Challenges and Opportunities for Renewable Ammonia Production via Plasmon-Assisted Photocatalysis

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Despite its severe operating conditions, associated energy consumption, and environmental concerns, the manufacture of nitrogen-rich fertilizers still relies heavily on producing ammonia in centralized chemical plants via the Haber–Bosch process. A distributed and more sustainable scheme considers the on-site production of carbon-neutral fertilizers at ambient conditions in photocatalytic reactors powered by sunlight. Among the different strategies proposed to boost the nitrogen reduction ability of conventional catalysts, the incorporation of plasmonic nanomaterials is gaining widespread interest owing to their unique optical tunability and their potential to improve the efficiency and selectivity of many chemical transformations. This Perspective examines the state-of-the-art for the nitrogen reduction reaction via plasmon-driven photocatalysis and discusses design principles for advancing it. The different physical mechanisms underlying the operation of plasmonic materials in a catalytic setting, and the dimensions along which the catalysts can be tuned to harness them are detailed. Paths to overcome current frontiers in the field, including design strategies of plasmonic photocatalysts, the development of complementary characterization techniques, the standardization of the reaction conditions and ammonia quantification methods, and the possibilities offered by theoretical methods to drive material discovery, identifying fundamental bottlenecks, and proposing directions for the advancement of this emerging field are outlined.

1. Introduction

Ammonia is an essential key raw material for the synthesis of nitrogen-rich chemicals in the modern industry. Besides its agricultural applications (76% of the synthetic NH3 is used to produce fertilizers), NH3 is used in the manufacture of plastics, synthetic fibers, explosives, and numerous chemical compounds, and it also provides safe storage of hydrogen for energy applications owing to its high energy density (13.6 GJ m⁻³) and easy transportation. In nature, NH3 is directly synthesized from atmospheric N₂ under ambient temperature and pressure conditions with the aid of nitrogenase enzymes. The large amount of energy (~500 kJ) required to fix 1 mol of N₂ is directly obtained from the sun via photosynthesis. However, the natural production of NH3 is not sufficient to fulfill the needs of our modern industrial society. Since its introduction in 1909, the production of NH3 still relies on the industrial Haber–Bosch process. Currently, the global production of NH3 through this process is about 150 million metric tons per year, and is expected to increase by 2–3% on a yearly basis from the growing demand arising from a booming world population. However, although the fixation of N₂ to NH₃ is an exothermic reaction (N₂ (g) + 3H₂ (g) → 2 NH₃ (g), ΔH (25 °C) = −92.2 kJ mol⁻¹), it does not occur spontaneously under mild conditions due to the strong N≡N bond (with a dissociation energy of 941 kJ mol⁻¹), high ionization potential (15.85 eV), and low electron affinity (~1.90 eV). Instead, high temperatures (300–600 °C), high pressures (150–300 atm), and purified N₂ and H₂ are required. As a consequence, the Haber–Bosch process accounts for 1–2% of the world’s total energy consumption and consumes ca. 50% of the global H₂ production, which is nowadays largely based (>95%) on transformations of...
fossil resources.\textsuperscript{[11]} As a result, approximately 2 tons of carbon dioxide accompanies the production of each ton of NH\textsubscript{3}, which represents around 3% of the total emissions of the greenhouse gases.\textsuperscript{[12–14]} Moreover, Haber–Bosch plants typically operate in a centralized and continuous manner and are economically feasible only on the scale of thousands of metric tons per day, which poses major constraints for the on-site small-scale production of NH\textsubscript{3}.\textsuperscript{[12–15]} Therefore, the development of sustainable and distributed alternatives for the production of NH\textsubscript{3} with a neutral carbon footprint is imperative.

Alternative approaches aim to decouple the synthesis reaction from fossil resources by facilitating the integration of renewable energy and CO\textsubscript{2}-free H\textsubscript{2}, in addition to improving the energy efficiency of the process.\textsuperscript{[16]} Apart from the biocatalytic processes based on nitrogenase enzymes,\textsuperscript{[17–19]} and homogeneously-catalyzed \textit{N}\textsubscript{2} reduction using metal complexes,\textsuperscript{[20,21]} alternatives include non-thermal plasma catalysis,\textsuperscript{[22]} electrocatalysis,\textsuperscript{[23,24]} and photocatalysis.\textsuperscript{[25,26]} Non-thermal plasma catalysis requires a renewable electrical energy input and comes accompanied by the challenges associated to selectivity control and by-product formation owing to the evolution of excited molecules, radicals, and ions, as well as high energy electrons generated in non-thermal plasmas. Electrochemical ammonia synthesis is by far the most investigated alternative approach for NH\textsubscript{3} synthesis. It requires a relatively simple electrolysis setup, and both complementary half-reactions can progress in the same cell.\textsuperscript{[27]} However, the favored formation of H\textsubscript{2} over transition metals at lower overpotentials than NH\textsubscript{3}, the limited N\textsubscript{2} solubility in aqueous electrolytes, and the required renewable energy input to power the electrocatalytic process are obstacles for its upscaling.\textsuperscript{[28,29]} Likewise, photochemical NH\textsubscript{3} synthesis also suffers from the occurrence of the competitive H\textsubscript{2} evolution reaction and limited N\textsubscript{2} solubility\textsuperscript{[30,31]} but does not rely on any external electrical supply as it is directly powered by renewable solar light. On account of the parallelism between the natural photosynthetic process and the herein considered on a N\textsubscript{2} basis, the term “artificial photosynthesis” emerges to describe a process able to produce NH\textsubscript{3} from air, water, and sun, an attractive alternative for renewable ammonia synthesis.

Since the foundational work by Schrauzer and Guth on the photocatalytic reduction of N\textsubscript{2} into NH\textsubscript{3} using Fe-doped TiO\textsubscript{2} under UV light,\textsuperscript{[32]} important efforts have been dedicated to increase the solar to chemical energy conversion of this process. To this end, different strategies have been investigated over the last decades aiming at maximizing the absorption of light and the charge transfer at the catalyst surface while simultaneously minimizing electron-hole recombination. These include morphology optimization and crystal regulation, introduction of surface defects, heteroatom doping, facet engineering, atom speciation, or the addition of co-catalysts and photosensitizers by forming heterogeneous hybrids. As a result, efficient charge separation and improved surface redox reactions led to improved performance and higher apparent quantum efficiencies (AQEs). Recently, the potential of plasmonics as a means to drive the photocatalytic nitrogen reduction reaction (NRR) more efficiently has been at the center of many scientific efforts. The present Perspective is focused on the role that plasmonic nanoparticles (NPs) play both as photosensitizers and photocatalysts in improving the performance of photocatalytic NRR. To that end, and after a brief presentation of the most recent achievements in the field, we lay down different experimental and theoretical aspects that should be taken into consideration when designing novel plasmon-based photocatalysts for the NRR. We believe that the synergic combination of the different practices discussed herein can help bridge the gap between the state-of-the-art and the requirements of the industry, thus moving toward an efficient and affordable alternative to the Haber–Bosch process.

2. Photocatalytic Nitrogen Reduction Reaction

The traditional approach to photocatalytic NRR starts when a semiconductor, appropriately selected according to the energy alignment of its band edges, is irradiated with light whose energy is equal or greater than its bandgap, exciting the electrons in the valence band to the conduction band and leaving holes in the former, thus creating electron-hole pairs. Then, these charge carriers migrate to the surface, with redox potentials able to reduce N\textsubscript{2} to NH\textsubscript{3} and oxidize water to O\textsubscript{2}.\textsuperscript{[33]} In order for these reactions to occur, N\textsubscript{2} must be first adsorbed on the catalytic active sites, which will be followed by hydrogenation, N≡N bond cleavage, and finally desorption of the NH\textsubscript{3} product. The N\textsubscript{2} fixation mechanism can be either dissociative or associative depending on the adsorption and hydrogenation modes (Figure 1).\textsuperscript{[22,34]} In the dissociative mechanism, attributed to the Haber–Bosch process, the triple N≡N bond of the N\textsubscript{2} molecule is first cleaved and then the hydrogenation reaction follows. In contrast, in the associative mechanism, the hydrogenation of N\textsubscript{2} leads to the synthesis and release of one NH\textsubscript{3} molecule, leaving one N atom adsorbed on the catalyst surface for further hydrogenation to NH\textsubscript{3}. In this case, the nitrogen atoms of the adsorbed N\textsubscript{2} molecules can be either hydrogenated alternatively (associative alternating pathway) or the terminal nitrogen atom is hydrogenated preferentially (associative distal pathway).

To utilize solar energy efficiently, the largest possible portion of the solar spectrum should be harvested, which strongly relies on the engineering of the bandgap of the semiconductor. However, tuning its bandgap may compromise the energy alignment of the photoexcited charge carriers, so that the semiconductor might not be able to reduce the N\textsubscript{2} molecule. In the particular case of NRR, the energy level of the conduction band of the semiconductor should be higher (more negative) than the reduction potential of the N\textsubscript{2} hydrogenation (+0.55 V vs NHE at pH 0). Similarly, if the valence band potential of the semiconductor is higher than the oxidation potential of water (+1.23 V vs NHE at pH 0), it is thermodynamically feasible for photo-generated holes to react with water to generate O\textsubscript{2}, or possibly even strongly oxidizing reactive oxygen species such as OH\textsuperscript{−} and H\textsubscript{2}O\textsubscript{2}. These species may oxidize NH\textsubscript{3} to nitrate,\textsuperscript{[35,36]} which, in addition to the favored formation of H\textsubscript{2} at lower overpotentials than NH\textsubscript{3} over transition metals could compromise the selectivity (vide infra, Figure 4a) of the photocatalyst. To overcome the poor ability for water oxidation of certain semiconductors, a hole scavenger (i.e., Na\textsubscript{2}SO\textsubscript{3}, amines, alcohols, and ethylenediaminetetraacetic acid) is needed to consume the accumulated holes and improve the efficiency of N\textsubscript{2} photoreduction.\textsuperscript{[37]} An ideal photocatalyst has therefore to i) have the ability to absorb a large fraction of the impinging
solar spectrum without compromising the reduction potential of photoinduced electrons, ii) minimize the recombination of electrons and holes in order to enhance the solar conversion efficiency, and iii) have appropriate active sites to enhance the affinity towards N₂ molecules, ease the activation, facilitate the reduction, and suppress the H₂ evolution reaction.

