PERSPECTIVE
Jingrun Ran, Shi-Zhang Qiao et al.
Two-dimensional building blocks for photocatalytic ammonia production
Two-dimensional building blocks for photocatalytic ammonia production

Jingrun Ran,†,* Bingquan Xia, Yanzhao Zhang and Shi-Zhang Qiao†,*

Owing to its extensive utilization in fertilizer generation and as an energy carrier, ammonia (NH\textsubscript{3}) is deemed to be one of the most essential chemicals. Currently, NH\textsubscript{3} generation mostly depends on the Haber–Bosch approach under harsh conditions, resulting in tremendous energy usage and environmental problems. Photocatalytic NH\textsubscript{3} generation represents a clean, inexpensive and environmentally friendly method to transform water and nitrogen into ammonia utilizing sunlight under ambient conditions. Recently, two-dimensional (2D) building blocks have received great attention in the photocatalysis field thanks to their outstanding features of high surface area, plentiful reactive sites, ultrathin thickness and short charge-to-surface transfer distance. This perspective summarizes the design and synthesis of photocatalysts prepared utilizing 2D building blocks towards light-driven NH\textsubscript{3} production. Our contribution highlights the in-depth and comprehensive structure/composition–performance relationship in 2D building block based photocatalysts for light-induced NH\textsubscript{3} production. We also discuss the delicate and insightful reaction mechanisms in 2D building block based photocatalytic NH\textsubscript{3} production. Finally, we propose the possible opportunities in merging advanced characterization techniques as well as powerful theoretical computations towards the rational design and fabrication of high-performance 2D material based photocatalysts towards light-induced NH\textsubscript{3} generation.

1. Introduction

As a pivotal feedstock for synthesizing fertilizers and an important energy carrier, ammonia (NH\textsubscript{3}) is produced in an amount of ca. 150 million tons annually worldwide.\textsuperscript{1–23} Presently, industrial-scale preparation of NH\textsubscript{3} still depends upon the conventional Haber–Bosch approach developed in the early 1900s. But this Haber–Bosch process is performed under harsh conditions: elevated temperature (350–550 °C) together with high pressure (150–350 atmosphere pressure) using iron-based catalysts, which utilizes ca. ~1% of global energy supply and large amounts of fossil fuels to produce hydrogen (H\textsubscript{2}) as a feedstock.\textsuperscript{1–33} Hence, the development of a sustainable and environmentally benign strategy to produce NH\textsubscript{3} is of paramount significance.

Dr Jingrun Ran received his BE and ME degrees in Materials Science and Engineering from Wuhan University of Technology, and PhD degree in Chemical Engineering from the University of Adelaide. Now he is working as an ARC DECRA Fellow in Prof. Shi-Zhang Qiao’s group, focusing on the atomic-level design and synthesis of photocatalysts for producing energy fuels and value-added chemicals using renewable solar energy. Dr Jingrun Ran has been recognized as a Clarivate Highly Cited Researcher in 2020.

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Photocatalytic NH₃ production is a clean, cost-effective, and eco-friendly technique capable of converting nitrogen (N₂) and water (H₂O) into NH₃ using renewable solar energy at room temperature and under atmospheric pressure. To realize industrial-scale photocatalytic NH₃ production, the core target is the exploration of highly active, strongly reliable and inexpensive nanostructured materials. Recently, two-dimensional (2D) materials have garnered tremendous attention in a variety of fields (e.g., electronics, catalysis and optoelectronics) ever since the discovery of graphene. Their distinctive features of high surface area, abundant reactive centres, ultrathin thickness and short bulk-to-surface distance make them outstanding building blocks to construct high-performance photocatalysts.

A range of 2D building blocks, e.g., graphitic carbon nitride (g-C₃N₄), BiOCl, BiI₃OBr, BiOBr, layered double hydroxides (LDHs), TiO₂, MoS₂, and SmOCl, have been developed as single-component 2D photocatalysts for NH₃ production. Accordingly, a variety of strategies, e.g., elemental doping, creating vacancies, modification on the termination, producing porosity, and/or crystal facet engineering, have been adopted to tailor the physicochemical characteristics of the above 2D building blocks for achieving enhanced activity, selectivity and stability in photocatalytic NH₃ generation. Besides, heterojunctions based on 2D building blocks have also been designed and prepared for light-driven NH₃ production. A series of binary heterojunctions, i.e., zero-dimensional (0D)/2D, 2D/2D and three-dimensional (3D)/2D, as well as ternary heterostructures, have been explored as efficient, highly selective and robust photocatalysts towards light-induced generation of NH₃.

In this perspective, we for the first time summarize all the photocatalysts synthesized utilizing 2D building blocks towards photocatalytic NH₃ production. The in-depth and overall structure/composition–performance relationship in these 2D building block based photocatalysts is discussed. Additionally, the insightful and delicate reaction mechanisms in photocatalytic NH₃ production are also explained. Finally, we propose the possible opportunities in this research field with special focus on merging the advanced characterization techniques, e.g., aberration-corrected scanning transmission electron microscopy (AC-STEM), synchrotron-based X-ray absorption spectroscopy (XAS), in situ Raman, and in situ Fourier transform infrared (FTIR) spectroscopy, and powerful theoretical calculations, to develop high-performance photocatalysts based on 2D building blocks for NH₃ generation.

2. Merits of 2D building blocks in photocatalytic NH₃ production

The distinct physicochemical features of 2D building blocks endow them with many outstanding merits in photocatalytic NH₃ production: (i) their large surface area and abundant reactive sites facilitate the adsorption/activation/reduction of N₂ into NH₃; (ii) their ultrathin thickness benefits the dissociation and migration of photo-induced charge carriers from the bulk onto the surface; (iii) their large surface area facilitates the formation of electronic coupling with other materials for efficient interfacial charge carrier separation and migration; (iv) their tailorable thickness allows the alteration of band gap width via the quantum confinement effect, accompanied by modulation of light absorption capacity and conduction/valence band edge positions; (v) their highly exposed surface atoms also facilitate the adoption of various engineering strategies (e.g., doping, creating vacancies and single-atom anchoring) to acquire the desired properties and functions.

It should be noted that various types of active sites, e.g., cation/anion vacancies, incorporated heteroatoms, and anchored single atoms, have been developed on 2D material based photocatalysts for efficient
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adsorption, activation and reduction of N₂ to produce NH₃. Each of the above types alone or two types of active sites together could apparently promote the adsorption/activation/reduction of N₂ molecules, as confirmed by experimental characterization, e.g., N₂ temperature-programmed desorption (TPD) and/or theoretical computations, thus leading to apparently improved activity and selectivity in photocatalytic N₂-to-NH₃ conversion.

