonia photo-production.

![Figure 10](image)

**Figure 10.** (A) Schematic illustration of the photocatalytic N\textsubscript{2} fixation model in which water serves as both the solvent and proton source, as well as the reversible creation of light-induced oxygen vacancies; (B) Theoretical prediction of N\textsubscript{2} activation on the OV of BiOBr (001) surface. (a) Side and (b) top view of (001) surface of BiOBr with an OV. (c) The adsorption geometry of N\textsubscript{2} on the OV of BiOBr (001) surface. (d) The charge density difference of the N\textsubscript{2}-adsorbed (001) surface; (C) Adsorption of N\textsubscript{2} on the (001) and (010) facets of BiOCl. (a) Crystal structure of BiOCl and the corresponding cleaved (001) surface. (b) The terminal end-on adsorption structure of N\textsubscript{2} on (001) surface of BiOCl; (c) the side-on bridging adsorption structure of N\textsubscript{2} on (010) surface of BiOCl; (D) Schematic illustration of the photocatalytic N\textsubscript{2} fixation over Bi\textsubscript{5}O\textsubscript{7}I (001) and (100) facers. (Reproduced with permission from the respective publishers; Figures 10–10 from the References [55], [31], [59], and [60], respectively).

In 2015, Zhang and Li studied the effect of oxygen vacancies on the exposed (001) facets BiOBr nanosheets to fix nitrogen under ambient condition [31]. The theoretical analysis calculated the extension of the N–N triple bond increased by 0.055 Å as absorbed N\textsubscript{2} molecules are activated by oxygen vacancies (Figure 10B). Also, the oxygen vacancies as the initial electron acceptor can avoid the electron-hole recombination and considerably promote the interfacial charge transfer. In this paper, the UV-Visible light driven N\textsubscript{2} fixation rate was measured to be 223.3 μmol g\textsuperscript{−1} h\textsuperscript{−1} without using sacrificial agent and a noble-metal cocatalyst. As a succession of the previous study, Zhang’s group clarified that two distinct structure of surface oxygen vacancy on different facets of BiOCl nanosheets completely determine the N\textsubscript{2} fixation mechanisms [59]. For instance, the N\textsubscript{2} reduction reaction on the oxygen vacancies of BiOCl (010) facets followed a symmetric alternating pathway which generates N\textsubscript{2}H\textsubscript{2}-level and N\textsubscript{2}H\textsubscript{4}-level species. Whereas, an asymmetric distal mechanism selectively produces ammonia (001) facets without involving the generation of N\textsubscript{2}H\textsubscript{2} or N\textsubscript{2}H\textsubscript{4}. By DFT calculation, the accepted adsorption possibility of N\textsubscript{2} on BiOCl surfaces was investigated. On the (001) facets, absorbed N\textsubscript{2} combines with two nearest Bi atoms in the sublayer to form a terminal end-on bridging, consequently, the activation exhibited the increasing N–N bond length to 1.137 Å (Figure 10(Ca)). Separately, different absorbed N\textsubscript{2} performs a larger extent of N\textsubscript{2} activation and elongates bond length to 1.198 Å (Figure 10(Cb)) through a side-on bridging mode (dinitrogen interacts with two nearest Bi atoms in the outer layer and the one next nearest Bi atom in the sub-layer on the (010) facet).
Respectively, the quantum yields under UV irradiation were 1.8% h\(^{-1}\) and 4.3% h\(^{-1}\) on the (001) and (010) surface of BiOCl. Inspired by Zhang’s group, Bai et al. examined the photocatalytic activity of different Bi\(_2\)O\(_3\)I facets over solar-driven N\(_2\) fixation reaction \([60]\). At 356 nm UV-light irradiation, the apparent quantum efficiency of (001) surface Bi\(_2\)O\(_3\)I was 5.1%, which is 2.2 times higher than that of (100) planes (Figure 10D). After exposure to (001) facets, the charge carrier separation and mobility were dramatically boosted, elucidating the enhancement of photoactivity on (001) Bi\(_2\)O\(_3\)I facets.

Although most publications highlight noteworthy attention on the exposure of different facets, it is more possible that the combined effects facet-dependent studies and oxygen vacancies-dependent studies will open a new and interesting perspective and provide inspiration for the development of advanced photocatalysts for N\(_2\) photoreduction. In addition, the combination of experimental data and theoretical simulations is highly necessary to fully interpret the N–N triple bond activation and pathway the NH\(_3\) formation mechanism. Thus, further study on the facet controlled and vacancy-mediated bismuth oxyhalides should be dedicated in the future to emphasize the scientific aspects and reveal the appropriate reaction steps for the N\(_2\) photofixation.

4.2.2. Nitrogen Vacancies

The introduction of defects in photocatalyst materials is completely considered as an effective method to enhance the photocatalytic nitrogen fixation. Instead of oxygen vacancy, another alternative strategy for using non-metal vacancy to fix nitrogen has been to utilize nitrogen vacancies in order to absorb and weaken N\(_2\) molecules. Because nitrogen vacancies have the same size and shape as the nitrogen atoms in di-nitrogen, nitrogen vacancies (NVs) are favorable in the selective chemisorption and activation of N\(_2\) \([66]\). This interprets why the N\(_2\) fixation rate remained unchanged when N\(_2\) was replaced by air as the N\(_2\) source. In addition, nitrogen vacancies significantly improved the separation of charge carriers by trapping photo-excited electrons and facilitating the interfacial charge transfer to the adsorbed N\(_2\).

