



Morphology-Governed Performance of Multi-Dimensional Photocatalysts for Hydrogen Generation

Zhishun Wei^{1,*}, Tharishinny Raja Mogan², Kunlei Wang^{2,3}, Marcin Janczarek⁴ and Ewa Kowalska^{2,*}

- ¹ Hubei Provincial Key Laboratory of Green Materials for Light Industry, Hubei University of Technology, Wuhan 430068, China
- ² Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan; rajamogan.t@cat.hokudai.ac.jp (T.R.M.); kunlei@cat.hokudai.ac.jp (K.W.)
- ³ Northwest Research Institute, Co., Ltd. of C.R.E.C., Lanzhou 730000, China
- ⁴ Faculty of Chemical Technology, Institute of Chemical Technology and Engineering, Poznan University of Technology, 60-965 Poznan, Poland; marcin.janczarek@put.poznan.pl
- * Correspondence: wei.zhishun@hbut.edu.cn (Z.W.); kowalska@cat.hokudai.ac.jp (E.K.)

Abstract: In the past few decades, extensive studies have been performed to utilize the solar energy for photocatalytic water splitting; however, up to the present, the overall efficiencies reported in the literature are still unsatisfactory for commercialization. The crucial element of this challenging concept is the proper selection and design of photocatalytic material to enable significant extension of practical application perspectives. One of the important features in describing photocatalysts, although underestimated, is particle morphology. Accordingly, this review presents the advances achieved in the design of photocatalysts that are dedicated to hydrogen generation, with an emphasis on the particle morphology and its potential correlation with the overall reaction performance. The novel concept of this work-with the content presented in a clear and logical way-is based on the division into five parts according to dimensional arrangement groups of 0D, 1D, 2D, 3D, and combined systems. In this regard, it has been shown that the consideration of the discussed aspects, focusing on different types of particle morphology and their correlation with the system's efficiency, could be a promising route for accelerating the development of photocatalytic materials oriented for solar-driven hydrogen generation. Finally, concluding remarks (additionally including the problems connected with experiments) and potential future directions of particle morphology-based design of photocatalysts for hydrogen production systems have been presented.

Keywords: water splitting; hydrogen generation; heterogeneous photocatalysis; vis response; nanoparticles; nanotubes; nanosheets; quantum dots

1. Introduction

Green and sustainable materials have attracted a lot of interest in the use of renewable energy sources instead of environmentally harmful and nonrenewable fossil fuels [1–3]. The renewable sources (e.g., water, tide, wind, and solar energy) are attractive options in comparison to conventional fuels [4–6]. Hydrogen molecules could be used as a clean and efficient carrier of energy, since they produce only water during combustion [7,8]. The other way around—water splitting into hydrogen and oxygen—could be realized by either solar or electrical power [9,10]. Commonly, solar-driven water splitting is considered to be a better choice than electrically powered systems, since it is eco-friendly.

Utilization of solar energy to generate hydrogen through water splitting is an ultimate strategy for solving the energy and environmental challenges caused by exhausting fossil fuels; additionally, it is a solution to the emission of greenhouse gases that originate from the combustion of fuels. Accordingly, photocatalysis is a potential method for the efficient use of solar energy, directly through hydrogen production from water. Many photocatalysts,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). such as various oxides [11], nitrides [12], and sulfides [13], have been fabricated and tested for hydrogen generation after the pioneering work of Fujishima and Honda in 1972 [14].

While the term "photocatalysis" might suggest that it is a simple combination of irradiation ("photo") and catalysis (i.e., the acceleration of the reaction rate in the presence of a photocatalyst), it should be pointed out that, usually, the photocatalytic reactions do not proceed in the absence of a photocatalyst nor in the dark. Therefore, the photocatalyst does not only accelerate the reaction rate, but it is necessary for the reaction to happen, as clearly discussed in the review papers by Ohtani [15,16]. In the case of heterogeneous photocatalysis, wide bandgap semiconductors are usually used as photocatalytic materials, since they have good redox properties. In brief, under irradiation, the photocatalyst is excited if the energy of photons is equal to or larger than its bandgap, causing electrons to be excited to the conduction band (CB), leaving the holes in the valence band (VB). Accordingly, the photogenerated charge carriers might either migrate to the surface of the photocatalysts, where they initiate the redox reactions, or recombine with each other, which causes activity loss. Obviously, much effort has been taken for the inhibition of charge carriers' recombination to get high quantum yields of photocatalytic reactions. Moreover, the difference between the photocatalytic and photosynthetic processes has also been pointed out by the authors of Refs. [17,18], where the former and the latter deal with thermodynamically downhill ($\Delta G < 0$) and thermodynamically unfavorable ($\Delta G > 0$) processes (e.g., oxidative degradation of organic compounds and water splitting), respectively. Accordingly, water splitting is commonly classified as "artificial photosynthesis" that mimics natural photosynthesis in green plants. However, it must be realized that in the case of natural photosynthesis, there are two main reagents (i.e., water and carbon dioxide); thus, simple water splitting does not solve the problem of CO₂ excess in the atmosphere (i.e., its capture and conversion). Accordingly, more advanced systems with simultaneous CO₂ reduction (into useful fuels) and H₂O oxidation have also been proposed that could be named as "artificial photosynthesis", without any doubt [19–23].

Titania (TiO₂—titanium dioxide) is probably the most broadly investigated semiconductor (SC) photocatalyst because of its low cost, nontoxicity, and abundance. Moreover, many other novel photocatalysts have also been designed and developed with different dimensions and morphologies for high activity in hydrogen production from water splitting. There are huge numbers of research papers on photocatalytic hydrogen evolution and even overall water splitting [24–29], accompanied by comprehensive reviews [30–32]. Many of these papers deal with the challenge how to synthesize novel chemical compounds with new intrinsic properties (i.e., bandgap energy and levels of conduction band (CB) and valence band (VB)) for both water reduction and water oxidation, preferably without the addition of any sacrificial reagent. Although these studies are considered as the most important for future development of solar energy technologies (i.e., vis-responsive materials), the morphology of photocatalytic materials are also very important for possible commercialization. It has been well presented by Liu et al. that photocatalysts' morphology might be a decisive factor for increasing the reaction selectivity and efficiency; additionally, the morphologically oriented studies enable the complex design of photocatalysts dedicated for a specified application, which might increase the chances of their successful commercialization [33]. However, there are only several review papers that deal with morphology, mainly focusing on 1D [34] and 2D materials [35–37], for hydrogen generation. Therefore, in this paper, we would like to present the recent trends in the development of novel photocatalysts with different morphologies, compositions, and performances. In order to make the content clear and logical, the present manuscript has been divided into five parts according to the dimensions of the photocatalysts; i.e., (i) zero-dimension (0D), (ii) one-dimension (1D), (iii) two-dimension (2D), (iv) three-dimension (3D), and also (iv) the composite photocatalysts constructed from two or even more dimensional structures (e.g., 0D/1D, 0D/2D, 1D/2D and so on). Of course, in some cases, the classification is not so obvious, but we have tried to organize this review in a reader-friendly matter.

In general, 0D nanomaterials include nanoclusters, quantum dots (QDs), and nanoparticles (NPs). Nanotubes, nanorods, nanowires, nanorings, nanobelts, and nanofibers belong to 1D nanomaterials. The 2D nanostructures might be recognized as nanofilms, nanoplates, nanosheets, and nanoflakes, etc.; whereas, 3D nanomaterials usually include meso/macroporous structures, flower-like materials, and honeycomb hierarchical (photonic crystals) composites that are constructed/accumulated by one or more types of 0D, 1D, and 2D nanostructures.

2. Zero-Dimension (0D) Photocatalysts

The first group of photocatalytic nanomaterials with the simplest structure is characterized by 0D morphology (i.e., nanoclusters, QDs, and NPs), as summarized in Table 1. Of course, NPs are the most broadly used and investigated for photocatalysis and other applications due to the easiest and fastest preparation methods. Usually, commercial photocatalysts (e.g., famous P25) belong to this group. Although, Fujishima and Honda showed water splitting on irradiated titania [14], the photocatalytic activity was low; thus, various studies have been performed on activity enhancement. One of the first approaches dealt with platinized photocatalysts, as it has been shown that photogenerated electrons in irradiated titania are quickly scavenged by platinum deposits, hindering charge carriers' recombination and working as co-catalysts for hydrogen evolution [38-43]. An interesting study has been performed by Wang et al., who showed that, in the case of commercial photocatalyst P25, platinum is preferably deposited on rutile first, and then on anatase [44]. Moreover, it has been concluded that one platinum deposit on the surface of large aggregates of titania (aggregation caused by thermal treatment) is enough to cause efficient hydrogen evolution under UV irradiation (CH₃OH as a hole scavenger), thanks to interparticle electron transfer (IPCT) between even the same kinds of titania NPs (anatase-anatase or rutile–rutile) in one aggregate, as shown in Figure 1.



Figure 1. Hydrogen evolution on titania modified with platinum: (a) Dependence of photocatalytic activity on the amount of Pt loading on homogenized P25 (HomoP25), HomoP25 annealed at 200 °C (HomoP25-200), and isolated phases from HomoP25 by the chemical dissolution method, followed by purification by thermal treatment: isolated anatase (ANA) and isolated rutile (RUT); (b) Schematic drawing showing IPCT on aggregated single-phase titania particles, e.g., Pt@ANA and Pt@RUT. Copyright 2018 Elsevier.

The importance of platinum localization on different parts of a two semiconductor photocatalyst has also been investigated for polypyrrole (PPy)–titania nanocomposites [45]. It has been found that platinum should be deposited on both semiconductors simultaneously, resulting in high hydrogen evolution rate (CH₃OH as a hole scavenger) (i.e., 125.1 and 3.2 mmol g⁻¹ h⁻¹ under UV and vis (>420 nm) irradiation, respectively), which is

much higher than that when platinum is only deposited on one component (ca. five or ca. seven times lower UV activity for Pt deposited only on titania or only on PPY, respectively), probably due to efficient multiple electron transfer pathways. Similarly, Abe et al. have pointed out that the localization of platinum is also very important for the suppression of a backward reaction for water splitting under vis irradiation (410 nm > λ > 800 nm; Pt as a co-catalyst), according to two-step photoexcitation: dye-sensitized layered niobate and tungsten oxide photocatalysts in the presence of shuttle redox mediator (triiodide/iodide) [46]. It has been shown that a Pt co-catalyst loaded inside the interlayer of H₄Nb₆O₁₇ allows the reduction of water in the presence of I₃⁻, because of the inhibited access of I₃⁻ to the reduction site (co-catalyst localized inside the structure) by the electrostatic repulsion between the negatively charged (Nb₆O₁₇)⁴⁻ layers and triiodide anions.