3. Single-component 2D photocatalysts

Up to now, various single-component 2D photocatalysts have been developed and utilized in photocatalytic NH₃ generation (see Table 1). A series of approaches, e.g., heteroatom incorporation, generation of vacancies, morphology control and surface modifications, have been explored to engineer the properties of these single-component 2D photocatalysts for highly efficient, highly selective and steady light-driven NH₃ generation. They are classified into four categories: (1) g-C₃N₄ based 2D photocatalysts; (2) bismuth based 2D photocatalysts; (3) LDH based 2D photocatalysts; and (4) other 2D photocatalysts, which are introduced in detail as follows.

3.1 g-C₃N₄ based 2D photocatalysts

In recent years, g-C₃N₄ has attracted enormous attention in the photocatalysis field thanks to its appealing properties of appropriate band gap width, favourable band edge positions, reliable stability, earth abundance and excellent processability. Particularly, several g-C₃N₄ based 2D photocatalysts are designed and prepared towards photocatalytic NH₃ generation. Various techniques, including elemental doping, vacancy defect creation, terminal modification and/or porosity generation, have been applied to engineer the physiochemical characteristics and optimize the photocatalytic NH₃ production performance of 2D g-C₃N₄.

Xue et al. reported the synthesis of porous g-C₃N₄ nanosheets with cyano groups and nitrogen defects by alkali-assisted calcination of urea. The as-prepared porous g-C₃N₄ nanosheets with cyano groups and nitrogen defects present an enhanced photocatalytic N₂ fixation rate of 1590 µmol h⁻¹ g⁻¹ in comparison to pure g-C₃N₄ without any co-catalyst under simulated solar irradiation (AM 1.5G). The elevated photocatalytic activity is caused by the synergistic impacts of strengthened light harvesting, advanced photo-induced charge carrier migration and adsorption of N₂ gas molecules. In another study, Zhang et al. synthesized ultrathin g-C₃N₄ nanosheets with abundant carbon vacancies on the surface via the thermal exfoliation route. The as-prepared ultrathin g-C₃N₄ nanosheets display a photocatalytic NH₃⁺ production rate of 54 µmol L⁻¹ in 100 min in the presence of no co-catalysts or sacrificial reagents, about 2.25 times larger than that of bulk g-C₃N₄. Such an improved activity originates from the carbon vacancies on the surface and ultra-small thickness, which favour the efficient charge carrier dissociation and transfer both in the bulk and on the surface. Wang et al. prepared g-C₃N₄ nanoribbons with intercalated K⁺ and cyano groups (mCNN). Compared to the scanning electron microscopy (SEM) (see Fig. 1a) and transmission electron microscopy (TEM) (see Fig. 1a inset) images of pristine g-C₃N₄, the SEM (Fig. 1b) and TEM (Fig. 1b inset) images of mCNN display its ribbon-shaped structures with uniform size, due to the scissoring out effect of molten KOH in the preparation process. A visible-light-driven photocatalytic NH₃ production activity of 3.42 mmol g⁻¹ h⁻¹ was obtained on the as-prepared mCNN, obviously larger than...
that on pristine g-C$_3$N$_4$ (1.11 mmol g$^{-1}$ h$^{-1}$) as displayed in Fig. 1c. Fig. 1d presents the photocatalytic NH$_3$ production amounts of pristine g-C$_3$N$_4$ and mCNN photocatalysts utilizing N$_2$ or Ar as the feed gas. As Ar was utilized as the feed gas without N$_2$, pristine g-C$_3$N$_4$ and mCNN photocatalysts present average photocatalytic NH$_3$ production activities of 0.23 and 0.52 mmol g$^{-1}$ h$^{-1}$, respectively. These results indicate that the nitrogen source of the produced NH$_3$ arises from photocatalysts, as Ar is utilized as the feed gas. Both experiments and theoretical computations support that the cyano group in mCNN is regenerated with the assistance of intercalated K$, similar to the Mars–van Krevelen process. The regeneration of the cyano group results in the improved activity and stability of mCNN. In another study, g-C$_3$N$_4$ porous nanosheets with doped sulphur and carbon vacancies (SCNNNSs) have been prepared via heating melamine and thiocyanuric acid together. A photocatalytic NH$_3$ generation activity of 5.99 mM h$^{-1}$ g$^{-1}$ was acquired in the as-synthesized SCNNNSs using simulated sunlight illumination. This activity is 280% times larger than that of bulk S doped g-C$_3$N$_4$. It was found that the porous sheet structure, ultra-small thickness, and incorporation of sulphur and carbon vacancies induce better photocatalytic performance.

Apart from the above studies, investigations based on theoretical calculations have been applied to study the g-C$_3$N$_4$ photocatalyst for NH$_3$ production. For instance, Lv et al. utilized density functional theory (DFT) based computations to explore the single B atom loaded on holey graphitic carbon nitride (B@g-CN) towards the photocatalytic nitrogen reduction reaction (NRR). The DFT computation results indicate that efficient N$_2$-to-NH$_3$ conversion can be achieved via the enzymatic pathway on B@g-CN with a very low activation barrier of 0.61 eV and overpotential of 0.15 V. These values are lower than those of many metal-based catalysts. Besides, the photo-excited electrons on B@g-CN can sufficiently enable the NRR against the hydrogen evolution reaction (HER). In another study, on the basis of DFT calculation results, Ren et al. found that nitrogen vacancies not only boost the dissociation of photo-excited electron–hole pairs in g-C$_3$N$_4$, but also increase the light absorption. Besides, they also found that the corrugated configuration structure of g-C$_3$N$_4$ favours the N$_2$ adsorption ability, thus improving the photocatalytic N$_2$ fixation activity.