From the time when the first report on graphitic carbon nitride (g-C\(_3\)N\(_4\)) in 2009, this metal-free polymeric photocatalyst has received tremendous interest, due to its specific properties such as excellent stability, cost-effectiveness, and environmental benignity. Recently, graphitic carbon nitride containing nitrogen vacancies has been employed as a photocatalyst for reduction of nitrogen to ammonia. In 2015, the first introduction of nitrogen vacancies induced g-C\(_3\)N\(_4\) for visible light driven NH\(_3\) production was reported by Dong \([66]\). After 15 h of light illumination, nitrogen vacancies incorporated g-C\(_3\)N\(_4\) generated 1.24 mmol h\(^{-1}\) g\(^{-1}\) of photofixation rate while bare g-C\(_3\)N\(_4\) show no catalytic activity, suggesting the indispensable role of nitrogen vacancies in promoting photoactivity. However, lacking nitrogen in defects modified carbon nitride structure slightly enlarged bandgap energy than that of pristine samples, resulting in a reduction of visible light absorption ability. In contrast to Dong’s research, Li suggests that even the influence of nitrogen vacancies on the band structure decrease the bandgap energy, it is not the main factor that affects the photocatalytic nitrogen reduction. Li et al. have fabricated nitrogen vacancies assisted g-C\(_3\)N\(_4\) by infrared ray assisted microwave (IM-CN(x), where x denotes the time) \([67]\). Under microwave treatment, abundant nitrogen vacancies were formed and served as chemical absorption centers. By DFT calculation, it was found that chemisorbed N–N triple bond is elongated from 1.107 Å to 1.242 Å due to the formation of \(\sigma\) bond between N\(_2\) molecule and the nearest C atom. Consequently, the NH\(_4^+\) evolution rate obtained by IM-CN(30) sample was 5.1 mg L\(^{-1}\) h\(^{-1}\) gcat\(^{-1}\), which is 5-fold and 2.5-fold higher than those of bulk CN\(_{520}\) and microwave treated CN(20). Similarly, Ma and Li have prepared high specific surface area carbon nitride by a dissolve-regrowth method, which is capable of N\(_2\) photoreduction \([68]\). Based on experimental results and theoretical simulation, Ma demonstrated the possible nitrogen photofixation over large surface area g-C\(_3\)N\(_4\) containing N-vacancies (Figure 11). First, absorbed N\(_2\) molecule in N-vacancy is activated by four-electron which occupies the anti-bonding orbitals of N atoms, then H\(^+\) reacts with the activated N\(_2\) molecule to produce NH\(_3\) and finally form NH\(_4^+\).
Besides using nitrogen vacancy active sites, nitrogen defects is also applied for producing NH$_3$ under solar simulation. Li et al. introduced cyano-deficient onto bulk g-$\text{C}_3\text{N}_4$ by cleavage C=N bond via KOH etching treatment [69]. The as-prepared g-$\text{C}_3\text{N}_4$ (ACN) possesses a porous structure with ladder-like thin layers. Li concluded that the presence of cyano groups not only reduce conduction band of bulk g-$\text{C}_3\text{N}_4$, but also act as an electron acceptor, capturing electrons and inhibiting electron-hole recombination. Moreover, the existent of cyano defects conduct more adsorption site for the N$_2$ activation. Therefore, the formation of cyano groups by etching bulk g-$\text{C}_3\text{N}_4$ with KOH is the main reason for the enhanced photocatalytic N$_2$ fixation activity. After 4 h testing catalytic activity, the NH$_4^+$ concentration of ACN-10% increase to 51.65 mg/L, which is 7.6 times higher than bulk samples. Figure 12 shows the formation of cyano deficient g-$\text{C}_3\text{N}_4$ and N$_2$ photofixation mechanism.

![Figure 11. The possible nitrogen photofixation process proposed by Ma et al. (Reproduced with permission from Elsevier [68]).](image1)

Figure 11. The possible nitrogen photofixation process proposed by Ma et al. (Reproduced with permission from Elsevier [68]).

The cyano defects were successfully introduced into the g-$\text{C}_3\text{N}_4$ framework by KOH etching and could contribute to improving the nitrogen photofixation ability of g-$\text{C}_3\text{N}_4$. (Reproduced with permission from Elsevier [69]).

**Figure 12.** The cyano defects were successfully introduced into the g-$\text{C}_3\text{N}_4$ framework by KOH etching and could contribute to improving the nitrogen photofixation ability of g-$\text{C}_3\text{N}_4$. (Reproduced with permission from Elsevier [69]).

4.2.3. Sulfur Vacancies

Due to similar chemical properties with oxygen, Hu hypothesized that sulfur vacancies have N$_2$ absorption ability as oxygen vacancies [70]. In his study, a tri-component metal sulfide of Zn$_{0.1}$Sn$_{0.1}$Cd$_{0.8}$S was prepared by the hydrothermal process. Under visible light irradiation, the photocatalyst performs an outstanding activity in nitrogen fixation, because of containing a
A strategy of coupling carbon nitride with sulfur vacancies doped metal sulfide was applied for the reduction of N\textsubscript{2} under visible light. At the same time, two similar heterojunction system of g-C\textsubscript{3}N\textsubscript{4}/ZnSnCdS and g-C\textsubscript{3}N\textsubscript{4}/ZnMoCdS were assembled by Cao et al. [71,73]. In general, the photo-induced electrons will be excited and migrated from g-C\textsubscript{3}N\textsubscript{4} to the quaternary metal sulfide whereas the photo-generated holes are transferred in the reversed direction and consumed by hole scavenger. Additionally, the sulfur vacancies could trap immigrated electrons form g-C\textsubscript{3}N\textsubscript{4} and intrinsic electrons in metal sulfide then transport immediately to activated N\textsubscript{2}. The schematic of electron-hole separation and transportation is depicted in Figure 13b. As the photoinduced electrons and holes are spatially separated, the charge recombination will be drastically inhibited, which is of highly beneficial for enhancing the photocatalytic activity. Under visible light irradiation, the highest NH\textsubscript{4}\textsuperscript{+} evolution rates of g-C\textsubscript{3}N\textsubscript{4}/ZnSnCdS and g-C\textsubscript{3}N\textsubscript{4}/ZnMoCdS are 7.5 and 3.5 mg L\textsuperscript{-1} h\textsuperscript{-1} gcat\textsuperscript{-1}, respectively, which is 33.3 and 13.5 times higher compared to those of individual g-C\textsubscript{3}N\textsubscript{4}.

