A Recent Developments in Photocatalytic Water Splitting by TiO₂ Modified Photocatalysts

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Abstract

As populations grow, global energy consumption in the next 30 years is predicted to rise by nearly 50%. Nowadays and many years before, the most energy worldwide is provided by fossil fuel which leads to severe pollution and contributes to the greenhouse effect. Hydrogen is the most ideal alternative clean energy, but currently, there is no significant hydrogen production from renewable sources. Hence, there is an urgent need for the development of new photocatalysts which will allow a water splitting for hydrogen production. The photocatalytic water splitting using TiO₂ offers a promising approach for clean, low-cost, and environmentally friendly production of hydrogen as a sustainable fuel. This paper reviews some recently used methods of synthesis such as hydrothermal, rapid breakdown anodization method, impregnation method, and sol-gel synthesis for the preparation of modified TiO₂ materials. These methods of synthesis provide the production of ultra-thin mesoporous TiO₂ nanosheets, nanorods, and nanotubes as well as heterojunction structures. Some investigations show that introduction of Ti³⁺ atomic defects is beneficial for the photocatalytic water splitting for hydrogen generation. Some progress has been achieved by heterocoupling the two or more semiconductors. There is experimental evidence that in the presence of alcohol as a sacrificial agent, H₂ production rates decreased from a higher number of hydroxyl groups i.e. in order 3>2>1. The H₂ generation is also larger when TiO₂ is modified with the addition of small quantity of metal nanoparticles such as Pt, Pd, and Ni. One study has shown that the samples sensitised with Pt nanoparticles were superior to Pd and Ni modified TiO₂, the other has shown that the co-catalyst activity followed the order Pd>Pt≈Au.

Keywords: Photocatalysis; Water splitting; Hydrogen production; Modified TiO₂; Nanoparticles

Introduction

As populations grow, global energy demands together with their potential environmental impact are expected to increase even more in the coming years. According to the U.S. Energy Information Administration (EIA), between 2018 and 2050, the world energy consumption is predicted to rise by nearly 50% [1]. In 2010, fossil fuels provided about 80% of all primary energy worldwide [2]. The combustion of fossil fuels lead to severe pollution and contributes to the greenhouse effect. Climate is a main driver for hydrogen in the energy transition. Limiting global warming to below 2 degrees Celsius (°C) requires that CO₂ emissions decline by around 25% by 2030, from 2010 levels, and reach net zero by around 2070 (IPCC, 2018) [3]. For a reasonable likelihood to stay below 1.5 °C of warming, global net anthropogenic CO₂ emissions should decline by around 45% by 2030, from 2010 levels, reaching net zero by around 2050 [3].

The world must therefore balance the role of energy in social and economic development with the need to decarbonise, reduce our reliance on fossil fuels, and transition towards lower-carbon energy sources. Hence, there is an urgent need for the development of clean and sustainable sources of energy. Hydrogen is considered to be the most ideal alternative clean energy because of its high calorific value, zero pollution, and storability, and it is widely considered to be the future clean energy carrier in many applications, such as environmentally friendly vehicles, domestic heating, and stationary power generation. Today, around 95% of
all hydrogen is generated from natural gas and coal resulting in the release of 70 to 100 million tonnes CO$_2$ annually in the EU (EC, 2020) [4].

For hydrogen to contribute to climate neutrality, it needs to achieve a far larger scale and its production must become fully decarbonised. Around 5% is generated as a by-product from chlorine production through electrolysis. In the iron and steel industry, coke oven gas also contains a high hydrogen share, some of which is recovered. Currently there is no significant hydrogen production from renewable sources. However, this may change soon. Currently, hydrogen is used mostly in oil refining and to produce ammonia [5].

Water splitting and alcohol photo-reforming using semiconductor photocatalysts and sunlight are promising future technologies for H$_2$ production. Water splitting plays an important role in producing of green and clean energy in the form of H$_2$ for the next generation. The generation of chemical fuels from water and sunlight is one of the key scientific challenges for the 21st century. Nowadays, hydrogen is being produced in large quantities for industrial and commercial purposes. Yet only 5% of commercial H$_2$ is produced through electrolysis of water and the rest entirely depends on the fossil fuel sources [6,7].

