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New opportunities for efficient N₂ fixation by nanosheet photocatalysts

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Catalytic ammonia synthesis from dinitrogen (N₂) under mild conditions has been considered to be the "holy grail" of N₂ fixation, which is one of the most important chemical processes in the agriculture, biological and industrial fields. Given that current artificial N₂ fixation is still dominated by the energy-intensive Haber–Bosch process, solar N₂ fixation represents an encouraging and fascinating route for carbon-free and energy-saving N₂ fixation. However, its practical application is seriously hampered by surface sluggish reaction kinetics. In this minireview, we share our perspectives on the use of two-dimensional (2D) nanosheets for the manipulation of photocatalytic N₂ fixation. Nanosheet photocatalysts serve as the perfect platform for the engineering of surface active sites, including defects and iron, all of which can not only bolster photon–exciton interaction toward robust charge carriers generation upon light absorption, but also mimic the function schemes of MoFe-cofactor in nitrogenase toward sufficient N₂ binding and activation. These merits endowed by nanosheets photocatalysts provide instructive information on exploring the rich nitrogen photochemistry on solid surfaces and offer new opportunities for the design of novel photocatalysts towards efficient N₂ fixation.

1. Introduction

Naturally occurring N₂ fixation has failed to meet the demands of fertilizer industry in modern times due to explosion of the world's population, making it critical to pursue artificial N₂ fixation technology.^{1,2} The first pioneering large-scale N₂ fixation industry was discovered and advanced by Fritz Haber and Carl Bosch using metal catalysts in the early 1990s. For now, Haber–Bosch process constitutes a key part of earth nitrogen circle and generates 450 million tons of fixed nitrogen a year.³ Unfortunately, positive impacts of industrial N₂ fixation are counterbalanced by its energy-intensive nature. Nonpolar N₂ has a strong N–N triple bond, high ionization energy, and negative electron affinity.⁴ This is the reason why Haber–Bosch process has to be carried out under harsh condition, necessitating both red-hot temperature (300–600 °C) and high pressure (150–250 atm). Besides, Haber–Bosch requires pure H₂ as the feedstock, which is typically supplied from the energy-consuming reaction of methane steam reforming. As a consequence, such a H₂ production process consumes nearly 2% of the annual global supply with a considerable amount of global greenhouse gas being released.¹ Therefore, the develop-

ment of a sustainable N₂ fixation strategy has been a demanding and compelling challenge.

In stark contrast to industrial Haber–Bosch process, nature accomplishes N₂ fixation through nitrogenase enzymes in certain bacteria under ambient temperature and pressure. The large difference in the reaction condition between industrial and biological N₂ fixation raises the question as to why nitrogenase is superior to Haber–Bosch catalysts. The most common nitrogenase complex is composed of two proteins that work collectively: homodimeric Fe protein and heterotetrameric MoFe protein.⁵ Homodimeric Fe protein possesses a high reducing power to supply electrons while the heterotetrameric MoFe protein manipulates the electrons provided to reduce N₂ to NH₃ (Fig. 1a).⁶ The key center residing in MoFe protein is the FeMo-cofactor, which is capable of binding, activation and reduction of N₂. Although the precise mechanistic

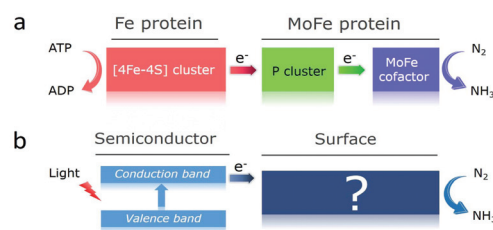


Fig. 1 Schematic illustration of fundamental processes of (a) biological and (b) photocatalytic N₂ fixation.

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details are unclear for now, biological N_2 fixation is still a touchstone and representative model for the development of alternative routes to the Haber–Bosch process by constructing functional models with nitrogenase-like activity.