Figure 13. (a) Nitrogen photofixation performance of the as-prepared catalysts as a function of the sulfur vacancies concentration [70]; (b) The schematic of electron–hole separation and transport at the g-C\textsubscript{3}N\textsubscript{4}/ZnMoCdS heterojunction interface [71]. (Reproduced with permission from the respective publishers).

Hu also discussed the role of Zn, Sn metal doping in the creation of sulfur vacancies rather than act as active sites to promote catalytic ability. The proof of elongated N–N triple bond from 1.164 Å to 1.213 Å over sulfur vacancies proves that sulfur vacancies can aid the activation of N\textsubscript{2} instead of doped metal. In this regard, Hu’s group continues to investigate the effect of different metal doping on ternary metal sulfide. Mo and Ni doped CdS can distort the crystal structure, leading to the formation of sulfur vacancies in obtained tri-component metal sulfide [72]. In order to compare the influence of sulfur vacancies, the as-prepared samples were calcined in O\textsubscript{2} gas to remove sulfur vacancies. In results, the photocatalytic NH\textsubscript{4}\textsuperscript{+} generation rates of Mo\textsubscript{0.1}Ni\textsubscript{0.1}Cd\textsubscript{0.8}S photocatalyst is 3.2 mg L\textsuperscript{-1} h\textsuperscript{-1} gcat\textsuperscript{-1}, which is 10-folds higher in comparison with the oxidized sulfur vacancies sample of Mo\textsubscript{0.1}Ni\textsubscript{0.1}Cd\textsubscript{0.8}SO. Hu concluded that the sulfur vacancies not only act as chemical absorption sites, but also capture photo-generated electrons, suppress charge recombination and encourage interfacial charge transfer.

High concentration of sulfur vacancies. This research implied that the photocatalytic nitrogen fixation activity is linearly dependent on the sulfur vacancy concentration. The NH\textsubscript{4}\textsuperscript{+} production rates over the various vacancy concentrations were compared and illustrated in Figure 13a, confirming that the concentration of sulfur vacancies plays a significantly pivotal role in the N\textsubscript{2} photofixation ability.
4.3. Metal Cocatalyst and Plasmon Enhancement

4.3.1. Metal Cocatalyst

In addition to the introduction of interior active sites, transition metals can be employed as exterior active sites by loaded on the semiconductor photocatalysts, namely cocatalyst. Cocatalysts play a critical role in photocatalysis. As electron acceptor, cocatalysts promote electron-hole separation and impede photogenerated charge carrier recombination. Among a variety of cocatalyst, platinum and ruthenium have been considered as the most effective cocatalyst, particularly in hydrogen evolution and CO₂ conversion. Inspired by prior research, Miyama engaged Pt loading TiO₂ and CdS for the improvement of N₂ photoreduction [74]. For both TiO₂ and CdS, the yield of ammonia was increased approximately 1.5 times after introducing noble metal cocatalyst. Several years later, Mirza group applied both Pt and RuO₂ as a reduction and oxidation cocatalyst in CdS [75]. The Pt particles in this system act as electron trapping centers which capture photoexcited electrons and perform reduction reaction. Whereas, the RuO₂ serves as a hole scavenger to consume generated hole, balancing electric charge. Figure 14a demonstrates the mechanism of photocatalytic ammonia evolution based on CdS/Pt/RuO₂ photocatalyst.

*Figure 14. (a) the mechanism of photocatalytic N₂ fixation over CdS/Pt/RuO₂ [75]; (b) M–H bond Strength vs. yield ammonia [76]. (Reproduced with permission from the respective publishers).*

In 1996, Ranjit et al. systematically investigated the impact on photocatalytic NH₃ evolution by the nature and amount of four noble metals decorated TiO₂ [76]. It is worth noting that ammonia was not produced by using pure TiO₂ photocatalyst. However, the metallization of titania results in the increasing of ammonia generation rate. It was found that the production rate is depended on several factors. First, the noble metals form the ohmic contact with semiconductor and serve as electron sinks where can easily accommodate the flow of electron transfer, suppressing electron-hole recombination. Secondly, the report supposed that the key role of the installed metal is to stabilize H₃ads formed on the metal, thus enhancing the ammonia yield. Figure 14b illustrates the linear dependent between the Metal-H₃ads bond strength and the yield of ammonia. This proposal is consistent with another work investigating Ru, Fe, and Os cocatalysts [77], where it was found that metal cocatalysts for NH₃ production needed to have a high over-potential for H₂ evolution; where the metals with high over-potentials for the hydrogen evolution reaction (Ru and Fe) having higher NH₃ activity than the metals with low hydrogen evolution reaction over-potential. Based on experimental data, Ranjit deduced that the catalytic activity of the nanocomposite photocatalyst is observed in the trend Ru > Rh > Pd > Pt. It is clearly seen that the trend is reversed in the hydrogen evolution reaction. Medford suggested that the role of the metal site is to minimize hydrogen evolution rather than being a cocatalyst for NH₃ synthesis [78].
4.3.2. Plasmon Enhancement