As most traditional unmodified semiconductors, e.g., TiO₂, CdS, or C₃N₄, cannot meet these requirements, a number of commonly utilized strategies to improve the activity of heterogeneous catalysts have been proposed (Figure 1). Although these approaches have already been covered by several excellent reviews,[26,31,34,38,39] we will recap some important general aspects for completeness. Vacancies are the most common active sites in photocatalysis. They can be formed during the synthesis of the material, after the synthesis -via chemical reduction or thermal treatment methods-, or be induced through light irradiation, and can be classified as surface, subsurface, and bulk defects depending on their location. Vacancies can serve as electron traps, alter the band structure of catalysts, and provide additional adsorption sites. Surface and subsurface defects in photocatalysts generally possess a strong binding to N₂, generating adsorbed N₂²⁻ while the electron-rich cations around defects promote the reduction of adsorbed N₂ through proton-coupled electron transfer (eT) via HN—NH and —NH₂ intermediates.[40] However, they may not be associated exclusively with beneficial effects as they may also act as recombination centers or undesired trap states, especially in the case of bulk defects, thus reducing the photocatalytic activity.[41]

As such, improving our understanding of the structure and properties of defects would help the rational design of high-performance semiconductor photocatalysts. Oxygen vacancies are responsible for N₂ photofixation in In(OH)₃/C₃N₄ catalysts,[42] bismuth oxyhalide-based materials,[43] TiO₂-containing catalysts,[40] In₂O₃/In₂S₃,[44] W₁₉O₄₉-based materials,[45] or
Fe-doped SrMoO<sub>4</sub>.<sup>[46]</sup> They act as chemisorption sites for N<sub>2</sub> molecules which are subsequently reduced via the photoexcited electrons that are transferred from the catalyst surface. Nitrogen and carbon vacancies in C<sub>3</sub>N<sub>4</sub> and co-doping with non-metal atoms, such as P, S, O, B, etc. have also been explored as active sites for N<sub>2</sub> photofixation.<sup>[18,19,47-49]</sup> Similarly, iodine, sulfur, and fluorine vacancies have been reported as being beneficial for the photocatalytic activity. In addition to defect engineering, doping the semiconductor with heteroatoms provides an effective way to generate more active sites for the adsorption and activation of N<sub>2</sub>. In this regard, doping of defect-rich W<sub>18</sub>O<sub>49</sub> nanowires with Mo, C<sub>3</sub>N<sub>4</sub> with Fe, TiO<sub>2</sub> with Ru, and doping of C<sub>3</sub>N<sub>4</sub> or ZnO with Mo, Co, Li, Ag, Ce, and Te have been reported, in which the transition metal acts as active center for photocatalytic NRR.<sup>[50-58]</sup> Engineering specific exposed facets constitute another typical approach to enhance the activity of traditional semiconductors. Theoretical calculations predicted that high-index facets provide abundant sites for N<sub>2</sub> adsorption and activation, which was experimentally demonstrated over tetrahedral Au nanorods and bismuth oxyhalide-based materials.<sup>[59,60]</sup> Owing to their unique electronic structure and high atom utilization efficiency, single atom, and cluster catalysts constitute two classes of systems that are recently receiving increasing attention as they display unprecedented activity and selectivity toward a wide range of catalytic reactions.<sup>[61]</sup> Their distinct catalytic activities are the result of the low-coordination environment of the metal center, quantum size effects, and metal-support interactions. In the particular case of N<sub>2</sub> fixation, single Ru, Pt, Mo, B, or Fe atoms decorate a number of different carriers including TiO<sub>2</sub> nanosheets, TiO<sub>2</sub>-SiO<sub>2</sub>, C<sub>3</sub>N<sub>4</sub>, or covalent triazine framework nanosheets.<sup>[52,62-68]</sup> The fabrication of hybrid structures is another feasible strategy to improve the performance of heterogeneous catalysts. Examples include ZnMoCdS,<sup>[34]</sup> BiO quantum dots,<sup>[69]</sup> or γ-Ga<sub>2</sub>O<sub>3</sub> combined with graphitic C<sub>3</sub>N<sub>4</sub>,<sup>[70]</sup> graphene quantum dots-modified Bi<sub>2</sub>WO<sub>6</sub> or Bi<sub>S<sub>2</sub></sub>Se<sub>Br</sub> hybrid structures among others.<sup>[71]</sup> In addition to the strategies mentioned above, the utilization of the localized surface plasmon resonance (LSPR) effect to improve the photocatalytic performance of NRR is recently attracting increasing attention.<sup>[72,73]</sup> This hybrid approach is the focus of this Perspective and will be discussed in detail in the next sections.

3. Plasmonics for Enhanced Photocatalysis

Plasmon-induced photocatalysis has gained traction as a promising means to efficiently drive chemical reactions using light.<sup>[74-76]</sup> This novel field of research has generated a completely new landscape of chemical reactivity by improving the efficiency of chemical transformations while allowing an extraordinary modulation of selectivity. In this manner, processes with a high societal impact such as CO<sub>2</sub> photo(electro) reduction<sup>[77,78]</sup> or water-splitting reactions,<sup>[79]</sup> to name a few, may be developed in a greener and cost-efficient manner.

Plasmonic photocatalysis is the result of the unique optoelectronic properties of conducting NPs, with noble metal NPs being the most studied systems.<sup>[80]</sup> These objects support LSPRs, which are resonant modes of the collective oscillations of the conduction electrons in the metal, that can be excited by incoming electromagnetic fields. As a consequence of this, materials such as Ag, Au, or Cu NPs present very high absorption cross-sections in the visible and near-infrared regions of the electromagnetic spectrum.<sup>[81]</sup> LSPRs are responsible for the intense electromagnetic fields generated at the surfaces of the nanostructures, a property with important repercussions in sensing<sup>[82]</sup> and theranostic<sup>[83]</sup> applications. Importantly, the features of plasmonic NPs can also modulate chemical reactivity. The energy of a photoexcited plasmonic mode can be shared with its environment through several distinct channels, so that plasmonic photocatalysis can be driven by three different photoactivation mechanisms: the local enhancement of the electromagnetic field,<sup>[84,85]</sup> the injection of charge carriers,<sup>[74,86,87]</sup> and the increase of temperature produced through photoheating.<sup>[88,89]</sup> These channels, together with radiative relaxation, that is, scattering, can coexist in a given system and can thus participate simultaneously in the same photochemical reaction, although the adequate engineering of the catalyst can balance their relative relevance or even suppress some of them. The drawing in Figure 2a depicts a plasmonic NP, surrounded by semiconductor NPs and excited resonantly by light. The coherent plasmonic mode can then share its energy with the environment through the aforementioned mechanisms, that are arranged in Figure 2 attending to the degree of order in the system, from the radiative relaxation of the plasmon to the dissipative heating of the NP environment. The diagram noting typical relaxation timescales in a plasmonic system (Figure 2c) is helpful in visualizing the progressive disordering of the energy stored in the internal degrees of freedom of the metal NP, starting from the collective plasmonic mode, passing from incoherent electronic excited states, and finishing by reaching a thermal equilibrium with its surroundings.

The far-field reemission of photons, or scattering, can in principle contribute to increasing the external quantum yield of a photocatalyst by extending the effective optical thickness of a sample including other absorbing materials, such as TiO<sub>2</sub>. The schematic spectral diagram in Figure 2b depicts the required spectral overlap between plasmonic scattering and semiconductor absorption that could make this approach useful. Using plasmonic nanoantennas with high-energy resonances can thus in principle shrink a photocatalytic system while preserving its activity, but this mechanism lacks other interesting properties that make plasmonic photocatalysis exciting, and can actually be considered a hindrance that limits the internal quantum yield of the plasmonic photocatalyst.<sup>[84]</sup> In the next sections, we will briefly discuss the three relaxation channels through which the plasmon can deposit energy locally, constituting the main energy-transfer mechanisms in plasmonic photocatalysis.

3.1. Near-Field Enhancement

Plasmonic photocatalysis can be achieved by taking advantage of the near-field enhancement generated at the surface of plasmonic NPs. In this case, the noble metal NP works as an antenna, focalizing the incoming light and leading to a localized increase in the density of photonic states that can be used to enhance the absorption of a near by acceptor. This interaction can be used to activate a catalyst such as a semiconductor.
Figure 2. a) Schematic representation of the available channels of relaxation for a plasmon. The scheme in the left depicts an optically excited plasmonic NP, surrounded by semiconductor photocatalysts and reagents. b) Depending on the energy-transfer mechanism involved, plasmonic NPs can simply increase the effective optical thickness of the setup, or sensitize it to a wider spectral region. Adapted with permission.© 2021, Wiley-VCH. c) Typical relaxation timescales for the decay of a plasmon into internal degrees of freedom, as they would occur after excitation with an ultrashort light pulse. Importantly, under continuous illumination all these steps occur concurrently. Adapted with permission.© 2020, American Chemical Society. d–f) Near-field enhancement. (d) Scheme of the enhanced promotion of e-h pairs by a nearby plasmonic NP. (e) Theoretical data depicting the excitation of a Pt NP co-catalyst by a plasmonic NP. The metals are separated by an insulation SiO2 layer. Reproduced with permission.© 2017, American Chemical Society. (f) Data of molecular fluorescence versus distance from a metal tip. The theoretical data in the panel is obtained by modeling the competition between enhancement and quenching by the metal. Reproduced with permission.© 2016, American Physical Society. g–j) Carrier injection. (g) Schematic diagram of Au bands and the physical processes exciting its electrons under illumination. Reproduced with permission.© 2019, Elsevier. (h) Schematic diagram of the injection of hot holes from the d band of Au, using a p-type semiconductor to direct them towards the reagents. Reproduced with permission.© 2018, American Chemical Society. (i) Schematic diagram showing indirect (left) and direct (injection) processes. (j) Direct carrier injection, also known as chemical interface damping, broadens the plasmonic peak. Adapted with permission.© 2017, American Chemical Society. k–m) Photoheating. (k) Theoretical temperature map of an isolated plasmonic NP under CW illumination. Reproduced with permission.© 2011, American Physical Society. (l) Theoretical temperature maps of two 2D plasmonic ensembles under CW illumination. Reproduced with permission.© 2010, American Physical Society. (m) Scheme of an NRR photocatalytic setup taking advantage of photogenerated temperature gradients to separate and protect the synthesized NH3 molecules. Reproduced with permission.© 2019, American Chemical Society.
or a non-plasmonic noble metal, for example, Pd, Pt, without interfacial exchange of charge carriers. The former situation is described schematically in Figure 2d, where the optical transition in the semiconductor is promoted by the proximity of the plasmonic particle. When it promotes a direct optical transition in a nearby semiconductor or molecule, the plasmonic resonance ought to overlap spectrally with their absorption bands to enhance the optical excitation in these materials (as in Figure 2b). The latter case, working in tandem with metal co-catalysts, has the conducting electrons of the two-metal antenna excited in coupled modes. This is exemplified in Figure 2e, showing simulation data for a system where the plasmonic near-field is responsible for exciting neighboring Pt NPs.[84] The advantage of this configuration is that the plasmonic mode does not need to overlap spectrally with semiconductor catalysts or reagents, as it aims to excite the metal co-catalyst instead (or, rather, the light excites the coupled bimetallic NP pair).[99] thus sharing with the other mechanisms discussed below the potential of extending the usable region of the solar spectrum.

