

Energy Advances

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Efficiency in Photocatalytic Production of Hydrogen: Energetic and Sustainability Implications

View Article Online
DOI: 10.1039/D4YA00361F

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Abstract

Hydrogen generation through a photocatalytic process appears a promising technology to produce this energy vector through a novel, efficient, green, and sustainable process. The fruitful use of sunlight as excitation source and renewable bio-derived reactants as well as the development of highly efficient catalysts are required to achieve this goal. In this perspective article, we focus on describing how to braid energy and sustainability sides of the hydrogen photo-generation into a single parameter, allowing quantitative measurement and trustful comparison of different catalytic systems. Starting from the energy-related efficiency parameters defined by the IUPAC, we present novel approaches leading to parameters enclosing energy and sustainability information. The study is completed with the analysis of other, non-IUPAC, parameters of broad use such as the Solar-to-Hydrogen observable. To set of results available in the literature for the water splitting reaction and the use of bio-derived sacrificial molecules is reviewed to assess the potential of such reactions in the energy-efficient and sustainable production of hydrogen.

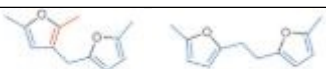
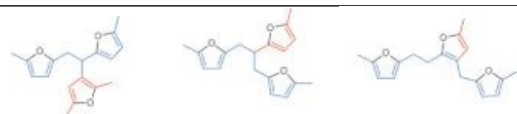
Keywords

Hydrogen; Photocatalysis; Energy; Sustainability; Efficiency

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Acronyms	View Article Online DOI: 10.1039/D4YA00361F
APY: Apparent Photonic Yield	
2,5-DMF: 2,5 Dimethylfuran	
COF: Covalent organic frameworks	
	
C12 Dimers: $C_{12}H_{18}O_2$	
EB: Erythrosin B	
EY: Eosin Y	
MgPc: Magnesium phthalocyanine	
Opt.: Mass of the catalysts optimized	
P25: TiO_2 (Evonik ©)	
PcNc: Phthalocyanine	
P-CTFs: Phosphorus-doped covalent triazine-based frameworks	
PHI: Poly (heptazine imide)	
PTFE: Photochemical Thermodynamic Efficiency Factor	
Pt NCs: Platinum Nanoclusters	
PY: Photonic Yield	
QE: Quantum Efficiency	
STH: Solar to Hydrogen	
STOS: $Sm_2Ti_2O_5S_2$	
TEOA: Triethalonamine	
Tetramers: $C_{24}H_{26}O_4$	
	
C18 Trimers: $C_{18}H_{20}O_3$	
ZnMT ₃ PyP: Zinc-5-(4-carboxyphenyl)-10,15,20-tri(3-pyridyl)porphyrin	
ZnPc: Zinc phthalocyanine	
ZnPyd: Zn-metalloporphyrins	



1.- Introduction

Hydrogen is a key molecule in many chemical industry processes related to the production of fuels and commodity molecules, high added value chemicals through hydrogenation reactions and others, and appears as a new energy vector with implications in many new fields including transportation, household and industrial processes. The use of this molecule in such a broad number of chemical processes would be supported by its good properties, in one way or another related to the relatively wide availability on earth due to its huge abundance in terms of mass concerning other elements, its high reactivity and reasonable energy storage capability, as well as the fact that energy release can take place without generating harmful products to the environment or humans. Catalysis and, particularly, photocatalysis can play a role in the hydrogen economy, working on both sides of production and consumption, as part of green and environmentally respectful processes.^{1,2}

Photocatalysis uses light to trigger a significant number of chemical reactions and can profit from the use of sunlight as a natural and renewable energy source.³⁻⁵ The setting-up of true green processes for hydrogen generation not only requires a renewable energy source but also renewable reactants. Water is a paradigmatic case but if seawater cannot be directly utilized, the massive use of this molecule to produce hydrogen would be detrimental for other uses and hydrogen photo-production would thus compete with water supply for human and agriculture related needs. Also, another critical aspect concerns the physical separation of hydrogen and oxygen, ideally carried out concomitantly with their production, to achieve affordable or competitive cost if compared with the nowadays dominant production from methane reforming and/or the electrolysis of water.^{6,7} Alternative molecules generated from bio-based processes can be also good candidates for the massive production of hydrogen. Fermentation derived bio-molecules, typically alcohols but also blend with other molecules