### 3.2 Bismuth based 2D photocatalysts

Due to the fascinating features of adjustable light-harvesting ability, internal electric field, easy creation of surface oxygen vacancy and photochemical stability, 2D Bi-based photocatalysts have drawn tremendous attention recently. Different 2D Bi-based photocatalysts, e.g., BiOCl, Bi$_2$O$_2$Br, and BiOBr, were prepared and adopted for photocatalytic NH$_3$ production. For example, Wu et al. prepared Br doped BiOCl micro-sheets with abundant O vacancies and exposed {001} facets (Br–BiOCl–OV) using a surfactant assisted solvothermal approach and a subsequent ion-exchange method. An NH$_3$ production activity of 6.3 µmol h$^{-1}$ was achieved on the optimized Br–BiOCl–OV utilizing visible light, ca. 150% larger than that of bare BiOCl. The incorporation of the Br ion not only leads to a better N$_2$ activation effect based on theoretical calculations, but also narrows the band gap width as well as raising the conduction band position, resulting in enhanced light absorption and stronger reduction capacity. Besides, Br–BiOCl–OV also presents improved dissociation of photo-induced excitons. The aforementioned effects synergistically cause the elevated photocatalytic NH$_3$ generation rate of Br–BiOCl–OV.

Di et al. synthesized single-unit-cell (SUC) Bi$_2$O$_2$Br nanosheets with confined defects using a polyvinylpyrrolidone (PVP) self-assembly approach. The TEM image of SUC Bi$_2$O$_2$Br nanosheets is displayed in Fig. 1e, confirming their 2D ultrathin nanosheet structure. Abundant point defects are observed on SUC Bi$_2$O$_2$Br nanosheets as shown in the aberration-corrected atomic-resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image (Fig. 1f). The structure model in Fig. 1g presents the surface point defects in Fig. 1f. Accordingly, the line profiles in Fig. 1h indicate that the numerous point vacancies correspond to Bi vacancies confined in SUC Bi$_2$O$_2$Br NSs. The presence of Bi vacancy can significantly increase the production of oxygen vacancies as confirmed by both theoretical computations and experimental results. Fig. 1i exhibits the positron annihilation lifetime spectra of SUC Bi$_2$O$_2$Br NSs with abundant defects and Bi$_2$O$_2$Br with few defects. The acquired positron annihilation lifetime parameters indicate the higher concentration of Bi surface defects in defect-rich SUC Bi$_2$O$_2$Br NSs compared with that of defect-deficient Bi$_2$O$_2$Br NSs. As displayed in Fig. 1j, after one-hour reaction, the defect-rich SUC Bi$_2$O$_2$Br NSs exhibit a larger amount of NH$_3$ (25.4 µmol L$^{-1}$) in a N$_2$ atmosphere, about 9.2 and 30.9 times larger than that of Bi$_2$O$_2$Br NSs with deficient defects and bulk Bi$_2$O$_2$Br, respectively. Besides, no apparent decrease of the photocatalytic NH$_3$ production activity is observed after four cycles (Fig. 1k), suggesting the good stability of defect-rich SUC Bi$_2$O$_2$Br NSs. The enhanced photocatalytic NH$_3$ production performance arises from the efficient dissociation and transportation of photoexcited electrons and holes, owing to their SUC configuration and surface defects. Moreover, Xue et al. fabricated oxygen vacancy engineered BiOBr ultrathin NSs mainly exposed with {001} crystal facets through utilizing PVP in the hydrothermal procedure. The BiOBr ultrathin NSs with oxygen vacancies exhibit about 10 times larger photocatalytic NH$_3$ production rate (54.70 µmol g$^{-1}$ h$^{-1}$) compared to BiOBr nanoparticles in the absence of any oxygen vacancies (5.75 µmol g$^{-1}$ h$^{-1}$). They found that the engineering of oxygen vacancies in BiOBr ultrathin NSs not only reduces the band gap and strengthens the light harvesting, but also raises the conduction band position for stronger reduction capability of photo-induced electrons. Besides, both the experiments and theoretical computations indicate that the adsorption and activation of N$_2$ molecules could be promoted by oxygen vacancies.

### 3.3 LDH based 2D photocatalysts

As a novel category of metal-to-metal charge-transfer (MMCT) based system, LDHs are highly promising in the photocatalysis...
field, owing to their adjustable metal cation components and tailorable thickness combined with engineering of defects and band structures. Thus, a range of LDH based photocatalysts have been developed. For instance, etched ZnCr–LDH presents a photocatalytic NH$_3$ production activity of 33.19 μmol g$^{-1}$ h$^{-1}$ with an apparent quantum efficiency (AQE) of 0.11% at 550 nm, ca. 1000% times larger in contrast to that of un-etched ZnCr–LDH (3.15 μmol g$^{-1}$ h$^{-1}$). The alkali-etching approach not only elevates the conduction band edge of ZnCr–LDH to improve the reduction capacity of photo-induced electrons, but also reduces its band gap for stronger absorption of visible light. Besides, the alkali-etching approach generated vacancies in ZnCr–LDH, which act as trapping centres for photo-induced electrons and elongate the charge-carrier lifetimes. Moreover, unsaturated Zn sites created by the alkali-etching method further favour the adsorption and activation of N$_2$. Hence, boosted photocatalytic NH$_3$ production activities are achieved on the etched ZnCr–LDH. In another report, a facile co-precipitation method was employed to synthesize a range of M$^{III}$M$^{II}$ (M$^{II}$ = Mg, Zn, Ni, Cu; M$^{III}$ = Al, Cr) LDH ultrathin NSs. The TEM images of CuCr LDH ultrathin NSs, suggesting their NS structure with an averaged lateral size of about 20 nm and a thickness of approximately 2.5 nm. The high-resolution (HR)-TEM image of CuCr LDH ultrathin NSs (Fig. 2c) displays a d spacing of 0.24 nm, ascribed to the (009) facet of CuCr LDH ultrathin NSs. As presented in Fig. 2d, the averaged length of the first Cr–O shell within CuCr-NS is 1.989 Å, smaller than that acquired within CuCr-bulk. Furthermore, the Cr in CuCr-NS shows a decreased coordination number of 5.5, in comparison to the Cr in CuCr-bulk (6.0). This result suggests a seriously distorted structure around Cr cations within CuCr-NS, in agreement with the presence of plentiful oxygen vacancies. As presented in Fig. 2f, many LDH NSs exhibit photocatalytic NH$_3$ production activities utilizing visible light ($\lambda > 400$ nm). Particularly, CuCr–LDH NSs display the highest photocatalytic NH$_3$ generation rate of 142.9 μmol L$^{-1}$. Additionally, an apparent quantum yield (AQY) of 0.10% at 500 nm was also obtained on CuCr–LDH NSs. To study the adsorption/activation/reduction of N$_2$ in situ diffuse reflectance infrared Fourier transform spectroscopy was adopted to probe the reaction intermediates on the CuCr–LDH NS surface (Fig. 2g). The characteristic bands at 1661, 1557 and 1448 cm$^{-1}$ correspond to the antisymmetric as well as symmetric deformations of surface NH$_4^+$ species. Both the adsorption/activation of N$_2$ and H$_2$O molecules are promoted via the abundant O vacancies in CuCr–LDH NSs. In addition, the structure distortions and compressive strain caused by the incorporation of Cu$^{2+}$ also result in enhanced interaction between N$_2$ and LDH, thus increasing NH$_3$ production. Furthermore, Zhang et al. have prepared ZnAl–LDH NS with incorporated Cu$^{2+}$ and plentiful oxygen vacancies utilizing an easy co-precipitation route. The Cu modified ZnAl–LDH NS exhibits an outstanding photocatalytic NH$_3$ production activity of 110 μmol g$^{-1}$ h$^{-1}$ in pure water using UV-visible illumination. Excellent robustness in photocatalytic NH$_3$ production was also found on this Cu modified ZnAl–LDH NS. Its outstanding photocatalytic performance arises from the presence of numerous oxygen vacancies...
and electron-rich Cu\textsuperscript{4+} advancing the N\textsubscript{2} adsorption/activation as well as electron–hole dissociation and transportation.

