

## *Supplementary information*

*for*

### **Photocatalysis with atomically thin sheets**

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## 1. Synthesis of atomically thin sheets

Developing convenient, feasible and reliable approaches to fabricate atomically thin sheets with high quality is greatly necessary for studying their properties, function, and photocatalytic applications. By virtue of the continuous progress of material science, a variety of effective preparation methods have been proposed, along with new strategies constantly been updated. Herein, we give a systematic summary of the various kinds of synthetic strategies of atomically thin sheets for photocatalysis, mainly including mechanical cleavage, liquid exfoliation, chemical vapor deposition (CVD), molecular beam epitaxy (MBE) and wet-chemical synthesis, which all have their particular superiorities and limitations. Ideally, all these methods can be divided into two categories: top-down strategies and bottom-up strategies. The top-down strategy refers to the exfoliation of layered bulk materials into few/single-layer atomically thin sheets, during which the weak interlayer interaction (van der Waals) of layered bulk materials was broken by various driving forces, while the covalent bonding in each layer cannot be destroyed. Mechanical cleavage and liquid exfoliation are the two typical top-down methods. The bottom-up strategy refers to the direct fabrication of atomically thin sheets by the regular collection of small building block molecules through chemical reactions, in different precursors at certain experimental environments. CVD growth, MBE, and wet-chemical synthesis are the representative bottom-up methods.

### Mechanical cleavage

Mechanical cleavage, a classical strategy for the exfoliation of layered bulk materials, along with the obtaining of corresponding atomically thin sheets. In a typical process, two pieces of Scotch tape are first attached onto the two parallel surfaces of the layered bulk materials. After that, tear off one piece of the Scotch tape from the bulk materials, during which the number of layers of the bulk materials will be reduced. By repeating the above steps, the thickness of the acquired materials can be effectively controlled. After getting thin-enough target materials on the surface of Scotch tape through several repeated operations, transfer them on the pre-prepared substrate (*e.g.*, the traditional SiO<sub>2</sub>/Si) under gentle pressure. Finally, the Scotch tape is peeled off from the substrate and the target few/single-layer atomically thin sheets is obtained. After the first report of the mechanical cleavage fabrication of single-layer graphene by Geim's group<sup>1</sup> in 2004, many other atomically thin sheets have been successfully prepared by this method, including h-BN, TMDs (MoS<sub>2</sub>, WS<sub>2</sub>, TiS<sub>2</sub>, TaS<sub>2</sub>, NbSe<sub>2</sub>, WSe<sub>2</sub>,

TaSe<sub>2</sub>, *etc.*), BP, MOFs, metal oxides, *etc.* The superiorities of this method are as follows: (1) theoretically, this method can be used to exfoliate all of the layered bulk materials to generate the corresponding atomically thin sheets; (2) by virtue of the no occurrence of chemical reactions during the whole exfoliation process, the generated target atomically thin sheets keep the same crystal structures as their bulk materials. Therefore, the generated target atomically thin sheets possess outstanding crystal quality, and can be acted as the ideal platform for the exploration of their intrinsic properties. In addition to the superiorities, there are also several limitations, restricting its further practical applications: (1) the generation yield of target atomically thin sheets is quite low, and it is almost impossible to meet the actual production applications; (2) normal, a substrate is needed to provide a place for the products to attach, which is unrealistic in business applications; (3) it is relatively difficult for the controlling of the thickness, size, and shape of the produced target atomically thin sheets.

### **Liquid exfoliation**

Liquid exfoliation is another classical top-down fabrication strategy for atomically thin sheets, including direct liquid exfoliation, ion intercalation-assisted liquid exfoliation, molecules intercalation-assisted liquid exfoliation, ion exchange-assisted liquid exfoliation, oxidation-assisted liquid exfoliation, and selective etching-assisted liquid exfoliation.

The direct liquid exfoliation method refers to the direct exfoliation of layered bulk materials into atomically thin sheets in solvents, by breaking the weak van der Waals interaction via sonication or shear force. It is worth noting that suitable solvents can make the layered bulk materials expand slightly, thus enlarging the interlayer spacing and weakening the interlayer interaction. What's more, the suitable solvents can also stabilize the as-fabricated target atomically thin sheets, avoiding their agglomeration. Therefore, selecting suitable solvents is very important for this method. However, the commonly used solvents of this method are organics, *i.e.*, N-methyl-pyrrolidone (NMP) and dimethylformamide (DMF). Up to now, various atomically thin sheets have been successfully exfoliated from their layered bulk materials by this method, including graphene, h-BN, TMDs (*e.g.*, MoS<sub>2</sub>, WS<sub>2</sub>, *etc.*), BP, COFs, MOFs, metal oxides (*e.g.*, MoO<sub>3</sub>, WO<sub>3</sub>, MnO<sub>2</sub>, *etc.*), and coordination polymers *etc.* Simple operation steps, low cost and high-yield make it show great potential in

commercial application. However, there are also several limitations, restricting its further practical applications: (1) It is relatively hard to obtain single-layer nanosheet with large transverse size; (2) The commonly used solvents of this method are organics, which are toxic and harmful to human health. Considering the toxicity of organic solvents, efforts have been made to find the nontoxic solvent using in this method. Fortunately, environment-friendly solvents, which are suitable for this method have been developed. In 2011, Zhang's group<sup>2</sup> found that the mixture of water (with high surface tension) and ethanol (with low surface tension) can be as the green solvent for the fabrication of inorganic graphene analogues (MoS<sub>2</sub>, WS<sub>2</sub>, and BN) by direct liquid exfoliation method. Besides, Xie's group using water as the green solvent successfully fabricated ultrathin 2D g-C<sub>3</sub>N<sub>4</sub><sup>3</sup> and BP<sup>4</sup> by this method.

Using sonication or shear force the weak van der Waals interaction can be broken during the direct liquid exfoliation process, thus achieve the successful exfoliation. However, it is hard to directly exfoliate the layered bulk materials with strong van der Waals interaction. In view of this, various auxiliary exfoliation methods have been developed to reduce the interlayer force and achieve the exfoliation purpose, including ion intercalation-assisted liquid exfoliation, molecules intercalation-assisted liquid exfoliation, ion exchange-assisted liquid exfoliation, oxidation-assisted liquid exfoliation and selective etching-assisted liquid exfoliation.

