

Review

Two-Dimensional Photocatalysts for Energy and Environmental Applications

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Abstract: The depletion of fossil fuels and onset of global warming dictate the achievement of efficient technologies for clean and renewable energy sources. The conversion of solar energy into chemical energy plays a vital role both in energy production and environmental protection. A photocatalytic approach for H₂ production and CO₂ reduction has been identified as a promising alternative for clean energy production and CO₂ conversion. In this process, the most critical parameter that controls efficiency is the development of a photocatalyst. Two-dimensional nanomaterials have gained considerable attention due to the unique properties that arise from their morphology. In this paper, examples on the development of different 2D structures as photocatalysts in H₂ production and CO₂ reduction are discussed and a perspective on the challenges and required improvements is given.

Keywords: artificial photosynthesis; photocatalysis; hydrogen; carbon dioxide; two-dimensional



Citation: Ioannidou, T.; Anagnostopoulou, M.; Christoforidis, K.C. Two-Dimensional Photocatalysts for Energy and Environmental Applications. *Solar* **2022**, *2*, 305–320. <https://doi.org/10.3390/solar2020017>

Academic Editor: Jürgen Heinz Werner

Received: 30 April 2022

Accepted: 6 June 2022

Published: 10 June 2022

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1. Introduction

Recent advances in nanotechnology and, in particular, precise materials engineering have allowed the development of many different nanomaterials that present unique physiochemical properties. Research in this specific topic has revealed the importance of the precise control of composition, morphology, structure and size in directing their optical, electronic, chemical, mechanical and thermal properties. All these properties play a crucial role in the efficiency of a specific application, especially in the field of clean energy production and environmental depollution. Therefore, the recent advances in the field of materials engineering open up new applications for known materials.

In our way to achieve sustainability, clean energy production and environmental pollution are among the greatest challenges that we are facing. Despite the great efforts of the last decades, there are still many technological barriers that need to be overcome. Many different approaches have been developed and applied in all the above-mentioned issues, including biotic [1,2] and abiotic methodologies [3–5]. Among the different technologies, abiotic methodologies, including catalytic processes that are based on the development of novel nanomaterials, have gained importance in recent years.

For all the above-mentioned fields, of particular interest is the development of novel photo-sensitive nanomaterials applied as photocatalysts. As in all technologies that rely on the use of nanomaterials, precise materials engineering has played a key role in the observed progress in these specific fields, allowing the development materials with specific properties via controlling composition, morphology, structure and size in directing their optical, electronic, chemical, mechanical and thermal properties. Since efficiency is closely related to materials properties, advancements in materials engineering are a prerequisite towards improving efficiency.

In addition to composition, morphology at the nanoscale plays an important role in the final properties that regulate efficiency. Among the different nanomaterials developed, of particular importance are two-dimensional materials. This stands especially for applications that are critically dependent on the available surface area together with advantageous charge-handling properties. Therefore, materials possessing a 2D structure have gained considerable attention in recent years. In order for a material to be characterized as 2D, it must contain a sheet-like morphology. The lateral size may vary from nanometers up to micrometers. In addition, the thickness of the layer should range from a single to few atomic thick layers. Their size constrains and the electron confinement in two dimensions offer them unique properties that are difficult to be found in their bulk counterparts [6].

The advancements presented in 2D materials and specially in those applied in light-triggered reactions are mostly linked with their improved physical, electronic and optical properties. This stands mostly for traditional photocatalysts and not for highly porous structures, such as metal–organic frameworks. Two-dimensional materials present a significantly larger specific surface area as compared with the corresponding bulk structures. A large specific surface area is one of the targeted properties in heterogeneous photocatalysis since both applications are related to surface reactions. Enhanced efficiency is linked with more available active sites, superior efficiency in light harvesting and mass transport and interaction with the substrate. In addition, the thickness of the structure may control the electronic properties via a multi-route approach. It may affect light absorption, the actual electronic band structure (a parameter that controls the performance of a specific reaction) and the availability of charges via controlling the abundance and stability of the photogenerated charges (electron and hole pairs, e^-/h^+). Thin 2D structures offer shorter pathways for charges to reach the surface where reactions occur, decreasing the migration distance and thus allowing a faster transfer and higher availability of charges. This is critical considering the required solar energy flux to complete reactions such as water splitting and CO_2 reduction [7,8]. An additional benefit of 2D structures is that they can also act as excellent supports for the development of multicomponent materials, allowing a higher interaction between the different parts.

In this review article, we focus on the recent progress on typical photosensitive single-phase 2D structures as well as composites and heterojunctions, applied as photocatalysts for sustainable energy production. Attention is paid to photocatalytic H_2 production and CO_2 reduction. Before discussing recent contributions in materials development, the fundamental principles and elementary steps in each application are explained.

2. Photocatalysis Based on 2D Materials

2.1. Fundamental Steps in Photocatalysis

Heterogeneous photocatalysis mimics the mechanism of natural photosynthetic centers. Under light irradiation, redox equivalents are formed and perform a chemical reaction. Lately, the term artificial photosynthesis has been used for any reaction that is initiated by light, ideally solar light, which stores energy (i.e., solar) in the form of chemical energy. As a consequence, the term solar fuel is used to characterize fuels produced using sunlight energy.

The advantage of the photocatalytic process is mostly reflected on the potential to use a free and endless energy, e.g., solar energy. The surface of the Earth annually receives solar energy (e.g., 1.3×10^5 TW) that is, by far, greater than the estimated future global energy demands (28–35 TW per year global energy demand by 2050) [9]. In addition, in contrast to other chemical processes, it may be applied under ambient conditions (pressure and temperature). Furthermore, the process is truly sustainable when suitable substrates are used, i.e., water. Considering the different systems developed, the use of semiconductors (SCs) in the heterogeneous photocatalytic process offers the advantages of the easy separation and reuse of the catalyst compared with homogeneous photocatalysts.

