Supported Plasmonic Nanocatalysts for Hydrogen Production by Wet and Dry Photoreforming of Biomass and Biogas Derived Compounds: Recent Progress and Future Perspectives

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Nowadays, the pursuit of a circular economy and sustainability pushes the world’s efforts toward less fossil fuel-dependent energy production strategies. The sense of sustainability, thus, means searching for effective approaches involving ecological fuels, and processes with a little environmental concern. Approaches for utilization of such renewable resources like solar energy as a driving force, and biomass-derived compounds as feedstocks for simultaneous hydrogen production as the most promising energy carrier, are currently gaining their momentum as the solutions for sustainable energy generation and tackling climate change. In this paper, we review the scientific advances in photocatalytic hydrogen production from biomass-derived compounds via wet- and dry- photoreforming over metal-loaded-semiconductor photocatalysts. Based on the recent literature reports, we narrowed focus particularly to designing the state-of-the-art photocatalysts which renders substantial enhancement of their performance possible via localized surface plasmon resonance effect.

1. Introduction

Over the last decade, the constant growth of energy demands, by 1.7% annually, is observed. Concerns are growing regarding such increment, because the global energy economy strongly relies on fossil fuels whose transformation into energy implies a major global challenge – greenhouse gas emission into the atmosphere. Current policies, restructuring programs, and global endeavors are undertaken towards new fuel options to better fulfill the potential of renewable resources in sustainable energy production.

Hydrogen is deemed a perfect candidate for the status of the “fuel of the future” and the ‘energy vector’\(^{[1]}\) for a future decarbonized energy system\(^{[2]}\) due to its highest energy density, zero-emissivity,\(^{[3]}\) and the highest mass abundance amongst elements on the Earth. A popular classification, related to used feedstocks and carbon emissions during the production process, distinguishes three main types (“colors”) of hydrogen i.e. gray, blue and green.\(^{[4]}\) The most attractive and desired “color” of the hydrogen, as a clean and sustainable fuel, is green which is the cleanest one due to zero carbon emissions.\(^{[5]}\) Green hydrogen is mostly generated via electrolysis powered by electricity from renewable energy sources. Thus, producing large amounts of green hydrogen requires appropriately larger electrical energy generation capacities (from renewable sources) which must be affordable if the economic competitiveness of the green hydrogen is expected. Industrially-efficient hydrogen production is mostly realized via the steam reforming of methane from natural gas,\(^{[6,7]}\) but the generation of carbon dioxide as a product disqualifies this method from being sustainable. Besides, natural gas hydrogen can be a product of transformation of hydrogen-containing resources such as coal, biomass components and derivatives,\(^{[8–11]}\) or water through gasification, thermal decomposition, electrolysis, or photolysis.\(^{[12]}\) Regrettably, most of these methods require external maintenance energy i.e., heat or electricity, or even the utilization of non-renewable \(\text{H}_2\) sources. Presently, processes utilizing water as a feedstock are the most energy-consuming so thus they allow generation amounts of hydrogen related to its world production.

Hydrogen production by means of photocatalytic methods emerges as a renewable alternative for broadly utilized techniques relied on fossil fuels as well as a solution to achieving sustainable energy soon. Therefore, the Sun provides enormous, in terms of reserves and renewability, energy of 1022 J that arrives at the Earth’s surface daily.\(^{[13]}\) Solar energy-driven catalytic processes are challenging both, in terms of materials (catalysts) and process design, but very prospective for the creation of environmentally benign processing routes that inspired many scientific explorations to date.\(^{[14–15]}\) Besides being clean and sustainable, direct solar-to-hydrogen photovoltaic processes (photocatalytic, photoelectrochemical, photobiological, photovoltaic)\(^{[16]}\) may be conducted at near-ambient conditions and are less complex comparing to solar-thermal systems. Photocatalytic hydrogen generation may be carried out in aqueous organic solutions containing sacrificial agents such as alcohols (methanol, ethanol, 2-propanol) or organic acids (formic or acetic acid)\(^{[17]}\). Photocatalytic water splitting, is particularly demanding from the thermodynamics point of view\(^{[18–20]}\) but offers unquestionable advantages allowing simultaneous hydrogen generation and wastewater remediation (removal of organic contaminants) and cultivation.\(^{[21–22]}\) Organic compounds, called sacrificial agents, are substances having an unique capabilities to more effective (than water) combine with the photo-generated valence band
holes more, and to be subjected to valorization. Such process resulting in the elimination of organic contaminants, particularly biomass-derived, from wastewater under solar irradiation is called photo-reforming and currently gains its momentum as a reasonable alternative for its conventional counterpart (steam reforming of methane; SMR) broadly applied in the industrial practice. However, in the case of photogenerated hydrogen, economic and environmental interests are strongly affected by the efficiency and the cost of hydrogen generation per one kilogram of feedstock that originate from poor quantum efficiency of conversion of the energy of photons into hydrogen. It constitutes the real limitation, by far, for large-scale applications, and one possible solution is boosting the photocatalyst efficiency by a combination of the most beneficial features of conventional, thermal catalysis and highly efficient solutions for solar energy harnessing. To this end, nanophotocatalysts, in particular their metal/semiconductor heterojunctions, have to be properly designed allowing efficient collection of photons, induction of localized surface plasmon resonance (LSPR), and local thermal effect by a generation of significant portion of heat in the nanoscale regions. Thermo-photocatalytic system conditions are induced with no need of heating the entire system (avoiding thermal cycling limitations). Literature reports focus mostly on metal-loaded semiconductor nanoparticles as photocatalysts for H₂ production consisting of the hetero-junctions of Au, Ag, Cu, and Pt (with many possible morphological variations) as plasmonic-metal part with sulfides (ZnS, CdS, ZnCdS, ReS₂, MoS₂) or TiO₂ semiconductors as the semiconductor support. Specifically, “function-oriented” design, via shaping elemental composition or morphology, enables plasmon nanocatalysts to achieve substantially boosted photocatalytic activity in H₂ evolution that is unable to achieve by their counterparts separately.

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Reliable way of reporting the activity of photocatalysts in H₂ production is currently a subject of growing debate. The evaluation of the activity of the photocatalysts expressed as the amount of evolved hydrogen gas per weight of photocatalysts is the most common way used by the authors. Unfortunately, this unit may not give a comprehensive insight on all determinants of their performance. Many relevant factors, i.e. reactor and irradiation conditions or morphological characteristics of the material, should be identical whether the comparison is to be reliable. If they are not identical, the activity should be additionally described using other, already proposed measures i.e. internal quantum yield (IQY) or apparent quantum yield (AQY), and solar-to-hydrogen (STH) conversion efficiency, in order reflect different aspects of the photocatalyst performance. However, detailed information of the set-up or irradiation, needed for calculation of these parameters, are not easy to find or simply unavailable in published reports. Therefore, in the present review, to summarize available data, we decided to use hydrogen production rate per gram of a catalyst per time (μmol g⁻¹ cat⁻¹ h⁻¹) which is still the widespread unit in the literature.

In this review, we summarize the current scientific achievements which reflect the progress in the field of supported plasmonic nanocatalysts development and both, wet- and dry-, photoreforming of biomass-derived compounds for sustainable hydrogen production. In the Introduction (Section 1), we would like to emphasize the value of the “green hydrogen”, together with the great importance of solar irradiation incorporation into hydrogen generation with the particular attention to plasmonic-enhanced photoreforming of biomass-derived compounds. Next Sections – 2 and 3 – we would like to devote a literature review on the current status of the development of plasmonic nano-photocatalysts regarding their chemical composition, structure, and performance in H₂ generation from the 1st and 2nd generation of biofuels, respectively. As the most attractive 1st generation biofuels, we have chosen methanol, ethanol, and glycerol, while as 2nd generation, cellulose and its valuable derivative – glucose. As the process of huge importance for world energy conversion industry, we propose to similarly comment on the dry methane reforming process (DRM) in Section 4. Finally, in the last Section 5, we sum up the challenges ahead the photo-hydrogen production from biomass-derived compounds by plasmonic photocatalysis and the outlook for its rewarding implementation on a large, industrial scale.

2. Plasmonic Enhanced Hydrogen Production from the 1st Generation of Biofuels

2.1. Photoreforming of methanol

Methanol contains only one hydroxyl group and one atom of carbon, thus, it is the simplest alcohol considered as the model molecule for the photocatalytic hydrogen production reaction as well as, looking perspective, the basic energy feedstock. This one-carbon substrate is attractive due to its low price, easy handling and abundant availability. Methanol is currently of huge interest in the chemical industry, because half of its world’s resources are used in various chemical applications and production of chemicals, and the other half is used in energy-related applications.

In the field of energy-related applications, biodiesel must be mentioned as well as the applications of methanol as cooking or marine fuels, which meet emissions regulations and constitute clean-burning alternatives for gasoline. Due to the compatibility with the existing petroleum infrastructure, methanol is called “the next chemical vector” after petrol. The most advantageous feature of methanol, from the future prospect point of view, is that it can be easily turned into hydrogen through catalytic processes incorporating solar irradiation as a renewable driving-energy resource.

Hydrogen generation by photoreforming of methane was the first time reported in 1980 by Kawai and Sakata. The proposed reaction mechanism proceeded through the subsequent steps: formation of formaldehyde, its oxidation to formic acid, and decomposition to carbon dioxide and hydrogen, as follows [Eqs. (1–3)]:

\[
\begin{align*}
\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2 \\
\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{H}_2 \\
\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\]

The fundamental work was continued by IR spectroscopy measurements and, based on the results, the alternative path involving two reactions [Eqs. (4) and (5)] in the presence of water has been proposed. The additional conclusion is that when the carbon dioxide is present, the water splitting reaction occurs.

\[
\begin{align*}
\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2
\end{align*}
\]

A mechanism proposed for catalytic photoreforming of methanol on Pd/TiO₂, based on further studies, is summarized in Figure 1. A detailed description of the subsequent steps in the reaction mechanism [Eqs. (6–10)] can be written as follows:

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{S} \rightarrow \text{CO} + 2\text{H}_2 \\
\text{TiO}^{2+} + \text{hv} \rightarrow \text{Ti}^{3+} + \text{O}^- \\
\text{CO} + \text{O}^- \rightarrow \text{CO}_2 + \text{S} + \text{V}_o \\
\text{H}_2\text{O} + \text{V}_o \rightarrow \text{O}^- + \text{H}_2 \\
\text{Ti}^{3+} + \text{O}^- \rightarrow \text{TiO}^{2+}
\end{align*}
\]
and schematically illustrated in Figure 2.  

According to the cycle mechanism proposed, the photo-reforming process begins when methanol adsorbs on the active surface of the catalysts. After that, it is dehydrogenated, and CO is strongly bonded at the surface therefore can poison the catalyst – reaction [Eq. (6)]. The catalyst surface is unblocked once the catalyst is irradiated by light, and bandgap excitations induce creation of reactive forms of oxygen – reaction [Eq. (7)], and CO after interaction with that species is removed as CO$_2$ – reaction [Eq. (8)]. CO$_2$ desorption leaves a vacant site on the metallic surface, which constitutes an active site for methanol re-adsorption and liberation of 2 moles of hydrogen. Anion vacancy created at the catalyst surface is refilled by water adsorption and dissociation – reaction [Eq. (9)]. Consequently, the third mole of hydrogen is liberated, and the system returns to the initial state, and the photo-catalytic cycle can be processed again.

Most of the catalysts examined in the literature are titania-based systems. Pure titania (mostly P25 anatase), however, represents very poor reactivity in photoreforming of methanol with water at ambient temperature, but it is strongly determined by the ratio of methanol to water in the solution. It has...
been stated that the rate of hydrogen liberation due to the photoreforming of methanol over titania are substantially higher for higher methanol concentrations and reach the optimum level, in terms of hydrogen yield, with approximately a 1:1 MeOH/H₂O solution.[22] The reaction may be also carried out in the gas phase, but anion vacancies re-oxidation is a very slow process on P25 titania, thus, the overall efficiency is poor. Many scientific efforts in the last decades were focused on the functionalization of TiO₂ (or other semiconductors as support) by nanoplasmonic plasmonic metal (co-catalysts) to improve the efficiency in low-temperature, photocatalytic reforming of methanol.[13,18,44,46] Therefore, it has been postulated and proven that H₂ evolution takes place on the co-catalyst.[45,46] Based on a systematic study of TiO₂ with noble metals (Ag, Au, Pt) as co-catalysts, a correlation between activity and the amount of co-catalyst and the work function values of the co-catalyst was observed. Generally, the enhancement of photoactivity of metal loaded-TiO₂, as a consequence of Schottky barrier formation, can be ordered as follows: Ru/TiO₂ < Ag/TiO₂ < Rh/TiO₂ < Pd/TiO₂ < Au/TiO₂ < Pt/TiO₂.[13,45,46] Similarly, to pure titania, hydrogen evolution over metal co-catalyst-loaded titania proceeds at higher rates in the gas phase than in the liquid phase, and when the methanol concentration is higher in the solution. For the Pd/TiO₂ (rutile) catalyst the H₂ production rate is even 10 times higher for gas phase versus liquid phase.[45]

As can be seen from all the given examples, in order to obtain a powerful photocatalytic system utilizing the plasmonic effect, a plasmonic metal nanoparticle is coupled in various configurations with a semiconductor exhibiting photocatalytic properties. The authors of the article[46] drew attention to the role of the size and shape of the semiconducting support, TiO₂ in this case, decorated with metallic particles, i.e. Pt, on the efficiency of methanol photocatalysis. By varying the shape of anatase crystals and the resulting different exposure of the crystal planes, they obtained high volumes of evolved hydrogen (up to 2.1 mmol·h⁻¹·g⁻¹) under simulated solar illumination.

Overview of the performance of various photocatalysts in aqueous methanol photoreforming toward hydrogen is summarised in Table 1.

As can be inferred from the data presented in Table 1, among the most efficient photocatalysts for photoreforming of methanol are Au/TiO₂,[45,47,49] CuO/TiO₂,[50] Pd/TiO₂,[45] Pt/TiO₂,[45,51] Au–Ag/TiO₂,[47] and Cu/(Au)–TiO₂.[52]

Upon UV/Vis illumination, 1% Au/TiO₂ nano-photocatalyst (APS < 3 nm) fabricated by deposition-precipitation processes (thereafter denoted as AuP25-DP; Figure 3c) reached an H₂ production rate of 33000 μmol·g⁻¹·h⁻¹.[49]

Scheme of the postulated charge transfer mechanisms in Au–TiO₂ photocatalytic NP system in a H₂O/MeOH mixture is depicted in Figure 4 and described in detail in [52,54].