(like the ABE mixture, e.g. acetone, butanol and ethanol), would be thus desirable candidates in the quest of producing renewable hydrogen.⁸⁻¹¹

A key aspect common to all photocatalytic processes and thus for those aiming to produce hydrogen is the bottleneck derived from the efficiency of the processes.³⁻⁵ Although increasing the always limited efficiency of photocatalytic processes is a must, a previous, seminal question concerns how to define, measure and interpret efficiency. Efficiency is primarily an energy-related parameter associated with any chemical process but a full understanding of the efficiency of a photocatalytic reaction requires including chemical information with implications on sustainability. As a case study, the analysis of the efficiency of the production of hydrogen from alcohols and, generally speaking, carbon-containing molecules, should take into account the evolution of such molecules and the corresponding carbon-containing products generated during reaction. The (carbon-based) product selectivity would have energy-related implications, in this case mainly although not exclusively connected with the consumption of charge carrier species and, in turn, photons during the reaction. Of course, a global understanding of energy related issues requires a full knowledge of the thermodynamics and kinetics of the reaction. On the other hand, as will be shown below, sustainability issues can be connected with the atom selectivity to the target product, in this case hydrogen, as often, several hydrogen-containing molecules are produced in the reaction, with the exception of the splitting of water reaction. Other relevant issues for photocatalytic hydrogen production would be connected with environmental and economic issues, also primarily affected by the products generated during the reaction. Although we would not consider in detail these last two due to their limited relationship with the efficiency parameter, it can be noted that the production of hydrogen from waste or the co-production of hydrogen with carbon-containing added value products are research fields with significance in relation to the just mentioned environmental or economic aspects of the process.^{5,8}



By analyzing the new perspectives available in the literature, here we will carry out a complete study of the key energy and sustainability related aspects of the reaction with connection with the efficiency of the process. This would provide a holistic view of the measurement and interpretation of the mentioned parameter. In this context, we would note that a survey of literature results provides, as a first impression, that a rigorous measurement of the efficiency for a light related catalytic process is significantly more complex than in thermal or classical counterparts. Moreover, it is relatively scarce the information that can allow a real comparison of the performance of photocatalysts coming from different studies. Both facts are intimately linked with the analysis of the light distribution at the reaction medium for any photoreactor configuration as well as for any photocatalytic reaction, and thus for hydrogen production. Measuring and modeling light intensity at a reactor can be carried out at different levels of accuracy mostly as a result of the complex nature of the experimental measurement as well as the computational effort required to achieve an error below experimental uncertainty in the spectral/spatial/directional description of the intensity of light.^{12,13} Despite that, the literature presents several parameters that can provide different levels of understanding of the efficiency of a photocatalytic process.^{14,15} In fact, a myriad of parameters attempts to measure efficiency, and here we will analyze systematically most significant ones. The way they are defined and the corresponding experimental/modelling tools required can classify them in a simple way. As outlined above, some of them require the measurement of experimental observables but, in some cases, they also require the above mentioned modeling of the light distribution in the reaction. Rather than showing the mathematical part of the study, the pros and cons as well as the quality of the information extracted from the most representative efficiency parameters for the photocatalytic production of hydrogen will be discussed here. The holistic view attempts to facilitate the progress of the field and to set-up the conditions to promote the quantitative measurement of



activity in the photocatalytic production of hydrogen and, by extension, for any photocatalytic reaction.