Since the first discovery of photocatalytic water splitting on a TiO$_2$ electrodes observed by Fujishima [8] researchers have focused on it using a variety of semiconductors such as TiO$_2$ [9], graphitic-carbon nitride [10], and CdS [11]. Among them, TiO$_2$ attracted much attention of many research groups and quickly became the most studied and used semiconductor for photocatalysis [12-15]. TiO$_2$ is considered as a promising semiconductor because of the advantages such as low cost, harmlessness, resistance to photo-induced corrosion and ease of handling but its performance is still limited due to its large bandgap, approximately 3.2eV for the anatase phase in powders [16-19].

Thus, to address these difficulties, it is extremely desirable to search for new materials that could split water by absorbing visible light. In this regard, modifications in titania for accelerating photocatalytic hydrogen generation from water is a favorable approach. Various attempts have been carried out to modify TiO$_2$ in order to present a response with visible light [20]; some techniques include the doped with metals [21] and non-metals [22], as well as several sensitization methods with dyes [23], quantum dots [24], and coupling of other semiconductors (as a heterojunction composite) [25,26], among others.

TiO$_2$ has a wide range of applications and it was extensively discussed in previously published papers for wastewater treatment such as photocatalytic degradation of organic compounds, as well as micro- and nano-plastics, etc. [27-31]. During photocatalytic water splitting the hydrogen is produced. Many research studies have shown that higher amount of hydrogen is produced in the presence of an electron donor such as alcohol (methanol, other primary alcohols, or polyols such as ethylene glycol) i.e. in the water-alcohol solution and differently dopped TiO$_2$ photocatalysts [32].

Alcohol as a sacrificial agent has lower splitting energy than water. Many published papers mention that “water splitting” are actually related to redox of the additives or probably corrosion and therefore do not deal with water splitting [33,34]. In a last decade, different type of nanomaterials and its composites have been developed and used for a wide range of applications which among others include photocatalytic reactions and hydrogen production and fuel cells [35-39].

Figure 1 shows a plot of number of publications about “photocatalytic water splitting” versus publication year [ScienceDirect on 23.07.2020]. The figure shows increasing numbers of publications in last ten years which indicate very high interest in photocatalytic water splitting from year to year. Nevertheless, hydrogen production systems based on heterogeneous photocatalysis are in constant development and change, as researchers look for more environmentally friendly photocatalytic processes.

Figure 1: Number of publications about “photocatalytic water splitting” versus publication year
Methods of synthesis

In this section an overview of different methods of synthesis such as hydrothermal approach, sol-gel method, rapid breakdown anodization will show different shapes of TiO₂ and its photocatalytic properties.

Hydrothermal synthesis of ultra-thin mesoporous TiO₂ nanosheets: The study carried out by Li et al. [40] offers inspiration for designing efficient photocatalysts and provides valuable insights towards defect engineering in photocatalysts. They were successfully synthesized ultra-thin mesoporous anatase TiO₂ nanosheets for hydrogen evolution from water splitting. The synthesized mesoporous TiO₂ has optimum aperture almost keeps around 2nm and the surface area is around 152.938 m²/g and pore volume 0.162 cm³/g.

Ultra-thin mesoporous TiO₂ nanosheets with high crystallinity have been obtained through a facile hydrothermal approach with the assistance of chloride ions, which is not only beneficial for obtaining stable mesoporous TiO₂ with high crystallinity, enlarging surface area to 178.496 m²/g and the pore volume to 0.201 cm³/g. Although the surface area and pore size have less decrease after ethylene glycol treatment, the pore volume enhances. It thus demonstrated that this facile Cl ions assisted method could lead to obtaining stable anatase TiO₂ nanoparticles with high crystallinity while retaining or even enlarging surface area. Ti^{4+} atomic defects in the ultra-thin mesoporous TiO₂ play a crucial role in suppressing the recombination of electron-hole pairs and enhancing the photocatalytic H₂ production rate. They explored the photocatalytic activity of the mesoporous TiO₂ towards photocatalytic water splitting under simulated solar light irradiation without filter. The experimental results have shown that H₂ generation yield of pristine mesoporous TiO₂ is only 2.845 mmol h⁻¹ g⁻¹, while it reaches to 3.157 mmol h⁻¹ g⁻¹ in high crystallinity TiO₂ and 4.543 mmol h⁻¹ g⁻¹ after further introducing Ti⁺⁺ defects. As expected, the increase rate of TiO₂ with Ti⁺⁺ defects reach 59.66%, which far exceeds that of others. It further confirms that the introduction of Ti⁺⁺ atomic defects is beneficial for the photocatalytic water splitting for hydrogen generation. They found a H₂ yield of 3.507 mmol h⁻¹ g⁻¹ without the Pt particle deposition indicating that Ti⁺⁺ point defects are beneficial for photocatalysis performance. They conclude that removing excess unfavourable defects and reintroducing advantageous ones is a promising way to improve photocatalysis performance.

