Recent Progress, Challenges, and Prospects in Two-Dimensional Photo-Catalyst Materials and Environmental Remediation

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HIGHLIGHTS

- Current progress in preparations, structures, and physicochemical properties of two-dimensional photo-catalyst materials and environmental remediation.
- Propose approaches of diverse of two-dimensional photo-catalyst materials-based nanoplatforms, optimization strategies to enhance activity, and their diverse applications.
- Current challenges and potential advancement of the emerging of two-dimensional photo-catalyst materials.
ABSTRACT The successful photo-catalyst library gives significant information on feature that affects photo-catalytic performance and proposes new materials. Competency is considerably significant to form multi-functional photo-catalysts with flexible characteristics. Since recently, two-dimensional materials (2DMs) gained much attention from researchers, due to their unique thickness-dependent uses, mainly for photo-catalytic, outstanding chemical and physical properties. Photo-catalytic water splitting and hydrogen (H\textsubscript{2}) evolution by plentiful compounds as electron (e\textsuperscript{-}) donors is estimated to participate in constructing clean method for solar H\textsubscript{2}-formation. Heterogeneous photo-catalysis received much research attention caused by their applications to tackle numerous energy and environmental issues. This broad review explains progress regarding 2DMs, significance in structure, and catalytic results. We will discuss in detail current progresses of approaches for adjusting 2DMs-based photo-catalysts to assess their photo-activity including doping, hetero-structure scheme, and functional formation assembly. Suggested plans, e.g., doping and sensitization of semiconducting 2DMs, increasing electrical conductance, improving catalytic active sites, strengthening interface coupling in semiconductors (SCs) 2DMs, forming nano-structures, building multi-junction nano-composites, increasing photo-stability of SCs, and using combined results of adapted approaches, are summed up. Hence, to further improve 2DMs photo-catalyst properties, hetero-structure design-based 2DMs’ photo-catalyst basic mechanism is also reviewed.

KEYWORDS Two-dimensional materials; Photo-catalysts; H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}-production; Pollutant degradation; CO\textsubscript{2} reduction

1 Introduction

The sustainable energy and chemical supplies demands are very essential for modern society that is necessary for our transportation, prosperity, and daily simplicity. The world’s almost 85% energy demands are fulfilled by fossil fuels-based energy production. Therefore, an increasing progress in modern society for pollution-free energy production gains attention of the researchers in all fields. In the past, larger part of worldwide energy formation was based on fossil fuel, which increases environment pollution and hence causes global warming [1–14]. In this modern society, development in different industries causes rapid population growth, which is further estimated to increase by two factors: the current energy required by 2050 to run industries around globe and their household uses [2–4, 15–26]. Presently, world’s energy supplies are mainly reliant on fossil fuels, for example, coal, petroleum, and natural gases, which are quickly being spent. Utilization of fossil fuels will certainly cause particular gases’ emission which are very injurious to the environment. Consequently, innovative findings in science and engineering are proceeded to address the barriers for efficient energy formation and environmental safety. Hence, production of the sustainable/renewable energy is a solution to meet up the rising worldwide energy demand and especially to solve environmental pollution issues [2–4, 27]. Conversely, fossil fuel-based energy is also widely used in chemical production on industrial level via inorganic/organic transformations by applying high-temperature/pressure circumstances. Although fossil fuel supplies are possibly sufficient for some next generations, durable cost of fossil fuels is undesirable because of un-sustainability of fossil fuels recognized as partial assets and rising greenhouse gases certified to enormous release of CO\textsubscript{2}-like hazard gases. The technical challenges to increase an industrially talented chemical process to protect a clean, renewable energy and to reduce harmful ecological impact are connected with the use of fossil fuels [2, 3, 19, 22]. In this regard, renewable sustainable energy production is one of the significant solutions, especially hydrogen (H\textsubscript{2})-based energy creation by photo-catalysts as well as electrocatalysts [2–4, 18, 19, 21, 25]. Here, we will mainly concern on photo-catalysts. The H\textsubscript{2} has the maximum energy contented per weight in combustion fuels and manufactures simply water (H\textsubscript{2}O) as by-product [3, 4, 19]. Thus
far, straightforward transfer of solar energy to fuel energy (H₂) and chemical energy was viewed as one of the green renewable ways to deal with energy and environmental pollution issues in the future [2–4, 17, 18, 21, 23–25]. Hence, H₂ is considered as an ultra-clean, powerful, environment friendly, and hopeful another choice for meeting the future fuel necessities with environmental safety by less release of greenhouse gasses [2–4, 17–19, 21, 23, 24].

2 Basic Properties of Photo-catalysis

2.1 Merits of Photo-catalysis

The considerable reliance of worldwide economy on non-renewable and geopolitical susceptible fossil fuel energies has led to necessity in advance technologies to protect alternative clean and renewable energy supplies. In between different renewable energy sources (i.e., wind, tidal, hydroelectric, ocean currents, biomass, geothermal, and solar), solar energy is by far the most abundant, low cost, pollution free, and sustainable. Even though the total solar energy the earth receives for one hour is greater compared to annual global energy expenditure, the most serious challenge remains collection and storage of this very diffuse form of energy to facilitate real-world application and non-interrupted fuel supply. Photo-catalysis can be basically explained as a method wherein photo-generated electrons (e⁻) and holes (h⁺) induce targeted redox reactions on light absorbers and/or co-catalysts loaded on it. A range of other invented renewable energy schemes, semiconductor (SC)-based photo-catalysis, in which infinite and clean solar energy can be acquired as a possible technology [28] achieved great interdisciplinary concentration for their various probabilities in energy and environmental uses. Efficient transformation of solar energy to solar fuel using photo-catalytic method was measured as very eventual enduring maneuver to resolve global energy and environmental concerns [29]. Naturally abundant sunlight and H₂O splitting-based production of H₂ by using sunlight were verified as regenerative, environment friendly, and vast techniques to resolve energy disaster and environmental pollution. In photo-catalysis method, a steady and capable photo-catalyst is an important aspect to attain a high efficiency of H₂. For energy crises as well as environmental issues, SC-based photo-catalysis has enormous ability to guarantee long-lasting and sustainable development, because of direct consumption of green solar energy for formation of important H₂ fuels and degradation of organic pollutants. Generally, four steps take place in the photo-catalytic process:

1. Light absorption
2. Creation of photo-generated (e⁻–h⁺)-pairs
3. Movement and recombination of photo-generated (e⁻–h⁺)
4. Redox reactions at photo-catalysts surface

How to understand it proficiently is very demanding, both kinetically and thermodynamically. The complexities lie in the subsequent features:

1. Maximum yielding of solar energy (mainly visible (vis) light) to produce enough energetic e⁻/h⁺
2. High mobility and long dispersion length of photo-generated e⁻/h⁺s to suppress bulk recombination
3. Sufficiently strong reduction power of photo-generated e⁻ and h⁺s to persuade reactions, specially H₂O oxidation that demands four e⁻
4. Plentiful surface locations for forward target reactions as an alternative of back reactions (e.g., H₂ and O₂ reaction to fabricate H₂O)

Such four subjects represent a significant research pathway. Moreover, three steps span a huge timescale from 10⁻¹⁵ to 10⁻¹ s. What’s more demanding are intrinsic conflicts between necessities for three key steps. Minimum three factors are considered here:

1. Increasing light absorption range (reduced bandgaps) generally leads to small reduction capability of photo-generated e⁻ and/or a lower oxidation capability of photo-generated h⁺;
2. The very low mobility of h⁺s compared to e⁻ in most SCs does not support rate-determining H₂O oxidation reactions,
3. The difference in random distributions of oxidation and reduction reaction sites and required migration of e⁻/h⁺ in diverse directions.

The strong underlying conflicts connected with photophysical process, electronic properties, and catalysis principles build recognition of highly efficient photo-catalysis as a very challenging process. To solve these challenges, it is significantly important to accurately control every fundamental step depending on a comprehensive consideration of
photo-catalysis and structure property interactions. Therefore, first we are going to explain SC materials' suitability for photo-catalytic nature.

### 2.2 General Selection of SC Photo-catalytic Materials

Generally, the photo-catalysis is an accelerated photo-reaction method in existence of SC photo-catalyst, in which photons with energy $hv \geq E_g$ ($E_g$ = band gap (BG) energy) of photo-catalyst are adsorbed to photoexcite free electrons ($e^-$s) to conduction band (CB), creating holes ($h^+$s) in valence band (VB). Photo-generated ($e^-–h^+$)-pairs participate in an important part for solar energy transfer method, for example, solar $H_2O$ splitting, $CO_2$ reduction, and photo-catalytic pollutant degradation. Although photo-generated carriers in excited states are less stable, they recombine easily, which results in low conversion effectiveness of photo-catalysis [30]. By the way, since discovery of photo-catalytic $H_2O$ splitting with $TiO_2$ in 1972, great effort was applied in progress of photo-catalysts for an efficient photo-catalytic method [31]. The SC-based photo-catalysis concerned huge research attention, [32] since it was considered very novel solution to manage energy deficiency and environmental pollution problems [33]. The sunlight as an exterior driving force can split $H_2O$ into $H_2$ and $O_2$, reduce $CO_2$ to chemical and valuable fuel, as well as terminate pollutants entirely [34]. Normally, the main significant efforts in the photo-catalytic development are categorized as light absorption, charge separation, transfer, and surface redox responses. By irradiation of photo-catalysts, it absorbed sunlight, which excites to produce ($e^-–h^+$)-pairs, when $hv \geq E_g$, leaving $e^-$s in CB and $h^+$s in VB, respectively. After that, photo-generated $e^-$s and $h^+$s are diffused to material surface and also transferred to surface active sites, prior to connection with surface reactions. Sometimes, charge carrier’s recombination occurs and crystal structure, particle size, crystallinity, surface morphology, etc., strongly influenced separation efficiency. At last, target molecules are adsorbed on the surface of materials and experience charge addition development and desorption to make final results [35].

In between ($e^-–h^+$)-recombination process, unnecessary heat is created, which causes a negative role in photo-catalytic production. In the photo-catalysis method, a stable and efficient photo-catalyst is an imperative feature to get high efficiency of $H_2$. Additionally, the driving force of solar light photo-catalysis demands suitable SCs to perform various photo-catalytic responses, for example, $H_2O$ splitting to manufacture $O_2$ and $H_2$, $CO_2$ reduction to hydrocarbon fuels, degradation of organic pollutants, disinfection of bacteria, and selective formation of organic compounds [36]. The milestone occurrence of photo-catalytic $H_2O$ splitting, by $TiO_2$-based electrodes in an ultraviolet (UV) light, was started from revolutionary research co-authored by Fujishima and Honda [37]. In 1976, photo-catalytic degradation of organic contaminants was studied by Carey et al. [38] using $TiO_2$ in aqueous suspension. In 1979, Inoue and co-authors examined photo-catalytic reduction of $CO_2$ to a range of organic compounds by SC materials, for example, $TiO_2$, $SiC$, $ZnO$, $CdS$, and $GaP$, in aqueous solution. After that, various considerable progresses were made in the formation of very proficient SC-based photo-catalysts. Up to now, several SC photo-catalysts were explored and utilized in $H_2O$ splitting. Based on composition, photo-catalysts are usually classified into three kinds:

1. Metal oxides (MOs)
2. Metal chalcogenides
3. Metal-free photo-catalysts

So far, hundreds of SC materials are discovered for different photo-catalytic uses by tuning a range from composition, electronic, and crystal structure. While important accomplishment was achieved in optimizing photo-catalytic performance, most photo-catalysts still suffer from relatively low photo-catalytic efficiencies that are much lower compared to the necessities for probable realistic uses. Based on previous research investigation, probable UV–Vis-active and vis-light-active photo-catalysts included $TiO_2$, $ZnO$, $Fe_2O_3$, $CdS$, $Bi_2WO_6$, $BiVO_4$, $Ta_2O_5$, $Ta_3N_5$, $TaON$, $C_3N_4$, and so on [39]. To date, emerging high-quality SC photo-catalyst for surmount recovery of energy deficiency and environmental hazards is a great research field [36]. Despite quick progress of conventional photo-catalysts, they are still facing numerous major challenges:

1. Many SCs, particularly MOs, can absorb UV light because of their wide BG [40]
2. A few SCs are not appropriate for entire $H_2O$ splitting, due to their inappropriate band location and because they only show either $H_2O$ oxidation or reduction activity [41]
3. In relocation of photo-generated charge carriers to surface reactive sites, charge recombination happens simply for bulk and on photo-catalysts’ surface [42].

4. The majority of bulk SC reaction active sites cannot be exposed to surface and are utilized in the photo-catalytic process [29].

Therefore, key issues to attain an excellent photocatalytic performance depend on normal mean of high-efficiency photo-catalysts. In recently discovered new potential photo-active materials, 2DMs got much consideration. Bearing in mind various characteristics and advantages, the promising 2DMs with suitable energy band configuration can stimulate new visions [14, 43, 44]. Recent research in 2DMs has advanced the modernized attention in p–n junction; the oldest electrical mechanism was employed in electronics and optoelectronics devices research. The 2DMs offer an amazing flexibility to propose a novel (p‑n)‑junction device configuration, not workable through usual 3D bulk SCs. The 2DMs signify a promising category of materials that have NSs-like configuration with thickness of just one or few atoms [45]. Attempts were ignited through innovation of graphene (G) in 2004, a single-layer (SL) carbon material along outstanding thermal, mechanical, and electrical characteristics [46]. Ever since, a range of G-like 2D photo-catalysts became a relevant topic in photo-catalysis field. The 2D photo-catalysts showed special chemical and physical properties in contrast to their bulk counterparts. Emerging 2DMs with unique structural and electronic properties and appropriate band structure have showed huge potential of achieving the desired photo-catalytic efficiency.

There are numerous features which influence the photocatalytic efficiency of photo-catalysts, e.g., composition, BG, crystallinity, surface state, and morphology of SC materials, and interfacial properties of components for composite photo-catalysts.

In view of necessities for competent light adsorption and photo-generated carrier separation and transport, if possible, a photo-catalyst must contain an elevated specific surface area (SSA), good crystalline structure, stability, and an appropriate band structure [29]. The 2DMs arrangement can supply huge SSA and a large fraction of low coordinated surface atoms to produce further UV light, whereas photon absorption in bulk materials or nanoparticles (NPs) is frequently inadequate through transmittance of light and reflection at grain boundaries [47]. Furthermore, as a result of atomic size thickness significantly decreases the migration distance; charge carriers produced in 2DMs interior will be quicker to transfer on surface compared to bulk materials (Fig. 1a). It will significantly decrease recombination chance of photo-generated carriers and support photo-catalytic method. Finally, regarding surface redox reactions, distinctive 2DMs configuration along elevated ratio of surface atoms to whole atoms can cause new SAS to speed up the reaction development. Additionally, atomic breakdown energy develops into comparatively minute when thickness decreased to atomic level and so additional surface defects will come into view. These surface defects will promote and improve target molecule adsorption to make strong interaction, easy charge transfer, and better activation procedure.

Photo-catalysts with such characteristics and 2DMs configuration receive high interest, and a great number of related studies were performed [32].

To concentrate on these challenges, formations of new and more competent photo-catalysts are required to energetically investigate in this field [49]. The 2D structures along with foreign electronic properties and a high SSA are formed from layered [50] and non-layered [48] materials. The layered materials are identified through strong in-plane bonds and weak van der Waals (vdWs) force in layers. On the other hand, Ajayan and co-workers [48] recently discovered an efficient formation approach via the progressive conversion of non-vdW solids to 2D vdWs transition metal chalcogenide (TMDCs) layers with recognized 2H (trigonal prismatic)/1T (octahedral) segments (Fig. 1b, c). Conversions, obtained after exposing non-vdWs solids to chalcogen vapors, were controlled utilizing enthalpies and reaction products vapor pressures. Heteroatoms-substituted (e.g., phosphorus and yttrium) TMDCs were also formed by the same scheme, so a general formation scheme is allowed to form phase-selected TMDCs’ 2D configurations with excellent stability at elevated temperatures (about 1373 K) and obtain scalable manufacture of SLs. These 2D TMDCs have wide uses in catalysis, electronics, and energy storage applications. On account of remarkable structure-based, chemical and physical, properties of 2DMs, the construction of few-layer (FL) or single-layer (SL) 2DMs provokes broad attention as talented photo-catalysts with numerous benefits:
1. The BG and light absorption of 2D-SC can adjust via altering layers number [51].
2. The (e⁻–h⁺)-recombination in case of bulk can decrease because of atomic size of 2DMs [52].
3. The SSA of the SCs is significantly enhanced, and most of the SASs can be exposed at surface and included in photo-catalytic reaction [47].

Along with the different 2D photo-catalysts with only FLs or SL structure, G-based photo-catalysts, 2D oxides, 2D chalcogenides, 2D graphitic carbon nitride (g-C₃N₄), and other 2D-SCs started gaining huge attention in photo-catalysis [49]. Although 2D photo-catalysts are viewed as talented materials to exchange solar energy into chemical energy as...
H₂-formation, there are a number of hurdles, which limit their uses [49], as follows:

1. The exciton binding energy in 2DMs-based photo-catalysts was significantly enhanced because of smaller unfavorable e⁻-screening than bulk material [53].
2. Some 2DMs-based SCs are not stable in aqueous solution or air; thin-layer 2D SC can be assembled collectively or oxidized through photo-generated h⁺'s during reaction, which leads to deterioration in photo-catalytic activity [54].
3. While (e⁻–h⁺)-pairs recombination is less compared to bulk SCs, it still resides in 2D photo-catalysts [55].
4. Reduction potential and oxidation potential of few 2D-SCs are not enough in overall H₂O splitting [55].

To address such issues, a range of approaches were designed to increase photo-catalytic activity of 2DMs-based photo-catalysts, for example, doping with a metal or nonmetal elements, inducing defects, and coupling with metal or SCs, which will be discussed in detail in the upcoming sections [56]. In fact, photo-activity of photo-catalysts relies on their properties, for instance, electron affinity, crystal structure, BG, and interface in photo-catalyst as well as co-catalyst [57]. Consequently, for well-organized transfer of H₂O to H₂, the mixing of photo-catalyst and co-catalyst required novel interface structure. This kind of interface can optimize absorption of light for photo-catalysts and support e⁻/h⁺ separation. Normally, bigger contact area at interface can offer enough charge transfer and trapping channels for parting (e⁻–h⁺)-pairs generated by incident light [49]. The above-mentioned problem has one another solution, which is the hetero-structure formation of 2DMs. In contrast to 0D–1D, 1D–1D, 0D–2D, and 1D–2D interfaces, 2D–2D coupled hetero-structure-based interfaces concerned broad concentration in photo-catalysis due to their particular advantages, as follows [49]:

1. The creation of intimate interface in two SCs is in support of exciton dissociation, which enhances the photo-catalytic quantum efficiency [58].
2. It is simplistic and proficient to structure the intimate interface in 2DMs-SCs, even if they have some mismatch of lattices [59].
3. Large lateral size along with high SSA leads to huge contact area in 2D/2D photo-catalysts that advance (e⁻–h⁺)-pairs’ separation and transfer [60].
4. The band potential coordinated to overall H₂O splitting by integrating H₂/O₂-evolution photo-catalyst. Therefore, oxidation and reduction influence of SCs is balanced for H₂O splitting [61].
5. Creation of 2D/2D hetero-structure is advantageous to develop stability of photo-catalyst because of increase in photo-corrosion and agglomeration [62].

As a sustainable technology, the SC photo-catalysis has gained significant attention in the recent decades due to possible ease/resolve energy and environmental pollution concerns. Therefore, due to 2D/2D interface advantages, many 2D/2D structures are formed recently to improve photocatalytic performance of photo-catalysts [63, 64]. Based on these advantages, we are going to summarize most of the related topics, which can further improve the photo-catalytic phenomenon for H₂O splitting (H₂O oxidation and H₂ evolution), CO₂ reduction, N₂ fixation, organic production, removal of pollutants based on G-based photo-catalysts, 2D oxides, 2D-chalcogenides, 2D g-C₃N₄, and some other 2D-SCs. The 2DMs reviewed here are considered as low-dimensional materials with thickness ranging from SL to few nanometers (nm) by means of basal plane controlling total surface area, and 2DMS-based SCs photo-catalysis principles, synthesis, and stability will be briefly reviewed. Here, up-to-date development of 2DMs-based photo-catalysts is summarized, and significant evaluations of categorizing and convenient production method of 2DMs-based photo-catalysts are presented. To further boost these results, different policies to engineer electronic structure of 2DMs-based photo-catalysts are summed up, such as component tuning, thickness tuning, defect, and doping engineering. Hybridization with insertion of outside components and keeping 2D structure is explained to improve photo-catalytic efficiency, for example, quantum dots (QDs)/2DMs, single atoms/2DMs, molecular/2DMs, and 2D–2D stacking materials. Therefore, we will give a concise explanation of recently developed 2DMs, their applications in photo-catalysis, and the promising approaches for the photo-activity progress from the perspective of chemical doping, hetero-structure layout as well as functional structural design assembly. More importantly, attention will be paid to advancement of versatile photo-catalytic applications of 2DMs-based photo-catalysts in H₂O oxidation, H₂ evolution, CO₂ reduction, N₂ fixation, organic synthesis, and elimination of pollutants.
Besides, manufacture approaches and characterization methods of 2D/2D photo-catalysts are also reviewed. Finally, ongoing opportunities and challenges for upcoming progress of 2DMs-based photo-catalysts in this exhilarating yet still upcoming area of research will be projected [29, 32, 49] and a short summary of present research position and challenges, with respect to 2DM-based photo-catalysts for photo-catalysis applications, will also be explained [29]. It is extremely important and insistent to present a timely updated widespread review on this matter to endorse further progress in the upcoming direction [32].

2.3 Benchmark Photo-catalysts

As it appears that too long step is in our conviction also a little that considered in future investigations that are association derived from present price of photo-catalytic materials. This feature looks alienated to laboratory-level work, deals with elementary information, and consequently accords with the rule not to be hampered by funds restrictions. On the other hand, we must admit that exploration is increasingly related to industry, and funding is governed through financial analysis of project, so this feature can no longer be ignored. In recent publications, it is expected to go forward in claims on importance of reported materials due to the absence of precious metals that were still considered as co-catalysts [65]. It is a too common assumption that does not inform the features of cheaper material; consequently, not including a precious metal (frequently applies in small quantity) is not essentially an economic choice, because material still depends on expensive starting materials, or tiresome reaction conditions (purification, temperature, solvent, etc.) that finally end up in inflating the cost of the proposed catalyst. It may take time to endeavor a little quantitative cost estimation to propose photo-catalyst, not only because the time is a necessary feature, but also getting support for optimizations in this field from other researchers [66]. Coming to the point, the following three key components are proposed to be explored to compare the built-in photonic effectiveness of a variety of photo-catalyst materials in laboratories.

1. Incident photon flux (photon numbers with respect to wavelength per time).
2. “Optimum rate” (achieve the highest photo-catalytic rate through changing photo-catalyst quantity in a specified reactor).
3. Rate of reactant expenditure or product evolution (at optimum rate under diverse reaction conditions).

The increase in heterogeneous photo-catalysis interest and other solar fuel conversion schemes will unavoidably lead to more research in this area. Unfortunately, many research works enclose imprecision while studying photo-catalytic measurements, particularly while reporting gas evolution [67]. It is taken toward benchmark materials’ selection difficulties as there is non-reliability in efficiency measurements. In the literature, some common errors are observed in expectancy of increasing overall quality this direction. It is recommended that classification for exploring photo-catalytic rate is given as follows:

1. Reactant conversion kinetic or product formation rates.
2. Incident photon flux with respect to wavelength.
3. Activities or partial pressures of reactants and sacrificial reagents.
4. Solution type, electrolyte concentration, and pH.
5. Quantity of photo-catalyst, co-catalyst, and solution.
6. Flow rate of reactor and volume/dimension of reactor.