In a typical process of ion intercalation-assisted liquid exfoliation strategy, some ions are first intercalated between each layer, to enlarge the interlayer spacing and weaken the interaction. Then, exfoliate the intercalated compounds with weakened interlayer forces into ultrathin 2D target products under mild sonication treatment. Various types of ions have been used in this method, such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cu<sup>2+</sup> *etc.* Among them, Li<sup>+</sup> is the most commonly used one, because it is easy for Li<sup>+</sup> to be introduced into the space of each layer owing to its small radius. What's more, H<sub>2</sub> will be generated owing to the reacting of intercalated Li<sup>+</sup> and water, which could further increase the layer spacing. It is worth mentioning that ion intercalation assisted liquid exfoliation method can be divided into chemical method and electrochemical method, according to the ways of ion introduction. Chemical ion intercalation-assisted liquid exfoliation method was first reported by Morrison's group<sup>5</sup> in 1986 for the fabrication of single-layer MoS<sub>2</sub> using n-butyllithium as the intercalator. Up to now, various types of layered bulk materials have been successfully intercalated into atomically thin sheets by this

method, such as MoS<sub>2</sub>, TiS<sub>2</sub>, WS<sub>2</sub>, ReS<sub>2</sub>, MoSe<sub>2</sub>, and Cu<sub>2</sub>WS<sub>4</sub>. The superiorities of this method are as follows: (1) Phase transformation can be induced during the process of ion intercalation, such as the transformation of 2H to 1T of TMDs nanomaterials, which endows them the research value of phase engineering; (2) The as-fabricated ultrathin 2D target products possess rich positive charge, which is beneficial for the adsorption and activation of reaction molecules during the photocatalytic reactions. In addition to the superiorities, there are also several limitations, restricting its further practical applications: (1) Up to now, it is only effective for the fabrication of metal sulfide and graphene, while, metal oxides, MOFs, COFs, *etc.* nanomaterials can't be prepared by this method; (2) The realization of the intercalation of Li ions normally needs high reaction temperature (over 100 °C) and long time (almost 72 h) for some nanomaterials. In view of this, and inspired by Li ions battery system, Zhang's group <sup>6</sup> proposed a novel introduction way of Li ions, that is electrochemical Li ions intercalation, which was driven by electrochemical force and Li foil. Up to now, electrochemical Li intercalation-assisted exfoliation strategy has been widely developed to fabricate various of atomically thin sheets, including graphene, *h*-BN, TMDs (e.g., MoS<sub>2</sub>, WS<sub>2</sub>, TiS<sub>2</sub>), and other metal chalcogenides (e.g., Sb<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>).

Molecule intercalation-assisted liquid exfoliation strategy, whose basic principle is similar to the above-mentioned iron intercalation-assisted liquid exfoliation strategy, has also been widely used for the fabrication of atomically thin sheets. In a typical process, some guest molecules, such as NH<sub>3</sub>, alkyl amines, crystal water, intercalate between each layer, thus enlarging the interlayer spacing and achieving the exfoliation fabrication of ultrathin 2D target products under mild sonication treatment. It is necessary to mention that in 2015, Cheon's group <sup>7</sup> proposed a novel tandem molecule intercalation-assisted liquid exfoliation strategy for the effective exfoliation of transition metal chalcogenides. The basic idea of tandem molecule intercalation is first open the interlayer space by short intercalated molecules, and then further enlarge the opened interlayer space by long intercalated molecules.

The basic principle of ion exchange-assisted liquid exfoliation strategy is to replace the original small radius ions existing in the interlayer with guest large radius ions through an ion exchange process, so as to increase the interlayer spacing and weaken the interlayer interaction. Up to now, various

atomically thin sheets have been successfully exfoliated from their layered bulk crystals, including metal oxides, LDHs, and metal phosphorus trichalcogenides. The exchanged ions can be divided into cation and anion. The cation exchange process occurs in the exfoliation of layered metal oxides and metal phosphorus trichalcogenides, while anion exchange process occurs in fabrication of LDHs. In spite of the large-scale production of target atomically thin sheets, there are also several limitations of this method: (1) Up to now, it is only effective for the fabrication of some metal oxides, metal phosphorus trichalcogenides, and LDH, while, MOFs, COFs, h-BN, TMDs, *etc.* nanomaterials can't be prepared by this method; (2) During the fabrication of LDH, some toxic organic solvents (*e.g.*, formamide) are used, which are difficult to remove owing to their high boiling point. Besides, owing to the taking place of chemical reactions in this method, the chemical formula of the as-prepared atomically thin sheets is a little different from the original bulk material.

Selective etching-assisted liquid exfoliation strategy, a typical method for the fabrication of MXenes by exfoliating the bulk layered MAX phases, was first developed by Gogotsi's group<sup>8</sup> in 2011. In a typical process, the strong M-A metallic bonding interlayer forces are broken by the strong etching agent (*e.g.*, HF), etching away the A layers. After that, the remaining  $M_{n+1}X_n$  holds loose packaging and can be easily exfoliated into single/few-layer ultrathin 2D MXenes with the help of subsequent mechanical force. Up to now, various types of MXenes have been successfully fabricated by this method, such as  $Ti_2C$ ,  $Al_3C_3$ ,  $Ti_4N_3$ ,  $V_2C$ ,  $Ti_3CN$ ,  $Ta_4C_3$ ,  $Mo_2TiC_2$ . The most obvious advantage of this method is that there are abundant functional groups (such as OH, F, O, H) on the surface of the synthesized MXenes material, which is conducive to the stability of the MXenes and the photocatalytic reaction. The limitation of this method is that it is only effective for the fabrication of MXenes, and not all the MXenes can be prepared from the MAX phases by this method. Besides the uses of strong corrosive chemical (HF) makes this method is relatively dangerous.

### **Chemical vapor deposition growth**

CVD growth is a classical bottom-up strategy for the fabrication of atomically thin sheets on substrates (*e.g.*, the traditional  $SiO_2/Si$ ). In a typical process, the vaporized reactive precursors pass through the surface of the target substrate with the specific gas flow under high temperature and high vacuum environment, during which the precursors undergo reaction and/or decomposition, in situ nucleation

and growth on the substrate surface, thus forming the ultrathin 2D films. After the reported of the fabrication of few-layer graphene via CVD growth strategy in 2006<sup>9</sup>, various types of atomically thin sheets, such as TMDs, metal oxides, h-BN, and topological insulators (such as, In<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub>) have been successfully prepared by this method. The most obvious superiority of this method is that it can produce size-thickness-controllable and high-quality atomically thin sheets in large quantities. However, there are also some limitations, which hinders its further applications: (1) The working environment is relatively harsh, always needs high temperature and high vacuum; (2) A original substrate is needed to provide a plane for the target 2D products to grow, which adds the extra step of transferring the products from original substrate to desired substrate for further explorations and applications. Therefore, efforts should be made to try to realize the growth of target product on arbitrary substrates, thus avoiding the extra and complicated transfer process. Besides, trying to achieve the high-quality growth of target product at low temperature is also worth the efforts.