The interaction of a plasmonic NP with other elements in the system through its near-field does not require their physical contact. What is more, close proximity between the plasmonic metal and the element whose optical excitation has been promoted can become a hindrance, as the metal can quench the processes downstream of the optical excitation by offering a large number of empty states to which the excited electron can relax into. The study presented by Novotny and coworkers has the conducting electrons of the two-metal antenna excited in coupled modes. This is exemplified in Figure 2e, showing simulation data for a system where the plasmonic near-field is responsible for exciting neighboring Pt NPs.[84] The advantage of this configuration is that the plasmonic mode does not need to overlap spectrally with semiconductor catalysts or reagents, as it aims to excite the metal co-catalyst instead (or, rather, the light excites the coupled bimetallic NP pair).[99] thus sharing with the other mechanisms discussed below the potential of extending the usable region of the solar spectrum.

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3.2. Charge Carrier Injection

Among the non-radiative LSPR decay mechanisms, the collective charge carrier oscillation can cohere and move its energy into single-electron degrees of freedom, giving rise to electrons and holes with high energies, up to the total energy of the incoming photon with respect to the Fermi energy of the metal. Here, it is relevant to differentiate between intraband carrier excitation, in which electrons from the metal conduction band are promoted within it, and interband excitations, in which electrons from a deeper band are promoted to empty states in the conduction band. This distinction is particularly relevant in Au, a material in which these interband transitions appear at relatively low energies, of approximately 2.3 eV or 540 nm, and allow the reliable targeting of hot hole excitation in the d band (Figure 2g,h).[94,105]

These excited hot electrons or holes can have enough energy to surpass the potential barrier between the metal and its environment. Under continuous wave (CW) irradiation, and although such non-thermalized hot charge carriers have very short lifetimes (<100 fs), they are constantly excited so that there is a steady-state population of carriers susceptible of leaving the metal.[106] Given their high energies, such photon-generated hot electrons and holes can drive reduction and oxidation reactions, respectively. Nevertheless, once excited, they thermalize rapidly into a Fermi-Dirac distribution via electron-electron and electron-phonon scattering (100 fs–1 ps), with their energy finally dissipating into the environment in the form of heat (wide infra). In order to collect them and increase their lifetime, the plasmonic metal has to be coupled with an acceptor such as a molecular adsorbate or a semiconductor. The interaction between metal NPs and large bandgap semiconductors has proven to be particularly efficient since the photosensitization capabilities of the former can complement the high photocatalytic activity of the latter, leading to a hybrid material with broadband features and improved efficiencies.

When considering the injection of carriers excited in the plasmonic material, it is key to have a suitable interface between it and the acceptor material, such that it can allow the exchange of charge. A relevant factor controlling the injection efficiency is the magnitude of the energy barriers separating the Fermi sea of the metal from the conduction (valence) band of the n-type (p-type) semiconductor, or the orbitals of an adsorbed molecule. Figure 2i depicts a typical Schottky barrier at the metal-semiconductor interface. Another relevant possibility for the injection of charge carriers from the metal is the direct excitation of electrons across the material interface, as schematically depicted in Figure 2i. The difference between these two modalities of injection is not necessarily apparent in a photocatalytic setting, but the additional plasmon dephasing channel opened by the direct charge injection can be observed by the broadening of the optical spectrum of the plasmonic nanoantenna. Figure 2j shows a typical signature of this effect, also known as chemical interface damping,[107] occurring due to a coating layer of molecular acceptors.[95] Distinct coatings affect the injection probability and plasmon broadening differently, depending on the electronic configuration formed at the interface.[108] Interestingly, theoretical models point out the possibility of direct charge transfer being more efficient in small systems.[109] Working with small plasmonic nanostructures can in general be a fruitful strategy for charge carrier injection, as their large surface to volume ratio also promotes the excitation of intraband hot electrons and holes,[100] although manufacturing larger NPs with strong hot spots has also been shown to favor this process.[111,112] Moreover, direct charge injection can be an important tool towards reaction selectivity, using the unique tunability of the optical properties of plasmonic NPs to target specific reaction pathways.[113]
### 3.3. Photoheating

Ultimately, the relaxation of the plasmon into incoherent excited electronic states leads to the temperature increase of the medium surrounding the NP. The diagram in Figure 2c illustrates the processes leading through this path, and the simulation data in Figure 2k exemplifies the typical diffusive temperature profile created by an isolated NP. This ability to generate heat has been already applied in different fields such as medicine or solar light harvesting.[89] Similarly, the temperature increase at the surface of a plasmonic NP under CW irradiation can also be used to enhance the rate of chemical reactions. Even though thermoplasmonics can create local temperature increase at the surface of a plasmonic NP under CW irradiation, its effect into account, as it can noticeably change the dynamics with plasmonic systems, and it is in general important to take its effect into account, as it can noticeably change the dynamics when using temperature-sensitive photocatalysts.[116]

### 4. State-of-the-Art Plasmonic Catalysts for Photocatalytic Nitrogen Reduction Reaction

In this section, we discuss recent advancements in plasmonic photocatalysis for N₂ fixation into NH₃. The available literature is divided into two classes: gold-based materials, representing the vast majority of studies currently reported, and photocatalysts based on alternative plasmonic materials, which include Ru, Cu, Ti₃C₂Tx, MoO₃-x, and SrMoO₄ (Table 1).

#### 4.1. Gold-Based Plasmonic Photocatalysts

Yang et al. reported Au NPs anchored on ultrathin TiO₂ nanosheets with oxygen vacancies (Au/TiO₂-OV) as an efficient photocatalyst for NRR (Figure 3a).[117] TiO₂ nanosheets provide a large specific contact area that increases the probability of excited charge carriers to interact with the reaction solution, along with the oxygen vacancies which offer the sites for the chemisorption, activation, and subsequent reduction of N₂ to NH₃. Hot electrons generated on Au under visible light irradiation are injected into the conduction band of defective TiO₂ nanosheets and diffuse and get trapped at the defect states of the oxygen vacancies, enabling the N₂ fixation. The design of plasmonic hybrid catalysts composed of Au NPs and C₃N₄ was

#### Table 1. Summary of experimental results of plasmonic catalysts for photocatalytic N₂ fixation. OV, NV, and SV indicate oxygen, nitrogen, and sulfur vacancies, respectively. n.a.: not available.