The analogous photocatalysts, namely 1 wt.% Au/TiO₂, have been examined in [45] and [47]. Au/TiO₂ nanoparticles used therein were prepared by the deposition of surfactant-stabilized preformed metal NPs on commercial titania powders (Nano-Active®, NanoScale Co., USA, and P25 Degussa respectively), using a reverse micelle approach (cf. Ref. [55]), from chloroauric acid as a precursor. However, the morphologies were similar, but the sizes of silver NPs were in the range of 1–6 nm – Figure 5a and 3–8 nm – Figure 6E (cf. < 2 nm in Ref. [49]).

| Photocatalyst | Hydrogen production rate[a] [μmol·g⁻¹·h⁻¹] | Sacrificial agent (aqueous methanol solution) | Light source | Ref. |
|---------------|------------------------------------------|---------------------------------------------|--------------|------|
| RuO₂–TiO₂–Pt  | –1733                                    | methanol water 1:1 (v:v%)                   | 500 W Hg-Xe lamp | [34] |
| TiO₂–Pt       | –1553                                    | methanol water 1:1 (v:v%)                   | 500 W Hg-Xe lamp | [34] |
| TiO₂–Pd       | –733                                     | methanol water 1:1 (v:v%)                   | n.a.         | [46] |
| RuO₂–TiO₂     | –123                                     | methanol water 1:1 (v:v%)                   | 300 W Hg-Xe lamp | [50] |
| TiO₂–(Ph₂)P₆R₆Cl | –163                                    | methanol water 1:1 (v:v%)                   | 100 W Hg-Xe lamp | [49] |
| TiO₂–MV–Pt–Al₂O₃ | –330                                    | methanol water 1:1 (v:v%)                   | 120 W Hg-Xe lamp | [49] |
| Cu/TiO₂       | –160                                     | methanol water 1:1 (v:v%)                   | 300 W Hg-Xe lamp | [49] |
| CuO/TiO₂      | 675                                      | methanol water 1:1 (v:v%)                   | 120 W Hg-Xe lamp | [52] |
| Au/TiO₂       | 24830                                    | methanol water 1:1 (v:v%)                   | 2.47 mM gas phase | [41] |
| Cu/(Au)–TiO₂  | 2400 (Vis)                               | methanol water 1:1 (v:v%)                   | 2400 (Vis)    | [41] |
| Cu/(Au)–TiO₂  | 33000 (UV/Vis)                           | methanol water 1:1 (v:v%)                   | 5200–11000 (UV/Vis) | [41] |
| Pd/TiO₂       | –1600                                   | methanol water 1:1 (v:v%)                   | 3.3 W UV LEDs | [51] |
| Pd/TiO₂       | –3140                                   | methanol water 1:1 (v:v%)                   | Solar Simulator (LOT-Oriel) | [48] |
| Cu/(Au)–TiO₂  | –940                                    | methanol water 1:1 (v:v%)                   | 150 W Xe lamp | [48] |
| Cu/(Au)–TiO₂  | 21350                                   | methanol water 1:1 (v:v%)                   | 21350 N     | [47] |
| Cu/(Au)–TiO₂  | 18600                                   | methanol water 1:1 (v:v%)                   | 18600 N     | [47] |
| Cu/(Au)–TiO₂  | 7750                                    | methanol water 1:1 (v:v%)                   | 7750 N     | [47] |
| Cu/(Au)–TiO₂  | 8360                                    | methanol water 1:1 (v:v%)                   | 8360 N     | [47] |

[a] If the units for hydrogen production rate in quoted references are different, the proper unit is given in the right-hand column. [b] FP: flame pyrolyzed.
methanol aqueous-solution. Application of that photocatalyst allowed reaching a substantial photocatalytic hydrogen generation rate measured at 24830 μmol g⁻¹ h⁻¹. That highest hydrogen yield has been achieved for the catalyst containing 0.19 at.% of copper (denoted as T-3 therein; Figure 7) and was three orders of magnitude higher compared to the pristine TiO₂ (30 μmol g⁻¹ h⁻¹; Figure 8).

As the reasoning behind the enhancement of the photocatalytic performance of TiO₂ catalyst, the Authors stated that the presence of Cu₂O broadened the light absorption to the range from the UV region to approx. 515 nm, and induced formation of the Cu₂O-TiO₂ heterojunction promotes the separation of photogenerated e⁻/h⁺ pairs and enhances the photocatalytic performance. The electrons photogenerated in Cu₂O are transferred to the titania and react with water to produce hydrogen, and the h⁺ are consumed by the sacrificial agent. Moreover, both, photocatalytic and chemical stability has been proven for the best used catalyst by repeatedly high hydrogen generation rates even after ten cycles of reuse, and by detecting no observable structural changes using XRD analysis after 10 h of operation.

Much attention has been given to the Pt/TiO₂ systems in the application for photoreforming of methane. The most efficient Pt/TiO₂ nanocatalysts were fabricated with 0.5 and 1 wt.% of Pt content by the immobilization of surfactant-stabilized preformed metal NPs on titania powders (commercial P25 or homemade flame-pyrolyzed titania[56] denoted as FP-TiO₂), using a reverse micelle approach (cf. Ref. [55]), from hexachloroplatinic acid as a precursor or flame pyrolysis similarly to TiO₂ (sample denoted as – FP-0.5 wt.%Pt/TiO₂).[47]

The morphologies of the prepared photocatalysts were depicted in Figure 6a, b and c. The examined materials may be ordered in terms of H₂ production rates as follows 1 %Pt/TiO₂, FP-0.5 %Pt/TiO₂, 0.5 %Pt/FP-TiO₂, and 0.5 %Pt/TiO₂ achieving 18600, 14230, 8360, and 7750 μmol g⁻¹ h⁻¹. It may be inferred that the Pt content (0.5 vs 1 wt.% Pt) as well as the preparation method of metallic and semiconductor parts of NPs, play a significant role in tuning photoactivity. Nanoparticles prepared by flame-pyrolysis (FP) reached higher hydrogen production rates than their deposited counterparts, but the greater influence may be noticed in the case of a metallic parts. The results of measured H₂ generation rates together with selectivity toward CO and CO₂ are summarized in Figure 9.

Another 1 wt.% Pt/TiO₂ photocatalyst, fabricated by Pt deposition onto TiO₂ from H₂PtCl₆ water solution has been examined in [45]. The morphology and Pt NPs’ size distribution is depicted in Figure 5b, d and f. When tested for the photo-reforming 20 vol.% CH₃OH/H₂O vapors, 1 wt.% Pt/TiO₂ photocatalyst reached outstanding H₂ evolution rate of 21350 μmol g⁻¹ h⁻¹ (Figure 10) which is close to 15% better than the analogous catalyst reported in [47].

An interesting example of titania loaded by noble (plasmonic) metal alloy, Au and Ag, has been reported in [47]. For the photocatalyst nanoparticles preparation, commercial P25 Degussa TiO₂ powder was used, and surfactant-stabilized preformed 1 %Au–1 %Ag alloy nanoparticles were deposited onto TiO₂ powders.[56] As it was expected, the prepared 1 %Au–
1%Ag/TiO$_2$ catalyst demonstrated the lower activity than 1% Au/TiO$_2$. The measured H$_2$ evolution rate for 1%Au–1%Ag/TiO$_2$ and 1%Au/TiO$_2$ were 12820 and 13300 μmol g$^{-1}$ h$^{-1}$, respectively. The silver emerged as less effective co-catalyst since the H$_2$ production rate measured therein for 1%Ag/TiO$_2$ catalyst was substantially lower – 1170 μmol g$^{-1}$ h$^{-1}$. The decrements for Ag-containing catalysts may be associated with the effect of Ag addition, which work function is very close to TiO$_2$, and thus, the electron trapping ability in 1%Ag/TiO$_2$ system is rather scarce. All the above-mentioned catalysts from Au–(Ag)/TiO$_2$ system were examined in [47] under the same conditions.

Likewise, mixed Cu- and Au-plasmon nanoparticles loading onto titania resulted in enhanced hydrogen photogeneration. The best-tested variant with mixed metal loading – Cu/Au/TiO$_2$ synthesized by stepwise precipitation, generated H$_2$ from water methanol solution at $r_{H_2} = 11000$ μmol g$^{-1}$ h$^{-1}$ upon UV/Vis illumination conditions. The Authors repeated the photocatalytic tests each time with freshly prepared catalyst but reported variations 5–25%, in the measured volumes of obtained hydrogen. Besides the measurement errors of the applied setup, the variations were attributed to the reproducibility of the catalyst synthesis protocol.

Summing up, liquid and gas phase photoreforming of methanol are very prospective technologies and their contributions to enabling the circular economy are of the highest value. Further development of materials dedicated for photoreforming of methanol, particularly in terms of efficient solar energy harvesting, conversion rates and selectivity, is still needed, although state-of-the-art nanophotocatalysts reach high H$_2$ production rates. Still, the repeatability of material preparation as well as maximization of their chemical stability, photo-stability, and overall durability are undoubtedly of the highest priority for the implementation at a commercial scale.

### 2.2. Photoreforming of ethanol

Ethanol is another biomass-derived product that may serve as a sacrificial electron donor and be utilized in the “clean” hydrogen production process. Bioethanol is obtained by fermentation from first-generation biomass, e.g., corn, sugarcane, beetroot, sweet sorghum, or – what is more important from the world’s energy demands point of view, as it has a lesser impact on the food chain – from second-generation “non-edible” biomass, e.g., lignocellulose originating from woody and agricultural residues. This variety, widespread, and universality of renewable raw materials for bioethanol production open up an attractive route for the photo-driven bioethanol-based output of hydrogen as well. Harnessing of solar energy in possibly the most efficient manner by engineering the photocatalyst specially tailored for the ethanol conversion into hydrogen has been the target of scientists for over a quarter of a century.

This chapter presents the main issues related to the ethanol photoreforming process and describes the photocatalytic solutions developed for its implementation, starting from well-researched TiO$_2$–supported noble metal catalysts, common for all biomass-based photocatalytic processes, to the most sophisticated nanostructured catalysts synthesized in laboratories over the
past few years. All outlined catalysts utilize, in a more or less disclosed way, the plasmonic effect for the enhancement of phototransition effectiveness.

Among the chemical transformations of ethanol induced by light, one can distinguish the complete photoreforming, when the molecule is fully converted into hydrogen and carbon dioxide [Eq. (11)].

\[
C_2H_5OH + 3H_2O + hν \rightarrow 6H_2 + 2CO_2 
\]  
(ethanol photoreforming)

Comparing to other sacrificial biomass-derived compounds such as higher alcohols (propanol, butanol), acids, and aldehydes, complete conversion of ethanol to CO\(_2\) is one of the easiest due to the simpler structure of the ethanol molecule. Fewer carbons in the structure result in fewer intermediate reactions and limited formation of by-products. Ethanol photoreforming reaction may be divided into two predominant primary reactions [Eqs. (12) and (13)]:

\[
C_2H_5OH + hν \rightarrow H_2 + CH_3CHO 
\]  
(ethanol dehydrogenation)

\[
CH_3CHO + 3H_2O + hν \rightarrow 5H_2 + 2CO_2 
\]  
(acetaldehyde photoreforming)

Other possible reaction involved in ethanol photoreforming process are [Eqs. (14) and (15)]:

\[
CH_3CHO \rightarrow CH_4 + CO 
\]  
(acetaldehyde decomposition)

\[
CO_2 + H_2 \rightarrow CO + H_2O 
\]  
(water-gas shift)

The acetaldehyde may continue photoreforming process to carbon dioxide [Eq. (13)] or decompose to form methane and carbon monoxide [Eq. (14)]. CO and CO\(_2\) may be converted to each other through a water-gas shift reaction [Eq. (15)].

As opposed to methanol photoreforming, in which CO\(_2\) is clearly detectable in the product stream, only traces of it can be
found in the case of ethanol, which means that the second of the primary reactions (acetaldehyde photoreforming) proceeds to a small extent. The amount of acetaldehyde is predominately in good stoichiometric agreement with the amount of H₂ obtained. That implies that dehydrogenation of alcohol is facile, while the that limits the comprehensive ethanol oxidation is oxidation of the aldehyde group. This is due to the high energy needed for the breaking of the bond between two carbons in the molecule. Photocatalytic conditions are usually too mild for it to happen. Activation is of C–C bond easier in case of sacrificial agents with more than one OH group inherent in the molecule structure, e.g., glycerol, sugars.

The reaction pathway involved in the photoreforming of ethanol is presented in Figure 11.

In the literature, one can also meet by-products of ethanol photoreforming such as ethane, propane, 1-ethoxyethanol, acetic acid, 1,1-diethoxyethane, 2,3-butandiol and others, depending on the reaction phase and conditions. Common property of these compounds is that they are usually present in only trace amounts and do not compete with hydrogen and acetaldehyde in terms of selectivity.

Complete photoreforming may seem beneficial considering the hydrogen output, which is six molecules per one ethanol molecule according to the reaction scheme (Eq. 11). It turns out, however, that more advantageous is to dehydrogenate ethanol molecule, obtaining H₂ and the main intermediate product of photoreforming, namely acetaldehyde, both in a stoichiometric ratio of 1:1 to the substrate. Such co-production of hydrogen and valuable acetaldehyde, characterized by good selectivity and free from greenhouse gas generation, is featured by 3–3.5 times more beneficial economics in terms of product value than alternative complete ethanol photoreforming.

Various factors affecting H₂ generation efficiency were considered in the literature. The nature of the found relationships and the impact of individual factors, however, depended on the adopted systems and conditions. Generally, both the electronic structure and structural form of the catalyst system are essential for functional performance of the catalyst. At the same time, the photoreforming efficiency and selectivity depend on solvent composition (water and ethanol concentrations), temperature, atmosphere, by-products accumulation, light wavelength, etc.

Supported plasmonic nanocatalysts for hydrogen production consists essentially of plasmonic metal nanoparticle immobilized on the semiconductor base. As described in more details in previous sections, the metallic nanoparticle should have the following features: 1) It should retard the recombination of electrons and holes through electron trapping, 2) It needs to be efficient for physisorbed atomic hydrogen recombination, 3) It should stable and resistant to oxidation, 4) It should exhibit plasmonic properties (dependent on metal type, size, and shape) in the UV-Vis range, to facilitate the catalytic process by generating “hot electrons”. At the same time, semiconductor should possess: 1) the proper bandgap energy; and 2) good organic reactant adsorption ability.

The exact mechanisms of the reactions taking place on the catalyst will depend on the composition of the gas phase (e.g., presence of oxygen) and the liquid medium (e.g., presence of water). In the absence of oxygen, the ethanol oxidation reaction may occur through two alternative pathways, namely the direct hole transfer and the formation of highly oxidizing hydroxyl radicals (·OH). Let us consider the hole transfer mechanism of ethanol oxidation using benchmark supported photocatalytic material – a TiO₂ with a metal nanoparticle. As can be seen in Figure 12, which demonstrates the process of an M/TiO₂ catalyst photoexcitation, and its interaction with ethanol, an adsorbed alcohol molecule donate an electron and becomes an ethoxide radical, converted subsequently into the acetaldehyde, while an excited electron reduces hydrogen ion.

Donating of an electrons to the valence band by ethanol molecule and capturing of electrons in the conduction band by metal nanoparticle is the most effective if proceeds through adjacent sites, which minimizes diffusion and side reactions. Thus, for an efficient reaction, the site of substrate adsorption must be located at the metal-support interface, so the diffusion and side reactions are minimized.

Ethanol is more favorably adsorbed on the TiO₂ surface because of the oxide higher heat of the adsorption in comparison to metals. The first step of the ethanol photoreforming reaction is the dissociative adsorption of the alcohol molecule on the TiO₂ surface to ethoxides and surface hydroxyls (Figure 13). The surface reaction may be described as [Eq. (16)]:

\[
\text{CH}_3\text{CH}_2\text{OH}(a) + \text{Ti}(s) \rightarrow \text{CH}_3\text{CH}_2\text{OTi}(s) + \text{HO}(s)
\]  

where (a) and (s) stand for adsorbed and surface, respectively. Upon UV light irradiation, the most active species are in close proximity to metal particles. The electrons which are trapped by

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**Figure 7.** (a) SEM and (b) TEM, (c) HRTEM images, and (d) corresponding FFT diffraction pattern of the selected area in (c) of Cu₃O/TiO₂ nano-photocatalyst containing 0.19 at.% of copper (therein denoted as T-3). Reprinted with permission from Ref. [50]. Copyright (2019) American Chemical Society.
metal particles and excited due to plasmonic effect, reduce hydrogen atoms of surface hydroxyls. Holes, in turn, oxidize chemisorbed ethoxide species.