Dosado et al. [41] were prepared a series of titania nanorods with different phase compositions and surface areas by calcination of hydrogen titanate (H₂Ti₃O₇) nanotubes at temperatures (150-1000 °C). Sodium titanate (Na₂Ti₅O₁₄) nanotubes were synthesized by alkaline hydrothermal treatment of the anatase TiO₂ powder. Hydrogen titanate (H₂Ti₃O₇) nanotubes were synthesized from the Na₂Ti₅O₁₄ nanotubes by ion exchange. Briefly, the sodium titanate nanotubes were dispersed in 1 M HCl (500 mL) for 2 h. Gold nanoparticles were deposited on the H₂Ti₃O₇ nanotubes, TiNTₓ (x=calcination temperature=350-1000) and Degussa P25 supports at nominal Au loading of 0.5, 1.0, 1.5 or 2.0 wt.% using the deposition-precipitation with urea method. The results of their research showed that 0.5 wt.% Au/TiNT600 photocatalyst has excellent H₂ production activity in all the alcohol-water systems, performing similarly to a 1.5 wt.% Au/P25 reference photocatalyst. For both the 0.5 wt.% Au/TiNT600 and 1.5 wt.% Au/P25 photocatalysts, H₂ production rates decreased in the order triol (glycerol) > diol (1,2-ethanediol ≈ 1,2-propanediol) > ethanol > 1-propanol. Good correlations were found between the H₂ production rates and alcohol properties such as the number of hydroxyl groups, polarity, or standard oxidation potential.

Rapid breakdown anodization method: Manovah et al. [42] have prepared TiO₂ nanotubes powders via rapid breakdown anodization sensitized with Pt, Pd and Ni nanoparticles (NPs) for photocatalytic water splitting i.e. for photogeneration of H₂. The samples sensitized with Pt NPs were superior to Pd and Ni sensitized TiO₂ NTs powders. Noticeably, the smaller the quantity of the NPs loaded over the TiO₂ NTs better the photogeneration of the H₂ molecules. They have found that the H₂ generation is larger with the addition of metal NPs and moreover lower quantity deposits produced better results. Pt NPs addition was better among the group in terms of H₂ generation over the other metals of the same group. The Pt/TiO₂ NTs with 5% metal sensitization generated H₂ with a specific release rate of 241.8 μmol g⁻¹ min⁻¹ [42].

Impregnation method: Salas [43] in his PhD dissertation demonstrates that hydrogen can be produced photocatalytically using a modified Degussa P25 (TiO₂)-Pt photocatalyst in a slurry medium under near-UV irradiation and having ethanol as a sacrificial reagent (hole scavenger). The system employed for the photocatalytic hydrogen generation was the Photo-CREC Water II Reactor. This unit was used with a specially designed H₂ collector tank and a BLB Lamp that permits the entire use of the near-UV irradiation spectrum.

The modified DP25-Pt photocatalyst was prepared using the incipient wetness impregnation technique. The Pt modified photocatalyst exhibited a 2.73 eV reduced band gap. The use of 2v/v% ethanol as a sacrificial reagent enabled producing significant hydrogen amounts with the simultaneous formation of CH₄ and C₂H₆ by products. It is proven that hydrogen formation in the presence of ethanol is a function of water solution pH and Pt loading on the TiO₂ photocatalyst. Concerning energy efficiencies, it was observed that the best results obtained are at pH=4 with 7.9% quantum yield for hydrogen production.

In Table 1 is summarized the influence of method of synthesis and modification of TiO₂ reaction medium on H₂ yield.