A fundamentally different approach for loading transition metal supported fixing nitrogen has been demonstrated to enhance light absorption through the surface plasmonic enhancement [79–83]. In order to increase the NH₃ production rate by harnessing the localized surface plasmon resonance, most recent studies have focused on using gold nanoparticles as a plasmonic structure. Owing to high light-harvesting properties, gold in a nanoparticle can absorb visible light and induce surface plasmon effect, which can inject hot electrons into the semiconductor conduction band. Oshikiri and his partner assembled a photoelectrode, with Au nanoparticles and Ru cocatalyst co-loaded Nb-SrTiO₃ [80]. The hypothesized mechanism was proposed that the excited hot electron is transferred to SrTiO₃ semiconductor and continuously injected into Ru cocatalyst. At the Ru surface, nitrogen and proton are reduced to ammonia. In contrast, the generated holes localize near the Au/Nb-SrTiO₃/water interface and immediately oxidize hydroxyl ions and ethanol (Figure 15a). The ammonia production was observed at long wavelengths up to 800 nm, implying plasmon-induced charge separation promoted nitrogen reduction in the cathode and oxidation in the anodic side. However, Ru cocatalyst not only accelerates N₂ reduction, but also for H₂ evolution because of stable absorption of H₂ onto a Ru surface. Later, a replacement of Ru cocatalyst with Zr/ZrOₓ cocatalyst was reported by the initial group in 2016 [81]. In the Au/Nb-SrTiO₃/Zr/ZrOₓ system, the NH₃ generation rate is prominently higher than that of Ru system, due to Zr prefers binding N* adatoms rather than H* adatoms. DFT calculation proved that the Zr is effective at limiting the hydrogen evolution reaction. An energy diagram of this system is provided in Figure 15b.

![Figure 15. A schematic illustration of the NH₃ synthesis device using a Nb-SrTiO₃ photoelectrode loaded with Au nanoparticles [80]; (b) Energy level diagram of the plasmon-induced NH₃ synthesis device [81]. (Reproduced with permission from the respective publishers).](image-url)

Furthermore, Zheng, Terazono, and Tanuma attempted to synthesize ammonia at room temperature using Os-Au nanocomposite catalyst which was prepared by directly sputtered Os onto Au layer [79]. The generation of ammonia was observed under visible light irradiation between 550 and 650 nm, corresponding to the conversion rate of 0.003% at 550 nm. Originally, neither pure Au nor Os nanoparticle showed photoactivity in ammonia synthesis. Although pure Au nanoparticles exhibit LSPR effect of photon energy absorption to generate electron, but are unable to encourage the N₂ reduction reaction. Whereas, Os nanoparticle is active for N₂ fixation, but inactive in the visible light region. Therefore, the assembly of Au–Os nanocomposite motivates the photon energy resonance transfer from Au nanoparticles to Os layer (Figure 16a), enhancing NH₃ yield. By contrast, for the first time, Ali and his colleagues hypothesized that gold nanoparticles can serve as reduction cocatalyst [82]. In his work, solar-driven nanostructured plasmon enhanced black silicon photoelectrode produces ammonia yield of 320 mg m⁻² in a day. The variety of controlled experiment confirm the roles of individual layers, which is described in Figure 16b. Gold nanoparticles (GNP) loaded black silicon (bSi) provide reduction active sites, receiving transferred electron form photon absorber bSi. While Cr layer acts as sacrificial hole sink where scavenge photogenerated holes by the oxidation of sulfite...
ions. In results, the NH$_3$ production of the GNP/bSi/Cr cell increases to around two-folds that of the GNP/bSi and eight-folds that of pure bSi.

**Figure 16.** (a) A schematic illustration the mechanism of Au-Os nanocomposite for NH$_3$ photofixation [79]; (b) Schematic diagram of photochemical nitrogen reduction of Au/bSi/Cr [72]. (Reproduced with permission from the respective publishers).

5. Conclusions

Utilization of solar light for energy production and environmental protection is one of the most critical challenges in the near future for researchers and scientists. Photocatalyst based on semiconductors is an effective route to employ the plentiful energy from the sun. Unfortunately, industrial application of this strategy is still limited by ineffective light absorption and fast electrons-holes recombination process of photocatalyst semiconductor. Thus, the development of the active photocatalyst system is required. A variety of methods have been introduced to improve the photocatalytic efficiency, such as combining multicomponent semiconductor together, metal or non-metal doping, usage of cocatalyst, and plasmon-enhancement. The main purposes of these methods are to enhance the visible light absorption ability, to narrow band gap energy of semiconductor, to increase the charge separation, to decrease charge-recombination and to supply more active sites on the surface of the nanocomposite semiconductor.

Over the last decade, nitrogen photofixation has been attracted many interests for the synthesis of ammonia by nitrogen and water under solar irradiation. There are two main strategies for developing efficient photocatalyst of nitrogen reduction. Introduction of metal active sites or non-metal vacancies not only provide more active centers to absorb nitrogen, but also weaken and activate N-N triple bond. Whereas, noble metals, such as Pt, Ru, Pd, Rh loaded photocatalysts can act as electron acceptors, promoting charge carrier separation and suppressing electron hole recombination. In addition, loading gold nanoparticle induces LSPS effect, which can enhance visible light absorption effectively. In this review report, we have demonstrated the advantages and disadvantage of each group of active centers-based semiconductors. Understanding the strong points and drawbacks of these materials is a very important step to develop new effective photocatalyst for NH$_3$ evolution based on solar-driven nitrogen fixation.