Interesting studies have been performed for faceted anatase particles modified with different noble metals (i.e., Pt, Au, Cu, and Ag) by the photodeposition method in the presence of methanol as a hole scavenger [43]. It has been found that the photodeposition of gold and platinum is very fast (>5 min is sufficient for the complete deposition of 2 wt%), as shown in Figure 2a. In contrast, the photodeposition of copper and silver needs a much longer irradiation time (8 and 45 min, respectively). The hydrogen evolution rate correlates well with the reduction ability of cations (induction period), i.e., an increase in the induction period correlates with a slower rate of H₂ generation. It has been proposed that rates of formation of deposits of noble metals and hydrogen evolution correspond to electron affinity of semiconductors and the work function of metal, i.e., the formed Schottky barrier. Interestingly, slightly different activities have been achieved for metal pre-modified titania samples, i.e., photocatalytic activities measured, not during, but after metal deposition samples were first prepared with in situ hydrogen evolution (as illustrated in Figure 2a), then dried and used as photocatalysts (activities shown in Figure 2b). This difference could be explained by a higher content of oxidized forms of metals (especially lesser noble metals, i.e., silver and copper). For example, the co-catalytic function of CuO (similar electron scavenging ability to zero-valent copper) has been found for CuO/WO₃, with a multiple-electron reaction on the surface of cupric oxide [47]. Moreover, the participation of mixed oxides, such as cuprous and cupric oxides, in hydrogen evolution must also be considered, since such activity has been confirmed [48].



Figure 2. Hydrogen evolution on octahedral anatase particles (OAP): (**a**) during metal deposition; (**b**) after metal deposition. Copyright 2017, Creative Commons Attribution License.

Zero-valent copper has been proposed as a promising co-catalytic material for photocatalysis, since copper has similar electronic properties to silver and gold, and is much cheaper. However, copper is easily oxidized when kept under ambient conditions (as discussed above) [42,43,49,50]. Therefore, formed, less active copper species (though probably re-reduced under reductive conditions during hydrogen generation [43]) could seriously limit the practical application of copper-based photocatalysts [51]. In order to solve this problem, two approaches have been proposed. First, the stabilization of Cu NPs by titania when copper is built in titania aerogel structure [52]. Second, in situ encapsulation of copper NPs with N-graphitic carbon layers (N/C-coated Cu) [51]. The N/C-coated Cu–TiO₂ composite possesses better photocatalytic properties than the uncoated Cu NPs, and 27 times higher activity for hydrogen generation than pristine titania. It has been proposed that the coating of Cu with N/C both improves the stability and accelerates the interfacial charge migration. The encapsulation of copper can be easily obtained by using polyethylenimine as a surfactant, where the use of a surfactant with large carbon and nitrogen density favors the formation of N-graphitic carbon coatings. This synthesis approach allows to prepare a cheap, stable, and efficient zero-valent Cu, and it has been proposed that other non-noble metal catalysts could also be fabricated by this method [51].

It should be mentioned, that H₂ evolution (or even overall water splitting) was firstly, carried out only under UV irradiation, as pristine titania is inactive under vis irradiation. Then, modified titania (via doping or surface modifications), e.g., with nonmetals [53,54], metals [55,56], and by coupling with other materials [57], has been applied. Interestingly, it has also been found that noble metals could be used for titania activation towards vis response because of plasmonic properties ("plasmonic photocatalysts") [58–61]. However, it should be stressed that, considering the mechanism via charge transfer, the direction of electron transfer is opposite during plasmonic photocatalysis than that during hydrogen evolution, i.e., from noble metal to titania. Therefore, though plasmonic photocatalysts are active under vis irradiation for various reactions, usually there is no (or very low, as compared with that under UV light) activity for hydrogen generation under sole vis irradiation [62–65]. Accordingly, either two kinds of metals (first for plasmonic excitation and second for hydrogen evolution) or more advanced structures (for example, the "advanced superstructure system", i.e., the composite of titania meso-crystals with deposits of noble metals [66,67] (discussed in Section 6)), have been proposed.

For example, Yu et al. have obtained efficient hydrogen evolution on TiO₂-based nanoheterostructures modified with Pt and Ag [68]. The development of metal-semiconductormetal nano-heterostructures for improving photocatalytic activity has been proposed, considering that they are not only the more efficient in harvesting light, but also in the spatial separation of charge carriers, which are important factors for high activity. The semiconductor NPs have been combined with two metals, and the disordered layers have been formed on the titania surface (self-doped (or hydrogenated) titania) to enhance the light harvesting efficiency [69]. Therefore, the n-n⁺ junction is obtained at the interface between stoichiometric (n-TiO₂) and disordered (n⁺-TiO₂) titania. Additionally, the Schottky diode and Ohmic contact (on n-TiO₂ and n⁺-TiO₂, respectively) result in multi-junctions ("multiple continuous built-in electric fields"), and thus, significantly improve carriers' separation. The multi-junctions' heterostructure (Pt–TiO₂–H–Ag; Figure 3) shows highly enhanced photocatalytic activity. The photocatalytic activity for H₂ evolution on Pt–TiO₂–H–Ag under solar illumination is 8.3, 9.3, and 1.5 times higher than that on platinized samples P25 (Pt–P25), TiO₂ (Pt–TiO₂), and hydrogenated TiO₂ (Pt–TiO₂–H), respectively. Additionally, the photocatalytic performance under vis irradiation has been improved for Pt–TiO₂–H–Ag in comparison to platinum-modified samples, reaching 2382.7 μ mol h⁻¹ g⁻¹, i.e., being about 15.1, 17.2, and 1.4 times higher than that on Pt-P25, Pt-TiO₂, and Pt-TiO₂-H, respectively. Furthermore, the photocatalyst shows good stability (five re-cycles), suggesting that simultaneous extension of photoabsorption and improvement of the spatial separation of charge carriers could be used also for other wide bandgap metal-oxide semiconductor photocatalysts [68].



Figure 3. Scheme with photographs for the fabrication of Pt–TiO₂–H–Ag nano heterostructure. Copyrights 2020 Elsevier [68].

It should also be mentioned that other metals have been used for titania modification towards hydrogen evolution. For instance, Luna et al. have modified titania NPs with two types of metals, i.e., noble and non-noble (Pd and Ni [70], and Au and Ni [56]). In both cases, the synergistic effect has been observed between both metals (Ni existing in both zero-valent and oxidized forms), and based on the investigation on the light absorption, the charge-carrier dynamics (time-resolved microwave conductivity; TRMC) and the photocatalytic performance (action spectra), it has been concluded that the main role of metal NPs is to act as catalytic sites for the recombination of atomic hydrogen. Unfortunately, hydrogen has been mainly generated at the UV range of solar spectrum, and only slight vis response has been noticed ($\lambda < 420$ nm).

Huang et al. have synthesized titania co-modified with two non-noble metals (Sn and Ni) by surface organometallic chemistry [71]. The photocatalytic activities of the prepared photocatalysts have been evaluated by photocatalytic H₂ evolution in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA). The synergistic effect between the atomically separated centers of Ni and Sn has been noticed for solar-to-hydrogen conversion, and about one order improvement of hydrogen generation has been achieved for optimal photocatalysts (Sn_{1.12}/Ni_{0.98}/TiO₂), in comparison with a pristine titania sample under solar light illumination. It has been proposed that the synergistic effect relates to the heteroatomic clusters with the cyclic structure of eight members, i.e., [-O-Ti-O-Sn-O-Ni-O-Ti-I] (Figure 4). Accordingly, efficient separation of charges and excitons are caused by an electron delocalization loop generated in Ni–O–Ti molecular linkages (Figure 5).



Figure 4. The schematic mechanism for the proposed formation of titania modified with Sn/Ni. Copyrights 2015 ACS. [71].



Figure 5. The scheme of the ring mechanism for electron delocalization. Copyrights 2015 ACS [71].

It should be pointed out that the experiments under solar (simulated or natural) radiation are very important for possible applications, but they do not lead to fruitful conclusions on the mechanism for titania-based photocatalysts, since titania is also excited due to the presence of UV light in the solar spectrum.

As already mentioned, faceted nanocrystals might be a promising base for efficient hydrogen generation. Both octahedral anatase particles with only [101] facets [72,73] and decahedral anatase particles with eight {101} and two {001} facets [74,75] (i.e., OAPs and DAPs, respectively) show very high activity for hydrogen generation under UV irradiation, when modified with NPs of noble metals. In contrast, though noble metal-modified faceted samples are also active under vis irradiation, due to plasmonic photocatalysis for oxidative decomposition of organic compounds [42,43,50,76,77], the negligible activity for hydrogen evolution has only been observed (electron-deficient metal after "hot" electron transfer from noble metals). However, faceted titania nanocrystals modified with nanoclusters of indium oxide (In₂O₃) have shown to be good candidates for hydrogen generation in the absence of a noble metal co-catalyst under solar irradiation [78]. Development of a new type of nanoheterostructure, consisting of fine nanoclusters of In₂O₃ (i.e., alike to fine species "doped" on the surface of TiO_2 nanocrystals with {101} and {001} exposed facets), developed through a facile hydrothermal method, has resulted in remarkable hydrogen production under visible light (LED source) and solar simulated light (AM 1.5G). It has been proposed that photogenerated electrons migrate from the CB of indium oxide to the CB of titania, what is responsible for the observed vis response. Additionally, it has been found that In₂O₃-modified titania single crystals with two kinds of facets ({101} and {001}) exhibit higher (1.3×) H₂ generation under vis irradiation than nanocrystals with only one type of facets ({101}). It has been proposed that high photocatalytic activity is caused by

the synergism between indium oxide and titania, the enhanced absorption of visible light, a unique morphology and high crystallinity [78].

Core-shell NPs are also considered as another 0D morphology with interesting properties due to the formation of a functional system from the integration of individual components, improving chemical and physical properties, such as dispersibility, functionality, and stability, that might not be obtained for sole components [79,80]. The core-shell titania-structured materials are considered as highly wanted, not only due to enhanced stability and activity, but also because of improved recycling ability when a magnetic component is used in the composite [81,82]. Indeed, Bielan et al. have found that the modification of magnetic core-shell particles (Fe₃O₄@SiO₂/TiO₂) with NPs of platinum and/or copper has resulted in a high enhancement of hydrogen evolution (methanol as a hole scavenger) even by two orders of magnitude under UV/vis irradiation [83]. Unfortunately, similar to other plasmonic photocatalysts, though vis activity has been observed for oxidative decomposition of phenol, negligible evolution of hydrogen has been noticed under vis irradiation. An interesting approach has been designed by Wang et al. for coreshell $Cu_xO@TiO_2$ formation by microemulsion method [57]. It is well known that coupled oxides, such as titania and copper/silver oxides-despite their enhanced activity under UV irradiation due to the inhibition of charge recombination (either via heterojunction type II or Z-scheme mechanism [84])—are often not stable under irradiation in contrast to titania, as these oxides with a narrower bandgap suffer from photocorrosion [85–87]. However, obtained core-shell Cu_xO@TiO₂ photocatalysts have exhibited high photocatalytic activity under long (6 h) and repeated (3 cycles) UV irradiation [57]. Additionally, based on XPS analysis showing the reduction of copper species, it has been concluded that enhanced activity is caused by Z-scheme mechanisms both for hydrogen generation (methanol as a hole scavenger) and oxidative degradation of acetic acid. Unfortunately, core-shell structures with vis-responsive material as a core usually means vis inactivity, due to the lack of electron donor inside the core-shell structure. In contrast, Zubair et al. have shown enhanced activity of core-shell TiO2@CdS photocatalysts, fabricated by a hydrothermal process (two steps) [88]. However, activity has been measured under simulated solar radiation, and thus it is difficult to estimate the reason for this enhancement (UV or vis range). Authors have optimized the shell thickness of titania by adjusting the amount of TiO_2 precursor, and the optimized TiO_2 @CdS sample exhibits much higher photocatalytic activity for hydrogen generation than pristine TiO₂ and CdS samples.