Sol-gel synthesis of TiO₂ thin films: Thin titanium dioxide (TiO₂) films show good electrochemical and photocatalytic properties for photocatalysis applications. The textural properties such as thickness, surface roughness, grain or particle size, pore size distribution and porosity of the TiO₂ films influence on photocatalytic activity [44].
**Table 1:** Influence of method of synthesis, modification of TiO<sub>2</sub> and reaction medium on H<sub>2</sub> yield.

| Modified TiO<sub>2</sub> | Method of Synthesis | Reaction Medium | Yield of H<sub>2</sub> (mmol h<sup>-1</sup> g<sup>-1</sup>) | Yield of H<sub>2</sub> (μmol min<sup>-1</sup> g<sup>-1</sup>) | Yield of H<sub>2</sub> (cm<sup>3</sup> h<sup>-1</sup>) | Ref |
|------------------------|---------------------|-----------------|---------------------------|---------------------------|---------------------------|-----|
| 1                      | TiO<sub>2</sub> pristine High crystallinity nanosheets with Ti<sup>3+</sup> defects without Pt | hydrothermal | water | 2.845 | 3.157 | 4.543 | 3.507 | [40] |
| 2                      | TiO<sub>2</sub> nanotubes with Pt, Pd and Ni nanoparticles TiO<sub>2</sub>NTs 5%Pt NPs 10%Pt NPs 5%Pd NPs 10%Pd NPs 5%Ni NPs 10%Ni NPs | breakdown anodization | water | 2.676 | 44.6 | 14.508 | 241.8 | [42] |
| 3                      | Pt modified Degussa P25 DP25;0% Pt DP25;0.06% Pt DP25;0.2% Pt DP25;1.0% Pt | Impregnation | 2v/v% ethanol; pH=4 | 0.66 | 1.71 | 3.99 | 7.83 | [43] |
| 4                      | M/TiO<sub>2</sub>(M = Pd, Pt, Au) 1 wt.% Pd/TiO<sub>2</sub> | deposition precipitation with urea method | glycerol–water mixtures 1,2-ethanediol–water mixtures | 47.5 | 44.5 | | | [32] |

These textural properties depend on the sol properties (sol reactivity, viscosity, water-to-alkoxide ratio, precursor concentration, complexing agent, surfactant) [45,46]. The sol properties can be controlled by varying its composition. Spin-coating of TiO<sub>2</sub> sol-gel is the common deposition method used to coat TiO<sub>2</sub> thin films on the glass substrates due to its low cost, experimental simplicity, easy scale-up ability [47]. In the sol-gel method, hydrolysis of metal alkoxides occurs first followed by the polycondensation of hydroxyl and/or alkoxy groups thus forming the oxide polymer network of TiO<sub>2</sub> via Ti-O-Ti route [48]. Two main reactions in the sol-gel process are hydrolysis of titanium tetraisopropoxide (TTIP) with water and condensation of hydrolyzed TTIP.

The faster hydrolysis of the TTIP with water results in the rapid precipitation of hydrolyzed TTIP due to high reactivity, which in turn leads to non-homogeneity in the films. Therefore, the hydrolysis rate needs to be controlled in order to avoid precipitation and to achieve sol-gels with desired properties to obtain highly homogeneous TiO<sub>2</sub> thin films [49,50].

**Effect of sacrificial agent on water splitting**

Many research studies carried out in the last thirty years have shown that direct photocatalytic water splitting to H<sub>2</sub> and O<sub>2</sub> using a wide range of semiconductor photocatalysts is too low to justify industry uptake. H<sub>2</sub> production rates can be increased by several orders of magnitude using renewable sacrificial agents such as...
ethanol or glycerol, though further work is necessary to realise target H₂ production rates of 2-3 mmol gcat⁻¹ min⁻¹ under direct sunlight that are needed to attract industry interest.

For example, in a Pt/TiO₂-water-methanol system, methanol is oxidized by means of the photogenerated valence band (VB) holes on the metal-decorated photocatalyst thus permitting the reduction of water to hydrogen by photogenerated electrons in the conduction band (CB). Such sacrificial reagents react irreversibly with the photogenerated holes and enhance consequently the electron/hole separation. This concept could be used for the photocatalytic production of hydrogen with simultaneous degradation of pollutants or what is known as photo reforming [7].