Electron and hole pairs (e^-/h^+) are formed in a SC when it is exposed to light greater than the energy difference between the bottom level of the conduction band (CB) and the

top level of the valence band (VB). Ideally, the energy source must be solar irradiation in order to totally explore the sustainable character of the process. This mechanism adds the first restriction for the formation of the redox equivalents, that is, the development of photocatalysts activated by solar energy. Considering that a major part of solar energy is in the visible region, photocatalysts that are activated under visible light irradiation are preferred. However, this should not be pursued in the expense of the targeted energy of the charges. e^- and h^+ pairs may undertake several paths upon their formation. Charge recombination either in the bulk or on the surface of the catalyst must be avoided. Therefore, strategies in this direction have been studied, including compositional modification and size constrains, but shape control as well. Figure 1 presents the elemental steps and fundamental reactions that take place on a photocatalyst focusing on H_2 production and CO_2 reduction. An important parameter that must always be taken into account is the energy of the photogenerated charges, which depends solely on the actual band structure of the SC.

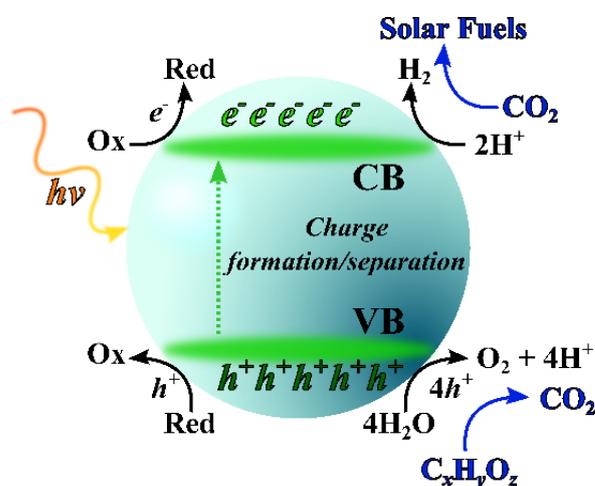


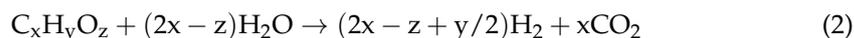
Figure 1. Schematic illustration of e^-/h^+ pairs formation upon the irradiation of a SC with the energy of incident light greater than the band gap energy and their participation in redox reactions for solar fuel production. Adopted from Ref. [10].

Solar fuel production using photocatalysis has been explored focusing on the production of H_2 and mainly C_1 and C_2 products from CO_2 reduction. H_2 may be produced via the photocatalytic route from the so-called water splitting process that converts water into H_2 and O_2 . Water oxidation is a highly demanding step since it is a four e^- process. Alternatively, H_2 may be produced by the photoreforming of oxygenated organic substrates. The reactions are given in the following formulas:

Overall water splitting process:



Photoreforming process:



In the latter, instead of water, an organic substrate is oxidized. This offers two key advantages. Firstly, the organic substrate may be oxidized easier than water, eliminating the rate limiting step of the water splitting process. Secondly, the oxidation of the organic substrate may provide protons for H_2 production. However, the proper choice of organic substrate defines the sustainability of the process. The importance of H_2 as a fuel is expressed by its zero greenhouse gas emissions when combined with O_2 in the fuel cell technology. Therefore, green hydrogen is produced via the photocatalytic process using solar energy and water as a substrate. On the other hand, CO_2 may be reduced into a variety of valuable

chemicals used as fuels (i.e., CH₄) or in other important aspects in the chemical industry, i.e., production of high-added-value chemicals. Depending on the targeted CO₂ reduction product, the process may be characterized as carbon neutral or carbon negative. The latter takes the carbon-neutral concept a step further since it removes more CO₂ than it emits.

Both photocatalytic CO₂ reduction and H₂ productions share similarities and were demonstrated over the same period [11,12]. However, H₂ evolution reaction has progressed significantly more compared to CO₂. This is mostly attributed to the challenges of the latter reaction. The multi-electron transfer process, C–C coupling and hydrogenation reactions required in the CO₂ reduction reaction highlight the more challenging thermodynamic and kinetic barriers. Furthermore, the photocatalytic conversion of CO₂ may result in different products (Table 1), a fact that may require additional complex separation processes or the development of highly selective photocatalysts. The low solubility of CO₂ in water is another practical issue. High pressures or the use of chemicals with a high CO₂ affinity (i.e., solvents) may be applied to avoid this issue, increasing the process complexity, but also reducing the environmental character of the overall process. Finally, we should also highlight that the two reactions are competing reactions since both require the use of photo-generated e[−]. Considering that H₂O is the ideal electron donor in a CO₂ photocatalytic reduction reaction, the competition between H₂O and CO₂ for e[−] consumption highlights the importance of selectivity towards accomplishing a specific reaction.

Table 1. Required redox potential of selected reactions [10].

| Reactions | E ⁰ (SHE, pH 7) |
|---|----------------------------|
| H ₂ O + 4h ⁺ → 4H ⁺ + 2O ₂ + 4e [−] | +0.81 |
| H ₂ + 2e [−] → H ₂ | −0.42 |
| CO ₂ + e [−] → CO ₂ [−] | −1.90 |
| CO ₂ + 2H ⁺ + 2e [−] → HCOOH | −0.61 |
| CO ₂ + 2H ⁺ + 2e [−] → CO + H ₂ O | −0.53 |
| CO ₂ + 4H ⁺ + 4e [−] → HCHO + H ₂ O | −0.48 |
| CO ₂ + 6H ⁺ + 6e [−] → CH ₃ OH + H ₂ O | −0.38 |
| CO ₂ + 8H ⁺ + 8e [−] → CH ₄ + 2H ₂ O | −0.24 |

Overall, based on the above analysis, an efficient photocatalyst must contain several characteristics. Among others, the catalyst must have a suitable band structure in order to utilize solar light and generate charges of a specific energy, generate sufficient charges avoiding recombination phenomena, present high specific surface area and exposed active sites and also be selective towards a specific reaction, especially in the case of CO₂ reduction. By the definition given above, 2D structures present a high specific surface area and, therefore, increased surface active sites as well as favorable charge-handling properties compared with their bulk counterparts. These characteristics make 2D structures as promising materials in photocatalysis and sparked intensive research over the last years.