2. Photocatalytic N_2 fixation

Similar to nitrogenase, semiconductor-based photocatalysis can also achieve N_2 fixation under ambient temperature and pressure. This strategy is very promising due to H_2 not being used, and as inexhaustible solar energy and water can provide active electrons and protons for direct N_2 fixation.⁷ However, contemporary photocatalytic N_2 fixation still suffers from poor quantum yield. The first obstacle limiting the photocatalytic N_2 fixation efficiency arises from the poor interfacial charge transfer that leads to intensive electron–hole recombination, manifesting a weak photon–exciton interaction towards the exciton dissociation.⁸ The second obstacle can be ascribed to the poor energetics of photogenerated electrons. This fact can be exemplified by the direct or proton-coupled one-electron N_2 reduction ($N_2 + e^- \rightarrow N_2^-(aq)$, -4.2 V vs. NHE; $N_2 + H^+ + e^- \rightarrow N_2H$, -3.2 V vs. NHE), both of which are not energetically possible for electrons of most semiconductors.⁹ Considering the function mode nitrogenase, the reason why biological N_2 fixation process appears less “up-hill” can be attributed to the enhanced binding and activation of N_2 on the MoFe-cofactor. In the light of this point, chemists have been attempting to activate the strong N–N triple bond through coordinating N_2 to the unsaturated transition metal complexes (metal = Fe, Mo, Ru and Co) for stoichiometrically transforming coordinated N_2 into NH_3 or N_2H_4 .¹⁰ Photocatalytic N_2 fixation differs from homogeneous N_2 reduction by transition metal complexes or MoFe-cofactor as it is a chemical process occurring on the surface of semiconductors. Hence, its catalytic efficiency is intrinsically related to the surface chemistry of semiconductors. Therefore, it is of great significance to fabricate semiconductors with well-designed surface catalytic sites to ensure efficient charge carriers generation and also mimic the functionality of MoFe-protein for the N–N triple bond activation to improve the overall N_2 fixation efficiency (Fig. 1b).

3. Two-dimensional (2D) nanosheets photocatalysts

Recently, 2D nanosheets catalysts have attracted considerable research attention because of their novel electrical, optical, electronic and mechanical properties, which have found wide applications in energy and environmental fields. Meanwhile, nanosheet photocatalysts can also act as a good model to gain deep insights into the correlations between atomic/electronic structures and their intrinsic properties, as summarized by several pioneering reviews.^{11–13} As for photocatalysis, nanosheets enable facile surface functionality towards the formation of active sites. First, surface defects, can be easily

created on nanosheets with well-engineered surface bond length, dangling bond and disorder degree. Second, nanosheets provide an ultrahigh surface area for the loading of active co-catalysts. As for photocatalytic N_2 fixation, surface defects and co catalysts are able to influence charge carrier kinetics and also affect the kinetics of the surface reaction.

We share our perspectives on the use of 2D nanosheets for the manipulation of photocatalytic N_2 fixation in this minireview. According to the published results, new opportunities can be opened by nanosheets for efficient photocatalytic N_2 fixation. This is because nanosheets photocatalysts can be used as the perfect platform for the engineering of surface active sites, including defects and iron, all of which have been shown to bolster photon–exciton interactions resulting in the generation of facile charge carriers upon light absorption. In addition, they also mimic the roles of MoFe-cofactor in nitrogenase to achieve sufficient N_2 binding and activation.

4. Nanosheets photocatalysts for N_2 fixation

4.1 Oxygen defects of bismuth oxyhalides

Oxygen vacancies (OVs) are the most widely studied and common surface anion defects on oxide surfaces possessing low formation energy. According to our previous results, on a prototypical ternary oxide material of BiOBr, OVs influenced photocatalytic N_2 fixation in two ways.¹⁴ First, the presence of OVs inhibited the electron–hole recombination, according to the enhanced defects emission in the steady-state photoluminescence (PL) spectra, thus facilitating photon–exciton interaction toward robust charge carriers generation *via* trapping hot electrons (Fig. 2a and b). Interestingly, in the N_2 atmosphere, such a PL peak was remarkably quenched due to the accelerated interfacial transfer from BiOBr to N_2 . This phenomenon was closely related to another role played by OVs for reliable N_2 activation. OVs are coordinating unsaturated centers for direct N_2 adsorption, and also prominently electron-rich centers with localized electrons capable of activating N–N triple bond *via* a charge back-donation (Fig. 2c). As supported by density functional theory (DFT) calculations, instant N_2 activation was evidenced by an increased N–N bond length of 1.133 Å between the N–N triple bond (1.078 Å) and double bond (1.201 Å). Since N_2 could be activated on OVs, which was similar to that on MoFe-cofactor in nitrogenase, efficient N_2 fixation was expected due to the facile electron transfer from OVs to the π antibonding orbital of N_2 . According to the work reported by Ye *et al.*, a similar N_2 activation scheme could also be realized on the OVs of Bi₅O₇Br, an important derivative of BiOBr with a novel light-switchable OVs generation characteristic (Fig. 2d).¹⁵

To shed light on the influence of different OV structures on N_2 fixation, and clarify the detailed mechanistic steps of photocatalytic N_2 fixation, we employed BiOCl nanosheets with two surface exposure models as the model photocatalysts.^{16,17} N_2 exhibited a terminal end-on adsorption structure on the OV of BiOCl (001) surface, while on the OV of the (010)