### 3.4 Other 2D photocatalysts

Apart from the above-mentioned 2D photocatalysts, other 2D photocatalysts, such as TiO\textsubscript{2} NSs,\textsuperscript{38} MoO\textsubscript{3–x} nanobelts,\textsuperscript{37} ultrathin MoS\textsubscript{2} NSs\textsuperscript{38} and amorphous SmOCl NSs,\textsuperscript{39} have also been explored for photocatalytic NH\textsubscript{3} generation. For example, Zhao et al.\textsuperscript{36} doped copper in TiO\textsubscript{2} NSs for producing more oxygen vacancies and massive compressive strain. X-ray absorption fine structure (XAFS) was adopted to study the local atomic structure and cation coordination in X\%–TiO\textsubscript{2} \((X = 0, 1, 3, 6, 8)\) resulting from Cu incorporation in the TiO\textsubscript{2} NSs. Fig. 2h presents the magnitude of \(k^2\)-weighted Fourier transforms of Ti K-edge EXAFS for X\%–TiO\textsubscript{2} \((X = 0, 1, 3, 6, 8)\) and bulk-TiO\textsubscript{2}. It is observed that the Ti–O shell peak intensity is increasingly lowered upon the increase of Cu concentration in TiO\textsubscript{2} from 0% to 6%, in agreement with the increase of O vacancies. Fig. 2i seen from Fig. 2j, 6%-TiO\textsubscript{2} presents the largest photocatalytic NH\textsubscript{3} production activities of 1.54 and 0.72 \(\mu\text{mol} \text{g}^{-1} \text{h}^{-1}\) utilizing 600 nm and 700 nm illumination, respectively. Moreover, 6%-TiO\textsubscript{2} shows the excellent reliability of photocatalytic NH\textsubscript{3} production in 5 cycles of testing. The outstanding photocatalytic NH\textsubscript{3} production performance is ascribed to the ample oxygen vacancies and compressive strain arising from the Jahn–Teller distortion via doping Cu, which are supported by a series of characterization techniques, e.g., X-ray diffraction (XRD), XAFS and electron paramagnetic resonance (EPR) spectroscopy, together with theoretical calculations. Moreover, the preparation of oxygen vacancy-rich MoO\textsubscript{3–x} nanobelts was accomplished through adopting a hydrothermal approach.\textsuperscript{40} The oxygen vacancies are found on the \(001\) and \((100)\) crystal facets of MoO\textsubscript{3–x} nanobelts confirmed by the scanning transmission electron microscopy (STEM) characterizations results. Efficient photocatalytic generation of NH\textsubscript{3} via \(\text{N}_2\) reduction was realized on oxygen vacancy-rich MoO\textsubscript{3–x} nanobelts, thanks to the existence of oxygen vacancies benefiting the chemisorption/activation of \(\text{N}_2\) molecules.

The preparation of ultrathin MoS\textsubscript{2} using a hydrothermal method was presented by Sun et al.\textsuperscript{41} The ultrathin MoS\textsubscript{2} exhibits a photocatalytic NH\textsubscript{3} generation activity of 325 \(\mu\text{mol} \text{g}^{-1} \text{h}^{-1}\) utilizing no electron donor or co-catalyst. This excellent photocatalytic activity of ultrathin MoS\textsubscript{2} arises from the light-induced trions activating and converting \(\text{N}_2\) molecules into NH\textsubscript{3} through a simultaneous six-electron reduction procedure.

Hou et al.\textsuperscript{42} have prepared amorphous SmOCl nanosheets (A-SmOCl) utilizing graphene oxide (GO) as a template by a wet-chemical approach. The as-fabricated A-SmOCl displays a photocatalytic NH\textsubscript{3} generation rate of 426 \(\mu\text{mol} \text{h}^{-1} \text{g}^{-1}\) under xenon light illumination (320–780 nm), with an AQY efficiency of 0.32% at 420 nm. Its impressive photocatalytic activity is ascribed to the presence of plentiful O vacancies in A-SmOCl enhancing the \(\text{N}_2\) adsorption/activation and increasing the light absorption range. Besides, the O K-edge XAS result corroborates the strengthened Sm–O covalency, which advances the migration of photo-induced electrons to the chemisorbed \(\text{N}_2\) molecules, thus increasing the photocatalytic activity of A-SmOCl.

For most single-component 2D photocatalysts discussed in Sections 3.1–3.4, the generation of vacancies (e.g., O vacancies, N vacancies and C vacancies) is a general and effective strategy to apparently boost the adsorption of \(\text{N}_2\) molecules and promote their subsequent activation and reduction. Thus, the light-induced \(\text{N}_2\)-to-NH\textsubscript{3} conversion performance is greatly enhanced on these single-component 2D photocatalysts engineered with vacancies.