The QDs-semiconductor composites have been intensively investigated because of the specific optical, electronic, and structural properties that result from the quantum confinement effect and large surface-to-volume ratios. There are various types of QDs with unique physicochemical properties. Recently, carbon QDs (CQDs) have been proposed for the modification of semiconductors [89], since they are non-expensive, non-toxic, and soluble in water. For hydrogen generation under vis irradiation (LED of 420 nm), Dong et al. have prepared an efficient and stable ternary photocatalyst—Ni₄P₂-CQDs@CdS, produced by chemical precipitation and photoreaction process [90]. Photocatalytic hydrogen generation (145 μ mol g⁻¹ h⁻¹) from pure water without any sacrificial reagents has been achieved by employing CdS, CQDs, and Ni_4P_2 as a light harvester, an electron acceptor (and a donor), and a catalyst, respectively. The experimental results demonstrate the electrons transfer from CdS via CQDs to Ni₄P₂ (catalyst), upon which, accumulated electrons facilitate hydrogen generation. An interesting study on overall water splitting has been performed with plasmonic excitation of CuNi bimetal NPs modified with CQDs [91]. Here, under plasmonic excitation, "hot" electrons were transferred to CQDs, working as a co-catalyst for hydrogen evolution, as shown in Figure 6.



Figure 6. A scheme showing the mechanism of water splitting on CuNi/CQDs photocatalyst. Copyrights 2019 Elsevier [91].

Additionally, more advanced carbon structures (i.e., graphene QDs (GQDs)), have also been used because of the large content of active sites, high photostability, low toxicity, high biocompatibility, and chemical inertness [92,93]. It is known that graphene could enhance the photocatalytic activity of semiconductors, hindering charge carriers' recombination, and also working as a co-catalyst for hydrogen evolution [94]. Indeed, GQDs have successfully been applied for solar water splitting [91,95,96]. For example, ternary photocatalyst nitrogen-doped GQDs (NGQDs)-ZnNb₂O₆/g-C₃N₄ exhibits visible light hydrogen generation ($\lambda > 420$ nm) [96]. It has been shown that the mole ratio of ZnNb₂O₆/g-C₃N₄ (Zn/CN) and the amount of NGQDs influence the efficiency of hydrogen generation. Accordingly, the highest hydrogen evolution rate of 0.34 mmol h⁻¹ g⁻¹ has been obtained on optimized photocatalyst, i.e., Zn/CN with a mole ratio of 1/7 and 5% NGQDs. It has been proposed that the best photocatalytic activity could be caused by the cooperative effects of heterojunction and NGQDs, resulting in the formation of a large number of charge carriers and the acceleration of their separation.

Moreover, other types of QDs have been applied for hydrogen generation. An interesting study has been carried out by Qian et al. on the application of $CeO_2 - CuO QDs$ for efficient solar-driven hydrogen evolution [97]. The p-type CuO/n-type CeO₂ heterojunction has been synthesized by the hypha assistance process on graphene. The filamentous fungus (Geotrichum candidum) has been used for the preparation of the hyphal structure of graphene microtubules, embedded with $CeO_2 - CuO QDs$. The prepared material exhibits high efficiency of hydrogen generation in the presence of a low amount of a sacrificial agent and without noble metals. The observed H₂ evolution rate has reached 2481 μ mol·h⁻¹·g⁻¹, being constant during four cycles of reaction. Another approach with QDs has been proposed by Lee at al., in which CdSe QDs have been covered with an amorphous titania layer (a-TiO₂) and applied for hydrogen generation from water [98]. Although a-TiO₂ is often considered as an ineffective photocatalyst, due to its rich crystalline disorder and defects [99], the improved photocatalytic activity of CdSe QDs—when covered with a-TiO₂—also indicates that amorphous titania might enhance the photocatalytic activity when it is in the form of a thin layer. It has been proposed that an electron transfer to a-TiO₂ depends on the position of the CB edge of CdSe NCs (The dependence on the size indicates that improved electron injection is expected for the energy level offset between CdSe and TiO₂.). It has been concluded that both charge mobility and absorption ability should be considered for the development of highly active QD-based photocatalysts for water splitting.

As summarized in Table 1, the exceptional photocatalytic properties have been reported in the case of titania 0D systems modified with copper or Ni/Sn. Furthermore, noble metal particles significantly improve the photocatalytic activity of such photocatalysts under both UV and vis irradiation. Interestingly, it has been found that even amorphous titania might improve photocatalytic activity if applied in the form of monolayer. Unfortunately, most experiments are performed in the presence of scavengers, mainly alcohols, and also other compounds, such as EDTA and Na₂S/Na₂SO₃. Therefore, in some papers the "alcohol dehydrogenation" term is clearly stated rather than "water reduction/splitting" [42,43,50,57]. Obviously, water reduction in the absence of any hole scavenger is most recommended, but it is hardly succeeded, due to positive change in Gibbs free energy (as already pointed in the Introduction), i.e., "photosynthetic process". Generally, it might be summarized that photocatalysts with 0D morphology have various advantages, such as a large specific surface area, a large number of active sites and fast charge carrier migration. However, they might aggregate easily, losing these profits. Additionally, their nano-sized dimensions result in serious difficulty for the recovery/recycling process, and also causes environmental threats, as they can be considered as secondary pollutants.

 Table 1. Examples of 0D photocatalysts for photocatalytic hydrogen evolution.

SCs	Modification on SCs	Irradiation Source	Scavenger	Findings	Ref.
TiO ₂	Cu loading	Xe lamp	CH ₃ OH	18 imes enhancement	[55]
TiO ₂	Pt-H-Ag deposition	Xe lamp (>420 nm)	CH ₃ OH	$17.2 \times$ enhancement	[68]
TiO ₂	Ni/Sn loading	Xe lamp (>200 nm)	EDTA	20 imes enhancement	[71]
TiO ₂	octahedral	Hg lamp (290 nm)	CH ₃ OH	1.5 imes enhancement	[73]
TiO ₂	Ag loading	Xe lamp	CH ₃ CHOHCH ₃	improved activity	[76]
TiO ₂	Au loading	Xe lamp (>420 nm)	CH ₃ OH	$8.3 \times$ enhancement	[77]
TiO ₂	In ₂ O ₃ loading	LED lamp/solar simulator	CH ₃ OH	high activity	[78]
TiO ₂ -CdS	core-shell	Xe lamp	Na ₂ S/Na ₂ SO ₃	1.4 imes enhancement	[88]
graphene	CeO ₂ -CuO QDs loading	Xe lamp	CH ₃ OH	2481 $\mu mol \ g^{-1} \cdot h^{-1}$	[97]
CdSe	TiO ₂ coating	AM 1.5 light	Na ₂ S/Na ₂ SO ₃	$2.7 \times$ enhancement	[98]

3. One-Dimension (1D) Photocatalysts

Nanotubes, nanowires, nanofibers, nanorings and nanobelts belong to 1D-structured materials. It is thought that nanotubes have been the most frequently studied among them for various photo-electrocatalytic reactions. In the case of titania nanotubes (TNTs), Grimes [100] and Schmuki [101] were probably first to investigate them, and they have popularized the global study of TNTs. Their research groups have performed various studies on: (i) synthesis optimization (mainly the anodization of titanium foil), (ii) characterization, (iii) growth mechanism, (iv) modification with different components (e.g., for vis activity), and (v) possible applications [102–107]. Subsequently, study of TNTs has been extensively performed by many research groups for both environmental purification [108–110] and solar energy conversion, including hydrogen generation, as shown in Table 2 [111].

For example, Chun et al. prepared a TiO_2/Ti_2O_3 photocatalyst consisting of TNTs (in situ grown; mixed anatase/rutile) on the bulk Ti_2O_3 support, as shown in Figure 7 [112]. Under sunlight irradiation (and without any co-catalyst), high rates of hydrogen evolution (1440 µmol g⁻¹ h⁻¹) have been observed. It has been proposed that the photogenerated electrons from anatase could migrate via rutile to Ti_2O_3 ; of course, this also means that titania must be excited, and thus, only the UV part of the solar spectrum is used. Moreover, it has been suggested that the synergism between bandgap alignments, improved light harvesting ability, and enhanced density of charge carriers generated by the heterojunctions between the Ti_2O_3 and TiO_2 are responsible for the high efficiency of hydrogen generation.





Figure 7. Scheme of TiO_2/Ti_2O_3 synthesis via hydrothermal treatment, acid washing, and calcination of bulk Ti_2O_3 . Copyright ACS [112].

Another approach that emphasizes the role of nanotubular structures was designed by Yang et al. [113]. The 1D mesoporous anatase TNTs with engineered surface defects were successfully synthesized via a combination of the solvothermal method and the high temperature surface hydrogenation process. It has been found that high temperature surface hydrogenation results in the formation of surface oxygen vacancies, which efficiently enhances the light absorption and spatial charge separation. The optimized sample (H400-TiO₂) shows a high rate of photocatalytic hydrogen generation of 9.8 mmol $h^{-1} g^{-1}$, which is ca. 2.5 times higher than that of TNTs without defects. It has been suggested that noticeably high photocatalytic activity might be due to more efficient photoabsorption because of the presence of surface defects; additionally, the special one-dimensional mesoporous nanotube structure contributes to the efficient spatial charge separation on the horizontal-vertical dimension (Figure 8).



Figure 8. The schematic mechanisms of charge transfers in anatase TNTs under solar light irradiation (**left**) and charge recombination in the case of bulk titania (**right**). Copyrights 2021 Elsevier [113].

Highly defective TNTs have also been investigated by Liu et al. who have prepared black TNTs, composed of anatase, with high contents of Ti^{3+} , by a high pressure H_2 treatment [114]. It has been proposed that a high rate of open-circuit photocatalytic generation of hydrogen (under UV excitation), without the presence of a co-catalyst, is caused by a stable and isolated Ti^{3+} defect structure acting as a co-catalytic center for hydrogen generation.

For vis response, TNTs have also been modified and/or doped with various elements. For example, N-doped TNTs have been prepared by treatment with NH_4F during the TNT synthesis by electrochemical anodization [115]. It has been found that the quantity of NH_4F significantly influences the N-doping level and the tube length; thus, influencing

the optical and photocatalytic properties. It has been proposed that a "suitable" N-doping level accelerates the electrons/holes separation, improving the photocatalytic activity for hydrogen evolution and RhB degradation under UV/vis irradiation (Xe lamp with a VisREF filter; 350 nm > λ > 780 nm).