The second type of anaerobic oxidation mechanism, i.e. the formation of highly oxidizing hydroxyl radicals, is not desirable. It causes the uncontrollable oxidation of organic compounds, thereby reducing selectivity, producing greenhouse gases and various organic by-products. The possibility of this mechanism to occur should be considered when a deep valence band semiconductor as TiO$_2$ is to be used as a support.

The reaction atmosphere is also essential for the efficiency of the process. When photoreaction is conducted in the oxygen-rich atmosphere, then competitive organic photooxidation takes place. Excited electrons are utilized for the reduction of oxygen rather than hydrogen ions, resulting in the superoxide radicals ($^\cdot$O$_2^-$) generation.

The selectivity may be tuned up by the water-free photoreforming of ethanol. The absence of an oxygen source results in the generation of an aldehyde with high selectivity, as further oxidation reactions on the semiconductor and the co-catalyst are avoided.$^{[66]}$ However, it is demanding to separate pure ethanol from an azeotropic mixture of ethanol and water. In this context, the flexibility in using an aqueous ethanol solution at various concentrations is economically important asset as the solution derived from biomasses fermentation plants do not need to be subjected to highly energy-consuming purification by distillation.

Pt deposited on TiO$_2$ is the most thoroughly studied supported catalyst structure being a reference for other systems. Despite the Pt is not usually associated with plasmonic application, and in the photocatalytic field it serves rather as a co-catalyst (excited electrons reservoir), it exhibits a plasmonic peak in the UV light range and therefore might enhance the reaction driven by the proper wavelength. Until today many other metals such as noble Pd, Rh, Ag and Au, and transition Cu and Co have been deposited on active titania and tested against the ethanol photoreforming enhancement.
In one of the earliest works on ethanol photoreforming, Bamwenda et al. compared the photocatalytic activity of \( \text{H}_2 \) generation between Au/TiO\(_2\) and Pt/TiO\(_2\) prepared by deposition-precipitation, impregnation, photodeposition, and simple mixing with colloidal metal suspension methods. Among many conclusions of these studies, one may notice the existence of optimal metal loading at around 0.3–1% and the higher overall activity of Pt samples compared to Au, which yielded in 8.94 and 7.81 \( \mu \text{mol g}^{-1} \text{min}^{-1} \text{m}^{-2} \) respectively. In other work, Puga and coworkers used the deposition-precipitation method to prepare gold nanoparticles of 1.5–6.5 nm diameter immobilized on the TiO\(_2\) surface and tested them both under UV and simulated solar light and under Ar and CO\(_2\) atmosphere. The results demonstrated a very good >99% selectivity towards \( \text{H}_2 \) production. Other minor gaseous products present were (in decreasing order of molar production): \( \text{CH}_4 > \text{CO} > \text{C}_2\text{H}_4 > \text{CO}_2 > \text{C}_2\text{H}_6 > \text{C}_3\text{H}_8 \). Under the CO\(_2\) atmosphere the photoactivity of the catalyst was lower than under the inert Ar. Authors obtained hydrogen yields up to \( 30 \text{ mmol g}^{-1} \text{h}^{-1} \) under UV illumination, increasing with gold loading. Simulated solar light conditions provided lower \( \text{H}_2 \) yields of 5–6 mmol g\(^{-1}\)h\(^{-1}\), which might, however, still be considered significant.

Photocatalytic production of hydrogen from ethanol using Rh/TiO\(_2\), Pd/TiO\(_2\), and Pt/TiO\(_2\) catalysts (Figure 14) was investigated by Yang et al. Both Pd and Pt deposited on TiO\(_2\) showed a strong catalytic activity and a quantum yield of about 10% at 623°C. Rh modified anatase was over one order of

![Figure 11. The scheme of the mechanism of \( \text{H}_2 \) production from ethanol.](image)

![Figure 12. The photocatalytic process of ethanol decomposition into hydrogen and acetaldehyde on the TiO\(_2\) supported metal nanoparticle.](image)

![Figure 13. Schematic of ethanol phototransition on Pt/TiO\(_2\) catalyst surface. Reprinted with permission from Ref. [62]. Copyright (2006) Elsevier.](image)
The influence of the metal-loaded TiO$_2$ catalyst on the production of hydrogen was observed to be significant. A fraction of Rh nanoparticles was found to be non-metallic, presumably caused by weak electron transfer capability in comparison with Pt or Pd. A significant fraction of Rh nanoparticles was found to be non-metallic.

The study by Murcia-López et al. was devoted to the influence of metal-loaded TiO$_2$ with Cu and Ag, and bimetallic Cu–Ag and Cu–Pt synthesis on the efficiency of ethanol photoreforming. They demonstrated that studied bimetallic catalysts were superior to the single-metal ones in terms of H$_2$ productivity, H$_2$/CO ratio, and catalyst stability. Cu–Pt/TiO$_2$ presented the highest H$_2$ yield (see Figure 15). Presence of Cu nanoparticles aided to control the extent of the oxidation resulting in a lower CO$_2$ formation than in case of Pt/TiO$_2$. However, Cu–Pt/TiO$_2$ was less efficient in ethanol photoreforming than the reference Pt/TiO$_2$ catalyst.

The presence of bimetallic Pt-Au nanoparticles and of Ti$^{2+}$ sites/O$_2^-$ vacancies in the bulk structure of reduced anatase were recognized by Gallo et al. as two key parameters for maximization of light absorption and feedstock activation. Experiments under the simulated solar light indicated that reduced state of TiO$_2$ is more efficient for the proton reduction to gaseous H$_2$ than the light absorption through surface plasmon resonance of Au-containing nanoparticles. Authors claim that the lower quantum efficiency of the samples containing Au is due to the fact that if photons are absorbed through the LSPR band in effective for production of hydrogen, the number of photons absorbed by reduced TiO$_2$ is lower. Therefore higher quantum yield is observed for Pt, as the photons are not absorbed by the resonance band of surface plasmons.

Montini et al. produced active and cheap nanocomposites by photodeposition of Cu on the TiO$_2$ supports. The activity of the catalyst was again strongly influenced by its structural characteristics. The high number of defects in a multiphasic support results in a very high dispersion of the metal and higher activity for the production of H$_2$, which is an effect of increased oxidation rate of the sacrificial agents.

Gold nanoparticles were also widely studied on the supports different from TiO$_2$. Carraro et al. considered Au and Ag nanoparticles deposited on the ε-Fe$_2$O$_3$ nanorod array for ethanol photoreforming. They obtained promising results concluding that loading of Au nanoaggregates onto ε-Fe$_2$O$_3$ enables a significant hydrogen production even when exposed solely to visible light (8 mmol h$^{-1}$ m$^{-2}$). The presence of Au characterized by LSPR phenomena adds the second mechanism to the conventional metal-semiconductor photocatalysis which is absorption of UV photon by ε-Fe$_2$O$_3$, resulting in formation of electron-hole pair. LSPR enhances visible light absorption and raises the catalyst activity by electron transfer from the metal to the semiconductor.

The effect of Au nanoparticles loading on ZnO on the photocatalytic performance of hydrogen generation from ethanol was evaluated by Sampaio et al. Incorporating gold nanoparticles onto zinc oxide nanowires surface significantly increased its H$_2$ yield. The photocatalyst with the smallest Au nanoparticles (5.4 nm) was the most active one, with a H$_2$ production rate of 427 μmol g$_{cat}^{-1}$ h$^{-1}$.

This study also demonstrated an impact of support morphology on hydrogen production. It was hypothesized that the particles with the most intricate shape (Figure 16) might scatter the incident light, enhancing light absorption and photoreaction efficiency.

The role of the morphology of the semiconductor part (support) was also investigated by Cargnello et al. They showed that H$_2$ production in uniform, one-dimensional brookite titania nanorods is highly enhanced by engineering their length. The anisotropic structure was found to improve the separation of charge carriers, in experimental studies giving even 65% quantum yield for hydrogen production from ethanol.

Another excellent example of the support structure effect on photocatalytic hydrogen generation can be found in the article by Paik et al. Reduced WO$_3$ nanowires, thanks to an increased amount of oxygen vacancies, possess the broadened bandgap. Conduction band in reduced WO$_3$ NWs becomes more negative than the standard hydrogen reduction potential, which is not achievable in bulk WO$_3$.

The review article by Czelej et al. describes in detail how engineering the individual building blocks of a plasmonic photocatalyst can improve the efficiency of hydrogen production.

It is worth mentioning a study by Barreca et al. on supported Mn$_3$O$_4$ nanosystems, both pure and functionalized with Au nanoparticles. Pure Mn$_3$O$_4$ nanosystems demonstrated a constant production rate of hydrogen at 10 mmol h$^{-1}$ m$^{-2}$, while modified with Au nanoparticles exhibited an almost 7-fold increase in efficiency. The second important conclusion was that increase of Au nanoparticle size from ~6 nm up to ~15 nm caused the decrease of LSPR intensity and also a lower interfacial contact between Au and Mn$_3$O$_4$, which reduced electron transfer efficiency and, therefore, hydrogen production rate.
Other studies were devoted to even more complex systems with a hierarchical structure. Luo et al. reported the synthesis of Cu$_2$O/TiO$_2$ p-n junction with site-specific deposited Au. The Au nanoparticles (with the size of approximately ~2.5 nm) were selectively deposited onto TiO$_2$ nanorods (Au@TiO$_2$/Cu$_2$O), Cu$_2$O nanocubes (Au@Cu$_2$O/TiO$_2$) or both TiO$_2$ and Cu$_2$O (Au@TiO$_2$/Cu$_2$O@Au) with the same Au loading. Under simulated solar light, Au@TiO$_2$/Cu$_2$O catalyst possessing Au@TiO$_2$ interface, and the TiO$_2$/Cu$_2$O p-n junction demonstrated the highest H$_2$ production rate of 8.5 mmol g$_{\text{cat}}$ h$^{-1}$. Matching of energy levels of the p-n junction accelerates charge separation and photo-generated hole transfer and thus dehydrogenation of ethanol to acetaldehyde at the junction site.

An interesting concept was presented by Chen et al. They demonstrated dual-porosity 3D TiO$_2$ nanotube array intended for the photocatalytic production of hydrogen from ethanol solution. Catalyst array consisted of a commercial sintered titanium web on which a uniform array of TiO$_2$ nanotube has been grown. The addition of well-distributed Pd nanoparticles with size of 4–5 nm to the TNTA-web caused an increase in hydrogen production to 130 mmol h$^{-1}$ m$^{-2}$. A solar-to-fuel efficiency was found to be 0.45%. The authors claim that by plasmon resonance caused by the absorption of visible light by Pd nanoparticles is not a significant mechanism for increasing the catalysis efficiency in case of the considered system.
Hierarchical MWCNT/Pd@TiO$_2$ hybrid photocatalysts were tested for hydrogen production from biomass-derived alcohols by Beltram et al.$^{[63]}$ Catalysts showed high activity both upon UV light irradiation and simulated solar light, with the performance of 25 mmol g$^{-1}$ h$^{-1}$ and 1.5 mmol h$^{-1}$ g$^{-1}$, respectively.

Another carbon-based hierarchical material proposed for ethanol photoreforming is the carbon nanocone/Pd@TiO$_2$ catalyst synthesized by Melchionna et al.$^{[76]}$ Carbon nanocones (CNC) hybridized with inorganic layer of nanocrystalline TiO$_2$ containing Pd nanoparticles and after calcination at 350°C were found to display H$_2$ production of 600 mmol g$_{\text{cat}}^{-1}$ under UV, and 32 mmol g$_{\text{cat}}^{-1}$ under solar irradiation. The evident impact of the CNC on the catalytic activity has been attributed to the delay of charge carrier recombination caused by the exceptionally strong electron sink characteristics of carbon nanotubes.

The last but very interesting material to be mentioned in this section is NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Au/CdS activated by near-infrared light with Au nanoparticles acting as a plasmonic nanoantenna. A sandwich structured NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Au/CdS particles were proposed by Feng et al.$^{[77]}$ Authors explain that besides acting as the nanoantenna harvesting larger fraction of incident light, Au has several other functions. It acts as an energy relay in synergistic Förster resonance energy transfer (FRET) and plasmonic resonance energy transfer (PRET) from NaYF$_4$:Yb$^{3+}$, Er$^{3+}$ to CdS. Au nanoparticle serves also, as many other noble metals mentioned before, as an electron sink to promote separation of electrons and holes. It acts, further, as a co-catalyst for activation of the ethanol to hydrogen transition. NaYF$_4$:Yb$^{3+}$, Er$^{3+}$/Au/CdS, unlike the previous materials, focuses on the utilization of NIR radiation, which accounts for about 44% of the solar energy, utilizing so-called up-conversion a non-linear optical process in which a sequential absorption of two photons leads to the emission of the photon higher energy and thus of shorter wavelength. The NYF/Au/CdS catalyst with plasmonic Au-mediator exhibited enhanced activity for hydrogen production from ethanol solutions, both, under NIR and simulated solar light illumination.

The performance of all the catalysts for hydrogen ethanol photoreforming discussed in this chapter is summarized in the Table 2.

### 2.3. Photoreforming of glycerol

Among several options of renewable hydrocarbons, aqueous glycerol, a side effect product of triglyceride transesterification process and wastewaters containing polyol, received notable attention in recent years.$^{[8,81,82]}$ The significance of glycerol increased with that of biodiesel, which has currently attracting wide global interest as a renewable energy source from biomass.$^{[83–85]}$ The glycerol molecule has an advantageous chemical structure for photochemical transformations due to the appropriate ratio between carbon, oxygen, and hydrogen atoms (a proportionally large number of H to C and O atoms), which in terms of hydrogen production make glycerol very attractive compared to other sacrificial agents.