### 4. 2D material based heterostructured photocatalysts

The unique properties (e.g., large surface area and highly exposed surface atoms) of 2D building blocks benefit their electronic coupling with other materials to achieve efficient interfacial dissociation and transportation of photo-induced charge carriers. In addition, a robust combination can also be achieved to realize high stability in photocatalytic NH\textsubscript{3} production. Hence, various 2D material based heterostructured photocatalysts have been designed and synthesized towards photocatalytic \(\text{N}_2\) reduction (see Table 2).\textsuperscript{43–51} They can be categorized into 0D/2D binary heterostructures,\textsuperscript{43–46} 2D/2D binary heterostructures,\textsuperscript{47,48} 3D/2D binary heterostructures\textsuperscript{49} and ternary heterostructures.\textsuperscript{50,51}

#### 4.1 0D/2D binary heterostructures

0D/2D heterostructured photocatalysts are the most extensively studied binary heterostructured photocatalysts. Based on the intrinsic features of the formed heterojunction, they are classified into metal/semiconductor 0D/2D heterostructures,\textsuperscript{43–44} semiconductor/semiconductor 0D/2D heterostructures,\textsuperscript{44,45} and semiconductor/semimetal 0D/2D heterostructures.\textsuperscript{46}

For instance, Liu et al.\textsuperscript{46} anchored single-atom Ru on TiO\textsubscript{2} NS by impregnation and calcination in an Ar–H\textsubscript{2} atmosphere. Both the aberration-corrected HAADF-STEM and synchrotron-based EXAFS spectra confirm the existence of single-atom Ru on the TiO\textsubscript{2} NS surface. The DFT calculations further reveal the largest adsorption energy of the Ru–O–Ru structure in defective TiO\textsubscript{2} with O vacancies, indicating that the formation of O vacancies via thermal H\textsubscript{2} treatment could stabilize the atomic dispersion of Ru on the TiO\textsubscript{2} NS surface. The single-atom Ru anchored TiO\textsubscript{2} NSs exhibit a higher photocatalytic NH\textsubscript{3} production activity (56.3 \(\mu\text{g} \text{h}^{-1} \text{g}^{-1}\)) than unloaded TiO\textsubscript{2} NSs (22.2 \(\mu\text{g} \text{h}^{-1} \text{g}^{-1}\)) utilizing xenon light. This elevated photocatalytic NH\textsubscript{3} production rate arises from the presence of single-atom Ru facilitating the charge separation/migration via accepting the photo-induced electrons into the empty d orbitals as well as...
## Table 2 Heterostructured 2D photocatalysts for NH₃ production