Following combined experiments carried out to assess photo-catalytic performance in likely comprehensive approach, the next step is to comprehend how recently studied photo-catalyst ranks in between present photo-catalysts. Benchmark cannot recommend from all considerations mentioned previously. A lot of investigations have been inadequately performed on this significant part of work, and only contrast materials are benchmark reference catalysts, for instance TiO2 Degussa P25. It certainly offers an early essence of photo-catalysts, but all the time comparison cannot provide a good judgment and is not enough to validate the published results. It might appear understandable, but arises a first theoretical question: Is model reported activity vs. Degussa P25 still possessed nowadays? We are bombarded with a variety of novel guidelines of editors, industries, grant agencies, and so on, that it is vital that upcoming photo-catalytic studies must concentrate on utilization of vis-light irradiation. It is a logical insight that provided strong relationship of photo-catalysis with sustainability, future realistic growth should take toward green energy, and process must hinge on utilization of sun light. A lot of energy is irradiated through solar spectrum in the range of vis spectrum (43%), but still more is in fact irradiated through IR rays (52%), yet at this moment it is complicated
to utilize it for SC photo-catalysis. It is confined energy to produce requisite charge separation in the majority of SCs-based photo-catalysts. However, it is valuable to note that only some ground-breaking works on exploitation of IR radiation have come forward [68–71], that hold interesting promises for future research development. Indeed, UV region (5%) is far too little, and so there is commonsense that wide BG (≥ 3.0 eV) SCs by themselves can no longer participate in leading role and become outdated unless investigated for development of strategies built around multi-component structural arrangements, for example Z-schemes and p–n junctions. Therefore, it looks conflict that activity must be indefinitely benchmarked against a UV-active SC, i.e., Degussa P25.

In these days, state-of-the-art catalysts’ table of comparisons are emerging more frequently in research work. These are more helpful, if selected with care. Tables should not evaluate one but maximum possible activity potential factors. A comparison between QY does not reveal a lot about catalyst selectivity and stability, which are the two equal significant conditions of comparison. The experiment duration choice for calculating QY is arbitrary and thus can be simply turned to researchers’ expediency, losing objective, particularly while kinetics of product formation are not steady. Furthermore, a photo-catalyst with superior AQY or QY could be simply synthetically better, as exclude a donation to evolve product through other mechanisms working in dark. One more significant feature is that AQY experiments are generally performed with monochromatic light source, and as declared already, QY differs along excitation wavelengths. Tables of comparison completely conversed on QY preferably demand of comparison depend on polychromatic lights sources or as a minimum between photo-catalysts mainly absorbing in same narrow wavelengths range (a situation hard to attain). It is obvious to compare standard catalyst and synthetic catalysts discovered under similar catalytic conditions. Terminology is an additional feature not to be underestimated, as it can be the source of perplexity. As distinct earlier QY and AQY refer to quantity of consumed reactant (or product formation), other International Union of Pure and Applied Chemistry definitions more frequently utilized in heterogeneous photo-catalysis regarded as photonic efficiency (PE) and quantum efficiency (QE):

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\text{QE} = \frac{\text{photochemical events}}{\text{absorbed photon flux}}
\]

\[
\text{PE} = \frac{\text{photo-reaction rate}}{\text{rate of incident photons}}
\]

Researchers need confirmation whether they are comparing the same factors. In general, we discourage a benchmark prepared completely for QY, PE, or QE, as in our estimation it is imperfect and deceptive [73]. Other activity data can propose extra basic information: Reporting product formation rates over unlimited time offers evaluation of catalyst stability and not very precise suggestion of probable diverse system, as well as a comparison on such terms is necessary for designing catalysts to be formed at commercial level. Compared rates should be studied for catalyst per both surface area and mass, for cause elucidated above.

3 Classification of 2DMs for Photo-catalysts

Advancement in material and engineering science over the past years has allowed huge development in catalysis, sustainable energy production, sensor, and electronics. Novel spectroscopy and nano-fabrication techniques offered tools to comprehend primary materials’ properties and to materialize their functionalities by adjusting their configuration and composition. It leads to enormous advancement in multi-component industrial catalysts [73] (e.g., become weak after treatment [74]), excellent chemical production, electrocatalysis (e.g., fuel cell catalysts [75]), and photocatalysis [76]. This growth was not only governed through turnover and market demands but also through elevating community understanding, rules for environmental safety, and sustainable growth. Currently rising sustainable development and technologies create utilization of a broad range of components, of which some are rare and unequally spread on earth and therefore have economic viability and at probable risk supply. In some way ironically, sustainability and risks associated with material are frequently ignored in academic-level investigation. It is due to functionality and performances during working conditions generally prevailed over synthesis and takes apart costs; hence, evaluation of material criticality and its viability is very intricate and basically goes ahead [77]. However, a basic point of view is materials’ sustainability for final target in renewable energy synthesis. Certainly, as clean energy is almost limitless (e.g., solar, wind), materials and chemicals utilized to transfer it to real electrical energy are obtain rarely. Notably, precious metals group (i.e., platinum), rare-earth elements, gallium, aluminum cobalt, and many others [78] are indispensable components of immensely utilized commercial catalysts. If
dependence can be decreased via replacement, such materials would be recycled more competently in the future to circumvent economic disturbances and increasing reserved competition [79]. These materials should have the following properties:

1. Catalyst durability upgrading through material design (post-modifications, confinement)
2. Lowering noble/rare metal loadings, whereas upholding high activity, through maximizing active surface area (atomic-level thickness in low-dimensional materials)
3. Substituting significant components with cost-efficient and abundantly accessible ones (base metals, carbon-catalysis)
4. Enhancement of durability in catalysts’ synthesis and removal (green chemistry-based catalyst recycle)
5. Evaluation of toxicity and environmental effect of catalyst materials

The catalysts’ nano-structure is another supreme feature to be considered as it can be used to analytically study and compare diverse catalysts to realize tendency in activity. Generally, the size of photo-catalyst materials also affects their electronic arrangement originated through quantum confinement effects (less than 10 nm) and degree of interface with support, as smaller sized photo-catalyst materials have a larger portion of atoms at metal support edge [57]. For example, Taehung Paik et al. [80] defined the optical BG increased in tungsten oxide (WO$_3$) NWs compared to stoichiometric WO$_3$ bulk counterpart, because of Burstein-Moss shift. This increment confirmed direct photo-catalytic H$_2$ evolution from WO$_3$ NWs via alcohol photo-reform. The stable H$_2$ production on platinized WO$_3$ NWs is pragmatic under conditions where platinized bulk WO$_3$ and bulk WO$_{2.9}$ powders either do not show activity or show very low rates, proposing that enhanced surface area is the answer for enhanced activity. As a result, controlled size and composition can cause unanticipated and important alterations in SC photo-catalytic materials properties [81].

As an ideal candidate for photo-catalysis, the mainly studied 2DMs-based photo-catalysts can be divided into different types: counting, MOs, metal composite oxides, MHOs, bismuth-based materials, metal chalcogenides, and metal-free photo-catalysts. Based on photo-catalyst compositions, the 2DMs used in photo-catalysts can be mainly categorized as illustrated in Fig. 2. The 2DMs can be synthesized either through exfoliation of

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**Fig. 2** Scheme of 2DMs synthesis and strategies toward 2DM-based photo-catalyst design
parent layer material through top-down method or formed from small molecules using bottom-up self-assembly technique. Synthesis of 2DMs with tunable layer number, edge morphology, and degree of crystallinity is vital for utilizing these materials for elevated activity catalytic applications and is also discussed in our recently published reviews [3, 4, 19]. Therefore, in this part, we will only provide a concise introduction for basic properties with small explanations about the synthesis strategies of such three types of 2DMs, which are utilized for photo-catalysis applications.

### 3.1 2D metal Oxides (MOs) NSs

The MOs are broadly studied for photo-catalysts. Certainly, fabricating 2DMs-based MOs is considered as an efficient way to maximize SSA and charge migration and hence gets a competent photo-catalytic performance [32]. So far, numerous MOs with 2DMs structures have been formed and used in photo-catalysis applications, for example TiO₂, Fe₂O₃, Cu₂O, ZnO, WO₃, SnO, In₂O₃, CeO₂, HNb₃O₈, etc. [82]. Due to the basic non-layered structure feature, some 2D-MOs were complex to be formed by facile ultrasonic exfoliation technique from their bulk counterparts. So, numerous other means were applied for controlled formation of 2D-MOs. For example, a lamellar inorganic–organic hybrid intermediate policy was planned to form ultra-thin TiO₂ NSs [82]. Utilizing Ti-isopropoxide as a Ti source, octylamine as a capping reagent, 2-phenyl ethanol as solvent, lamellar TiO₂-octylamine hybrid precursors were obtained via solvothermal process (Fig. 3) [32]. The ultrasound-based exfoliation-resulted powder was washed to eliminate octylamine and get clean, ultra-thin TiO₂ NSs. The AFM result showed

![Fig. 3](image) The ultra-thin TiO₂ flakes. a Synthesis scheme. Adapted with permission from Ref. [82]; b AFM image, c height profiles correspond to AFM image in b. Adapted with permission from Ref. [32]
that TiO2 NSs’ average thickness was about 1.66 nm. A lot of other types of MOs-NSs, such as Cu2O [83] and In2O3 [84], were also formed via a similar technique. Taking advantage of ultra-thin size, the enhanced density of states (DOSs) by Fermi level (FL) and enhanced charge density on TiO2 NSs surface were obtained. For this reason, TiO2 NSs displayed quick transport of carriers and therefore achieved 450 times improved photo-catalytic activity as compared to bulk TiO2 for CO2-reduction for formate fabrication. Additionally, exfoliated single-crystalline WO3 NSs were formed by Bi2W2O9. On account of layered Bi2WO6 structure that is composed of [W2O7]2− and [Bi2O2]2+ layers, the WO3 layers were attained through careful etching of [Bi2O2]2+ layers via processing of acids like HCL and the stabilized WO3 layers can be obtained through the tetrabutylammonium hydroxide surfactant. These exfoliated WO3 NSs showed an improved BG as compared with bulk-WO3, caused by quantum confinement effect. With exception of an exfoliation method, the direct preparation development of MOs-NSs was obtained by wet chemical technique. Utilizing surfactant’ self-assembly approach through polyethylene oxide–polypropylene oxide–polyethylene oxide and ethylene glycol as co-surfactant, various MOs with ultra-thin thickness were formed, for instance TiO2, Fe3O4, Co3O4, ZnO, MnO2, and WO3 [32].

In the last four decades, various MOs, e.g., TiO2, ZnO, SnO2, WO3, and Fe2O3, were broadly examined as photo-catalysts [42, 85]. Among them, TiO2 was the most explored one due to its good stability, biocompatibility, and favorable electronic structure as well as light absorption nature [34]. The 2D-TiO2 NSs obtained from the exfoliation of layered titanate have drawn attention in utilizing them as photo-catalysts [86]. The 2D-TiO2 NSs showed SC nature similar to their bulk cousins and include rutile and anatase form of TiO2, but with somehow superior BG because of the size quantization. For instance, Ti0.91O20.36-NSs exhibited a BG of ~3.8 eV that was higher than that for anatase TiO2 (3.2 eV) [87]. Top-down multi-step access found on intercalation and exfoliation of layered MOs was well recognized to form MO-NSs [88]. For example, for TiO2-NSs, layered titanates were initially formed by high temperature, conventional solid-state reaction of TiO2, and mixture of alkali metal carbonates (Fig. 4).

After that, it was developed with an acid solution to generate protonated intermediate by ion-exchange route. The interlayers of protonated titanate were more extended by changing protons with a definite quantity of bulky organic ions, such as tetrabutylammonium cations (TBA+). In suitable condition, layered configuration was exfoliated induced via weak shear force, for instance, mechanical shaking in aqueous solution. Different kinds of layered MOs-NSs, such as WO3, titanoniobate [89] (TiNbO5, Ti2NbO7, and Ti5NbO14), perovskite oxides [90] (K2Ln2Ti3O10, Fig. 4)

![Fig. 4](https://example.com/fig4.png)

Scheme showing the crystal structure of lepidocrocite kind titanate and its exfoliation into TiO2 NSs. Adapted with permission from Ref. [29]
together with KLnNb2O7 and RbLnTa2O7 (here Ln stands for lanthanide ions), HNb2O6, HCa2−xSrxNb3O10, and HCa2−yTayO10 [91], were formed through analogous solid-state reactions method and wet-chemical exfoliation methods. For instance, titanoniobate NSs have exhibited enhanced photo-catalytic performance in organic pollutant removal [92]. Recently, Tae et al. studied the formation of numerous diamond-shaped titanate NSs with a normal lateral size < 30 nm, by applying a straightforward wet-chemical technique [93]. In very recent times, Zhou et al. formed freestanding, SL Bi2WO6 MSs by wet-chemical technique via using cetyltrimethylammonium bromide. Bi-atoms on SL were not saturated; hence, introduced numerous active sites on surfaces, which generated h+s directly under light irradiation. An excellent photo-catalytic performance of SL Bi2WO6 for photo-degradation of RhB was recognized by fast charge carrier separation at highly photo-active surface [94].

3.2 Metal Composite Oxides

Compared to MOs, metal composite oxides also showed advantages to photo-catalysis, and numerous metal composite oxides were formed with ultra-thin thickness [91]. Consistent with acid/base effect and ion intercalation supported exfoliation method, HNbWO6 NSs were obtained by dispersing the layer HNbWO6·1.5H2O into tri-ethanolamine aqueous solution [95]. The results based on AFM calculations showed that HNbWO6 NSs thickness was about 1.8 and 2.0 nm, which are in agreement with SL significance. As-synthesized HNbWO6 NSs suspensions displayed a proficient activity for photo-catalytic H2-evolution with a moderate rate of 158.9 µmol h−1. Furthermore, ion-exchange approaches through utilizing ultra-thin precursor were used for synthesis of metal composite oxides. For instance, SnNb2O6 NSs were obtained through K4Nb6O17 NSs and SnCl2 as precursors [96]. Through K4Nb6O17 ultrathin thickness, it was preserved in SnNb2O6 with ~3 nm thickness, as confirmed through AFM study. In comparison with bulk SnNb2O6, the SnNb2O6 NSs were having improved BG and more negative CB potential, denoting good reduction capability for photo-catalytic-based H2-evolution. Furthermore, charge transfer effectiveness in SnNb2O6 NSs was also enhanced because of ultra-thin thickness. Additional research showed that the outstanding vis-light H2-evolution activity was acquired over SnNb2O6 NSs, approximately 14 times superior to bulk SnNb2O6.

3.3 Metal Hydroxides (MHOs)

Ultra-thin MHOs were increasingly considered as significant class in 2DMs, which showed an exciting view in numerous sectors, for example catalysis, energy storage, and conversion. On account of simplicity of guideline for cations, the preferred BG was formed in MHOs by incorporating particular photo-active metal cations. So, the ultra-thin 2D-MHOs structure showed a great potential toward photo-catalytic uses. For example, ZnAl-layered double hydroxide (LDH) 2D-NSs were formed via a reverse micelle technique and used as photo-catalyst for converting CO2 to CO [97]. By means of sodium dodecyl sulfate as surfactant, 1-butanol as co-surfactant, translucent and stable reverse emulsion structure was created in an iso-octane/H2O mixed solution. Following Al and Zn sources addition to mix solution, urea was used to generate alkaline condition and formed ZnAl-LDH with ultra-thin configuration. Thickness was about 2.7 nm in standing NSs in TEM image and is equivalent to the thickness of 2D-LDHs’ layers. Due to the ultra-thin thickness, O2 vacancies (V_o) were formed in ultra-thin ZnAl-LDH NSs, resulting in the creation of Zn+−V_o complexes. The DFT-based study showed a novel defect-level hybridization with both occupied Zn 4s orbitals and O2p orbitals emerging in BG of ultra-thin ZnAl-LDH NSs compared with bulk ZnAl-LDH. The Zn+−V_o complexes can provide e− trap sites for CO2 photo-reduction. Consequently, an appreciably amplified photo-catalytic activity for CO2-reduction was obtained for ultra-thin ZnAl-LDH NSs compared with bulk ZnAl-LDH. Except ZnAl-LDH, several new MHOs with ultra-thin thickness, for example CoOOH [98], NiTi-LDH, and ZnTi LDH [99], also showed wonderful performance for diverse photo-catalytic uses.

3.4 Metal Chalcogenides

The TMDs have gained much interest because their mechanical, optical, and electrical characteristics were explored for a wide range of applications, for instance biosensors, catalysis, lithium battery cathodes, transistors, memory devices, photovoltaics, photodetectors, photo-catalytic solid lubricants, and PEC conversions. The TMDs (e.g., MoS2, WS2, and
TiSe$_2$) are a large group of layered materials with common representation as “MX$_2$,” where M is a transition metal element of group 4–10 ((Ti, Hf, Zr), (Ta, V, Nb), and (W, Mo)) and X is the chalcogen atom (S, Se, Te). The TMD NSs have different functions in PC and PEC applications. They behave as a photo-sensitizer via increasing light harvest ability in vis region of sun irradiation, a charge separator throughout appropriate energy band arrangement, and a charge carrier. Correct function of 2D nanosheets (NSs) depends on utilization of reaction scheme. In consequence of special electronic configuration, in general metal chalcogenides showed a comparatively broad light absorption area (Fig. 5), which were measured to be a group of talented materials having photocatalytic uses. Normally, the stoichiometry of TMDs can be expressed through formula MX$_2$, in which M and X signify a chalcogen and a transition metal, respectively. The single layer of a TMD involves three atoms, where M is situated in two X (Fig. 5a, b). The configurations of 1T and 2H phases of MoS$_2$ are shown in Fig. 5c.

Recently, many 2D metal chalcogenides have been formed and showed an excellent photo-catalytic performance, e.g., CdS, MoS$_2$, SnS$_2$, SnS, In$_2$S$_3$, ZnIn$_2$S$_4$, ZnSe, and SnSe [101]. The synthetic techniques of such 2D metal chalcogenides generally concentrate on exfoliation, because of essential layer structures. Taking hexagonal SnS$_2$ (h-SnS$_2$), such as h-SnS$_2$ SLs, can be attained through refluxing bulk-SnS$_2$ in formamide to rupture interlayer vdWs’ interactions [102]. Almost transparent aspect of SnS$_2$ NSs in TEM image exposes ultra-thin thickness, and it was described to be 0.61 nm via AFM, well matched with SL-SnS$_2$ slab along [001] direction. As a result of SL configuration, electronic structure of SLs-SnS$_2$ experienced discrete changes, with increased BG, higher DOSs at VB edge, and faster interfacial charge transfer. Therefore, SLs-SnS$_2$ delivers a surprisingly improved photo-catalytic H$_2$O splitting activity (70 times development) compared to bulk-SnS$_2$, under vis-light. The 2D metal chalcogenide NSs, for example MoS$_2$ [103], SnS$_2$ [104], TiS$_2$ [105], WS$_2$ [106], MoSe$_2$ [107], WSe$_2$ [103], etc., are rising as a new significant class of 2DMs in the photo-catalysis applications because of their good electronic properties [108]. Taking MoS$_2$ as an example, bulk-MoS$_2$ materials have indirect BG of 1.2 eV that is not suitable for photo-catalytic reactions caused by the lack of oxidation or reduction potential ($E_0$) for activating photo-catalytic method. However, MoS$_2$-NSs had been established with having a direct BG of ~ 1.96 eV because of quantum confinement effect that provides MoS$_2$-NSs along appropriate band positions and capability for vis-light absorption. In contrast to most of the layer MOs, vdWs bonding of metal chalcogenide interlayers creates exfoliation of these layers easily. Until now, a lot of top-down approaches are described for the formation of SL or FL metal chalcogenide NSs, for example lithium intercalation–exfoliation, mechanical exfoliation,
and liquid phase ultrasonic exfoliation [109]. Furthermore, bottom-up chemical production and chemical vapor deposition (CVD) techniques suggested potential influential alternatives such as exfoliation techniques for fabricating metal chalcogenide NSs. For example, Cheon et al. introduced disk-shaped ZrS₂ NSs with <2 nm thicknesses and lateral size ranging from 20 to 60 nm via reacting ZrCl₄ and CS₂ in oleylamine [110]. This method was, soon after that, extended for other transition metal selenide and sulfide NSs. The MoS₂ NSs were formed via solvothermal techniques using (NH₄)₆Mo₇O₂₄·4H₂O and thiourea as precursors [111].

3.5 Bismuth-Based Materials

Recently, bismuth (Bi)-based materials have been broadly investigated and studied for their photo-catalysis applications because Bi₆s in Bi(III) can hybridize with O₂p orbitals to generate novel favorable hybridized VB and BG of Bi-based materials which are narrowed for absorption of...
vis-light. Due to continuous improvement in photo-catalytic performance, numerous Bi-based materials with controlled ultra-thin thickness are formed, for example Bi₂WO₆ [112, 113], Bi₂MoO₆ [85], BiVO₄ [114], Bi₂SiO₅ [115] (BiO)₂CO₃ [94], Bi₃ NbO₇ [116], BiOX (X = Cl, Br, I) [117], and Bi₂O₃/Bi₂O₄− nano-composite [118]. The SL Bi₂WO₆ NSs were formed via surfactant cetyltrimethylammonium bromide (CTAB)-supported hydrothermal technique [94], where Br-ions from CTAB were adsorbed at SL Bi₂WO₆ surface and produced Coulomb repulsion forces, which delayed stacking of SLs Bi₂WO₆. Furthermore, hydrophobic long-chain cationic CTA⁺ at Bi₂WO₆ acts as active sites. After irradiation with light, h⁺s is produced in vis-light. photo-catalytic activity toward pollution deduction in interface, sandwich [BiO]+–[WO₄]²−–[BiO]+ substructure was achieved, as supported from AFM analysis (Fig. 6a–d). Plentiful coordinative unsaturated Bi-atoms were exposed at SL Bi₂WO₆ SNs and act as active sites. After irradiation with light, h⁺s is produced in [BiO]⁺ as e−s in [WO₄]²−. Resembling hetero-junction interface, sandwich [BiO]+–[WO₄]²−–[BiO]⁺ substructure permits efficient interface for space charge separation. Therefore, SL Bi₂WO₆ displayed significantly improved photo-catalytic activity toward pollution deduction in vis-light.

In addition, as-synthesized SL Bi₂WO₆ illustrated H₂-evolution activity under vis-light, even if Bi₂WO₆ nanocrystal in fact holds no H₂-evolution activity. Altering the surfactant type to polyvinylpyrrolidone (PVP), ultra-thin BiOCl NSs were attained by means of a solvothermal treatment [119]. The BiOCl nanoplate’s thickness (≈ 30 nm) was reduced to 2.7 nm, while PVP was applied as a capping agent, as verified through the AFM analysis. The polyvinyl skeleton structure of PVP prevented more development of the BiOCl nano-crystal by generating passivation layer about BiOCl cores via strong interaction with Bi³⁺, N, and O atoms of pyrrolidone ring. This suppressed the agglomeration of BiOCl nano-crystal along c-axis during repulsion forces in between polyvinyl groups. Therefore, ultra-thin BiOCl NSs were prepared via the PVP-assisted solvothermal treatment and this method was further used for synthesis of ultra-thin BiOBr and BiOI 2D form [120]. The attained ultra-thin thicknesses give BiOCl NSs with upshifted CB and VB potentials and reduced the BG relative to BiOCl nano-plates. As such, effective division of photo-induced (e−–h⁺)-pairs was obtained and caused an increase in photo-catalytic activity for pollutant removal [32]. Paolo Fornasiero and co-workers also explored Bi₂O₃/Bi₂O₄– composite that functions as a potential photo-catalyst (Fig. 6e–g). The aim of the study was to begin active species on photo-catalyst surface via utilizing a non-traditional advancement. Therefore, they utilized (UV–Vis)-light to stimulate alterations in Bi₂O₃ surface that produces Bi₂O₃/Bi₂O₄– nano-composite arrangement. So, for methylene blue (MB) such surface modifications bring significant enhancement in photo-catalytic performance. The wide BG with respect to Bi₂O₃ along excitation considerations proposes that analogous photo-induced crystal modifications, although exist, should be insignificant for TiO₂-based materials. Until now, only careful designed thermal treatments were able to make exciting anatase/rutile nano-composites with outstanding photo-catalytic performance [118].