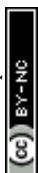
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2.- Efficiency: energy and sustainability

As efficiency is primarily an energy related parameter, a basic definition comes out from IUPAC recommendations and common sense. It would describe efficiency as the ratio between the input and output energy of the reaction, measured joule-to-joule. In photocatalysis, this parameter takes form considering the number of photons, the source of the energy, per unit time (the rate of energy production) involved in the reaction.¹⁶ Work carried out in recent years attempts to provide parameters rendering the real or approximate estimations of the efficiency.^{13,14,17} Table 1 summarizes the general formulation of the efficiency in photocatalytic measurements as well as some simple parameters attempting to provide alternative (and more feasible or practical) formulations. A few of the calculations are specific and display wide application within the (sub)field of hydrogen production. Note that Table 1 collects parameters expressed as a fraction (of unity), although parallel formulations can be presented in percentage (x100).

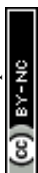
2.1.- Global Efficiency

The global efficiency of a photoreaction reaction (second row of Table 1) can be defined conceptually as composed of three different terms. Each term can have an associated parameter. They define the different parts of the process to extract a rational interpretation of the losses taking place and thus to provide a complete answer to the interpretation of the efficiency. A first point to note is that some of these parameters can be calculated or approximated by a single parameter and, as said, can be estimated using different degrees of approximation.



The first term of the global efficiency is η_{Source} . If the energy source is the sun, we can consider that this parameter would take the unit value although the analysis of the “efficiency” in collecting sunlight at a reactor using parabolic or other concentrators would provide a different value.¹⁸ If an artificial source is utilized, the efficiency is always below 1 and depends primarily on the type of lamp. Obviously, LED lamps would have higher efficiency than mercury or xenon lamps as they have lower heat losses. Complete information about how to calculate this factor using artificial sources within the context of a photocatalytic process can be found in refs^{19–23}.

The second term concerns the reactor under illumination, η_{reactor} . Sometimes is called the reactor radiation incidence efficiency. Measuring (experimentally) the photons at each point of a reactor cannot be accounted for in most experimental conditions as the light-measurement equipment will interfere with light, cannot be physically allocated at the reactor, and/or the corresponding measurement cannot achieve adequate spatial discrimination. Moreover, if the dispersion of light is a relevant contribution to the matter-light interaction process, light intensity at any point of a reactor is intimately associated with the catalyst presence at the reaction medium. In brief, from a practical point of view, this term corresponds to a loss term mainly associated with the radiation losses taking place through all the walls of the reactor. On occasions, the coupling of $\eta_{\text{reactor}} \times \eta_{\text{Abs}}$ is the one calculated and reported. For some of the IUPAC definitions, such as the photonic yield, the experimental measurement of light intensity, or more properly, the number of photons per unit time, after the illuminated reactor wall/window(s) is required.¹⁶ So, not all radiation losses will be accounted for while using the IUPAC defined parameter. The light intensity after the corresponding wall/window illuminated is, on the other hand, a boundary condition included in the calculation of the last term presented in the global efficiency, η_{reaction} .^{12,13} As it is obvious, η_{reactor} cannot achieve a unity value. The corresponding value depends primarily on



the geometry of illumination and reactor configuration but also on catalyst concentration and physico-chemical properties.

Most of the literature concerns the calculation of the η_{reaction} term. As the central piece of the formulation, this term contains the calculation of the so-called “quantum efficiency” of the process, η_{ϕ} . Rigorously, the parameter requires to measure/calculate the rate of reaction and of the rate of photon absorption. The difficulty in providing an accurate value for the last parameter leads to different ways of calculation as well as the use of alternative parameters substituting it. In this context, we stress the fact that illumination in a photocatalytic reactor is carried out using multi-wavelength sources. This is the case of sunlight but also of artificial light sources with reasonable light intensity. Other valuable experiments with relatively poor control of hydrodynamic conditions (using reaction chambers rather than reactors) and/or model conditions can use monochromatic, laser-type sources. The multi-wavelength nature of the source of interest defines the way the quantum efficiency parameter is calculated in photocatalysis and here utilized. Nevertheless, parallel definitions are available for efficiency parameters measuring η_{reaction} for monochromatic light sources.¹⁶