Nanorods are another type of 1D structure applied for H₂ evolution processes. For example, anatase nanorods have been successfully prepared by thermal treatment of H₂Ti₃O₇ nanotubes [116]. It has been found that nanorods with different properties (such as crystallite sizes, aspect ratios, and specific surface areas) might be prepared by adjusting the calcination parameters. Optimized calcination conditions (600 °C for 20-180 min or 700 $^{\circ}$ C for 10 min) results in the preparation of anatase nanorods with large specific surface areas, high crystallinity, and the best photocatalytic performances towards methylene blue photodegradation and H₂ evolution in alcohol-water systems by modification with metallic co-catalysts (Au, Pd or Au/Pd) under UV irradiation ($365 \text{ nm}, 6.5 \text{ mW cm}^{-2}$). The best sample (Pd-Au/600TiO₂(20)) has reached H₂ generation rates of 37.2, 44.0, and 45.6 mmol $g^{-1} h^{-1}$ in 10% vol. ethanol–water, ethylene glycol–water, and glycerol–water systems, respectively. In the other work, Galdamez-Martinez et al. have prepared ZnO nanowires via a vapor-liquid-solid (VLS) process, using Au as a catalyst [117]. Different morphologies, e.g., homogeneously grown vertically orientated nanowires, nanowires with random orientation (grown also at a tilted angle of ca. 65° , i.e., less homogenous), heterogeneously grown nanowires (a lack of the anisotropic crystallization), and highly heterogeneous nanostructure (disorder), have been obtained by adjusting the growth conditions during the VLS process. It has been found that nanowires with random orientations and optimal diameters exhibit the best photocatalytic activity under UV/vis for hydrogen generation from water; whereas, the sample with a disorder structure shows the worst activity.

Next, nanowires with vis responses have also been designed. For example, self-doped Ta₂O₅ nanorods with efficient light harvesting ability (absorption from 400 to 800 nm), prepared by a simple hydrolysis method, could generate hydrogen under vis irradiation (23.35 μ mol g⁻¹ h⁻¹) in contrast with an inactive commercial Ta₂O₅ sample [118]. Self-doping results in the significant narrowing of the bandgap from 3.88 eV to 2.93, 2.83, 2.75, and 2.53 eV for samples prepared at different temperatures of 180, 200, 220, and 240 °C, respectively. Moreover, the specific surface area of self-doped samples (the mesoporous structure) has reached up to 237.89 m² g⁻¹. It has been proposed that the formation of Ta⁴⁺ species, high crystallinity, large specific surface area and mesopores are responsible for high photocatalytic activity. The proposed mechanism of vis-induced hydrogen generation (Figure 9) considers that a new energy level (between the VB maximum and CB minimum) is formed (due to Ta⁴⁺ species localized near oxygen vacancies), effectively narrowing the bandgap. Therefore, under vis irradiation the photogenerated electrons from the VB are excited to the new energy level, and then transferred to the CB (no discussion on the reason of their transfer to CB).



Figure 9. The schemes showing the proposed mechanism of visible light hydrogen generation on self-doped Ta₂O₅ nanorod. Copyrights 2017 Elsevier [118].

Furthermore, nanowire-based composites have also been proposed for photocatalytic hydrogen generation processes. An interesting approach has been presented for TiO₂/ZnO nanowire arrays, prepared by a two-step hydrothermal route on stainless steel mesh, in which a combination of solar (50 W) and ultrasonic (50 W) energy accelerates hydrogen generation [119]. It has been found that the co-utilization of solar and mechanical energy results in high activity (hydrogen-generation rate reaching 3.052 μ mol·g⁻¹·h⁻¹, ~1.6 times that under only solar radiation) and also good recyclability and stability. Moreover, nanowires in the core-shell arrangement have also been adopted for hydrogen evolution. For example, CdS-ZnO core-shell nanowires show high photocatalytic activity, and it has been proposed that the ZnO shell does not only prevent photocorrosion of cadmium sulfide but also improves the charge carriers' separation [120]. The CdS–ZnO nanowires exhibit better stability in acid solution and in the enhancement of photocatalytic hydrogen generation rates by more than two orders in magnitude under UV/vis than sole CdS nanowires. Nanorods in core-shell configuration have also been prepared by sulfidation of ZnO nanorods on stainless steel wire mesh by Hsu et al. [121]. It has been suggested that photogenerated charges carriers, generated in ZnS under vis irradiation, might be effectively separated by the migration of electrons to CB of Ag_2S , or to steel wire mesh (Figure 10). It has been found that, besides the enlargement of the specific surface area, the core-shell structure has also changed the surface character from hydrophobic to superhydrophilic. The high photocatalytic activity for hydrogen generation, reaching 5870 and 168 μ mol g⁻¹ h⁻¹ under UV and visible light irradiation, respectively, is probably caused by the formation of an Ag₂Scoupled ZnO-ZnS heterojunction on a conductive support (metal mesh) that improves the following: (i) the light absorption, (ii) the separation efficiency of photogenerated charge carriers, and (iii) the contact with the reactants.



Figure 10. Schematic mechanism of hydrogen evolution on Ag₂S-ZnO@ZnS/mesh photocatalyst. Copyrights 2016 ACS [121].

Table 2, with summarized examples of 1D photocatalysts dedicated for hydrogen generation, shows the potential of heterojunction structures such as CdS–ZnO core-shell nanowires. For vis photocatalytic activity, a very promising performance has been found for self-doped Ta_2O_5 nanorods, but without detailed mechanism clarification.

In summary, there are the following advantages of 1D morphology: high aspect ratio, directed migration of electrons (spatial separation of charge carriers), and large specific surface area. However, the size-controllable synthesis and efficient dispersion are remaining challenges. Similar to 0D photocatalysts, hole scavengers are commonly applied; that is, mainly methanol, but also other organic (ascorbic acid) and inorganic (Na₂S/Na₂SO₃/NaCl) compounds are used. Unfortunately, it is difficult to compare the photocatalytic activity of different photocatalysts, since significantly different experimental conditions have been used, including the most important factor of irradiation conditions (i.e., lamp type, wavelengths' range, irradiation intensity, irradiation distance, etc.), as well as the type and concentration of scavengers, and the photoreactor type (light distribution, mass transport, diffusion/kinetic-control, with or without hydrogen uptake, etc.), which all differ between research groups. However, it is clear that modifications and new structures ZnO

proposed by authors have exhibited promising activities for possible commercialization. Obviously, the change in the synthesis conditions influences the properties of the final structure. For example: (i) N-doping does not only change the photoabsorption properties, but also the length of TNTs; (ii) the calcination conditions affect the properties (specific surface area, crystallinity, etc.), and thus, the photocatalytic activity of titania nanowires. It should be pointed out that 1D as well as 2D morphologies could be easily used as (photo)electrode materials; thus, these also apply for (photo)electrocatalytic purposes.

SCs Modification on SCs **Irradiation Source Findings** Scavenger Xe lamp (full-sunlight 1440 μ mol g⁻¹ h⁻¹ TiO₂ NTs TiO₂/Ti₂O₃ CH₃OH filter) 9.8 mmol $h^{-1} g^{-1}$, TiO₂ NTs Pt loading Xe lamp(AM 1.5 G) CH₃OH $2.5 \times$ enhancement Ti³⁺ TiO₂ solar simulator (AM 1.5) CH₃OH enhanced H₂ rate halogen lamp (5% UV $3.77 \text{ mmol cm}^{-2} \text{ h}^{-1}$ TiO₂ NTs N-doped CH₃OH light) $45.6 \text{ mmol g}^{-1} \text{ h}^{-1}$ 100 P/F lamp (365 nm) Pd/Au/Pd-Au TiO₂ nanorod alcohols 23.35 mmol g^{-1} h⁻¹ Ta⁴⁺ Ta₂O₅ Xe lamp (>400 nm) CH₃OH $1.985 \ \mu mol \cdot \tilde{g}^{-1} \cdot h^{-1}$ TiO₂/ZnO nanowires Xe lamp (200-2500 nm) CH₃OH more than 1200 CdS-ZnO Core-shell nanowires Xe lamp ascorbic acid $\mu mol{\cdot}g^{-1}{\cdot}h^{-1}$

Table 2. Examples of 1D photocatalysts for photocatalytic hydrogen evolution.

4. Two-Dimension (2D) Photocatalysts

visible light

Ag₂S-ZnO@ZnS

core-shell nanorods

Among various 2D nanostructures (nanofilms, nanoplates, nanosheets, nanoflakes), one might conclude that nanosheets have been the most popular in the investigation of hydrogen evolution. For example, hydrogenation combined with gas-assisted liquid exfoliation has been proposed for the fabrication of ultrathin TiO_2 nanosheet assembly (Figure 11 and Table 3) [122]. It has been proposed that hydrogenation is responsible for the formation of surface-point defects (e.g., oxygen vacancy), while keeping the ultrathin 2D structure without any damage. It has been found that 2D structures have large specific surface areas and high contents of low-coordinated surface atoms. Additionally, surface lattice distortion (oxygen vacancies and low-coordinated surface atoms) results in a reduction of bandgap and an upshift of the CB minimum. Accordingly, the structure exhibits narrow bandgap and its significant content of surface reactive sites, and thus, its efficient solar-light utilization, which causes high photocatalytic activity for hydrogen generation (540.7 μ mol·h⁻¹) and good stability during recycling under simulated solar radiation.

Na2S/Na2SO3/NaCl



Figure 11. The schematic mechanism of assembly formation of titania ultrathin nanosheets. Copyright 2018 Elsevier [122].

The defective nanosheets have also been proposed by Liu et al. [123]. Herein, anatase nanosheets with defects at different locations (i.e., either on the surface or in the bulk) have been successfully fabricated by the adjustment of temperature and HF contents during hydrothermal process. It has been found that surface defects are preferable for efficient

Ref.