### **Wet-chemical synthesis**

Wet-chemical synthesis, a typical bottom-up strategy for the fabrication of atomically thin sheets by solution chemical reactions, during which specific surfactants are normally added to achieve the goal of regulating and stabilizing target products. Up to now, various types of wet-chemical synthesis strategies have been developed, including hydro/solvothermal method, hot-injection method, 2D-oriented growth, self-assembly growth, 2D-templated growth, interface-mediated synthesis, and on-surface synthesis. Their overall superiority includes: (1) These methods can be used to fabricate almost all of the nonlayer structured 2D nanomaterials, *e.g.*, Au, Pd, TiO<sub>2</sub>, CeO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, PbS, CuS; (2) Their high-yield, easy-control and low-cost features endow them great application prospect in industry. However, the limitation of these methods is that the synthesis process is easily affected by the reaction conditions (*e.g.*, temperature, time, types and concentrations of precursors, solvents, and surfactant), which makes it difficult to synthesize monolayer nanomaterials.

Hydro/solvothermal method is a typical wet-chemical synthesis strategy, which occurs under high temperature and high pressure in a sealed vessel and uses water/organic solvent as the reaction medium. Various ultrathin 2D photocatalysts, especially inorganic semiconductor photocatalysts have been fabricated by this method, such as transition metal oxide (TiO<sub>2</sub>, WO<sub>3</sub>, ZnO, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>), TMDs

(MoS<sub>2</sub>, *etc.*). In addition to the common superiority and limitations of chemical method, hydro/solvothermal synthesis method also has its own unique characteristics. Due to the limitation of reaction place (sealed autoclave), it is difficult to study the growth mechanism of target atomically thin sheets during the synthesizing process, which makes it hard to extend this method to other atomically thin sheets' synthesis.

The hot-injection method is considered to be an effective strategy for colloid synthesis, which can induce chemical reaction by rapidly injecting active reactant molecules into a hot solution containing special surfactants (long chain oleylamine and/or oleic acid). After the first report of the hot-injection fabrication of cadmium chalcogenide (CdSe) nanocrystals by Bawendi's group<sup>10</sup> in 1993, many atomically thin sheets (especially 2D metal chalcogenide) have been successfully prepared by this method, including CdTe, GeS, GeSe, CuS, TMDs (*e.g.* TiS<sub>2</sub>, ZrS<sub>2</sub>, TaS<sub>2</sub>, TiSe<sub>2</sub>), *etc.* As an effective method for the preparation of ultrathin 2D colloidal metal chalcogenide with excellent quality in dispersion, purity and uniformity, hot-injection method also shows some limitations: (1) The uses of hard-to-remove surfactants (long chain oleylamine and oleic acid) are unfavorable for photocatalytic applications; (2) The uses of high boiling point solvent lead to the needs of high reaction temperature (over 300 °C); (3) The special operation of the precursor injection leads to the impossibility of mass production.

Self-assembly growth is another promising wet-chemical synthesis strategy used for the fabrication of atomically thin sheets. In a typical process, 0D or 1D nanocrystals are directionally connected and fused with each other to form the target atomically thin sheets. In this process, the driving force of directional control is dipole moment, or/and small positive charge, or/and directional hydrophobic attraction. After the first report of the fabrication of ultrathin 2D CdTe nanomaterial by self-assembly growth of thin CdTe nanocrystals by Kotov's group<sup>11</sup> in 2006, various ultrathin 2D CdTe nanomaterials have been successfully prepared by this method, such as ultrathin 2D Cu, ultrathin 2D Au, ultrathin 2D PbS, and ultrathin 2D Eu<sub>2</sub>O<sub>3</sub>, *etc.*

The 2D-oriented attachment is an effective wet-chemical synthesis strategy for the fabrication of nanomaterials with ultrathin 2D structure, which is actually belongs to the self-assembly growth strategy and is worth discussing separately owing to its well-studied and widely-used features. In a



typical process, tiny nanocrystals are directionally connected to each other by sharing the specific high energy crystal plane to form ultrathin 2D nanostructure. In 2010, Weller's group<sup>12</sup> firstly reported the 2D-oriented attachment fabrication of ultrathin 2D PbS nanomaterials from tiny PbS nanocrystals. Since then, various atomically thin sheets have been prepared by this method, such as PbSe, SnSe, Bi<sub>2</sub>Se<sub>3</sub>, *etc.*

2D-templated growth is considered to be an effective strategy for the synthesis of 2D anisotropic nanostructures, which uses the pre-fabricated 2D nanosheet or bulk substrates as guide-templates. Up to now, a variety of 2D-templated growth fabrication of atomically thin sheets have been reported, such as the preparation of ultrathin 2D *hcp* Au square by using the GO nanosheet as template, the fabrication of ultrathin 2D  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheet by using CuO nanoplate as the template, the synthesis of ultrathin 2D NiO nanosheet by using layered  $\alpha$ -Ni(OH)<sub>2</sub> nanosheet as the template, and the synthesis of ultrathin 2D CuInS<sub>2</sub> nanosheet by using CuS nanoplate as the template.

Interface-mediated synthesis, the basic principle of which is to confine the organic ligand at the air/water interface before reacting with metal source dissolved in water, has been considered as an effective strategy for the fabrication of ultrathin 2D metal organic nanomaterials. In a typical process, organic ligand is first dissolved in volatile organic solvents (*e.g.*, chloroform). Then, drop the solution onto the top of the metal salt aqueous solution. With the rapid volatilization of organic solvents, the organic ligand will be confined at the air/water interface owing to the low solubility in water of organic ligand. Finally, organic ligand reacts with metal ion at the 2D air/water interface to form 2D target product, can be expediently transferred to any target substrates. In 2011, Schlüter's group<sup>13</sup> first reported the fabrication of ultrathin 2D coordination polymers (CPs) nanomaterials at the water/air interface. Since then, this method has been widely used to prepare other atomically thin sheets, especially for polymers (COFs, MOFs, *etc.*). Besides, ultrathin 2D inorganic nanosheets, such as ZnO, have also been successfully prepared by this method.

On-surface synthesis has been regarded as a promising strategy for the fabrication of ultrathin 2D COF nanomaterials. In a typical process, some certain monomers of the corresponding COF are first casted on the substrate surface. Then, these monomers polymerize with each other to form ultrathin 2D COF nanomaterials under the surface confinement of solid substrate. In 2013, Lei's group<sup>14</sup> first achieved

the fabrication of ultrathin 2D imine-based COF by this method on the surface of highly oriented pyrolytic graphite. An important requirement of on-surface synthesis method is that one of the monomers must be more volatile than the main monomer. The purpose of this request is to ensure that the main monomer does not decompose before the volatile monomer evaporates.