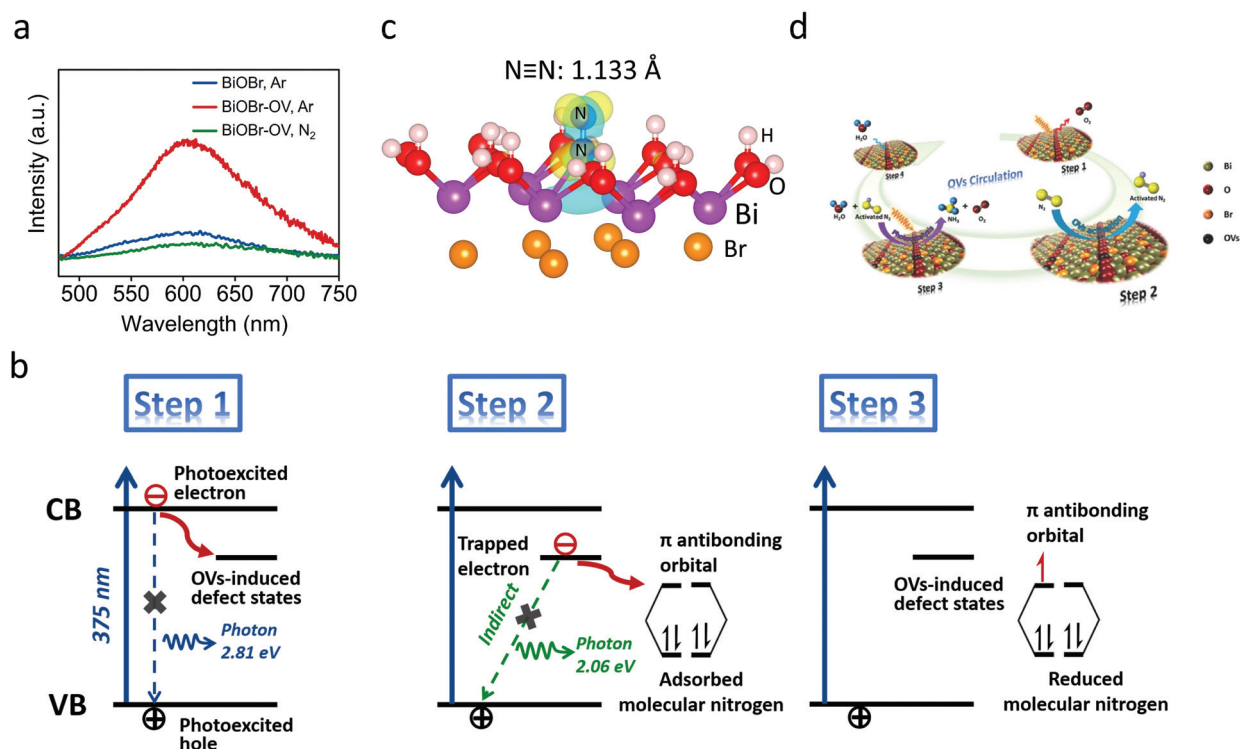


Fig. 2 (a) Steady PL spectra of the as-synthesized BiOBr in different atmosphere. (b) Schematic illustration for OVs-associated interfacial electron transfer for N₂ fixation. (c) Terminal end-on adsorption structure of N₂ on the OV of BiOBr. (d) Schematic illustration of light-switchable OVs generation for N₂ fixation on Bi₅O₇Br. Reprinted with permission from ref. 14 and 15.

surface, it was in a side-on bridging adsorption mode (Fig. 3a and b). On the OV of BiOCl (001) surface, the triple N–N bond was activated to 1.137 Å, while on the OV of the (010) surface it was further elongated to 1.198 Å; close to the value of N–N double bond of N₂H₂ (1.201 Å).

Two widely-accepted mechanisms are proposed over photocatalytic N₂ fixation: **distal and alternating**.^{18,19} In the distal

mechanism, hydrogenation of the uncoordinated N atom in N₂ occurs consecutively to form a terminal nitride intermediate, generating the first NH₃ molecule. Then, the single coordinated N will be converted into another NH₃ molecule (Scheme 1). In contrast, in the alternating mechanism, hydrogenation occurs alternately on the two coordinating N atoms of N₂, generating key intermediates like metal-bound diazene (HN=NH) and hydrazine (H₂N–NH₂) (Scheme 1). Theoretical calculation further revealed that fixation of N₂ in a terminal end-on coordination structure was expected to proceed *via* an asymmetrically distal pathway, in which N₂ fixation preferentially occurred on the N atom away from the OV (Fig. 3c). Coordinating N began to be fixed only after distant N was fully hydrogenated. The fixation of N₂ in the side-on bridging mode was achieved *via* a symmetrically alternative pathway because both the coordinating N atoms shared the same possibility