[112]

[113]

[114]

[115]

[116]

[118]

[119]

[120]

[121]

 $168 \ \mu mol \ l \ g^{-1} \ h^{-1}$

hydrogen generation (simulated solar radiation), because of their dual functions: (i) trapping of photogenerated charges; and (ii) adsorption of reagents. Similarly, Liu et al. have investigated defective titania nanosheets [124]. Titania nanosheets were prepared by a solvothermal method and treated with N₂ plasma at atmospheric pressure to generate defects, i.e., oxygen vacancy and Ti³⁺ ions. The photocatalytic hydrogen formation (under UV/vis) in the defective titania (8.1 mmol $g^{-1} h^{-1}$) was 14.85 times higher than that in bare titania nanosheets. Advantageous action of defective titania has also been shown for a single-atomic Pt site photocatalyst, constructed using defective titania nanosheets as a photocatalytic support for hydrogen production from water splitting [125]. It has been suggested that the oxygen vacancy on the surface of titania could effectively stabilize the atomic platinum by constructing the Ti-Pt-Ti structure. Accordingly, stabilized platinum sites by a three-center structure could promote the separation and migration of photogenerated charges, enhancing the hydrogen production. This photocatalyst has shown the improved performance under UV/vis irradiation, where the hydrogen evolution rate is up to 13460.7 μ mol·h⁻¹·g⁻¹, i.e., ca. 29.0 and 4.7 times higher than that on titania nanosheets and titania modified with Pt NPs, respectively. Platinum and defects have also been applied in bimetallic (Pd-Pt)/mesocrystalline Ta_2O_5 nanosheets with high vis absorption abilities, mainly because of the creation of oxygen vacancies [126]. The highest photocatalytic activity for hydrogen formation on Pd-Pt/mesocrystalline Ta₂O₅ nanosheets reaches 21529.52 $g^{-1} h^{-1}$ (being ca. 21.2 times higher than that on the commercial Ta_2O_5) with apparent quantum efficiency of ca. 16.5% at 254 nm. It has been proposed that highly improved activity is mainly caused by the significant roles of Pd-Pt NPs for increasing the charge separation and transport. Similar to single-atomic Pt site photocatalyst, isolated Co atoms grafted on the titania nanosheet (with the thickness of 6 nm) surface via Co-O electronic coupling, have been proposed for hydrogen formation [127]. Indeed, this photocatalyst shows efficient hydrogen generation under UV/vis irradiation, exceeding the activity of bare titania nanosheets by 12 times. Based on the theoretical and experimental results, it has been confirmed that Co atoms work as reactive sites, and also that the electron transfer and hydrogen adsorption/desorption processes might be significantly enhanced via the effective Co–O electronic coupling in atomic scale, causing an acceleration in hydrogen production. A unique nanosheet-based system for simultaneous degradation of pollutants and water splitting has been proposed by Wu et al. [128]. The Co_3O_4 -{001}/{101}-TiO_2 nanosheets with unique p-n/facet heterojunction structure have been used for treating pharmaceutical-contaminated water. Under UV/vis irradiation, a strong internal electric field (well known for decahedral anatase) forced electron transfer and hole transfer to $\{101\}$ facets and Co_3O_4 NPs, respectively. Accordingly, the dual (p–n/surface) heterojunction structure enables the spatial separation of charges. The holes, primarily accumulated on Co_3O_4 NPs, might efficiently oxidize the pharmaceutical pollutants (enrofloxacin, ciprofloxacin, and ibuprofen); whereas, the electrons accumulated on {101} facets of titania nanosheets might simultaneously reduce water molecules to hydrogen.

The second important group of 2D structures is based on nanoplates. Feng et al. have prepared cadmium sulfide nanoplates with rough surfaces through an ionic exchange process, and then modified them with in situ photo-deposited Pt NPs [129]. The rate of photocatalytic hydrogen generation on Pt/CdS reached 3.75 mmol h⁻¹ g⁻¹, which was much higher than that on pristine CdS. Additionally, the Pt/CdS has shown a good stability in continuous solar hydrogen production, even after 16 days. It has been proposed that the rough structure (plate-like) and the presence of platinum as a co-catalyst could efficiently improve the photoabsorption ability and the charge carrier separation (providing reactive sites), respectively. Application of a pyroelectric material (BiOIO₃ nanoplates) to separate charge carriers by internal polar field, and thus, to enhance the efficiency of photocatalysis, has been proposed by Su et al. [130]. The thickness of nanoplates has been shown to be decisive for the efficiency of photocatalytic hydrogen production, i.e., seven times enhancement has been achieved for 150 nm-thick nanoplates in comparison to 25 nm-thick ones. It was concluded that the enhanced internal polar field resulting from the increased thickness of the BiOIO₃ nanoplates ensures a tightly bound layer of the adsorbed ions on the surface of nanoplates, and also acts as an accelerator to separate the photoexcited carriers.

A very popular material for vis photocatalysis, $g-C_3N_4$, has also been used for water splitting. For example, ultrathin $g-C_3N_4$ nanosheets with large specific surface areas have been fabricated by a liquid exfoliation process from bulk $g-C_3N_4$ in isopropanol [131]. The $g-C_3N_4$ nanosheets are shown to be more efficient for hydrogen generation than the bulk sample under solar radiation, probably due to their more efficient photoabsorption and larger specific surface area. Additionally, modification of $g-C_3N_4$ with CuS nanoplates (hexagonal) by a hydrothermal process has an enhanced charge separation efficiency, and $g-C_3N_4$ -CuS exhibits a much higher hydrogen generation rate (126.5 μ mol h⁻¹) than the bare $g-C_3N_4$ nanosheets.

An interesting approach, using a new type of WS_2/WO_3 photocatalyst with layered structure to mimic photosynthesis (i.e., Z-scheme heterostructure), has been proposed by Zhang et al. [132]. The composite-monoclinic WO₃ nanoplates (m–WO₃), with a few layers of hexagonal WS₂ with semiconducting 2H (2H–WS₂), has been fabricated via a sulfurization (in situ) of hydrous nanoplates of WO₃, prepared by a hydrothermal process. It has been proposed that the electronic interaction between two components follows a direct Z-scheme mechanism; thus, it decreases the recombination of charge carriers, while keeping the redox ability of both components. Moreover, the formation of the transition layer ("S-W-O"), due to the contact between 2H–WS₂ and m–WO₃, could further shorten the migration path of charges, smoothing their interfacial transfer. Accordingly, about five times higher activity has been achieved with a photocatalyst with optimized properties for hydrogen generation under UV/vis irradiation than the few-layered 2H–WS₂ alone.

The highlighted examples of 2D-ordered photocatalytic materials (Table 3) show that defective Pt-loaded titania nanosheets have exceptional photocatalytic properties under solar-simulated light, similar to bimetallic Pd-Pt/mesocrystalline Ta₂O₅ nanosheets. Similar to 0D and 1D photocatalysts, various scavengers (methanol, triethanolamine, ENR, CIP, IBU, lactic acid, and so on) are commonly used for photocatalytic hydrogen evolution; however, an interesting approach to the use of wastes (pharmaceutical wastewater) as a hole scavenger has also been proposed. Moreover, it has been confirmed that the structure and the morphology are decisive for the overall activity. For example, the localization of defects (on the surface or in the bulk), the thickness of the nanosheets (5× broader causing 7× higher activity for BiOIO₃, probably a product of the increased interpolar field, and thus, the enhanced charge carrier separation), the superiority of organized structure (nanosheet) above the bulk (e.g., for g-C₃N₄), and the isolated atomic metals (Ti-Pt-Ti and Co-O) and nonmetals (S-W-O) resulting in an efficient charge-carrier transfer and hydrogen generation, have been found for 2D nanostructures.

SCs	Modification on SCs	Irradiation Source	Scavenger	Findings	Ref.
TiO ₂	ultrathin nanosheets	AM1.5	CH ₃ OH	540.7 μ mol g ⁻¹ h ⁻¹	[122]
TiO ₂	Ti ³⁺	simulated solar light	CH ₃ OH	28.8 μ mol g ⁻¹ h ⁻¹	[123]
TiO ₂	N-doping	simulated solar light	TEA	$14.85 \times$ enhancement	[124]
TiO ₂	Pt loading	Xe lamp (solar simulator)	CH ₃ OH	13,460.7 μ mol g $^{-1}$ h $^{-1}$	[125]
Ta_2O_5	Pd-Pt loading	Xe lamp	CH ₃ OH	21,529.52 μmol g ⁻¹ h ⁻¹	[126]
TiO ₂	Co loading	Xe lamp	CH ₃ OH	$12 \times$ enhancement	[127]
TiO ₂	Co ₃ O ₄ loading	Xe lamp (400 nm)	ENR/CIP/IBU	$3.75 \text{ mmol } \text{h}^{-1}\text{g}^{-1}$	[128]
CdS	Pt loading	Xe lamp (435 nm)	Na ₂ S /Na ₂ SO ₃	improved activity	[129]
BiOIO ₃	nanoplates	UV-vis	CH ₃ OH	7 imes enhancement	[130]
$g-C_3N_4$	CuS loading	simulated solar light	TEA	126.5 μ mol g ⁻¹ h ⁻¹	[131]
WO ₃	WS ₂	Xe lamp	lactic acid	$673 \ \mu mol \ g^{-1} h^{-1}$	[132]

Table 3. Examples of 2D photocatalysts for photocatalytic hydrogen evolution.

CIP-ciprofloxacin; ENR-enrofloxacin; IBU-ibuprofen; TEA-triethanolamine.

5. Three-Dimension (3D) Photocatalysts

In this group, one can distinguish meso/macro-porous structures, flower-like composites, and honeycomb-like hierarchical materials that have been constructed/accumulated from one or more kinds of 0D, 1D, and 2D nanostructures. For example, titania with a 3D urchin-like structure has been synthesized by a single-step process (to control both the crystal phase and morphology of titania) via a surfactant-free solvothermal method [133]. The best-performing mixed-phase (anatase/rutile) photocatalyst exhibits remarkable durability up to 25 h and an ability to generate hydrogen at the rate of $3522 \,\mu mol g^{-1}$ under natural sunlight (with Na₂S/Na₂SO₃ as sacrificial reagents). Moreover, titania coupled with other materials has also been investigated, e.g., flower-like nanostructures of TiO₂@Ni(OH)₂ core-shell microspheres [134]. The 3D nanostructure, composed of well-arranged $Ni(OH)_2$ nanoflakes on the titania microspheres, has resulted in six-fold improvement of hydrogen production (simulated solar radiation, with EDTA-Na2 as a sacrificial reagent), than that by pristine titania. It has been proposed that p-n type heterostructures facilitate the separation and the transfer of charge carriers, and provide large quantities of active sites for photocatalytic hydrogen evolution. Titania has also been used to construct unique, black, flower-like nanostructures with solar-driven photocatalytic activity for hydrogen evolution [135]. In this study, a mild method has been developed for the preparation of a black 3D N-TiO₂-x@MoS₂ core-shell structured photocatalyst (Figure 12). Titania has been co-doped with Ti³⁺ and N and additionally coupled with MoS₂, forming a core-shell nanostructure. It has been proposed that successful doping results in vis light absorption; whereas, type II heterojunction hinders charge carriers' recombination. The decomposition of methyl orange (vis) and the hydrogen-production rate (solar simulator, with CH₃OH as a sacrificial reagent) have reached 91.8% and 1.882 mmol $h^{-1}g^{-1}$, respectively.



Figure 12. Schematic diagram for the formation of the N-TiO₂-x@MoS₂ nanocomposites. Copyrights 2017 Elsevier [135].

The unique combination of flower-like structures and sheets has been studied by Lv et al. [136]. The perovskite NPs and graphene oxide (GO) have formed the 3D nest-like LaCO₃OH/Ni(OH)₂@graphene (RGO) hierarchical composite, as shown in Figure 13. GO has been used as both carbon source (self-sacrificial) and morphology-control agent. The photocatalytic performance has been significantly improved, thanks to this morphology, benefiting from the fast electron transfer on the uniform nanosheets of Ni(OH)₂@RGO and the efficient light harvesting of the 3D nest- and flower-like structure of LaCO₃OH-Ni(OH)₂@RGO. The photocatalytic activity for hydrogen generation achieves ca. 1.38 mmol·h⁻¹·g⁻¹, being 13-fold higher than that for bare LaCO₃OH. Unfortunately, the experiments have been performed under strong UV irradiation (Hg lamp; 250 nm > λ >



650 nm); thus, it is impossible to conclude if this photocatalyst might be active under sole vis irradiation.