3.6 Metal-Free NSs

Excluding metal containing SC 2DMs, metal-free 2DMs were also formed as photo-catalysts. Recently, new classes of metal-free 2DMs have been introduced from lightweight and abundant elements, such as carbon, phosphorus, and binary carbon nitride, boron carbide, and hexagonal boron nitride (h-BN) that reveal new prospects for photochemistry. The 2D-G with hexagonal sp²-hybridized structure is inspiring great research concern in a range of energy-related uses because of its elevated carrier mobility. The high flexibility and larger SSA alone from accessibility of solution processable graphene oxide (GO) allows 2D-G NSs to simply merge with other SCs to form electronic bridges [121]. Recently, 2D-G have been intensively studied in photocatalytic fields and demonstrated as competent e−-acceptor to improve the charge transfer and reduce (e−–h⁺)-pair’s recombination to improve photo-catalytic activity of composite photo-catalysts [3, 4, 18, 19]. More interestingly, although SL 2D-G is recognized as a semimetal with a zero BG, which is not suitable in light absorption, numerous scientists have confirmed that functionalized 2D-G base analogy like 2D-GO could be promising materials for nonmetal photo-catalysts as band structure of GO is associated with its degree of oxidation that can be engineered via choosing appropriate preparation methods. For example, Yeh et al. observed a 2D-GO that could work as active photo-catalyst...
in H₂O splitting [122] and can gradually produce H₂ from 20 vol% methanol solution in H₂O and pristine H₂O after irradiation with UV/Vis-light. After that, Hsu et al. studied 2D-GO and showed an elevated photo-catalytic efficiency for transformation of CO₂ to methanol (CH₃OH) by solar light irradiation [123]. As an equivalent of 2D-G, g-C₃N₄ NSs were rapidly rising because of their excellent chemical and electronic properties [124]. Bulk g-C₃N₄ has a layered 2D configuration and proper BG (~2.7 eV) for light absorption in visible range. The g-C₃N₄ NSs were obtained through delaminating bulk layered g-C₃N₄ that is usually formed via pyrolysis of N₂-rich precursors through bulk reaction or polycondensation.

A new metal-free photo-catalyst, with outstanding photocatalytic proficiency of g-C₃N₄ NSs under vis-light irradiation, was verified in many photo-catalytic uses. For example, Niu et al. [125] studied a simple top-down approach to form g-C₃N₄ NSs via oxidation etching of bulk g-C₃N₄ in air under high temperature (Fig. 7). The acquired g-C₃N₄ NSs thickness was about 2 nm with SSA 306 m² g⁻¹, which was high in comparison with bulk phase. Quantum confinement effect causes enhanced e⁻-transfer ability toward in-plane

Fig. 7  a Scheme shows bulk g-C₃N₄ and g-C₃N₄ NS structures. Adapted with permission from Ref. [29].  b Scheme to fabricate g-C₃N₄-NSs through thermal oxidation etching of bulk g-C₃N₄ at 500 °C in air.  c TEM image,  d AFM analysis of g-C₃N₄-NSs. Adapted with permission from Ref. [32]
direction, and the lifetime of photo-generated charge carriers was improved. Therefore, photo-catalytic performance of g-C3N4 NSs for H2-production process was really enhanced. In recent times, other liquid phase exfoliation techniques are formed to synthesize g-C3N4 NSs from bulk counterpart. For instance, Yang et al. prepared freestanding g-C3N4 NSs through liquid phase exfoliation of g-C3N4 powder in isopropanol; this exhibited good photo-catalytic effectiveness for H2-evolution by applying vis-light irradiation. Photocatalytic efficiency of exfoliated NSs was higher >17 factor contrast to non-exfoliated counterpart and with a factor of >8 than already described g-C3N4 NSs [126]. Apart from distinctive energy band configuration, g-C3N4 is more active toward many photo-catalytic uses, for example H2-evolution, CO2-reduction, pollutant deduction, disinfection, etc. As a result of in-plane graphite-like layer configuration with strong C–N covalent bonding and interlayer weak vdW’s forces, bulk g-C3N4 was accountable to be exfoliated and obtained in FL or even SL form. Generally, there are two methods for g-C3N4 exfoliation, i.e., thermal oxidation and ultra-sonication-based liquid exfoliation techniques. In view of that, H2-bond coherent strands of polymeric melon units in layers were not sufficiently stable beside oxidation. Liu et al. [125] formed a thermal oxidation exfoliation method to form an ultra-thin g-C3N4 NSs. Thicknesses of bulk g-C3N4 were steadily reduced with increasing times through layer-by-layer etching method (Fig. 7b–d). After 120 min, thermal oxidated g-C3N4 NSs with almost 2 nm thicknesses were obtained. Since quantum confinement effect and increased BG promoted e−’s migration rates along in-plane direction, H2-evolution activity improved 5.4 times, as compared to bulk counterpart. Encouraged by this synthesis method, numerous advance researches achieved organizing ultra-thin g-C3N4-NSs via modified techniques [127, 128]. The ultra-sonication assisted liquid exfoliation was observed as another effective technique to attain ultra-thin g-C3N4 NSs because of fundamentally layered structure.

In exfoliation process, the efficiency is affected due to surface energies, and when solvent and bulk materials match each other, exfoliation was extremely good. The calculated g-C3N4 surface energy was almost 115 mJ m−2, in a good agreement with H2O (~ 102 mJ m−2). Thus, with the use of H2O in g-C3N4 liquid exfoliation, exfoliated NSs with almost 2.5 nm thickness were acquired [129]. Based on the analogous law, Ajayan and co-workers [130] calculated g-C3N4 exfoliated by isopropanol. The as-formed g-C3N4-NSs were having homogeneous thickness of ~2 nm. This ultra-thin thickness of g-C3N4-NSs displayed an improved BG as well as charge migration rate in contrast to bulk g-C3N4. This caused a 9.3 times higher photo-catalytic-based H2-evolution. Similarly, other solvents were also searched to form ultra-thin g-C3N4 and obtained improved photocatalytic performance [131]. Despite g-C3N4, other metal-free materials were also formed, which act as photo-catalysts for different uses [132]. For example, ultra-thin silicon NSs controlled synthesis via molten salt-induced exfoliation and chemical reduction of natural clay [133]. Ultra-thin silicon NSs (≈ 5 nm thickness) showed an excellent H2-evolution performance from a H2O methanol mixture. Advanced investigations showed that proficient H2O splitting was obtained over ultra-thin silicon NSs lacking addition of co-catalyst or sacrificial agent [134]. Unfortunately, ultra-thin silicon NSs have experienced serious activity decline by extended time. How to approve suitable approach to increase stability might be heart of H2O splitting over ultra-thin silicon NSs [32].

### 3.7 Other Metal Containing 2D-NSs

In addition to aforementioned different types of materials, other recently introduced 2DMs, for example layered metal oxy-nitride and oxy-halides, and metal carbides, also have a great potential for photo-catalysis uses after chemical doping or combining with other SCs. For instance, bismuth oxy-halides (BiOX, X = Cl, Br, and I) were gotten increasing interest because of their outstanding photo-catalytic nature, that are analogous to or even greater than those of the anatase TiO2 [119]. Moreover, neutral layers of the Ti3C2(OH)2 formed through HF-assisted exfoliation of metal carbides, for example Ti3AlC2, were verified as competent photo-catalyst for adsorption and photo-catalytic decomposition of organic molecules in an aqueous atmosphere [135].

### 3.8 2D/2D Hetero-structures

Properly developing the 2D/2D hetero-structures confirmed the most talented form for further boosting the photo-catalytic activity, because of that hetero-junction interfacial effect [136]. The hetero-junction interfacial effect can encourage separation and therefore extend lifetime of the photo-generated (e−–h+) pairs in catalyst that directly or indirectly contributes to redox reaction of photo-catalytic
H₂-production or organics degradation. Several attempts were applied to engineer 2D-component or reinforce the interfacial acting force to form the capable 2D/2D photocatalysts. Although hetero-junction found on a range of dimensions (e.g., 2D/2D, 3D/3D, and 2D/3D) with exposed interface put right contact, they are all possible efficient catalysts. The 2D/2D hetero-junctions have different advantages for catalysis, as follows:

1. High catalytic active sites because of great SSA/inter-face area and ultra-thin thickness.
2. Charges are easily transferred because of small basic resistance and short transport path in 1D of the ultra-thin 2D components.
3. Transparency consequence from ultra-thin thickness is helpful in light absorption.

Therefore, plan as well as the use of 2D/2D layered hetero-structures has rapidly become the most up-to-date research topics. Recently, the family of ultra-thin, 2D layered materials formed significantly. Further, other than presently used ultra-thin 2D-NSs, for example 2D-G, TMDCs, and noble metals, there are many other 2D-NSs with changeable electronic and physical properties formed from the last few years, e.g., MOFs, h-BN, black phosphorus, metal–organic frameworks (MOFs), organic crystals, and covalent organic frameworks (COFs) [136].

### 4 Electronic Structure Engineering

Engineering an electronic configuration, the properties of ultra-thin 2DMs are experiencing a different variation, offering probabilities to enhance or even provoke novel photocatalytic activity. There are a range of ways to engineer the electronic structure of ultra-thin 2DMs, e.g., thickness tuning, component tuning, defect engineering, doping, and so

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**Fig. 8** a–c TEM results of TBA⁺-exfoliated Ca₂₋ₓSrₓNb₃O₁₀⁻⁻-NSs. d, e Raman spectra and UV–Vis diffuse reflectance spectrum of restacked HCa₂₋ₓSrₓNb₃O₁₀⁻⁻ and HCa₂Nb₃₋₉Ta₉O₁₀ NSs. Adapted with permission from Ref. [137]
on. Now, we will explain most of them in detail in the next section.

4.1 Component Tuning

For photo-catalytic employment, component of SC establishes band configuration. As reactivity of the photo-generated e−s and h+ s toward resultant surface redox reactions was usually defined by band edge potentials, component of SC demonstrates a vast effect on photo-catalytic performances. Particularly, for ultra-thin 2DMs, the electronic configuration strongly relies on equivalent constituent. Maeda et al. [91] formed HCa2−xSrNb3−yO10 and HCa2−xTa5+xO10 NSs with restricted energy band structure via interlayer exchange K+−ions with protons in layered KCa2−xSrNb3−yO10 as well as KCa2−xTa5+xO10 and after that more undergo exfoliation. By gradually engineering atomic component in NSs, the optical absorption of materials is deeply suffered (Fig. 8).

Thoroughly, commencement of absorption edge in HCa2−xSrNb3−yO10 showed a clear redshift with improved Sr-content, accompanying via BG energy reduced from 3.59 (x = 0) to 3.40 eV (x = 2). Additionally, onset of blueshift absorption edge was determined for KCa2−xTa5+xO10 with higher Ta contents. The substitution of Nb5+ by Ta5+−ions caused more negative CB potential, which was liable for blueshift of the onset absorption edge. Thus, tunable light absorption performance was obtained by altering component and further showed an important effect on the photo-catalytic H2-evolution reaction. By utilizing an analogous plan, energy band structure of ternary sulfides, H2−zZnx−yIn2S4, was efficiently engineered with ZnIn2S4 and showed optimal photo-catalytic H2-evolution rate [138]. Another significant case was tuning of halogen/O2 ratio in the bismuth oxy-halide to tune electronic structures. In accordance with DFT calculations, VB top of bi-oxy-halide was mainly composed of O2p and Xnp (n = 3, 4, and 5 for X = Cl, Br, and I) hybrid orbitals, while CB was primarily comprised of Bi6p orbitals. In the course of engineering O, X elements, BG and band edge potentials were efficiently engineered. Thus far, a number of Bi oxy-halide NSs with tuned O, X component were synthesized, for example Bi12−xO17−yC12 [139], Bi4O5SBr2 [140], Bi2O2I2 [141], and so on. In general, with decreasing Br or Cl content, acquired materials showed narrowed BG than that of resultant BiOCl or BiOBr and reduction of I content resulted in an increase in BG comparative to BiOI.

Benefiting from energy band structure range, tuned bi-oxy-halide ultra-thin NSs are showing superiority toward various photo-catalytic employments.

4.2 Thickness Tuning

SC thickness is an important factor to an electronic structure engineering and photo-catalytic performance optimization. As a result of known quantum confinement effect, BG of SC undergoes an increase, when materials thickness is reduced. Moreover, surface effect is aggravated as thickness reduced to an atomic size. The electronic DOSs can improve at the surface of ultra-thin 2DMs in comparison with interior of bulk materials. Such characteristics showed a significant impact on photo-catalytic efficiency of ultra-thin 2DMs. Based on thermal oxidation etching way, ultra-thin C3N4 NSs with thickness of ~ 2 nm were formed [125]. As thickness reduced to atomic size, electronic structure of C3N4 suffers from major difference. Consequently, due to quantum confinement effect, BG increased from 2.77 eV for bulk C3N4 to 2.97 eV in ultra-thin 2D-NSs. Simultaneously, thickness reduction grants guarantee to improve an electron transport capability toward in-plane direction and enhanced duration of photo-generated charge carriers.

Additional research originates in which CB edge of ultra-thin C3N4 NSs showed upshift in comparison with bulk counterpart [142]. So, photo-generated e−s holds strong reduction capability and helps in improving the photo-catalytic H2-evolution performance. Despite C3N4, electronic structure tuning is gained within other SCs through thickness engineering. Through thickness reduction of bulk SnNb2O6 to 50 and 3 nm, resultant BG increased from 2.30 to 2.35 and 2.43 eV, respectively, causing upshifting of CB edge [96]. It is suggested that thickness engineering was an efficient way to alter energy band configuration of SCs. Moreover, when bulk materials thickness is regularly decreased to an atomic size thickness or even SL, the ratio of exposed surface atoms to whole atoms can be prominently improved. Lack of nearby atoms formed plentiful coordination on unsaturated surface atom with dangling bonds and is leaning to bond with other atoms to attain stability. So, these surface atoms displayed a high surface energy and chemical reactivity. The free-standing SnSe and SnS NSs with all exposure surface atoms were acquired through exfoliating their bulk counterparts in mixed solvent of H2O and ethanol [143]. Taking
SnS as an example, with large-area NSs resembling morphology with lateral size of almost 500 nm, their transparent properties were studied by TEM investigation, showing ultra-thin thickness of as-synthesized material (Fig. 9). The average height of SnSe NSs, calculated by AFM, was about 0.57 nm that agrees with thickness of half unit cell. Hence, these SL-exfoliated NSs calculated band structures which proposed a change from an indirect SC in bulk SnS to direct SC for SnS SLs. In comparison with bulk SnSe, enhanced DOSs were obtained at VB edge of SL SnS, which were enabling SL SnS with improved carrier transport efficiency. To get benefit from SL structure, SLs SnS showed improved photo-absorption and charge separation efficiency and later supported H2O splitting performance.

4.3 Doping

The appropriate doping was observed as a competent approach for engineering physicochemical property of 2DMs. Conscious manufacturing of extrinsic metal or nonmetal species into SC lattice presents the prospect to adjust electronic or surface configurations of host material for enhancing photo-catalytic performance. Types and allocation of dopants are very important to control properties of host SCs. Advantages of atomic size of 2DMs; doping perhaps is a very sufficient plan to influence properties of ultra-thin 2DMs. Normally, doping always happens on bulk materials’ shallow surface due to lack of atoms accessing gallery that demonstrated a small manipulation.
on their total performance. Concerning ultra-thin 2DMs, atomic thickness permits efficient doping of dopants and just needs small diffusion penetration. So, it is enviable to tailor heteroatom into 2DMs and builds high competence methods.

### 4.3.1 Metal Doping

Metal ions incorporation into crystal lattice causes a rise in impurity levels in SCs forbidden band. Onset light absorption edge redshift is frequently examined that is recognized to cause
a transition of impurity quantities to CB or VB. Normally, the very capable doped photo-catalysts primarily depend on doping alteration of metal ions that satisfied the criteria, i.e.,

1. The $e^-$s and $h^+$s can be trapped through dopant and make sure efficient confined separation.
2. The captured $e^-$s and $h^+$s are generated and transferred on surface successfully.

Xie and co-authors [145] doped In$_2$S$_3$ NSs with Co to optimize photo-catalytic H$_2$O splitting. Through a lamellar inorganic–organic hybrid intermediate approach, Co-doped In$_2$S$_3$ NSs (0.59 nm thick) along with 3-atomic layers thickness were formed (Fig. 10). The electronic configuration of In$_2$S$_3$ using three atomic layers and Co-doped In$_2$S$_3$ was first verified via DFT simulations. To simulate existence of Co-dopant, certain ultra-thin In$_2$S$_3$ NSs with noticeably enhanced DOS are developed at conduction band maximum (CBM) as compared with perfect, ultra-thin In$_2$S$_3$ NSs. Additionally, Co-ion doping provides a Co-doped In$_2$S$_3$ material with numerous other energy levels that were resultant from Co$_{3d}$ splitting. Under light irradiation, $e^-$s was simply excited through $d \rightarrow d$ internal transition of the Co-ions in tetrahedral coordination, allowing generation of more photo-generated ($e^-$–$h^+$)-pairs. These results were confirmed through light absorption difference of In$_2$S$_3$ NSs and Co-doped In$_2$S$_3$ in (UV–Vis)-diffusion reflectance spectrum. Considerable advancement in light absorption was viewed from 600 to 2000 nm that was consigned to creation of dopant energy levels of Co. To get advantages from doping of Co, photo-generated charge separation effectiveness enhanced about 25-fold increase in average recovery duration, as practiced through an ultrafast transient absorption spectroscopy (UTAS). Therefore, Co-doping permits 10 times developed photo-catalytic activity for H$_2$O splitting compared to perfect In$_2$S$_3$ NSs. Similarly, other metal elements were also utilized for doping to engineer electronic structure of ultra-thin 2D-hosted photo-catalyst, for instance Pt, Rh, Cr, Fe, Cu, and so on [146]. For example, Fe was doped into ultra-thin BiOCl NSs, which extended light absorption range from UV to Vis-light. Photo-catalytic activity for pollutant removal and H$_2$-evolution was increased. These results certainly verified that metal element doping is an efficient way to tune electronic structure of ultra-thin 2D photo-catalysts and can promote photo-catalytic performance.

### 4.3.2 Nonmetal Doping

Concerning nonmetal elements doping, two direct theories were suggested to modify an electronic arrangement and hence influence photo-catalytic performance. First, dopants can generate localized states between forbidden bands and one advantage is fusing of dopant-occupied positions with VB and upshifting of valence band maximum (VBM). Such two diverse techniques normally originate from different doping types, where surface doping will cause development of localized states and uniform doping will promote VBM [148]. As mobility of $h^+$s in localized states is slow and after that restricts photo-catalytic efficiency, offering uniform allocation of dopant to upshift VBM and encourage $h^+$s relocation is preferred much. The atomic thickness of the 2DMs facilitated a uniform doping because little doping depth is specifically needed [149]. By tailoring O$_2$-atoms for 2D ZnIn$_2$S$_4$ NSs to replace sulfur atoms lattice, electronic configuration suffered by diverse differences from the pristine ZnIn$_2$S$_4$ NSs [150]. So, the DFT-based calculations showed that O$_2$-doping effectively reinforces DOS at VBM versus pristine ZnIn$_2$S$_4$, enlightening creation of enhanced charge density around VBM. Both of CB and VB edge in O-doped ZnIn$_2$S$_4$ showed the upshift concerning ZnIn$_2$S$_4$ NSs, as verified through UV–Vis absorption spectrum and XPS VB spectrum. It enhanced CBM as well as improved the VB distance across obtained with very superior mobility and improved the expenditure of photo-generated $h^+$s, thus to support H$_2$ production. Wang and co-authors studied that C-atoms doping can efficiently refrain electronic configuration of h-BN (Fig. 11) [151]. So, the DFT simulation showed that BG of h-BN was obtained to be 4.56 eV. After C-doping in structure, BG was notably reduced. Regarding B$_{11}$C$_{12}$N$_9$ compounds, BG was narrowed to 2.00 eV, through VB and CB edges which mostly consist of C$_{2p}$ orbitals. B$_{11}$C$_{12}$N$_9$ VB top states were not localized in comparison with pure BN. Taking advantage of C-doping with $sp^2$-delocalization system, ultra-thin C-BN NSs with thickness of almost 3–4 nm were achieved and displayed an outstanding vis-light photo-catalytic performance to evolution of H$_2$ and reduction of CO$_2$. Considering insulator characteristic of pristine h-BN, it is illustrated that nonmetal doping can endorse photo-catalytic performance and also create promising photo-catalytic performance.
4.4 Defect Engineering

Aside from doping, defect engineering also demonstrates an important effect on ultra-thin 2DMs, in case of photo-catalysis. Owing to 2D atomic size thin structure, in the presence of defects, it has strong influence on fundamental properties, in spite of a very low-level doping. In relation to huge surface defects formation in the bulk materials, ultra-thin 2DMsNSs with relatively small atomic escape energy can propose an important chance to get a range of defects. So, it is necessary to construct surface defects, for instance anion, cation vacancies, pits, vacancy association, and distortions, to efficiently optimize electronic configuration of ultra-thin 2D photo-catalysts.
4.4.1 Anion Vacancies

In anion vacancy type, V\(_{O}\) was broadly studied due to its small creation energy and prevalence in the oxide materials [152]. For example, Fengcai Lei et al. [84] studied that by fast heating of intermediate In(OH)\(_3\) NSs in O\(_2\) or air, V\(_{O}\)-rich and V\(_{O}\)-deficient In\(_2\)O\(_3\) NSs were formed in fully controlled way, respectively. Figure 12 shows the AFM image, which showed thickness of In\(_2\)O\(_3\) NSs to be almost 0.9 nm, enlightening controlled formation of In\(_2\)O\(_3\) materials with atomic thickness. ESR and XPS spectrum results showed the presence of V\(_{O}\). The observed 531.4 eV peak showed V\(_{O}\)-rich ultra-thin In\(_2\)O\(_3\) NSs, which have maximum peak area, signifying that more V\(_{O}\)-rich ultra-thin In\(_2\)O\(_3\) NSs were formed compared to V\(_{O}\)-poor ultra-thin In\(_2\)O\(_3\) NSs and bulk counterpart. Moreover, sharp V\(_{O}\) signal at g = 2.004 in ESR spectrum was also observed that shows V\(_{O}\)-rich In\(_2\)O\(_3\) NS sample holds the highest level of V\(_{O}\). In V\(_{O}\) engineering, electronic configuration of In\(_2\)O\(_3\) NSs with rich V\(_{O}\) will experience noticeable change. As authorized
through DRS analysis and the XPS VB spectrum, $V_o$-rich In$_2$O$_3$ NSs showed a narrowed BG and upshifted VB edge. DFT simulations clearly show that enhanced DOS at VBM was created and a novel defect concentration showed $V_o$-rich In$_2$O$_3$ than $V_o$-poor In$_2$O$_3$ NSs. So, the $V_o$-rich In$_2$O$_3$ NSs acquired higher carrier level and enhanced electric field in
space charge regions. The e−s were further simply excited into CB in irradiation. Therefore, V_o-rich In_2O_3 NSs showed 2.5 and 15 times enhanced photo-catalytic performance as compared to V_o-poor In_2O_3 NSs as well as bulk In_2O_3, correspondingly, for H_2O oxidation. Such outcomes certainly verified the efficient role of anion vacancy in electronic configuration engineering.