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Synthesis method</th>
<th>Light source</th>
<th>Reactant solution</th>
<th>NH₃ production</th>
<th>Activity (µmol h⁻¹ g⁻¹)</th>
<th>Quantum efficiency (%)</th>
<th>Stability</th>
<th>Detection method</th>
<th>References (year)</th>
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</thead>
<tbody>
<tr>
<td>0D/2D Ru/TiO₂</td>
<td>Impregnation and calcination in H₂/Ar</td>
<td>Xe lamp</td>
<td>20 vol% ethanol aqueous solution</td>
<td>ca. 3.3</td>
<td>&gt;2 hours</td>
<td>Indophenol blue method</td>
<td>40 (2019)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0D/2D Cu/g-C₃N₄</td>
<td>Impregnation and annealing treatment in N₂</td>
<td>Xe lamp (780 nm &gt; λ &gt; 420 nm)</td>
<td>20 vol% ethanol aqueous solution</td>
<td>186</td>
<td>1.01 at 420 nm</td>
<td>&gt;3 hours</td>
<td>Nessler’s reagent</td>
<td>41 (2018)</td>
<td></td>
</tr>
<tr>
<td>0D/2D Au/TiO₂</td>
<td>Self-assembly via electrostatic attraction</td>
<td>Xe lamp (λ &gt; 420 nm)</td>
<td>10 vol% methanol aqueous solution</td>
<td>130.5</td>
<td>0.82 at 550 nm</td>
<td>&gt;9 hours</td>
<td>Indophenol blue method</td>
<td>42 (2018)</td>
<td></td>
</tr>
<tr>
<td>0D/2D Au/(BiO)₂CO₃</td>
<td>Hydrothermal method and chemical bath deposition</td>
<td>Xe lamp</td>
<td>Milli-Q water</td>
<td>38.23</td>
<td>&lt;1 hour</td>
<td>Indophenol blue method</td>
<td>43 (2017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0D/2D AgInS₄/MXene</td>
<td>Hydrothermal method</td>
<td>Xe lamp (λ &gt; 400 nm)</td>
<td>20 vol% methanol aqueous solution</td>
<td>38.8</td>
<td>0.07 at 420 nm</td>
<td>&lt;15 hours</td>
<td>Indophenol blue method</td>
<td>44 (2019)</td>
<td></td>
</tr>
<tr>
<td>0D/2D AgCl/d-Bi₂O₃</td>
<td>Hydrothermal controllable precipitation approach</td>
<td>Xe lamp (λ &gt; 400 nm)</td>
<td>Deionized water</td>
<td>606</td>
<td>&gt;3 hours</td>
<td>Nessler’s reagent</td>
<td>45 (2019)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0D/2D POM/RGO</td>
<td>Stirring at 85°C using l-ascorbic as the reducing reagent</td>
<td>Xe lamp</td>
<td>Distilled water</td>
<td>130.3 µmol L⁻¹ h⁻¹</td>
<td>&gt;1 hour</td>
<td>Nessler’s reagent</td>
<td>46 (2019)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D/2D MoO₃/BiOCl</td>
<td>Mechanical mixing</td>
<td>Xe lamp (λ &gt; 420 nm)</td>
<td>Deionized water</td>
<td>35</td>
<td>&gt;5 hours</td>
<td>Nessler’s reagent</td>
<td>47 (2019)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D/2D BP/g-C₃N₄</td>
<td>Ultrasound, drying and calcination</td>
<td>Xe lamp (λ &gt; 420 nm)</td>
<td>5 vol% methanol aqueous solution</td>
<td>347.5 µmol L⁻¹ h⁻¹</td>
<td>&gt;20 hours</td>
<td>Nessler’s reagent</td>
<td>48 (2018)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D/2D PrCO₃OH/g-C₃N₄</td>
<td>Hydrothermal method</td>
<td>Xe lamp</td>
<td>10 vol% methanol aqueous solution</td>
<td>8900</td>
<td>&gt;5 hours</td>
<td>Nessler’s reagent</td>
<td>49 (2018)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ternary MoS₂/C–ZnO</td>
<td>Hydrothermal, calcination and photo-deposition</td>
<td>Xe lamp (λ &gt; 420 nm)</td>
<td>5 vol% ethanol aqueous solution</td>
<td>245.7 µmol L⁻¹ g⁻¹ h⁻¹</td>
<td>&gt;24 hours</td>
<td>Nessler’s reagent</td>
<td>50 (2018)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ternary TiO₂@C/g-C₃N₄</td>
<td>One-step calcination</td>
<td>Xe lamp (λ &gt; 420 nm)</td>
<td>20 vol% methanol aqueous solution</td>
<td>250.6</td>
<td>0.14 at 420 nm</td>
<td>&gt;10 hours</td>
<td>Nessler’s reagent</td>
<td>51 (2019)</td>
<td></td>
</tr>
</tbody>
</table>
enhancing the N2 adsorption and activation. In another study, single-atom Cu anchored g-\(\text{C}_3\text{N}_4\) was fabricated by Huang et al.\textsuperscript{43} The as-prepared Cu loaded g-\(\text{C}_3\text{N}_4\) displays a photocatalytic NH3 generation rate of 186 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) utilizing visible-light illumination (\(\lambda > 420\) nm) and a quantum efficiency of 1.01% at 420 nm. Such an activity is ca. 8 times larger than that of unmodified g-\(\text{C}_3\text{N}_4\). The improved photocatalytic performance is ascribed to the active isolated \(\pi\) electrons as well as excellent adsorption capacity on the positively charged Cu ions, as corroborated by EXAFS, \textit{operando} FTIR, \textit{operando} EPR and theoretical computation results. Moreover, Yang et al.\textsuperscript{42} reported the preparation of Au nanosphere loaded TiO2 ultrathin nanosheets (UNSSs) with oxygen vacancies (Au/TiO2\textsubscript{OV}). Fig. 3a shows that Au nanospheres are uniformly dispersed on the surface of TiO2 UNSSs with O vacancies (TiO2\textsubscript{OV}). The existence of OVs was tested by low-temperature EPR analysis. TiO2 and Au/TiO2 exhibit no EPR signals (Fig. 3b). TiO2\textsubscript{OV} and Au/TiO2\textsubscript{OV} display a peculiar OV signal with a \(g\) factor of 1.998, indicating the existence of OVs (Fig. 3b). \(N_2\) TPD was applied to analyze the \(N_2\) adsorption ability of all the as-prepared samples. Both TiO2 and Au/TiO2 samples merely display an adsorption peak, resulting from \(N_2\) physisorption. In comparison, apart from the physisorption peak, both TiO2\textsubscript{OV} and Au/TiO2\textsubscript{OV} exhibit a peak located at a higher temperature, attributed to the \(N_2\) chemisorption (Fig. 3c). This result indicates that \(N_2\) chemisorption occurs at the OV sites on the TiO2 NS surface. The electron migration from OV-induced Ti\textsuperscript{3+} and \(N_2\) is deemed to be the major cause of the \(N_2\) chemisorption. As shown in Fig. 3d, Au/TiO2\textsubscript{OV} presents a photocatalytic NH3 production activity of 78.6 \(\mu\)mol h\(^{-1}\) g\(^{-1}\), ca. 98 and 35 times higher than those of Au/TiO2 and TiO2\textsubscript{OV}, respectively. No noticeable decrease in the photocatalytic NH3 generation rate of Au/TiO2\textsubscript{OV} is observed over five cycles of testing, suggesting its good stability. Fig. 3e illustrates the photocatalytic NH3 production mechanism of the Au/TiO2\textsubscript{OV} system. Under light illumination, hot electrons are produced in Au nanospheres and injected into the TiO2 NS conduction band. Then the hot electrons are trapped in defect states caused by the OV in TiO2 NSs. Subsequently, the hot electrons reduce the N2 molecule adsorption and activation at the OV sites. In the meantime, the hot holes in the Au nanospheres are mainly used up by the methanol as an electron donor. This highly efficient “working-in-tandem” photocatalytic mechanism leads to the outstanding NH3 production performance in the Au/TiO2\textsubscript{OV} system. Furthermore, a chemical bath deposition (CBD) approach was adopted by Xiao et al.\textsuperscript{44} to load Au nanoparticles (NPs) on the surface of [\(\text{BiO}_2\text{CO}_3\)] nanodisks (NDs). An improved photocatalytic NH3 generation activity of 38.23 \(\mu\)mol mg\(^{-1}\) h\(^{-1}\) was observed on the as-prepared Au NP deposited [\(\text{BiO}_2\text{CO}_3\)] NDs in comparison to that of [\(\text{BiO}_2\text{CO}_3\)] NDs alone. This is because Au NPs can increase light absorption and generate hot electrons for N2 reduction as well as rapidly accepting the photo-excited electrons and promoting electron–hole separation.

Several semiconductor/semiconductor 0D/2D heterojunctions have also been developed for photocatalytic NH3 production.\textsuperscript{44,45} For example, 0D AgInS2 NP loaded 2D MXene Ti\textsubscript{1}C\textsubscript{2} NSs were fabricated \textit{via in situ} growth utilizing a hydrothermal method.\textsuperscript{46} The as-fabricated 0D/2D AgInS2/Ti\textsubscript{1}C\textsubscript{2} heterostructure displays a photocatalytic NH3 production activity of 38.8 \(\mu\)mol g\(^{-1}\) h\(^{-1}\) utilizing visible light (\(\lambda > 400\) nm) in 20% methanol aqueous solution. An AQE of 0.07% at 420 nm was also achieved on this 0D/2D AgInS2/Ti\textsubscript{1}C\textsubscript{2} heterostructure. The origin of the excellent photocatalytic NH3-production activity was studied by both experimental characterization and theoretical calculations. The 2D morphology of Ti\textsubscript{1}C\textsubscript{2} NSs and the Z scheme heterostructure formed between AgInS2 and Ti\textsubscript{1}C\textsubscript{2} apparently benefit the photo-induced electron–hole pair dissociation as well as movement. The high specific surface area of Ti\textsubscript{1}C\textsubscript{2} NSs with ample surface reactive sites facilitates the adsorption/activation/reduction of N2. Furthermore, the DFT based theoretical computations also corroborate the spontaneous activation of N2 molecules on Ti\textsubscript{1}C\textsubscript{2} NSs \textit{via} a di-nuclear end-on bound structure. In addition, Gao et al.\textsuperscript{46} fabricated a p–n heterojunction of AgCl/\(\delta\)-Bi\textsubscript{2}O\textsubscript{3} ultrathin NSs by a two-step
approach of hydrothermal reaction and precipitation. The AFM characterization indicates a uniform thickness of ca. 2.7 nm for the AgCl/β-Bi2O3 NSs. Both the high-resolution XPS spectra of O 1s and EPR spectrum confirm the presence of oxygen vacancies. The as-prepared AgCl/β-Bi2O3 NSs present a photocatalytic NH3 generation activity of 606 μmol h⁻¹ g⁻¹ utilizing visible light (λ > 400 nm), apparently higher than that of β-Bi2O3 alone. The boosted photocatalytic activity originates from the construction of a p–n heterojunction suppressing the electron–hole recombination and the oxygen vacancies promoting the chemical adsorption/activation of N2. Besides, the ultrathin 2D NS morphology also facilitates the migration of electrons and holes, thus contributing to the improved photocatalytic activity.