Given that the photocatalytic activity greatly depends on the physicochemical properties of the photocatalyst as well as on the specific conditions used in the reaction and especially the intensity and the wavelength of the incident radiation, it is rather difficult to compare the performance of the different systems tested. Production rates are usually reported in μmol h^{−1} g^{−1}; however, the normalization of the activity to the specific surface area of the catalyst may be also applied. Quantum yields (QY) or apparent quantum yields (AQY) have been introduced as a way to compare the efficiency of photocatalysts tested in different setups. In this process, the number of the reacted electrons (based on the product, i.e., 2e[−] per H₂) over the number of absorbed/incident photons is reported. However, instead of the “apparent,” the so-called “true” quantum efficiency should be reported. The latter process offers the benefit of providing the accurate values of the efficiency since, for the optical properties of the catalyst, its behavior in the media of the reaction is taken into account [13].

2.2. Heterojunctions

An efficient approach to improve several important aspects of a photocatalyst is the coupling with another SC, i.e., the formation of a heterojunction. Visible light response may be given to a wide E_g SC through its coupling with a narrow E_g SCs. This may offer a better control of the light absorption properties compared with other competing approaches, such as the widely studied doping process. Furthermore, many examples in the literature have demonstrated that efficient charge separation may be also achieved in heterojunctions [14]. However, special attention must be given on the actual band structure of the coupled SCs in order to realize such improvements. Charge separation may be accomplished via two mechanisms. In both cases, the fundamental condition that must be fulfilled is that the CB of the one SC must lie within the band gap of the second. The formation of type-II heterojunctions (Figure 2) is the most common case. In such systems, the difference in the band energy level controls the migration of the charges. h^+ are directed in one SC, while e^- follow the opposite direction. Therefore, efficient charge separation occurs. The major issue in type-II heterojunctions is that e^- and h^+ lose part of their energy since they are spontaneously transferred from bands of high energy to those of lower. This shortcoming is bypassed when charge migration occurs via the Z-scheme mechanism (Figure 2), where e^- on the low energy CB recombines with h^+ on the low energy VB. Usually, in such systems, a charge mediator may be required, allowing the recombination of e^- on the low energy CB with h^+ on the less positive VB [15].

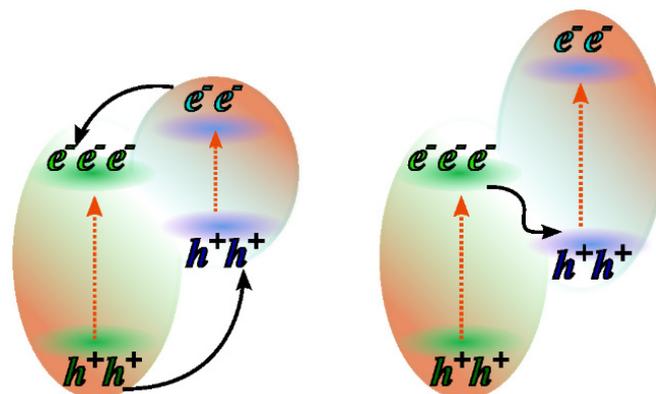


Figure 2. Charge transfer in a type-II (left side) and a Z-scheme (right side) heterojunction. Adapted from Ref. [10].

Charge separation in heterojunctions requires the formation of a tight interface between the different parts. Therefore, the large lateral size of 2D structures offers the benefit of providing a large contact area between the coupled systems [15]. Therefore, 2D structures may be used as excellent platform to be coupled with materials of other morphologies, but charge separation via interface is manifested when forming 2D/2D heterostructures [14]. Exciton dissociation is favored in 2D/2D heterojunctions even in the presence of a lattice mismatch compared with heterojunctions of different morphology [16].

3. Solar Fuel Production Using 2D Materials

Many different photocatalysts have been developed and applied in H_2 production and CO_2 reduction, of which TiO_2 nanomaterials occupy the vast majority. Among the different TiO_2 photocatalysts, 2D TiO_2 structures are of particular importance. Facets with the lowest surface energy define the morphology of the crystal. Surfactants are mostly used to control the shape of the TiO_2 crystal. In anatase TiO_2 , {101} surfaces are predominately exposed, resulting in a bipyramid structure. The formation of 2D anatase single crystal structures with preferentially exposed {001} facets has been achieved using fluorine as a capping agent under hydrothermal conditions [17,18]. Most importantly, the exposed surfaces may control the activity of the catalyst. For many reactions, it has been shown

that {001} facets offer higher activity, a fact that has been attributed to the chemistry of the different facets and, in particular, the coordination number of the terminated Ti centers [19]. However, controversial results have been reported regarding the activity of anatase crystals with different exposed surfaces. The actual conditions of the synthesis affect important parameters of the catalyst. This could be the case for the different activity reported, a fact that highlights the importance of more studies being required in this field, including a complete physicochemical characterization to identify key material parameters. For example, Liu et al. reported that the exposed crystal facets in 2D anatase TiO₂ together with the primary particle size and the proper removal of the capping agent control H₂ production [20]. Structures with a smaller particle size after the complete removal of fluorine were significantly more active. A synergy was suggested for the enhanced activity, including an improved surface area and the shift of the CB minimum to more negative levels. Surface heterojunctions may be also formed by controlling the ratio of the co-exposed facets. This has been suggested using theoretical calculations on anatase TiO₂ nanocrystals with co-exposed {001} and {101} facets [21]. The {001}/ {101} ratio of the facets was controlled using different amounts of the capping agent and the spatial separation of the charges (Figure 3) was suggested as being the main contributor in the improved CO₂ reduction reaction.