So, through the need of obtaining the rate of photon absorption, the rigorous calculation of the quantum efficiency requires careful measurement of the boundary conditions using actinometry and/or radiometry and the use of numerical procedures to obtain the intensity of light at each point of the reactor. The rate of photon absorption is the product of the absorption coefficient of the catalyst multiplied by the intensity of light at each point of the reactor. The interaction of light with matter in a photocatalytic reactor defines two types of systems. A first one is called pseudo-homogenous and typically corresponds to suspended solids. Dispersion of light plays a key role although is not the single light-matter effect of relevance as absorption, reflection and refraction of light should be considered. Three methods are the most popular to obtain the rate of photon absorption through the solving of



the integro-differential radiative transfer equation. These are the discrete ordinate method, the finite volume method or the Monte Carlo method. They are exact as far as true convergence is obtained in the spectral/spatial/directional representation of light at the reactor. As they all imply intensive computational effort, more simple methods taking advantage of a limited representation(s) of the directional properties of light at the reactor or other simplifications have been implemented. These methods facilitate the solving of the integro-differential radiative transfer equation through the use of (semi-) closed (analytical) formulae instead of the use of numerical (accurate) tools.^{12,13,24} New methods recently proposed in the literature used machine learning and literature results to set-up alternative procedures to calculate η_{reaction} without detailed analysis of the light-matter interaction taking place under reaction conditions. They provide an alternative way of measuring η_{reaction} to the one presented in Table 1, although the results show that similar observables to the rate of photon absorption should be utilized in order to provide meaningful results.²⁵ The second type of systems is called heterogeneous and the main light-matter events are absorption/transmittance, reflection and refraction. They mostly relate to supported catalysts although some systems specifically designed for multiple scattering (like photonic materials) would not be considered “heterogeneous”. In any case, here the obtaining of the relevant optical properties of the solids and the rate of photon absorption take place with the help of experimental measurements of the above mentioned optical properties and boundary conditions and the application of classical optics.^{12,13,18}

As it will be shown hereafter, for hydrogen photo-production, water splitting reports display relatively low values (except for tests using monochromatic sources) of the efficiency parameters. Higher values are typically encountered for the production of hydrogen using sacrificial molecules. In any case, realistic calculations would lead to a value below 0.3-0.2 in the best cases. Considering that η_{Source} could be considered unity for the best case but η_{reactor}



has inherent losses for all configurations reported and thus a value below unity, the maximum (true) efficiency reported would never exceed 0.3 or 30 %. This appears a reasonable upper bound limit. Values reported above this point would suffer from severe simplifications, in most cases associated with the analysis of the relevant properties of the illumination source. These typically concern (i) the handling of the total photon flux of the light source as monochromatic (using a central wavenumber which, even using filters, is incorrect); (ii) the use of the nominal power of the source or a simple evaluation of the radiation field intensity; and/or (iii) restrict radiation–catalyst interaction model to absorption events.

For our purposes, a critical issue, connected with (the not so obvious) relationship in the sustainability of the chemical process, comes out from the dimensionality of the quantum efficiency parameter as defined in Table 1. The physical units of the parameter are mole of the target molecule per mole (Einstein) of photons. To provide a dimensionless efficiency parameter, the so-called “selectivity” factor should be included in the denominator of η_{ϕ} . The new efficiency parameter is called the fraction of useful photons, η_{Θ} . Such parameter uses the selectivity factor ($S = \sum n_i S_i$) that can be calculated as the summation (expressed, i , on the basis of the molecule utilized to measure the reaction rate present at the numerator of the efficiency parameter, in our case, hydrogen) over all products of the reaction of the inverse of the number of charge carrier species (n_i) involved in the generation of the product multiplied by its fractional selectivity (S_i). Considering the one photon is used to generate one (electron-hole) charge carrier pair, the units of the selectivity factor are mole of the target molecule per Einstein of photons.¹³ Through the selectivity factor, the inclusion of chemical information in the quantum efficiency parameter leads to a new dimensionless parameter that allows measuring the real fraction of (the initial) photons involved in the reaction. It takes into account that the different products of a reaction consume a different number of charge carrier species and in turn photons. This is easily visualized considering that the oxidation or the