## 2. Family members of atomically thin sheets

Atomically thin sheets hold abundant family members, including graphene, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), hexagonal boron nitride (h-BN), black phosphorus (BP), transition metal dichalcogenides (TMDs), layered double hydroxides (LDHs), metals, MXenes, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), to name but a few. Additionally, the 2D structures of some classical photocatalysts have also been successfully prepared, such as TiO<sub>2</sub>,<sup>15</sup> WO<sub>3</sub>,<sup>16</sup> Bi<sub>2</sub>O<sub>3</sub>,<sup>17</sup> BiVO<sub>4</sub>,<sup>18</sup> InVO<sub>4</sub>,<sup>19</sup> Bi<sub>2</sub>WO<sub>6</sub>,<sup>20</sup> CdS,<sup>21</sup> ZnIn<sub>2</sub>S<sub>4</sub>,<sup>22</sup> and BiO(Cl, Br, I),<sup>23</sup> which enrich the family members of atomically thin sheets. Besides, some newly developed atomically thin sheets, such as ferroelectric AgBiP<sub>2</sub>Se<sub>6</sub>,<sup>24</sup> graphdiyne,<sup>25</sup> germanium telluride (GeTe),<sup>26</sup> hematene,<sup>27</sup> and gersiloxene (HGeSiOH),<sup>28</sup> have also shown application prospects in the fields of photocatalysis.

**Graphene.** Graphene, an allotrope of carbon, possesses a 2D single-atom-layer structure. In the monatomic layer, each carbon (C) atom is connected with three neighboring C atoms by  $\sigma$ -bond, forming a hexagonal-close-packed carbon network structure. Graphene has been widely used as cocatalyst in the field of photocatalysis because of its excellent properties. Its ultra-high carrier transfer rate at room temperature can promote the transmission of photogenerated electrons, accelerate the separation of photogenerated electron-hole pairs, inhibit their recombination, and improve the quantum yield of photocatalytic materials. It can expand the light absorption range and enhance the light absorption intensity of the photocatalysts. Its large specific surface area and excellent physical adsorption performance are also one of the main reasons to improve the photocatalytic efficiency. In addition to the above functions, it can also be used as a support carrier, which can make the photocatalyst disperse evenly and effectively inhibit its agglomeration; it can also be used as a light stabilizer to inhibit the photochemical corrosion of photocatalyst, etc.

**g-C<sub>3</sub>N<sub>4</sub>.** The g-C<sub>3</sub>N<sub>4</sub>, an analogue of graphite, shows typical 2D layered structure. In the monatomic layer, alternating carbon (C) and nitrogen (N) atoms are connected by sp<sup>2</sup> bond, forming a N-substituted graphite framework structure. g-C<sub>3</sub>N<sub>4</sub> holds a suitable band gap (~2.7 eV), visible-light-responsivity, high stability, and has become a new research hotspot in the field of photocatalysis.

**h-BN.** Single-atom-layer h-BN, also be called white graphene, holds a typical 2D layered structure

with similar structural features and lattice parameters as graphene. In the monatomic layer, alternating boron (B) and nitrogen (N) atoms are connected by covalent bond, forming a hexagonal-close-packed network structure. Besides, the adjacent layers, with a distance of 3.3 Å, are held together by van der Waals forces. h-BN nanomaterial possesses wide band gap (~5.5 eV), excellent chemical, thermal stability and wide range of photocatalytic applications, including H<sub>2</sub> production, CO<sub>2</sub> reduction, and organic pollutants degradation.

**BP.** BP, the most stable form of the allotrope of phosphorus, possesses a 2D layered structure similar to graphene. In the monatomic layer, each phosphorus (P) atom is connected with three neighboring P atoms by covalent bond, forming a corrugated honeycomb structure. What's more, the adjacent layers, with a distance of 5.4 Å, are held together by van der Waals forces. BP nanomaterial holds a tunable band gap (0.3 -2 eV), endowing it a wide range of optical properties from visible to near infrared (NIR) region.

**TMDs.** TMDs, commonly marked as  $MX_2$  ( $M$ : transition metal elements from group IVB to group VIII;  $X$ : S, Se and Te elements of group VIA), are also typical atomically thin sheets. Each TMD monolayer contains three atom-layers, forming a “ $X-M-X$ ” sandwich structure. Besides, the adjacent monolayers, with a distance of 6-7 Å, are held together by van der Waals forces. Similar to BP, 2D TMDs nanomaterials also possess tunable band gap. With MoS<sub>2</sub> as exemplification, the indirect band gap bulk MoS<sub>2</sub> semiconductor with 1.3 eV band gap gradually changes to direct band gap ultrathin 2D MoS<sub>2</sub> semiconductor with 1.8 eV band gap, as the number of layers decreases. The suitable band positions of monolayer MoS<sub>2</sub> making it to be a potential photocatalytic material for H<sub>2</sub> production.

**LDHs.** LDHs, also known as anionic clays, possess host-guest layered structures, which are composed of positively charged metal cation layers and charge-balancing anion layers or guest solvation molecules and introduced interlayer water molecules. Their general chemical formula is  $[M^{z+}_x M^{3+}_x (OH)_2]^{m+} [A^{n-}]_{m/n} \cdot yH_2O$  ( $M^{z+}$ : divalent metal ions, such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>;  $M^{3+}$ : trivalent metal ions, such as Al<sup>3+</sup>, Fe<sup>3+</sup>, Mn<sup>3+</sup>;  $A^{n-}$ : anion or solvation molecules, such as SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, RCO<sub>2</sub><sup>-</sup>, locating in the void of water bearing interlayer). The metal cations occupy the centers of octahedra whose vertexes, containing hydroxide ions, are shared and connected together to form 2D layers. Owing to the variousness of metal cations ( $M^{z+}$  or  $M^{3+}$ ), the interlayer anion and solvation

molecules ( $A^{n-}$ ), and the different value of  $x$ , LDHs involve rich isostructural materials. Besides, in virtue of their easily tuned cation-anion properties, their band gap can be effectively regulated.

**Metal.** The metal atoms are closely connected with the surrounding ones and commonly form three different crystal structures, that is face center cubic (*fcc*) structure, hexagonal close-packed (*hcp*) structure, or body center cubic (*bcc*) structure. In the *fcc* unit cell, there are one atom in each of the centers of the 6 faces and the 8 corners. Besides, each face atom is shared by the adjacent face of other unit cell, and each corner atom is shared by 8 unit cells. In terms of the *hcp* structure, there are one atom in each of the 12 corners of the unit cell to form a hexagonal cylinder, what's more, there are also one atom in the center of the upper and lower surfaces, and three atoms in the inner middle layer of unit cell. Besides, each face atom and corner atom are shared by 2 unit cells, and 6 unit cells, respectively. In the *bcc* unit cell, there are one atom at its the center, and eight atoms at its corners. Besides, each corner atom is shared by 8 unit cells. Most noble metals (*e.g.*, Au, Ag, Ir, Rh, Pt, Pd, *etc.*) show *fcc* structure, except Ru and Os metals, which possess *hcp* structure. The role of metal atoms in photocatalysis is similar to that of graphene. It can accelerate the separation of photogenerated electron-hole pairs, expand the light absorption range and enhance the light absorption intensity of the photocatalysts, and act as the photocatalytic reaction sites.