Figure 13. Scheme showing the fabrication of LaCO₃OH-Ni(OH)₂@RGO composite. Copyrights 2020 Elsevier [136].

Furthermore, flower-like Bi₂WO₆-Bi₂O₃ structures have been prepared by a twostep process, including an ionic liquid-assisted solvothermal step and calcination [137]. The addition of ionic liquids during the preparation of Bi₂WO₆ based-materials causes an increase in photocatalyst size and the creation of more petal sheets in the flowerlike microspheres. The Bi₂WO₆-Bi₂O₃ flower-like photocatalyst shows higher activity for H_2 generation under UV/vis (Xe lamp) irradiation than the Bi_2WO_6 photocatalyst, probably due to improved light absorption, enlarged specific surface area, and matched band structure (type II heterojunction), and thus, inhibited charge carriers' recombination. Finally, a flower-like nanostructure has also been tested for hydrogen evolution under vis ($\lambda > 420$ nm) irradiation. The Sn₃O₄ has been prepared in the form of a flower by a hydrothermal method without templates or surfactants [138]. It has been found that a platinized flower-like nanostructure is much more efficient (85%) than platinized sheets, reaching 184 μ mol·h⁻¹·g⁻¹ hydrogen evolution (CH₃OH as a sacrificial reagent). Moreover, another flower-like nanostructure, composed of Ag₂S and CdS, has also exhibited vis activity for hydrogen evolution ($\lambda > 420$ nm; TEOA) [139]. Cadmium sulfide consisting of self-assembled nanosheets (4.7 nm-thick) has been prepared via solvothermal method assisted with microwaves, and an in situ ion exchange method has been used to deposit Ag_2S NPs on the nanosheets' edges (Figure 14. The photocatalyst has shown high activity for H₂ evolution, reaching 375.6 μ mol·h⁻¹·g⁻¹, which is 11.5-fold higher than that of pristine CdS. It has been proposed that the effective separation of charge carriers, the low overpotential of Ag_2S , and the utilization of the near-infrared (NIR) light by Ag_2S are responsible for the improved performance in photocatalytic hydrogen generation [41].



Figure 14. Schematic illustration of synthesis procedure for hierarchically structured CdS–Ag₂S nanocomposites. Copyrights 2019 Elsevier [139].

Mesoporous structures also play an important role in the 3D group. Zhang et al. have utilized the concept of defect engineering for the preparation of defective mesoporous titania microspheres, where defects are formed by NaBH₄ in the mesopore space [140]. Interestingly, it has been found that through changing the temperature of reduction, the migration of defects occurs, from the nanocrystalline-exposed surfaces to the interfaces between phase junction (Figure 15), which enables a well-tuned localization of defects. It has been reported that the reaction rates of hydrogen evolution (CH₃OH as a sacrificial reagent and Pt as a co-catalyst) under simulated solar radiation (AM 1.5G) and vis ($\lambda > 420$ nm) irradiation reach 1065·µmol·h⁻¹ and 42.6·µmol·h⁻¹, respectively.



Figure 15. Schematic illustration of the synthesis of defective mesoporous titania microspheres with phase junctions via a facile confinement reduction method. Copyrights 2019 Elsevier [140].

Titania has also been used in another mesoporous structure, considering the famous P25; thus, a uniformly ordered mesoporous titania microsphere, with a tuned ratio of anatase to rutile, and radially oriented meso-channels, has been constructed, through a coordination-mediated self-assembly method [141]. The obtained microspheres have a similar anatase/rutile ratio to that in P25, but larger specific surface area (78.6 m² g⁻¹) and larger pore volume (0.39 cm³ g⁻¹). It has been found that mesoporous microspheres exhibit a much higher solar-driven hydrogen generation rate (with Pt and CH₃OH as a co-catalyst and a hole scavenger, respectively) than commercial P25 (simulated solar radiation). Moreover, microspheres could also generate hydrogen under vis irradiation (420 nm and 520 nm) in contrast to inactive P25.

Next, the composites of titania with other compounds were investigated, e.g., $TiO_2/$ Cu_2O [142], $TiO_2/g-C_3N_4$ [143], TiO_2/CdS [144], and $NH_4TiOF_3/TiO_2/g-C_3N_4$. [145]. The Cu_2O/TiO_2 photocatalysts with oxygen vacancies have been prepared through a adsorption-reduction strategy of Cu²⁺ ions with Cu₂O NPs, decorated on/within mesoporous titania microspheres [142]. It has been proposed that high activity for hydrogen evolution (CH₃OH as a hole scavenger) under UV/vis irradiation (Xe lamp) is due to allsolid, direct Z-scheme mechanisms between defective titania and cuprous oxide. Moreover, it has been shown that hydrogen can also be evolved from sea water, with reaction rates of 5.1 mmol h^{-1} g^{-1} and 11 mmol h^{-1} g^{-1} for seawater and water, respectively. It was concluded that (i) the Z-scheme mechanism, (ii) a high specific surface area (more photocatalytic active sites for both Cu₂O and TiO₂), and (iii) improved stability (consumption of holes from Cu₂O by the oxygen vacancy), result in high photocatalytic performance of these microspheres. Another titania-based composite (TiO_2/CdS) has been designed by Meng et al., in which a hierarchical structure, consisting of titania spiny nanosheet microspheres with CdS NPs, has been synthesized by a SILAR method (successive ionic layer adsorption and reaction), as shown in Figure 16 [144]. The hybrid photocatalyst has shown a significantly enhanced photocatalytic hydrogen evolution rate of 51.4 µmol h⁻¹ under UV/vis (Xe lamp; CH₃OH as a hole scavenger), in comparison to almost inactive components. It



has been proposed that the Z-scheme mechanism, hierarchical structures, and efficient charge carriers' separation and migration are responsible for high photocatalytic activity.

Figure 16. Schematic illustration for the fabrication of TiO₂/CdS photocatalyst. Copyrights 2017 Elsevier [144].

Similarly, it has been shown that hierarchical titania/graphitic carbon nitride nanofibers (meso/macro-porous), constructed by combined electrospinning and calcination, exhibit enhanced hydrogen evolution under simulated solar irradiation [143]. The hierarchical composite shows much higher activity than reference samples (non-hierarchical composites and porous titania nanofibers) for hydrogen evolution (CH₃OH as a hole scavenger) under solar radiation. Moreover, only composites with $g-C_3N_4$ (hierarchical and non-hierarchical) show vis response ($\lambda > 420$ nm; no details on the irradiation setup). Therefore, it has been proposed that hierarchical meso/macro-porous structures might increase the migration of charge carriers and the diffusion rate of product molecules, while supplying a large specific surface area and plentiful reactive sites. Graphitic carbon nitride and titania have also been combined with NH₄TiOF₃, forming 3D camellia-like structures [145]. It has been proposed that the 3D hierarchical structure enables multiple refractions and reflections of light within the material, which significantly enhances the sunlight harvesting efficiency. The photocatalytic hydrogen generation under UV/vis (Xe lamp; TEOA and Pt as a hole scavenger and a co-catalyst, respectively) irradiation at the rate of 3.6 mmol $g^{-1} h^{-1}$ exceeds that by pure g-C₃N₄ by ca. four times. It has been proposed that high photocatalytic activity is due to the Z-scheme mechanism between $g-C_3N_4$ and titania; additionally, NH₄TiOF₃, evenly dispersed on titania, improves the interface performance of both main components by hindering the rapid recombination of charge carriers.

The sole 3D g-C₃N₄, in the form of a multi-hole hexagon with nitrogen defects and a high specific surface area, has been synthesized by thermal polymerization via addition of EDTA into hydrothermal-treated dicyandiamide, as shown in Figure 17 [146]. The photocatalytic activity for hydrogen generation under vis irradiation ($\lambda > 420$ nm; Xe lamp with cut-off filter; TEOA and Pt) for the optimal photocatalyst reaches 5839 µmol·g⁻¹·h⁻¹, which is 102-fold higher than that of bulk g-C₃N₄. It has been proposed that the combined effects of enhanced light harvesting, enlarged specific surface area (129 m²/g), hindered recombination of charge carriers, negatively shifted CB position, and an efficient exposure of active sites, are responsible for high photocatalytic activity (Figure 18).



Figure 17. Scheme of the synthesis for multi-hole hexagon of g-C₃N₄. Copyrights 2020 Elsevier [146].



Figure 18. Scheme of the morphology superiority for the photocatalytic H_2 production for defective hexagon of $g-C_3N_4$ under vis irradiation. Copyrights 2020 Elsevier [146].

Another specific 3D structure has been presented by Gultom et al.; a nanodiode of Ag₂O and Zn(O,S), deposited on the surface of mesoporous silica to form the p-n heterojunction SiO₂ / Ag₂O/Zn(O,S), as illustrated in Figure 19 [147]. It was found that the photocatalytic hydrogen generation has been obviously enhanced for the composite of n-Zn(O,S) with p-Ag₂O (outward for improvement of reduction reactions, and inward for modulating the built-in electrical nanofield). The best hydrogen generation rate (under UV irradiation) of 9.2 mmol·g⁻¹·h⁻¹, corresponding to an apparent quantum yield of 10.3%, has been achieved by the optimization of the Zn(O,S) content and p-Ag₂O localization, which was about 2.7 times higher than that by pristine Zn(O,S). The remarkable enhancement of activity has been ascribed to the synergy between components via the following: (i) three-dimensional multi-bandgap quantum-well (3D MQW) band structure, (ii) improved photoabsorption, (iii) activity of surface oxygen, (iv) separation of charge carriers, (v) longer lifetime of charges, (vi) low charge transfer resistance, and (vii) the p-n heterojunction in the photocatalyst.



Figure 19. Schematic illustration for the synthesis of SiO₂/Ag₂O/Zn(O,S). Copyrights 2019 ACS [147].

Hierarchical honeycomb structures of anatase, co-doped with Br- and N- (HC-Br,N/Ana), have been proposed by Zhang et al. [148]. It was found that HC-Br,N/Ana exhibits a high efficiency of hydrogen-generation rate under vis ($\lambda > 420$ nm) of 2247 µmol h⁻¹ g⁻¹, which is much higher than that by single doped titania (Br- or N- of 0 or 63 µmol h⁻¹ g⁻¹, respectively); thus, synergy between Br and N was suggested. It has been proposed that the co-doping of titania with Br and N reduces its bandgap (to 2.88 eV), and that the holes on N acceptor level could passivate the electrons on Br donor level; thus, hindering the charge carriers' recombination.