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reduction of a chemical species can progress with the formation of different products. For example, in the case of a sacrificial molecule utilized for hydrogen production, the oxidation of the molecule would progress up to carbon dioxide through several intermediates usually containing a higher proportion of oxygen than the initial molecule. As shown later in this work, as there is a univocal correlation between the number of charge carrier species and the production of hydrogen, the fraction of useful photons also provides the ground for a measure of the sustainability of the reaction through the relationship with the atom efficiency on a hydrogen basis.

2.2.- Other parameters

A second point to mention in the context of analyzing η_{ϕ} is the formulation of alternative parameters that would be easier to obtain and would substitute the quantum efficiency parameter. For polychromatic sources, the IUPAC defines the so-called “quantum yield” for this purpose. As mentioned, such a definition eliminates the calculation of the rate of photon absorption in η_{ϕ} and utilizes the rate of incident photons inside the irradiated window of the reactor.¹⁶ So, instead of using the absorbed photons, the quantum yield uses the impinging photons once the reactor losses are considered in a first approximation (radiation losses inherent to the illuminated but not all walls of the reactor). A trivial inspection of Table 1 indicates that this parameter would not allow obtaining a meaningful value for the (global) efficiency, η , of the process but can serve as a guide to estimate η_{reaction} . As trivially deduced from its definition, the photonic yield renders a lower bound to the accurate calculation (e.g. using the quantum efficiency) for the η_{reaction} . Note however, that a significant number of reports do not use the IUPAC definition(s) to report efficiency and typically use the total incident photon flux (instead of the rate of photon absorption or the photon flux inside the irradiated window) to provide a different parameter, called commonly “apparent quantum efficiency” or by the IUPAC “apparent (photonic) yield”. This parameter, not included in

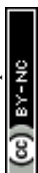


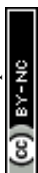
Table 1, is obsolete according to the IUPAC. Nevertheless, due to its broad use, we will collect information in following section(s) using such parameters.¹⁶

In the way to provide simple estimations of the efficiency and thus to avoid the complex experimental-modeling methodologies required for accurate estimation, other simple parameters have been implemented by several authors. The most popular by far is the so-called solar-to-hydrogen STH parameter. The parameter measures the chemical energy of the hydrogen produced vs. the incident sunlight energy. The incident energy is referenced to the Air Mass 1.5 Global (AM 1.5G; 100 mW cm⁻²) standard. Although initially developed for (photo)electrochemical methods, the application of STH as collected in Table 1 has been utilized by many authors in the photocatalysis field.^{26–28} STH is a parameter originally designed for the pure water splitting reaction, but the literature shows its use for reactions utilizing sacrificial agents. The maximum value would depend on the solar range (source) to be used. If the UV/Visible/IR component is the target source, the maximum of the parameter is around ca. 3.3/43/53 %. Of course, the sun provides IR photons at sea level up to ca. 2500 nm (in fact, up to 1800 nm as CO₂/water essentially absorbs all photons above such cut-off), but no single material is able to use (relatively) low energy photons. Likely, the harvesting of nearIR photons up to the cut-off energy just mentioned would require the use of carbonaceous-type materials and/or lanthanides with an engineering f-electron subshells. These options appear to be able to profit from the solar spectrum up to a wavelength of ca. 1150 nm (1.08 eV). An additional option for the future could be the use of double-photon technologies but nowadays these are rather inefficient and typically utilize rather toxic and/or unstable (under reaction conditions) materials.²⁹ From the above discussion, a target value of 10 % requires the use of the visible and/or the nearIR contributions of sunlight and, if the profit is limited to ca. 1150 nm, top values above 65-70 % are unattainable. Such a maximum does not consider any type of losses and thus is an upper bound.