| Plasmonic material | Catalyst | Light source | Light power | Medium | NH₃ yield | AQE | Ref. |
|--------------------|----------|--------------|-------------|--------|-----------|-----|------|
| Au                 | Au/BiO₂CO₃ | 300 W Xe lamp (solar simulator) | n.a. | H₂O | 38.2 µmol g⁻¹ h⁻¹ | n.a. | [120] |
| Au                 | Au/TiO₂-OV | 300 W Xe lamp (λ > 420 nm) | n.a. | H₂O | 78.6 µmol g⁻¹ h⁻¹ | 0.82% (at 550 nm) | [117] |
| Au                 | Au/endo-CeO₂ | (1) 808 nm diode laser, 1.6 W (2) 1 W | 8 W cm⁻² | H₂O:CH₃OH = 80:20 | (1) 1.14 µmol g⁻¹ h⁻¹ | (2) 2.56 µmol g⁻¹ h⁻¹ | n.a. | [121] |
| Au                 | AuRu₀.₃ | 300 W Xe lamp | 400 mW cm⁻² | H₂O (2 bar) | 101.4 µmol g⁻¹ h⁻¹ | 0.021% (at 350 nm) | 0.017% (at 550 nm) | [125] |
| Au                 | Au/endo-CeO₂ | 300 W Xe lamp | 400 mW cm⁻² | H₂O (2 bar) | 101.4 µmol g⁻¹ h⁻¹ | 0.021% (at 350 nm) | 0.017% (at 550 nm) | [125] |
| Au                 | Au/hollow C₃N₄-NV | 300 W Xe lamp (λ > 420 nm) | n.a. | H₂O:CH₃OH = 80:20 | 783.4 µmol g⁻¹ h⁻¹ | 0.64% (at 550 nm) | [118] |
| Au                 | Au/C₃N₄-NV | 300 W Xe lamp | | H₂O | 184 µmol g⁻¹ h⁻¹ | n.a. | [119] |
| Ru                 | r-Ti₃C₂Tx/Au | 300 W Xe lamp | | H₂O | approx. 32 µmol g⁻¹ h⁻¹ | 0.697% (at 520 nm) | [122] |
| Ru                 | Au/Mo-doped W₁₀O₃₀ | 300 W Xe lamp | | H₂O:CH₃OH = 4:1 | 399 µmol g⁻¹ h⁻¹ | 0.611% (at 540 nm) | [123] |
| Ru                 | Au@UO₂-66 | 300 W Xe lamp (>400 nm) | 40 mW cm⁻² | K₂SO₄/H₂O (0.5 m) | 263 µmol g⁻¹ h⁻¹ | 0.97% (at 520 nm) | [124] |
| Ru                 | K/Ru/TiO₂-H₂ | 300 W Xe lamp | | gas phase | 112.6 µmol g⁻¹ h⁻¹ | n.a. | [126] |
| Ru                 | Ru-SV-Co₅S₄C₃N₄ | 300 W Xe lamp (λ > 420 nm) | n.a. | H₂O:CH₃OH = 10:1 | 438 µmol g⁻¹ h⁻¹ | 1.28% (at 400 nm) | [127] |
| Cu                 | Cu₉₅Fe₄ | 320–780 nm Xe lamp | 250 mW cm⁻² | H₂O | 342 µmol g⁻¹ h⁻¹ | 0.13% (at 535 nm) | [128] |
| Ti₃C₂Tₓ | Ti₃C₂Tₓ/TiO₂ | Xe lamp | 250 mW cm⁻² | H₂O | 422 µmol g⁻¹ h⁻¹ | 0.07% (at 740 nm) | [129] |
| MoO₃₄ | MoO₃₄ | 300 W Xe lamp | | H₂O | 326 µmol g⁻¹ h⁻¹ | 0.31% (at 808 nm) | [130] |
| SrMoO₄ | SrMoO₄ | 300 W Xe lamp | | H₂O | ca. 90 µmol g⁻¹ h⁻¹ | 1.24% (at 808 nm) | [131] |
Figure 3. a) Schematic illustrating the plasmonic hot electron generation, injection, and N₂ reduction processes in the N₂ photofixation with the Au/TiO₂-OV catalyst under visible light. Reproduced with permission.[117] Copyright 2018, American Chemical Society. b) Illustration for direct NRR on Au NPs encapsulated in UiO-66 matrix. The synergistic LSPR effects, including hot electron generation, electron transfer (ET), energy transfer (ET), and localized-EF-polarization effects, are all involved in the activation of adsorbed N₂ molecules (*N₂) and other key reaction intermediates (e.g., *NNH). Reproduced with permission.[124] Copyright 2021, American Chemical Society. c) Schematic illustration of solar thermal NH₃ synthesis on Ru/TiO₂-xHₓ. Reproduced with permission.[126]. d) Fourier-transformed EXAFS spectra in R space of porous Cu₉₆Fe₄. Reproduced with permission.[128] Copyright 2017, Elsevier. e) Photocurrent responses of WₓO₄₉, Mo-doped WₓO₄₉, and Au/Mo-doped WₓO₄₉ at a bias potential of 0.2 V versus Ag/AgCl. Reproduced with permission.[123] Copyright 2021, The Royal Society of Chemistry. f) Proposed photocatalytic NRR pathway on Ru-SV-CoS/C₃N₄. Reproduced with
also reported. Guo et al. used Au NPs uniformly embedded in the mesopores of nitrogen-deficient hollow C \textsubscript{3}N\textsubscript{4} spheres for efficient N\textsubscript{2} photofixation (Figure 3h).\textsuperscript{[118]} The authors demonstrated that the photocatalytic NRR activity depends strongly on the shell thickness, as this determines the charge carrier transport ability of the catalyst. Varying the shell thickness affects the interplay of the total number of active sites on the outer/inner surface and in the mesopores with ease of access to the active sites. The reaction mechanism is elucidated by the combination of photocurrent measurements and Density Functional Theory (DFT) calculations and is governed by the presence of nitrogen vacancies. They provide the active sites for the chemisorption of N\textsubscript{2} as well as the trapping sites for the electrons photogenerated from the C \textsubscript{3}N\textsubscript{4} and the plasmon excitation of the Au NPs. Similarly, Wu et al. reported C\textsubscript{3}N\textsubscript{4} nanosheets loaded with Au NPs as efficient photocatalysts for NH\textsubscript{3} synthesis.\textsuperscript{[119]} Combining experimental results and DFT calculations, the authors conclude that the nitrogen vacancies are responsible for the observed performance as they promote N\textsubscript{2} chemisorption, polarization of N\textsubscript{2}, and N—N bond cleavage. The hot electrons generated at the plasmonic element can be injected efficiently into the adsorbed N\textsubscript{2}, favoring its reduction to NH\textsubscript{3}. Additional semiconductors have been applied in combination with Au NPs. For instance, Xiao et al. reported (BiO\textsubscript{3})\textsubscript{2}CO\textsubscript{3} nanodisks modified with Au NPs for efficient NRR.\textsuperscript{[120]} In this case, Au can extend the light absorption of the semiconductor in addition to its role as a hot electron collector to efficiently separate the photogenerated electrons and relative holes, thus increasing the N\textsubscript{2} reduction rate. On a different note, Jia et al. reported a facile wet-chemistry route for the selective growth of crystalline cerium oxide at the ends of Au nanorods in the presence of a small amount of K\textsubscript{3}PtCl\textsubscript{4} (Figure 3g).\textsuperscript{[121]} The surface of grown CeO\textsubscript{2} is rich in oxygen vacancies, that is, Ce\textsuperscript{3+}, which facilitate the adsorption and activation of N\textsubscript{2} and their reduction via the plasmonic hot carriers. Meanwhile, the hot holes generated under the plasmon excitation are consumed by methanol that is used as a hole scavenger at the lateral facets of the Au nanorods to close the photocatalytic cycle. Therefore, the spatial separation design of the Au/end-CeO\textsubscript{2} nanostructures offers reaction sites for both reduction and oxidation, with the reduction of N\textsubscript{2} occurring on the surface of CeO\textsubscript{2} and the consumption of hot holes on the side surface of the Au nanorods. The NRR performance of this structure presents an 8.9- and 5.0-fold increase with respect to that of bare Au nanorods and fully coated Au@CeO\textsubscript{2} core@shell nanostructures, respectively. Au nanospheres on partially reduced Ti\textsubscript{3}C\textsubscript{2} (r-Ti\textsubscript{3}C\textsubscript{2}) were also reported as selective photocatalysts for NRR. In this case, the expanded layer spacing of r-Ti\textsubscript{3}C\textsubscript{2} exhibits abundant low-valence Ti (Ti\textsuperscript{4+−5+}) sites, as confirmed by the low-temperature electron paramagnetic resonance (EPR) spectra (Figure 3k). These centers effectively capture and activate N\textsubscript{2}, while Au nanospheres offer plasmonic hot electrons for the reduction into NH\textsubscript{3}, being the competing H\textsubscript{2} evolution reaction greatly suppressed.\textsuperscript{[122]} Additionally, plasmonic Au NPs anchored on Mo-doped W\textsubscript{18}O\textsubscript{49} nanowires (denoted as Au-MWO) were also reported for NRR.\textsuperscript{[123]} N\textsubscript{2} chemisorption occurs on the low valence Mo sites, which is mainly caused by the electron injection effect of the antibonding orbital of N\textsubscript{2} when adsorbed on the defect sites. Similar to other photocatalysts, sufficiently energetic electrons produced from the plasmonic Au NPs inject into MWO, enabling the reduction of activated N\textsubscript{2}. The improved N≡N bond activation ability was further verified by the photocurrent response in N\textsubscript{2} and Ar saturated atmospheres (Figure 3e). Mo-doped W\textsubscript{18}O\textsubscript{49} and Au/Mo-doped W\textsubscript{18}O\textsubscript{49} display a more pronounced photocurrent decrease than W\textsubscript{18}O\textsubscript{49} (i.e., 25% and 38% vs 10%, respectively), which suggests a favorable electron transfer to the adsorbed N\textsubscript{2} molecules in the case of Mo-doped tungsten oxide. The highest photocurrent reduction of Au/Mo-doped W\textsubscript{18}O\textsubscript{49} may be attributed to the favorable activation of N\textsubscript{2} by surface plasmons. DFT calculations demonstrate that the N\textsubscript{2} photofixation on MWO goes through an alternative pathway being the NH\textsubscript{3} desorption the rate-determining step.

Even though hybrid systems consisting of a plasmonic material with a semiconductor are the most explored plasmonic photocatalysts, a few studies are reported in which the plasmonic material is able to simultaneously activate and reduce N\textsubscript{2} (Figure 4d). For instance, Chen et al. reported Au NPs embedded within a UiO-66 MOF for renewable NH\textsubscript{3} synthesis.\textsuperscript{[124]} The MOF matrix serves as a versatile substrate that can not only anchor the Au NPs to ensure their optical/catalytic property and stability, but also provides interconnected nanoreactors with ultrahigh surface areas for the diffusion and collision of N\textsubscript{2} and hydrated protons to the plasmonic NPs. DFT calculations demonstrated that N\textsubscript{2} reduction follows the associative mechanism, and that the rate-determining step is the reduction of N\textsubscript{2} to NH\textsubscript{3}. The activation of N\textsubscript{2} and other key intermediates, for example, NNH, occurs via the synergistic LSRR effects, which include the direct injection of hot electrons generated on the Au NPs upon visible irradiation along with non-radiative energy transfer and localized-electric-field polarization (EF-polarization) effects as illustrated in Figure 3b. On a different note, Hu et al. reported a hybrid structure composed of a plasmonic Au core and a Ru antenna as a suitable platform for fine-tuning the energy flow from the plasmonic metal to neighboring catalytic Ru sites.\textsuperscript{[125]} N\textsubscript{2} can be chemisorbed efficiently at Ru sites through an end-on configuration to form a Ru–N\textsubscript{2} complex in close proximity to the enhanced electromagnetic field generated by the plasmonic component. This hybridized state may allow the LSPR to excite directly the charge carriers within the complex to induce...
N₂ dissociation, thus forming chemisorbed ≡N as evidenced by near-ambient pressure X-ray photoelectron spectroscopy (XPS, Figure 3j). The surface plasmon-driven N₂ fixation system may involve indirect and direct injection of hot electrons, and, importantly, a major contribution from the local enhanced electric field.