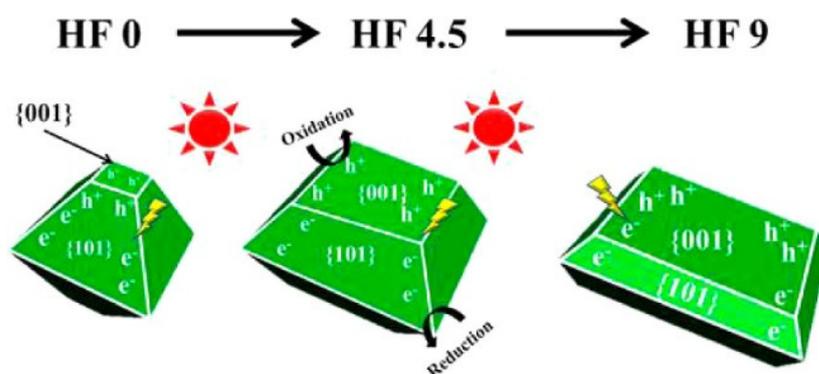


Figure 3. Spatial separation of charges in anatase TiO₂ of varying {001} and {101} facets ratio. Reprinted with permission from Ref. [21]. Copyright 2014, American Chemical Society.

As a way to improve the main inherent drawback of anatase, i.e., being inactive under visible light irradiation, a doping method was applied to improve the electronic properties linked with light absorption. The nitrogen doping of anatase TiO₂ sheets expanded light absorption to the visible region. The corresponding N-modified photocatalyst presented considerable activity in H₂ evolution under pure visible light irradiation, while it improved activity under UV-Vis irradiation compared with the non-doped TiO₂ [22]. Black titania is another example of improving visible light response. Such structures are usually developed through a hydrogenation treatment at high temperatures that induces surface defects' formation. Defect formation may present strong morphology dependence as demonstrated in TiO₂ nanosheets with {001} exposed facets [23]. Titanate 2D structures are another interesting class of materials applied in photo-triggered reactions. Rh doping in exfoliated protonated titanate nanosheets induced new mid-gap states and H₂ production under UV-light irradiation was controlled by the dopant content [24]. The activity of the layered titanate nanosheets is critically affected by the chemical exfoliation as well as by the co-catalyst and the nanosheets have been proven active even using non-precious CdS quantum dots as co-catalysts [25].

In addition to attempts to control the properties of single-phase 2D TiO₂ nanostructures, considerable attention has been paid to the construction of composite materials based on TiO₂ sheets. She et al. coupled TiO₂ nanosheets with 2D SnS₂ [26]. The 2D/2D SnS₂/TiO₂ heterojunction was applied in CO₂ reduction and exhibited a 10-times increased CH₄ production compared with bare TiO₂ nanosheets. The authors suggested that the observed significant enhancement of the activity originated from the reduced recombination

rates of the charges due to the increment in the contact between the two parts. The enhancement of the photocatalytic H_2 production from H_2O /methanol solution was attributed to the same reason in composites of TiO_2 with exposed $\{001\}$ facets coupled with layered MoS_2 [27]. Most importantly, the 2D/2D TiO_2 /MoS₂ junction was more active than the TiO_2 nanosheets when Pt was used as a co-catalyst. We obtained similar results in a 2D/2D heterojunction composed of TiO_2 and carbon nitride (CN) nanosheets [14]. By applying a facile one-pot synthesis strategy, TiO_2 nanocrystals with a specific morphology were deposited on ultrathin CN nanosheets (Figure 4). Composites of CN with TiO_2 nanocrystals with a bipyramidal or nanosheet morphology were developed in the presence or the absence of a capping agent. Bare TiO_2 nanosheets presented a significantly lower activity than the non-shaped TiO_2 in gas-phase CO_2 reduction. When both TiO_2 structures were coupled with 2D CN nanosheets, they exhibited improvement in photoactivity compared with their individual counterparts. Surprisingly, the 2D/2D CN/ TiO_2 junction was more active than the corresponding composite bearing unshaped TiO_2 (i.e., 2D/3D junction). Charge dynamic analysis using transient absorption spectroscopy revealed that interfacial charge transfer was favored in the 2D/2D structure, reducing charge recombination and increasing the availability of photo-induced electrons. This is attributed to the increased contact between the two-dimensional phases of the composite. This is a clear example of the benefits in charge separation efficiency in heterojunctions developed through the coupling of 2D structures.

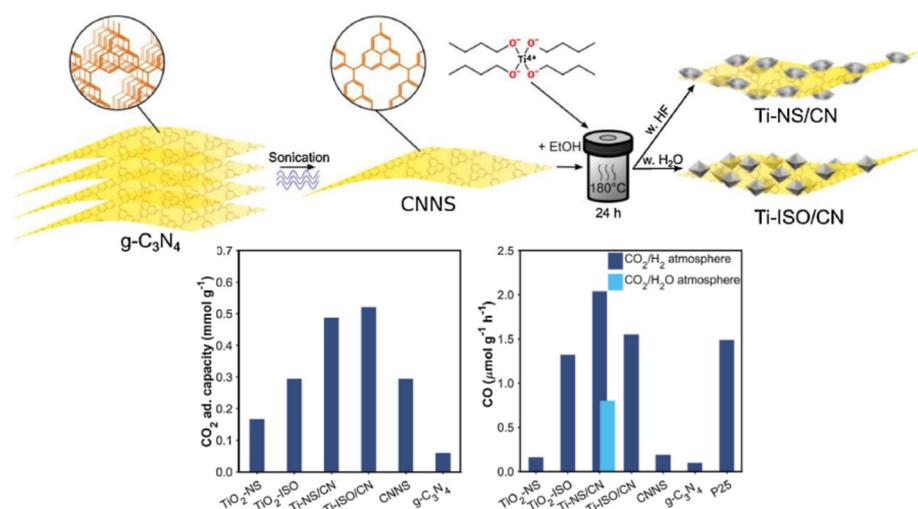


Figure 4. Schematic representation of the synthesis protocol for the coupling of ultrathin CN structures (CNNS) with TiO_2 nanosheets (Ti-NS) or unshaped TiO_2 nanoparticles (Ti-ISO) (top). CO_2 adsorption ($25^\circ C$ and 1 bar) and photocatalytic CO production under the UV-Vis irradiation of pure TiO_2 and the corresponding composites with CNNS (bottom). Reprinted with permission from Ref. [14]. Copyright 2019, Elsevier.