In 2015 Al Azri et al. [32] found that M/TiO₂ (M=Pd, Pt, Au) photocatalyst activity for H₂ production depends on both the metal co-catalyst (M) and the reaction medium (different alcohol-water mixtures). They were prepared photocatalysts using Degussa P25 TiO₂, at metal loadings of 0.5 and 1.0 wt.% for Pd, and 1.0 wt.% for Pt and 1.0 wt.% for Au. The activities of the M/TiO₂ photocatalysts for H₂ production were evaluated in a wide range of alcohol-water mixtures (alcohol concentration 10 vol. %) under UV (365nm, 5mWcm⁻²). H₂ production rates in the alcohol-water mixtures were dependent on (i) the metal co-catalyst; (ii) the co-catalyst loading; and (iii) the alcohol type. Co-catalyst activity followed the order Pd>Pt>Au. Metal co-catalyst particle size was not important for achieving high hydrogen production rates in the M/TiO₂ systems, at least within the size range 1-6nm. The highest H₂ production rates were achieved for the 1.0 wt.% Pd/TiO₂ photocatalyst in glycerol-water mixtures (47.5 mmol g⁻¹ h⁻¹) and 1.2-ethanediol-water mixtures (44.5 mmol g⁻¹ h⁻¹). H₂ production rates decreased in the order glycerol > 1,2-ethanediol > 1,2-propanediol > methanol > ethanol > 2-propanol > tert-butanol ≫ water. For each M/TiO₂ photocatalyst, correlations were established between the rate of H₂ production and specific alcohol properties, especially alcohol polarity and the exponential of the alcohol oxidation potential.

Heterojunction structures

In order to prevent the rapid charge carrier recombination and to isolate the redox sites on the catalytic surface separately, it is essential to spatially separate the electrons and holes in different compartments which can be accomplished by heterocoupling the two or more semiconductors. Recently heterojunctions formed between two solid materials have attracted more attention, including semiconductor-semiconductor S-S, semiconductor-metal S-M, and semiconductor-carbon S-C (carbon nanotubes, graphene, etc.) heterojunctions [51].

Some progress has been achieved in the use of complex oxides (RhSrTiO₃ [52], PbBi₂NbO₆ [53], Sr₂NbO₅ [54] and oxynitrides SrNbO₃N [55], LaTiO₂N [56], and TiON [57]) for overall water splitting under visible light but these materials are either difficult to synthesise in pure form, or the efficiencies reported are comparatively moderate. However one of the most promising, but lesser studied oxynitrides for overall water splitting under visible light is Ta₂O₃ (CBE at -0.3 V vs. NHE, pH 0), which has recently received much attention through its incorporation into a heterojunction, for example with CaFe₂O₄ [58], N-doped TiO₂ [59], and Cu₂O [60]. It is clear that transition metal oxynitrides have great potential in the future for utilization in water splitting systems, however more research into this emerging family of photocatalyst materials is required, particularly their incorporation into junction architectures.

During the composite formation, defect density at the interface minimizes and the new functionalities arising at the interfacial structure that is normally not attained in their respective single phases. The coupling of ZnO with TiO₂ overlayer avoids the photo corrosion of ZnO and also improves the light absorption properties of ZnO-TiO₂ as ZnO owns high absorption efficiency compared to pure TiO₂ [61]. Electron transfer takes place from ZnO to TiO₂ because electron derived from ZnO is more negative, while inter component hole transfer may not be significant as VB edge position of both ZnO and TiO₂ are almost same. Along with the latter, absorption range of this composite is not altered as both are wide gap in nature. Therefore, ZnO-TiO₂ composite may not be beneficial in all the cases. However, pronounced blue shift up to 3.8 eV was noticed for this composite when fabricated through combined sol-gel technique and dip coating on the quartz substrate [62].

Mechanisms of semiconductor photocatalytic water-splitting

TiO₂ is a semiconductor consists of valance band (VB) and conduction band (CB). Energy difference between these two levels is said to be the band gap, E₇. Without excitation, both the electrons and holes are in valence band. When semiconductors are excited by photons with energy equal to or higher than their band gap energy level, electrons receive energy from the photons and are thus promoted from VB to CB if the energy gain is higher than the band gap energy level.

The photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactants adsorbed by the semiconductor. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production. Thermodynamically, the water splitting reaction is an uphill process, i.e. is an endothermic reaction requiring a minimum energy of 1.23eV because the Gibbs free energy change ΔG° = 237.2kJ mol⁻¹ or 2.46eV per molecule of H₂O and therefore requires high overpotentials [63]. Nature itself demonstrates an efficient strategy to utilise solar irradiation (near unity quantum yield) by spatially separating electrons and holes in wireless photosynthesis reactions. The process of water splitting can be envisaged as two half reactions: water oxidation, and secondly, proton reduction to hydrogen fuel.

For hydrogen production, the CB level should be more negative than hydrogen production level (E₇/H₂O) while the VB should be more positive than water oxidation level (EO/H₂O) for efficient oxygen production from water by photocatalysis [7]. In the case of photocatalytic water splitting, a catalyst absorbs photon energy
and consequently, electrons are transferred from its valence band to its conduction band. If its band gap is large enough, above that needed for water splitting (1.23 eV), and its band edges meet the thermodynamic requirement for the charge transfer to occur, then in principle, excited electrons can reduce hydrogen ions and holes can oxidize oxygen anions [64].

The photocatalytic hydrogen production from water splitting by TiO$_2$ is shown in Figure 2. Theoretically, all types of semiconductors that satisfy the above-mentioned requirements can be used as photocatalysts for hydrogen production. Having strong catalytic activity, high chemical stability and long lifetime of electron/hole pairs, TiO$_2$ is the most widely used photocatalyst.

![Figure 2: Mechanism of TiO$_2$ photocatalytic water splitting for hydrogen production.](image)

According to the proposed mechanism when metal nanoparticles (NPs) are used for sensitizing TiO$_2$ upon exposure to UV light of 365nm, TiO$_2$ NPs form electrons and holes [65]. The electrons first move to the CB of the TiO$_2$ and from there it interacts with the metal NPs. It is the interaction of these electrons with the metal NPs that decide the photocatalytic route to be taken by each of the sample. Moreover, the photoexcited e- transfers from TiO$_2$ to Pt until the Fermi level equilibrium is attained resulting in high conductivity, largely reducing the possibility of recombination. Now, the electrons from Fermi level of Pt NPs interact with the hydrogen ion (H$^+$) to form hydrogen molecule (H$_2$). In the case of Pd NPs, the metals form a surface metal oxide and when the e$^-$ is transferred from TiO$_2$, the metal ions get reduced to metal (Pd0) in the case of Pd [66]. The electrons held by Pd are then transferred to hydrogen ion to eventually form gaseous H$_2$ molecule. Interestingly, the involvement of ethanol is observed to act as a better electron donor [6]. During the prolonged separation of the e$^-$/h$^+$ pairs, the e$^-$ from the electron donors interacts irreversibly with h$^+$ in the VB of TiO$_2$ further separating thereby increasing the quantum efficiency. Furthermore, it suppresses the backward reaction [67].

### Discussion

In order to start water splitting reaction it is need to supply some energy since it is an endothermic reaction requiring a minimum energy of 1.23 eV because the Gibbs free energy change for the reaction is $\Delta G^\circ=237.2$kJ mol$^{-1}$ or 2.46 eV per molecule of H$_2$O. This required energy coming from modified TiO$_2$ species after its activation with certain wavelength light.

It was seen that modification of TiO$_2$ is possible to carry out using different methods of synthesis as well as different selection of starting compounds (presence or absence of sacrificial agent) and co-catalysts. It should be emphasized that in the presence of sacrificial agents not only hydrogen is produced but also is evident simultaneous formation of CH$_4$ and C$_2$H$_6$ by products. Someone should also study selectivity of the prepared photocatalysts regarding the presence of by-products. From all mention above methods of synthesis, the best yield of hydrogen is achieved with the method of nanoparticles modification of TiO$_2$ and in the presence of water-alcohol mixtures.

### Conclusion

Photocatalytic water splitting and hydrogen production as a clean way of energy can contribute to replacing fossil fuel and reduce greenhouse gas emissions. It has been studied different methods of synthesis of photocatalytic materials based on TiO$_2$ and its use for the photocatalytic water splitting for hydrogen generation. This review paper has shown that there are advances and achievements in the development of new photocatalysts for water splitting, but more research is required especially if someone wants to scale up this process and become alternative related to the current way of hydrogen production.

### Conflict of Interest

There are no conflicts to declare.

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