Figure 4. a) Band structure of different semiconductors used in the photocatalytic NRR and reduction potentials related to photocatalytic NH₃ synthesis. VB and CB denote valence and conduction bands, respectively. b) AQE versus NH₃ formation rate for different plasmonic metal-containing materials and the corresponding references. c) Impact of the introduction of a plasmonic material over a semiconductor on the NH₃ production rate for different plasmonic material/semiconductor systems and the corresponding references. d) Schematics illustrating the interband excitation of a traditional semiconductor (left); intraband and interband excitation of a plasmonic metal (second left); (c) intraband excitation of a plasmonic semiconductor (third left); and (d) plasmonic carrier excitation and injection into a semiconductor (right) to later generate reductive electrons for molecular N₂ fixation.
Apart from the above-compiled experimental studies, Au-based photocatalysts for photocatalytic NRR were also reported in theoretical studies. To this end, the reactivity toward $N_2$ of transition metal (M)-doped Au(III) (M: Fe, Co, Ni, Mo) systems which combine the strongly plasmonic nature of Au and the ability of M metals to catalyze NRR were evaluated.\[133]\ The authors found that AuMo achieves the best catalytic activity but it is prone to oxidation. In contrast, AuFe alloys exhibit the best compromise between stability with respect to phase separation, reversibility of Fe oxidation and reduction, and reactivity. For this system, the authors calculated the excited-state potential energy surfaces for dissociation of $N_2$ via density functional embedding theory, that accounts for the effect of the cluster’s environment.\[134]\ They determined the ground-state dissociation activation energy to be 4.74 eV$/N_2$, with Fe as the active site on the surface. This energy barrier may be overcome through consecutive resonance energy transfers that are facilitated by the presence of electronic excited states with intermediate energies at the metal surface, potentially coupling to states of the Fe-dopant and the adsorbate molecule. The crossing between excited states may effectively lower the dissociation barrier of $N_2$ to 1.33 eV.

### 4.2. Alternative Plasmonic Materials for Photocatalytic Nitrogen Reduction Reaction

Apart from Au, hybrid materials based on Ru, Cu, Ti$_3$C$_2$, MoO$_3$, and SrMoO$_4$ have been also presented in the literature. Yuan et al. reported Ru/$\text{CoS}$ with S-vacancies on graphitic C$_3$N$_4$ nanosheets (Ru-SV-CoS/C$_3$N$_4$) as an efficient catalyst for NRR.\[127]\ The two nitrogen atoms are bridged to a Ru-Co bimetal center and the asymmetrical electron donation from Ru and Co to $N_2$ polarizes the molecule, weakening the N≡N bond (Figure 3f). In addition to this phenomenon, the plasmonic electric-field-enhancement effect enables the Ru/CoS$_x$ interface to boost the generation of energetic charge carriers, accelerates charge separation and transfer, and thus kinetically facilitates $N_2$ fixation. Mao et al. reported a highly efficient solar $N_2$ synthesis over K/Ru/TiO$_2$-H$_x$.\[126]\ Both K and the electron-rich TiO$_2$-$x$H$_x$ support exhibit abundant oxygen vacancies that can tune the electronic structure of Ru by accepting H atoms from it, subsequently delivering them to the Ru-activated $N_2$ to form NH$_3$ (mechanism I, Figure 3c). Additionally, NH$_3$ could be also produced via the reaction between N activated by Ru and the reversibly incorporated H atoms on the TiO$_2$-$x$H$_x$ surface (mechanism II, Figure 3c). Different from thermal catalysis, this solar thermal strategy confined electromagnetic and thermal energy in a small volume around the Ru cluster due to SPR effects, exhibiting reduced activation energy and enhanced reactivity. Porous Cu$_{60}$Fe$_{4}$ photocatalyst for NRR was reported by Hou et al.\[128]\ In situ X-ray absorption near-edge spectroscopy (XANES) and Fourier-transformed extended X-ray fine structure (EXAFS) spectra revealed the formation of nitrogen-containing complexes on the surface of porous Cu$_{60}$Fe$_{4}$, responsible for the increase of valence state and coordination numbers of Fe atoms during the catalytic reaction (Figure 3d). DFT calculations demonstrated that the presence of Fe atoms contributes to the polarization of the $N_2$ molecule, thus decreasing the reaction barrier substantially. The reaction follows the distal pathway, being the reduction of $N_2$ to N$_3$ the rate-limiting step. Overall, surface Fe species including Fe single atoms, Fe dimers, and Fe clusters served as the active sites to efficiently absorb and activate $N_2$ molecules, while Cu frameworks generated hot electrons by LSPR. The same authors reported Ti$_3$C$_2$T$_x$/TiO$_2$-400 as an efficient photocatalyst for NH$_3$ synthesis.\[129]\ Similarly to the Au-TiO$_2$ hybrid system, oxygen vacancies in TiO$_2$ serve as active centers to adsorb and activate $N_2$ molecules, as demonstrated by DFT calculations, while the plasmonic Ti$_3$C$_2$T$_x$ enables the harvesting of NIR light to generate hot electrons. Furthermore, semiconducting plasmonic MoO$_3$-$x$ nanosheets were reported by Wu et al.\[130]\ Specifically, the coexistence of the low valence state of Mo with the oxygen vacancies within the same nanostructure enables a sufficient amount of active sites for $N_2$ absorption with broad-spectrum plasmon-induced hot electrons, which facilitates the photochemical transformation of $N_2$ without any other co-catalyst (Figure 4d). On one hand, the intrinsic oxygen vacancies introduce extra electrons into the conduction band, providing the ability to support the LSPR for broad-spectrum absorption (visible to NIR, Figure 3i) and the generation of energetic hot electrons with high reduction potential. On the other hand, the low-valence Mo moieties function as $N_2$ chemisorption active sites via electron back-donation. By using spheres of the same material, Bai et al. reported the oxygen vacancies as the sites inducing the injection of hot charge carriers from the LSPR. The hot electrons are granted free movement in the conduction band to maximize their participation in the NRR, while the defect electronic states prolong the carrier lifetime through the prevention of immediate carrier recombination.\[131]\ Similarly, plasmonic SrMoO$_4$ was developed by regulating the concentration of oxygen vacancies that are formed in the reduction process from Mo$^{6+}$ to Mo$^{4+}$.\[132]\ Upon excitation, plasmonic hot electrons jump from states close to the Fermi level to the conduction band or higher energy levels, allowing the efficient harvesting of the visible and NIR light. The energetic electrons from both the intrinsic band excitation and the LSPR excitation enable the thermodynamic reduction of $N_2$ to NH$_3$ in ultrapure water.

In summary, the majority of the reports are based on the formation of hybrid materials in which a photocatalytic component is combined with a plasmonic resonator (generally Au). In most of the reported systems, the occurrence of anion (N, C, O, S) vacancies on the photocatalytic semiconductor was observed to promote $N_2$ fixation, thanks to their ability to bear excess electronic charge and unsaturated metal centers for the chemisorption, activation, and subsequent reduction of $N_2$ to NH$_3$. A generally reported photoactivation mechanism boosting the ammonia formation is the injection of hot electrons, generated on the plasmonic metal, into the conduction band of the semiconductor or directly into the $N_2$ molecules chemisorbed on its defect sites. Figures 4b,c compiles key performance metrics of different published reports. Figure 4b maps the AQE versus NH$_3$ formation rate for different plasmonic metal-containing materials, while Figure 4c shows the impact of introducing a plasmonic material over a semiconductor compared to the bare semiconductor on the NH$_3$ production rate. As observed from Figure 4b, for a given NH$_3$ formation rate, Ru, Au, and MoO$_3$-$x$-based materials are those
that exhibit the highest AQE. Complementary, the results presented in Figure 4c reveal the beneficial impact of introducing a plasmonic material to productivity. The NH$_3$ formation rate increases in all cases when compared to the performance of the bare semiconductor, which is more prominent for the TiO$_2$-, Mo-doped W$_{18}$O$_{49}$-, and CoS/C$_3$N$_4$-based systems.

5. Outlook and Conclusions

5.1. Plasmonic Features and Catalyst Design Principles for Photocatalytic Nitrogen Reduction Reaction

Work in photocatalytic NRR is providing an increasing number of examples of the potential of using plasmonic nanostructures as photosensitizers. These can act in a system in a variety of ways, through the different energy-transfer mechanisms outlined in Section 3, and whose balance can be influenced by changing the material, size, and surface properties of plasmonic NPs. The operation of plasmonic photocatalysts also depends on other factors, such as their abundance relative to other active materials within the photocatalytic system.\[135\] Accordingly, a number of design decisions are necessary when including plasmonic nanostructures in a photocatalytic system. In particular, changing the material and shape of a plasmonic nanoantenna determines its optical properties, and these impose downstream consequences on the evolution of the reaction. For instance, tuning the main plasmonic mode at wavelengths that do not overlap with the absorption bands of semiconductor photocatalysts reduces the likelihood of the electromagnetic enhancement of the semiconductor contribution to the reaction, but at the same time makes the system capable of extracting a wider spectral range. An efficient implementation of plasmonic materials in photocatalytic strategies critically depends on deploying nanostructures that complement the overall photocatalytic strategy, and whose potential hindrances, such as reaction quenching through charge back-transfer, are minimized. Furthermore, fundamental questions about the detailed properties of the interaction mechanisms between plasmonic NPs and the environment can benefit from additional clarification.\[136,137\]

Because of the strong tunability of the optical properties of plasmonic NPs and their multi-mechanistic route for contributing to chemical reactions, experimental progress in plasmonic photocatalysis has been often aided by theoretical and computational efforts. Much of this work is devoted to describing and modeling the optical response of plasmonic nanostructures and their physical energy-transfer mechanisms.\[138\] Computing the optical response of conductive nanostructures can be reliably done with classical methods that describe the collective charge oscillation of the free carriers in a nanostructure, described as continuous matter,\[139\] thus allowing the study of large systems such as complex metamaterials operating in the IR.\[140\] However, theoretical models in plasmonics need to be extended with explicit non-local or quantum-mechanical considerations when studying small NPs,\[141\] or when describing mechanisms involving single-electron processes such as direct\[142\] or indirect\[140,143,144\] hot carrier injection. Some researchers have also approached the study of plasmonic hot carriers through purely quantum mechanical techniques, for example, modeling direct charge transfer between small metal and semiconductor clusters,\[140\] phonon-assisted hot-electron excitation in metals,\[145,146\] or near-field enhancement in small particles described with atomic resolution.\[147\]