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References

1. Service, R.F. New recipe produces ammonia from air, water, and sunlight. *Science* **2014**, *345*, 610. [CrossRef] [PubMed]

2. Licht, S.; Cui, B.; Wang, B.; Li, F.-F.; Lau, J.; Liu, S. Ammonia synthesis by N2 and steam electrolysis in molten hydroxide suspensions of nanoscale Fe2O3. *Science* **2014**, *345*, 637–640. [CrossRef] [PubMed]

3. Linsebigler, A.L.; Lu, G.; Yates, J.T. Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758. [CrossRef]

4. Datta, R.S.; Ou, J.Z.; Mohiuddin, M.; Carey, B.J.; Zhang, B.Y.; Khan, H.; Syed, N.; Zavabeti, A.; Haque, F.; Daeneke, T.; et al. Two dimensional PbMoO4: A photocatalytic material derived from a naturally non-layered crystal. *Nano Energy* **2018**, *49*, 237–246.

5. Daeneke, T.; Khoshmanesh, K.; Mahmood, N.; de Castro, I.A.; Esrafilzadeh, D.; Barrow, S.J.; Dickey, M.D.; Kalantar-zadeh, K. Liquid metals: Fundamentals and applications in chemistry. *Chem. Soc. Rev.* **2018**, *47*, 4073–4111.

6. Kisch, H. Semiconductor Photocatalysis-Mechanistic and Synthetic Aspects. *Angew. Chem. Int. Ed.* **2015**, *52*, 812–847. [CrossRef] [PubMed]

7. Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Anpo, M. Charge Carrier Dynamics of Standard TiO2 and Other Semiconductors. *J. Phys. Chem. B* **1999**, *103*, 3120–3127. [CrossRef] [PubMed]

8. Habisreutinger Severin, N.; Schmidt-Mende, L.; Stolarczyk Jacek, K. Photocatalytic Reduction of CO2 on TiO2 and Other Semiconductors. *Angew. Chem. Int. Ed.* **2013**, *52*, 7372–7408. [CrossRef]

9. Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering heterogeneous semiconductors for solar water splitting. *J. Mater. Chem. A* **2015**, *3*, 2483–2534. [CrossRef]

10. Schiavello, M.; Augugliaro, V.; Palmisano, L. An experimental method for the determination of the photon flow reflected and absorbed by aqueous dispersions containing polycrystalline solids in heterogeneous photocatalysis. *J. Catal.* **1991**, *127*, 332–341. [CrossRef]

11. Kisch, H.; Bahnemann, D. Best Practice in Photocatalysis: Comparing Rates or Apparent Quantum Yields? *J. Phys. Chem. Lett.* **2015**, *6*, 1907–1910. [CrossRef] [PubMed]

12. Buriak, J.M.; Kamat, P.V.; Schanze, K.S. Best Practices for Reporting on Heterogeneous Photocatalysis. *J. Phys.* **2004**, *127*, 297–2245. [CrossRef] [PubMed]

13. Khan, S.U.M.; Al-Shahry, M.; Ingler, W.B. Efficient Photochemical Water Splitting by a Chemically Modified n-TiO2. *Science* **2002**, *297*, 2243–2245. [CrossRef]

14. Jing, D.; Guo, L. A Novel Method for the Preparation of a Highly Stable and Active CdS Photocatalyst with a Special Surface Nanostructure. *J. Phys. Chem. B* **2006**, *110*, 11139–11145. [CrossRef] [PubMed]

15. Cao, J.; Sun, J.Z.; Hong, J.; Li, H.Y.; Chen, H.Z.; Wang, M. Carbon Nanotube/CdS Core–Shell Nanowires Prepared by a Simple Room-Temperature Chemical Reduction Method. *Adv. Mater.* **2004**, *16*, 84–87. [CrossRef]

16. Wang, X.; Liu, G.; Lu, G.Q.; Cheng, H.-M. Stable photocatalytic hydrogen evolution from water over ZnO–CdS core–shell nanorods. *Int. J. Hydrogen Energy* **2010**, *35*, 8199–8205. [CrossRef]

17. Hou, J.; Wang, Z.; Kan, W.; Jiao, S.; Zhu, H.; Kumar, R.V. Efficient visible-light-driven photocatalytic hydrogen production using CdS@TaON core-shell composites coupled with graphene oxide nanosheets. *J. Mater. Chem. A* **2012**, *2*, 7291–7299. [CrossRef]

18. Khan, S.U.M.; Majumder, S.A. Optimization of p-silicon surface by etching and electrodeposition of Pt and Ni for photosplitting of water. *Int. J. Hydrog. Energy* **1989**, *14*, 653–660. [CrossRef]

19. Gurunathan, K. Photocatalytic hydrogen production using transition metal ions-doped γ-Bi2O3 semiconductor particles. *Int. J. Hydrog. Energy* **2004**, *29*, 933–940. [CrossRef]

20. Jang, J.S.; Yoon, K.Y.; Xiao, X.; Fan, F.-R.F.; Bard, A.J. Development of a Potential Fe2O3-Based Photocatalyst Thin Film for Water Oxidation by Scanning Electrochemical Microscopy: Effects of Ag–Fe2O3 Nanocomposite and Sn Doping. *Chem. Mater.* **2009**, *21*, 4803–4810. [CrossRef]