**MXenes.** MXenes, with common formula of  $M_{n+1}X_nT_x$  ( $n=1, 2$  or  $3$ ;  $M$ : transition metal element;  $X$ : carbon and/or nitrogen element;  $T_x$ : -OH, -F, or -O functional group), holds a graphene-like 2D structure. Different types of MXenes possess distinctive band gaps from 0 to 2 eV. For instance,  $M_2C$  ( $M = Ti, Zr, Hf, Sc$ ) nanomaterial have the band gaps between 0.24 and 1.8 eV. It is noteworthy that, there are rich hydroxy group on the surface of MXenes, which can be acted as the anchor sites for the adsorption and activation of organic reactant molecules.

**COFs.** COFs, new organic porous crystalline materials, hold periodic porous COF ordered framework structure. This ordered structure was built by the covalently connected organic units, which are composed of light elements, such as H, O, C, N, and B. 2D COFs nanomaterials show layered structure. In the monolayer, organic units were connected by strong covalent bonds. Besides, the adjacent monolayers are held together by van der Waals forces, forming periodically aligned channels parallel to the stacking direction. 2D COFs nanomaterials possess excellent crystal structure, uniform pore

structure, and controllable band gap, endowing them great potential for photocatalytic applications. Note that, the band gap of COFs can be effectively regulated by decorating some active functional groups (carboxyl, hydroxyl, amino, *etc.*) on their framework.

**MOFs.** MOFs, a kind of crystalline porous compound materials, possess a periodic grid structure. This grid structure was constructed by the connecting metal/metal oxygen clusters through oxygen/nitrogen-containing multidentate organic ligands. Depending on the diversity of coordination modes composed of organic ligands and metal/metal oxygen clusters, multifarious types of MOFs with distinctive crystal structures can be formed. It is worth pointing out that the metal-oxygen units of 2D MOFs nanomaterials can be seen as the isolated semiconductor quantum dots (QDs). What's more, the charge transitions also occur between organic ligands and metal/metal oxygen clusters, resembling the process of charge transition from VB to CB in semiconductor materials. These unique features of 2D MOFs endow them the properties of semiconductor photocatalyst. Besides, the photocatalytic properties of 2D MOFs can be adjusted by altering the species of metals center and organic ligands.

### 3. Why choose atomically thin sheets for photocatalysis

The extraordinary properties of atomically thin sheets lead to unprecedented superiorities in photocatalysis. These superiorities include quantum confinement effect, short transmission distance of carriers, high charge density, ultrahigh specific surface areas, rich low-coordinated surface atoms, well-dispersion in solutions, *etc.* (1) The atomic-level thickness of atomically thin sheets will undergo remarkable quantum confinement effect, leading to broaden of band gap and shift of the CB and VB position. This will enhance the redox ability of the photocatalysts. For instance, the CB position of bulk BP (0.3 eV of band gap) is lower than the  $H^+/H_2$  potential, which does not meet the thermodynamic requirements of  $H_2$  evolution reaction. While atomically thin BP sheet with single-atomic-layer thickness holds broader band gap of 2.0 eV and the CB position shifted to more negative direction than  $H^+/H_2$  potential, making it possible for the occurrence of  $H_2$  production reaction. (2) Their atomic-level thickness also helps to shorten the carrier diffusion distance from internal to the surface, leading to the effective suppression of bulk recombination of carriers. (3) The high charge density on the surface of atomically thin sheets makes possible high-speed migration of photogenerated carriers to reaction sites, leading to an effective suppression of surface recombination of carriers. (4) The ultrahigh specific surface areas of atomically thin sheets allow more frequent contact between the reactants and catalysts. (5) Atomically thin sheets possess a large number of low-coordinated surface atoms, which are the adsorption and activation sites of typical reactant molecules. This is conducive to the efficient photocatalytic reactions. Besides, the low-coordinated surface atoms can also be acted as the anchor point of single atom catalysts, which is good for the cooperation of single atom catalysis and 2D catalysis, thus further improving the photocatalytic efficiency. (6) Due to the existence of a large number of low coordination surface atoms on the surface of atomically thin sheets, strong electrostatic repulsion will be formed between the sheet to sheet of atomically thin sheets. The strong electrostatic repulsion prevents atomically thin sheets from sinking/agglomeration, thus leading to the well dispersion in solutions. This allows them to expose rich photocatalytic sites for photocatalytic oxidation-reduction reaction. Besides, this also makes them highly optical transparent, which effectively reduces the light shielding effect in photocatalytic oxidation-reduction reaction.

Besides, the unique structural features and properties of the atomically thin sheets endow them as an ideal platform to demonstrate some specific principles and phenomena in the process of photocatalysis.

(1) Controllable synthesis of pure single crystal facet is relatively easy for atomically thin sheets, which allows them acting as an ideal platform for studying the selective correlation between defined crystal facet and photocatalytic reactivity. (2) Although doping engineering is considered as an effective strategy for the improvement of photocatalytic performance, the enacted role of dopants in photocatalytic reaction is still controversial, owing to the possible existence of negative effects of dopants originating from acting as the recombination centers for the photo-generated carriers. Note that the heteroatoms tend to irregularly distribute in the interior of bulk materials, which enhances the occurrence probability of the recombination of photo-generated carriers. In view of this, atomically thin sheets are ideal acceptors for doping, which could offer favorable thin layer to achieve surface heteroatom doping and avoid the negative effects of dopants as much as possible. Moreover, atomically thin sheets have also been commonly used as the ideal model to deeply revealed the relationship between doped heteroatoms and photocatalytic performance from the atomic level. (3) The ultrahigh specific surface areas and rich exposed surface atoms of atomically thin sheets provide great convenience for the formation of vacancies. In addition, the high charge density on their surface reduces the barrier of electron migration. This endows them as an ideal platform to explore the role of vacancy in the electron-hole separation deeply and atomically. (4) Photocatalytic heterojunctions composed of atomically thin sheets would provide abundant 2D/2D interfaces, making them an ideal model to study the role of interface in photocatalysis.



## 4. Modification of atomically thin sheets for photocatalysis

In this section, we give a systematic summary of the various kinds of modification strategies of atomically thin sheets for photocatalysis, including thickness engineering, porous engineering, defect engineering, doping engineering, phase engineering, facet engineering, and composite construction (0D/2D, 1D/2D, 2D/2D).