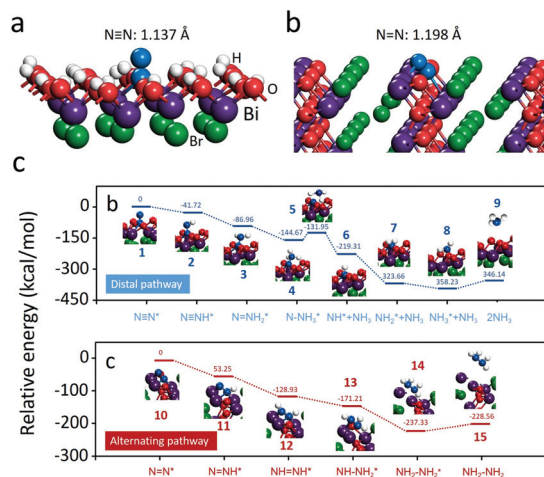
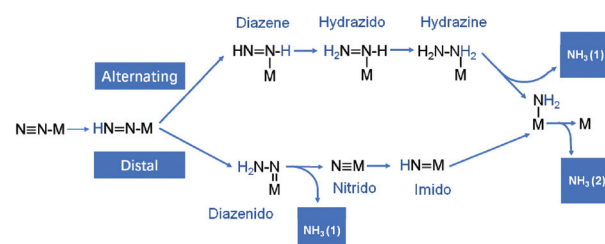


Fig. 3 N₂ adsorption structures on the OV of (a) BiOCl(001) and (b) BiOCl(010) surface. (c) OV-mediated N₂ fixation pathways. Reprinted with permission from ref. 16.



Scheme 1 Distal and alternating pathway for N₂ fixation.

towards hydrogenation, thus generating possible intermediates, including N_2H_2 and N_2H_4 (Fig. 3c). Noticeably, in contrast with uncatalyzed free N_2 fixation which faced high thermodynamic barriers towards the formation of N_2H_2 or N_2H_4 , N_2 fixation on the $\text{BiOCl}(001)$ or (010) surface was thermodynamically accessible due to the presence of molecular steps in low energy created by surface OV. Intrinsic thermodynamically promoted N_2 fixation occurred due to the increase in the Lewis acid/base reactivity upon activation, thus speeding the subsequent electron transfer and proton attack in water.

4.2 Oxygen defects of layered-double-hydroxide

Layered-Double-Hydroxides (LDH) are a new class of promising 2D photocatalysts, because both the constituent metal cation and thickness can be tuned for band structure engineering (Fig. 4a). Zhang *et al.* proposed that OVs or coordinately unsaturated sites could be easily generated when the size of LDH nanosheets was controlled to a few nanometers.²⁰ Well-designed CuCr-LDH nanosheets (CuCr-NS) were synthesized, in which Cr^{3+} showed strong absorption to visible light, while Cu^{2+} acted as the divalent cation to promote defects formation. According to the Cr K-edge extended X-ray absorption near-edge fine structures (EXAFS), distance of first shell Cr-O bond length was around 1.1989 Å, much shorter than that observed on conventionally synthesized bulk CuCr-LDH (CuCr-Bulk) because of the severe structure distortion around the Cr cations, which could be explained by the structural com-

pression in the *ab*-plane in the presence of OVs (Fig. 4b and c). As for photocatalytic N_2 fixation in water, CuCr-NS exhibited superior activity than the bulk counterpart under visible light (Fig. 4d). Presence of OVs within CuCr-NS strongly affected its photocatalytic N_2 fixation performance in two ways. First, OVs introduced prominent defect levels to the CuCr-LDH bandgap with compressive strain, arisen from unoccupied Cr 3d orbitals. These new energy states strengthen photon-exciton interaction *via* promoting the light response region of CuCr-LDH and facilitating the electron-hole separation. Second, OVs increased N_2 adsorption energy and also activated the N-N bond like MoFe-cofactor for kinetically enhanced N_2 reduction after photoexcitation.