Considering the interpretation of the STH observable, a key point, repeatedly mentioned in the literature, is that the useful range of the solar spectrum utilized in the photocatalytic process depends primarily on the band gap energy of the catalyst and there is no direct or straightforward way of introducing such information into the STH parameter. In fact, the STH parameter is a kind of black box, as the losses cannot be associated with confidence in any physical parameter of the reactor or the reaction (including the photocatalyst) that would allow the optimization of the process. As mentioned before, the adequate measure of the effects of light absorption under reaction conditions can be only achieved through the rate of photon absorption or equivalent formulations and, in general, the full knowledge of the η_{Source} , η_{reactor} , η_{reaction} efficiencies is required. Nevertheless, the strongest point of the STH parameter comes out from the relatively easy calculation of the maximum achievable for a specific material (primarily defined by the band gap energy) as well as its wide application. Valuable tests for different reactor configurations, semiconductors with different band gap energies covering the UV, visible and nearIR ranges have been presented in the literature.^{30,31}

As a representative example of other useful parameters of relatively limited application for measuring efficiency in hydrogen production, we can present the so-called “photochemical thermodynamic efficiency” factor. Table 1 shows that this parameter replaces, in the formulae of the quantum efficiency, the rate of target molecule production by the rate of formation of the primary radical involved (for our purposes, hydrogen production, hydroxyl type radicals). The parameter will thus provide a way to measure the ratio between the energy consumed in the reaction vs. the input energy. Depending on the path for hydroxyl generation, the maximum PTEF achieved can be different. In the absence of oxygen, hydroxyl radicals can be formed exclusively from holes and a unity value appears as the maximum value. In the presence of oxygen, the maximum value can be up to 1.3.^{32,33}

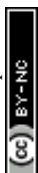


3.- Production of hydrogen: efficiency

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Once the different efficiency parameters were presented and their interpretation discussed, we will review the literature data. To this end, we will present data corresponding to water splitting as well as the reforming type reactions taking place with the help of most frequently used sacrificial agents such as alcohols, acids, sugars and others. Some reports provide information concerning several sacrificial molecules and are considered separately for each case included in the study. The summary of the literature attempts to illustrate the dual (energy but also sustainability related) information enclosed in the studies reported. This implies that the perspective article focuses attention on two types of studies. First, we selected works carrying out the analysis of light intensity at the reactor to report the IUPAC recommended parameters and/or the analysis of efficiency parameters presented in Table 1. Second, other works are selected as they provide a complete report about the selectivity of the reaction when sacrificial agents are used. Although the set of results presented may not provide a complete view of the field of the photocatalytic production of hydrogen, it is ideally suited to sustain the analysis of the efficiency of the reaction in terms of energy and sustainability issues. In this context, we note that full information about the different catalyst formulations and characteristics is available in many review articles, as those described in the introduction section.^{3,4,6,8-11}

For each “type of” substrate (water, carbon-containing molecules) mentioned, we summarize the relevant information in two tables enclosing the information of the efficiency and, when required and/or available, the selectivity of the reaction. Concerning the efficiency, we summarize results considering five-six different parameters encountered in the literature. Here such results are defined in terms of the mathematical process utilized rather than the efficiency parameters claimed to be calculated by the authors. These are: the (i) quantum efficiency (QE) and (ii) photonic yield (PY) parameters reported in publications following the