4.4.2 Cation Vacancies

Besides anion, cation vacancies are extremely efficient approach to cause useful electronic structure modification of ultra-thin nano-structure due to multifarious electron arrangement and orbit. For example, vanadium (V) vacancies (V_v) were initiated in single-unit-cell BiVO_4

Fig. 14 Scheme showing the crystal structure of BiOCl. a 3D-projection. b, c [Bi_2O_2]^{2+} layers along with the [010] and [001] directions, correspondingly. d TEM/HR-TEM of BiOCl NSs. e Positron lifetime spectra of ultra-thin BiOCl NSs and BiOCl NPs. f, g Scheme showing trapped positrons of VBi"defect and VBi"VO VBi"-associated vacancy, correspondingly. Adapted with permission from Ref. [119]
NSs (1.28 nm) along diverse quantities (Fig. 13) [153]. The atomic level concentration of the V{sub}v was done through positron annihilation spectrometry (PAS) and X-ray fluorescence (XRF). For BiVO{sub}4 the shortest life component (τ{sub}1, around 200 ps) approved from PAS that trapped at V{sub}v, helpful for subsistence of V{sub}v for two samples. Comparative positron intensity duration for V{sub}v-rich BiVO{sub}4 NSs was denoted for higher V{sub}v level. Furthermore, elemental ratio of t V and Bi was verified to be 0.914 and 0.976 in V{sub}v-rich BiVO{sub}4 NSs and V{sub}v-poor BiVO{sub}4 NSs, in that order proposing concentration difference of V{sub}v. Benefiting from incidence of V{sub}v, a novel defect level can be produced in BG of BiVO{sub}4, as confirmed via DFT simulation, which leads e{sup}−′s further capable to be excited into C.B. Additionally, higher DOS at VB edge was achieved because of V{sub}v engineering. So, engineered vacancies increased the light harvest and promoted electronic conductivity for V{sub}v-rich BiVO{sub}4. Simultaneously, abundant V{sub}v allowed an efficient charge separation that prolonged carriers’ lifetime from 74.5 to 143.6 ns. Taking advantages from such V{sub}v, an advanced photo-catalytic performance was attained from methanol synthesis rate up to 398.3 µmol g{sup}−1 h{sup}−1.

4.4.3 Associated Vacancies

The lost surface atoms not just introduced mono-vacancy but also vacancies associated were able to appear. As a result of multi-atomic vacancy coupling, vacancy associated can strongly engineer electronic structure and cause amazing electronic performance. For instance, triple vacancy of VBi""VO VBi"" were built in ultra-thin BiOCl NSs (thickness = 2.7 nm) with dimension engineering (Fig. 14) [119]. Generated associated triple vacancy VBi""VO VBi"" was verified through PAS. When Bi-atoms’ outer surface was exposed in BiOCl crystal configuration, it is very likely to break out from lattice to make vacancy. While thickness was decreased to an atomic size, O{sub}2-atoms that linked to Bi-atoms in an internal layer also escaped more effortlessly. So, control defects in BiOCl nano-plates were separated VBi"", whereas that changed its associated vacancy VBi""VO VBi"" in ultra-thin BiOCl NSs. Different defect types certainly affect the electronic structure that guarantees BiOCl NSs with enhanced adsorption of RhB molecules due to further negative charge. Benefiting from defect types changing from VBi"" to VBi""VO VBi"", ultra-thin BiOCl NSs showed both upshifted CB and VB potentials that favor charge mobility and therefore allowed enhanced separation of (e{sup}−–h{sup}+) pairs. Therefore, ultra-thin BiOCl NSs showed great solar photocatalytic activity toward removal of pollutants.

4.4.4 Distortion

Besides the vacancies, other defects, for instance, distortions and pits were also sufficient policies for changing electronic structure of the ultra-thin 2D photo-catalysts. For instance, O’Hare and his research team [99] formed NiTi-LDH NSs through controlled thickness during reverse micro-emulsion approach. As obtained NiTi-LDH NSs, local atomic arrangement was examined through the X-ray absorption near-edge spectroscopy (XANES). While thickness significantly decreased, the titanium cation (Ti{sup 4+}) with lowered oxidation state was achieved in NiTi-LDH NSs (≈ 2 nm thickness), whereas it is approximately completely Ti{sup 4+} in bulk NiTi-LDH. In comparison with bulk NiTi-LDH, lower coordination numbers of Ti-cations were seeing in NiTi-LDH NSs and experience severe crystal deformations. Consequently, NiTi-LDH NSs showed distinguishing electronic crystal lattice and enhanced e{sup −} transfer effectiveness comparative to bulk NiTi-LDH.

4.4.5 Pits

Pits formation gives a good technique to enhance surface defects which produced more coordinated unsaturated atoms with dangling bonds around pits in NSs. Through thermal treatment of bulk g-C{sub}3N{sub}4 in NH{sub}3 environment, NSs are efficiently exfoliated and many in-plane pits were built in g-C{sub}3N{sub}4 NSs [124]. In-plane pits formation damaged g-C{sub}3N{sub}4 plane structure and supplies promising active sites with dangling bonds. These dangling bonds serve as cross-plane diffusion pathways to speed up mass transfer and charge diffusion. Furthermore, formed pits are promoted as a result in creation of C-vacancies owing to unbalance structure. So, g-C{sub}3N{sub}4 NSs showed improved BG and absolute light absorption area matching with bulk counterpart. Simultaneously, pit-rich g-C{sub}3N{sub}4 NSs guarantee superior CB and VB potential and give advanced e{sup −} donor density. Thus, 20 times high photo-catalytic H{sub}2-evolution activity was attained in vis-light irradiation. The aforementioned investigation results give a new and
deep insight to comprehend method of action of surface defects in supporting photo-catalytic activity from energy band structure, surface charge, and SASs. Usually, as relative to defect poor counterpart, engineered defects in ultra-thin 2DMs can alter electronic configuration, generally with improved DOS at edge of VB or CB, or even create a novel defect concentration in between forbidden band. Generally, light absorption possibility of genuine materials with redshift and hence light harvesting capability can be improved. At surface, limited charge density can also be altered and might make possible adsorption and activation of the target molecules. Simultaneously, formed surface defects can develop carrier level in the photo-catalysts and provide charge separation centers to entrap the carriers, encouraging consumption effectiveness of h⁺s and e⁻s for analogous interfacial redox responses.

4.5 Anisotropic Effects in Catalysis

Photo-catalytic routes could show vital to sustainable manufacturing of fuels and chemicals necessary for carbon–neutral society. An (e⁻–h⁺) recombination is a serious issue that has till date limited efficiency majority of potential photo-catalysts. Therefore, Matteo Cargnello et al. [155] showed the efficiency of anisotropy in enhancing charge separation and thus increasing activity of TiO₂ photo-catalytic method. Particularly, they showed that H₂ fabrication in homogeneous, 1D brookite-TiO₂ nano-rods was highly improved through engineering their length. Utilizing respective characterization techniques to separately investigate excited e⁻ and h⁺, linked high observed reaction rates to anisotropic arrangement support competent carrier use. The QY for H₂-fabrication from C₃H₆OH, C₅H₈O₃, and C₆H₁₂O₆ as high as 65%, 35%, and 6%, correspondingly, showed generalization of this method for enhancing the photo-activity of SC-NMs for a broad range of reaction systems.

5 Hybridization

Unlike bulk materials, 2DMs have become a hot topic in academic field due to their atomic layer thickness, broadband absorption, and ultrafast optical response, which have been widely applied in the ultrafast laser generation [156–183], optical switching and modulators [184–197], optoelectronics devices [183, 198–203], and biosensor and biotherapy [14, 44, 204–214]. 2DMs have an ultra-large SSA to make sure that surface state is even more significant compared to bulk inside. Photo-generated charge carriers will be distributed at surface to engage in the redox reactions, to be discussed next. So, surface hybridization to present size element to support consumption effectiveness of charge carriers is enviable below precondition of 2D arrangement. Consistent with surface hybridization, numerous representative hybridizations with 2D structure are introduced, e.g., QDs/2DMs, single atoms/2DMs, molecular/2DMs, and 2D–2D stacked materials.

5.1 Quantum Dots/2DMs Hybridization

Coordinated unsaturated surface atoms of NPs have dangling bonds that used energy. To further decrease NPs’ size, bigger part of surface atoms compared with total atoms will be attained and their regular atom binding energy must be high. So, if the size of NPs can control the QDs and modify 2DMs, interfacial strong coupling among them can be manufactured. Furthermore, QDs can show high dispersion on 2DMs because of their small size; those probably effective co-catalysts furthermore enhance the photo-catalytic activity. To develop operation effectiveness of Ag, Ag-QDs with size > 5 nm were formed. After hybridization with BiOBr NSs, photo-catalytic activity has been significantly boosted to degrade tetracycline hydrochloride, ciprofloxacin (CIP), and rhodamine B after vis-light irradiation. It was studied that tailored Ag-QDs activate molecular O₂ through hot e⁻ which decrease after vis-light exposure. The Ag-QDs can concurrently provide charge separation centers, adsorption centers, and photo-catalytic reaction centers, which are dependable on enhanced photo-catalytic efficiency. To decrease service of noble metals, non-noble metals or even metals-free QDs are taken as other choice. Also, thickness of subjected 2DMs can be further decreased to SL, in order to get improved dispersion and interfacial contact. For example, nitrogen-doped carbon QDs (N-CQDs) through 3 nm size were formed by facile hydrothermal method and later modified at BiOI NSs’ atomically thin surface [120]. The AFM analysis showed that average thickness of BiOI was almost 0.9 nm, proposing SL arrangement.
After N-CQDs, the N-CQDs/BiOI matters introduction displayed significantly extended lifetime of photo-generated charge carriers, as showed through time-resolved transient photo-luminescence (PL) decay and immediate photo-current. BiOI atomic-level configuration makes sure prominently quick bulk charge diffusion to surface and conjugated π-modified N-CQDs configuration, which effectively endorse surface charge separation, resulting in longer carrier duration. Therefore, the photo-catalytic activity and the N-CQDs/BiOI materials active species concentration enhanced considerably. Kang and co-authors also confirmed that C-QDs can work as chemical catalyst to really improve the photo-catalytic H2O splitting via C3N4 [215]. Different from traditional single step 4e− reaction from H2O splitting, 2e−/2e− two-step path was followed by the C-QDs-C3N4, where C3N4 is added to transfer H2O to H2 and H2O2. Moreover, C-QDs are accountable in H2O2 decomposition and O2 evolution. Therefore, outstanding photo-catalytic H2O splitting effectiveness can be obtained, with 2.0% solar to H2 efficiency and robust stability in 200 recycle run after 200 days. Similarly, there are also some other systems concerning QD/2DMs hybridization to further enhance photo-catalytic efficiency, for example CdSe QDs, Zn–Ag–In–S QDs, NiS2 QDs, and so on [216]. Such findings certainly verified superiority of QD modification, and QD/2D arrangement might be efficient substitute for configuration to get improved photo-catalytic performance.

5.2 Single Atoms/2DMs Hybridization

To further enhance photo-catalytic activity, size reduction of NPs to single atoms is possibly a probable plan. However, fraction of unsaturated coordination bonds of monoatom maximizes and enables a strong surface effect [217]. The first studied monoatom-based catalysis by Zhang et al. [218]
became an interested topic in photo-catalysis direction. The monoatom-based photo-catalyst was based on isolated single atom on support materials surface, in the form of dispersion or coordination. Monoatoms-based strategy can improve photo-catalytic activity and offer another technique to alter the selectivity. As well, active single atom, chemical bonding in metal single atom, and 2D M SSs-based supports have become a strong and simpler charge transfer method. So, it is very attractive to create a single-atom/2DMs hybridization to obtain a high photo-catalytic activity [219]. Wu and co-workers [220] studied single Pt-atom as co-catalysts to advance photo-catalytic H2 evolution activity of C3N4 NSs. A simple liquid phase reaction with C3N4 and H2PtCl6-coupled low-temperature annealing was applied to form Pt-single atoms/C3N4. High-angle annular dark-field STEM (HAADF-STEM) was utilized to establish allocation and arrangement of Pt. The individual clear spots matching to Pt-atoms were viewed to be consistently dispersed on g-C3N4, with ~99.4% Pt size of >0.2 nm, showing a Pt sub-sist completely as monooatoms. On the other hand, when the Pt loading quantity reaches 0.38%, the Pt-atoms dispersion was denser and formed numerous sub-nanometer clusters. Extended X-ray absorption fine structure (EXAFS) spectroscopy was utilized to investigate local atomic configuration of the Pt/C3N4. The Pt-atoms coordination number was about 5, through bond distance of ~ 2.03 Å, exposing those Pt-atoms that were dispersed on the top of C3N4 system. Following production of single Pt-atom/C3N4 arrangement, photo-catalytic H2-evolution activity was significantly enhanced. The H2-evolution rate of Pt/C3N4 (0.16 wt% Pt loading) achieved was almost 318 μmol h⁻¹, about 50 times advanced, as compared to pristine-C3N4. Simultaneously, single Pt-atom/C3N4 showed admirable stability for H2-evolution and isolated single Pt-atom still stays at C3N4 after circulations. The desirable quality of UTAS, surface trap states of C3N4 verified was basically changed because of isolated single Pt-atom that extends the carrier duration and provides more chances for e⁻ s to engage in H⁺-reduction method. Moreover, separated single Rh-atoms were spread on 2D-TiO2 NSs along with homogeneous 0.7 nm thickness via calcination, protonation, and coupled exfoliation method [221]. In HAADF-STEM image, separated brightest spots were observed that showed Rh-atoms but intermediate brightness spots symbolized Ti-atoms. The EXAFS showed that Rh species in single Rh-atoms/TiO2 displayed an analogous chemical setting as Rh₂O₃ showed bonding to O-atoms which was hence oxidized. Mono-Rh-atom co-catalysts were served as a reaction core for photo-catalytic-based H2-evolution, consistent with DFT simulations. So, H2-evolution rate was boosted 10 times as compared to pure TiO2 NSs. Although single atoms were engaged in catalysis, there were also existed numerous matters to be determined. Normally, the sustained content of monoatom was comparatively small and noble metal single-atom showed main types. It is very attractive to boost quantity of supported metal atoms with isolated single-atom arrangement and broaden it to other non-noble metals. Moreover, it is required to promote the stability, in order to meet potential industrial uses. The facts that single isolated metal atoms had high surface energy were shown, in which isolated metal atoms strongly cooperate with support surfaces. Through influenced metal atoms interactions with surface defects (elevated energy sites) on support, hybridization energy scheme might turn into a local minimum. Consequently, mono-metal atoms can be fastened as well as kept stable. Particularly in ultra-thin 2DMs, surface defects are liable to be generated because of ultra-large SSA and minute atomic flee energy. So, it is possible to construct monoatom anchored surface DR ultra-thin 2D arrangement to elevate photo-catalytic activity.

5.3 Molecular/2DMs Hybridization

Despite single isolated atoms, single molecule materials can also be used to engineer electronic structure by acting as a co-catalyst to enhance photo-catalytic activity [222]. Profiting from sub-nano-pores in C3N4, molecular TiO2 was included into C3N4 NSs by facile polycondensation of precursors with dicyandiamide and TiO2-ions [223]. The morphology of clean ultra-thin TiO-C3N4 NSs was obtained and confirmed by TEM analysis, with thickness of about 3−3.3 nm. From HAADF-STEM analysis and elemental mapping, TiO2 was originated to be consistently dispersed on C3N4 framework with isolated format. These results suggested that molecular TiO2 was effectively built in C3N4 framework equally. Local Ti–O geometrical and electronic structures in sub-nano-pores of C3N4 NSs were found through XAFS. Usually, anatase-TiO2 displayed well-defined triple pre-edge characteristics that can be recognized to distort TiO6 pattern with six coordinated O₂⁻-atoms. Dissimilar from TiO2 result, Ti–O in C3N4 exhibited a single pre-edge feature with non-symmetric structure. The
EXAFS showed that Ti-atoms were located in C₃N₄ h⁺s that was coordinated with six N₂-atoms in C₃N₄ and one O₂ atom out of plane in C₃N₄. Benefiting from TiO₂ molecule insertion, TiO-C₃N₄ NSs displayed a narrowed BG in comparison with pristine C₃N₄ with a reduction in CB position. It is resultant from more electron involvement of Ti–O into C₃N₄ and enhances π–e⁻ delocalization in conjugated structure. TiO-C₃N₄-engineered electronic structure can also enhance charge carrier separation. Therefore, TiO-C₃N₄ enhanced the photo-catalytic performance for ·OH generation and removal of pollutant. In photo-catalytic method, h⁺s transfer slower kinetics which brings massive carrier recombination in Achilles’ heel of photo-catalytic conversion activity. Even though ultra-thin 2D-structure permits quick charge migration in bulk phase, lack of surface charge separation centers will also spoil overall photocatalytic activity. Utilizing strategy to encourage surface charge separation, particularly h⁺s transfer is extremely required. Instead, it looksfeasible to utilize H₂O soluble molecular materials as homogeneous co-catalyst and hence also optimize photo-catalytic performance. Wu and his research team [220] formed H₂O-soluble molecular trifluoroacetic acid (TFA) as co-catalysts to enhance photo-catalytic H₂-evolution performance of K₄Nb₆O₁₇ NSs. Taking advantage of reversible redox couple TFA/TFA⁻ as well as high active intermolecular radical responses, TFA molecule served as strong h⁺s-shuttle, allowing efficient move of the photo-generated h⁺s and ensuing elevated charge separation effectiveness. The TFA increment enhanced H₂-evolution rate regularly and the maximum rate reached 6344 µmol g⁻¹ h⁻¹, when TFA/K₄Nb₆O₁₇ molar ratio was 25.6. This optimum H₂ yielding rate was ~ 32 times higher compared to pristine K₄Nb₆O₁₇ NSs, certainly signifying this molecular co-catalyst. As solid-state co-catalysts, they are restricted from limited contact areas in co-catalysts and host photo-catalyst, and surface charge separation cannot be completely definite. When overmuch solid-state co-catalysts were anchored on photo-catalyst, the SASs will be covered that deficient in the satisfactory active sites easy to get reactant molecules. As a result, H₂O-soluble molecular materials such as molecular co-catalysts can equally disperse in the solution and give greatest available area to host photocatalysts. So, developed molecular co-catalyst approaches perhaps are a possible way in a competent separation of photo-generated carriers and therefore improve photo-catalytic performance.

5.4 2D–2D Stacking Materials Hybridization

While constructing 2D–2D stacks, it is a largely applied method to boost photo-catalytic efficiency. Particularly for layered materials, lattice mismatch was reduced due to comparable layered structures, and 2D–2D stacking with close associates was formed. For example, Zhang and co-workers [139] studied SL Bi₁₂O₁₇Cl₂ with surface Vᵥ via Li-intercalation-based exfoliation approach. Afterward, SLs MoS₂ NSs were assembled onto SL-Bi₁₂O₁₇Cl₂ through surface Vᵥ and build Bi-S bonds in Bi₁₂O₁₇Cl₂ and MoS₂. TEM image well matched with an elemental mapping results proposed that numerous tiny MoS₂ NSs were strongly anchored on a large Bi₁₂O₁₇Cl₂ NS to make 2D stacking hetero-structure (Fig. 16); normal thickness of large size and small size NSs was ~ 0.717 and 0.686 nm that concurred with Bi₁₂O₁₇Cl₂ and MoS₂ SLs, in that order.

The atomic resolution HAADF-STEM analysis and resultant EELS elemental mapping showed that it was obviously studied and SLs-MoS₂ were anchored selectively on (Bi₁₂O₁₇) end faces to construct (Cl₂)–(MoS₂)–(Bi₁₂O₁₇). As charge density surrounding (Bi₁₂O₁₇)₂⁺ layer was superior compared to (Cl₂)²⁻ layer, photo-generated e⁻s and h⁺s were ambitious to (Bi₁₂O₁₇)⁺ end faces under irradiation, correspondingly. Photo-generated e⁻s flowed in between MoS₂ SLs through formed Bi-S bonds and enable efficient charge separation (ultra-long duration of carrier 3446 ns), as proofed through TA spectroscopy. Taking advantage of atomic size thickness, efficient directed interface charge separation, and plentiful H₂-evolution sites in MoS₂, acquired MoS₂/Bi₁₂O₁₇Cl₂ bilayers displayed great vis-light photo-catalytic H₂-evolution performance. Using ascorbic acid as h⁺s sacrificial agent, H₂-evolution rate can turn up 33 mmol h⁻¹ g⁻¹ and quantum effectiveness of 36% at 420 nm. Other than MoS₂/Bi₁₂O₁₇Cl₂, there are several investigations about 2D stacking to optimize photo-catalytic efficiency, for instance NiO/C₃N₄/Co₃O₄ [225], MoS₂/TiO₂ [224], MoS₂/CdS [226], WS₂/CdS [226], MoS₂/C₃N₄ [227], SnS₂/C₃N₄ [228], Fe₂O₃/C₃N₄ [229], C₃N₄/Bi₂O₃I₂, ZnCr-LDH/layered titanate [230], and ZnIn₂S₄/MoSe₂. For example, a distinctive 2D stacking structure has more benefits. It increased the available area about planar interface in 2D/2D structures and reduced barriers for e⁻ transportation via co-catalyst, and therefore promoted the interfacial charge transfer development through e⁻ tunneling effect. Furthermore, these 2D thin layers can ease light blocking effect of
co-catalyst; therefore, sufficient light can contact the host photo-catalyst. It is required to alter 2D-components and reinforce interfacial acting force to promote highly efficient 2D/2D photo-catalysts.

6 Photo-catalytic Applications

Based on the aforementioned consequences, ultra-thin 2DMs displayed huge benefits for the photo-catalysis from micro-structure, BG, electronic configuration, and surface nature. Thus far, advanced ultra-thin 2DMs NSs were functional as photo-catalysts for diverse photo-catalytic uses. So, development of flexible photo-catalytic uses by 2DMs for \( \text{H}_2\text{O} \) oxidation, \( \text{H}_2 \)-evolution, \( \text{CO}_2 \) reduction, \( \text{N}_2 \)-fixation, organic synthesis, and pollutants removal will be explained in detail in the next section.

6.1 Water (\( \text{H}_2\text{O} \)) Oxidation

Hydrogen (\( \text{H}_2 \)) that has the highest energy density is measured as one of the potential energy carriers for storing solar energy in chemical bond energy form between two H atoms.

![Image](https://example.com/image.png)
In between different methods for conversion of sunlight and H₂O into H₂, photoelectrochemical (PEC) H₂O splitting using SC photo-electrodes has gained most interest due to three main benefits:

1. Production of H₂ and O₂ at respective electrodes that eradicate separation problems.
2. Operation potential under environmental conditions.
3. Potential for manufacturing of a system which consists of just stable and copious inorganic materials.

Designing vis-light-active SCs for H₂O splitting needs an appropriate BG and band position, efficient charge separation, fast charge movement, and longtime durability in aqueous solutions. An attractive design approach to fulfill these requirements is to merge 2D materials (e.g., graphene, MoS₂, g-C₃N₄) with appropriate SCs. It is usually known that H₂ is very potential green fuels with benefits, for example high specific energy, multiple use approaches, and pollution-free combustion product. It displayed magnificent view in prospect of sustainable energy use, if it is created through sustainable skill. The photo-catalytic H₂O splitting into H₂ and O₂ is viewed as Holy Grail infield of chemistry through just sustainable solar light as energy input, photo-catalysts as medium, and H₂O as reaction source. As major forward step was accomplished, effectiveness of H₂O splitting is still restricted in majority of photo-catalytic methods. Usually, H₂O-oxidation is efficiency, limited method in photo-catalytic H₂O splitting schemes because of complex

Fig. 17  a Se and Zn K-edge extended XAFS oscillation function kχ(k). b Equivalent Fourier transforms; red, blue, and black lines show ZnSe SLs, ZnSe-pa SLs, and bulk ZnSe, in that order. c Simulated DOS; black, blue, and olive lines show total, Se sp, and Zn sp state densities, correspondingly. d Photo-current density versus utilized potential curves in chopped 300 W Xe-lamp irradiation. Adapted with permission from Ref. [233]
four \( h^+ \)'s complex redox method. So, it is highly in demand and imperative to propose photo-catalyst with robust solar \( H_2O \)-oxidation method. Recent studies illustrated that 2DMs-based photo-catalysts are very capable choice for solar \( H_2O \)-oxidation [231, 232]. The freestanding SLs ZnSe with four-atomic thickness was formed through ultrasonic exfoliation from lamellar hybrid intermediate \((Zn_2Se_2)(pa)\) (pa represents n-propylamine) [231]. The U-XAFS, local atomic structures, and electronic configurations of the ZnSe SLs were studied. For Zn K-edge \( k\chi_{ik} \) oscillation curves as shown in (Fig. 17a), the ZnSe SLs displayed clear distinction comparative to ZnSe-pa SLs and bulk ZnSe, showing significant variation of local atomic arrangement. The R-space curves of ZnSe samples showed that peaks positioned at 2.11 and 3.63 Å were attributed to the nearest Zn–Se and next nearest Zn–Zn coordination in bulk ZnSe (Fig. 17b). While ZnSe size was decreased to an atomic level, local atomic configuration experiences outstanding changes. ZnSe peak was shifted to 2.17 Å, and next the nearest Zn–Zn distances (3.85 Å) were decreased. Simultaneously, Se–Se distances in SLs ZnSe NSs were extended from 4.012 to 4.11 Å of bulk ZnSe. Such findings certainly showed reality of surface distortion in SL structure that reduced surface energy and allowed exceptional stability of ZnSe SLs. Moreover, surface deformation of SL ZnSe will consequently be in the form of enhanced DOSs at CB edge that might further make sure a high charge carrier transfer rate (Fig. 17c).