The amount of hydrogen produced in the process largely depends on the concentration and the nature of the substrates (sacrificial agents) as well as the photocatalyst that is used. In the glycerol photoreforming process 7 moles of H$_2$ per one mole of a sacrificial agent can be produced following the stoichiometry of the reaction [Eq. (17)]. While oxygen is present during the reaction, glycerol is oxidized to carbon dioxide (CO$_2$) [Eq. (18)].
Table 2. The photocatalytic performance of the supported plasmonic metal photocatalysts in photoreforming of the ethanol. (For the sake of comparison, the values of power, temperature, conversion, and production rates from different references were converted to the same units. The experimental data extracted from graphs were marked with tilde).

| Photocatalyst | Hydrogen production rate\(^a\) \([\text{μmol g}^{-1} \text{h}^{-1}]\) | Sacrificial agent (aqueous ethanol solution) | Light source | Ref. |
|---------------|---------------------------------|---------------------------------|------------|-----|
| 1% Au/TiO\(_2\) | 469 \(\text{μmol g}^{-1} \text{h}^{-1}\) | aqueous solution of 5 M ethanol | 500 W Hg lamp (30 mW cm\(^{-2}\)) | [57] |
| 0.4% Pt/TiO\(_2\) | 536 \(\text{μmol g}^{-1} \text{h}^{-1}\) | pure ethanol | 100 W ultraviolet Hg lamp | [62] |
| 1% Pd/TiO\(_2\) | 3300 \(\text{μmol g}^{-1} \text{h}^{-1}\) | | | |
| 1% Pt/TiO\(_2\) | 3000 \(\text{μmol g}^{-1} \text{h}^{-1}\) | | | |
| 1% Rh/TiO\(_2\) | 1200 \(\text{μmol g}^{-1} \text{h}^{-1}\) | | | |
| Pt/TiO\(_2\) | \(-27000\) | 0.57 M | 450 W Xe-Hg lamp | [58] |
| Pt/TiO\(_2\) | \(-5400\) | 1.37 M | 280 W Xe lamp | [72] |
| 1 wt.% Pt/WO\(_3\) | \(-460\) | ethanol \((50 \% \text{v/v})\) | 150 W Hg-Xe arc lamp | [71] |
| 1 wt.% Pt-brookite nanorods | \(-45000\) | ethanol \((50 \% \text{v/v})\) | 150 W Xe lamp | [71] |
| 1% Cu/TiO\(_2\) | \(-1600\) | ethanol \((50 \% \text{v/v})\) | 125 W Hg lamp | [60] |
| 1% Au/TiO\(_2\) | \(-700\) | ethanol \((50 \% \text{v/v})\) | 150 W Xe lamp | [59,68] |
| 1% Pt/TiO\(_2\) | \(-4800\) | ethanol \((50 \% \text{v/v})\) | 125 W Hg lamp | [59,68] |
| 0.5% Au-0.5% Pt/TiO\(_2\) | \(-7400\) | (150 W Xe lamp) | | |
| 1% Au\(-1 \% \text{Pt/TiO}_2\) | \(-1700\) | | | |
| \(\varepsilon\)-Fe\(_2\)O\(_3\) NR | \(-20000\) | ethanol \((50 \% \text{v/v})\) | 150 W Xe lamp | [69] |
| Ag/\(\varepsilon\)-Fe\(_2\)O\(_3\) NR | \(-24000\) | | | |
| Au/\(\varepsilon\)-Fe\(_2\)O\(_3\) NR | \(-45000\) | | | |
| 0.45% Au/TiO\(_2\) | 23180 (9930) | pure ethanol | 125 W Hg lamp | [78] |
| 0.57% Au/TiO\(_2\) | 21152 (11427) | Ar atmosphere | | |
| 1.0% Au/TiO\(_2\) | 28542 (15402) | \((\text{CO}_2 \text{atmosphere})\) | | |
| 1.7% Au/TiO\(_2\) | 29677 (18453) | | | |
| 1.0% Au/TiO\(_2\) | 11242 | ethanol \((50 \% \text{v/v})\), Ar atmosphere | 125 W Hg lamp | [78] |
| 0.45% Au/TiO\(_2\) | 5919 | pure ethanol, simulated solar light | | |
| 1.0% Au/TiO\(_2\) | 6151 | Ar atmosphere \((100 \text{ mW cm}^{-2})\) | | |
| 0.5% Au/TiO\(_2\) | 5539 | pure ethanol, simulated solar light \((100 \text{ mW cm}^{-2})\) | | |
| 1.0% Au/TiO\(_2\) | 5219 | | | |
| CNC/Pd@TiO\(_2\) | 1200 | | | |
| CNC/Pd@TiO\(_2\)-350 | 30000 | | | |
| 0.38% Au/ZnO-n | 280 | ethanol \((20 \% \text{v/v})\) | 300 W Hg-Xe lamp | [70] |
| 0.90% Au/ZnO+ | 226 | | | |
| 0.29% Au/ZnO-f | 427 | | | |
| 0.35% Au/ZnO-t | 211 | | | |
| 0.74% Au/ZnO-c | 197 | | | |
| NaYF\(_4\)-Yb\(^{3+}\), Er\(^{3+}\) /Au/CdS | 0.59 (NIR) | 12 wt% ethanol | 300 W Xe lamp with filters | [77] |
| | –230 (UV-Vis-NIR) | solution in water | for NIR, simulated solar light, and UV-Vis | |
| MWCNT/Pd@TiO\(_2\) | 25000 | ethanol \((50 \% \text{v/v})\) | 125 W Hg lamp | [63] |
| | 1500 | | | |
| Pd/TiO\(_2\) nanotube array | 130000 | \(\text{μmol h}^{-1} \text{m}^{-2}\) | simulated solar light \((100 \text{ mW cm}^{-2})\) | [75] |
| Au/MnO\(_x\) | –66000\(^H\) | \(\text{μmol h}^{-1} \text{m}^{-2}\) | 150 W Xe lamp | [75] |
| Cu/TiO\(_2\) | –3800 | \(\text{μmol h}^{-1} \text{m}^{-2}\) | 150 W Xe lamp | [73] |
| Cu–Ag/TiO\(_2\) | –3000 | \(\text{μmol h}^{-1} \text{m}^{-2}\) | 300 W UV-Vis lamp \((100 \text{ mW cm}^{-2})\) | [67] |
| Cu–Pt/TiO\(_2\) | –4700 | | | |
| Au@TiO\(_2\)-NR | 5152 | pure ethanol | simulated solar light \((100 \text{ mW cm}^{-2})\) | [79] |
| Au@TiO\(_2\)-NR-8 | 5341 | | | |
| Au@TiO\(_2\)-NR-6 | 5812 | | | |
| Au@TiO\(_2\)-NR-4 | 6305 | | | |
| Au@TiO\(_2\)-NR-2 | 7093 | | | |
| Au@TiO\(_2\) nanoflowers | –24000 | 10 vol.% ethanol | UV lamp, 365 nm \((6.5 \text{ mW cm}^{-2})\) | [80] |
| Au@TiO\(_2\)/CuO | 8548 | pure ethanol | 300 W Xe lamp \((100 \text{ mW cm}^{-2})\) | [74] |
| Au@CuO/TiO\(_2\) | 6932 | | | |
| Au@TiO\(_2\)/CuO@Au | 7348 | | | |
| Au@TiO\(_2\) | 7143 | | | |
| CuO/TiO\(_2\) | 830 | | | |

\(^a\) If the units for hydrogen production rate in quoted references are different, the proper unit is given in the right-side column; \(^b\) Peak value.

The photoreforming reactions:

\[ \text{C}_2\text{H}_5\text{O}_3 + \frac{7}{2} \text{H}_2 \xrightarrow{\text{hv}} 4\text{H}_2\text{O} + 3\text{CO}_2 \]  
(17)

The photocatalyst due to its benefits such as high photoactivity,

Most works about valorization of glycerol use TiO\(_2\) as a photocatalyst due to its benefits such as high photoactivity,
relatively low price, thermal stability, nontoxicity, and accessibility. The most commonly used structure of TiO2 for this type of application is the commercial P25 (composed of 75-80% anatase and 20–25% rutile).\(^1\)\(^{2}\)\(^{3}\)\(^{4}\)\(^{5}\) To enhance its photocatalytic properties, the NPs of metal oxides (doping agents) have been frequently used as cocatalysts for a long time. For instance, a small amount (even less than 1 wt.%) of some noble metals, e.g., Pt, Pd, Ag, Au, Ru, Rh, and Ni\(^6\)\(^{7}\)\(^{8}\)\(^{9}\)\(^{10}\) can improve H2 evolution compare to bare TiO2 or another semiconductor (La-CNT, CdS, g-C3N4, ZnO, BiO2, WO3).\(^{11}\)\(^{12}\)\(^{13}\)\(^{14}\)\(^{15}\) In addition, some research have been focused on the formation of Z-scheme systems, i.e., composites consisting more than one semiconductor.\(^{16}\)\(^{17}\) Overview of the performance of various photocatalysts in aqueous glycerol photoreforming to hydrogen is summarized in Table 3.

Among various noble metals incorporated in the photocatalysts, the most attractive one seems to be Pt. This is due to its lowest value of overpotential, and Pt usually achieves the highest activity in the hydrogen generation process. Photo-reforming, photooxidation, and water splitting mechanisms of glycerol proposed for Pt/TiO2 catalysts have been shown in Figure 17.

In the environments containing oxygen, glycerol can be directly as well as indirectly oxidized toward CO2 while electrons from conduction band reduce oxygen to generate further oxidizing species, which can get involved into the oxidation reactions. Under unaerated conditions, the photoreforming reaction takes place. The organic compounds are oxidized by using photo-generated holes, while electrons can be used to reduce water to H2. The tests of glycerol photooxidation and photoreforming were conducted at over 80 mg TiO2 and 0.5 wt.% Pt/TiO2 (Pt were deposited on TiO2 by impregnation method) photocatalyst suspension with the initial glycerol concentration of 20 mM, T = 40 °C.\(^{18}\) A solar light-simulating source (Osram XBO 450 W) source was used to photocatalytically

| Table 3. Photocatalysts used for valorization of the glycerol into H2. |
|---------------------------------------------------------------|
| **Photocatalyst**    | **Hydrogen production rate** \(\text{mol} \text{g}^{-1} \text{h}^{-1}\) | **Sacrificial agent** | **Light source** | **Ref.** |
|----------------------|----------------------------------------------------------|----------------------|------------------|--------|
| Cd(7%)-SnO2/(CdS)x | 290 | 1 M | 500 W Hg-Xe | [96] |
| Pt/TiO2             | -700 | | 150 W Xe lamp Solar simulator (Lot oriel) | [68] |
| Au/TiO2             | -500 | | | |
| Pt-Au/TiO2          | -550 | | | |
| PtO2.5-Au3/TiO2     | -1100 | | | |
| 0.5% Au-WO4/TiO2   | 8600 | | | |
| Pt/TiO2 (anatase)   | 0.1 | \(\mu\text{mol min}^{-1}\) | 5 vol.% glycerol | 35 W HID lamp (20 mW cm\(^{-2}\)) | [97] |
| NIO/TiO2 (anatase)  | 1230 | | 20 mW Xe lamp (≥ 420 nm) | | [98] |
| NIO/TiO2 (anatase)  | 258 | | 450 W Osram XBO | | [98] |
| NIO/TiO2 (anatase)  | 900 | | 500 W high-pressure Hg lamp (Ushio USH-500SC) | | [89] |
| Cu-Pt/TiO2          | 1313 | | 500 W high-pressure Hg lamp (Ushio USH-500SC) | | [88] |
| 3.0% β-Bi4O5g-C3N4 | 8585 | | | |
| (~2%) CuO/TiO2      | 4.68 | | | |
| Au-1.5%TiO2 (DP)    | -19.11 | | | |
| Au-3%TiO2 (DP)      | -23.00 | | | |
| Pt-3%TiO2 (DP)      | -16.61 | | | |
| Pt-0.5%TiO2 (IMP)   | -10.43 | | | |
| Pd-0.5%TiO2 (DP)    | -6.11 | | | |
| 0.3% wt Pt/TiO2     | -1.42 | | | |
| 1 wt.% PdAu/TiO2    | 19.6 | mol kg\(^{-1}\) h\(^{-1}\) | 25 vol.% glycerol | 400 W metal halide lamp | [100] |
| Ag2O-TiO2           | 175 | | Medium pressure | | [92] |
| Bi2O3-TiO2          | 133 | | | |
| ZnO-TiO2            | 90.3 | | 125 W Hg lamp | | |
| 1 wt.% Ag/TiO2 (P25) | 23 | mmol g\(^{-1}\) (22 h) | 5 vol.% glycerol | solar simulator, ABET technologies, LSseries light source | [103] |
| 1% Rh/TiO2 (P25)    | 143 | \(\mu\text{mol h}^{-1}\) | 20 mM | 300 W Xe lamp | [94] |
| SG1(25%)TiO2/MC-H   | -36 | 75 mg photocatalyst | 20 mW Xe lamp | | |
| SG1(10%)TiO2/MC-H   | -17 | (6 h) | 125 W, 254–579 nm, mercury lamp | | [104] |
| SG1(40%)TiO2/MC-H   | -9 | | | |
| SO2TiO2 P25/com-HKUST-1 | 2.9 | mmol g\(^{-1}\) h\(^{-1}\) | | | |
| SO2TiO2-ST/com-HKUST-1 | 2.4 | 1:9 | 150 W, solar simulator Model 9600 Newport Corporation | | [105] |
| SO2TiO2 P25/syn-HKUST-1 | 4.5 | | | |
| Ag2O-TiO2 (20% AS and AP 80%) | -190 | | | |
| [a] If the units for hydrogen production rate in quoted references are different, the proper unit is given in the right side column; [b] Sample calcined, temp: 450 °C; [c] DP – deposition-precipitation; [d] IMP – impregnation; [e] SG1 – Sol Gel Synthetic Method; [f] MC-H – Mesoporous Carbon Functionalization. |
tests. For two photocatalysts (TiO$_2$ and Pt/TiO$_2$), the rates of generated H$_2$ and CO$_2$ in reaction environment, with and without O$_2$, as functions of illumination time are presented in Figure 18.

When the reaction takes place under photoreforming conditions, in absence of oxygen, unmetallized TiO$_2$ was almost inactive. There is a large H$_2$ generation overpotential on the surface of TiO$_2$, and as a result, the water reduction driving force due to photogenerated electrons is small. Even low dispersion of Pt resulted in a significant increase in the reaction production rate and lead to the transformation of both, CO$_2$ and H$_2$ in the gas phase. In particular, the maximum rates of H$_2$ production over the Pt/TiO$_2$ were higher by a factor of 25 compared to the TiO$_2$ photocatalyst. Moreover, quantities of H$_2$ and CO$_2$ generated over the Pt/TiO$_2$ under glycerol photoreforming conditions agree very well with those anticipated from the stoichiometric reaction equations, confirming that sacrificial agents and all semi-products are fully transformed into CO$_2$ and H$_2$. More detailed information concerning the reaction pathways that may occur under photooxidation and photoreforming conditions of glycerol over irradiation Pt/TiO$_2$ photocatalyst suspension can be found in ref.[98]

The information about photocatalytic reforming of glycerol on Rh/TiO$_2$ photocatalyst has been reported in [94]. As demonstrated by the authors, the reaction leads to continuous generation of H$_2$ and CO$_2$ by simultaneous formation of organic semi-products through anodic oxidation. It can involve different reaction pathways, see Figure 19. Experiments are conducted over TiO$_2$, with Rh nanoparticles (particle size 1.9 ± 0.7 nm) on the surface as a co-catalyst (1 wt.% loading) (see Figure 20), at a dispersion level of 57%. The Rh/TiO$_2$ photocatalyst was prepared via incipient wetness impregnation. Irradiation was provided by a 300 W Xe lamp. Reaction conditions: temperature 15 °C, pressure 1 bar Ar, 75 mg of Rh/TiO$_2$ dispersed in 100 mL of a 20 mM aqueous reactant solution.

Figure 17. Scheme of simplified, mechanism of potential reactions upon illumination of Pt/TiO$_2$ suspensions under conditions of water splitting (a and b), glycerol oxidation (c and d), and glycerol photoreforming (a and d). Reprinted with permission from Ref. [98]. Copyright (2012) Elsevier

Figure 18. Evolution of (A) CO$_2$ and (B) H$_2$ over irradiation time for two photocatalysts (TiO$_2$ and Pt/TiO$_2$) in environment with and without O$_2$. Reprinted with permission from Ref. [98]. Copyright (2012) Elsevier.

Figure 19. Conceptual scheme of three possible reaction pathways for photoreforming of glycerol on Rh/TiO$_2$. Reprinted with permission from Ref. [94]. Copyright (2016) Elsevier Inc.
Glycerol is transformed via direct as well as indirect hole transfer pathways which can result in [94].

Path 1 – C–C bonds are ruptured as a results of oxidation. Glycerol is oxidized to glyceraldehyde (GDA). The next steps pass through sequential cleavage of formic acid through intermediate glycolaldehyde (Cn-1 aldehyde), and formaldehyde (Cn-2 aldehyde) toward total mineralization to CO₂.

Path 2 – Oxidation to the corresponding aldoses or ketoses. Two electron oxidation of glycerol to form dihydroxyacetone (DHS). Consecutive dihydroxyacetone conversion via glycolic acid yields CO₂ and two equivalents of formaldehyde.