### 4.1 Thickness engineering

Layer thickness control can effectively regulate the intrinsic properties of atomically thin sheets, including the band structure, electronic structure, charge transfer, and some surface features (*e.g.*, defects, active sites), all of which play the important role in the photocatalytic reaction. With the decrease of the thickness of ultrathin 2D photocatalysts to several nanometers, the quantum confinement effect will be strengthened, which could enlarge the bandgaps along with regulating the band positions. For example, the bandgap of bulk ZrS<sub>2</sub> is 1.66 eV, whereas when the thickness of ZrS<sub>2</sub> decreases to three layers, two layers, and monolayer, their corresponding bandgap increases to 1.94 to 1.97 and 2.01 eV, respectively<sup>29</sup>. Besides, reducing thickness could also induce the occurring of defect energy level in original band structure, which could also effectively regulate the band gaps. In addition, the thickness decrease also could make the indirect bandgap materials change to the direct bandgap materials. Take MoS<sub>2</sub> as an example, the bulk MoS<sub>2</sub> possesses an indirect bandgap (1.2 eV), whereas when the thickness decreases to single-layer, the ultrathin 2D MoS<sub>2</sub> has a direct bandgap of 1.9 eV<sup>30</sup>. Reducing thickness also allows enhanced photon collection, decreased carrier transfer distance, rich defects production, and abundant active sites exposure. Therefore, it has been widely used for the enhancing of photocatalytic performance of atomically thin sheets. For instance, in 2018, Zhang's group<sup>21</sup> demonstrated the fabrication of ultrathin 2D CdS nanosheet via a simple oil-bath method and systematically turning the thickness of 2D CdS nanosheet by adjusting the added amount of sodium citrate. The results showed that with the thickness decrease, the photocatalytic performance of CdS for H<sub>2</sub> evolution increase. The thinnest ultrathin 2D CdS nanosheet with 1.5-nm-thickness showed best photocatalytic performance with a H<sub>2</sub> evolution rate of 2155 μmol·g<sup>-1</sup>·h<sup>-1</sup>, which was almost 2.7 times higher than that of CdS nanoparticles.

### 4.2 Pores engineering

Holes in the atomically thin sheets can bring the following benefits to the materials. (1) They can effectively enhance the specific surface area, offer rich boundaries and edges sites, and provide more coordination unsaturated atoms, all of which could be acted as the photocatalytic reaction center. (2) They can also alter the band gap and band position of 2D photocatalysts owing to the electron confinement effect caused by electrons being pressed around the hole. As a typical example, the bandgap of holey ultrathin 2D  $\text{WO}_3$  nanosheet can be enlarged from 2.25 eV of intact  $\text{WO}_3$  nanosheet to 2.92 eV<sup>31</sup>. Besides, the VBM is more positive and the CBM is more negative of holey ultrathin 2D  $\text{WO}_3$  nanosheet, which greatly increase its photocatalytic oxidation-reduction ability. (3) Holes in the atomically thin sheets can deservedly shorten the charge migration distance, thus effectively sending more carriers to the reaction sites. Therefore, pores surface design has been regarded as an effective strategy for the enhancing of photocatalytic performance of ultrathin 2D photocatalysts. As a typical example, Yang's group<sup>32</sup> rationally designed and fabricated a holey ultrathin 2D g- $\text{C}_3\text{N}_4$  nanosheet, holding rich in-plane pores, via a simple heat treatment process, during which bulk g- $\text{C}_3\text{N}_4$  was heated under an  $\text{NH}_3$  atmosphere. The abundant holes on the surface of ultrathin 2D g- $\text{C}_3\text{N}_4$  nanosheet increased the specific surface area, as well as the number of active edges and through-plane diffusion channels, which remarkably promoted the transformation of reactant molecules and the photogenerated carriers. Benefiting from the pores surface advantages, the as-fabricated holey ultrathin 2D g- $\text{C}_3\text{N}_4$  nanosheet exhibited superior photocatalytic performance with  $\text{H}_2$  production rate of  $82.9 \mu\text{mol}\cdot\text{h}^{-1}$ , which was almost 19 times higher than that of bulk g- $\text{C}_3\text{N}_4$ .

### 4.3 Defect engineering

Recent studies have proven that introducing defects in photocatalyst can effectively enhance the photocatalytic performance of nanomaterials, owing to its turning functions for the physicochemical properties of photocatalysts, such as the migration of photo-generated carriers, light absorption, surface acidity and basicity, surface active reaction sites, adsorption and dissociation properties, and electronic structures. Therefore, defect engineering in photocatalysis has dramatically attracted tremendous attentions. Benefit from their ultrathin thickness, ultrahigh specific surface areas, and rich low-coordinated surface atoms, evenly introducing rich defects on the surface of ultrathin 2D photocatalysts is relatively easier. Vacancy defects is the most widely studied defect structure in defect engineering in recent decades. In 2019, Xie's group<sup>17</sup> rationally designed and fabricated the oxygen

vacancies-rich ultrathin 2D Bi<sub>2</sub>O<sub>3</sub> nanosheets with the thickness of above 0.68 nm via in situ oxidation of freshly exfoliated Bi nanosheets. Using the fabricated oxygen vacancies-rich ultrathin 2D Bi<sub>2</sub>O<sub>3</sub> nanosheets as ideal model and with the help of various advanced theoretical and experimental techniques, they offered a deep and atomic-level understanding of the role of oxygen vacancies in the CO<sub>2</sub> photofixation. Density-functional calculations uncovered that oxygen vacancies on the surface of ultrathin 2D Bi<sub>2</sub>O<sub>3</sub> nanosheets can decrease the CO<sub>2</sub> adsorption energy, which is conducive to the activation of CO<sub>2</sub>. Using photoluminescence (PL) characterization, they revealed that oxygen vacancies are beneficial to hinder the recombination of photogenerated carriers. Besides, through the in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFT) measurement, it can be found that oxygen vacancies-rich ultrathin 2D Bi<sub>2</sub>O<sub>3</sub> nanosheets hold enhanced capacity for the generation of ·CO<sub>2</sub><sup>-</sup> species. By virtue of the above excellent properties, the as-fabricated oxygen vacancies-rich ultrathin 2D Bi<sub>2</sub>O<sub>3</sub> nanosheets showed an extraordinarily enhanced photocatalytic CO<sub>2</sub> fixation activity with a dimethyl carbonate (DMC) conversion yield of about 18% in the presence of methanol, which was almost 9-fold higher than that of the oxygen vacancies-poor Bi<sub>2</sub>O<sub>3</sub> nanosheets. Based on the advanced theoretical and experimental analysis, they proposed the oxygen-vacancy-associated single electron transfer pathway for the photofixation of CO<sub>2</sub> to long-chain chemicals.