Similar OV-mediated efficient sunlight-driven nitrogen fixation could be also achieved over ultrathin TiO_2 nanosheets and Bi_2MoO_6 , another Bi based nanosheet. Using OVs as the N_2 activation sites and plasmonic Au as the hot electrons source, Yang *et al.* achieved a high apparent quantum efficiency of 0.82% at 550 nm for N_2 fixation.²¹ Dong *et al.* purposely introduced unsaturated Mo atoms on the edge *via* oxygen defects through hydrogenation.²² According to the N_2 reduction curves, hydrogenated Bi_2MoO_6 ($\text{H-Bi}_2\text{MoO}_6$) was demonstrated to drive N_2 fixation under low working potential of 0.36 V vs. SCE, much lower than that of conventional Bi_2MoO_6 ($\text{C-Bi}_2\text{MoO}_6$) without defects (Fig. 4e).

4.3 Nitrogen vacancies

Nitrogen vacancies (NVs) are common defects observed in graphite carbon nitride ($\text{g-C}_3\text{N}_4$), a metal-free 2D polymeric photocatalyst consisting of repeating units of tris-triazine in each layer and van-der-Waals force between layers. Similar to OVs, NVs have also been demonstrated to largely improve the photocatalytic performances of $\text{g-C}_3\text{N}_4$ by extending its photo-response, promoting charge carriers separation and enhancing reactant adsorption.^{23–26} Due to the metal-free polymeric character of $\text{g-C}_3\text{N}_4$ with the diverse nitrogen environment, tuning of NVs during synthesis is more facile than that of OVs. Niu *et al.* introduced NVs located at N_{2c} lattice sites *via* controlling the polycondensation temperature. $\text{g-C}_3\text{N}_4$ with NVs displayed enhanced light absorption, restrained charge carriers' recombination and improved performance to generate $\cdot\text{OH}$ radicals.²³ Hong *et al.* prepared nitrogen-deficient $\text{g-C}_3\text{N}_4$ *via* a hydrothermal treatment using ammonium thiosulfate as an oxidant and improved the photocatalytic H_2 evolution rate of pristine $\text{g-C}_3\text{N}_4$ 2 fold.²⁴ Ding *et al.* found presence of NVs within the framework of C_3N_4 due to the loss of NH_x species displayed improved reactivity for the aerobic oxidation of aromatic alcohols to aldehydes under simulated sunlight.²⁵ The concept of NVs for possible N_2 activation was introduced by Dong *et al.*²⁷ They suggested that NVs could behave like a N_2 -imprinted polymer due to its size being similar to that of the N atom in N_2 . Enhanced adsorption and activation of N_2 on NVs was therefore expected. Besides, NVs could also trap photoexcited electrons to facilitate the generation of charge carriers just like OVs. NVs were introduced *via* simply calcining $\text{g-C}_3\text{N}_4$ at 520 °C under a N_2 flow for 2 h (Fig. 5a). Control

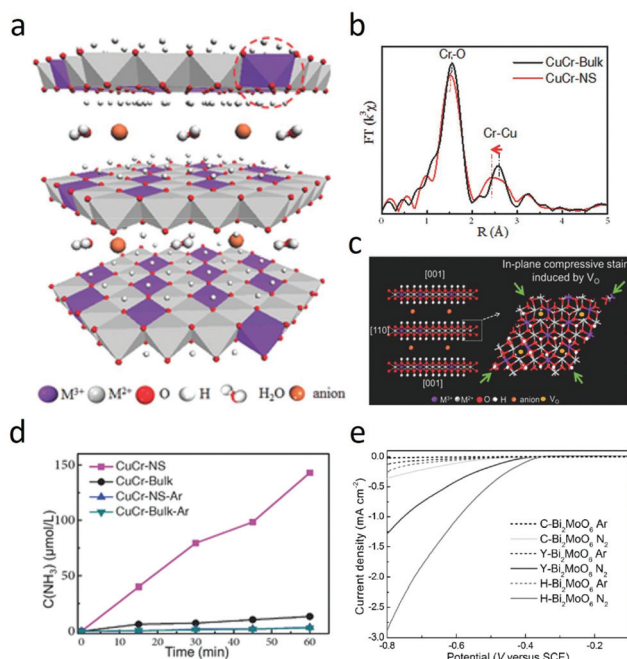


Fig. 4 (a) Schematic illustration of the ultrathin LDH structure. (b) k^2 -weighted FT of Cr K-edge EXAFS spectra. (c) Schematic of the in-plane biaxial compressive strain in CuCr-NS. (d) Photofixation of N_2 fixation over the as-prepared CuCr-LDH in different atmosphere. (e) N_2 reduction and HER polarization curves for $\text{H-Bi}_2\text{MoO}_6$ in comparison with $\text{C-Bi}_2\text{MoO}_6$. Reprinted with permission from ref. 20 and 22.