In addition to metal oxides, metal sulfides and phosphides have also been coupled with 2D CN structures [28,29]. CN decorated with SnS_2 particles presented an impressive $6305.18\ \mu mol\ h^{-1}\ g^{-1}$ without the use of expensive noble metals as co-catalysts under pure visible light irradiation [28]. Three-dimensional NiCoP coupled with two-dimensional CN nanosheets presented improved H_2 evolution rates compared with the corresponding CN photocatalyst bearing Pt as a co-catalyst. More importantly, the NiCoP/CN heterostructure presented a stable H_2 production rate for up to 60 h [29]. The strong interaction between the two phases (CN and NiCoP) was ascribed to the formation of Co–N and Ni–N bonding states and was identified as the key parameter for the improved stability and activity. Two-dimensional heterojunctions composed of CN and BiOCl provided structural defects at the interface enhancing CO_2 reduction [30]. Once again, efficient charge separation,

which increased the availability of the charges, was the main reason for the improved photocatalytic activity.

Perovskite-based materials are another interesting family of photoactive materials that can possess a 2D structure. Inorganic as well as hybrid organic/inorganic perovskites have been developed and applied in photocatalysis. $\text{HfCa}_2\text{Nb}_3\text{O}_{10}$ nanosheet structures obtained via chemical exfoliation presented an impressive 16-fold enhanced H_2 photocatalytic production compared to the bulk structure [31]. The enhancement was even greater in Rh-doped $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets compared with the bulk layered oxide [32]. In these materials, the chemical composition controls the actual band structure, which may have a great effect in activity [33]. Shifting the CB to more positive levels results in reduced activity due to the less energetic CB e^- . Two-dimensional organic-inorganic hybrid perovskites were also proven to be active in H_2 [34]. Recently, phenylmethylammonium lead-iodide 2D perovskites achieved a record-high solar-to-chemical conversion efficiency (H_2 production) for hybrid perovskites [35]. The length of the perovskites' organic cation determined the photocatalytic activity. Two-dimensional perovskites with the shortest organic cation exhibited a faster charge separation and transportation, producing $333 \mu\text{mol h}^{-1}$ of H_2 using Pt as a co-catalyst in aqueous solutions under visible light irradiation.

Layered double hydroxides (LDHs) are another class of inorganic 2D materials that have been applied in CO_2 photocatalytic reduction and H_2 production. The composition of these layered materials is tunable, and they possess ion exchange abilities, a property that can be used to anchor chemical moieties and provide specific properties with applications in photocatalysis. Cu_2O particles formed in situ from Cu-Zn-Cr LDHs were proven to be more active than the pristine material in the CO_2 reduction to CO [36]. Cu_2O nanoparticles promoted charge separation and acted as active centers for CO_2 reduction. The suppression of the charge recombination rate was also suggested for the improved photoactivity in MTi-LDH (M: Ni, Zn, Mg) by anchoring TiO_6 octahedra units on the surface of the LDH structure, a process that also modified the band structure [37]. In such systems, the content of the immobilized heterostructure plays a crucial role in the activity as demonstrated in CdSe nanocrystals deposited on ZnCr-LDH forming a heterojunction (Figure 5) [38].

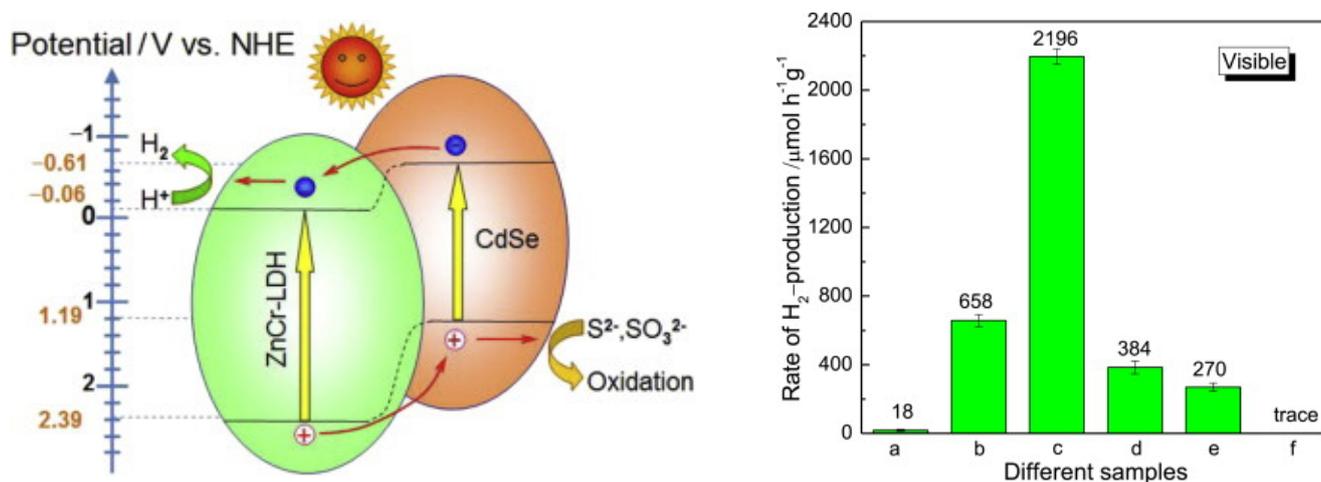


Figure 5. Charge separation in the CdSe/ZnCr-LDH heterojunction (left panel) and H_2 evolution (right panel) activity of the ZnCr-LDH having different CdSe contents under visible light ($\lambda > 420 \text{ nm}$). Reprinted with permission from Ref. [38]. Copyright 2015, Elsevier.