#### 4.4 Doping engineering

The past few years have witnessed a remarkably increase in research progress on the doping engineering for the modification of ultrathin 2D photocatalyst. Introducing heteroatom can bring various attractive advantages to the ultrathin 2D photocatalysts. The generated defect levels caused by the introduction of heteroatoms can adjust the band gaps of photocatalysts. For instance, the introduction of Ni heteroatom made the bandgap of 2D Ni-doped BiO<sub>2</sub> nanosheet reduce from 1.46 to 1.40 eV, leading to the light absorption edge extend to 885 nm from 850 nm<sup>33</sup>. Besides, introducing heteroatom can also effectively tune the surface properties of photocatalysts (e.g., surface species, specific surface area, and morphology, etc.), form defects or vacancies (like, oxygen vacancies), and modify the optoelectronic properties (such as effectively extending the light absorption range and improving conductivity). Therefore, doping engineering has been widely used for enhancing the photocatalytic performance of atomically thin sheets. For instance, in 2019, a novel Cu-doped 2D ultrathin ZnIn<sub>2</sub>S<sub>4</sub> nanosheet for the boosting of photocatalytic H<sub>2</sub> evolution was reported by Zhan's

group<sup>22</sup>. More importantly, by deeply exploring the structural and functional properties of Cu-doped 2D ultrathin ZnIn<sub>2</sub>S<sub>4</sub> nanosheet, they offered an atomic insight for the role of Cu atom played in the modification of ZnIn<sub>2</sub>S<sub>4</sub> nanosheet and offered atomic level origin of the effect of optimum and excess doping. In their work, pristine and a series of Cu-doped ultrathin 2D ZnIn<sub>2</sub>S<sub>4</sub> nanosheet (Cu<sub>x</sub>-ZnIn<sub>2</sub>S<sub>4</sub>) with the average thickness of about 5 nm (roughly equivalent to four Zn-In-S molecular layers) were successfully fabricated via hydrothermal method. Using X-ray absorption near edge structure (XANES), X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), Raman spectra and X-ray photoelectron spectroscopy (XPS) technologies, the chemical states of doped Cu atoms in ZnIn<sub>2</sub>S<sub>4</sub> lattice were explored. The results exhibited that the Cu atoms were existed in the form of Cu<sup>2+</sup> both in Cu<sub>0.5</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub> and Cu<sub>3.6</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub>, and the Cu-S bonds were similar to that of CuS. In order to clarify the doping sites (substitute In or Zn atom), the formation energy (*E<sub>s</sub>*) for the corresponding substitution doping was calculated, which showed that the *E<sub>s</sub>* of substitution Zn (1.316 eV) was lower than that of In (1.965 eV), indicating that Cu atoms were doped into the ZnIn<sub>2</sub>S<sub>4</sub> lattice by substituting Zn atoms. Furthermore, EXAFS fitting further revealed that Cu<sub>0.5</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub> ultrathin nanosheet still maintained the metal-S<sub>4</sub> coordination, while the atomic structure of Cu<sub>3.6</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub> was distorted and showed Cu-S<sub>3.6</sub> coordination. Additionally, systematic theoretical calculation (density of states and electron difference density analysis) and experimental characterization (photoluminescence spectra, time-resolved photoluminescence decay spectra, and surface photovoltage spectroscopy) revealed that Cu<sub>0.5</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub> ultrathin nanosheet possessed unfilled acceptor states in the valence band top, while Cu<sub>3.6</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub> showed greatly upshift of VB maximum, which correspondingly led to the effective separation and heavy recombination of photogenerated carriers, respectively. Owing to the above-mentioned reasons, the Cu-doped ZnIn<sub>2</sub>S<sub>4</sub> ultrathin nanosheet with the optimal doping concentration of 0.5% showed outstanding photocatalytic performance for H<sub>2</sub> evolution with a rate of 26200 μmol·h<sup>-1</sup>·g<sup>-1</sup>, which was almost 4-fold than that of the pristine ZnIn<sub>2</sub>S<sub>4</sub> nanosheets (6500 μmol·h<sup>-1</sup>·g<sup>-1</sup>) and 29-fold than that of the excess Cu dopants ZnIn<sub>2</sub>S<sub>4</sub> (Cu<sub>3.6</sub>-doped ZnIn<sub>2</sub>S<sub>4</sub>, 6500 μmol·h<sup>-1</sup>·g<sup>-1</sup>).

#### 4.5 Phase engineering

Phase engineering plays an important role in adjusting the photocatalytic performance of atomically thin sheets, owing to the differences in atomic arrangement and electronic structure of different crystal

phases. More importantly, the atomically thin sheets with coexistence of polycrystalline phases can effectively induce the carriers migration and separation, thus enhancing the photocatalytic performance. In 2008, Li's group<sup>34</sup> first reported the boosting photocatalytic performance of TiO<sub>2</sub> surface phase engineering. Since then, phase engineering has been widely used in photocatalysis, especially the atomically thin sheets based photocatalysis. As a classic example, Ozin's group<sup>35</sup> demonstrated the controllable fabrication of ultrathin 2D WS<sub>2</sub> nanosheets with distinctive crystal phase via a simple hot-injection method and investigated their functions in photocatalytic H<sub>2</sub> production system. By adjusting the injecting precursors, the crystal phase of ultrathin 2D WS<sub>2</sub> nanosheets can be effectively tuned. Specifically, through pouring CS<sub>2</sub> (as sulfur source) and WCl<sub>6</sub> (as tungsten source) precursors into hot oleylamine solution (320 °C), distorted octahedral (1T') phase ultrathin 2D WS<sub>2</sub> nanosheet with monatomic layer thickness was successfully obtained. While, during the fabrication process, by adding a few hexamethyldisilazane into the reaction system, hexagonal (2H) phase ultrathin 2D WS<sub>2</sub> nanosheet was obtained. The electronic band alignment and photocatalytic performance test results showed that ultrathin 2D 1T-WS<sub>2</sub> nanosheet can act as an efficient H<sub>2</sub> production cocatalyst, whereas the ultrathin 2D 2H-WS<sub>2</sub> nanosheet showed functions as a visible light sensitizer. Besides, the decreased photoactivity of 2H-WS<sub>2</sub>/TiO<sub>2</sub> nanocomposite can be attributed to the fact that 2H-WS<sub>2</sub> can also acted as the electron-hole recombination centers.

#### **4.6 Facet engineering**

Facet engineering also plays a key role in regulating the photocatalytic performance of atomically thin sheets, owing to the following points. (1) Each facet often has its own unique atomic arrangement, crystal orientations, electronic structure, and geometrical morphology, which leading to its unique physical, chemical and optical properties. Therefore, by controlling the exposure of specific crystal facet of atomically thin sheets, their photocatalytic performance can be effectively adjusted. (2) Each facet also possesses unique charges trapping capability, which can induce effective carriers migration and separation, thus making the photooxidation and photo reduction reactions take place on different crystal facets. For instance, Huang's group<sup>36</sup> successfully fabricated the 2D BiOIO<sub>3</sub> nanoplates with (010) and (100) facet exposed. The facet - induced carriers migration and separation was observed in the fabricated 2D BiOIO<sub>3</sub> nanoplates by the photo - deposition tests. Profiting from the effective

separation of photo-generated electrons and holes, the fabricated 2D BiOIO<sub>3</sub> nanoplates with the exposure of (010) and (100) facet in proper proportion showed excellent photocatalytic performance for CO<sub>2</sub> reduction.