Finally, probably the most prospective structure for efficient light harvesting is presented: photonic crystals (PCs)—a periodic optical nanostructure that affects the motion of photons. Although various types of structures could be considered (1D, 2D, and 3D), they are presented here together (considering honeycomb structures as the most typical) for clarity of presentation. The uniqueness of PCs is the formation of photonic bandgap (PBG), where light at certain frequencies is forbidden from propagation, due to refractive periodicity of the material [149]. An occurrence of PBG causes multiple scatterings of light at the edges, resulting in a decrease in photons' group velocity—known as slow photons—that could be efficiently utilized with photo-absorbing materials for amplified light harvesting [150]. It should be pointed out that the PBG effect is dependent on the angle of the irradiation [151,152], the diameter of the void spaces or inner spaces [153,154], the distance between tubes (nanotubes), and the thickness of the periodic nanostructure's wall [155].

In recent years, several studies have been reported on the correlation between the PBG effect of PCs and their photocatalytic activity for hydrogen production. Accordingly, Chiarello et al. have shown that the total amount of generated H₂ increases linearly with the enlargement of the inner diameter of titania, indicating the confinement and manipulation of light that entered within the material. In contrast, enhanced photoelectrochemical hydrogen evolution has been reported for quantum dots-sensitized TiO₂ inverse opal PCs with the smallest void spaces [156]. Moreover, an enhanced "energy production" from water/biomass could depend not only on the nanovoid spaces of the designed PCs, but also other factors, such as co-modifications performed on the periodic nanostructure, as summarized in Table 4.

The overlapping of the slow photons region (PBG effect) and the absorption edge of the backbone PC material, has emerged as a successful technique for promoting light harvesting; thus, they can amplify the photocatalytic performance. Liu et al. have shown the enhanced hydrogen evolution for Pt-loaded titania inverse opal (IO) with a nanovoid diameter of 133 nm, which allows more precise overlapping between slow photons and a titania electronic absorption at approximately 360 nm, in comparison with smaller/larger nanovoids with a slow photons effect at shorter/longer wavelengths [157]. Similarly, Waterhouse et al. have succeeded in matching the wavelengths of the PBG effect and titania

absorption edge through precise tuning for Au/TiO₂ PC, with a stopband position located at 357 nm, which has exhibited efficient hydrogen generation from photoelectrochemical water splitting [158].

Apart from that, an increase in overall activity could be evident by the overlapping of the slow photons at either blue or red edges with any photo-absorbing material, such as noble metals (plasmonic effect) [159] and dye sensitized molecules. Accordingly, enhanced hydrogen evolution has been observed by tuning the arise of slow photons at ca. 518 nm that overlapped precisely with the localized surface plasmon resonance (LSPR) effect from Au NPs, deposited on titania nanorod PCs [160]. Similarly, the amplified photoelectrochemical water splitting has been achieved after matching the wavelengths of LSPR and PBG (at 513 nm), owning to the noble metal incorporated within the material and slow photons from the bismuth vanadium-based photoelectrode, respectively [161]. However, it should be highlighted that the precise matching between slow photons and plasmon effect could not be proven by polychromatic source of irradiation, as PCs material such as titania could also absorb light under vis range up to 450 nm (due to defects and impurities), as shown in a recent study [162].

Fabrication of well-ordered multi-array PCs is identified as one of the important aspects in governing the overall photocatalytic performance, as the trapping and multi-scattering of photons is more evident in such materials. Accordingly, Cui et al. have reported much higher hydrogen evolution during water oxidation in the presence of the CdS–Au–WO₃ heterostructure PCs in comparison with the crushed ones, highlighting the reduced slow photons enhancement in the latter sample [163]. A similar observation has been highlighted in a study performed for the photodegradation of organic pollutants, where the grounded PCs sample exhibits much lower activity in comparison with the undestroyed ones [164], indicating the importance of the well-ordered multi-array PC structures in the overall photocatalytic activity.

In summary, 3D photocatalysts have been usually constructed from one or more kinds of 0D, 1D, and 2D morphologies, and thus, the 3D morphologies could accumulate their various advantages. Undoubtedly, the morphology-governed activity has been confirmed in various studies. For example, 3D organized structures, such as hierarchical TiO₂/g- C_3N_4 , 3D TiO₂ with oriented radially meso-channels, and 3D g- C_3N_4 multihole hexagon, were shown to be much more active than respective materials with irregular morphologies. Moreover, photocatalysts with 3D morphology exhibit higher activity than 2D ones, e.g., platinized flower-like Sn_3O_4 compared with platinized sheets of Sn_3O_4 . Additionally, a uniform dispersion of one component on another might also improve the photocatalytic performance, e.g., NH₄TiOF₃ dispersed on the titania surface in a TiO₂/g-C₃N₄ composite. Usually, it is proposed that an organized morphology results in an efficient charge carriers' migration, and thus, in higher photocatalytic activity. Moreover, 3D structures have also been proposed as profitable materials for an efficient light harvesting, e.g., the camelia-like structure of $TiO_2/g-C_3N_4/NH_4TiOF_3$ and all PCs. The light harvesting ability of PCs is their main advantage, and thus, is commonly used for various applications. The most recommended option is to overlap the photonic bandgap edge position (slow photon effect) with the absorption ability of SCs, which results in a significant enhancement of photocatalytic activity. Moreover, an addition of modifiers with the ability of vis absorption, and the subsequent tuning the position of PBG edge (by void/sphere diameter) to overlap with the absorption of modifiers, results in significant enhancement of activity, even in the visible range of the solar spectrum. The important morphology is probably the most evident for PCs, since even slight destruction of their structure causes a significant decrease in the activity.

Table 4 presents the examples of different types of PCs applied for hydrogen generation. Similar to other structures hole scavengers, i.e., alcohols (methanol, ethanol, ethylene glycol), triethanolamine, and Na₂S/Na₂SO₃, etc., are commonly used for the hydrogen evolution process. Notwithstanding the scavengers' use, the presented enhancements in

PCs	Modification on PCs	Irradiation Source	Scavenger	Findings	Ref.
TNTs	-	Xe lamp	-	improved activity	[154]
TiO ₂	Pt loading	Xe lamp	CH ₃ OH	2× enhancement *	[157]
IOT	Au loading	UV lamp (>365 nm) and solar	C ₂ H ₅ OH	high activity	[158]
TiO ₂ nanorods	Au NP loading	Xe lamp (>420 nm)	-	improved activity	[160]
Mo:BiVO ₄ IO	Au NP deposition	solar light stimulator	-	$4 \times$ enhancement	[161]
WO ₃	Au/CdS loading	Xe lamp (>420 nm)	Na ₂ S/Na ₂ SO ₃	high activity *	[163]
TiO ₂	Au/CdS loading	Xe lamp (>420 nm)	Na ₂ S/Na ₂ SO ₃	high activity	[165]
TNTs	Cu NP loading	Xe lamp (>420 nm)	ethylene glycol	high activity	[166]
IOT	F_IOT/Au infilt.	Hg/Xe lamp	C ₂ H ₅ OH	high activity	[167]
IOT	CuO/BiVO ₄ loading	Hg lamp (365 nm)	C ₂ H ₅ OH	enh. Activity **	[168]
IOT	Ti ³⁺ /Au–Pt NPs load.	UV lamp (<400 nm)	C ₂ H ₅ OH	high activity	[169]
CdS IO	-	$\lambda \geq 420 \text{ nm}$	Na ₂ S/Na ₂ SO ₃	2× enhancement *	[170]
TNTs	Ti ³⁺	Xe lamp	-	10 imes enhancement *	[171]
g-C ₃ N ₄ IO	-	Xe lamp	TEA	6× enhancement *	[172]
IOT	Ag NP loading	Xe lamp	-	high activity	[173]

the photocatalytic activity confirm that significant developments of new efficient materials based on PCs is highly recommended.

Table 4. Examples of photonic crystals applied for photocatalytic hydrogen evolution.

*—compared to reference; **—enhanced activity dependent on BiVO₄ and CuO amount; infilt.—infiltration; IO—inverse opal; IOT—inverse opal titania; F_IOT—fluorination of IOT; Ti³⁺—self-doping.

6. Composite-Structure (Multi-Dimensional) Photocatalysts

Multi-composite photocatalysts, constructed from two (or even more) dimensions structured together (e.g., 0D/1D, 0D/2D, 1D/2D), have also been proposed for photocatalytic hydrogen evolution. Obviously, application of fine deposits (0D: QDs, NPs, nanoclusters) on the surface of more complex structures is the most popular. Although QDs have shown remarkable merits (e.g., large specific surface area, efficient light harvesting ability, and adjustable bandgap), which are beneficial for vis photocatalysis, the utilization of QDs is also connected to serious issues of charge recombination and possible aggregation. Accordingly, the stabilization of QDs on the support should be beneficial for the overall performance. Indeed, stable and highly active photocatalysts have been prepared when 0D Zn-AgIn₅S₈ (ZAIS) QDs are deposited onto 2D α -Fe₂O₃ nanosheets through electrostatic attractions, i.e., a difference in Zeta potential results in a uniform dispersion of ZAIS QDs on nanosheets, as shown in Figure 20 (Table 5) [174]. It has been confirmed that the introduction of α -Fe₂O₃ nanosheets enhances the mobility and separation of charge carriers. Additionally, high conductivity of α -Fe₂O₃ can lead out the photogenerated charge carriers, and thus, hindering their recombination. It has been proven that appropriate band alignment is beneficial for the construction of Z-scheme heterostructures (as confirmed by EPR), which improves the redox properties and prevents the charge carriers' recombination. The best nanocomposite, with 3 wt% α -Fe₂O₃, causes hydrogen evolution under vis irradiation (>420 nm; ascorbic acid as a hole scavenger) at the rate of 1.7 mmol \cdot g⁻¹ h⁻¹, that is 3.5 times higher than that on pristine QDs, with an apparent quantum efficiency of 7.48% at 450.nm.



Figure 20. Schematic illustration for synthesis of ZAIS/ α -Fe₂O₃ via electrostatic adsorption of the ZAIS QDs on α -Fe₂O₃ nanosheets. Copyrights 2021 Elsevier [174].

NPs are probably more popular than QDs for the modification of other structures due to their usually easier and cheaper synthesis methods. For example, Liu et al. have prepared a 0D/2D TiO₂/CoP photocatalyst via in situ growing of titania NPs on the CoP nanosheets by hydrothermal process [175]. It has been found that the optimized composite (1wt% CoP) exhibits the best activity for H_2 generation under UV/vis (Xe lamp; CH₃OH), which is ten times higher than that by pristine titania. It has been proposed that small work function and high conductivity of nanosheets causes the formation of an Ohmic-junction with titania, which can efficiently enhance the charge carriers' separation, thus increasing the photocatalytic activity. In contrast, Bian et al. have used 2D titania structures (mesocrystals) modified with 0D deposits of noble metals as plasmonic photocatalyst [66,67]. It has been proposed that the position of noble metals is detrimental for the overall activity; thus, gold should be deposited on the basal rather than the lateral surface, resulting in electrons migration via titania mesocrystals. In the case of hydrogen evolution under vis irradiation (460 nm > λ > 700 nm; 2-propanol), a second metal should be deposited as a co-catalyst for hydrogen generation (electron transfer from first metal via plasmonic excitation to titania and then to second metal). Therefore, it has been proposed that gold should be deposited on the basal surface, with platinum on the lateral one, causing efficient hydrogen evolution even under vis irradiation.