Metal chalcogenides have been widely applied as photocatalysts in many reactions, including solar fuels production. One of their main advantages is the short band gap energy that allows the utilization of the visible part of solar irradiation. Among the different materials in this family, CdS has been extensively studied since it is an exceptional photocatalyst. Nevertheless, stability issues due to photocorrosion and high toxicity are the top drawbacks that need to be addressed. Over the last decade, molybdenum dichalcogenide has also

been proven suitable for solar fuel production [39]. MoS₂ has been used as a co-catalyst in H₂ evolution by CdS [40]. A correlation between H₂ production and MoS₂ thickness was revealed. Photoactivity was improved via decreasing the MoS₂ thickness. Such studies are very important since expensive noble metals are usually used as co-catalysts in H₂ evolution reaction. The development of inexpensive co-catalysts, such as MoS₂ or SnS₂ [13], would be a significant step forward in the field. In a similar study, Yin et al. systematically studied the thickness and lateral size of MoS₂ as co-catalysts deposited on CdS in H₂ production [41]. The thickness was tuned using a facile exfoliation process followed by centrifugation. In addition to thickness, lateral size also affected activity. The decrease in lateral size increased H₂ evolution. Improvements in activity were attributed to the shorter distance from the basal plane to the active sites at the edges of the MoS₂ sheet. The MoS₂ edges are considered highly active for many critical reactions, including CO₂ reduction [42]. Hierarchical CdS-Au/MoS₂ core/shell nanostructures composed of CdS nanorods and MoS₂ nanosheets (Figure 6) presented excellent photocatalytic H₂ production [43]. Improvements in visible light absorption, charge separation through the formation of a heterojunction and the increased number of active sites at the edges of the MoS₂ structure due to the 2D morphology were responsible for the observed enhanced H₂ production. The coupling of MoS₂ with other nanosheets has also been performed. MoS₂ nanosheets were deposited on 2D Cu₂S (Figure 7) [44]. The morphology of both nanostructures played a crucial role in the activity, regulating the light trapping and scattering ability, charge separation and specific surface area. In this type of materials, exchange reactions may be applied to change the composition of the structure due to the presence of chalcogens and transition metals. However, such approaches are challenging. For example, CdIn₂S₄ nanosheets have been successfully supported on Co₃O₄, forming a p-n heterojunction [45]. The in situ synthesis process allowed the formation of a tight interface, improving stability and the selective reduction of CO₂ to CO (5300 μmol h⁻¹ g⁻¹) under visible light irradiation due to the efficient charge separation.

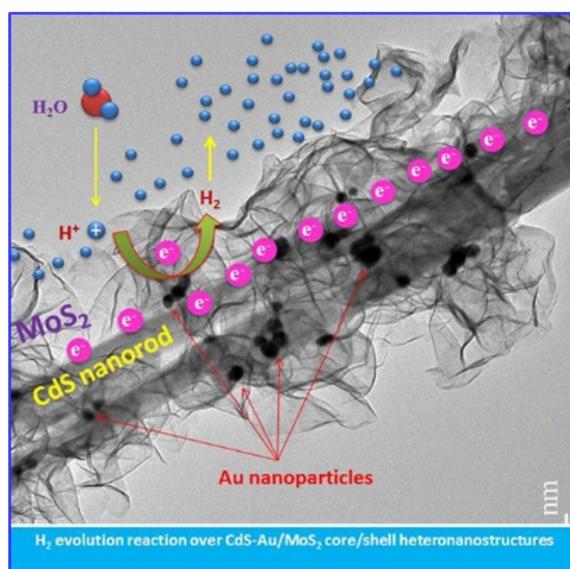


Figure 6. Hierarchical CdS-Au core/shell nanostructures and H₂ production on MoS₂. Reproduced with permission of Ref. [43]. Copyright 2018, American Chemical Society.

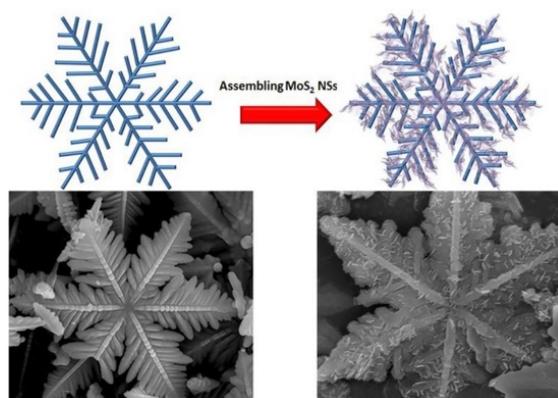


Figure 7. Formation of MoS₂ nanosheets/Cu₂S snowflake nanocomposite for efficient H₂ production. Reprinted with permission from Ref. [44]. Copyright 2018, Elsevier.