Path 3 – Dehydration evolving at cathode, derived by the light. Light-driven dehydration of glycerol to produce hydroxyacetone (HA). Consecutive oxidation of HA leads to the production of acetic acid, and formaldehyde semi-products toward total mineralization to CO₂.

After 12 h of PR H₂ and CO₂ reached respectively (see Table 4).

It can be seen that the amounts of H₂ and CO₂ evolved during PR of HA are substantially lower (~80%) lower than that for other compounds (DHA, GAD, glycerol). Photoreforming evolution rate of H₂ over time is presented in Figure 21.

Four different photocatalysts for H₂ production process by means of photoreforming were prepared, as reported in [68]. Apart from metallic (Pt, Au) nanoparticles deposited on reduced TiO₂ (anatase phase) nanocrystals, the bimetallic Pt–Au nano-

| Table 4. H₂ and CO₂ evolved during 12 h PR of glycerol, GAD, DHA, HA. |
|-------------------|-------------------|-------------------|-------------------|
| Glycerol          | 1405              | 1264              | 1247              |
| GAD               | 366               | 387               | 686               |
| DHA               | 222               | 57                |
| HA                |                   |                   |

Figure 20. (A) 1 wt.% Rh/TiO₂ TEM image (B) photocatalyst nanoparticle size distribution. Reprinted with permission from Ref. [94]. Copyright (2016) Elsevier Inc.

Figure 21. (A) Evolution rate of hydrogen rates during C3-oxygenates photoreforming process. (B) H₂/CO₂-ratios. Curved lines are drawn for the sake of clarity. Dashed horizontal lines in (B) denote the stoichiometric ratios anticipated from the overall reaction equations. Reprinted with permission from Ref. [94]. Copyright (2016) Elsevier Inc.
crystals were used for photoreforming process as attractive photocatalysts with relatively high activity in H₂ production. In the tests 1 M aqueous solutions of glycerol were used as a sacrificial agents. The photocatalysts are labeled as Pt₁, Au₁, Pt₁–Au₁, and Pt₀.₅–Au₀.₅. The numbers next to the element symbol denote the nominal wt.% of the metal. The results for the monometallic (Pt or Au)/TiO₂ were compared to bimetallic systems (see Table 3). Under UV-A, the higher hydrogen production rates are achieved for the bimetallic Pt–Au. form of photocatalysts may promote hydrogen desorption. For Pt₀.₅–Au₀.₅ samples higher activity can be observed in comparison to Pt₁–Au₁ forms. In each of the above samples, the presence of the crystalline TiO₂ (anatase) favors the activity of photocatalysts. Tests conducted under simulated sunlight revealed lower photocatalytic activity in comparison UV-A irradiation. It may be related to the lower percentage of UV photons in the sunlight irradiation. Experiments under simulated solar irradiation show that stable hydrogen production is obtained even after 65 h.

Wang et al.⁹¹ proposed to utilize the Ag₂O–TiO₂ composite in their experiment due to its strong photocatalysis ability and narrow band gap. The reaction mechanism of the LSPR effect under solar irradiation for Ag₂O-doped TiO₂ used as photocatalyst and glycerol used as sacrificial agent is depicted in Figure 22. In the first step, Ag₂O particles have to be reduced to metallic form Ag⁰ and the next LSPR effect triggers the transition electrons by visible light from Ag₂O particles to the conduction band of TiO₂. Furthermore, UV irradiation may photogenerate electrons and holes which will additionally lead to harnessing a wide range of sunlight spectrum.

Dispersion stability may be increasing and H₂ production performance may be improving by the novel method of mixing Ag₂O–TiO₂ photocatalysts particles with different morphologies: nanosphere (AS), nanoplates (AP), nanotubes (AT) was implemented, as presented in [106]. Precursors of TiO₂ with different morphologies were prepared in the hydrothermal process, and then, by using the the precipitation, corresponding Ag₂O–TiO₂ photocatalysts were synthesized.⁹¹ NPs with different shape and histogram of particle size distribution have been shown in the HRTEM image (see Figure 23). A series of NPs with different shapes were synthesized and investigated in terms of their performance. The most interesting results were obtained for AS, AP types of Ag₂O–TiO₂ particles (see Table 3). Photocatalysts mixed and with different morphology were suspended in an aqueous solution of glycerol. The excellent colloidal dispersion has been achieved use of any dispersant for dispersion stability. The H₂ production rate observed in photoreforming process from this particles mixture was 1.1–2.3 fold higher than that for the system with single-component.

The H₂ production experiments by means of photoreforming were carried out in ambient temperature and 0.1 MPa pressure. In this experiment the light source (300 W Xe arc lamp) at the range of 320–780 nm was applied and 0.1 g of catalyst was dispersed in 100 ml aqueous glycerol solution (7 vol.% of glycerol). As observed, the H₂ production yield follows AP < AT < AS for the single-catalyst systems. The results also show that the dispersion stability is important parameter and has a strong impact on the performance of H₂ production. It has been proposed that mixing method of catalyst nanoparticles with different morphology and shapes can open up an interesting avenue to energy-efficient heterogeneous catalysts dedicated to H₂ production process.

Various systems such as metal Pt, Au, Pd–TiO₂ in a photocatalytic transformation can exhibit different mechanisms of charge transfer. Due to a higher energy band gap between the conduction band of TiO₂ and a Pd plasmon metallic state than in the case of Pt, the recombinition in Pd/TiO₂ system occurs more rapidly than in the Pt/TiO₂. In the Au/TiO₂ system the recombination events are mitigated, because the in the Au-related metallic state the energy level is lower in comparison to the conduction band of TiO₂, what may be related to higher participation of generated electrons in the

---

Figure 22. Scheme of the mechanism of the LSPR effect in transformation of glycerol under solar irradiation in Ag₂O/TiO₂. Reprinted with permission from Ref. [103]. Copyright (2017) Elsevier Ltd.
Some examples of experiment of glycerol PR over a 0.5% Pd/TiO$_2$ and for 2% Au/TiO$_2$ were proposed in [109]. In this study, only the UV light interacts with the catalysts. Pd, although applied in lower loading than Au, proved to be around twice as active.

More detailed investigations are conducted in [101], where during experiment 0.2 g of 0.3 wt.% Pd/TiO$_2$ catalyst was suspended in 100 ml deionized water. 100 μL of glycerol was added and illuminated with a 400 W Xe arc lamp (Oriel model 66084). Rate of hydrogen production, \(1.4 \text{ ml } \text{H}_2 \text{ (g) min}^{-1}\text{mol}^{-1}\); rate of \(\text{H}_2\) per mole alcohol \(\sim 0.2 \text{ mL s}^{-1}\text{mol}^{-1}\) (stoichiometric number)\(^{-1}\), where “hydrogen stoichiometric number” is the amount of hydrogen gas generated per mole of alcohol (in the cases PR of glycerol, the hydrogen stoichiometric number is 7). The reaction mechanism for Pd-based photocatalysts was proposed based on tests performed to determine the impact of molecular structure on the amount of \(\text{H}_2\) generation (see Figure 24).\([101,110]\) After chemisorption of the alcohol on Pd, rapid reaction occurs leading to the formation of a strongly chemisorbed CO on the palladium surface is inhibited. Then, photon absorption leads to a generation of active oxygen species which removes CO as \(\text{CO}_2\) by the photo-generated reaction.

![Figure 23. HR-TEM images of Ag$_2$O–TiO$_2$: (a) nanosphere (AS), (b) nanoplate (AP), (c) nanotube (AT), (d) HR image of TiO$_2$ and Ag$_2$O, and (e) particle size distributions of Ag$_2$O on AS, AP, and AT, respectively. Reprinted with permission from Ref. [106]. Copyright (2020) 2020 Yang, Zhong, Chen, Wang, Mo, Zhang, Shu and Song.](image)

![Figure 24. Scheme of photoreforming mechanisms of primary alcohol on Pd/TiO$_2$ catalysts. \(V_0\) indicates a lattice vacancy. Reprinted with permission from Ref. [101]. Copyright (2011) Elsevier B.V.](image)
holes. When desorption of carbon dioxide occurs the vacant site at the metal surface or at the metal/titania interface is available for further alcohol adsorption.

The results published in Ref. [102] demonstrate that by fine-tuning of the composition and a structure of the metal Pd$_{\text{shell}}$–Au$_{\text{core}}$ NPs immobilized on TiO$_2$ result in extraordinarily high quantum efficiencies for H$_2$ generation using glycerol as a sacrificial agents (see Table 3).

To effectively improve TiO$_2$ photocatalytic performance, using of the noble metals as a cocatalysts is the most common approach, however their high price encourages researchers to pay more attention to Earth-abundant metals as co-catalysts. One of most investigated non-noble co-catalyst used for transformation of glycerol valorization to H$_2$ is Cu. Some comparisons of results of Cu/TiO$_2$ and CuO$_x$/TiO$_2$ shows that the second one was more active for valorization of glycerol to H$_2$.

Jung and coworkers[99] consider the promotional effect of bimetallic Cu and Pt nanoalloys loaded onto TiO$_2$ for H$_2$ photogeneration. CuO$_x$–PtO$_2$ composites were immobilized on TiO$_2$ particles by impregnation process followed by heat treatment in the air. The results show that Pt increased the photocatalytic activity about 3 folds, whereas for Cu only there was no significant effect. Compared to above-mentioned observations, co-deposition of Cu–Pt increased the photoactivity around 4.5 times. Theoretical studies (Density Functional Theory, DFT, calculations) indicated the increased electron density in the Pt component of the deposits, attributed to the interaction between the Cu and Pt, which left it in a more reducible state. It is believed that Pt, where the greater charge density is present, has positively contributed for the initial deposit reduction step as well as for H$_2$ evolution rate. The Cu–Pt alloy also appears to promote the charge separation of photogenerated electrons, especially in the reduced state, which may further improve photocatalytic H$_2$ production. The scheme of photocatalytic H$_2$ generation processes is depicted in Figure 25. It is worth mentioning that studies on the coupling inorganic semiconductors together with metal organic frameworks (MOFs) for photocatalytic applications in has been successfully conducted in [114–116], including photoreforming of aqueous glycerol mixture under simulated solar irradiation, in which the hydrogen was obtained as a product.[105,117]

Nickel is another example of non-noble metal which is widely used as TiO$_2$ co-catalyst for hydrogen generation. Liu et al.[88] report that photocatalytic production of H$_2$ over NiO$_x$/TiO$_2$ depends substantially on the calcination temperature during catalyst preparation, which would impact the formation of n-type semiconducting NiO$_x$ and p-type (TiO$_2$) junction. The maximum photoactivity can be achieved after calcination at 450°C. Moreover, the band gap energy of composite system is decreased (0.58 eV) with respect to TiO$_2$. For calcination in
higher temperature, reduction of the catalytic performance is observed due to a significant decrease in the surface area. Fujita et al.\textsuperscript{[20]} noted that the amount of NO\textsubscript{2} loaded onto TiO\textsubscript{2} is the important factor affecting the photocatalytic performance. Two competitive effects, related to the NO\textsubscript{2} amount used, are observed. The energy gap decreases with increasing NO\textsubscript{2} loading, but on the other hand, the amount of generated H\textsubscript{2} becomes lower, due to the reduction of the exposed surface area of TiO\textsubscript{2} that can be illuminated by the light.

Non-TiO\textsubscript{2} based photocatalysts research conducted in last years were also proposed and tested in hydrogen generation via photoforming process.\textsuperscript{[17,95,118,119]} Among them, one of the most common choice under visible light irradiation is CdS (n-type semiconductor with bandgap energy of 2.4 eV). The CdS has some drawback such as its tendency to cadmium leaching, which is a result of photooxidation related with rapid recombinination of photogenerated electron and hole pairs.\textsuperscript{[96,120–123]}

Pechini’s method was used for producing a type II heterostructure Cd(7\%)-SnO\textsubscript{2}/(CdS)\textsubscript{0.3}. When the initial solution had the same amount of Cd and Sn,\textsuperscript{[94]} The synergistic effect on the photocatalytic activity in hydrogen production (290 µmol g\textsuperscript{-1} h\textsuperscript{-1}) for this composite can be attributed to two factors, the first one is the presence of CdS which acts as the absorbing species and the second is related to Cd(7\%)-SnO\textsubscript{2} which prevents the charge recombination phenomenon.

Xiang et al.\textsuperscript{[122]} reported oil-soluble CdS quantum dots (QDs) prepared by means of a solvent-thermal process for which H\textsubscript{2} generation. In this research, the glycerol was used as sacrificial agent and reaction was conducted under visible light illumination. They observed that pristine water-soluble CdS QDs show a very low H\textsubscript{2} production rate (0.067 mmol g\textsuperscript{-1} h\textsuperscript{-1}) due to high recombination rate of electron and hole and overpotential of hydrogen evolution reaction. The presence of Sn\textsuperscript{2+} co-catalyst in the solution leads to significantly increased hydrogen transformation rate. For the concentration of Sn\textsuperscript{2+} equal 0.2 × 10\textsuperscript{-3} M, the amount of generated hydrogen is 24 times higher (1.61 mmol g\textsuperscript{-1} h\textsuperscript{-1}). It is attributed to the adsorption of Sn\textsuperscript{2+} ions on the surface of CdS QDs, which in the next step is reduced to Sn atoms by the photogenerated electrons from the conduction band of CdS QDs upon light illumination. The concentration of Sn\textsuperscript{2+} is increased in the solution, which cause a decrease in the amount of produced H\textsubscript{2}. It is explained by the fact that excess amount of Sn\textsuperscript{2+} can possibly block the light absorption by CdS QDs.

Another example of non-TiO\textsubscript{2} based photocatalysts is described by Vaiano et al.\textsuperscript{[7,17]} The presence of Cu in the ZnO crystal lattice leads to a significant enhancement in photocatalytic H\textsubscript{2} production from an aqueous glycerol solution (initial concentration − 5 wt.% under visible light illumination. The best results of H\textsubscript{2} production rate (2600 µmol L\textsuperscript{-1}) were achieved under Cu loading 1.08 mol\% (photocatalyst dosage 1.5 g L\textsuperscript{-1}, solution pH equal to 6). By increasing up to 10 wt.% the initial glycerol concentration, the hydrogen production rate was increased to about 4770 µmol L\textsuperscript{-1}. The doping with Cu inhibits the recombination rate of the photogenerated electron-hole pairs, which cause that catalyst can produce hydrogen. Authors proved that the Cu-doped ZnO-based photocatalysts have to be active for several reuse cycles, maintaining the same hydrogen production and evidencing the absence of photocorrosion phenomena in the optimized operating conditions, and what is more important, the catalyst is able to produce hydrogen under visible light without the presence of noble metals in a sample formulation.

Z-scheme systems heterojunction photocatalyst is based on mixing of at least two semiconductorsto achieve composite materials one is responsible for the photogeneratore holes, and another for photogenerated electrons.\textsuperscript{[124]} This approach may assure lower bandgap and better charge separation, stability and light absorption which in turn improve the photocatalytic activity.\textsuperscript{[95,97,118,125]} Tahir et al. analyzed Z-scheme Au-NPs embedded on dual photocatalysts WO\textsubscript{3}/TiO\textsubscript{2} for boosting photocatalytic hydrogen transformation from aqueous glycerol solution under visible light.\textsuperscript{[97]} For 0.5% Au-loaded WO\textsubscript{3}/TiO\textsubscript{2} the highest H\textsubscript{2} generation rate (of 17200 ppm g\textsubscript{cat} \textsuperscript{-1} h\textsuperscript{-1}) was achieved, which was 2.33, 4.46 and 5.89 folds higher in comparison to Au/TiO\textsubscript{2}, WO\textsubscript{3}/TiO\textsubscript{2} and pristine TiO\textsubscript{2} samples, respectively. The catalysts revealed test stability also in cyclic runs of continuous H\textsubscript{2} production. Researchers revealed that constructing heterojunction photocatalyst adjusted redox potential. Furthermore, faster charges separation under visible light irradiation may be achieved by decorating photocatalyst with plasmonic Au NPs (see Figure 26), which results in superior H\textsubscript{2} production rate.