Taking advantages from SL structure with surface defects, ZnSe SLs show strong light absorption, enhanced charge separation effectiveness, and small charge transfer resistance. Consequently, SLs ZnSe NSs exhibited 195 times superior photo-catalytic performance compared to bulk ZnSe for \( H_2O \) oxidation after Xe-lamp irradiation (Fig. 18d). As \( H_2O \) oxidation to evolve \( O_2 \) is completely \( h^+ \)-contributed reaction, enhancing \( h^+ \)-use rate perhaps is an efficient plan to enhance photo-catalytic \( H_2O \)-oxidation. Liu et al. [136] created several pore constructions in ultra-thin \( WO_3 \) NSs through fast-heating approach on earlier exfoliated \( WO_3 \cdot 2H_2O \) NSs. As migration direction of the photo-generated \( h^+ \)'s was along \{001\} [2–4, 16–26] facets

![Image](image-url)
in the x-direction in W–O–W chains on WO₃ NSs, with long itinerant pathway the photo-generated h⁺s certainly undergo several recombinations of charge carriers, which acutely prevent photo-catalytic performance. The created pores efficiently shorten diffusion way of h⁺s and conduce to H₂O oxidation to make O₂ at WO₃ surface. Additionally, plentiful dangling bond along pore environment created good circumstances to make easy chemisorptions of molecular reaction that finally boosted O₂-evolution kinetics. As a result, 18 times superior photo-catalytic H₂O oxidation was attained for pore-rich WO₃ ultra-thin NSs comparative to bulk WO₃. It shows significant strategy to promote conversion efficiency by using ultra-thin 2D configuration to the photo-catalytic H₂O oxidation. Additionally, many other photo-catalysts with ultra-thin 2D-structure can also show an exceptional photo-catalytic behavior toward H₂O oxidation, for instance SnS₂ [234], SnSe [235], SnS, Fe₂O₃ [236], NiTi-LDH, and also engineered materials like In₄O₃ with V₀ engineered [84], Co-doped In₄S₃ [145], pit-rich BiOCl [237], and so on.

6.2 H₂-Production

As innovative investigation for photo-catalytic H₂-evolution based on TiO₂ in 1972, photo-catalytic H₂-evolution from H₂O was at front position of chemistry research to solve worldwide energy problem. Many amazing catalytic materials were used in photo-catalytic H₂-production; majority are still said to have quite small photo-catalytic effectiveness, which could not meet the necessities of realistic uses on large industrial scale. Current research for the 2DMs established that rising 2D-SCs with suitable energy BG were a talented choice to get outstanding H₂-evolution performance [239]. In case of abundant SCs, the Cu₂O with unique CB, positioned at ~0.7 V negative as compared to H₂-evolution potential, is possibly a competent catalyst in H₂-conversion from solar. To realize elevated H₂-evolution efficiency, atomic-sized 2D-NSs, e.g., cubic Cu₂O, were formed. The AFM study showed thickness of about 0.62 nm, related to four-atomic-level thickness of Cu₂O in [01-1] direction. Therefore, surface energy of the cubic Cu₂O was conformed to the order of (111) < (100) < (110). As (110) and (01-1) surfaces are equivalent facets (01-1), facet in atomic-level thin Cu₂O NSs also showed a great surface energy that brings a good activity. From considerably reduced thickness, atomically thin Cu₂O NSs’ electronic structure was distinct from bulk equivalent. Utilizing DFT simulations, an atomically thin Cu₂O NSs showed really enhanced DOSs at edge of VB as compared to bulk Cu₂O. At similar time, extended CB edge was also studied in 2D Cu₂O NSs as compared to bulk Cu₂O, enlightening that atomic-level thick Cu₂O has high carrier mobility and small BG. Profiting from such advantages, above 36 times higher photo-catalytic H₂-evolution rate was reached from 2D Cu₂O NSs after vis-light irradiation. These results certainly illustrated that 2DMs can bring huge advantage for H₂-evolution as well as a series of extraordinary activities. In addition to the advancement in H₂-evolution, more modification in ultra-thin 2DMs structures was required. For instance, through doping O₂ into ZnIn₂S₄ NSs, H₂-evolution rate of O-doped ZnIn₂S₄ can attain 2120 µmol h⁻¹ g⁻¹ from aqueous solution containing 0.25 m Na₂SO₃ and 0.35 m Na₂S after visible light illumination lacking any co-catalyst that was 4.5 times high as compared to pure ZnIn₂S₄ [150].

Local atomic structures of formed materials were studied by XAFS. The O₂ doping in ZnIn₂S₄ NSs created high structure distortion through substitution of O₂-atoms for sulfur. The engineered local atomic and electronic structure will experience observable deviation. The DFT simulation showed that O₂ doping can boost DOS at VBM with respect to pure ZnIn₂S₄, signifying creation of enhanced charge density about VBM. XPS results showed the valence spectra and estimated BG, where CBM and VBM of O-doped ZnIn₂S₄ ultra-thin NSs show upshifting in comparison with pure ZnIn₂S₄. So, average recovery duration of carriers for O-doped ZnIn₂S₄ NSs was about 1.53 factors long-lasting relative to pure ZnIn₂S₄, attaining 110 ps. Hence, these advantages showed that O-doped ZnIn₂S₄ can show really enhanced photo-catalytic activity for H₂-evolution. These findings showed that doping was an efficient policy to alter local electronic and atomic structure of 2DMs that can influence charge separation or migration and at the end optimizes H₂-evolution.

Moreover, though considering major ultra-thin 2D-SCs NS materials lacks satisfactory H₂-evolving sites, it is necessary to establish plentiful H₂-evolution positions, for example, isolated Pt-atom or FL-TMDCs to more improve H₂-evolution performance. Therefore, Wang and co-authors [227] studied FL MoS₂ to C₃N₄ NSs to improve photo-catalytic H₂-evolution. In the formation method, C₃N₄ was
absorbed in (NH₄)₂MoS₄ H₂O solution and after that sulfidation was done through H₂S gas, at 350 °C. C₃N₄ and MoS₂ have equivalent layer formation, which can reduce lattice mismatch and help planar development of MoS₂ slabs after using C₃N₄ surface. Consequently, an inorganic–organic 2D–2D stacking was formed using G-like thin-layer hetero-nano building block. Moreover, dispersed MoS₂ thin layers on C₃N₄ surface can provide the superior effectiveness compared to multilayer MoS₂ because of e-tunneling effect via MoS₂ NSs surface can provide the superior effectiveness compared to multilayer MoS₂ because of e-tunneling effect via MoS₂ NSs surface. C₃N₄ and MoS₂ were also utilized as reducing co-catalysts after reacting with TiO₂ and increase photo-activity in the HER. Therefore, Ti₃C₂Tx gives a 2D-podium to interrelate with consistently fabricated TiO₂ to make possible partition of photo-generated (e⁻–h⁺)-pairs to slow charge recombination. Fascinatingly, TiO₂ NPs were well dispersed at Ti₃C₂Tx x, Nb₂CTx x, and Ti₂CTx 2D junctions exhibited better photo-catalytic H₂-evolution activity in comparison with pristine C₃N₄. The 0.2 wt% MoS₂ is the best sample that illustrated the highest H₂-evolving rate, with an obvious 2.1% QY recorded at 420 nm. Moreover, WS₂ can be utilized as a catalyst in WS₂/p-type Si photo-cathode hetero-junctions. Kwon et al. [238] examined WS₂/p-Si photo-cathode for photo-catalytic based HER. Figure 18a shows the as-prepared WS₂ thin film color changes from yellow to brown with increasing thickness, whereas absorbance of film regularly enhances. However, absorption peak position almost remains constant (Fig. 18b). The PEC demonstrated that photo-catalytic HER performance for 23 nm WS₂/p-Si showed the maximum current density of 8.375 mA cm⁻² at 0 V and 72% incident photon to current conversion efficiency (IPCE) (Fig. 18c, d). So, it shows that merger of TMDs (WS₂, MoS₂), along traditional SCs, for example Si, is capable for efficient PEC H₂O splitting. Similarly, Wang et al. [240] studied physicochemical nature of Ti₃C₂Tx MXene coupled with TiO₂ for photo-catalytic HER (Fig. 19a) [241]. The 5 wt% content of Ti₃C₂Tx x in TiO₂/Ti₃C₂Tx x nano-composite showed a 400% augmentation for the photo-catalytic HER than rutile TiO₂. Therefore, Ti₃C₂Tx x gives a 2D-podium to interrelate with consistently fabricated TiO₂ to make possible partition of photo-generated (e⁻–h⁺)-pairs to slow charge recombination. Fascinatingly, TiO₂ NPs were well dispersed at Ti₃C₂Tx x surface without harsh aggregation. Additionally, Ti₃C₂Tx x, Nb₂CTx x, and Ti₂CTx were also utilized as reducing co-catalysts after reacting with TiO₂ and increase photo-activity in the HER [240]. Fascinatingly, Nb₂CTx x and Ti₂CTx show better HER catalytic activity as compared to Ti₃C₂Tx x, while coupling with TiO₂ as co-catalysts (Fig. 19b). It can be dragged through Schottky barrier (SB) and work function of every...
enhanced photo-catalytic efficiency was observed by efficient charge transfer and separation due to the existence of SB to decrease H\(^+\) to H\(_2\). Similarly, Sun et al. [75] also studied g-C\(_3\)N\(_4\)/Ti\(_3\)C\(_2\) photo-catalysts, in which Ti\(_3\)C\(_2\)T\(_x\) with O-surface terminations enhances the separation of charges for improvement of 105% in the HER activity with apparent QY of 1.27%. The DFT simulations support it and showed that O-terminated Ti\(_3\)C\(_2\) with 25% H-atoms presents obvious free energy as low as 0.011 eV [241]. Giorgio Carraro et al. [81] explored enhanced \(H_2\) evolution via photo-reforming of sustainable oxygenates using nano-structure Fe\(_2\)O\(_3\) polymorphs. They studied that Fe(III) oxide polymorphs, \(\beta\)- and \(\varepsilon\)-Fe\(_2\)O\(_3\), have notable performance in solar spectrum for \(H_2\) production from solutions of renewable oxygenates (i.e., ethanol, glycerol, glucose). For \(\beta\)-Fe\(_2\)O\(_3\) and \(\varepsilon\)-Fe\(_2\)O\(_3\), \(H_2\) evolution rates up to 225 and 125 mmol h\(^{-1}\) m\(^{-2}\) are gained, along significant better activities in regard to commonly study \(\alpha\)-Fe\(_2\)O\(_3\).

### 6.3 Reduction of \(CO_2\)

Other than photo-catalytic \(H_2\) evolution, \(CO_2\) reductions to produce hydrocarbon fuels over photo-catalysts were observed as an efficient way to concurrently reduce energy crisis and greenhouse cause. Basically, combustion of fossil fuel develops a great quantity of \(CO_2\), causes an increase in greenhouse effect due to unstoppable increase in \(CO_2\). Significantly, conversion of \(CO_2\) to valuable fuels is an alarming challenge in the recent time. Certainly, \(CO_2\) composed a fundamental C1 building element for chemical industries, but its thermodynamic stability and very high kinetic blocked its broad industrial uses. The undeniable solution for this mystery is to discover C-neutral fuels for low-C market to a sustainable future without environment disadvantages [245]. Usually, the \(CO_2\) molecules are very stable with C=O bond dissociation energy higher than \(~750\) kJ mol\(^{-1}\). Thus, in \(CO_2\) photo-reduction method, higher energy is required to split O=C=O structure, that is very demanding compared to \(H_2O\) splitting into \(H_2\). Gateway for creation of a \(CO_2\) intermediate through single \(e^-\) transmission to activate a \(CO_2\) was observed as a rate-limited step to ensue proton-concerned reduction method. A theoretical potential of \(\sim 1.9\) V versus NHE is needed for initial startup, and a superior over-potential is necessary for actual utilized potentials. Furthermore, multiple
proton-coupled e− transfer methods are concerned in CO2 activation and reaction ways were quite difficult and varied with the synthesis of different products. In accordance with diverse number of injected e−s (2e−, 4e−, 6e−, and 8e−), the products, for example, are CO, HCHO, CH3OH, and CH4, correspondingly. Moreover, competition exists for CO2 photo-reduction and H2O reduction, because H2O reduction to produce H2 is energetically more encouraging that confines products selectivity. Current research explained that ultra-thin 2DMs-based photo-catalysts also displayed outstanding CO2 photo-reduction. For instance, Bi2WO6 layers with single-unit-cell thickness were formed through a lamellar hybrid intermediate plan [246]. Sodium oleate was used to provide oleate ions, thus to relate to Bi3+ via electrostatic interaction. Afterward, lamellar Bi-oleate was used to provide oleate ions, thus to relate through a lamellar hybrid intermediate plan [246]. Sodium of 75 µmol g−1 h−1 was obtained in methanol synthesis bubbled during solution for measurements. An average rate of 75 µmol g−1 h−1 was obtained in methanol synthesis over single-unit-cell Bi2WO6 layers for 5-h analysis that was almost 3 and 125 times higher comparative to Bi2WO6 nano-crystals and bulk Bi2WO6 correspondingly. Following six cycles, photo-reduction effectiveness remains the same and is not effected by any deterioration and shows an outstanding photo-stability. Recent research initiates that an excellent photo-catalytic performance was resulting from the novel geometrical configuration of single-unit-cell Bi2WO6 layers, as follows:

1. Initially ultra-large SSAs of single-unit-cell Bi2WO6 layers make sure 3 factors higher capacitance in CO2 adsorption that was a significant tip for CO2 activation and reduction.
2. The single-unit-cell thicknesses give advance charge separation and extend carrier duration as testified through time-resolved fluorescence emission spectrum calculations.
3. Single-unit-cell thickness carries almost higher DOS at CB edge as well as boosted surface charge density and hence promoted the 2D-conductivity.

Research certainly showed benefits of 2DMs photo-catalyst for CO2 photo-reduction. Adsorption of CO2 is a significant condition for CO2 photo-reduction, which considerably influences e− transfer method. Here, it is attractive to find suitable approach to boost adsorption site for CO2 adsorption and generate strong contact to make possible e−s transfer for efficient activation. Research concluded that generating surface defect sites is possibly another way [97]. Although with controlled synthesis, ZnAl-LDH ultra-thin NSs with thicknesses of 2.7 and 4.1 nm and bulk ZnAl-LDH with almost 210 nm thicknesses can be synthesized that are known as ZnAl−1, ZnAl−2, and ZnAl−3, correspondingly. While bulk ZnAl-LDH thickness is reduced to ultra-thin configuration, density of Vv defects is increased, so reduces coordination number of nearby Zn-ion and initiates several coordinative unsaturated Zn-ions. So, Zn+-Vv-complexes are built in ZnAl-LDH NSs as supported through XAFS, ESR, and PAS spectra calculations. In CO2 photo-reduction route, synthesized Zn+-Vv complexes can function as entrapping positions to encourage CO2 adsorption. Simultaneously, EIS and DFT simulation showed that Zn+-Vv complexes can provide e−s entrapping sites to improve charge separation effectiveness and make easy e−-transfer to CO2. Therefore, defect-rich ZnAl-LDH NSs showed great photo-catalytic activity for conversion of CO2 into CO through a 2e− method, with 7.6 µmol g−1 h−1 conversion efficiency for ZnAl-1. Further improved CO2 conversion competency, selectivity, and developed stability obtained by Xie et al. [154] tuned Vv into a single-unit-cell o-BiVO4 and then it is used as a photo-catalyst for CO2-reduction. Using cetyltrimethylammonium bromide, a lamellar hybrid half way plan was used for the formation of o-BiVO4 layers with single-unit-cell thickness. Regulating reaction time and temperature, Vv-rich and Vv-poor o-BiVO4 atomic layers were formed with [001] direction. Atomically thick o-BiVO4 NSs showed AFM and TEM results. As proved through PAS and XRF, Vv with discrete levels was formed on Vv-poor o-BiVO4 and Vv-rich o-BiVO4 NSs surface. Vv showed a significant function in photo-catalytic method for CO2-reduction. Firstly, Vv created a new defect concentration in BG and enhanced h+s level near the Fermi level. Therefore, light harvesting of Vv-rich o-BiVO4 was improved and electronic conductance was better. The Vv-rich o-BiVO4 showed an increased CO2-adsorption capacitance and stronger surface hydrophilicity comparative to Vv-poor o-BiVO4; this was certainly useful to CO2 reduction process. Finally, Vv improved charge
Fig. 20 a Lowest amount energy routes (PBE/DFT-D3 calculations) pursued for CO₂ into *CH₄ and **H₂O conversion, catalyzed by Mo₃C₂. Gray, lilac, red, and white spheres indicate C, Mo, O, and H atoms, correspondingly (Li et al. [248]). b Photo-catalytic CO and CH₄ evolution rates over P25, 5Pt/P25, 5TC/P25, and 5TC-OH/P25 (Ye et al. [249]). C–f Photo-catalytic CO₂RR of the TiO₂/Ti₃C₂ (TT-x) samples and P25 for the CH₄ formation (e) and FE-SEM images of TT550 (d, e) and TT650 (f) (Low et al. [250]). g, h Photo-induced e⁻ migration method at Ti₃C₂/Bi₂WO₆ hetero-interface (g) and photo-catalytic activity of Ti₃C₂/Bi₂WO₆ through diverse mass ratios of Ti₃C₂ to Bi₂WO₆ (0%, 0.5%, 1%, 2%, and 5%) (h). Adapted with permission from Ref. [251]
separation and efficiently boosted carrier lifetime that permits more e⁻s to engage in CO₂ photo-reduction. To get benefit from already discussed benefits, Vₓ-rich o-BiVO₄ showed improved conversion effectiveness with methanol production rate of 398.3 µmol g⁻¹ h⁻¹. In photo-reduction method, just small concentration of H₂ and trace amount of ethanol can be detected, signifying highly suitable method for product selection. Furthermore, the Vₓ-rich o-BiVO₄ can undergo continuous photo-reduction reaction up to 96 h, lacking any clear decrease in the photo-catalytic efficiency. The above such outcomes show that the 2D photo-catalysts are efficient choice for getting highly efficient CO₂ reduction. In case of pristine MXene, somehow the consideration of surface terminations (–OH and –O functional group) was very important to clarify reaction steps for CO₂RR. In case of surface terminations was active site in CO₂RR for high HCOOH. Obviously, whole energy barrier for CO₂ hydro-reduction into HCOOH at Oₓ in Ti₂CO₂ SL was very good with just 0.53 eV compared with other reduction products that needed superior kinetics. For example, Oₓ on O-terminated MXene was active site in CO₂RR for high HCOOH selectivity; therefore, MXene NSs can be used for broad range of applications.

Ye et al. [252] joined surface-alkalinized TiₓCᵧ MXene as co-catalysts with marketable P25 through a simple mechanical mixing technique for important improvement in photocatalytic CO₂RR. Following surface alkalinization, 5 wt% TiₓCᵧ(OH)ₓ-doped P25 (5TC-OH/P25) reveals obvious support in CH₄ release as compared to un-modified 5TC/P25 (Fig. 20b). The DFT study showed that adsorption energy of CO₂ on TC-F (F-termination) was superior to CO₂ on TC-OH (OH-termination). Thus, CO₂ molecules were easily adsorbed at TC-OH surface, leading to the synthesis of activated CO₃²⁻. So, encouraging charge separation, extraordinary electrical conductance, sufficient CO₂ adsorption, and activation sites on alkalinized MXene were main things contributed to photo-catalytic improvement. These clearly showed the major job of surface alkalinization of MXene, as a valuable metal-free co-catalyst for synthetic photo-synthesis.

Similarly, Low et al. [253] studied in situ formed TiO₂ NPs on conductive TiₓCᵧ to form TiO₂/TiₓCᵧ hybrids (TT-x, where x shows the calcination temperature) through thermal annealing for CH₄ production from CO₂RR (Fig. 20c). After –F functional groups removal at elevated temperature, it brings oxidation of TiₓCᵧ tuned with –O functional groups. The TT50 and TT650 morphology was clearly different from TiₓCᵧ but analogous to rice crust (Fig. 20d–f). High conductivity of TiₓCᵧ promotes e⁻-transfer from TiO₂ and exclusive rice crust analogue morphology with a large active site density, considerably push photo-catalytic activity. Referring to precede work which is discussed already, it was hard to straight evaluate both TiO₂/TiₓCᵧ-Tₓ photo-catalytic systems due to different synthesis methods, unlike TiO₂ phase, discrete difference in morphology, and diverse MXene surface modification. Therefore, it is sensible to embrace AQY for CO₂RR as a controlled tool to describe different future experiment conditions. In recent times, same group of researchers has formed ultra-thin 2D/2D TiₓCᵧ/Bi₂WO₆ hetero-junction hybrid nano-composites (Fig. 20g) [254]. Due to electronic coupling and intense physical effects, 2D/2D hetero-junction noticeably improves transfer and partition of photo-induced charge carriers to reduce charge recombination. 2 wt% TiₓCᵧ-modified Bi₂WO₆ NSs (NSs) (TBₓ) records the highest CH₄ release rate than other stoichiometry (Fig. 20h). Moreover, large interfacial contact surfaces of intimate 2D/2D hetero-junction donate more quick charge mobility in comparison with 0D/2D and 1D/2D hetero-junctions due to a decrease in charge transfer path. So, such stimulating investigation on parallel 2D/2D hetero-interfaces generates novel potential in material science for layered hetero-junctions design in electrocatalysis and photo-catalysis for energy conversion.

6.4 Nitrogen (N₂) Fixation

In comparison with CO₂RR, the photo-catalytic N₂-fixation is still more demanding as dissociation enthalpy of N₂ molecule triple bond (962 kJ mol⁻¹). Normally, catalyst
conversion for N\textsubscript{2} is enormously harsh as N\textsubscript{2} just weakly binds with solid-state catalysts and reaction entails high-energy intermediates. So, it is very much required to do an appropriate structure to support conversion competency of N\textsubscript{2} to NH\textsubscript{3}, E\textsubscript{0} to make the N\textsubscript{2}− is as high as −4.2 V versus NHE via N\textsubscript{2} + e\textsuperscript{−} → N\textsubscript{2}H\textsubscript{4} method, whereas proton-coupled e\textsuperscript{−} transfer reaction N\textsubscript{2} + H\textsuperscript{+} + e\textsuperscript{−} → N\textsubscript{2}H has more available E\textsubscript{0} of −3.2 V versus NHE [255]. Proton-supported exchange method might evade production of high-energy intermediates and therefore reduce thermodynamic kinetics for NH\textsubscript{3} formation. Current investigations showed that 2DMs are a talented applicant to get an efficient photo-catalytic N\textsubscript{2} fixation [249]. 