However, performing ab initio calculations within frameworks such as DFT is not commonplace in plasmonics. Their large computational requirements limit their usefulness to study small metal nanostructures with sizes that, although depending on methodology and available computational power, are typically below 10 nm,\[147,148\] hence significantly lower than those relevant in many experimental settings. On the other hand, they offer insights into the detailed dynamics of plasmonic systems.\[147\] In a catalytic context, they are also crucial for studying reaction kinetics\[149,150\] and the reaction evolution at catalytic sites in heterogeneous catalysis\[151\] which includes computing the stability of molecular adsorption in different materials and features, as well as the changes that such adsorption induces on the electronic states of the molecule. A complete computational description of plasmonic photocatalysis would therefore benefit from multiscale frameworks capable of integrating the optical response of large plasmonic systems with a detailed description of the reaction and the surface sites driving it at the atomic level. Moreover, the relevant physical and chemical phenomena also occur at disparate timescales, from fs to ns. Consequently, achieving a complete description of plasmonic photocatalysis at all the relevant scales with a single computational framework is not viable, and will require alternative approaches. A promising avenue is designing multiscale models of plasmonic photocatalysis, implementing lessons from other such models used in chemistry,\[150,152\] to simultaneously address questions about energy-transfer mechanism balance and aiding in photocatalyst engineering.\[153\]

5.2. Engineering of the Plasmonic Photocatalysts for Nitrogen Reduction Reaction

As discussed in Section 4.1, the majority of reports found in the literature devoted to plasmon-activated photocatalytic NRR are based on the formation of hybrid materials in which the photocatalytic component (generally a semiconductor such as TiO$_2$) is combined with a plasmonic resonator. In this manner, different parameters inherent to the formation of a heterogeneous nanohybrid (i.e., the physical heterojunction created between both components, their relative molar ratios, or the specific location of the photosensitizer onto the catalyst) could have a major impact not only on the electronic structure of the semiconductor component but also on its active sites, thus being key factors in determining the final photocatalytic properties of the ensemble. The rational modulation of such parameters can result in the improvement of the relatively low reaction yields that currently hinder further developments in this field.

The low photocatalytic activities inherent to semiconductor photocatalysts depend on several factors, being low light absorption capabilities and fast recombination of electron-hole pairs the most detrimental ones. As an alternative, the correct engineering of heterojunction photocatalysts is an opportunity to overcome such limitations.\[153,154\] In this case, the main use
of hybrid photocatalysts entails the formation of a physical interface between two or more components with different compositions, structures, or crystalline characters and the appearance of synergic features. In this vein, the interface created between the photocatalyst and the plasmonic photosensitizer presents several advantages: 1) The photogenerated electron-hole pairs can be spatially separated onto different components, restricting the recombination and leading to longer lifetimes and improved activities. 2) As a consequence, reduction and oxidation reactions are physically separated as well. 3) The combination of different surfaces in the same hybrid also means differential adsorption of molecular species, allowing improved reaction rates and better selectivities.[155] 4) Finally, the engineering of either Schottky or Ohmic contacts will also play a major role in the final photosensitization features. These two contact modes can produce different propagation directions of the photogenerated charge carriers, leading to different photocatalytic outputs.[156]

Another important limitation that hinders the implementation of plasmonic photosensitization in metal-semiconductor photocatalysts is the limited attention devoted to the amount of plasmonic component used. This parameter has proven to be particularly relevant, especially in photoactivation processes driven by the injection of hot charge carriers.[135] Accordingly, a certain metal concentration threshold is observed in these cases, above which a further increase in the amount of photosensitizer leads to a decrease in photocatalytic activity. Such behavior is explained as a consequence of the role played by the metal NPs as recombination centers, leading to faster electron-hole recombination dynamics and overall reduction in exciton lifetime. In this manner, a careful monitoring of the metal loading should be adopted in all experimental procedures in order to establish the ideal metal-semiconductor ratio for each hybrid system, leading to a maximization of the photocatalytic response. Presently, few examples show the importance of this parameter on the photocatalytic NRR. Among them, Yang and coworkers have shown that the amount of Au NPs adsorbed onto ultrathin TiO₂ nanosheets with oxygen vacancies plays a major role in the photoactivation mechanism.[117] Here, the best catalytic activity towards NRR was obtained with a metal loading of 2.53 wt.% with respect to the semiconductor. The authors explain the loss of catalytic activity associated with a further increase of Au as a consequence of the blockage of TiO₂ surface active sites.

The spatial disposition of the photosensitizer onto the photocatalyst is another important characteristic that should be taken into consideration when creating heterojunction materials. We have seen in previous sections that the use of photocatalytic semiconductors with anion (N, C, O, S) vacancies promote N₂ fixation, thanks to their ability to bear excess electronic charge and unsaturated metal centers.[157] Therefore, placing the metal component onto semiconductor facets enriched with anion vacancies will favor the injection of charge carriers and the subsequent transformation of the adsorbed molecules. Previous reports have shown that hot electrons injected from Au NPs adsorbed onto TiO₂ allowed the reduction of chemisorbed N₂ to NH₃.[117] Other authors have deposited a layer of amorphous TiO₂₃ₓ on Au-loaded crystalline TiO₂. Their results demonstrate that the close contact between the plasmonic resonator and the vacancies present on the external layer is the main responsible for the enhanced photocatalytic features of the sandwich structure.[158]

One of the main limitations of using the plasmonic photosensitization of photocatalysts bearing anion vacancies resides in the extremely high reactivity of these defects. For instance, oxygen vacancies are easily quenched by water and oxygen molecules under photocatalytic conditions, leading to the fast poisoning of the photocatalytic surface and the termination of the reaction. As an alternative, in situ photoinduced oxygen vacancies have been proposed as an easy means to boost the activity of different transition metal oxides.[159–161] This approach selectively produces surface over bulk defects, thus minimizing charge recombination in the crystal. A recent study shows that relatively small concentrations of photoinduced oxygen vacancies in ZnO and TiO₂ can play a major role in the photoactivation of the material given the relatively long lifetimes of such defects.[160] The implementation of this approach in plasmon-induced systems can be foreseen as an interesting route towards improved NH₃ yields.

In parallel to this, the development of materials containing active sites along with plasmonic properties in a single nanostructure, as described above for the MoO₃-x material,[130,131] emerges as an attractive approach. Semiconductor-based oxides, arsides, and phosphides, as well as transition-metal nitrides can be alternative plasmonic materials to noble metals in the near-IR and visible ranges, respectively.[162] The research in this direction is fairly open-ended, and provides an excellent opportunity to explore and develop new design dimensions. Research on plasmonic alloy photocatalysts is also expected to grow over the next years. In this regard, single-atom alloys in which small amounts of isolated metal atoms are present in the surface layer of a metal host are rapidly receiving increasing attention. To date, most of the work on these materials has focused on trace amounts of group 8, 9, and 10 transition metals (Pd, Pt, Rh, Ni, Ru) alloyed into group 11 metals (Cu, Ag, Au) with applications in thermal-driven catalysis such as selective hydrogenations, dehydrogenations, C=C and C=O coupling reactions, NO reduction, and CO oxidation, among others.[163] However, they have been barely explored for light-mediated reactions. In the context of methane dry reforming, Zhou et al. recently reported a plasmonic photocatalyst consisting of a Cu “antenna” NP with single-Ru atomic “reactor” sites on its surface with long-term stability and high selectivity to syngas.[164] The authors proposed that light-excited hot carriers, together with single-atom active sites led to the observed catalytic performance, that is primarily ascribed to the substantial reduction of the energy barrier for methane activation. All these approaches will allow researchers to move beyond the classical semiconductor/plasmonic material hybrids, thus offering unique opportunities in the design of novel photocatalytic materials.

5.3. Opportunities of Operando Characterization Techniques to Study Photocatalytic NRR

The rational design of heterogeneous photocatalysts with optimal performance relies heavily on the detailed understanding of the atomic and molecular interactions and
associated reactions at solid surfaces. Conventional characterization methods are limited in meeting the growing requirements of interrogating complex and sophisticated photochemical systems, which usually manifests complex dynamics in the nanoscale. In situ spectroscopic studies have significantly advanced catalysis science by providing fundamental information about catalytic structure and surface species under controlled environments. Sometimes under vacuum conditions with model catalytic systems and in other cases under in situ conditions in the presence of chemical probe molecules, reactive environments (reduction, oxidation, etc.) or in operando mode under reaction conditions (pressure, temperature, reactants, products, etc.), these different scenarios provide fundamental information about the electronic and molecular structures of the catalytic active sites and complex network of reaction pathways, thereby contributing to the understanding of the structure-performance relationships of heterogeneous catalysts.

In 2014, Baldi et al. were able to demonstrate the first experimental observations of H2 absorption and desorption within individual Pd NPs by implementing electron energy loss spectroscopy (EELS) to probe the bulk plasmon resonance.[165] Later on, the same research group demonstrated that plasmonics, combined with environmental transition electron microscopy (ETEM) and optically coupled transmission electron microscopy (OTEM), can be used to locally probe NP dynamics under optical excitation and in reactive chemical environments. In particular, these techniques were used to monitor how Pd nanocubes coupled to Au NPs interact with H2 in response to light with nanometer-to-atomic-scale resolution.[166,167] The authors found that under illumination, multicomponent plasmonic photocatalysts consisting of an Au NP “antenna” and a Pd “reactor” show clear α-phase nucleation in regions close to electromagnetic “hot spots”. Plasmons increase the rate of distinct reaction steps with unique time constants, thus enabling reaction nucleation at specific sites closest to the electromagnetic hot spots. Non-thermal effects imparted by plasmonic NPs, including electromagnetic field enhancement and plasmon-derived hot carriers, were crucial in explaining the site selectivity observed in PdHx phase transformations under illumination. Transmission electron microscopy will continue to play an important role in catalyst design and investigations with high spatial and temporal resolution will go along with new ensemble catalyst development.