Next type of hetero-structured nanocatalyst is described by Tahir.\textsuperscript{[126]} La-modified TiO\textsubscript{2}/CNTs was synthesized for photocatalytic H\textsubscript{2} production under visible light. The samples were prepared by sol-gel assisted with hydrothermath method. The highest photogeneration of H\textsubscript{2} from aqueous glycerol solution (17265 ppm g\textsubscript{cat} \textsuperscript{-1} h\textsuperscript{-1}) was obtained for 5%La-5% CNTs/TiO\textsubscript{2} nanoroads (HRTEM images of catalysts are shown in Figure 27). For this (5%La-5% CNTs/TiO\textsubscript{2}) catalyst produced H\textsubscript{2} amount was 1.14, 1.53 and 4.10 folds greater than for (I) 5%La-5% CNTs/TiO\textsubscript{2}, (II) 5%La/TiO\textsubscript{2} and (III) using bare TiO\textsubscript{2} NPs respectively. Significant enhancement of photoactivity is affected by the synergistic effect that occurs between La and CNTs, relatively larger BET surface area, cleavage of glycerol by La, as well as appropriate band structure, and hindered charge recombination rate. Interestingly, this catalyst also demonstrated prolonged stability with a steady H\textsubscript{2} generation in cyclic runs.

The Bi\textsubscript{2}O\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} nanocomposite has been proposed as an efficient hydrogen generation photocatalyst in the process of photoforming from glycerol-water mixture over visible light illumination.\textsuperscript{[98]} Depending on the contact degree developed amongst the Bi\textsubscript{2}O\textsubscript{3} particles and the g-C\textsubscript{3}N\textsubscript{4} sheets, type-\textit{p}−\textit{n} junctions (Figure 28A) or Z-scheme (Figure 28B) may be responsible for the efficient charge separation in the Bi\textsubscript{2}O\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} composites.\textsuperscript{[98]} Changing the Bi\textsubscript{2}O\textsubscript{3} content (0.5–5.0 molar %) a serious of nanocatalysts was synthesized by the sonication-mixture and two-step sol-gel method, using mesoporous β-Bi\textsubscript{2}O\textsubscript{3} and g-C\textsubscript{3}N\textsubscript{4}. The maximum H\textsubscript{2} production was achieved for Bi\textsubscript{2}O\textsubscript{3} at 3.0 molar % β-Bi\textsubscript{2}O\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4}, which was 20 times higher than that obtained for bare materials (8585 vs 400 µmol g\textsuperscript{-1}) respectively. It was possible due to the presence of effective heterojunctions that improved charge transference in material,
and decrease the level of recombination of photo-charges for nanocomposite.

In recent years, fast growth is expected in the photocatalytic conversion of glycerol to hydrogen. Among various methods, extensive research of the photocatalysis processes is focused on development of novel and effective deposition methods and their optimization to form active nanocatalysts with well-defined sizes, shape, and oxidation states on the semiconductor surface. The noble metals, in particular Pt, are found to be the most effective cocatalysts, but the academic society attention is focused on using Earth-abundant metals such as Ni or Cu as cocatalyst, due to their lower price. Heterojunction composites are also very promising materials due to their possibility of overcoming the thermodynamic limitations of semiconducting materials.

Figure 26. Scheme of photocatalytic glycerol aqueous transformation to H₂ over Au-NPs embedded WO₃/TiO₂ under visible light illumination. Reprinted with permission from Ref. [97]. Copyright (2019) Elsevier B.V.

Figure 27. HR-TEM images of La-modified TiO₂ NRs embedded over CNTs. (a–c) TiO₂ NRs dispersed over CNTs, (d–e) TiO₂ NRs/CNTs heterojunctions, (f) d-spacing of TiO₂ and CNTs. Reprinted with permission from Ref. [126]. Copyright (2018) Hydrogen Energy Publications LLC. Published by Elsevier Ltd.
3. Plasmonic Enhanced Hydrogen Production from the 2nd Generation of Biofuels

Cellulose is a carbohydrate polymer, also known as a polysaccharide. This polysaccharide constitutes more than 50% of lignocellulose which represents a copious renewable carbon resource for producing chemicals sustainably. Cellulose is structured centrally within the lignocellulosic body through interconnected semi-crystalline microfibers. Van der Waals forces and hydrogen bonding are significant interactions through the whole cellulose microfibril structure. D-Glucose (monomer of cellulose) is linearly connected thanks to β-1,4-glycosidic bonds with polymerization degree between 800 up to 10,000.

In the open literature already exist two excellent and complete review articles[129,130] that extensively summarize state of the art (till 2016) concerning photo-driven reforming of cellulose and glucose for the production of hydrogen. However, in none of the scientific works cited in this open literature, there were no discussions on the usage of supported plasmonic nanophotocatalysts. In this part of our review, we will focus on the research carried out during the last five years (since 2016). It is worth signalizing that, in the open literature of the last five years, the investigations on this specific subject are scarce.

3.1. Photoreforming of cellulose

First discovered (in 1980) by Kawai and Sakata, that the feedstock from plants such as carbohydrates could release H₂ upon a light sources coming from a Xe lamp. In an aqueous solution and RuO₂/TiO₂/Pt[131] and Pt/TiO₂[132] as photocatalysts, H₂ was formed with low rates of less than $<50 \text{µmol g}^{-1} \text{h}^{-1}$.

Cellulose is the main sources of glucose, and let’s start this section with the first example of improving the hydrolysis of cellulose to glucose (as an important step for hydrogen production) at visible-light published by applying TiO₂ nano-fibre (T)-supported zeolite HY adorned with Au nanoparticles (NPs), named as Au-HYT. To achieve a 48% of glucose yield, a 16 h of visible-light illumination at 140 °C was needed (without significant activity under dark conditions). These findings reveal that the tremendous improvement in hydrolysis mainly is due to the LSPR (Localized Surface Plasmon Resonance) effect of Au nanoparticles. It was postulated that the polarized electric field of zeolites might enhance the power of acidity throughout the LSPR. Following these lines, Li and collaborators reported another plasmonic metal (Ir)/zeolite composite dissociating the β-1,4-glycosidic bond in cellobiose (a simple model of cellulose). Ir/HY composite catalyst performed with high efficiency in hydrolyzing the β-1,4-glycosidic bond at a maximum temperature of 100 °C under visible-light. Additionally, the same composite material was active in the hydrolysis of crystalline cellulose, giving 5-hydroxymethylfurfural (HMF) glucose, and cellobiose as the most important produced chemicals.

As previously found in the literature, Pt (as any other metals) supported on surface of the TiO₂, has the role of an electron sink, improving the split of the photo-driven charge carriers and retarding the recombination of $e^-/h^+$ pairs. These carriers can primarily induce the reactions of water-splitting for hydrogen formation (Figure 29a).[130,135] After that, the generated glucose may proceed through several routes to produce hydrogen (Figure 29b).

None well-determined plausible reaction mechanism for photo-induced catalytic reforming of glucose has not been reported to date, and recently, a significant number of metal-
containing co-catalyst and its deposition methods on TiO$_2$ for photocatalytic hydrogen production from wastewaters or biomass has been reported.$^{[130]}$ However, the studies are not focused on plasmonic nano-photocatalysts.

In different studies, $\alpha$-cellulose was used as a model of lignocellulose since it is not completely a purified cellulose substrate, but a combination of cellulose and other polysaccharides (mostly xylan) easily produced from agricultural and forest wastes after pretreatment under very strong base-containing aqueous media. Considering these results, a relatively soft hydrolysis at 160°C was chosen as the right pretreatment to produce biomass-derived aqueous streams for the further photo-induced catalytic hydrogen production (Figure 30).$^{[36,137]}$

Recently, Lan et al. reported a concise study of the photo-driven catalytic reforming of cellulose over metal/TiO$_2$ (i.e. mixed TiO$_2$, 80% of anatase and 20% of rutile) catalysts in water.$^{[138]}$ m-TiO$_2$ was applied as the support to prepare the right material under study compared with the investigated catalysts based on TiO$_2$, P25. A systematic investigation was carried out to study Pt loading, the loading of cellulose and catalyst in the reaction setup, and the temperature of the reaction on the photocatalytic behavior. In this study, platinum-based catalysts immobilized on m-TiO$_2$ (Pt/m-TiO$_2$) were synthesized by a simple wet impregnation method followed by calcination in air at 500°C for two hours. Before the catalytic tests, Pt/m-TiO$_2$ catalysts were reduced in pure H$_2$ at 200°C for 30 min. According to the outcomes, the photo-driven catalytic reforming system applying cellulose is operated at 40°C with 1.0 g L$^{-1}$ of cellulose and 0.75 g L$^{-1}$ of 0.16 Pt/m-TiO$_2$ photocatalyst to obtain the optimum photo-driven catalytic efficiency of rH$_2$ = 9.95 μmol h$^{-1}$, and rCO$_2$ = 3.75 μmol h$^{-1}$. One more time, and what is commonly observed in the literature, in this work the LSPR was not investigated.

3.2. Photoreforming of glucose

Although so far, the plausible mechanism for the photo-induced reforming of glucose (Eq. (19), Figure 29b) is not

![Figure 29. Suggested model of the photoreforming for cellulose over metal/TiO$_2$: (a) The role of the metal as e$^-$ trappers for a better separation of photo-generated e$^-$/h$^+$ pairs; (b) The role of the metal in glucose photocatalytic dehydrogenation. Reprinted with permission from Ref. [130]. Copyright (2016) The Authors.](image-url)
entirely understood, all the investigations showed a constant degradation/oxidation route acting at the photo-generated holes, producing formic acid, and subsequently a mixture of hydrogen and CO/CO$_2$. A different plausible mechanism may be suggested that takes into account the metal as a catalytically active center (Figure 29b).\textsuperscript{[130]}

\[
C_6H_{12}O_6 \rightarrow 6CO + 6H_2
\]  
(19)

This reaction proceeds on metal-containing catalysts such as Pt via cleavage of C–C bonds, as it is known in the literature for reforming of glucose in water.\textsuperscript{[139]} This reaction would take place in the absence of light, and no further reactivity would be observed due to deactivation of Pt by chemisorbed CO. However, illumination of titania with UV light evoked e$^{-}$/h$^+$ pairs, with the hole possessing high electrophilic O$^-$ properties.\textsuperscript{[140]} These reactive oxygen species (ROS) reacted with CO chemisorbed on Pt, stimulating the production of carbon dioxide and further free active Pt site for the adsorption of more glucose. The formation of more hydrogen will be through the anion vacancy on the TiO$_2$ support after the interaction with water. The whole process is represented as follows [Eqs. (20–23)]:

\[
C_6H_{12}O_6 + Pt^\circ \rightarrow 6CO_{ad} + 6H_2
\]  
(20)

\[
TiO_2 + hv \rightarrow Ti^+++ + O^\cdot + O^{2-}
\]  
(21)

\[
CO_{ad} + O^\cdot \rightarrow CO_2 + Pt^\circ + V^o
\]  
(22)

\[
V^- + Ti^+++ + O^{2-} + H_2O \rightarrow TiO_2 + H_2
\]  
(23)

X. Wu et al. have prepared 1.7 wt.% initial cobalt content in CoO/g-C$_3$N$_x$, the photocatalyst synthesized by one-pot procedure presented the highest photo-induced catalytic activities with a H$_2$ production rate of approx. 60 $\mu$mol g$_{cat}$$^{-1}$ h$^{-1}$ in the course of PASC PR (phosphoric acid swollen cellulose (PASC) photoreforming).\textsuperscript{[137]} In the presence of CoO/g-C$_3$N$_x$ composite, the all glucose was entirely converted within 3 h with approx. 78 wt.% of the carbon in glucose converted to lactic acid, together with approx. 43 $\mu$mol g$_{cat}$$^{-1}$ of hydrogen (5 mg of hydrogen dissolved in 1 M NaOH solution containing 10 mg of CoO/g-C$_3$N$_x$ applying a 300 W Xenon lamp).

Different copper- or nickel-loaded TiO$_2$ photocatalysts have been compared by Bahadori et al., in photoreforming of glucose.\textsuperscript{[141]} The catalysts were synthesized starting from three titania-based materials, fabricated by precipitation and characterized by crystalline anatase with high surface area, or fabricated through flame synthesis, i.e., flame pyrolysis and the commercial P25, producing a mixture of rutile and anatase phases with smaller surface area. The best activity within the semiconductors was found for the commercial titania P25, while the modification with 1 wt.% CuO by precipitation led to the highest hydrogen productivity, i.e., 9700 $\mu$mol g$_{cat}$$^{-1}$ h$^{-1}$.

A methodical investigation on the solar-induced catalytic production of hydrogen (by photoreforming) for M/TiO$_2$ (M = Au, Ag, Cu, or Pt) applying glucose as a model molecule, and subsequent extended to lignocellulose hydrolysates and wastewaters, was published (Figure 30).\textsuperscript{[136]} Three methods metal (M) co-catalyst loading were studied: (i) Deposition-precipitation (DPM), (ii) impregnation and (iii) photodeposition (PDM). Deposition-precipitation (finishing with hydrogenation, H) or photo-deposition ensured more interesting results than conventional impregnation (finishing by calcination). Immobilizing of metal-containing co-catalysts by photo-induced deposition or deposition-precipitation methods gives considerable high H$_2$ productivity. In any case, either H$_2$DPM/TiO$_2$, and PDM/TiO$_2$ hydrogen productivity increases according to the following sequence: Ag < Cu < Au < Pt. The explanation by the authors for the

Figure 30. Photo-induced catalytic hydrogen production yields from rice husks or $\alpha$-cellulose hydrolysates prepared at 160°C on HDP/Cu/TiO$_2$ (HDP-decoration-precipitation of Cu followed by hydrogenation) by direct simulated sunlight illumination (direct simulated, AM1.5G, 1.0 kW m$^{-2}$), treated under UV (Hg lamp, $\approx$1.5 kW m$^{-2}$) irradiation, and simulated sunlight irradiation after the initial UV treatment. Reaction conditions: homogeneous suspensions of the photocatalyst (25 mg) in the biomass hydrolysate (25 mL) irradiated under argon environment (1.4 bar) at 25°C, $t$ = 2 h. Reprinted with permission from Ref. [136]. Copyright (2019) MDPI (Basel, Switzerland).
improved photocatalytic activity is probably connected to the predominant presence of reduced metallic nanoparticles, providing active sites for hydrogen production. The best results were obtained (1912.7 μmol g⁻¹ h⁻¹ of hydrogen) applying M/TiO₂ (M = Au, Ag, Cu, or Pt) under argon environment (1.4 bar) at 25 °C, and irradiation time of 120 minutes.