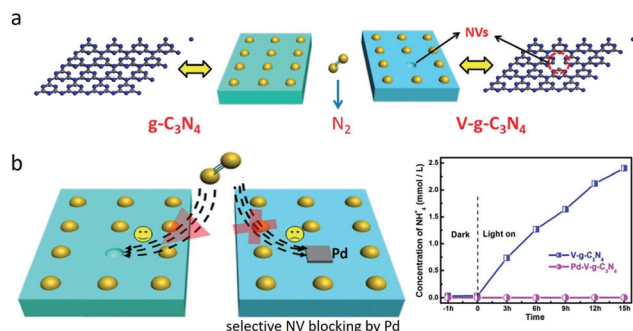


Fig. 5 (a) Preparation process for C_3N_4 with NVs. (b) NVs site blocking by Pd particles for suppressed photocatalytic N_2 fixation. Reprinted with permission from ref. 27.

experiments revealed that NH_4^+ could not be generated without visible light or NVs. $^{15}\text{N}_2$ isotopic labelling experiment further proved that N_2 was the source of the formed NH_4^+ . The strong chemical N_2 adsorption was associated with N_2 activation, as proven by increased N–N bond length (from 1.117 Å to 1.214 Å) according to DFT calculation. Meanwhile, selective block of NVs using metallic Pd completely suppressed the photocatalytic N_2 fixation performance of $\text{V-g-C}_3\text{N}_4$, further confirming N_2 was mainly adsorbed and reduced on NVs (Fig. 5b). $\text{g-C}_3\text{N}_4$ has also been recently demonstrated to be a reliable 2D component for the synthesis of nanocomposites, including $\text{C}_3\text{N}_4/\text{MgAlFeO}$, $\text{C}_3\text{N}_4/\text{graphene oxide}$, $\text{C}_3\text{N}_4/\text{W}_{18}\text{O}_{49}$, $\text{C}_3\text{N}_4/\text{Ga}_2\text{O}_3$, *etc.*, all of which could realize efficient charge carrier separation and photocatalytic N_2 fixation.^{28–31} Unfortunately, the decomposition of $\text{g-C}_3\text{N}_4$ would bring false positive results of NH_4^+ generation, which could not be ruled out by $^{15}\text{N}_2$ isotopic labelling experiments. This phenomenon should be carefully considered when some nitrogen containing photocatalysts or sacrificial reagents are used for photocatalytic N_2 fixation in the future.

4.4 Iron (Fe)

Fe, either in its cation state or metal state, is the key element for biological and industrial N_2 fixation. For instance, the preparation of Fe-based metal complexes for N_2 activation is inspired by the fine structure of FeMo-cofactor, and metallic Fe directly activates N_2 towards dissociation under certain conditions.^{32,33} In photocatalysis, iron doping or loading is a universal strategy to enhance photocatalytic performances of many semiconductor materials, including N_2 fixation. The feasibility of N_2 binding and reduction on Fe was first theoretically evaluated by Azofra and his co-workers.³⁴ Using a 2D MoS_2 as the platform, they theoretically proposed a hybrid structure, where single Fe atoms are deposited on the basal planes of 2H-MoS_2 , mimicking the FeMo-cofactor (Fig. 6a). Bader charge analysis revealed a net charge transfer from Fe to MoS_2 , making Fe a plausible binding site for lone pairs of N_2 . Nature of N_2 –Fe interaction was directly relevant to two major spontaneous $d(\text{Fe}) \rightarrow \pi^*(\text{N}_2)$ charge transfers responsible for the N–N triple bond elongation to 1.14 Å (Fig. 6b).