21. Jang, J.S.; Choi, S.H.; Kim, H.G.; Lee, J.S. Location and State of Pt in Platinized CdS/TiO2 Photocatalysts for Hydrogen Production from Water under Visible Light. *J. Phys. Chem. C* **2008**, *112*, 17200–17205. [CrossRef]
24. Maeda, K.; Xiong, A.; Yoshinaga, T.; Ikeda, T.; Sakamoto, N.; Hisatomi, T.; Takashina, M.; Lu, D.; Kanehara, M.; Setoyama, T.; et al. Photocatalytic Overall Water Splitting Promoted by Two Different Cocatalysts for Hydrogen and Oxygen Evolution under Visible Light. *Angew. Chem. Int. Ed.* 2010, 49, 4096–4099. [CrossRef] [PubMed]

25. Clavero, C. Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nat. Photonics* 2014, 8, 95. [CrossRef]

26. Ma, X.-C.; Dai, Y.; Yu, L.; Huang, B.-B. Energy transfer in plasmonic photocatalytic composites. *Light Sci. Appl.* 2016, 5, e16017. [CrossRef]

27. Mubeen, S.; Hernandez-Sosa, G.; Moses, D.; Lee, J.; Moskovits, M. Plasmonic Photosensitization of a Wide Band Gap Semiconductor: Converting Plasmons to Charge Carriers. *Nano Lett.* 2011, 11, 5548–5552. [CrossRef]

28. Fan, W.; Leung, M. Recent Development of Plasmonic Resonance-Based Photocatalysis and Photovoltaics for Solar Utilization. *Molecules* 2016, 21, 180. [CrossRef]

29. Cushing, S.K.; Li, J.; Meng, F.; Senty, T.R.; Suri, S.; Zhi, M.; Li, M.; Bristow, A.D.; Wu, N. Photocatalytic Activity Enhanced by Plasmonic Resonant Energy Transfer from Metal to Semiconductor. *J. Am. Chem. Soc.* 2012, 134, 15033–15041. [CrossRef]

30. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 1972, 238, 37. [CrossRef]

31. Li, H.; Shang, J.; Ai, Z.; Zhang, L. Efficient Visible Light Nitrogen Fixation with BiOBr Nanosheets of Oxygen Vacancies on the Exposed {001} Facets. *J. Am. Chem. Soc.* 2015, 137, 6393–6399. [CrossRef] [PubMed]

32. Yuan, S.-J.; Chen, J.-J.; Lin, Z.-Q.; Li, W.-W.; Sheng, G.-P.; Yu, H.-Q. Nitrate formation from atmospheric nitrogen and oxygen photocalysed by nano-sized titanium dioxide. *Nat. Commun.* 2013, 4, 2249. [CrossRef] [PubMed]

33. Bozso, F.; Ertl, G.; Grunze, M.; Weiss, M. Interaction of nitrogen with iron surfaces: I. Fe(100) and Fe(111). *J. Catal.* 1977, 49, 18–41. [CrossRef]

34. Tennakone, K.; Wickramanayake, S.; Fernando, C.A.N.; Ileperuma, O.A.; Punchihewa, S. Photocatalytic nitrogen photoreduction to ammonia over titanium dioxide powders doped with ferric ions. *Langmuir* 2007, 3, 303–304. [CrossRef]

35. Zhao, W.; Zhang, J.; Zhu, X.; Zhang, M.; Tang, J.; Tan, M.; Wang, Y. Enhanced nitrogen photofixation ability of honeycombed graphitic carbon nitride: The experimental and density functional theory simulation analysis. *Appl. Catal. B Environ.* 2017, 201, 58–69. [CrossRef]

36. Soria, J.; Conesa, J.C.; Augugliaro, V.; Palmisano, L.; Schiavello, M.; Sclafani, A. Dinitrogen photoreduction to ammonia over titanium dioxide powders doped with ferric ions. *J. Phys. Chem.* 1991, 95, 274–282. [CrossRef]

37. Rusina, O.; Linnik, O.; Eremenko, A.; Kisch, H. Nitrogen Photofixation on Nanostructured Iron Titanate Films. *Chem. A Eur. J.* 2003, 9, 561–565. [CrossRef] [PubMed]

38. Linnik, O.; Kisch, H. On the mechanism of nitrogen photofixation at nanostructured iron titanate films. *Photochem. Photobiol. Sci.* 2006, 5, 938–942. [CrossRef]

39. Lashgari, M.; Zeinalkhani, P. Photocatalytic N₂ conversion to ammonia using efficient nanostructured solar-energy-materials in aqueous media: A novel hydrogenation strategy and basic understanding of the phenomenon. *Appl. Catal. A General* 2017, 529, 91–97. [CrossRef]

40. Hu, S.; Chen, X.; Li, Q.; Li, F.; Fan, Z.; Wang, H.; Wang, Y.; Zheng, B.; Wu, G. Fe³⁺ doping promoted N₂ photofixation ability of honeycombed graphitic carbon nitride: The experimental and density functional theory simulation analysis. *Appl. Catal. B Environ.* 2017, 201, 58–69. [CrossRef]

41. Schrauzer, G.N.; Guth, T.D. Photocatalytic reactions. 1. Photolysis of water and photoreduction of nitrogen on titanium dioxide. *J. Am. Chem. Soc.* 1977, 99, 7189–7193. [CrossRef]