#### 4.7 Composite construction

Constructing heterojunctions is generally considered as an effective strategy to accelerate the migration and separation of photo-induced carries and extend the light-response range of photocatalysts. Owing to their ultrahigh specific surface areas, high charge density, and rich low-coordinated surface atoms, atomically thin sheets has become the ideal model for the effectively building of photocatalytic heterojunctions with compact interface contact. In recent years, various atomically thin sheets-based photocatalytic heterojunctions with matched electronic band structure and geometric configuration, including 0D/2D, 1D/2D, and 2D/2D heterojunctions, have been successfully fabricated and showed obviously enhanced photocatalytic performance for energy and environmental applications. For example, Zhang's group<sup>37</sup> demonstrated the rational design and construction of 2D/2D Janus Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub>/MoS<sub>2</sub> bilayer photocatalytic heterojunction by selectively and chemically attaching 1T MoS<sub>2</sub> monolayers on the (Bi<sub>12</sub>O<sub>17</sub>) end-faces of Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> monolayers. The as-constructed novel 2D/2D Janus Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub>/MoS<sub>2</sub> bilayer photocatalytic heterojunction exhibited outstanding photocatalytic activity with a hydrogen-evolution rate of 33 mmol·g<sup>-1</sup>·h<sup>-1</sup>. The excellent performance can be attributed to the efficient directional migration of photo-generated electron-hole pairs at the (Bi<sub>12</sub>O<sub>17</sub>)/(Cl<sub>2</sub>) end-faces and 2D/2D interface. Photo-generated electron of Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> will be directionally transferred to (Bi<sub>12</sub>O<sub>17</sub>) end-faces under the action of internal electric field, while hole will migrate to (Cl<sub>2</sub>) end-faces. Furthermore, the electron on the (Bi<sub>12</sub>O<sub>17</sub>) end-faces will be further transferred to MoS<sub>2</sub> via Bi-S bonds. The above-mentioned carriers migration and separation paths was proven by the photo - deposition tests. In addition to above mentioned 2D/2D Janus heterojunction, building 2D van der Waals heterojunction is also a good strategy to enhance the performance of photocatalytic composites. Especially the multilayer van der Waals heterojunction, as in building with atomic-scale Lego, may bring better advantages than expected to the photocatalytic composite system.

## **5. Summaries and discussions on the current research status, challenges in the area of atomically thin sheets for photocatalysis**

Almost all of the members of atomically thin sheet family have shown potential value in photocatalytic applications. However, in the current research, only a few types of atomically thin sheets have been widely studied for photocatalytic applications, for example, g-C<sub>3</sub>N<sub>4</sub>, metal oxides, mix metal oxides, and metal chalcogenides. Other atomically thin sheets, especially emerging 2D nanomaterials, such as BP, TMDs, MXenes, COFs, MOFs need to be put in more attention and efforts to further explored their photocatalytic applications both in performance and mechanism. What's more, the current reported members of atomically thin sheets family represent only the tip of the iceberg of this charming family. Inevitably, in nature, there are also many other atomically thin sheets that have not yet been developed, among which many possess the photocatalytic application value. Therefore, exploring and discovering new members of atomically thin sheets family for photocatalytic applications is an absolutely fascinating theme. The emergence of new atomically thin sheets is bound to benefit academia and industry circles, and even cause academic shock, just like the discovery of graphene, although it would be challenging.

Although rich top-down approaches and bottom-up approaches have been developed for the fabrication of atomically thin sheets for photocatalysis, it is still a huge challenge to meet all the requirement of controllable thickness, large-scale output, easy synthesis, and low cost. Note that, in terms of the large-scale industrial application, these requirements are essential. Therefore, great efforts still need to be made to develop scalable strategies for the large-scale and low-cost fabrication of high-quality ultrathin 2D photocatalysts. Herein, we give our perspectives of the directions worthy of efforts in the not too distant future. (I) Using in situ technique, such as in situ liquid cell transmission electron microscopy (in situ liquid cell TEM) to realize the visualization of the crystal growth behavior and obtain in-depth mechanism understanding of the fabrication process of atomically thin sheets<sup>38</sup>. After getting the direct and in-depth insights of the fabrication of atomically thin sheets, purposefully and reasonably improve the corresponding methods to make it simpler and more efficient. (II) Aside from improving the existing synthesis technology, developing new synthesis strategy undoubtedly is an attractive topic for future research, although it would be great difficult.

Various strategies have been developed for the modification of ultrathin 2D photocatalyst. However, the studies of these strategies are still in their early stage, and constant efforts are still required. There are still many applications to be expanded and the mechanism to be clarified. In the future research, efforts can be made from the following three aspects: (I) exploring simpler ways and easier experimental conditions to realize the modification of ultrathin 2D photocatalyst; (II) deeply and systematically clarifying the essential mechanism for the enhancement of photocatalytic performance of the various modification strategies.

Although atomically thin sheets have displayed great potential for photocatalytic applications, we also clearly understand that the photocatalytic efficiency of these materials is still far from industrial applications. Great challenges remain to be faced, and hard efforts still needed to be paid to realize the potential industrial applications. Doing the following well, but not limited to the following, is conducive to speed up the realization of industrialization. (I) Using various advanced characterization technologies (in situ TEM, in situ FTIR, GC-MS, *etc.*), to deeply understand the photocatalytic reaction mechanisms, and the thermodynamic and kinetic processes, guiding the design of more favorable reaction conditions, and more reasonable reaction device. (II) The structural decomposition, degradation, and collapse of atomically thin sheets often occurs during the photocatalytic chemical reaction. Therefore, it is necessary to develop simple and reliable methods to dramatically improve the stability and durability of atomically thin sheets during the photocatalytic reactions. (III) In liquid reaction environment, particulate catalyst always faces the problem of loss of active ingredients. Therefore, it is necessary to develop effective strategies to improve the recycling of nano-sized atomically thin sheets in practical applications, thus avoiding loss of active material, as well as preventing secondary pollution. These effective strategies include but not limited to, fixing catalysts on the flexible fabric<sup>39</sup>, designing and manufacturing self-catalytic reactors using metal 3D printing technology<sup>40</sup>, and fabricating integrated photocatalytic devices with additional functions preventing the loss of active nanomaterials. (IV) In the age of data science, as an effective means, mechanical learning technology will bring innovation to the development of traditional catalysis (both in industry and academia), and will promote the rapid progress of catalytic technology<sup>41</sup>. In view of this, it is urgent to seamlessly integrate the experiment, theory, and data science using the young and burgeoning machine learning technology to guide the discovery, design, synthesis, optimization of ultrathin 2D



photocatalysts, and help to deeply understand the relationships between the properties of ultrathin 2D photocatalysts and their catalytic activity, selectivity and stability.

To this end, being atomically thin sheets cannot resolve all the dilemmas faced by photocatalysis, but does provide new opportunities for further enhancing the photocatalytic performance, and open a door for understanding the photocatalytic principles or mechanisms at the atomic level. We sincerely hope that this tutorial review article has been able offer a systematic and comprehensive summary of the research advances in the synthesis, modification, and photocatalytic applications of atomically thin sheets. More importantly, we hope that the current challenges and future perspectives of atomically thin sheets for photocatalysis proposed in this article could bring some guidances and inspirations to the follow-up work. We confidently believe that more exciting progress will be achieved in this fascinating field in the near future.

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