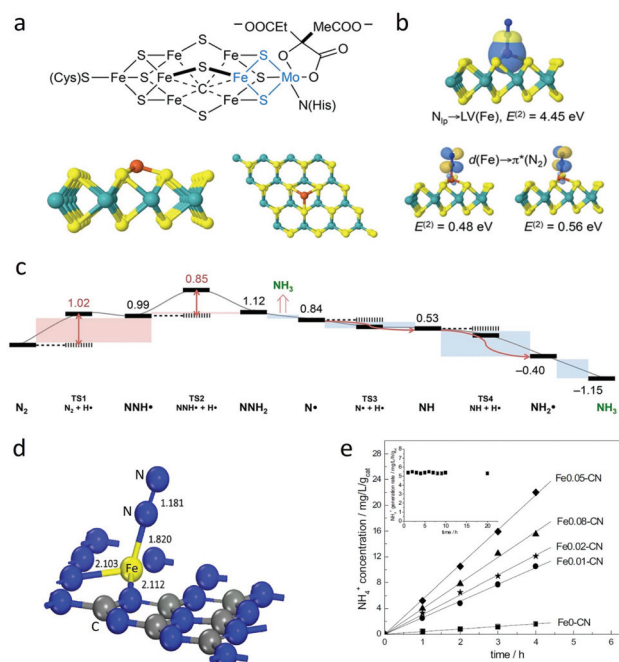


Fig. 6 (a) Schematic illustration of nitrogenase FeMo cofactor and optimized Fe deposited on 2D MoS_2 . (b) Adsorption N_2 on surface Fe atom of Fe-MoS_2 and the corresponding interfacial charge transfer process. (c) Minimum Gibbs free energy path corresponding to N_2 conversion into NH_3 catalyzed by Fe deposited on MoS_2 . (d) Optimized N_2 adsorption Fe-doped C_3N_4 . (e) Influence of Fe concentration on the photocatalytic N_2 fixation performance of C_3N_4 . Reprinted with permission from ref. 34 and 35.

Broader theoretical calculations suggested the N_2 fixation over Fe-MoS_2 would be realized under mild condition and that the rate-determining step is the first H^+/e^- pair with a 1.02 eV energy barrier along with complete N_2 hydrogenation to NH_3 (Fig. 6c). Using C_3N_4 as the substrate, Wu *et al.* directly prepared a Fe^{3+} -doped C_3N_4 (Fe-CN) and evaluated its photocatalytic performance for N_2 fixation.³⁵ Fe^{3+} was found to be directly inserted into the interstitials and was stabilized by C_3N_4 with an electron-rich character through the covalent Fe–N bond. Physical N_2 adsorption on pristine C_3N_4 was accompanied by release of $-14.6 \text{ kJ mol}^{-1}$ energy, while direct chemisorption of N_2 on Fe was evidenced by a large adsorption energy of $-134.8 \text{ kJ mol}^{-1}$ with a lengthened N–N triple bond of 1.181 Å (Fig. 6d). As for the N_2 fixation, Fe-CN with an optimized Fe loading amount showed 13.5-fold higher rate than that of undoped C_3N_4 (Fig. 6e).

Besides MoS_2 and C_3N_4 , graphene was also demonstrated to be an excellent promoter for N_2 fixation. Graphene is single-layered graphite and attracted enormous interest since its discovery due to its excellent mechanical, thermal and electric properties. It can be used as the perfect substrate for the development of functionalized nanocomposites for new applications. Recently, graphene is demonstrated to reach a reverse saturation state with abundant hot electrons above the Fermi level under visible light.³⁶ Following this discovery, Chen *et al.*

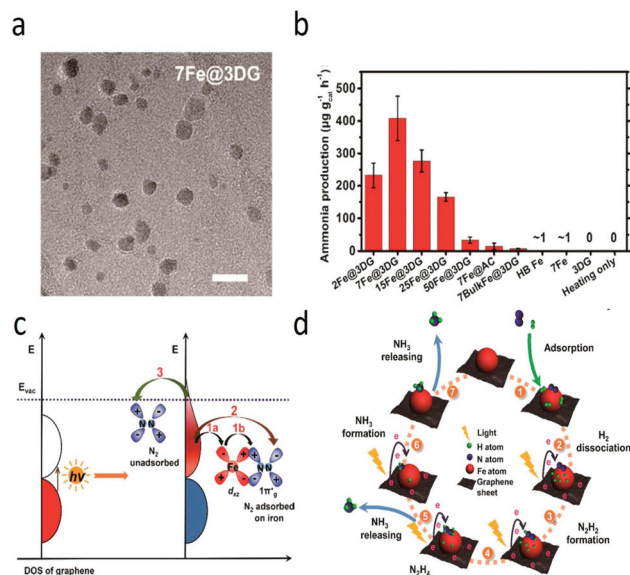


Fig. 7 (a) TEM image of a typical Fe@3DG nanocomposite. (b) Catalytic performance of Fe@3DG with different Fe loading under atmospheric pressure. (c) Proposed three paths of the hot electrons from light illuminated graphene toward prompted N₂ activation. (d) Proposed mechanism for NH₃ synthesis on Fe@3DG. Reprinted with permission from ref. 37.

took full advantage of the light-induced energetic hot electrons from graphene as the direct reducing species to fix N₂ under mild conditions.³⁷ They intentionally loaded iron oxide on a 3D cross-linked graphene material to synthesize a Fe@3DGraphene (Fe@3DG) nanocomposite (Fig. 7a). Under ambient conditions, Fe@3DG was able to synthesize NH₃ using a H₂/N₂ (3/1) mixture gas and an optimized N₂ fixation could be realized *via* tuning the iron loading amount (Fig. 7b). Remarkable N₂ fixation only happened under a certain threshold light intensity where reverse saturation state of graphene was simultaneously achieved. After the threshold, hot electron injection and N₂ fixation increased along with light intensity increase. Hot electrons of graphene can increase the electron density of the loaded Fe nanoparticles, or get

indirectly captured by N₂ *via* a tunneling path, or directly get transferred to N₂ adsorbed on graphene (Fig. 7c). Chen *et al.* proposed a general reaction mechanism associating the N–N dissociation enabled by a synergetic effect between iron and hot electrons of graphene, which proceeded through the intermediates of N₂H₂ and N₂H₄ (Fig. 7d).