Wang et al. synthesized three types of polyoxometalates (POMs)/reduced GO composites as semiconductor/semimetal 0D/2D photocatalysts for photocatalytic N2 reduction without any co-catalysts or electron donors. The largest photocatalytic NH3 production activity of 130.3 μmol L⁻¹ h⁻¹ was obtained on H4[PMo10V2O40]/reduced graphene oxide. They attribute the excellent performance to three reasons: (i) reduced aggregation of GO with more exposed reactive sites leading to enhanced N2 adsorption; (ii) broad light absorption range and good reductivity and (iii) GO boosting electron migration and inhibiting electron–hole recombination.

4.2 2D/2D binary heterostructures

The integration of two different 2D building blocks to establish a 2D/2D heterostructure is deemed to be an effective strategy because their intimate contact with large interfacial area greatly favours the dissociation and migration of photo-induced electrons and holes as well as strong interaction for achieving excellent stability. For instance, Xiao et al. have synthesized a 2D/2D MoO3/BiOCl composite via electrostatic adsorption. The as-prepared MoO3/BiOCl heterostructure displays an obviously improved photocatalytic activity of 35 μmol g⁻¹ h⁻¹ for N2 reduction to NH3, compared with either pure MoO3 or bare BiOCl, using xenon light irradiation. They ascribed the improved activity to the presence of MoO2 which not only promoted charge carrier migration but also facilitated the adsorption/activation of N2. Furthermore, Qiu et al. combined black phosphorus (BP) NSs with g-C3N4 NSs to form 0.05BPCNS via calcination in an Ar atmosphere. The SEM image of 0.05BPCNS displays a rough surface due to the loading of BP NSs (Fig. 3f). The thickness of 0.05BPCNS is shown to be ca. 4–5 nm in its AFM image (Fig. 3g). Furthermore, as displayed in Fig. 3h, 0.05BPCNS presents an averaged photocatalytic NH3 generation activity of 347.5 μmol L⁻¹ h⁻¹, much larger than that of g-C3N4 NSs (40.5 μmol L⁻¹ h⁻¹) or BP NSs (45.3 μmol L⁻¹ h⁻¹). The time course of photocatalytic NH3 production of 0.05BPCNS in Fig. 3i confirms its excellent robustness. The XPS characterization results indicate the formation of C–P covalent bonds between g-C3N4 NSs and BP NSs, bringing about improved charge carrier separation/transfer efficiency and increased stability owing to the occupation of lone electron pairs on the P atom. This is also corroborated by the time-resolved photoluminescence spectra (Fig. 3j), which indicate the longer charge carrier lifetime of 0.05BPCNS compared with that of CNS. The photocatalytic mechanism in Fig. 3k indicates that the photo-induced electrons on the CNS conduction band are transported to BPNS, where the N2 molecules are adsorbed and reduced to form NH3. In the meantime, the photo-induced holes in the CNS valence band oxidize the methanol.

4.3 3D/2D binary heterostructures

Feng et al. fabricated a LnCO3OH (Ln = La, Pr) coupled g-C3N4 heterostructure using a hydrothermal approach. Fig. 4a shows the TEM image of the LaCO3OH–CN composite. A hexagonal morphology is observed. Moreover, PrCO3OH with an irregular morphology is dispersed on CN (Fig. 4b). As shown in Fig. 4c, LaCO3OH/g-C3N4 and PrCO3OH/g-C3N4 exhibit improved photocatalytic NH3 generation activities of 8200 and 8900 μmol h⁻¹ g⁻¹, respectively. Their activities are much larger than that of g-C3N4 or hydrothermally treated g-C3N4. Besides, both LaCO3OH/g-C3N4 and PrCO3OH/g-C3N4 display robust stabilities over five cycles of reaction. The XRD and high-resolution XPS spectral results of the used LaCO3OH/g-C3N4 and PrCO3OH/g-C3N4...
also confirm the good stabilities of their crystal and chemical structures. Furthermore, the results of the EPR spin-trap test with DMPO in water (Fig. 4d) show four characteristic peaks with an intensity ratio of 1:2:2:1 on LaCO$_3$OH/g-$\text{C}_3\text{N}_4$, ascribed to DMPO$^·$OH. Thus, a Z-scheme heterojunction is proposed to form in LaCO$_3$OH/g-$\text{C}_3\text{N}_4$ (Fig. 4e). First, N$_2$ is adsorbed onto the photocatalysts surface. Upon light illumination, the photo-excited electrons in the LaCO$_3$OH conduction band recombine with the photo-excited holes in the g-$\text{C}_3\text{N}_4$ valence band. The photo-excited electrons on the g-$\text{C}_3\text{N}_4$ conduction band reduce the adsorbed N$_2$ to generate NH$_3$. Simultaneously, the photo-excited holes on the LaCO$_3$OH valence band oxidize the OH$^−$ to form ‘OH. The formed ‘OH is then captured by methanol as the scavenger. Therefore, they ascribe the excellent photocatalytic NH$_3$-production performance of 1 wt% MoS$_2$ loaded carbon coated ZnO (1% MoS$_2$/C/ZnO) to the strong chemical adsorption of N$_2$ and the efficient electron–hole separation caused by the Z-scheme heterojunction with the Ln–N electron migration channel.