In addition to the nature of the coupled materials and the composition of the final heterojunctions, precise materials engineering may control the actual coupling of two SC and provide advanced systems. This is highlighted in the work of Hu et al., in which the effect of the selective deposition of 2D MoS₂ on specific facets of TiO₂ nanosheets was reported [46]. Photocatalytic H₂ production was drastically improved when MoS₂ were deposited on the {101} facets of TiO₂. Through this approach, the {001} facets were exposed, while charge separation occurred due to the formation of a surface junction on TiO₂ and the formation of a heterojunction between MoS₂ and TiO₂ (Figure 8). The coupling of MoS₂ nanosheets with anatase/rutile mixed phase TiO₂ nanofibers has also been prepared and tested in CO₂ reduction (Figure 9) [47]. Two types of junctions were suggested by the authors: the formation of a heterojunction between TiO₂ and MoS₂ and a homojunction between the two phases of TiO₂ (anatase and rutile). A 2D/2D heterojunction was also formed by growing MoS₂ on TiO₂ nanosheets [48]. The presence of MoS₂ nanosheets as a co-catalyst presented a higher activity, but, most importantly, a higher selectivity for CO₂ conversion to CH₃OH than Pt, Au and Ag. The improved charge separation and the presence of highly active sites at the edges of MoS₂ were responsible for the enhanced activity. MoS₂ has also been effectively coupled with other SCs [49,50], while other 2D chalcogenides, such as Cu₂S and ZnS [51–53], have also been proven suitable for solar fuel production.

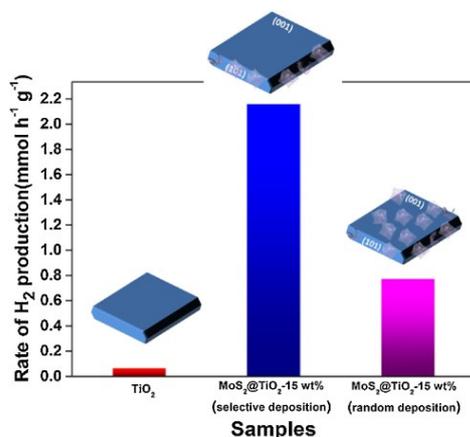


Figure 8. Rate of photocatalytic H₂ production by a TiO₂ NSs and MoS₂@TiO₂ composite (selective and random deposition). Reprinted with permission from Ref. [46]. Copyright 2019, Elsevier.

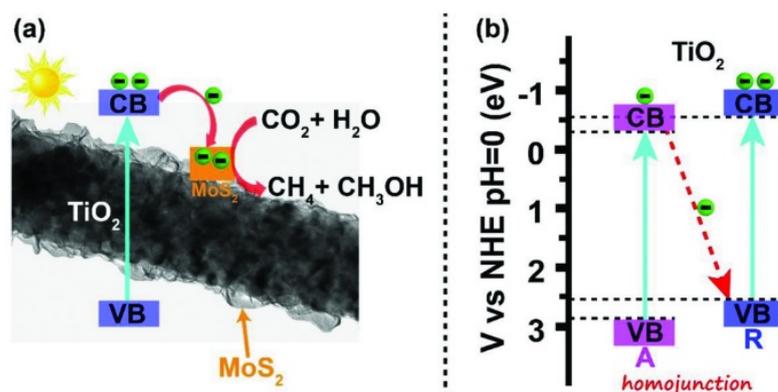


Figure 9. (a) Schematic representation of the $\text{TiO}_2/\text{MoS}_2$ heterojunction, charge separation under UV-Vis light irradiation and CO_2 reduction into CH_4 and CH_3OH . (b) The charge transfer mechanism in the homojunction formed between anatase and rutile. Reprinted with permission from Ref. [47]. Copyright 2018, John Wiley and Sons.

Carbon nitride (CN) is another interesting material that can possess a 2D structure under certain circumstances [54]. It is a promising SC, suitable for both photocatalytic H_2 production and CO_2 reduction due to its highly negative CB level. The low-cost, facile preparation protocols, visible light response and the organic character that allows easy modification sparked intensive research in the development of novel CN structures since as-synthesized CN usually possesses a bulk structure, but 2D morphology can be obtained using post-synthetic methodologies, such as sonication [14], thermal oxidation etching [55] and the intercalation of salts [56]. Thermal conditions, including the atmosphere of the thermal treatment, may regulate the properties providing defects and shape control [57,58]. Ou et al. reported an interesting study, in which a 2D/2D CN/ MoS_2 layered nanojunction was more active in H_2 production than using Pt as a co-catalyst [59]. Depending on the catalytic application, CN may be optimized towards enhancing activity. We have recently shown that, while H_2 evolution is controlled by the available CB e^- linked with light absorption and charge separation, CO_2 reduction is mostly regulated by CO_2 adsorption on the surface of CN [57]. Charge dynamics analysis using transient absorption spectroscopy (TAS) under real catalytic conditions revealed that the temperature of the thermal treatment has a crucial effect on the reactivity with a sacrificial agent that enables higher H_2 evolution rates. In addition, the thermal post-treatment of the preformed CN may result in the formation of intermediate mid-gap states, improving charge formation (Figure 10). Monometallic as well as bimetallic alloy nanoparticles (NPs) have also been efficiently coupled with 2D CN. In such heterostructures, of particular importance is the utilization of low-cost Cu NPs. AuCu alloy NPs on ultrathin porous CN nanosheets have proven particularly efficient in the photothermal CO_2 reduction to ethanol [58]. The strong coupling of the two phases is a prerequisite to allow the migration of photogenerated charges.

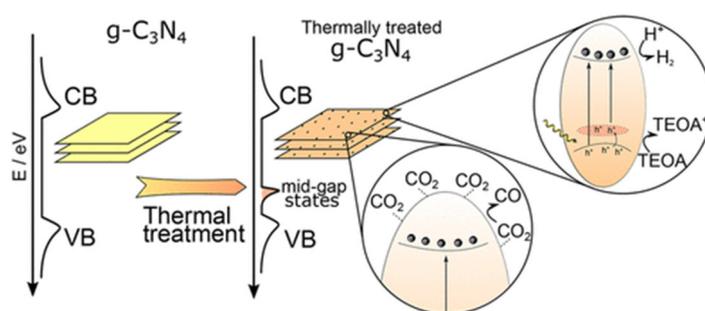


Figure 10. Photocatalytic H_2 production under UV-Vis and visible light irradiation (top) and mid-gap state formation (bottom) in the thermally treated CN. Reprinted with permission from Ref. [57]. Copyright 2018, American Chemical Society.