Zhang and co-workers [250] studied that V\textsubscript{o} formation in BiOBr NSs can efficiently boost N\textsubscript{2} fixation reaction. Theoretical study showed that N\textsubscript{2} adsorption onto the V\textsubscript{o} through an end on arrangement of adsorbed N\textsubscript{2} triple bond can be extended from 1.078 Å in original N\textsubscript{2} to 1.133 Å, signifying efficient N\textsubscript{2} activation. Generated e\textsuperscript{−}s in BiOBr can simply inject into N\textsubscript{2} π antibonding orbitals. Accessibility of localized π-back donating e\textsuperscript{−}s in V\textsubscript{o} might efficiently adsorb N\textsubscript{2} to generate activation. So, N\textsubscript{2} reduction to NH\textsubscript{3} catalyzed through the BiOBr with V\textsubscript{o} needs a very low reaction kinetic and a higher photo-catalytic performance can be obtained. N\textsubscript{2} conversion rate after vis-light and UV–Vis-light irradiation is 104.2 and 223.3 μmol g\textsuperscript{−1} h\textsuperscript{−1}, respectively, after without h\textsuperscript{+} scavenger or co-catalyst. Stimulated through V\textsubscript{o}-motivated N\textsubscript{2} activation, MoS\textsubscript{2} NSs with S-vacancy were formed and further utilized to N\textsubscript{2} fixation. The MoS\textsubscript{2} NSs showed NH\textsubscript{3} formation rate almost 325 μmol g\textsuperscript{−1} with 10-h measurement after simulated solar light irradiation. Although marketable bulk MoS\textsubscript{2} cannot give any photo-catalytic performance for NH\textsubscript{3} synthesis under similar test condition, it illustrates exclusive benefit of MoS\textsubscript{2} NSs for N\textsubscript{2}-reduction. According to Mott–Schottky spectra, MoS\textsubscript{2} NSs and bulk MoS\textsubscript{2} samples in CB positions were anticipated to be −0.35 and −0.24 V, correspondingly, that were positioned below thermodynamic reduction potentials of N\textsubscript{2} through one or two-e\textsuperscript{−} transfer method. So, it was presumed that N\textsubscript{2} reduction with MoS\textsubscript{2} NSs was multi-electron coupled proton transfer method. Due to n-type SC essence, there subsists many free e\textsuperscript{−}s in MoS\textsubscript{2} NSs and such free e\textsuperscript{−}s can pair with photo-generated excitons to form charge excitons (trions) that were mostly located around Mo-sites. Produced trions have manifold e\textsuperscript{−}s in one bound state that was useful to multi-e\textsuperscript{−} migration reactions. While N\textsubscript{2} is confined through S-vacancies, it was bounded via three 

Mo atoms with trions after irradiation. N\textsubscript{2} activated after e\textsuperscript{−}s donation from bonding orbitals and accepting e\textsuperscript{−}s to its antibonding orbitals results in a trion-supported six-electron reduction method. The significant photo-catalytic N\textsubscript{2} fixation resides in building adsorption site in N\textsubscript{2} molecule, e\textsuperscript{−}-rich systems for e\textsuperscript{−} donation, engineering band configuration through enough E\textsubscript{0} and coupling protons to decrease energy condition of intermediates. So, theoretical and experimental study showed that novel breakthrough on MXene-based composites for CO\textsubscript{2}RR and N\textsubscript{2}RR will appear in the frontline of technology and science, transferring them in future real energy applications.

6.5 Organic Synthesis

Idea of decreasing energy expenditure for chemically developed, solar light-driven chemical transformation through assist of the SCs holds huge view. Under irradiation, SCs can use solar light to make an exciton or hot carriers that can stimulate chemical reactions at surface of catalyst. Effectiveness and selectivity of the photo-catalytic conversion are still in adequate at large scale. Weak interaction of O\textsubscript{2}-molecule with photo-catalysts surfaces, particularly a defect-free surface, is a serious matter for poor effectiveness of photo-catalytic organic formations. Reaction involves O\textsubscript{2}, which needs efficient interfacial e\textsuperscript{−}-transfer, either directly as donor or indirectly as e\textsuperscript{−}-acceptor [256]. Additional significant subject is poor selectivity that might be obtained from photo-generated h\textsuperscript{+}s. Generally, generated h\textsuperscript{+}s has strong oxidizing capacity and is accountable for nonselective over-oxidation. In recent times, the 2D photo-catalysts displayed a huge promise for selective organic transformation using mild conditions. For example, Xiong et al. [257] formed V\textsubscript{o} into ultra-thin WO\textsubscript{3} NSs to make O\textsubscript{2}-molecules active and activate organic conversion. Defect-rich (DR) WO\textsubscript{3} NSs were formed through calcination of the first synthesized WO\textsubscript{3}H\textsubscript{2}O NSs in N\textsubscript{2}-environment, at 673 K, whereas defect-deficient (DD) WO\textsubscript{3} NSs were synthesized via calcination in atmospheric condition. From aberration-corrected HAADF-STEM, it is clear that DD WO\textsubscript{3} shows comparatively smooth and flat surface. Simultaneously, continuous and controlled lattice fringe was experienced from atomic resolution HAADF-STEM image (Fig. 21). Such outcomes conclusively proposed the defects deficiency in such DD WO\textsubscript{3} sample. In DR WO\textsubscript{3}, many small pits were formed,
with small lattice disorder, and dislocation appears in NSs that vigorously emphasize the presence of different defects.

To further reveal the presence of $V_o$, synchrotron radiation-related XAFS spectroscopy was performed. The DR WO$_3$ showed a clear diverse confined atomic configuration compared to DD WO$_3$, where W-atom coordination numbers decrease from 6 to 5.4 for DD WO$_3$ and DR WO$_3$, showing local deficiency of O$_2$-atom. ESR investigation was also used to calculate WO$_3$ samples. Noticeably, at $g = 2.002$ a symmetric ESR signal was experimented for

![Morphological study.](image)

**Fig. 21** a–f Morphological study. g Fourier transforms W L3-edge EXAFS spectra with respect to commercial WO$_3$. h ESR spectra at room temperature. i Scheme showing locations of $V_o$ in WO$_3$ lattice. j Cyclic analysis for defect-rich WO$_3$ in catalytic aerobic coupling of benzylamine after irradiation with $\lambda > 400$ nm at 298 K. k Scheme shows total light-driven catalytic reaction route. Adapted with permission from Ref. [257]
the DR WO₃, showing e⁻-entrapment at Vₒ. Joint STEM, XAFS, and ESR findings suggested that subsistence of Vₒ at precise sites induces few lattice distortion and displacement. After getting benefits from DR configuration, O₂ was chemisorbed at Vₒ of defect-rich WO₃ NSs through end on arrangement and associated with e-s transfer from coordinative unsaturated site to O₂. So, O₂ was efficiently activated to O²⁻ species over DR WO₃, and it was transformed from amines to respective imines with 6 times enhanced kinetic rate compared to DD WO₃. As reaction time increased to 8 h as conversion ratio of benzylamine was greater compared to 80% with an extremely high selectivity, no clear decline was observed within 6 times of catalytic cycles. Other than O₂-activation, hydrophobicity was another significant feature to affect photo-catalytic organic conversion method. Li and co-workers [258] studied colloidal formation approach information of BiOCl NSs. Through BiCl₃ hydrolysis in octa-decylene solution, supported by in situ preparation of H₂O via reaction in oleylamine and oleate solution, single-crystalline BiOCl colloidal NSs (BiOCl C-UTNSs) were obtained with almost 3.7 nm thickness. For comparison, BiOCl NSs were also formed through hydrothermal way, known as BiOCl H-UT-NSs. Surface H₂O contact angle (CA) measurement was utilized to establish wettability of as-synthesized BiOCl NSs. BiOCl C-UT-NSs showed a H₂O CA of 116.3°, which is hydrophobic. It occurs from detail that organic ligands have capped on BiOCl C-UT-NSs surface during colloidal formation. Conversely, BiOCl H-UT-NSs exhibited a H₂O CA of 0°, showing the super-hydrophilic nature of synthesized BiOCl H-UT-NSs. Huge difference in BiOCl C-UT-NSs and BiOCl H-UT-NSs may bring about important effect for photo-catalytic organic conversion method. Moreover, there subsist plentiful Vₒ on BiOCl C-UT-NSs, ensuing strong light absorption in vis-light range. To get benefit from hydrophobic character and enhanced light harvesting capability, BiOCl C-UT-NSs displayed greatly enhanced photo-catalytic activity for conversion of N-t-butylbenzylamine to N-t-butyl-benzylamine. The 78% conversion ratio was obtained from BiOCl C-UT-NSs, whereas BiOCl H-UT-NSs have only displayed about 15% conversion rate, from Xe lamp irradiation for 1 h. Furthermore, BiOCl C-UT-NS sample was more utilized for conversion of secondary amines to respective imines along increased conversion selectivity as well as efficiency. The 2D photo-catalysts were verified to be talented choice for the photo-catalytic organic formation, and such approach can broaden perceptive of organic conversion method and is favorable to establish further proficient organic transformation systems.

### 6.6 Removal of Pollutants

In the progress of financial and industrialization, environmental pollution is the main problem that threatens the public health. The photo-catalysis was considered as an efficient and financially viable technology to handle elimination of environmental pollutions. Due to exclusive advantages such as better adsorption capability of pollutants and strong light harvesting capacitance, 2DMs-based photo-catalysts showed a great hope for removal of pollutants. For instance, Xia and co-workers [140] formed ultra-thin Bi₄O₅Br₂ NSs through reactive ionic liquid supported via solvothermal method in combination with pH adjustment. In ionic liquids, long carbon chain served as a capping reagent which controls the crystal growth along c-axis. Simultaneously, reaction condition pH was adjusted to 11 that supplied OH⁻ to substitute Br- to execute de-halogenation in fabrication route of Bi₄O₅Br₂. So, both thickness and component-engineered Bi₄O₅Br₂ materials were formed and utilized in photo-catalytic degradation of an antibiotic CIP and tetracycline (TC) after irradiation with vis-light for 120 min. After irradiation, 75% of CIP is photo-degraded through Bi₄O₅Br₂, whereas BiOBr degradation rate was 51.4%. Furthermore, BiO₃Br₂ NSs showed 77.8% degradation rate for TC within 60-min irradiation, which is very high compared to BiOBr with just 31.7%. Changeable energy band configuration of Bi₄O₅Br₂ was verified to consider the increased photo-catalytic activity. More negative CB position of Bi₄O₅Br₂ will make easy development of more active O²⁻ species. Upshifting of CB position and broad VB will be advantageous to improve charge separation effectiveness. Thus, obtained Bi₄O₅Br₂ NSs displayed greater performance toward pollutant removal. To further enhance photo-catalytic performance in pollutant degradation, creating surface defects might be another approach. Therefore, Xie and co-workers [119] studied that while BiOCl thickness is reduced from 30 to 2.7 nm, in BiOCl defect type will vary from isolate defects VBi‴ along four negative charges, BiOCl NSs were additionally negatively charged as comparative...
to BiOCl nano-plates. As RhB was positively charged, the further negatively charged ultra-thin BiOCl NSs promoted RhB adsorption on BiOCl NSs’ surface. Moreover, the presence of vacancies can enhance light absorption and speed up separation of charges. As a result, ultra-thin BiOCl NSs exhibited a great solar photocatalytic activity for RhB removal. MXene shows outstanding performance in photocatalytic degradation of organic pollutants. Mashtalir et al. [135] utilized Ti3C2Tx to degrade MB (a cationic dye) and acid blue 80 (AB80) (an anionic dye) (Fig. 22a, b). The MB and AB80 degradation was augmented via UV irradiation.

In dark, MB level reduces due to negatively charged adsorption at Ti3C2Tx surfaces with MB. After UV irradiation, a substantial reduction in MB and AB80 concentration, with 81% and 62%, respectively, was experienced in existence of suspended Ti3C2Tx. It is observed that over longtime period, Ti3C2Tx oxidation to form TiO2 in dissolved O2 presence was obvious that merits wide ranging research in this field. Similar to G-TiO2 nano-composites, it was imagined that Ti3C2Tx-supported TiO2 may function as a possible catalyst that further promotes progress of this direction. While continuing such investigation for the design of hetero-junction
interfaces, Peng et al. [259] studied a composite of Ti3C2 and \{001\} facets-exposed TiO2 through hydrothermal incomplete oxidation of Ti3C2 (Fig. 22c–e).

In photo-catalytic reaction, TiO2 through preferential \{001\} facets creates e−s and h+s through UV light illumination and, afterward, Ti3C2 develops a Schottky junction with \{001\} -face n-type TiO2. It hinders recombination of e−s with h+s due to SB. Enriched e−s on TiO2 (001) might interact with dissolved O2 to generate superoxide radical anions (O2−) that further respond to H+ and e− to produce extremely reactive hydroxyl (OH) radicals, which increase photo-degradation. It is well recognized that photo-catalytic activity of TiO2 relies not only on particle shape but also on its exposed facets. It seems that \{001\} surface offers oxidation sites in photo-catalytic method, while \{101\} facets proceed as reductive sites. Therefore, TiO2 facet tuning using MXene has basic significance to systematically untangle underlying photo-catalytic system [241]. In addition, TiO2 metal sulfides are also utilized to join with Ti3C2Tx. Xie et al. [260] formed a 2D in-plane CdS/Ti3C2Tx onto sheet hetero-structures via electrostatic self-assembly method (Fig. 23a). In such catalytic system, the Ti3C2Tx Janus co-catalysts not just act as an e− mediator to augment e−s extraction from CdS but also restrain h+‐mediated photo-corrosion of CdS. Assigning Ti3C2T small Fermi level than CdS CB, photo-e − lifetime of CdS/0.5% Ti3C2Tx was longer as compared to bare CdS. Moreover, Ti3C2Tx can absorb Cd2+ ions that were produced during photo-catalysis (Fig. 23b) and, as a result, avoid Cd2+ ions dissolution in H2O to enhance photo-stability of CdS. For instance, double-gain strategy offers a conceptual idea to evade instability as well as photo-corrosion of CdS. Other than MXene-based binary hybrid nano-composites, prosperous study into ternary hetero-structures has become a mainstream in photo-catalysis area. Wang et al. [262] (2018) formed a new quasi-core–shell In2S3/anatase TiO2@metallic Ti3C2Tx MXene hetero-structure hybrids through in situ hydrothermal technique for degradation improvement in

**Fig. 23** a Scheme of CdS/Ti3C2Tx NSs to improved photo-activity and photo-stability. b Adsorption of Cd2+ over CdS NSs and Ti3C2Tx MXene in dark. Adapted with permission from Ref. [261]. c Charge migration. d Separation and reaction mechanism for MO degradation in In2S3/anatase TiO2@metallic Ti3C2Tx (InTi) system after vis-light and photo-catalytic degradation of MO over other In2S3-based binary hybrids. e In2S3, In Ti hybrids, and Ti3C2Tx. f In Ti-x indicates mass of Ti3C2Tx included during preparation (x ≥ 8, 16, 32, and 54 mg). Adapted with permission from Ref. [262].
methyl orange (MO). Fascinatingly, enhanced photo-activity of ternary nano-architectures was credited to numerous associated factors, such as well-designed type II band arrangement and noble metal-free-based Schottky junction with promising charge migrating channels (Fig. 23c, d). Specifically, such occurrence originates from synergistic contribution in between vis-light-responsive In$_2$S$_3$, upward band bending in TiO$_2$, and amazing electrical Ti$_3$C$_2$Tx conductivity. For example, optimal photo-catalyst in the presence of Ti$_3$C$_2$Tx content of 16 mg (InTi-16) evidents the highest photo-degradation competency for MO elimination, as well as more significantly, it exceeds other In$_2$S$_3$-based binary NSs (Fig. 23e, f). Progressing via this analysis, it can be elucidated that key to ameliorate dyes photo-catalytic degradation is to effectively separate photo-induced (e$^-$–h$^+$)-pairs to hold back charge recombination. Consequently, efficiently tuned vigorous hetero-structure system with distinct quality (e.g., intimate contacted hetero-interfaces, use broad solar spectrum to imitate natural sunlight, superior conductance, constructive charge transfer, and separation) is an urgent demand for boosting photo-catalytic degradation. Incidentally, extensive research in chemistry, materials arrangement, and optimization is the main requirement. In turn, it will open new prospects for separating charge carrier dynamics in synergistically speeded up photo-activity in practical photo-catalytic applications.

**6.7 Hydrogen Peroxide (H$_2$O$_2$) Production**

Since the first synthesis of H$_2$O$_2$ by Thenard (1818) as a result of barium peroxide reaction with nitric acid [263], H$_2$O$_2$ has gotten rising consideration in past 200 years due to which it was listed among the 100 most significant chemicals in world [264]. The anthraquinone oxidation (AQ) is mostly developed for H$_2$O$_2$ manufacture on industry level that is presently caused about 95% of total H$_2$O$_2$ formation. Normally, AQ method generally contains four steps [265]:

1. Hydrogenation of AQ in organic solvent by means of Ni/Pd catalyst.
2. Oxidation of hydrogenized AQ (HAQ) in air or O$_2$-enriched atmosphere with the help of catalysts.
3. Removal of H$_2$O$_2$ and recycling HAQ to AQ.
4. Refinement and concentration of H$_2$O$_2$.

The multi-step oxidation and hydrogenation response need an elevated applied energy. On the other hand, AO method is not environmentally benevolent, since large quantity of waste H$_2$O (for example, 2-ethyl-anthraquinone, tri-octyl phosphate, tert-butyl urea, and K$_2$CO$_3$ lye), exhaust gas (mesitylene isomers), and solid waste (activated alumina) was formed. It is well known that H$_2$O$_2$ is a very competent and ecological oxidant. It has maximum content of active O$_2$ (47.1% w/w), and no noxious side products are formed in its reactions, apart from H$_2$O and O$_2$. Due to these qualities, H$_2$O$_2$ has broadly applied in organic synthesis, [266] waste H$_2$O management, disinfection [267], and paper industry [268]. Nowadays, H$_2$O$_2$ is studied in energy field as both oxidant and reductant in innovative fuel cell [269]. The results illustrated that the theoretical output potential of the H$_2$O$_2$ fuel cell was 1.09 V that is analogous to traditional H$_2$-fuel cell (1.23 V). The H$_2$O$_2$ has established rising concentration as it is not only a mild and environment friendly oxidant but also a talented novel liquid fuel. Formation of H$_2$O$_2$ by photocatalysis is green, sustainable, and potential method, in view of its utilization in H$_2$O and O$_2$ as source materials and solar light as energy. Other advantage of H$_2$O$_2$ as compared to H$_2$ is that it is completely soluble in H$_2$O and simply transportable that paves it as energy carrier perfectly.

Synthetic photo-synthesis is a photochemical method to renovate sustainable resources into clean fuels and chemicals (for example, H$_2$O$_2$) through sunlight which was expected to solve rising energy requirements. Photocatalytic-based H$_2$O$_2$ formation is a talented approach to improve energy requirements, as H$_2$O$_2$ is significant liquid chemical and fuel. However, subsequent dilemma strictly limits the growth of this method:

1. Less selectivity.
2. Less stability (usually > 5 short-time cycles).
3. Quick charge recombination.
4. Support of hole scavengers.
5. Requirement of O$_2$ saturation.

TiO$_2$ is broadly considered as a photo-catalyst because of its crystal stability, optical, physical and electrical properties as well as biocompatibility [17, 18]. H$_2$O$_2$ manufactured by TiO$_2$ photo-catalytic attracted a great
concentration [19]. The TiO$_2$ CB (−0.19 V vs. NHE, pH 0) bottom is more negative than 2e$^-$ reduction of O$_2$ (0.68 V), which promotes reduction reactions for H$_2$O$_2$ fabrication, but pristine TiO$_2$ has few disadvantages for example, poor light absorption due to its large BG. Mainly, quantity of H$_2$O$_2$ generation is much low (<0.2 mM) over pristine TiO$_2$-based photo-catalyst that is away from reasonable level. This may be after the formation of H$_2$O$_2$; it straight away reacts with surf ace Ti–OH groups and forms Ti–OOH complexes. Secondly, Ti–OOH complexes dissociated to Ti–OH and OH$^-$ through e$^-$ reduction as:

$$\text{Ti} \ - \ \text{OOH} + \text{H}^+ + e^− \rightarrow \text{Ti} - \text{OH} + \text{OH}^-.$$ 

Numerous surface alteration approaches were applied to boost photo-catalytic fabrication of H$_2$O$_2$ in TiO$_2$-based photo-catalytic method, for example surface fluorination and surface complexation. The g-C$_3$N$_4$ is analog to graphite, and metal-free polymer n-type SCs have stacked 2D configuration of tri-s-triazine linked through tertiary amines [38]. In consequence of its exceptional structural, electrical, optical, and physicochemical properties, g-C$_3$N$_4$ is familiar as a novel class of multipurpose materials for catalytic, electronic, and energy uses [39]. Wang and co-authors (2009) first revealed photo-catalytic properties of g-C$_3$N$_4$ on H$_2$ and O$_2$ evolution [40], and g-C$_3$N$_4$-based photo-catalysts have attracted boosting interest worldwide [41]. BG of g-C$_3$N$_4$ is ~2.7 eV which is similar to optical wavelength of ~460 nm, that makes it a possible vis-light-active photo-catalyst. Additionally, g-C$_3$N$_4$ has photo-catalytic capability for H$_2$O reduction and oxidation because of its suitable BGs [42]. Hypothetically, g-C$_3$N$_4$ is a good photo-catalyst applicant for H$_2$O$_2$ formation [10] as its CB position (~1.3 V vs. NHE) is correctly located to make possible O$_2$ reduction (~0.28 V vs. NHE), while VB potential (1.4 V vs. NHE) is smaller compared to metal oxides that can efficiently avoid oxidative disintegration of H$_2$O$_2$. As such, g-C$_3$N$_4$ rapidly becomes attractive in the field of photo-catalysis H$_2$O$_2$ formation [43]. However, photo-catalytic H$_2$O$_2$ formation activity of g-C$_3$N$_4$ is still limited via low effectiveness in consequence of some adverse parameters, generally including lower surface area, inadequate vis-light harvesting, and quick recombination of photo-induced (e$^-$–h$^+$)-pairs. Protocols, for instance engineering structures, controlled defects, loaded noble metal nanoparticles, doping elements, and heterogenization, were later applied to improve g-C$_3$N$_4$-based photo-catalytic H$_2$O$_2$ formation.

### 7.1 Photo-catalytic H$_2$ Production

Since 1972, Fujishima and Honda [37] discovered H$_2$O splitting at TiO$_2$ electrode under UV light irradiation; at the same time, numerous efforts were dedicated to photo-catalytic H$_2$-production [136]. The photo-catalytic is a procedure that produces H$_2$ (and O$_2$) using reduced or oxidized adsorbed H$_2$O through photo-generated e$^-$s and h$^+$s at SC catalysts’ surface. Due to quick recombination of photo-generated (e$^-–h^+$) in catalysts, for H$_2$ production effectiveness was still far from prerequisite practical applications. Therefore, 2D/2D layered composite photo-catalysts with suitably formed hetero-junctions are moderately promising for increasing H$_2$-production effectiveness via supporting separation of photo-generated (e$^-–h^+$) [270]. In comparison with UV light with small percentage of the solar emission, vis-light (almost 50% of solar radiation) determined that the photo-catalysts are more capable for high proficient sunlight utilization and photo-catalytic activity. Zhang et al. [271] developed a type of “sheet on sheet” hierarchical hetero-structure for vis-light-based photo-catalytic H$_2$-production via in situ development of ZnIn$_2$S$_4$ 2D-NSs on sheetlike g-C$_3$N$_4$ surfaces. g-C$_3$N$_4$ was one of the most talented photo-catalysts because of its good stability, non-toxicity, exceptional electronic configuration, and cost efficiency. Its photo-catalytic effectiveness is restricted through poor light harvesting effectiveness and quick recombination of photogenerated charge carriers. Combining vis-active ZnIn$_2$S$_4$ 2D-NSs, the above shortcomings were overcome based on

### 7 2D/2D Hetero-junctions for Catalysis

The description of hetero-junction, initially developed from SC–SC (S–S) junction, now has been elaborated to scope metal–SC (M–S) junction and still nontypical hetero-structures of SCs and ionic conductors [136]. Mostly, edge coupling of two components in a hetero-junction could make band arrangement or repairing contact after Fermi levels equilibration (or work functions) at interface following Anderson’s rule or Schottky–Mott rule for S–S or M–S junctions, correspondingly. There is an agreement in previous work that re-localization of charge carriers at hetero-junctions edge may make easy catalytic activity of as-fabricated materials or devices.
hetero-junction contact interface that can persuade proficient interfacial transfer of photo-generated \((e^-h^+)\) from g-C_3N_4 to ZnIn_2S_4 and delayed charge recombination depending on measurement findings of surface photo-voltage and PL of ZnIn_2S_4/g-C_3N_4 hetero-structures. Both suppressed charge recombination on g-C_3N_4 NSs and enhanced photo-generated charge carriers in ZnIn_2S_4 NSs give amazing improvement on photo-catalytic activity of ZnIn_2S_4/g-C_3N_4 hetero-structures for H_2-production.