Furthermore, a more complex structure has also been proposed: 3D titania microflowers (prepared by the hydrothermal method) deposited on $g-C_3N_4$ sheets (prepared by calcination) via solution-mediated self-assembly, as shown in Figure 21 [176]. The photocatalytic activity of the optimized (50 w% $g-C_3N_4$) composite for hydrogen evolution under UV/vis (Xe lamp; TEOA and Pt) is 7.7 and 1.9 times higher than that on bare $g-C_3N_4$ and TiO₂, respectively. Accordingly, it has been suggested that the photo-induced electron/hole pairs in this 3D/2D could be separated efficiently via a direct Z-scheme mechanism.



Figure 21. Schematic representation for the fabrication of 3D TiO₂/2D g-C₃N₄ composites. Copyrights 2019 Elsevier [176].

Well-known sulfides are highly attractive for photocatalysis under vis irradiation due to a narrower bandgap than oxides, but their practical application is limited due to photocorrosion. Accordingly, modification of sulfides with other materials has been proposed to improve their stability and the overall performance of the composite materials [177–179]. For example, cadmium sulfide has been widely used for the formation of coupled materials with advanced morphology, forming efficient and stable photocatalysts, e.g., CdS/Co₉S₈ (3D/0D) [180], CdS/TiO₂ (1D/2D) [181], and CdS/MoS₂ (1D/2D) [182]. Although CdS, in the form of QDs (0D), is commonly applied in photocatalysis [183–185], other organized structures have also been proposed. For example, 3D hierarchical CdS supporting 0D Co_9S_8 NPs has been prepared via a facile solvothermal method [180]. It has been found that the photocatalytic activity (>420 nm; Na₂S/Na₂SO₃) of the optimized material exceeds H₂-generation rate of reference samples, i.e., CdS and Co₉S₈, by ca. 7 and 258 times, respectively. Accordingly, it has been proposed that a synergistic effect, including enhanced light absorption capacity, accelerated separation, and migration of charge carriers, as well as much stronger reduction ability of electrons in the CB of Co₉S₈ (Z-scheme mechanism), are responsible for activity enhancement. Another form of CdS that has been used for composite structures are nanowires (1D). For example, 2D titania with exposed $\{001\}$ facets (nanosheets), pre-modified with Pt NPs (as a co-catalyst for H₂ evolution), has been modified with CdS by reflux method [181]. It has been confirmed that the morphology controls the photocatalytic performance as $Pt/TiO_2(2D)/CdS(1D)$ exhibits 3.7 times higher hydrogen generation rate (>400 nm; lactic acid) than that of the Pt/P25/CdS composite.

Similar 1D structures of CdS (nanorods) have been used by Chava et al. for synthesis (by a two-step facile hydrothermal process; Figure 22) of 1D/3D CdS/MoS₂ heteronanostructures (HNSs) [182]. It has been found that the hydrogen evolution rate under vis irradiation (>420 nm; lactic acid) is 11 times higher than that on pure CdS nanorods. Accordingly, it has been proposed that a synergistic effect between components, due to matched energy band levels causing the inhibition of charges' recombination, is responsible for this enhanced activity, as shown in Figure 23.



Figure 22. Schematic illustration of synthesis protocol for the fabrication of 1D CdS/2D MoS₂. Copyrights 2018 Elsevier [182].



Figure 23. Schematic illustration of the proposed mechanism for enhanced photocatalytic activity during H₂ evolution. Copyrights 2018 Elsevier [182].

Although the majority of studies compare the novel photocatalysts (with well-organized morphology) with either bulk materials or commercial samples, some reports have discussed how slight changes in the morphology (e.g., of one component) might influence the photocatalytic performance. For example, an interesting study has been performed for a porous titania structure modified with CdSe (a sol-gel method with calcination and hydrothermal process) of different morphology, i.e., nanoplates, nanoprisms and nanopyramids [186]. It has been found that the composites with nanoplate-shaped CdS exhibit the highest rate for hydrogen evolution of 3.6 mmol $h^{-1} g^{-1}$ (>400 nm; Na₂S/Na₂SO₃), then nanoprisms (3.1 mmol $h^{-1} g^{-1}$) and nanopiramids (2.5 mmol $h^{-1} g^{-1}$), which additionally is much higher than the activity of bare samples, i.e., 0.5 mmol $h^{-1} g^{-1}$ for pristine CdSe and inactive titania.

As summarized in Table 5, the formation of coupled semiconductors' materials, especially CdS-based systems, is a desired direction for the development of efficient photocatalysts for H₂ evolution. Various scavengers (L-ascorbic acid, methanol, triethanolamine, Na₂S/Na₂SO₃, and lactic acid, etc.) have also been applied for multi-dimensional photocatalysts. Despite this, the effective optimization of multi-dimensional morphologies could combine advantages of mono-dimensional materials and avoid disadvantages of other morphologies, significantly improving the properties and photocatalytic activities. It is clear that organized and well-controlled morphology results in much higher photocatalytic activity also for multi-dimensional photocatalysts. Similar to other dimension structures, the localization of a co-catalyst could be decisive for the overall performance of photocatalysts.

SCs	Modification on SCs	Irradiation Source	Scavenger	Findings	Ref.
α-Fe ₂ O ₃	Zn-AgIn ₅ S ₈ QDs	Xe lamp ($\lambda \ge 420 \text{ nm}$)	L-ascorbic acid	$1.7 \text{ mmol g}^{-1} \text{ h}^{-1}$	[173]
CoP	TiO ₂	Xe lamp	CH ₃ OH	$0.06 \text{ mmol g}^{-1} \text{ h}^{-1}$	[174]
g-C ₃ N ₄	TiO ₂	Xe lamp	TEA	$7.7 \times$ enhancement	[175]
CdS	Co ₉ S ₈ nanoparticles	halogen light (5% UV light)	Na ₂ S/Na ₂ SO ₃	5.15 mmol h $^{-1}$ g $^{-1}$ 6.8× enhancement	[179]
TiO ₂ /CdS	Xe lamp (>400 nm)	Xe lamp (>400 nm)	lactic acid	$35.3 \ \mu mol \ g^{-1} h^{-1}$	[180]
CdS	MoS ₂	Xe lamp	lactic acid	11.85 mmol $g^{-1} h^{-1}$ 11× enhancement	[181]
TiO ₂	CdSe	UV cut-off filter ($\lambda \ge 400 \text{ nm}$)	Na ₂ S/Na ₂ SO ₃	$3650 \ \mu mol \ g^{-1} \ h^{-1}$	[185]

Table 5. Examples of multi-dimensional photocatalysts applied for photocatalytic hydrogen evolution.

7. Conclusions

The photocatalytic generation of hydrogen remains a challenge when it comes to practical applications. One might conclude that the overall efficiencies of this process, reported in the literature, are unsatisfactory. The problems relate, firstly, to the use of sacrificial reagents (electron donors). Considering the fast charge carriers' recombination and backward reactions, with the continuous addition of those substances which are indispensable to allow the reaction to proceed efficiently (half of the water splitting reaction to perform water reduction to hydrogen). Another problematic issue is connected with the nature of these sacrificial reagents, especially in the context of their costs vs. photocatalytic hydrogen generation total costs. Accordingly, the proposed application of wastewater as a hole scavenger is a very attractive possibility; potentially resulting in complete water purification and fuel generation. The crucial element of the considered photocatalytic system is the photocatalyst itself. The proper selection and design of photocatalytic materials can significantly improve the perspective applications of this process. The most often investigated issues determining the efficiency of photocatalysts are the band structure of semiconductor, crystallinity, crystal type and structure, and particle size. However, a photocatalyst morphology is quite rarely taken into consideration in the photocatalysts' design procedures, so far, despite it being known that, in some cases, even a slight change in the morphology could result in significant change in the photocatalytic performance (as also shown in this review). The various morphological configurations belonging to the main dimensional arrangement groups of 0D, 1D, 2D, and 3D, presented in this review, show that their utilization in the photocatalytic hydrogen production systems can provide a promising direction for significant enhancement of the efficiency of hydrogen generation.

One can expect that, probably, all structures of nanomaterials with any capacity to be active under irradiation have already been tested and likely recommended for hydrogen generation. Unfortunately, it is quite hard to compare different structures, as experiments are performed under significantly differing conditions. Additionally, there are some confusing reports, e.g., those suggesting solar water splitting (title or/and abstract) when water reduction in the presence of sacrificial reagents has been only performed under UV/vis irradiation. It should be remembered that bare titania is also active under solar radiation due to the UV part of the solar spectrum, and thus, vis activity for modified titania could not be proven under solar (or simulated solar) radiation. In some cases, authors do not write at all how photocatalytic experiments have been performed. Moreover, sometimes vis, solar, simulated solar, and UV/vis (Xe lamp) irradiation are used interchangeably. Another issue that could cause concern relates to unproven conclusions. It is thought that, in some cases when the study is focused on the morphology, the mechanism is little neglected (no need to answer the question: "why?"). Moreover, many photocatalytic materials are described as "excellent". Accordingly, it is hard to conclude which material is the best and the most highly recommended. Therefore, in general, after consideration of both the pros and cons of various structures (Table 6), it is thought that the composite nanostructure photocatalysts (formed from 0D, 1D, 2D, and 3D) might be the most highly

recommended by this review, since they usually retain the advantages of single components while simultaneously limiting their respective disadvantages.

Table 6. Advantages and disadvantages of different morphologies.

D	Advantages	Disadvantages	Ref.
0D	large SSA, many AS, fast CCM from bulk to surface	aggl.; AS inactivation (easily and uncontrollable), difficult recyc., secondary pollutants	[187–189]
1D	directivity and conductivity, large SSA, high aspect ratio, fast CCM along the axial direction—low E-HR and high PA	E-T-B uneven in size, poor dispersion	[190,191]
2D	large SSA, high stability, used to stabilize 0D (poor stability/aggl.) by loading 0D on 2D	E-T-B re-stacked due to the hydrophobicity and van der Waals force - reduces SSA	[192,193]
3D	easily recy., high stability, overcome shortcomings of 0D, 1D and 2D aggl., AS of each component, large SSA, high porosity and AS, improved CCM and absorbability	req. surfactants or template (secondary pollutant), a problem of subsequent removal (affecting integrity of the structure)	[194–196]

aggl.—agglomeration; AS—active sites; CCM—charge carriers' migration; D—dimension; E-HR—electron-hole recombination; E-T-B—easy to be; PA—photocatalytic activity; SSA—specific surface area; req.—mostly require; recy.—recycle/reuse.

To summarize, although there are many examples of efficient hydrogen evolution methods (even under vis irradiation) on novel photocatalytic materials, there is still insufficient discussion on the influence of the morphology on the photocatalytic activity, while also considering the mechanism clarification. It is thought that further studies should be performed via systematic investigation in this field, in order to understand key factors of photocatalytic activity and to propose commercially acceptable photocatalysts. This should be done while taking into consideration proper reactor design. As a result of further study, practical application of this method can be made possible.

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