In another very interesting work, but not deeply studied in terms of LSPR, Gao et al., investigated nanocomposites (SiO₂/Ag@TiO₂ core-shell) for a solar thermal collector which shows efficient photo-induced thermic features for the simultaneous production of desalinated seawater and hydrogen (Scheme 1). The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through SiO₂/Ag core for generation of heat that is concomitantly helpful for photocatalysis. The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through The whole system is designed for wide absorption of solar light where higher energy photons absorbed by TiO₂ shell are used for photocatalytic electron-hole pair formation, and lower energy photons are trapped through where the plasmonic-induced energy is traveling from the metal to the titania to magnify the formation of e⁻-h⁺ pairs in the semiconductor (in this case TiO₂)[142,146]. The hydrogen productivities were determined as follows: 150 μmol g⁻¹ h⁻¹ for TiO₂ spheres, 264 μmol g⁻¹ h⁻¹ for SiO₂@TiO₂ and 816 μmol g⁻¹ h⁻¹ for SiO₂/Ag@TiO₂ core-shell nanocomposites. Worth mentioning is the fact that no photo-driven catalytic hydrogen was observed (for all materials tested) when visible-NIR light was the unique source of illumination.

Photo-induced reforming of organics for hydrogen production by applying copper-containing TiO₂ photocatalysts is attracting a lot of attention[141]. In the investigation of Clarizia et al.[145] nanoparticles of TiO₂-P25 were applied as an active support for the preparation of Cu-containing photocatalysts using CuSO₄ and Cu₂O (alternatively) in an aqueous suspension of TiO₂-P25 before the irradiation. The ability of different organic acids and alcohols for hydrogen photoreforming was studied. Experimental results indicate the appearance on the catalysts surface of metal copper nanoparticles (for both CuSO₄ and Cu₂O together with TiO₂-P25). Additionally, a plausible mechanism of hydrogen formation through localized surface plasmon resonance (LSPR) was presented (Scheme 2).[146] Based on the best optimized experimental conditions ([Cu(III)]: 0.8 mM; TiO₂ load: 500 mg L⁻¹), the production rate of hydrogen under Cu-modified TiO₂ (H₂, CuTiO₂-P25) after 120 min of light irradiation was 2.50 μmol min⁻¹ in comparison with 0.34 μmol min⁻¹ for bare TiO₂-P25.

The lack of stability of Cu-based photocatalysts due to photocorrosion/leaching problems is an important issue that must be undertaken for future real applications, especially knowing that keeping the lab conditions (i.e.: reducing conditions: inert atmosphere, in the presence of a sacrificial agent, and Cu photodeposition under UV irradiation) to guarantee good acceptable stability is not sustainable under future industrial conditions (i.e.: exposure to air and in the presence of acidic reaction intermediates). In the open literature
there are strategies to improve such stability,\cite{147} such as the preparation of embedded CuOx@TiO$_2$ by a water-in-oil microemulsion method\cite{148} consisting in the synthesis of Cu nanoparticles in a microemulsion continued by hydrolysis and condensation of tetraisopropyl orthotitanate with the main goal of covering the protected copper NPs with a porous titanium oxyhydroxide layer.

The studies on the mechanism of glucose photo-induced catalytic reforming are not well-explored (especially in the case of plasmonic photocatalysis), and depends on several key parameters among them, the kind of selected photocatalyst. As an example, a plausible reaction mechanism for the H$_2$ production through photocatalytic transformation of glucose on Pt-F-TiO$_2$, showing the existence of gluconic acid in solution, is the following [Eqs. (24–27)].\cite{149}

\begin{align*}
  h^+ + H_2O &\rightarrow \cdot OH + H^+ \\
  h^+ + OH &\rightarrow \cdot OH \\
  H^+ + e^- &\rightarrow \frac{1}{2}H_2 \quad (on \text{Pt}) \\
  RCHO + \cdot OH &\rightarrow RCO' + H_2O \\
  \text{Or} \quad [\text{Eqs. (28–32)}] \\
  h^+ + RCHO &\rightarrow RCO' + H^+ \\
  RCO' + H_2O &\rightarrow RCOOH + \cdot H \\
  RCOOH + \cdot OH &\rightarrow R'OH(R^{'CHO}) + CO_2 + \cdot H
\end{align*}

Where:

\begin{align*}
  RCHO &= C_6H_{12}O_6 \\
  RCOOH &= C_6H_{12}O_7
\end{align*}

Based on the above equations, the reaction is started by the light-induced activation of Pt-F-TiO$_2$ photocatalyst, giving the generation of e$^-$–h$^+$ pairs. The holes (h$^+$) can be covered by water molecules on the surface or/and hydroxyl ions to create *OH radicals [Eqs. (24) and (25)]. Platinum (Pt) can capture photoformed electrons from the conduction band, and as a consequence, the protons H$^+$ (electron acceptors) react with the electrons to form gas hydrogen on Platinum [Eq. (26)]. Glucose (RCHO, adsorbed on the catalyst surface) reacts with *OH radicals [Eq. (27)], producing gluconic acid [Eq. (29)], which would react further with *OH radicals provoking a decarboxylation reaction to occur [Eq. (30)]. Potentially the h$^+$ (holes) can also react straightforward with glucose (acting as electron donor) [Eq. (28)]. The formed *H radicals can produce gas H$_2$ [Eqs. (31) and (32)]. The quantity of CO$_2$ formed [Eq. (30)] was observed to be higher in the presence of Pt-F-TiO$_2$ than for Pt–S–TiO$_2$, indicating the higher reactivity of unbounded *OH radicals (formed on Pt-F-TiO$_2$) than the *OH ones captured on the surface of the catalyst (formed on Pt–S–TiO$_2$).\cite{149}

As mentioned before, the literature closely connected to the studies on wet photoreforming of cellulose and glucose applying supported plasmonic nanoparticles is insignificant.
with just a few articles mentioning the general thermal effect connected to the photocatalytic effect of the material. One of the reasons for that is the lack of specialized methods to study LSPR in association with a thermophotocatalytic behavior of the material tested, especially working in situ-operando under such complex measurement conditions of wet photocatalytic reforming of biomass-based model compounds.

4. Plasmonic Enhanced Dry Reforming of Methane

Dry reforming of methane (DRM) has initiated a great scientific efforts in recent years since it enables the conversion of CH₄ and CO₂ into industrially important synthesis gas or (mixture of CO and H₂ also called syngas). Syngas is a basic ingredient for a large scale production of value-added chemical compounds, for example methanol (CH₃OH), formaldehyde (HCHO), methyl tert-butyl ether (MTBE), and dicarboxylic acid (H₂O₂C–R–CO₂H), as well as liquid synthetic motor fuels obtained via the Fischer-Tropsch synthesis, such as gasoline (C₅–C₁₂), naptha (C₁₂–C₂₀), kerosene (C₁₁–C₁₃), and diesel (C₁₂–C₂₂).[153] As hydrogen can be easily separated from syngas, the DRM process constitutes alternative source of H₂. In general, DRM is a complex endothermic process that involves 6 major chemical reactions [Eqs. (33–38)].

\[
\begin{align*}
CH₄ + CO₂ &\rightarrow 2CO + 2H₂ \quad \Delta H_{298K}^{°} = 247.3 \text{kJ mol}^{-1} ; \Delta G° = 66170 - 67.32T \\
CO₂ + H₂ &\rightarrow CO + H₂O \quad \Delta H_{298K}^{°} = 41.0 \text{kJ mol}^{-1} ; \Delta G° = -8545 + 7.84T \\
CH₄ + H₂O &\rightarrow CO + 3H₂ \quad \Delta H_{298K}^{°} = 206.0 \text{kJ mol}^{-1} \\
CH₄ &\rightarrow C + 2H₂ \quad \Delta H_{298K}^{°} = 75.0 \text{kJ mol}^{-1} ; \Delta G° = 2190 - 26.45T \\
2CO &\rightarrow C + CO₂ \quad \Delta H_{298K}^{°} = -171.0 \text{kJ mol}^{-1} ; \Delta G° = -39810 + 40.87T \\
CO + H₂ &\rightarrow C + H₂O \quad \Delta H_{298K}^{°} = -131.0 \text{kJ mol}^{-1}
\end{align*}
\]

Generally, the major DRM reaction (Eq. 33) occurs at high temperature range from 700 to 1000 °C and it is necessary to maintain such a high temperature in order to achieve high equilibrium conversion of substrates. The equilibrium of DRM, however, is impacted by the reverse water gas shift reaction (RWGS) (Eq. 34), leading to higher CO₂ conversion CO than CH₄. Therefore, the CO/H₂ ratio is usually less than 1. Limiting temperatures of various reactions associated with DRM are presented in Table 5.

The following conclusions can be drawn from Table 5: 1) the DRM reaction is goes along with methane cracking at temperatures > 640 °C; 2) the disproportionation of CO (Eq. 37) and RWGS reaction (Eq. 34) is hindered above 820 °C; 3) the most plausible range of temperature for deposition of carbon due to CH₄ cracking and CO disproportionation reaction is found to be 557–700 °C. However, the DRM process has a thermodynamic limitation. When the temperature of the reaction exceeds 727 °C, the reforming reaction becomes favorable. At high temperature, CO disproportionation reaction (Eq. 37) is hindered but the deep cracking of methane (Eq. 36) is promoted, resulting in the formation of carbon deposit, which primarily causes the catalyst deactivation. Although an extensive research has been conducted to tackle the problem, carbon deposition poses a serious threat to DRM process. Utilization of light energy has been proposed as a potential solution to this problem because the photocatalytic reaction usually takes place at relatively low temperatures range beyond the thermodynamic limit.

The first ever reported photocatalytic transformation of CO₂ and CH₄ was carried out over ZrO₂ powder photocatalyst under UV light. After 5 h of irradiation, 0.7 µmol of CO and very small amount (0.03 µmol of H₂) were present in the gas phase. When the sample was subsequently heated at 400 °C for 20 min, the production yield increased to 1.57 µmol of CO and 0.2 µmol of H₂, respectively. Shortly after, the same group reported that MgO exhibits activity toward the photoreduction of CO₂ to CO under UV illumination in the presence of CH₄, however, H₂ was not detected. The next interesting attempt to transform CO₂ and CH₄ into a mixture of CO and H₂ by means of photocatalytic DRM (photo-DRM) was made by Yuliati et al. Photo-DRM was carried out using a Ga₃O₅ photocatalyst powder with specific surface area around 2 m² g⁻¹ at mild 200 °C temperatures and compared to the thermal DRM reaction. Nevertheless, the photocatalytic activity of this system (1.1 µmol of CO and 2.5 µmol of H₂ after 3 h) was still insufficient even under UV illumination at 200 °C. Recently, Wibowo et al. have investigated the effect of UV light irradiation on DRM at 700 °C over several metal oxides: SrTiO₃, TiO₂, WO₃, and SnO₂. It was reported that SrTiO₃ particles with specific surface area 15.43 m² g⁻¹ demonstrated the highest performance for photo-DRM (0.35 µmol min⁻¹ of CO and 0.038 µmol min⁻¹ of H₂) among the investigated metal oxide.

| Reaction | Temperature [°C] |
|----------|-----------------|
| DRM [Eq. (1)] | Lower limit 640 |
| CH₄ cracking [Eq. (4)] | 557 |
| Boudouard reaction [Eq. (5)] | Upper limit 820 |
| RWGS reaction [Eq. (2)] | 1093 |
photocatalysts (see Figure 31), and at the same time exhibited high stability against coking at ~700 °C.

As can be seen, the major limitation of pristine metal oxides in photo-DRM is the necessity of UV light excitation due to relatively large bandgap values typical for these photocatalysts. Early attempts at performing photo-DRM process require significant external heating as well. For the effective utilization of solar irradiation, however, the photocatalysts that are active across the entire visible and also near infrared (Vis-NIR) light, and at the same time capable of driving low temperature photo-DRM are the most sought-after.

Over the past few years, a great effort has been devoted to couple the wide bandgap semiconductors with metallic NPs (predominantly plasmonic metals), in order to design efficient photocatalysts for photo-DRM reaction that could operate under whole UV-Vis-NIR spectrum and low temperature.\(^\text{[160-172]}\)

From the perspective of modifying metal type, one can distinguish four major groups of supported nanocatalysts for photo-DRM: 1) platinum-modified, such as Pt/black-TiO\(_2\)\(^\text{[166]}\) Pt/CeO\(_2\)\(^\text{[173]}\) Pt/SiO\(_2\)\(^\text{[172]}\) 2) rhodium-modified, such as Rh/SiO\(_2\)\(^\text{[161]}\) Rh/Al\(_2\)O\(_3\)\(^\text{[160]}\) Rh/SiTiO\(_2\)\(^\text{[160]}\) Rh/ZrO\(_2\)\(^\text{[166]}\) rh/ThO\(_2\)\(^\text{[166]}\) 3) nickel-modified, such as Ni/SiO\(_2\)\(^\text{[168]}\) Ni/Al\(_2\)O\(_3\)\(^\text{[163,165,169]}\) Ni/Ga\(_2\)O\(_3\)\(^\text{[165]}\) Ni/TiO\(_2\)\(^\text{[162]}\) Ni/CoO\(_2\)\(^\text{[170]}\) Ni/CoO\(_2\)/SiO\(_2\)\(^\text{[164]}\) and 4) bimetallic-modified, such as Pt-Au/SiO\(_2\)\(^\text{[172]}\) Rh-Au/SiO\(_2\)\(^\text{[161]}\) Cu-Ru/MgO-Al\(_2\)O\(_3\)\(^\text{[167]}\). The performance of the photocatalysts in photo-DRM reaction is summarized in Table 6.

The first noticeable progress in photo-DRM was reported for Pt-supported systems. For example, platinum coupled to black TiO\(_2\) crystals dispersed on the light-diffuse-reflection surface of silica exhibited a remarkable 57.8% photo-DRM quantum efficiency at 650 °C, which is 200 °C lower in comparison to that without light irradiation. This result demonstrates a large potential for performing photo-DRM reaction under thermodynamic limit. A unique photocatalyst nanocomposite composed of Pt NPs embedded partially in mesoporous CeO\(_2\) nanorods (see Figure 32) is the next interesting system for photo-DRM process. The photocatalyst was prepared by facile impregnation of CeO\(_2\) nanorods with Pt(NO\(_3\))\(_2\) aqueous solution and tested in photo-DRM under focused irradiation using a high power 500 W Xe lamp (any additional heating was not applied)\(^\text{[173]}\). As compared to the previous system, not only high syngas production rate was achieved, but also the CO/H\(_2\) ratio approaching 1.

The second very important class of nanocomposites dedicated to dry photoforming of methane are Rh-supported photocatalysts. Doubtlessly, special attention should be paid to Rh/SiO\(_2\) system, for which exceptionally large H\(_2\) production rate of ~240 mmol g\(^{-1}\) min\(^{-1}\) and CO/H\(_2\) = 1 were reported\(^\text{[161]}\). Although, to the best of our knowledge, this system together with the other bimetallic Rh-Au/SiO\(_2\) designed by the same authors exhibit the highest reported activity in photo-DRM, one should notice that the performance tests were carried out with the additional heating to 500 °C. Hence, this was rather thermocatalytic DRM process than photo-DRM. Recently, Shoji et al. have investigated several Rh-modified photocatalysts for photo-DRM reaction under UV light excitation and low temperature.\(^\text{[166]}\) One of the investigated nanocomposites, Rh/SrTiO\(_2\) (see Figure 33a), was found to efficiently promote the reaction.

It was demonstrated that Rh/SrTiO\(_2\) system is able to drive the photo-DRM yielding a remarkably high performance, triggers a stoichiometric reaction, and at the same time breaks the thermodynamic limitation of conventional catalyst for synthesis gas generation (see Figure 33b). In addition, the fabricated photocatalyst exhibited long-term stability and resistance to coking and aggregation of metallic NPs. Isotope analysis indicated that the lattice oxygen (O\(^{\text{2-}}\)) species generated by CO\(_2\) reduction mediate the uphill dry reforming of methane (see Figure 33c). The O\(^{\text{2-}}\) species react with residual carbon after methane cracking, yielding stoichiometric CO + H\(_2\) products and highly stable coking-resistant properties of the photocatalyst.