4.4 Ternary heterostructures

2D building blocks have also been applied in complex ternary heterostructured photocatalysts to achieve synergistically enhanced photocatalytic NH$_3$ generation.$^{50,51}$ For example, Xing et al.$^{50}$ fabricated a ternary photocatalyst of MoS$_2$ NP loaded carbon coated ZnO NSs (MoS$_2$/C-ZnO) via combining hydrothermal and photo-deposition approaches. The optimized 1 wt% MoS$_2$ loaded carbon coated ZnO (1% MoS$_2$/C-ZnO) shows the largest photocatalytic NH$_3$ production activity of 245.7 μmol L$^−1$ g$^−1$ h$^−1$ using simulated sunlight illumination. This activity is 9.3 and 4.0 times larger than that of ZnO and carbon coated ZnO (C-ZnO), respectively. They ascribed the high activity on 1% MoS$_2$/C-ZnO to the boosted dissociation/migration of charge carriers due to the presence of a carbon layer and MoS$_2$ as electron trappers. The enlarged surface area also contributes to the improved activity. In contrast, C-ZnO exhibits the largest photocatalytic NH$_3$ production activity under visible-light irradiation, since the mixed MXene Ti$_x$C$_{1-x}$Y and melamine was calcined to yield 2D carbon nanosheet-supported TiO$_2$ NPs wrapped with g-$\text{C}_3\text{N}_4$ NSs (TiO$_2$/C/g-$\text{C}_3\text{N}_4$)$^{43}$ The TEM image of TiO$_2$/C/g-$\text{C}_3\text{N}_4$ (Fig. 4f) indicates that TiO$_2$ NPs are dispersed onto the surfaces of C NSs and coupled with g-$\text{C}_3\text{N}_4$ NSs. The high-resolution XPS spectrum of Ti 2p confirms the presence of a large amount of Ti$^{3+}$ in TiO$_2$/C/g-$\text{C}_3\text{N}_4$. As presented in Fig. 4g, an excellent visible-light-driven photocatalytic NH$_3$ generation rate of 250.6 μmol h$^−1$ g$^−1$ accompanied by a quantum yield of 0.14% at 420 nm was obtained on the as-prepared TiO$_2$/C/g-$\text{C}_3\text{N}_4$. This activity is not only ca. 18 and 10 times higher than that of g-$\text{C}_3\text{N}_4$ and TiO$_2$/C, respectively, but also larger than that of a physically mixed TiO$_2$/C and g-$\text{C}_3\text{N}_4$ sample (TiO$_2$/C + g-$\text{C}_3\text{N}_4$). The authors attribute the outstanding activity of TiO$_2$/C/g-$\text{C}_3\text{N}_4$ to its ample surface defects, strong electron-donating capacity, suitable light absorption capability, efficient charge migration and outstanding N$_2$ activation capacity. Besides, the type II heterostructure established between TiO$_2$ and g-$\text{C}_3\text{N}_4$ also improves the efficient electron–hole dissociation and transportation (Fig. 4h).

For the 2D material based heterostructured photocatalysts discussed in Sections 4.1–4.4, it is of central importance to design and fabricate appropriate heterojunctions (e.g., type II heterojunction, p–n junction and Z scheme) with efficient interfacial charge transfer and a strongly bonded interface to accomplish high activity and stability in photocatalytic NH$_3$ production. Besides, both reduction and oxidation active sites could be accommodated on different components in the heterojunction on the basis of the migration direction of photo-induced electrons and holes. In particular, the unique advantages of 2D materials, e.g., high surface area, ultrathin thickness and abundant active sites, are greatly beneficial for achieving the above target.

5. Conclusions and outlook

In summary, the design and preparation of single-component and heterostructured photocatalysts using two-dimensional (2D) building blocks are summarized and introduced. The comprehensive and insightful composition/structure–performance relationships in these 2D material based photocatalysts for ammonia production are discussed. The precise and in-depth reaction mechanisms of these 2D material based photocatalysts are also elucidated. Although some achievements have been made in the above area, there are still many approaches to be developed. For example, it is of great importance to rationally design and fabricate single-component 2D photocatalysts with the following properties: (i) appropriate band gap width for a broad light-responsive range; (ii) desired band edge positions for sufficient redox ability of photo-induced electrons and holes towards the N$_2$ reduction reaction and oxidation reaction (e.g., water oxidation); (iii) ultrathin thickness and high crystallinity for efficient electron–hole dissociation and transportation; (iv) large surface area and massive active sites (e.g., cation/anion vacancies, doped heteroatoms and specific crystal facets with abundant undercoordinated surface atoms). Apart from the four intriguing above-mentioned properties, the rational design and synthesis of heterostructured 2D material based photocatalysts with the following characteristics is essential: (i) complementary band gap widths of different components in the heterostructures for maximizing the light absorption range; (ii) favourable band alignment (e.g., type II heterojunction, p–n junction and Z scheme heterojunction) for high-efficiency electron–hole separation and transfer; (iii) compatible crystal structures of different components for achieving strong binding, thus facilitating fast interfacial charge migration and high stability; (iv) creation of reduction and oxidation active sites on different components based on the electron–hole transfer direction in the heterojunction.

Furthermore, both state-of-the-art characterization techniques, e.g., aberration-corrected scanning transmission electron microscopy, synchrotron radiation-based X-ray absorption spectroscopy, in situ Fourier transform infrared spectroscopy and in situ Raman, and powerful theoretical calculations can be
combined together to explore the overall and in-depth composition/structure–performance correlation in 2D material based photocatalysts. Besides, a range of newly developed in situ or operando characterization methods, e.g., in situ transmission electron microscopy, in situ electron spin resonance spectroscopy, in situ Raman and operando synchrotron-based X-ray absorption spectroscopy, can be adopted to reveal the actual reaction mechanisms in the photocatalytic ammonia production procedure. The acquired insightful and overall composition–structure/performance relationship, together with the revealed reaction mechanisms will further contribute to the design and preparation of brand-new high-performance photocatalysts utilizing 2D building blocks towards light-driven ammonia generation. Moreover, it is highly promising to adopt powerful theoretical computations for a high-throughput screening of photocatalysts with novel compositions and structures. Then these predicted photocatalysts can be rationally designed and fabricated using advanced nanotechnology to achieve efficient, highly selective and steady light-induced ammonia production.

Conflicts of interest

There are no conflicts to declare.

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References

7 X. Yan, D. Liu, H. Cao, F. Hou, J. Liang and S. X. Dou, Small Methods, 2019, 3, 1800501.
8 M. Li, H. Huang, J. Low, C. Gao, R. Long and Y. Xiong, Small Methods, 2019, 3, 1800388.
10 D. Yan, H. Li, C. Chen, Y. Zou and S. Wang, Small Methods, 2019, 3, 1800331.