Enhanced photo-catalytic activity should also be contributed to increase in surface active sites and extension of light absorption via ZnIn_2S_4 NSs combination. The overall photo-catalysts-based H_2O splitting was also developed for production of O_2 and H_2 concurrently, but it is still a major confront [270]. To fulfill redox potential for overall H_2O splitting, photo-catalysts CBM must more negative as compared to E_0 of H^+/H_2 (0 V vs. normal H_2 electrode (NHE)) and VBM should be more positive compared to oxidation potential of O_2/H_2O (1.23 V). Over-potential related to charge transfer and minimum BG of photo-catalysts for efficient H_2O splitting is always superior compared to theoretical value (1.23 eV). Therefore, Liao et al. formed 2D MoS_2/AlN(GaN)-layered hetero-structures as extremely competent vis-light photo-catalysts for overall H_2O splitting. The H_2 and O_2 were formed at opposite surfaces of hetero-structures, because AlN (GaN) and MoS_2 SLs act as e^- donor and e^- acceptor in this hetero-junction photo-catalyst, respectively. Pristine MoS_2 using a direct BG of 1.9 eV was a potential vis-light-driven photo-catalyst and is confirmed not efficient in H_2O splitting. Group III nitrides (AlN or GaN) SLs with good thermal/chemical stability and highly thermal conductance have demonstrated a good option to manufacture SLs MoS_2 hetero-structures, to improve photo-catalytic activity. Moreover, there was only around 2% lattice mismatch among h-AlN (GaN) and MoS_2 SLs, which was major benefit for manufacturing of hetero-structures. The MoS_2/AlN and MoS_2/GaN hetero-structures were calculated to be capable photo-catalysts under vis-light irradiation because of proper BGs for H_2O splitting and good optical absorption [136].

In recent times, polymers were supposed to be one of the potential alternatives in photo-catalytic overall H_2O splitting.

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**Fig. 24** a TEM image. b NK-edge XANES of aza-CMP, C_2N, and aza-CMP/C_2N. c HAADF-STEM images and elemental mapping (Pt-labeled C_2N and Co-labeled aza-CMP). d Overall H_2O splitting activity. e Scheme showing aza-CMP/C_2N hetero-structures electronic band structures. f J–V curves of catalysts in dark and under light irradiation. Adapted with permission from Ref. [274]
because of its engineering molecular structures [272]. To remove limitation of single-element polymer with inadequate $E_0$, 2D/2D polymer hetero-junction photo-catalysts with Z-scheme configuration were designed from imitating two-step excitation way of plants, where light-driven two half reactions of $\text{H}_2\text{O}$ splitting and glucose formation are divided spatially [273]. The Z-scheme-based polymer derived from 2DMs was proved to be an effective pathway to get appropriate energy levels for enough reaction kinetics and allow proficient charge transfer in overall $\text{H}_2\text{O}$ splitting.

Wang et al. [270] synthesized hetero-structures (aza-CMP/C$_2$N) consisting of aza-conjugated microporous polymers (CMP) and C$_2$N NSs as 2D polymer-related Z-scheme systems for competent photo-catalytic overall $\text{H}_2\text{O}$ splitting. The aza-CMP/C$_2$N hetero-structures were synthesized via mixing and consequently annealing of CMP and C$_2$N NSs. The as-fabricated stacked NSs of aza-CMP/C$_2$N with abundant overlapped areas might be exposed via the TEM analysis in Fig. 24a. The XANES spectroscopy, HAADF-STEM image, and elemental mapping were utilized to show

![Figure 25](image)

**Fig. 25** a Photo-catalytic $\text{H}_2$ evolution based on different catalysts with $> 420$ nm. b Effect of BP/CN ratio in BP/CN on photo-catalytic $\text{H}_2$ production rate under vis-light irradiation for 3 h. c Cycle stability test on BP/CN photo-catalytic $\text{H}_2$ production under vis-light irradiation. d Photo-catalytic $\text{H}_2$ production based on BP/CN with $> 780$ nm light irradiation. e HAADF-STEM image. f Scheme for photo-catalytic $\text{H}_2$ evolution utilizing BP/CN. Adapted with permission from Ref. [275]
interlayer relations as well as homogeneous combination of aza-CMP and C2N NSs (Fig. 24b).

Investigation on photo-catalytic activity showed that H2 and O2 (molar ratio 2:1) were concurrently formed from pristine H2O with aza-CMP/C2N hetero-structures as photocatalysts under vis-light (> 420 nm) irradiation, whereas both aza-CMP and C2N components are inactive. In addition, aza-CMP/C2N hetero-structures with 1:1 mass ratio showed optimum photo-catalytic performance (H2 evolution rate: 5.0 mmol h⁻¹, solar to H2 conversion efficiency: 0.23%, evident QE at 600 nm: 4.3%) (Fig. 24c). Figure 24d presents the energy band position of aza-CMP/C2N hetero-structures, which indicates that photo-generated e⁻s in C > B of aza-CMP were quickly recombined with photo-generated h⁺s at VB, of C2N at their interface, while other photo-generated e⁻s and h⁺s participated in H2O redox reaction. Credit to as-constructed hetero-structures, both charge separation and transfer were assisted in aza-CMP/C2N composites (confirmed via outcomes of electrochemical impedance measurements and transient photo-current) and therefore increased photo-catalytic performance.

As a move toward green chemistry, sequence of metal-free photo-catalysts, e.g., g-C3N4, BP, boron nitride (BN), and boron carbide (BC), was highly preferred to be studied

| Materials | Co-catalyst | Light source | H₂ yield (μmol h⁻¹g⁻¹) | References |
|-----------|-------------|--------------|------------------------|------------|
| CdS       | 0.5 wt% Pd, 4 wt% MoS2, 5wt % polyaniline | Daylight fluorescent lamp | 570 | [278] |
| CdSe      | Pt          | λ = 300 W    | 1.65                   | [279] |
| UiO-66/CdS| 1.5 wt% MoS2 | λ ≥ 400 nm   | 12,426                 | [280] |
| InS/CdS   | 0.2 wt% MoS2 | λ ≥ 420 nm   | 625.8                  | [281] |
| CdS       | 0.4 wt% rGO, 2 wt% MoS2 | λ ≥ 420 nm | 6857                   | [282] |
| CdS       | 1.33 wt% graphene,0.67 wt% MoS2 | λ ≥ 420 nm | 9000                   | [283] |
| CdS       | 2 wt% single-layer (SL) MoS2 | λ ≥ 420 nm | 10,050                 | [284] |
| CdS       | 0.2 wt% MoS2 | λ ≥ 420 nm | 5330                   | [285] |
| CdS       | 0.2 wt% MoS2 | λ ≥ 420 nm | – 5400                 | [286] |
| CdS NSs   | 1% MoS2 NSs | λ ≥ 400 nm   | 8720                   | [287] |
| g-C3N4    | –           | λ > 420 nm   | 3.2                    | [288] |
| g-C3N4    | Pt          | λ > 420 nm   | 106.9                  | [288] |
| g-C3N4    | Pt          | λ > 300 nm   | 23,468                 | [288] |
| Graphene  | CdS         | 300 W Xe     | 1050                   | [289] |
| 1H-MoS2   | –           | 100 W halogen | 50                    | [290] |
| 1T-MoS2   | –           | 100/400 W halogen | 10.8/42 k   | [290] |
| 1T-MoSe2  | –           | 100 W halogen | 26,000                 | [291] |
| 1T-WS2    | TiO2        | 300 W Xe     | 2570                   | [292] |
| 2H-WS2    | TiO2        | 300 W Xe     | 225                    | [292] |
| MoS2      | CdS         | λ > 420 nm   | 1472                   | [293] |
| WS2       | CdS         | λ > 420 nm   | 1984                   | [24]  |
| SnS2      | –           | 300 W Xe     | 1060                   | [104] |
| ZnInS4    | –           | 300 W Xe     | 57                     | [294] |
| ZnInS4    | Pt          | 300 W Xe     | 213                    | [294] |
| Zn–In–S   | Pt          | 400 W Hg     | 229                    | [295] |
| Zn–In–S   | Pt + NaCl   | 400 W Hg     | 1056                   | [295] |
| TiO2      | Pt          | 350 W Xe     | 1667.5                 | [296] |
| CdSe      | 2%CoP       | 350 W Xe     | 56.3                   | [277] |
| CdS       | WS2         | 300 W Xe lamp | 14.1                  | [297] |
because of their profusion, inexpensive, and excellent stability. The study of a competent and stable metal-free photo-catalyst with broad spectrum solar absorption for photo-catalytic H₂-production remains a major issue. Zhu et al. [275] productively formed a 2D layered hetero-structures consisting of BP and graphitic carbon nitride (CN) (BP/CN) as metal-free photo-catalysts in H₂-evolution for vis to near-IR region for the very first time. Compared to a single element (BP or CN), BP/CN hetero-structures showed considerably enhanced photo-catalytic activity, and H₂-evolution for 3 h obtained 1.93 µmol, 0.46 µmol under > 420 nm > 780 nm light irradiation, respectively (Fig. 25a, d). It is mostly due to proficient interface charge transfer based on strong interface interaction in CN and BP that restrained recombination and improved the partition rate of photo-generated (e⁻–h⁺)-pairs (Fig. 25f). After excitation in vis-light, a charge migration from CN to combine BP stimulated through hetero-junction interfacial effect in BP/CN can be established through consequences of time-resolved diffuse reflectance spectroscopy. In NIR excitation case, just BP was excited and extensive excitation duration is obtained from competent electron entrapping via P-N coordinate bond at hetero-junction edge [136].

Jingrun Ran et al. [276] studied metal-free photo-catalysts of metal-free 2D/2D vdWs phosphorene/g-C₃N₄ hetero-structure. The synthesized nano-composite showed improved vis-light photo-catalytic H₂ production activity of ~571 µmol h⁻¹ g⁻¹ in 18 v % lactic acid aqueous solution. This enhanced activity occurs due to intimate electronic coupling at 2D/2D interface, which introduced a new metal-free phosphorene/g-C₃N₄ photo-catalyst and formed 2D/2D vdWs hetero-junction for uses in catalysis, electronics, and optoelectronics. Qixiao Gai et al. [277] synthesized 2D CdS and 2D CoP NSs, oxidation and phosphidation process. Then, 2D–2D CdSe/CoP photo-catalysts were formed by ultrasonically dispersing the mixed solution of CdS and CoP. The CdSe/CoP with 2% CoP loading amounts showed a maximum photo-catalytic performance of 56.3 mmol g⁻¹ h⁻¹ under vis-light irradiation that is 11.3 times as high as bare CdS. The improved photo-catalytic activity of CdS eCoP should be due to the following two points: (1) high catalytic activity of CoP; (2) highly proficient separation and transfer of (e⁻–h⁺)-pairs photo-generated in CdS because of synthesized 2D–2D hetero-structure. In Table 1, H₂-production-based photo-catalysts are summarized.

## 7.2 Photo-catalytic Pollutant Degradation

In industrial progress, mass discharge of poisonous wastes (e.g., agrochemicals, dyes, and antibiotics) [136] has become worldwide a rigorous hazard to H₂O resources and human physical condition [298]. Besides civilizing environment policies and system, development of an eco-friendly solution for eradicating pollution is dreadfully in demand. Among possible solutions, photo-catalytic decomposition of organic contaminants via in situ very reactive species is supposed to be green, cost-efficient, and talented move to deal with pollution matters. Even though numerous types of single ingredient photo-catalysts were developed, mostly suffer from a poor photo-catalytic activity and are not sufficiently efficient for real applications. A series of 2D/2D layered hetero-structures was generated for organic photo-degradation, showing potential uses. The 2D/2D hetero-structures consisting of AgIO₃ and g-C₃N₄ NSs (AgIO₃/g-C₃N₄-NS) were successfully formed for photo-catalytic waste H₂O treatment after vis-light exposure by Li et al. [299]. The ultra-thin g-C₃N₄ NSs as polymeric organic SCs material were exhibiting superior vis-light response. Photo-catalytic performance of AgIO₃/g-C₃N₄ NSs hetero-structures was considerably higher than that of single AgIO₃ or g-C₃N₄ NSs for organic dyes degradation. Noticeably, degradation reaction rate constant of rhodamine B (RhB) than as-synthesized AgIO₃/g-C₃N₄-NS sample was approximately 22.86 times higher as compared to hetero-structures composed of AgIO₃ and bulk g-C₃N₄ (AgIO₃/g-C₃N₄-B). It shows significance of 2DMs for construction of hetero-junction photo-catalysts (Fig. 26b).

A possible photo-catalytic method was also proposed in this work: The photo-induced e⁻’s on CB of g-C₃N₄-NS can move to AgIO₃ CB under vis-light irradiation that promoted photo-generated (e⁻–h⁺)-pairs separation in g-C₃N₄-NS (Fig. 26c). Considerably decreased steady-state PL spectra peak intensity and enhanced lifetime of charge carriers in PL spectra of AgIO₃/g-C₃N₄ NSs as compared with that of single g-C₃N₄ NSs indicated superior e⁻–migration and charge separation effectiveness at hetero-junction edge. To consider O₂⁻/O₂ reduction potential, the oxidative breakdown of the dye should be due to h⁺’s in VB of the g-C₃N₄ NSs and •O₂⁻ produced through e⁻’s reduction of O₂ from CB of g-C₃N₄ NSs. In another work, diverse quantity of BiOCl nano-plates is utilized to combine with g-C₃N₄ NSs via an easy calcination method. The face-to-face interaction edge
of as-synthesized BiOCl/C₃N₄ hetero-structures was studied, and the significance of contact area of two components was discussed. The superior photo-current intensity and weakened PL intensity of BiOCl/C₃N₄ hetero-structures as compared with those of C₃N₄ NSs illustrated separation and migration of photo-generated e−s at interface. The BiOCl/ C₃N₄ hetero-junction photo-catalysts were loaded with 70% BiOCl which showed the highest MO photo-degradation activity in vis-light irradiation. Wang et al. [300] prepared g-C₃N₄/Bi₂WO₆ 2D/2D hetero-structures consisting of g-C₃N₄ NSs and SL Bi₂WO₆ NSs for degradation of ibuprofen under vis-light irradiation. It shows that highly active photo-degradation system might be developed via navigation of charge division, transportation, and consumption at atomic level. Bera et al. [301] prepared a chain of hetero-structures consisting of rGO and CdS with diverse dimensionality (rGO/CdS) for photo-catalytic degradation of methylene blue (MB).

The 2D-G as an example of 2D-layered material, whose atomic thickness has outstanding charge transfer ability, can offer conducting e−-channels for separation of the photo-generated charges in the hetero-junction photo-catalyst composed of BG and SC. Through utilizing terephthalic acid (TA) as an example, the OH• radicals were established to be generated active species for the photo-catalytic decomposition. Therefore, improved rGO/CdS activity in comparison with the single CdS might be explained as follows: Under vis-light irradiation, photo-generated e− in CB of CdS is...
transferred to rGO surface and reacts with adsorbed O2 that consequently produces ·O2− and OH·. Oxidization of both OH• and photo-generated h+s leads to photo-catalytic decomposition of MB dye molecules. Charge migration from CdS to rGO takes place at rGO/CdS hetero-structures interface, as proved from considerably quenched PL of CdS components, promoting separation of photo-generated charges and therefore enhancing photo-catalytic activity [136]. In a few cases, the photo-catalytic activity of pollutant degradation might be increased through synergetic effect in hetero-junctions and other configuration tuning.

Yangyang Liu et al. [302] studied a 2D/2D nano-composite photo-catalyst (ZnO/MoS2) derived from P-doped ZnO NSs with large SSA and 2D-MoS2 for competent photo-degradation of organic dyes (Fig. 27a–f). The ZnO/MoS2 hetero-structures with different MoS2 loading amounts (mass ratio is 0, 0.01, 0.1, and 1 wt%) and commercial P25 are utilized as photo-catalysts for photo-degradation calculations that took place in similar experimental conditions (Fig. 27d, e). Comparative findings illustrate that ZnO/MoS2 with a small loading amount of MoS2 (0.1 wt%) would considerably improve photo-catalytic activity in comparison with pristine ZnO NSs. When MoS2 loading amount was increased from 0.01 to 0.1 wt%, photo-catalytic performance of ZnO/MoS2 was further improved, but reduced after loading amount of MoS2 and further enhanced to 1 wt%. A huge MoS2-doped concentration would block sunlight that was utilized to force photo-degradation of MB and therefore decreases the photo-catalytic performance. A photo-catalytic mechanism of ZnO/MoS2 hetero-structures is proposed in Fig. 27f [136]. Derived from interfacial effect between ZnO and MoS2, photo-generated e+s would migrate from CB of ZnO to that of MoS2 that considerably improved the separation of carriers and therefore increase catalytic activity. Increased transport and separation of photo-generated h+s and e−s stimulated through interfacial effect can be established through increased photo-current density of MoS2/ZnO hetero-structures after introduction of MoS2 components. The photo-generated charges react with O2 and H2O after
relocated to catalyst surface and generated much reactive radicals (OH and superoxide anion radicals) to degrade dye molecules. In addition to hetero-junction effect, P loading stimulated defects in ZnO NSs also support photo-catalytic activity as they can enhance light absorption via introduction of energy level between BGs [136].

Fig. 28  a TiO$_2$ and graphene NS structures. b TEM and element mapping of graphene/TiO$_2$ hetero-structure. c Photo-catalytic degradation of rhodamine B (RhB) over different photo-catalysts under irradiation of UV light. Adapted with permission from Ref. [304]. d Preparation of GCN samples through one-pot impregnation–thermal reduction approach. e Total CH$_4$ yield over as-synthesized photo-catalysts. f Photo-generated charge transfer in GCN system for CO$_2$ reduction with H$_2$O to make CH$_4$. Adapted with permission from Ref. [303]
7.3 Photo-catalytic CO₂ Reduction

The 2D materials aptitudes to boost the specific surface area to give elevated surface reactive sites make them a top precedence for photo-catalyst supports. Provided large contact area of 2D/2D composite, contact in graphene and photo-catalyst is anticipated to be enhanced that speeds up transfer and separation of photo-generated (e⁻–h⁺)-pairs, therefore enhancing their photo-catalytic CO₂ reduction activity. According to the above-discussed phenomena, J. Sun et al. [257] fabricated three classes of 2D/0D, 2D/1D, and 2D/2D graphene/TiO₂ hetero-structures through solvothermal method. So, the 2D/2D graphene/TiO₂ hetero-structure showed maximum photo-catalytic effectiveness in contrast to 0D/2D and 1D/2D graphene/TiO₂ hetero-structures and pristine TiO₂ NSs. This performance was ascribed due to stronger electronic and physical coupling in 2D/2D structure that provides more proficient electron transport (Fig. 28a–c). Also, Wee-Jun Ong et al. [303] studied 2D/2D sandwich-like graphene-g-C₃N₄ (GCN) composite formed by one-pot impregnation thermal reduction technique. It also shows a high photo-catalytic activity for CO₂ reduction to CH₄. The large contact interface in graphene and g-C₃N₄ plays a significant function to improve photo-catalytic CO₂ reduction by rising electron movement (Fig. 28d–f).

Furthermore, W. J. Ong et al. formed 2D/2D layered nano-structure of rGO/g-C₃N₄ by surface charge modification and protonation for improved photo-catalytic reduction of CO₂ to CH₄ [305]. The preparations involved ultrasonic dispersion with NaBH₄-reduction method (Fig. 29a). In comparison with pristine g-C₃N₄ and rGO/CN, optimized composite 15 wt% rGO/pCN (15rGO/pCN) showed high CH₄ production of 13.93 mmol g⁻¹cat with a photochemical QY of 0.560% (Fig. 29b, c). Since g-C₃N₄ also showed 2D π-conjugated structure, this quality improves the capability of catalyst to adsorb CO₂ molecules. When electrostatically charged with 2D conducting material rGO, pCN, and rGO created efficient interface, which caused improved performance for CO₂ reduction (Fig. 29d).

In addition, formation method of 2D/2D structure may affect photo-catalytic activity; for example, exfoliation production of graphene and g-C₃N₄ will expose defects present on surface those are helpful for CO₂ reduction, but surplus functional groups on catalyst surface will decrease conductance and number of active sites, therefore degrading activity. Therefore, Yu Teng Liang et al. [305] formed smaller quantity of surface defects that resulted in a higher...
photo-catalytic CO$_2$ reduction activity toward CH$_4$ formation as compared to their counterparts with high quantity of surface defects. In this method, graphene was formed by two different techniques that involved rGO solvent-exfoliated graphene (SEG) way and coupled with TiO$_2$ to make rGO-TiO$_2$ and SEG-TiO$_2$, correspondingly. Due to its outstanding electron conductivity, SEG-TiO$_2$ showed higher photo-catalytic CO$_2$ reduction activity compared to rGO-TiO$_2$. Hence, Table 2 shows the current developments in 2D materials for solar CO$_2$ reduction devices.

### 7.4 Photo-catalytic H$_2$O$_2$ Production

Carbonaceous nanomaterials (NMs) with unique characteristics of sp$^2$-hybridized carbon bonding with remarkable physicochemical nature at nanoscale usually show outstanding mechanical, chemical, and electrical properties [323]. In photo-catalysis research direction, carbonaceous NMs are frequently acted as e$^-$ transfer materials and photo-sensitizer that can widen adsorption edge and advance migration effectiveness of photo-induced e$^-$s [324]. While carbonaceous NMs are immobilized on g-C$_3$N$_4$ photo-catalyst, they can accept and transport photo-induced e$^-$s from CB level of g-C$_3$N$_4$ and boost the reduction reaction activity and so lead to superior photo-catalytic performance [325]. As typical carbonaceous NMs, CNTs with π-conjugative structure are able to accept, transport, and store e$^-$s [326]. So, g-C$_3$N$_4$-CNTs fabricated by incorporating the CNTs into g-C$_3$N$_4$ can advance photo-catalytic activity. Zhao and co-authors [327] applied the amination method to initiate CNTs in g-C$_3$N$_4$ NSs to make hybrid catalyst of g-C$_3$N$_4$/CNTs, where CNTs were covalently mixed with g-C$_3$N$_4$. The g-C$_3$N$_4$/CNTs hybrid photo-catalyst showed H$_2$O$_2$ formation rate of 32.6 μmol h$^{-1}$ that was noticeably higher than g-C$_3$N$_4$ (2.5 μmol h$^{-1}$). The CNTs covalent

| Photo-catalyst materials | CO$_2$ reduction product | Average rate (μmol g$^{-1}$ h$^{-1}$) | References |
|--------------------------|--------------------------|--------------------------------------|------------|
| TiO$_2$ NS-graphene | CH$_4$ | 9.5 | [306] |
| graphene-Ti$_{0.91}$O$_2$ hollow spheres | CH$_4$/CO | 1.14/8.91 | [307] |
| WO$_3$ NSs | CH$_4$ | 16 | [308] |
| MoS$_2$-TiO$_2$ | CH$_4$ | 10.6 | [309] |
| BiOCl nano-plates | CO | 8.1 | [310] |
| BiO/g-C$_3$N$_4$ | CO/CH$_4$ | 4.86/0.18 | [311] |
| Ag or Au/Zn-Ga-LDH | CO/CH$_3$OH | 300/2010 | [312] |
| carbon-doped BN NSs | CO | 9.3 | [313] |
| Sandwich-like graphene/g-C$_3$N$_4$ | CH$_4$ | 5.87 | [314] |
| rGO/protonated g-C$_3$N$_4$ | CH$_4$ | 13.93 | [315] |
| GO | CH$_3$OH | 0.172 | [316] |
| Boron-doped graphene (P25/B-GR) | CH$_4$ | 2.5 | [317] |
| Oxygen-rich TiO$_2$-doped graphene oxide (5GO-TiO$_2$) | CH$_4$ | 3.450 | [318] |
| Cu$_2$Se/graphene | CH$_3$OH | 2.63 | [319] |
| rGO-TiO$_2$ | CH$_4$ | 0.135 | [320] |
| Cu$_2$O/rGO | CH$_3$OH | 41.5 | [321] |
| CsPbBr$_3$ QDs/gO | CH$_4$ | 29.6 | [322] |
| TiO$_2$-CdS/rGO | CH$_4$ | 0.115 | [323] |
| WO$_3$ NS | CH$_4$ | 16 | [324] |
| MoS$_2$/Bi$_2$WO$_6$ | CH$_3$OH | 36.7 | [325] |
| MoS$_2$/TiO$_2$ | CH$_4$ | 10.6 | [326] |
| SnS$_2$ | CO | 12.28 | [327] |
| Bi$_2$WO$_6$ | Methanol | 75 | [328] |
| ZnAl-LDH NSs | CO | 7.6 | [329] |
| Vv-rich o-BiVO$_4$ | Ethanol | 398.3 | [330] |
| Ti$_3$C$_2$ with P25 | CH$_4$ | | [331] |
combined with g-C3N4 advanced e\textsuperscript{−} generation via higher reduction capability and favorably shifted CB level to improve single e\textsuperscript{−} reduction of O\textsubscript{2} to ·O\textsuperscript{2−}.