The rapid advancements in single-atom and sub-nanocluster catalysis and their susceptibility to undergo restructuring under reaction conditions impose major challenges for monitoring the dynamic behaviors of both the geometric structure and electronic environment of the catalytic sites at atomic scale. Additional questions arise when the catalytic effects are influenced by the presence of plasmonic materials, as in the case of plasmonic photocatalysis. Disentangling the individual contributions demands the development of multi-technique approaches to deeply understand the nature of the active sites and reaction mechanisms, advancing our comprehension of complex and dynamic surfaces at the atomic level. The integration of additional analytical techniques in the electron microscope such as electron- and light-stimulated Raman spectroscopy (ELISR), mass spectrometry, and ultrasensitive gas-phase molecular spectroscopy will be key in characterizing optically driven processes with high spatial and chemical resolution.[166] Among various vibrational spectroscopic methods, in situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) is a useful technique to monitor the photochemical fixation process. It enables the study of the time-dependent transformation of the functional groups on the catalyst surface providing insights into the NRR mechanism. In addition, the generally accessible Raman spectroscopy is particularly powerful as it can provide information at the molecular level when the access to a synchrotron light source is not possible. It can work in the presence of aqueous solutions as the Raman scattering intensity of water is weak, visible laser light can be used as the excitation source, and the full energy range of vibrational modes of chemical species can be detected.[168] In particular, electrochemical tip-enhanced Raman spectroscopy (EC-TERS) provides molecular fingerprint information with nanometer-scale spatial resolution, thus emerging as a promising complementary technique to surpass the currently existing barriers for plasmonic photocatalysts design. EC-TERS enables imaging the changes in the surface defect structure of photocatalysts, thus rendering a platform for real-time monitoring of the defects and its concentration during the NRR. In the case of plasmonic materials, the sensibility of surface-enhanced Raman spectroscopy (SERS) to the LSPR effect of noble metal nanostructures and the concomitant amplification of the Raman intensity of molecules on the metal surface makes SERS a suitable tool for studying the chemical processes occurring on the catalyst surface.[169] Independently from its usage as a characterization tool, SERS was also recently reported as a non-perturbative approach for NH3 detection.[170] This technique features chemical selectivity to NH3, allowing rapid detection of concentrations below 1 ppm in just under 1 s, which shows potential for ultra-sensitive chemical experiments both in situ and in operando modes.

Additional techniques to assist in probing the role of defects in NRR are EPR and near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). Unpaired electrons contained in the atoms or molecules of substances, that is, vacancy defects, lead to different g values and intensities, which are closely related to the type and relative concentration of defects. EPR enables the identification of both anion and cation vacancies, thus being a powerful technique for those materials in which the vacancies are the active sites. Similarly, atmospheric XPS appears as an appropriate technique to detect the surface defect type of a semiconductor photocatalyst, thus being able to probe chemical interactions on the atomic level for vapor/solid interfaces. The original defects or those created under reaction conditions can change the electronic structure and chemical environment of the elements, giving rise to differences in the spectrum, that is, peak shift, variations of the intensity, or the appearance of new peaks, which can be ultimately correlated with the catalytic performance.

X-ray absorption spectroscopy (XAS) constitutes another major characterization tool for the elucidation of the chemical and structural features of heterogeneous catalysts. Its convenience stems from the fact that XAS studies can provide a diverse range of information for a given catalyst (chemical composition, oxidation number, crystallographic information, presence of defects, surface roughness, or relative distribution of
different species) in a single experiment.\textsuperscript{174} In the particular case of the NRR, XAS has been recently used to study the enhanced photocatalytic features towards N\textsubscript{2} photofixation of ZnAl layered double hydroxides doped with Cu\textsuperscript{2+}.\textsuperscript{175} Spectroscopic data allowed to unravel the cooperative contribution of oxygen vacancies and electron-rich Cu\textsuperscript{2+} centers to promote the efficient separation of the photogenerated electrons and holes and the preferential adsorption of N\textsubscript{2}. In the last decade, major improvements in the development of operando XAS studies in a broad range of experimental conditions have allowed to gather important information related to the identity of the active sites and the stability of the material under realistic reaction conditions.\textsuperscript{171,173} One of the most important parameters in determining the (photo)catalytic features of a material is its oxidation state. As we have seen in previous sections, this is particularly relevant in semiconductors whose photocatalytic activity depends on the presence of anion vacancies and their consequent stability throughout the photocatalytic process. In this manner, XAS can provide useful information related to the oxidation state of the material, specially under operando conditions, by simply examining the absorption edge position of the spectra. Previous works have shown that both XANES EXAFS can give important insights into the formation of metal-nitrogen (M-N\textsubscript{x}) species in the electrochemical NRR over single atom Fe catalysts.\textsuperscript{174} Similarly, valuable information can be obtained for the photocatalytic NRR, shading light over the important role played by anion vacancies among other structural features of the photocatalyst. For instance, Qin and coworkers have studied N\textsubscript{2} photofixation in the presence of tunable hexagonal/trigonal mixed-phase ultrathin Mo\textsubscript{1-x}W\textsubscript{x}S\textsubscript{2} nanosheets.\textsuperscript{175} The authors found that the higher electron density of W 5d orbitals produces an electron transfer to the adsorbed N\textsubscript{2} molecules that enhances the activation process. The implementation of this technique in plasmon-induced photocatalytic processes can help us understand the nature of the charge transfer occurring at the metal/semiconductor interface.

5.4. Theoretical Methods Guiding Plasmonic Photocatalyst Design

Finding new and improved photocatalysts for NRR, engineering their surface to create active catalytic sites, and understanding the reaction kinetics in their presence can be greatly aided by ab initio studies, providing insights on the impact of changes of composition and structure to the evolution of the reaction. Tight-Binding and DFT are common theoretical frameworks for these simulations, with the latter being the most widely used, especially when taking into account its different variants and extensions. Such ab initio methods are critical tools for studying the fundamental processes at play in catalysis,\textsuperscript{180} from modeling the kinetics of a reaction\textsuperscript{180} to finding novel catalytic materials,\textsuperscript{185} passing from understanding the role of defects and dopants as reaction centers.

Much of the effort gone into studies using computational chemistry has been poured into modeling thermal catalysis and electrocatalysis,\textsuperscript{186} but are of course useful for understanding different aspects of photocatalytic system design as well. They can, for instance, inform the impact of NP geometry on the reaction kinetics,\textsuperscript{181} model in detail the reaction kinetics through the description of intermediate states,\textsuperscript{187–189} or compute the evolution of the system using molecular dynamics.\textsuperscript{190} Importantly, the efforts in developing different explicit and implicit solvation models in heterogeneous catalysis\textsuperscript{180,181} are also critical for developing useful multiscale models\textsuperscript{152,182} for photocatalytic processes. Using time-dependent DFT (TD-DFT) addresses more specific questions on photocatalysis or electrocatalysis, as they calculate neutral excitations of a material under a periodically oscillating external field.\textsuperscript{183,184} Refinements to computing the optical response of materials can be obtained by using many-body theories like the GW approximation or the Bethe Salpeter equation, providing precise results for systems out of their ground state.\textsuperscript{185,186} However, these are computationally costly, and have consequently a limited application in larger systems or in screening large numbers of them, so they are not completely standard in computational chemistry.

Particularly to the study of N\textsubscript{2} fixation catalysis, recent work includes ab initio models of N\textsubscript{2} adsorption,\textsuperscript{113} study of reaction kinetics on Fe surfaces\textsuperscript{149} or with single-atom catalysts.\textsuperscript{176} A recent study has used DFT techniques for probing alternative N\textsubscript{2} mechanisms on noble metal electrocatalysis, where the reaction is initiated by surface hydrogenation.\textsuperscript{187} In general, these methods can be used to approach modeling questions related to the engineering and functionalization of photocatalyst surfaces to improve selectivity of NH\textsubscript{3} synthesis over H\textsubscript{2} evolution,\textsuperscript{180} clarifying the reaction paths opened by using different materials as catalysts,\textsuperscript{180} explore different aspects of catalyst stability,\textsuperscript{180} and others. The potential of using ab initio methods to drive advances in materials science is only limited by their significant computational requirements, balanced with our reliance on different types of approximations.

Using DFT simulations facilitates the study of reactants, and the interactions between them and with the surface of catalysts, offering an a priori exact solution of the ground state of any system, with other methods such as those mentioned above opening up the simulation of their excited states. The accuracy of DFT is limited, however, by two main reasons: not knowing the exact form of the exchange-correlation (XC) potential between the exchange of indistinguishable electrons, and the intractable complexity that arises when increasing the number of degrees of freedom by considering systems with more electrons. The former is inescapable, but amenable to remarkable progress using different candidates for XC potentials.\textsuperscript{191} The latter limitation can be ameliorated by introducing approximations that reduce the degrees of freedom in the system, but it is nonetheless constrained by using finite computational resources. These cap the size of the system under simulation (or its duration, if considering molecular dynamics). Critically, this is a major difficulty in integrating optical models of plasmonic nanostructures with ab initio simulations of the reaction.\textsuperscript{181} Typical plasmonic nanostructures have features in the order of tens of nanometers, and even in the hundreds,\textsuperscript{182} whereas ab initio techniques are most capable when modeling systems under a few nanometers. Consequently, the study of plasmonic photocatalysis is particularly amenable to designing tailored multiscale models combining different theoretical frameworks, echoing the variety of multiscale approaches employed in computational chemistry.\textsuperscript{150,152,192–194}
approach that was recognized with a Nobel prize in chemistry in 2013.\textsuperscript{195} Multiscale models specifically tailored for plasmonic photocatalysis have the potential of clarifying the detailed dynamics of these complex systems, and move the field towards designing efficient hybrid photocatalysts that take full advantage of these conducting nanoantennas.