42. Tennakone, K.; Bandara, J.M.S.; Thamininulla, C.T.K.; Jayatilake, W.D.W.; Ketiparachchi, U.S.; Ileperuma, O.A.; Priyadarshana, M.K.A. Photoreduction of dinitrogen to ammonia by ultrafine particles of iron hydroxide oxide (Fe(O)OH) formed by photohydrolysis of iron(II) bicarbonate. *Langmuir* 1991, 7, 2166–2168. [CrossRef]

43. Lu, Y.; Yang, Y.; Zhang, T.; Ge, Z.; Chang, H.; Xiao, P.; Xie, Y.; Hua, L.; Li, Q.; Li, H.; et al. Photoprompted Hot Electrons from Bulk Cross-Linked Graphene Materials and Their Efficient Catalysis for Atmospheric Ammonia Synthesis. *ACS Nano* 2016, 10, 10507–10515. [CrossRef] [PubMed]
45. Tennakone, K.; Fernando, C.A.N.; Wickramanayake, S.; Damayanthe, M.W.P.; Silva, L.H.K.; Wijeratne, W.; Illeperuma, O.A.; Punchihewa, S. Photocatalytic reduction of nitrogen to ammonia with coprecipitated Fe(III) and Ti(IV) hydrous oxides. Sol. Energy Mater. 1988, 17, 47–53. [CrossRef]

46. Illeperuma, O.A.; Kiridena, W.C.B.; Dissanayake, W.D.D. Photoelectrodeposition of nitrogen and water on montmorillonite clays loaded with hydrous ferric oxide. J. Photochem. Photobiol. A Chem. 1991, 59, 191–197. [CrossRef]

47. Baumann, R.; Stumpf, R.; Davis, W.M.; Liang, L.-C.; Schrock, R.R. Titanium and Zirconium Complexes That Contain the Tridentate Diamido Ligands [(i-PrN-o-C6H4)2O]2-[(i-PrNON)2-] and [(C6H11N-o-C6H4)2O]2-[(CyNON)2-]. J. Am. Chem. Soc. 1999, 121, 7822–7836. [CrossRef]

48. Van Tamelen, E.E.; Fechter, R.B.; Schneller, S.W. Conversion of molecular nitrogen to hydrazine. J. Am. Chem. Soc. 1969, 91, 7196. [CrossRef]

49. Hirakawa, H.; Hashimoto, M.; Shiraishi, Y.; Hirai, T. Photocatalytic Conversion of Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. J. Am. Chem. Soc. 2017, 139, 10929–10936. [CrossRef]

50. Sun, S.; Li, X.; Wang, W.; Zhang, L.; Sun, X. Photocatalytic robust solar energy reduction of dinitrogen to ammonia on ultrathin MoS2. Appl. Catal. B Environ. 2017, 200, 323–329. [CrossRef]

51. Banerjee, A.; Yuhas, B.D.; Margulies, E.A.; Zhang, Y.; Shim, Y.; Wasielewski, M.R.; Kanatzidis, M.G. Photochemical Nitrogen Conversion to Ammonia in Ambient Conditions with FeMoS-Chalcogels. J. Am. Chem. Soc. 2015, 137, 2030–2034. [CrossRef] [PubMed]

52. Liu, J.; Kelley, M.S.; Wu, W.; Banerjee, A.; Douvalis, A.P.; Wu, J.; Zhang, Y.; Schatz, G.C.; Kanatzidis, M.G. Nitrogenase-mimic iron-containing chalcogels for photochemical reduction of dinitrogen to ammonia. Proc. Natl. Acad. Sci. USA 2016, 113, 5530–5535. [CrossRef] [PubMed]

53. Hoffman, B.M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D.R.; Seefeldt, L.C. Mechanism of Nitrogen Fixation by Nitrogenase: The Next Stage. Chem. Rev. 2014, 114, 4041–4062. [CrossRef] [PubMed]

54. Ye, L.; Han, C.; Ma, Z.; Leng, Y.; Li, J.; Ji, X.; Bi, D.; Xie, H.; Huang, Z. Ni3P loading on Cd0.5Zn0.5S solid solution for exceptional photocatalytic nitrogen fixation under visible light. Chem. Eng. J. 2017, 307, 311–318. [CrossRef]

55. Wang, S.; Hai, X.; Ding, X.; Chang, K.; Xiang, Y.; Meng, X.; Yang, Z.; Chen, H.; Ye, J. Light-Switchable Oxygen Vacancies in Ultrathin Bi5O7Br Nanotubes for Boosting Solar-Driven Nitrogen Fixation in Pure Water. Adv. Mater. 2017, 29, 1701774. [CrossRef]

56. Li, C.; Wang, T.; Zhao, Z.J.; Yang, W.; Li, J.F.; Li, A.; Yang, Z.; Ozin Geoffrey, A.; Gong, J. Promoted Fixation of Molecular Nitrogen with Surface Oxygen Vacancies on Plasmon-Enhanced TiO2 Photocathodes. Angew. Chem. Int. Ed. 2018, 57, 5278–5282. [CrossRef] [PubMed]

57. Sun, S.; An, Q.; Wang, W.; Zhang, L.; Liu, J.; Goddard Iii, W.A. Efficient photocatalytic reduction of dinitrogen to ammonia on ultrathin MoS2. Green Chem. 2018, 20, 5530–5535. [CrossRef] [PubMed]

58. Sun, S.; An, Q.; Wang, W.; Zhang, L.; Liu, J.; Goddard Iii, W.A. Efficient photocatalytic reduction of dinitrogen to ammonia on ultrathin MoS2. Chem. A Eur. J. 2017, 50, 112–121. [CrossRef] [PubMed]