Ni-supported photocatalysts represent the most intensely investigated group of nanocomposites for dry photoforming.

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**Figure 31.** a) The UV-vis reflectance spectra; b) CO production yield from dry reforming of methane at 700 °C under illumination with UV light (On) and under dark condition (Off) for various metal oxide catalysts. Reprinted with permission from Ref. [159]. Copyright (2018) The Chemical Society of Japan.
of methane in recent years. As can be seen in Table 6, either the additional heating or highly focused irradiation has to be applied to overcome sluggish kinetics of the reaction. The most active amongst Ni-supported systems for photo-DRM; the Ni–CeO$_2$/SiO$_2$ was designed and fabricated by Jiang et al. back in 2019.$^{[164]}$ Photo-DRM tests were carried out in a home-made continuous flow photoreactor under highly focused beam of UV-Vis-IR irradiation of 385.2 kW m$^{-2}$. Although the external heating was not applied, the real local temperature of the sample would have been even ~700 °C due to very high energy density of the light beam, resulting in photo-thermocatalytic reaction. The authors achieved extremely high hydrogen and carbon monoxide generation rates (33.42 and 41.53 mmol min$^{-1}$ g$^{-1}$) and remarkably high light-to-fuel efficiency of 27.4%, much higher than those of Ni/CeO$_2$. High photo-thermocatalytic activity of this system was explained by participation of oxygen from CeO$_2$ clusters on Ni nanocrystals in the RDS of DRM reaction. Based on extensive experimental investigations combined with DFT calculations, the activation energies for oxidation of C* and CH* radical species (which is the RDS) were significantly reduced. Considering the example of Ni-modified system investigated under mild conditions (low temperature and low intensity light), the Ni/Al$_2$O$_3$ turned out to be promising in photo-DRM.$^{[163,165]}$ The photo-DRM tests were conducted using a fixed-bed flow photoreactor at 200 °C and Vis-NIR illumination. It was found that the plasmonic Ni/Al$_2$O$_3$ photocatalyst containing 25% mass of Ni prepared by an impregnation method exhibits optimal CO and H$_2$ production rates, which are only slightly lower than in the case of corresponding Rh/Al$_2$O$_3$ system designed by the same authors (see Figure 34).

Bimetallic-supported photocatalysts have emerged recently as promising candidates for highly efficient photo-DRM. These systems can be either in the form of uniformly alloyed NPs or plasmonic antenna-reactor clusters coupled to non-metallic or semiconducting support. In particular, the latter was proven to be perfect choice for low-temperature methane dry photo-reforming. Recently, Zhou et al have developed such a system: a plasmonic photocatalyst composed of a Cu nanoparticle acting as “antenna” with Ru single atomic “reactor” sites on top of the nanoparticle surface with various concentration of Ru (see Figure 35).$^{[165]}$ The Cu$_{x}$/Ru$_{1-x}$ NPs were synthesized by coprecipitation onto MgO–Al$_2$O$_3$ composite support.

| Photocatalyst | Light source | T [°C] | Conversion rate [μmol/g/min] | Production rate [μmol/g/min] | Ref. |
|---------------|--------------|--------|-----------------------------|-----------------------------|------|
| Pt/black-TiO$_2$ | Solar simulator | 0.1 | 550 | – | – | 6167 | 2150 | [160] |
| Pt/CeO$_2$ | 500 W Xe lamp/200–2400 nm | – | 25$^\text{[a]}$ | –3100 | –2800 | 6000 | 5700 | [171] |
| Pt/SiO$_2$ | 300–800 nm | 0.6 | 400 | 46.6 | –35 | –80 | –60 | [172] |
| Rh/SiO$_2$ | Vis/490–550 nm | 0.22 | 500 | 126000 | –120000 | –240000 | –240000 | [161] |
| Rh/Al$_2$O$_3$ | 300 W Xe lamp/UV-Vis | 0.25 | 200 | – | – | 333 | 133 | [165] |
| Rh/SrTiO$_3$ | 150 W Hg-Xe lamp/UV | – | 100 | –500 | –500 | –920 | –920 | [166] |
| Rh/ZrO$_2$ | 150 W Hg-Xe lamp/UV | – | 100 | –420 | –450 | –750 | –820 | [166] |
| Rh/TiO$_2$ | 150 W Hg-Xe lamp/UV | – | 100 | –180 | –220 | –320 | –350 | [166] |
| Cu@TaC | Xe lamp/Vis | 1.5 | 600 | 20000 | 2700 | 18000 | 2850 | [162] |
| Ni/SiO$_2$ | Xe lamp/300–800 nm | 1.07 | 550 | –900 | –670 | –1400 | –1300 | [168] |
| Ni/Al$_2$O$_3$ | Xe lamp/300–800 nm | 1.07 | 550 | –64 | –62 | –130 | –130 | [168] |
| Ni/Al$_2$O$_3$ | 300 W Xe lamp/300–800 nm | 0.25 | 200 | – | | 104 | 67 | [163] |
| Ni/Al$_2$O$_3$ | 300 W Xe lamp/UV-Vis | 0.25 | 200 | – | | 294 | 128 | [165] |
| Ni/Ga$_2$O$_3$ | 300 W Xe lamp/UV-Vis | 0.25 | 200 | – | | –83 | –50 | [163] |
| Ni/TiO$_2$ | 300 W Xe lamp/UV-Vis | 0.25 | 200 | – | | –56 | –56 | [163] |
| Ni/CeO$_2$ | 500 W Xe lamp/200–2400 nm | 36.34 | 25$^\text{[a]}$ | –3200 | –3000 | 6270 | 6530 | [170] |
| Ni–CeO$_2$/SiO$_2$ | 500 W Xe lamp/200–2400 nm | 38.52 | 25$^\text{[a]}$ | –23000 | –18000 | 41530 | 33420 | [164] |
| Pt–Au/SiO$_2$ | Xe lamp/300–800 nm | 0.6 | 400 | 68.6 | –35 | –120 | –95 | [172] |
| Rh–Au/SiO$_2$ | Vis/490–550 nm | 0.22 | 500 | 216000 | –180000 | –372000 | –360000 | [161] |
| Cu–Ru/MgO–Al$_2$O$_3$ | Super continuum laser/white light | 19.2 | 25$^\text{[a]}$ | –16500 | –16500 | –33000 | –33000 | [167] |

[a] The local temperature of the catalyst generated by focused light beam was significantly higher.
The photo-DRM tests at room temperature revealed high CO and H\textsubscript{2} production rates, high selectivities (>99%) and significantly suppressed coking of Cu-Ru/MgO-Al\textsubscript{2}O\textsubscript{3} plasmonic antenna-reactor photocatalyst. Quantum mechanical simulations performed by authors suggest that doping of Cu(111) surface with the atomically dispersed Ru, coupled to the chemical reaction activation in the excited state, results in significant reduction of activation barrier for CH\textsubscript{4} (see Figure 36). It is proposed that generation of hot electrons is the major mechanism in photo-DRM, responsible for drastically different behavior in comparison to the thermally driven reaction considering the same catalysts. The hot electrons are responsible for enhancement of C-H activation rates on Ru sites, and the desorption rates of H\textsubscript{2} from the surface. This, in turn, leads to kinetic matching of the CO and H\textsubscript{2} formation rates, and hence minimization of RWGS rate and coking, enabling highly stable and selective photo-DRM.

To sum up, dry photoreforming of methane constitutes an exciting alternative for a sustainable hydrogen production with simultaneous environmental protection. After the initial attempts in the late 90s the main progress in photo-DRM have been made very recently. There are still many problems to solve, for example direct use of solar energy, efficient continuous flow photoreactors or higher conversion rates, before the first commercial implementation of this technology. Doubtlessly, further development of plasmonic systems, such as plasmonic antenna-reactor photocatalysts, will be beneficial for industrially relevant reactions such as dry reforming of methane where high positive reaction enthalpy limits the application of conventional catalysts.
Figure 33. a) HAADF-STEM image of the Rh/SrTiO$_3$. The red square indicates a magnified HAADF-STEM image; b) The temperature dependence of DRM reaction activity in the dark and under light illumination conditions. Rh/SrTiO$_3$ under light illumination (indicated by red squares), the limitation of the thermal system for DRM when a generic catalyst is used (indicated by dashed line), Rh/SrTiO$_3$ under dark conditions (indicated by grey line and white diamonds) and pristine STO under light irradiation (indicated by green line and green triangles); c) Tentative mechanism of photo-DRM over Rh/SrTiO$_3$. Reprinted with permission from Ref. [166]. Copyright (2020) Springer Nature.

Figure 34. Effect of Rh and Ni loading on the CO and H$_2$ production rates (a) and CO/H$_2$ ratio (b) in the photo-DRM reaction under Vis-NIR illumination at 200 °C. Reprinted with permission from Ref. [165]. Copyright (2020) Royal Society of Chemistry.
Figure 35. Ruthenium concentration vs the photocatalytic performance of Cu-Ru surface alloys. a) A model of a Cu NP – Ru single atom surface alloy photocatalyst together with the DRM reactants and products presented on the left; b) The CH$_4$ reaction rate as a function of Ru content and long-term stability; c) Selectivity of photo DRM under 19.2 W cm$^{-2}$ white light irradiation as a function of Ru content in the NPs; d–f) Schematics of the compositional dependence of the Cu$_x$Ru$_{x-1}$ NPs with respect to coke resistance. Reprinted with permission from Ref. [167]. Copyright (2020) Springer Nature.

Figure 36. The computed ground- and excited-state PES for CH$_4$ and CH dehydrogenation. RDS for a) CH$_4$ and b) CH activation on pure Cu(111) and CuRu(111), respectively. The left panel depicts reactant, the central - transition state, and the right – product structures. Red arrows indicate the detaching H. Ground- and excited-state energy plots for c) CH$_4$ activation on Cu(111) and d) CH activation on CuRu(111). Color saturation of the plots changes from dark to light from the ground to the highest energy excited state. Possible electronic excitation and relaxation channels indicated by vertical red arrows are displayed. Possible trajectories along both the excited-state (indicated by pink and green dashed lines as visual guides) and the ground-state (indicated by orange dashed lines) curves are marked. The ground-state activation barriers and the excited-state activation barriers are displayed as well. Reprinted with permission from Ref. [167]. Copyright (2020) Springer Nature.
5. Summary and Outlook

Dry- and wet-, LSPR-driven, biomass photoreforming processes emerge as crucial for further development of modern civilization, which is now experiencing constantly growing global warming effect, and facing significant issues in mitigating the climate change. Thus, the development of such modern technologies for simultaneous conversion of biomass-derived compounds or greenhouse gasses (like CO₂ or CH₄) into energy and hydrogen under the solar irradiation, together with wastewater recultivation is highly desired. Efficient solar-driven generation of hydrogen, the “fuel of the future”, via photoreforming poses a major challenge in terms of the entire photocatalytic system design but particularly the nano-photocatalysts’ design (morphology and chemical composition) enabling maximization of yield. Knowing the potential of solar- to-hydrogen conversion of biomass via photoreforming for building the sustainable future, the design of dedicated nano-photocatalysts has attracted many researchers’ attention. The reported examples demonstrate the superiority of plasmon nano-photocatalysts over conventional ones when the aspect of a sustainable and efficient H₂ production is taken into consideration. The differences between plasmonic and non-plasmonic nano-photocatalysts originate from the enhanced quantum efficiency of the former group in photon-to-hydrogen conversion. It is particularly governed by localized surface plasmon resonance, and large electric field enhancement, substantial increment in UV-vis electromagnetic radiation in near field, and the LSPR-induced heating (locally in nano-regions) that can vibronically excite the molecules, lowering the activation barriers of the surface reactions. By far, LSPR nanoparticles are composed mainly of noble metals, expensive and of limited availability, thus the earth abundant counterparts are suggested to be developed in the future.

Summing up the presented research status, it worth noting that presented activity data have been obtained under extremely varied experiment conditions (i.e., irradiation sources, light intensity, catalysts’ chemical composition, substrate contents, temperature, and pH). As we mentioned before, these conditions must be identical to perform reliable comparison between the photocatalysts. Unfortunately, many published works report the photocatalyst activity using only common measure expressed as the amount of evolved hydrogen gas per weight of photocatalysts (and time). In many cases it may not give all the premises necessary for understanding the intrinsic photonic efficiency of various photocatalyst materials in various conditions or leads to difficulties in benchmarking and moving forward the knowledge. In these terms, the quality of new literature reports should be improved by providing more important details of the applied set-ups. That will allow evaluation of the photocatalytic activity using independent, absolute parameters, comparison between the systems, unify the standards and protocols between different labs, and selecting better and better photocatalysts for sustainable applications. Stability of the photocatalysts is very important as well as their activity. In some cases very high activity is reported in short-term operation of the photocatalysts or hydrogen generation rate is measured after certain time, but it is not clearly indicated if that time can be taken as the photocatalyst’s overall stability. Generally, based on the literature survey, it may be inferred that the long term stability of the photocatalysts is the major obstacle for the progress in the field. Nevertheless, the hydrogen generation productivities based on the available data and summarized in the present review provides an informative compilation, and allows quantitative comparison of different systems.

LSPR-driven dry photoreforming of methane provides an exciting opportunity to overcome huge thermodynamic cost of DRM, which is the most environmentally benign and highly desired technology. As opposed to the wet photoreforming, dry photoreforming is carried out in a gas phase, enabling better control and utilization of local heat generated by the LSPR decay. Combining this local heating and the direct electron injection mechanism, it is possible to trigger the photo-DRM reaction pathway in the excited state PES and, as a result, boost syngas generation efficiency. As the photo-DRM is relatively new idea, there is still plenty of challenges to solve in order to make the process commercially attractive. For instance, novel efficient plasmonic nanocatalysts featuring high selectivity to syngas and fast adsorption of CO₂ and CH₄ must be developed. The second very important step is to design novel continuous flow photoreactors that maximize light utilization efficiency and the overall photocatalyst surface available for the molecules to adsorb and get converted into product.

Wet photoreforming is commonly considered to be more challenging than dry photoreforming, in terms of both process conditions optimization and reactor design. Recently, extensive efforts have been devoted to constructing efficient heterogeneous systems using single metal- or dual co-catalyst-loaded semiconductor (mainly TiO₂) photocatalysts that enable bandgap reduction, tuning the photooxidation pathways, improving the selectivity, and making hydrogen production form aqueous organic solutions more efficient and feasible. Although many of the reported photocatalysts demonstrated their potential by achieving high hydrogen production rates, several process conditions and engineering issues, particularly competition between water oxidation and organic oxidation and the photo-generated hydrogen mass transfer rate limitations in liquid-phase, are yet to be overcame. The main efforts should be devoted to developing of continuous-flow reactors with optimized chamber shapes and geometries that enable efficient harnessing of solar flux and thermal control. Full control of the plasmonic photochemistry, maintaining the nanocatalysts in operando stability and the LSPR localized surface plasmon resonance effect at long-term operation, achieving the maximum possible hydrogen production yield as well as the selectivity, now constitute the main challenges for further implementation of plasmon-photocatalytic flow systems dedicated to solar-to-hydrogen conversion via photoreforming of biomass solutions at industrial scale.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords: hydrogen · supported catalysts · photochemistry · surface plasmon resonance · biomass

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