While we advance toward the revolutionary promise promised by quantum computing to simulate the quantum behavior of matter beyond today’s capabilities,\textsuperscript{196} research in materials science keeps exploring new theoretical frameworks and computational schemes scaffolding the progress of nanotechnology. A good example of this drive is the wide adoption of techniques from the growing literature in machine learning (ML).\textsuperscript{197} The interaction between these statistical methods and the natural sciences has proven useful in a variety of problems, of which some examples centered around chemistry and nanophotonics include classification tasks of large molecular databases,\textsuperscript{198} rapid screening of candidate single-atom catalysts using predictive techniques generalizing from large datasets,\textsuperscript{199} or solving inverse problems where we need to find a system delivering a target response.\textsuperscript{200,201} Methodologically, these statistical techniques have strongly interacted with different ab initio frameworks, including DFT, to, for example, design new XC functionals,\textsuperscript{202–204} develop powerful hybrid methodologies with quantum mechanical,\textsuperscript{205–208} and molecular dynamics approaches.\textsuperscript{209} On the more applied side, the study of N\textsubscript{2} fixation is of course among the interesting targets of a combined utilization of ML and DFT techniques, and has been used to, for example, rapidly screen single-atom catalysts.\textsuperscript{210,211} MBenes\textsuperscript{212} candidate catalysts for this reaction, or high-entropy alloy catalysts using fully ML techniques.\textsuperscript{213} In the last decade, there have also been efforts to use ML to generate statistical ab initio methods, aiming to large speedups capable of sampling exceedingly large numbers of systems, such as in mapping the space of possible chemical compounds.\textsuperscript{214,215} But it is also important to remember that ML techniques can be also fruitfully applied in tandem with experimental data,\textsuperscript{216} shortening the exploration of the space of parameters underscoring the synthesis of novel materials, facilitating the interpretation of material characterization datasets, or guiding the sampling of catalysts candidates. In a recent example of this latter possibility, Williams et al. employ ML methods to accelerate the discovery of efficient catalysts in the context of NH\textsubscript{3} conversion.\textsuperscript{217}

5.5. Standardization of the Reaction Conditions and Metrics for Ammonia Quantification

In addition to the design of efficient catalytic systems, the reaction conditions, selectivity to the desired product, as well as the NH\textsubscript{3} detection methods should be taken into consideration. To date, reaction parameters, such as illumination source, wavelength range and intensity, solution pH, and catalyst loading, vary among the different available studies, making the comparison between them difficult. In order to facilitate future research, establishing experimental standards should be a community-driven effort. Most of the current studies focus on the use of solar light as an energy source. Therefore, Xe lamps equipped with filters are the most commonly used light sources. Using AM 1.5 G filters is recommended in order to avoid comparison bias concerning photocatalytic activity due to lack of information on optical characteristics. To further ensure comparability, the applied irradiance should be reported as well. Moreover, it is highly advised to report the absolute incident photon flux or the absolute incident radiation power.\textsuperscript{218} Incident photon flux inside the reaction solution may significantly vary (>30%) due to simple differences such as irradiation of a reactor from the bottom or the top.\textsuperscript{219} Semiconductor-plasmonic hybrid materials generally use methanol as a sacrificial hole scavenger to promote the NH\textsubscript{3} production rate.\textsuperscript{117,118,121,123} Apart from compromising the comparability, methanol-driven N\textsubscript{2} fixation can only be considered as a “partial solar-to-fuel-conversion” because a portion of the solar energy is stored in methanol oxidation products. As it was previously described, alternatives to these materials are metal-plasmonic hybrid structures and combinations of plasmonic properties and active sites in single nanostructures, such as MoO\textsubscript{3}-\textsubscript{125,128,130,131} The close proximity of the plasmonic metal and adsorbed N\textsubscript{2} in these systems can allow for faster hot electron injection rather than being mediated through a semiconductor, which can further improve NH\textsubscript{3} production rates without the use of scavengers. Therefore, these structures provide an excellent opportunity that should be further explored. Additionally, combination of defect engineering and external fields, for example, microwaves, electric field, and magnetic field is another promising strategy to further boost photocatalytic N\textsubscript{2} reduction reactions.

As a starting point, in order to standardize the reaction conditions, the N\textsubscript{2} fixation photocatalysis must be measured at environmental conditions, which means measuring the NH\textsubscript{3} production rate at standard temperature and pressure, neutral pH, without scavengers, and under illumination by an AM 1.5 G solar simulator. To directly compare efficiency, all experimental parameters must be the same. Additionally, when two or more products are obtained by N\textsubscript{2} fixation, comparing efficiencies is difficult. In such cases, AQE is more applicable. To determine practical suitability, solar-to-chemical conversion efficiency has been frequently used in most photocatalytic applications, such as water splitting and CO\textsubscript{2} reduction.\textsuperscript{220}

Regarding the selectivity, the N\textsubscript{2} fixation efficiency can be affected by different competitive reactions, most frequently H\textsubscript{2} evolution. The equilibrium potential of N\textsubscript{2} reduction to NH\textsubscript{3} (+0.55 V vs NHE at pH 0) or to NH\textsubscript{4}\textsuperscript{+} (+0.27 V vs NHE at pH 0) is more positive than that of the H\textsubscript{2} evolution, implying N\textsubscript{2} fixation is thermodynamically more likely to occur than H\textsubscript{2} evolution. However, H\textsubscript{2} evolution is kinetically favorable compared with N\textsubscript{2} fixation because H\textsubscript{2} evolution only involves a two-electron process, whereas an N\textsubscript{2} molecule needs six electrons for N\textsubscript{2} fixation. It is worth noting that the presence of H\textsubscript{2} is commonly verified by gas chromatography, which has led to the observation that different materials effectively suppress its production.\textsuperscript{122,128,131} Moreover, the produced NH\textsubscript{4} in the solution may easily be further oxidized to nitrite or nitrate by photogenerated holes and reactive oxygen species.\textsuperscript{221} Even though this issue has not yet received much attention, it is crucial to address it in the future. Exploring the construction of heterojunctions or the Z-schema to separate NH\textsubscript{3} production and water oxidation sites appear as interesting approaches to this problem.
The generally applied experimental setup consists of a double-phase system, where N\textsubscript{2} gas (or air) is blown into an N\textsubscript{2}-saturated water solution containing the uniformly dispersed photocatalyst. However, the poor solubility in water (1.0 mmol L\(^{-1}\) at 25 °C and 1 atm) and low diffusion coefficient (105 cm\(^2\) s\(^{-1}\)) of N\textsubscript{2} can result in mass transfer limitations and unfavorable N\textsubscript{2} adsorption/activation on the photocatalyst. Furthermore, low selectivity to NH\textsubscript{3} could be hardly avoidable in this situation and H\textsubscript{2} evolution could become the dominant process. To overcome these solubility and diffusion limitations, the use of triple-phase flow systems is becoming popular, although the effectiveness of such approach has only been demonstrated in other photocatalytic reactions (e.g., photo-degradation, CO\textsubscript{2} reduction, and bacteria inactivation).\textsuperscript{[222–224]}

In these systems, photocatalysts are suspended at the gas-liquid interface via surface tension regulation, and N\textsubscript{2} gas (or air) is continuously blown into the water/photocatalyst interface. Regarding the concentration of N\textsubscript{2}, which in gas phase is about 140 times higher than its saturation concentration in water, triple-phase systems afford a much higher concentration on the surface of the catalysts, thus potentially providing much higher NH\textsubscript{3} formation rates. In addition, O\textsubscript{2} and NH\textsubscript{3} are separated in both gas phase and water phase on the different sides of the photocatalyst, resulting in the inhibition of the NH\textsubscript{3} oxidation. Furthermore, air can be directly used instead of pure N\textsubscript{2} gas as the source of NH\textsubscript{3} synthesis which significantly reduces the cost of N\textsubscript{2} fixation reaction and contributes to simplifying and standardizing its implementation.\textsuperscript{[22,225]}

Taking into account the low reaction yields, the accurate quantification of NH\textsubscript{3}, which can be hindered by the presence of different interferences, is highly important. The most widely used methods of detection are spectrometric methods based on the Nessler’s reagent (K\textsubscript{2}HgI\textsubscript{4}) or indophenol blue due to the easy operation and cost. However, these methods have some associated shortcomings. An obvious disadvantage of Nessler’s reagent is the toxicity due to the presence of Hg. The reaction time of NH\textsubscript{3} with Nessler’s reagent also affects the accurate quantification of NH\textsubscript{3}. Indophenol dye gradually photodegrades and is prone to undesirable reactions with other amine groups present in the solution. Moreover, the spectroscopic results can be easily interfered by the pH of solution, some organic reagents, or metal ions. For instance, it has been found that methanol can seriously interfere with the detection results of both methods due to the presence of carbonyl compounds that lead to an additional light absorbance, leading to a false increase of the NH\textsubscript{3}
An alternative method to overcome the drawbacks associated with the spectrometric methods is ion chromatography. Compared with spectrophotometry, it has a lower detection limit and the interferences can be easily avoided by selecting the appropriate separation method, separation column, and detection method. In contrast, it is more expensive and requires more complex instrumentation.

In the process of photocatalytic N₂ fixation, various pollution sources such as NH₃ in the catalyst itself, N₂ or water source, or from the dissolution of gases in the environment, may increase the amount of NH₃ detected, causing false positives. Therefore, it is critical to conduct control experiments to distinguish the actual source of N₂ fixation. To this end, the photocatalytic reactions are conducted in a system with ¹⁵N₂ bubbling. Since a distinction can be made between nitrogen isotopes because NMR scalar coupling and molecular interactions between ¹H and ¹⁵NH₄⁺ split the ¹H resonance into a doublet signal with a spacing of 73 Hz, while resonance signals obtained from the ¹H and ¹⁴NH₄⁺ coupling are split into a relatively sharp triplet with a spacing of 52 Hz, the ¹⁵NH₄⁺ produced can be quantified by ¹H-NMR. Apart from the identification of the NH₃ source, quantitative analysis of both ¹⁴NH₃ and ¹⁵NH₃ isotopes can be carried out from the integrated peak areas.[29,226] In fact, NMR is currently considered the most accurate quantitative and qualitative detection method. However, analyzing NH₄⁺ concentrations in the 5–10 μm range with a 600 MHz NMR spectrometer requires acquisition times from 12 to 22 min and analyzing a 1 μm sample with a 900 MHz NMR spectrometer requires up to 1 h to obtain acceptable signal-to-noise.[228,229] Recently Kolen et al. reported a method based on ¹H NMR in which the time required to quantify NH₄⁺ in aqueous samples can be reduced by an order of magnitude by adding 1 mm paramagnetic Gd³⁺. This improvement makes ¹H NMR NH₄⁺ quantification more accessible and reduces the cost of control experiments. The proposed method can detect NH₃ over a wide pH range with high sensitivity (<2%) and exhibits good linearity (R² = 0.999).[230]

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