Table 1 summarizes the photocatalytic activities of as-mentioned nanosheets photocatalysts for N₂ reduction, which are not totally unified due to different experimental conditions, including light source, temperature, and concentration of the photocatalysts. Hopefully, apparent quantum yield may be generalized as a comparison standard in the future.

5. Summary and outlook

In this minireview, we share our perspectives on the use of 2D nanosheets for the manipulation of photocatalytic N₂ fixation by summarizing the results reported by our group and other groups. We firmly believe new opportunities can be opened by nanosheets for efficient photocatalytic N₂ fixation for two aspects. First, photon–exciton interaction toward facile charge carrier generation upon light absorption can be bolstered. Second, the surface active sites can mimic the function schemes of MoFe-cofactor in nitrogenase toward sufficient N₂ adsorption and activation. These merits endowed by nanosheets photocatalysts provide instructive information on exploring the rich nitrogen photochemistry on solid surfaces and offer new opportunities for the design of novel 2D photocatalysts towards efficient N₂ fixation. Despite many advantages of solar ammonia synthesis without the use of electricity or heat, it is also faced with grand challenges. For instance, produced ammonia can be further oxidized to nitrite or nitrate or photogenerated holes or activated oxygen, which can be circumvented if photocatalytic reactors can be designed well so as to separate these oxidative species with ammonia. Meanwhile, atomistic insights into fundamental mechanisms of photocatalytic N₂ fixation is still in the early stage and require a combination of theoretical calculations and modern *in situ* characterization techniques, including TEM, XPS and FTIR. Moreover, rational engineering of surface active sites on

Table 1 Summary of nanosheet photocatalysts for the reduction of N₂ to NH₃

Catalyst	Reaction medium	Light source	Scavenger	Ammonia generation rate
BiOBr ¹⁴	H ₂ O	λ > 420 nm	None	104.2 μmol g ⁻¹ h ⁻¹
Bi ₅ O ₇ Br ¹⁵	H ₂ O	λ > 400 nm	None	1380 μmol g ⁻¹ h ⁻¹
BiOCl ¹⁶	H ₂ O	Full spectrum	Methanol	92.4 μmol g ⁻¹ h ⁻¹
CuCr-NS ²⁰	H ₂ O	Full spectrum	none	184.8 μmol g ⁻¹ h ⁻¹
Au/TiO ₂ -OV ²¹	H ₂ O	Full spectrum	Methanol	78.6 μmol g ⁻¹ h ⁻¹
H-Bi ₂ MoO ₆ ²²	H ₂ O	Full spectrum	none	1.3 μmol g ⁻¹ h ⁻¹
V-g-C ₃ N ₄ ²⁷	H ₂ O	λ > 420 nm	Methanol	160 μmol g ⁻¹ h ⁻¹
C ₃ N ₄ /MgAlFeO ²⁸	H ₂ O	400–800 nm	Ethanol	417 μmol g ⁻¹ h ⁻¹
C ₃ N ₄ /W ₁₈ O ₄₉ ²⁹	H ₂ O	Full spectrum	Ethanol	144.5 μmol g ⁻¹ h ⁻¹
C ₃ N ₄ /graphene oxide ³⁰	H ₂ O	Full spectrum	Ethylendiaminetetraacetic acid	515 μmol g ⁻¹ h ⁻¹
C ₃ N ₄ /Ga ₂ O ₃ ³¹	H ₂ O	Full spectrum	Ethanol	281.2 μmol g ⁻¹ h ⁻¹
Fe-C ₃ N ₄ ³⁵	H ₂ O	λ > 420 nm	None	325 μmol g ⁻¹ h ⁻¹
Fe@3DG ³⁷	H ₂ /N ₂ , 473 K	UV	None	24 μmol g ⁻¹ h ⁻¹

2D photocatalysts is essential to maximize the overall photocatalytic N₂ fixation, and also enable the understanding of the active sites–catalytic activity relationship. We believe this mini-review will be helpful to researchers in the area of photocatalysis and N₂ fixation.

Conflicts of interest

There are no conflicts to declare.

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