59. Li, H.; Li, J.; Ai, Z.; Jia, F.; Zhang, L. Oxygen Vacancy-Mediated Photocatalysis of BiOCl: Reactivity, Selectivity, and Perspectives. Angew. Chem. Int. Ed. 2017, 57, 122–138. [CrossRef] [PubMed]
66. Dong, G.; Ho, W.; Wang, C. Selective photocatalytic N2 fixation dependent on g-C3N4 induced by nitrogen vacancies. J. Mater. Chem. A 2015, 3, 23435–23441. [CrossRef]

67. Li, S.; Chen, X.; Hu, S.; Li, Q.; Bai, J.; Wang, F. Infrared ray assisted microwave synthesis: A convenient method for large-scale production of graphitic carbon nitride with outstanding nitrogen photofixation ability. RSC Adv. 2016, 6, 45931–45937. [CrossRef]

68. Ma, H.; Shi, Z.; Li, Q.; Li, S. Preparation of graphitic carbon nitride with large specific surface area and outstanding N2 photofixation ability via a dissolve-regrowth process. J. Phys. Chem. Solids 2016, 99, 51–58. [CrossRef]

69. Zhou, N.; Qiu, P.; Chen, H.; Jiang, F. KOH etching graphitic carbon nitride for simulated sunlight photocatalytic nitrogen fixation with cyano groups as defects. J. Taiwan Inst. Chem. Eng. 2018, 83, 99–106. [CrossRef]

70. Hu, S.; Chen, X.; Li, Q.; Zhao, Y.; Mao, W. Effect of sulfur vacancies on the nitrogen photofixation performance of ternary metal sulfide photocatalysts. Catal. Sci. Technol. 2016, 6, 5884–5890. [CrossRef]

71. Zhang, Q.; Hu, S.; Fan, Z.; Liu, D.; Zhao, Y.; Ma, H.; Li, F. Preparation of g-C3N4/ZnMoCdS hybrid heterojunction catalyst with outstanding nitrogen photofixation performance under visible light via hydrothermal post-treatment. Dalton Trans. 2016, 45, 3497–3505. [CrossRef] [PubMed]

72. Cao, Y.; Hu, S.; Li, F.; Fan, Z.; Bai, J.; Lu, G.; Wang, Q. Photofixation of atmospheric nitrogen to ammonia with a novel ternary metal sulfide catalyst under visible light. RSC Adv. 2016, 6, 49862–49867. [CrossRef]

73. Hu, S.; Li, Y.; Li, F.; Fan, Z.; Ma, H.; Li, W.; Kang, X. Construction of g-C3N4/Zn0.11Sn0.12Cd0.88S1.12 Hybrid Heterojunction Catalyst with Outstanding Nitrogen Photofixation Performance Induced by Sulfur Vacancies. ACS Sustain. Chem. Eng. 2016, 4, 2269–2278. [CrossRef]

74. Miyama, H.; Fujii, N.; Nagae, Y. Heterogeneous photocatalytic synthesis of ammonia from water and nitrogen. Chem. Phys. Lett. 1990, 74, 523–524. [CrossRef]

75. Khan Mirza, M.T.; Bhardwaj Ramesh, C.; Bhardwaj, C. Catalytic Fixation of Nitrogen by the Photocatalytic CdS/Pt/RuO2 Particulate System in the Presence of Aqueous [Ru(Hedta)N2]⊖ Complex. Angew. Chem. Int. Ed. Engl. 1988, 27, 923–925. [CrossRef]

76. Ranjit, K.T.; Varadarajan, T.K.; Viswanathan, B. Photocatalytic reduction of dinitrogen to ammonia over noble-metal-loaded TiO2. J. Photochem. Photobiol. A Chem. 1996, 96, 181–185. [CrossRef]

77. Rao, N.N.; Dube, S.; Manjubala; Natarajan, P. Photocatalytic reduction of nitrogen over (Fe, Ru or Os) /TiO2 catalysts. Appl. Catal. B Environ. 1994, 5, 33–42. [CrossRef]

78. Medford, A.J.; Hatzell, M.C. Photon-Driven Nitrogen Fixation: Current Progress, Thermodynamic Considerations, and Future Outlook. ACS Catal. 2017, 7, 2624–2643. [CrossRef]

79. Zeng, H.; Terazono, S.; Tanuma, T. A novel catalyst for ammonia synthesis at ambient temperature and pressure: Visible light responsive photocatalyst using localized surface plasmon resonance. Catal. Commun. 2015, 59, 40–44. [CrossRef]

80. Oshikiri, T.; Ueno, K.; Misawa, H. Plasmon-Induced Ammonia Synthesis through Nitrogen Photofixation with Visible Light Irradiation. Angew. Chem. Int. Ed. 2014, 53, 9802–9805. [CrossRef]

81. Oshikiri, T.; Ueno, K.; Misawa, H. Selective Dinitrogen Conversion to Ammonia Using Water and Visible Light through Plasmon-induced Charge Separation. Angew. Chem. 2016, 128, 4010–4014. [CrossRef]

82. Ali, M.; Zhou, F.; Chen, K.; Kotzur, C.; Xiao, C.; Bourgeois, L.; Zhang, X.; MacFarlane, D.R. Nanostructured photovoltaical solar cell for nitrogen reduction using plasmon-enhanced black silicon. Na. Commun. 2016, 7, 11335. [CrossRef] [PubMed]

83. Ueno, K.; Oshikiri, T.; Shi, X.; Zhong, Y.; Misawa, H. Plasmon-induced artificial photosynthesis. Interface Focus 2015, 5, 20140082. [CrossRef] [PubMed]

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