In addition to the formation of junctions via the coupling of CN with other nanomaterials, CN-based homojunctions may also be formed. This originates from the organic character of the material that allows easy modification [60]. p–n homojunctions may be formed through the introduction of electron-acceptor groups into the CN structure [61]. This allows efficient charge separation, improving solar energy conversion.

Metal–organic frameworks (MOFs), a relatively new class of well crystalline and porous materials, are formed through the link between metal clusters and organic molecules. Structures containing MOFs have been applied for solar fuel production [14,18]. Their application in CO₂ photocatalytic reduction reactions offers the advantage of increasing the CO₂ concentration close to the active catalytic sites [18], eliminating one of the main rate-limiting steps of the process. Two-dimensional MOF structures have been also developed and applied in solar fuel production [62], despite such structures being difficult to obtain due to stability issues. A 2D/2D MOF/CN composite was developed by Liang et al. [63], improving H₂ production. In this study, the MOF structure was involved in the electron transfer from the catalyst to the Pt co-catalyst. A 2D Ni-based MOF structure was coupled with reduced graphene oxide (rGO) through via Coulomb interaction forming a 2D/2D heterojunction [64]. A ruthenium complex (Ru(bpy)₃) was used as light sensitizer and an electrostatic charge transfer from rGO to the MOF structure was suggested, promoting CO₂ adsorption. Another interesting approach of MOFs in the field is their use as precursors for the development of novel photocatalysts. Co₃O₄ 2D nanoparticles were developed using a modified version of ZIF-67 as a precursor (Figure 11) [65]. The obtained Co₃O₄ nanosheets were proven to be more active than the bulk Co₃O₄ in CO₂ photocatalytic reduction under visible light. However, a light sensitizer was used in these tests. Improvements in activity were attributed to the presence of defective oxygen in the structure, increasing the ability to capture CO₂.

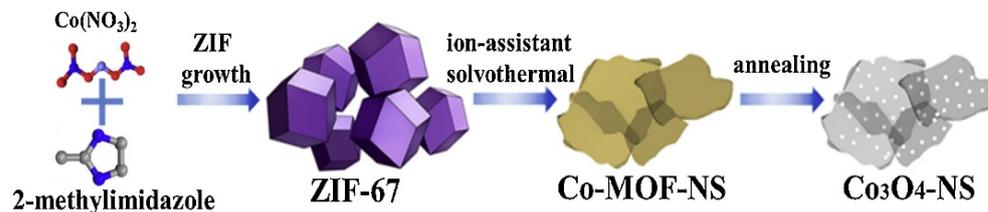


Figure 11. Schematic illustration for the development of ultrathin Co₃O₄ nanosheets using ZIF-67 as a precursor. Reprinted with permission from Ref. [65]. Copyright 2019, Elsevier.

4. Concluding Remarks and Directions

Both H₂O and CO₂ could be used as cheap and largely available feedstocks for chemical energy storage. The use of solar energy for fuel production through artificial photosynthesis is a simple process to obtain energy rich chemicals. The cheap photocatalytic conversion of CO₂ could be also coupled with the Carbon Capture Utilization and Storage technology (CCUS), a process that must be included in any future carbon management approach. However, many improvements are required in order to meet industrial needs for large-scale applications. In such systems, efficiency is defined by activity, stability and reproducibility as well as selectivity. All these critical parameters are not related to the fundamentals of the process itself, but rather with the properties of the material. Two-dimensional materials have proven to be more efficient than their bulk counterparts, and a variety of materials and protocols have been developed. Precise engineering allowed the perfect control of the composition, size and morphology that regulate their electronic and textural properties.

For any photocatalytic application, research must focus on the development of solar-light-activated catalysts. In the specific case of H₂ evolution reaction, future work should focus on improving light absorption properties and increase the availability of photo-generated e⁻. These could be achieved by optimizing single-phase materials or by the development of multi-component systems through the synthesis of heterojunctions and

heterostructures. In the specific case of composites, special attention must be paid to the development of the interface between the different parts, allowing their intimate coupling and interaction. On the other hand, CO₂ photocatalytic reduction is a more challenging. In addition to improvements in light absorption and charge availability, issues related to mass transfer as well as selectivity towards the production of a specific product must be solved. Therefore, materials with a high selectivity and ability to absorb higher amounts of CO₂ must be developed. In addition, the developed catalyst must be always fully characterized, including structural, morphological, compositional and electronic characterization as well as the utilization of techniques able to discriminate differences at the sub-nanometer scale at the bulk, but, most importantly, on the surface of the catalyst. Time-resolved in situ methodologies [13] and advanced operando [66] characterization techniques, both under real catalytic or synthesis conditions, could also significantly help in the identification of the reaction mechanism or understanding the development of the catalyst. This will give the opportunity to identify key material parameters and link them with catalytic activity. Based on the published contributions in the field of solar fuels in recent years, it seems that there is room for improvement in terms of efficiency and selectivity. Two-dimensional materials are expected to contribute in this direction given the documented advantages from recent years.

Author Contributions: Conceptualization, K.C.C.; methodology, T.I. and K.C.C.; formal analysis, T.I., M.A. and K.C.C.; investigation, T.I. and M.A.; resources, K.C.C.; writing—original draft preparation, T.I., M.A. and K.C.C.; writing—review and editing, T.I., M.A. and K.C.C.; visualization, T.I., M.A. and K.C.C.; supervision, K.C.C.; project administration, K.C.C.; funding acquisition, K.C.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work benefited from state aid managed by the French National Research Agency (ANR) under the Investments for the Future (program “Make Our Planet Great Again”) with reference ANR-18-MOPGA-0014. The research was partially funded by Democritus University of Thrace (project 82268).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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