When polyoxometalates (POMs) [328] are irradiated through plentiful light energy, excitation of charge transfer from O\textsuperscript{2−} to Mn\textsuperscript{+} (n = 5, 6) is observed, guiding to development of h\textsuperscript{+} center (O\textsuperscript{−}) and trapped e\textsuperscript{−} center (M\textsubscript{\textsuperscript{+}}\textsubscript{n\textsubscript{−1}} pair. So, excited POMs can provide e\textsuperscript{−} donors/acceptors. In addition, POMs have lesser recombination possibility of e\textsuperscript{−}s and h\textsuperscript{+}s, as a result of its distinct HOMO–LUMO BGs. Taking advantages of these, POMs have been broadly used in photo-catalysts areas, for example H\textsubscript{2}O oxidation [329], H\textsubscript{2}-evolution [330], CO\textsubscript{2}-reduction [331], etc. Thus far, POMs also combined with g-C3N4 for photo-catalytic H\textsubscript{2}O\textsubscript{2} evolution. Zhao and co-workers [332] combined POM cluster of [PW\textsubscript{11}O\textsubscript{39}]\textsuperscript{−7}(PW\textsubscript{11}) with 3D ordered macro-porous g-C3N4 (3DOM g-C3N4) for efficient photo-catalytic H\textsubscript{2}O\textsubscript{2} evolution. POM covalent cluster of PW\textsubscript{11} was covalently bonded with 3DOM g-C3N4 by captivating an organic linker approach. The quantity of synthesized H\textsubscript{2}O\textsubscript{2} by g-C3N\textsubscript{4}/PW\textsubscript{11} attained 3.5 μmol within 60 min, whereas catalytic activity of pristine 3DOM g-C3N4 was only 1.3 μmol. The CB and VB of 3DOM g-C3N\textsubscript{4}/PW\textsubscript{11} were more positive compared to 3DOM g-C3N4 that improved their potential for H\textsubscript{2}O oxidation and promoted 2e\textsuperscript{−} reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}. Similarly, they also studied a further POM cluster, [SiW\textsubscript{11}O\textsubscript{39}]\textsuperscript{8−}(SiW\textsubscript{11}), to covalently combine with g-C3N\textsubscript{4} [333].

Compared to PW\textsubscript{11}, the SiW\textsubscript{11} possessed more negative CB level, helping 2e\textsuperscript{−} reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}. Under sunlight irradiation (AM 1.5), H\textsubscript{2}O\textsubscript{2} photo-catalytic production of 15.2 μmol h\textsuperscript{−1} over hybrid g-C3N\textsubscript{4}/SiW\textsubscript{11} photo-catalyst was attained. Except for direct combination of POMs with g-C3N\textsubscript{4}, POMs-derived metal oxides were also incorporated with g-C3N\textsubscript{4} to make hybrid photo-catalysts. Since POMs-derived metal oxides can accept, transport, and store e\textsuperscript{−}s, resulting hybrid photo-catalysts are able to improve photo-induced e\textsuperscript{−}s generation and therefore increase performance of reduction reaction for H\textsubscript{2}O\textsubscript{2} formation. Zhao and Zhao [334] studied g-C3N\textsubscript{4}/PWO hybrid photo-catalyst through calcination of g-C3N\textsubscript{4} precursor and (NH\textsubscript{4})\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} (NH\textsubscript{4}·PW\textsubscript{12}) (POMs precursor). The hybrid g-C3N\textsubscript{4}/PWO photo-catalyst showed competent photo-catalytic appearance for photo-catalytic H\textsubscript{2}O\textsubscript{2} fabrication by vis-light in the absence of organic e\textsuperscript{−} donor. In addition, a similar group [335] utilized another POMs-derived metal oxide to include g-C3N\textsubscript{4}. The g-C3N\textsubscript{4}/CoWO hybrid photo-catalyst was fabricated via calcination of 3-amino 1, 2, 4-triazole (3-AT) and (NH\textsubscript{4})\textsubscript{8}Co\textsubscript{2}W\textsubscript{12}O\textsubscript{42} (NH\textsubscript{4}·Co\textsubscript{2}W\textsubscript{12}). Under vis-light irradiation, H\textsubscript{2}O\textsubscript{2} was rapidly generated over g-C3N\textsubscript{4}/CoWO and the amount of formed H\textsubscript{2}O\textsubscript{2} was 18.7 μmol in 60 min, while individual g-C3N4 offered very lower photo-catalytic activity (<0.1 μmol in 60 min). CoWO-incorporated g-C3N\textsubscript{4} framework could produce more e\textsuperscript{−} for O2 reduction, while negative shifts of CB level from g-C3N4 to g-C3N\textsubscript{4}-CoWO enhanced single e\textsuperscript{−} reduction of O2 to ·O2−. Also, incorporated CoWO advanced the oxidation of ·O2− to 1O2 by h\textsuperscript{+} and formed 1O2 proceeded 2e\textsuperscript{−} reduction to H\textsubscript{2}O\textsubscript{2}. Every one of these is related to enhanced photo-catalytic activity for H\textsubscript{2}O\textsubscript{2} production over g-C3N\textsubscript{4}/CoWO hybrid photo-catalyst.

Organic counterparts have advantages of economic, simple formation and mechanical flexibility [336]. Mainly, organic photo-catalysts are capable to concentrate on faults of their inorganic counterparts, for example heavy metal with sensitive toxicity and restricted level of active sites. g-C3N\textsubscript{4} were recognized as representative organic polymer SC photo-catalysts. Recently, other organic SCs were also employed as photo-catalysts, e.g., triazine and aromatic diimides. Aromatic diimides possess high e\textsuperscript{−} mobility and stability that are significant class of n-type organic SCs and incorporated with g-C3N\textsubscript{4} for photo-catalytic H\textsubscript{2}O\textsubscript{2} evolution. Shiraishi et al. [337] included facile way to aromatic diimide (pyromellitic diimide, PDI) in g-C3N\textsubscript{4} network by facile thermal condensation. These results showed that both CB and VB levels were developed into more positive via incorporation of PDI units in g-C3N\textsubscript{4} due to high e\textsuperscript{−} affinity of PDI. This detail exposed that g-C3N\textsubscript{4}/PDI photo-catalyst has superior ability for O2 reduction; therefore, H\textsubscript{2}O\textsubscript{2} evolution from H\textsubscript{2}O and O2 was promoted. Additionally, efficient synthesis of 1,4-endoperoxide species on photoexcited g-C3\textsubscript{3}N\textsubscript{4}/PDI suppressed 1e\textsuperscript{−} reduction of O2 and 4e\textsuperscript{−} reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}, thus promoting selective two-e\textsuperscript{−} reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2}.

Likewise, other categories of aromatic diimides were also incorporated with g-C3N\textsubscript{4}, for example biphenyl diimide (BDI) [338] and mellitic triimide (MTI) [339]. In pristine H\textsubscript{2}O with O\textsubscript{2}, both g-C3N\textsubscript{4}/BDI and g-C3N\textsubscript{4}/MTI catalysts successfully produced millimolar levels of H\textsubscript{2}O\textsubscript{2}. For further activity improvement, rGO is incorporated with g-C3N\textsubscript{4}/PDI catalyst [340] that takes advantage from 2D single-carbon monolayer property of rGO with high charge carrier mobility and high photochemical and
thermal stability. The g-C₃N₄/PDI/rGO nano-hybrids photo-catalyst was synthesized by hydrothermal–calcination process. The photo-catalytic reaction testing showed that g-C₃N₄/PDI/rGO₀.₀₅ produced the largest amount of H₂O₂ (29 μmol) under vis-light irradiation within 24 h, which was higher compared to g-C₃N₄ and g-C₃N₄/PDI. The SCC efficiency value of g-C₃N₄/PDI/rGO₀.₀₅ was up to 0.20% that was higher compared to other counterparts. In this photo-catalyst system, rGO not only encouraged efficient charge division but also increased selective 2e⁻ O₂ reduction. The activity of g-C₃N₄/PDI-rGO photo-catalyst could be further improved by introducing BN because of spatial separation of e⁻ and h⁺ onto rGO and BN, correspondingly [341]. Yang et al. [342] fabricated perylene imides (PI) on g-C3N₄ NSs to construct an all-solid-state Z-scheme hetero-junction. The hybrid g-C₃N₄/PI photo-catalyst with Z-scheme arrangement promoted spatial separation of charge carriers, where photo-induced e⁻s in PI recombined with h⁺s in g-C₃N₄, while remaining h⁺s and e⁻s were left on PI and g-C₃N₄, correspondingly. Consequently, more e⁻s from CB of g-C₃N₄ part reduced O₂ to produce more H₂O₂, while h⁺s of g-C₃N₄/PI oxidized OH⁻ to -OH that also later reacted to generate H₂O₂. The shift of H₂O₂ production from single-channel to two-channel leads to significant enhancement in photo-catalytic H₂O₂ evolution. In another study, anthraquinone (AQ) was fastened on g-C₃N₄ surface that attains analogous roles as other organic SCs [343].

Fei Xue et al. [344] studied efficient photo-catalytic pure H₂O₂ splitting for simultaneous H₂ and H₂O₂ fabrication. Photo-catalytic overall H₂O splitting for instantaneous H₂ and H₂O₂ generation via a 2e⁻ pathway can readily address these issues. A novel CoNi₃P cluster incorporated P-doped g-C₃N₄ photo-catalyst (CoNi₃P-PCN) by two-step phosphating method that presents such unique behavior for pure H₂O splitting into stoichiometric H₂ and H₂O₂. The highest H₂ production rate reaches 239.3 μmol h⁻¹ g⁻¹, achieved over CoNiP-PCN photo-catalyst that is among the best reported activities for overall H₂O splitting. It is found that both P and cluster co-catalyst are critical to remarkably improved photo-catalytic activity. Specifically, P as a substitution of C in PCN introduces a positive charge center (P⁺), reinforcing

### Table 3 Summary of photo-catalytic H₂O₂ production

| Material          | Sacrificial reagent | Photo-catalyst concentration | Irradiation conditions | H₂O₂ yields | References |
|-------------------|---------------------|------------------------------|------------------------|-------------|------------|
| TiO₂              | C₂H₅OH              | 10 mg mL⁻¹                  | > 280 nm               | 40 mM (12 h) | [345]      |
| TiO₂              | 2-C₃H₇OH            | 1 mg mL⁻¹                   | 365 nm                 | 423.2 μΜ (2 h) | [346]     |
| Cu/TiO₂           | –                   | 300 mg                      | 300–400 nm             | 8 μM (5 min) | [347]      |
| F-TiO₂            | HCOOH               | 0.5 g L⁻¹                   | 360 nm                 | 1–1.3 mM    | [348]      |
| Au/TiO₂           | HCOOH               | 1 mg mL⁻¹                   | > 420 nm               | 640–700 μΜ (1 h) | [349]     |
| CoPirGO/TiO₂      | 2-C₂H₅OH            | 0.5 g L⁻¹                   | > 320 nm               | 4.5 μM (3 h) | [350]      |
| TiO₂/WO₃/rGO      | 2-C₂H₅OH            | 1 mg mL⁻¹                   | AM 1.5                 | ~270 μΜ (1 h) | [351]     |
| Au/TiO₂           | CH₃OH               | 1 mg mL⁻¹                   | > 320 nm               | 1.06 mM (3 h) | [352]      |
| Au/SnO₂-TiO₂      | Alcohol             | 1 mg mL⁻¹                   | UV irradiation         | ~15 mM (25 h) | [353]      |
| g-C₃N₄            | Alcohol             | 4 mg mL⁻¹                   | > 420 nm               | 30 μmol (24 h) | [354]     |
| Mesoporous g-C₃N₄| EtOH                | 4 mg mL⁻¹                   | > 420 nm               | 90 μmol (24 h) | [355]      |
| AQ-augmented g-C₃N₄| 2-C₂H₅OH           | 0.5 mg mL⁻¹                 | AM 1.5                 | 361 μΜ (1 h) | [356]      |
| KPF₆/g-C₃N₄       | C₂H₅                 | 0.5 mg mL⁻¹                 | > 420 nm               | 1.5 μM (5 h) | [357]      |
| Holey defective g-C₃N₄| H₂O+IPA          | 0.83 mg mL⁻¹               | > 420 nm               | 12.1 μΜ (2.5 h) | [358]     |
| O₂-enriched g-C₃N₄| H₂O+CH₃OH           | 1 mg mL⁻¹                   | > 420 nm               | 300 μM (5 h) | [359]      |
| g-C₃N₄-SiW₁₁      | CH₃OH               | 1 mg mL⁻¹                   | AM 1.5                 | 15.2 μΜ (1 h) | [360]      |
| g-C₃N₄-CoWO       | Organic e⁻          | 1 mg mL⁻¹                   | ≥420 nm                | 9.7 μΜ (1 h) | [361]      |
| [RuII(Me₂phen)₃]²⁺ | O₂-saturated H₂SO₄ | 1.0 μM                      | > 420 nm               | 612 μΜ (9 h) | [362]      |
| Au/BiVO₄          | H₂O+EtOH            | 50 mg/30 mL                 | > 420 nm               | 40.2 μΜ (10 h) | [363]     |
| rGO/Cd₃(TMT)₂     | H₂O+CH₃OH           | 80 mg/20 mL                 | > 420 nm               | ~7 mM (24 h) | [364]      |
| Resins            | H₂O                 | 50 mg/30 mL                 | > 420 nm               | 99 μΜ (24 h) | [365]      |
chemical connection between PCN and CoNiP, in the form of $P^{+}–P^{δ−}–Co^{δ+/Ni^{δ+}}$. This unique bridging effect, together with extended light absorption by P doping and optimized surface redox potential by co-catalyst integration, stimulates efficient vectorial charge transfer between PCN and CoNiP and subsequent surface mass exchange. In contrast, this also shows that well-satisfied band structure of PCN can facilitate the $2e^−$ reaction pathway, which not only has implication for potential use of CoNiP-PCN as potential photo-catalyst for solar H₂ manufacture, and offers a new idea for pure H₂O splitting in particulate system [344]. Table 3 offers intuitive summary of photo-catalytic-based H₂O₂ production.

8 Future Perspective and Challenges

In this review, a large number of experimental as well as theoretical research works related to photo-catalysts are discussed. A lot of confronts are required to be solved for incorporation of 2D p–n junctions in mass production electronic elements. Two most imperative confronts are scalable production of 2D p–n junctions and environment degradation of 2DMs. Despite significant growth in ultra-thin 2DMs for photo-catalysis, it is still suffering from large number of challenges in this direction. First, apart from extensively developed ultra-thin 2DMs, for instance OH, MOs, and sulfides for photo-catalytic process, other types of probable ultra-thin 2DMs with novel structure or electronic properties for photo-catalysis should be investigated, for instance layer oxy-halides (e.g., FeOBr and Bi₂VO₆Cl), thiophosphates (e.g., CoPS₃), multi-metal chalcogenides (for instance Cu₂ZnGeS₄), or metal-free SCs (e.g., C₃N and C₂N). Specially, ultra-thin 2DMs by means of intrinsic non-vdWs’ layer structure have great potential in photo-catalysis, since plentiful surface atoms along dangling bonds can assist to construct outstanding chemical surroundings for supporting molecular reaction chemisorptions and enhance catalytic reaction dynamics. Second, there is an exceptional large-scale approach to yield ultra-thin 2D photo-catalysts with controlled thickness or crystal structures. The scalable manufacturing of ultra-thin 2D photo-catalysts has immense importance for possible commercial applications, and therefore more concentration should be given to cost-efficient scalable production approach. Third, atomic-scale thicknesses permit ultra-thin materials along simply adjusting electronic structures that show an important effect on photo-catalytic performance. In spite of defect engineering, element doping, etc., or other efficient approaches for instance, engineering or tensile strain of surface state should be modified to engineer electronic structure and therefore enormously promote photo-catalytic activity. Fourth, ultra-thin 2D arrangement offers a perfect material model to distinguish catalysts’ active site, additional types of tuning, and reaction centers quantity to fulfill definite catalytic process requirement.

8.1 Scalable Synthesis and Environmental Degradation

First major confront is concerned with scalable synthesis of engineered vdWs hetero-structures with well-controlled edges. Still if deterministic assigned methods are flourishing at experimental level, they are not suitable for commercial purposes. Growth methods, such as CVD growth, have already been proven proficient for the growth of high-quality 2DMs such as lateral and vertical hetero-structures at laboratory level. The VdWs epitaxial methods are even more promising for fabrication of high-quality 2D hetero-structures. Upscale of such growth methods is probable, and the upcoming years will realize the application of higher-quality devices. A second, potential approach is to upscale growth of 2D p–n junctions to merge development of single 2DMs (e.g., MoS₂) with different doping methods (frequently electrostatic or chemical). A second confront is environment degradation of numerous recognized 2DMs. For instance, while exposed to air, the BP in its ultra-thin structure is likely to absorb humidity that degrades material electronic properties. In context of BP, the most established degradation mechanism such as material reaction with O₂ alters material properties. One method that prevents this degradation is encapsulating air-sensitive material among h-BN flakes under O²⁻ and humidity-free conditions. One active area of 2DMs investigation is consequently devoted to upscale encapsulation methods. A special move, which is at present practiced, is active investigation for novel 2DMs that did not create degradation problems, which could arrive either from the preparation (e.g., TiS₃) or from natural resources (e.g., franckeite). Such, active search previously assisted to multiply number of present 2DMs only a handful more than twenty under 10 years.
8.2 Future Perspectives

Other than traditional optoelectronic applications, 2D p–n junctions have still a lot of unknown applications and fundamental problems. For example, thermoelectric applications of 2D p–n junctions were not yet completely studied. The conventional Peltier device, a component mainly utilized in electronics for cooling (and commonly less for heating), depends on p- and n-type SC thermally coupled in parallel and series. The VdWs hetero-structures could be utilized to manufacture atomic-level thin cooling (or heating) elements in combination with other smart properties of 2DMs, e.g., high transparency or flexibility. Another exciting way is the study of new p-n junction geometries (e.g., circular p-n junctions in recent times showed in G) or novel devices based on 2D p-n junctions, e.g., logic gates or memories. Genuine probabilities still buried in 2DMs are in all possibilities than one described and 2D p–n junctions grasp much promise in larger-scale applications. Such 2D-junctions are particularly attractive building blocks of inflexible and transparent electronics, e.g., light-emitting diodes (LEDs) or solar cells. One more application, which can advantage from ultra-thin structure of 2D p–n junctions, is light-sensing and harvesting applications for nano-photonics. The 2D p–n junctions can be utilized as photodetectors, and numerous material combinations are present, which can be utilized to propose devices with sensible wavelengths ranging from infrared to UV that have already been established.

9 Conclusion

In recent years, new p–n junctions manufacturing witnessed benefit of an ultra-thin nature of 2DMs. The top-down and bottom-up production methods have established competent generating p-n junctions with high optoelectronic properties. 2DMs continue to offer numerous prospects to manufacture new p-n junctions with exceptional properties, which unlock motivating scientific directions both in requisites of elementary questions and with respect to applications [32]. Ultra-thin 2DMs and their hybridizations through maintaining 2D arrangement are outstanding materials for elementary photo-catalytic investigation and promising marketable uses. This broad review highlights modern advancement in appliance of ultra-thin 2DMs for the photo-catalytic solar energy conversion. First, this review offers a complete outline of categorization and controlled fabrication mechanism of an ultra-thin 2D photo-catalyst. After that, approaches to modify electronic arrangement of ultra-thin2DMs and more effecting photo-catalytic properties are reviewed, that is, an element engineering, thickness engineering, defect engineering and doping. In addition, further hybridizations with upholding ultra-thin 2D characteristics are offered to further enhance photo-catalytic properties, such as QDs/2DMs, single atoms/2DMs, molecular/2DMs, and 2D–2D stacking materials. Lastly, a variety of photo-catalytic applications over ultra-thin 2D photo-catalysts were reviewed with emphasis on insights into structure–performance relationship, involving H2O oxidation, H2 evolution, CO2 reduction, N2 fixation, organic synthesis, and pollutants degradation. In conclusion, this review highlights universal approaches and current growth in 2D/2D hetero-junctions and hetero-structures that are outstanding candidates for basic investigation and possible catalyst applications because of their exclusive electronic structure and physicochemical properties:

1. Integrating their components’ advantages, for instance ultra-thin 2D configuration, large surface area, and electronic/physicochemical properties;
2. Partition or charge transfer can be encouraged for required function; and
3. Versatile options (such as thickness, elements, defects, fabrication expertise, and contact space) can be designed to engineer properties and therefore application activity [136].

Heterogeneous photo-catalysis has turned into a fast-growing galaxy with manifold miscellaneous matters being investigated and introduced. Driven through aforementioned benefits and possible standards of 2D/2D hetero-structures, increasing amount of extraordinary achievements were established in last few years. However, with challenges creating hurdles for real catalysis applications, e.g., catalyst competency, selectivity related to yield and pollution, environment friendly, and cost-efficient, there are still a lot of efforts to follow the purpose of developing required catalyst and reaction scheme for real-world applications. Catalysts grasp key for increasing effectiveness of catalytic reaction method which is the entrance of commercial practicable applications required to be prevailed over. The 2D/2D hetero-structures as photo-catalysts are planned with purpose to endorse light harvesting, charge carrier separation/transfer, redox reactivity, etc. In addition to sufficiently intriguing
benefits of 2D elements via very well engineering of structure, composition, BG, and surface reaction sites, interfacial tuning at nanoscale of 2D/2D hetero-structures is probable to further make easy photo-catalytic activity. Even though a lot of opportunities subsist for 2D/2D hetero-structures as electrocatalysts, this field is also facing a lot of challenges and research room:

1. Synthetic techniques are further required to be optimized to persuade commercial manufacturing demands.
2. Analysis techniques might be more superior for structure, physicochemical properties, and activity for these ultra-thin hetero-structures.
3. Clear comprehension of work mechanism, in particular reaction intermediates, of 2D/2D hetero-junction electrocatalysts is still now required.

In addition, aforementioned optimization method of designing catalyst, high products yield/selectivity, and development of novel organic materials preparation are all solutions for further investigation. As a result of quick advancement and affluent information accumulated in the 2DMs and hetero-structures in last year’s, one may anticipate that 2D/2D hetero-structures would participate in a significant role in resolving energy and environment confronts [136]. However, investigations concentrating on the photo-catalysis mechanism are still insufficient. A lot of hard work should be required to optimize the theoretical calculation setting, nearer to the industrial-scale practical reaction conditions. Parallel exploitation of theoretical approach along superior experimental approach can assist to get deeper understanding for connection between neighboring atomic microstructure and activity as well as elucidate reaction methods. Also, due to relevant limitations of every material, a preferred move to obtain optimal properties is performed to assemble diverse building blocks to produce supportive results. It is supposed that such a broad review will further put research in the field of 2DMs as a novel photo-catalysis [32].

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