IUPAC recipes, as discussed in the previous section. Connected with the QE parameter, we also investigated (iii) the fraction of useful photons. We also summarized data considering (iv) the apparent (photonic) yield (APY), calculated using the incident photon flux in the denominator of the efficiency parameter. As mentioned in the previous section, this is frequently called by certain authors as apparent quantum efficiency. Finally, the (v) Solar-to-Hydrogen (STH) and (vi) Photochemical Thermodynamic Efficiency Factor (PTEF) parameters are presented as defined in Table 1. A general point is that most of the quantum efficiency, photonic yield or apparent photonic yield data are calculated using a factor 2 multiplying the reaction rate. Although authors may not be aware, this constant is the selectivity factor for the photocatalytic generation of hydrogen. Thus, in the case of quantum efficiency, the reported parameter is, in fact, the dimensionless “fraction of useful photons”. In the other four parameters, the introduction of this factor is relatively meaningless although may find ground through the parallelism with the quantum efficiency. We will further discuss these points and their implications in subsequent paragraphs. Finally, a summary of the relevant information for the most studied reactions is depicted in an associated figure. This figure attempts to summarize the information of charge carrier species as well as the evolution of the reactants under reaction conditions. With the complete picture of the process, we would have the basis to rationalize the literature results reporting the efficiency of the photocatalytic process in terms of energy and sustainability issues.

3.1.- Water

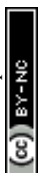
For the case of water splitting, Table 2 collects the data of efficiency. Of course, selectivity issues are trivial as hydrogen is the only possible product containing hydrogen atoms. Typical systems tested are composite systems based in oxides, oxysulfides, oxynitrides, nitrides and carbon nitride based systems. As well described in the literature, such catalysts work under different Z-scheme type schemes allowing efficient charge carrier species separation and



semi-reactions for hole and electron species at separated surface sites.^{3,27,28} Although results using monochromatic sources (the 3 entries listed at the end of Table 2) can reach high values, when attempting to profit from the whole visible range, performance is significantly affected. Under polychromatic excitation, note that some values reported in the table and using the apparent yield/quantum efficiency (APY) are relatively high. This would likely indicate that the simple way of measuring efficiency is not only obsolete, as dictated by the IUPAC, but likely would lead to unphysical values in a significant number of cases. The STH values provided are always below or around 1 %. Only in the case of a platinum promoted COF, we find a value exceeding the above mentioned cut-off.³⁴ Despite this, for a realistic test, using a 100 m² surface exposed to sunlight during a long period of time, the group of Domen obtained a 0.76 % value for the STH parameter (1st entry of Table 2).³⁵ The absence of information considering the measurement of the quantum efficiency can be noticed and thus the potential of the tested systems would need to be further assessed. Nevertheless, it can be concluded the current status for the water splitting is far for reaching the objective of using 10 % of the sunlight energy.

3.2.- Methanol

Methanol is selected as the initial carbon-containing sacrificial molecule here studied. It corresponds to the case more broadly studied. Also, the relative simplicity of the molecule allows for tracking all (carbon, oxygen and hydrogen containing) products potentially produced under reaction conditions. The summary of efficiency values reported is presented in Table 3. In this table, we selected as initial entries titania-based systems, promoted with Pt and other (noble, non-noble) co-catalysts as well as those systems obtained through doping of titania and/or composites with a dominant presence of the mentioned oxide. The corresponding results included in Table 3 are followed by other systems based on other oxides and thus other semiconductors, mostly sulfides and carbon nitride. Very high values

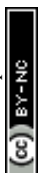


are typically encountered when using the apparent photonic yield (APY) also called apparent quantum yield. This has been commented already for the Table considering water splitting results. The titania-based systems are reported mostly under UV irradiation and, in some cases, under visible irradiation. Efficiency under visible light is always inferior except for cases concerning composite systems where a second semiconductor is specifically devised for it. In any case, for the complete UV-visible range of sunlight (ca. 280-760 nm), all systems display an efficiency below ca. 6-7 % (maximum achieved to our knowledge in ref. ³⁶). Higher values can be encountered under UV illumination. The maximum of 6-7 % could be achieved with other systems like carbon nitride, ZnIn₂S₄-based, or doped GaN systems (last entries of Table 3), although the absence of accurate calculations of the quantum efficiency does not allow to assuring this point with confidence for non-titania based systems. On the other hand, Table 3 would indicate the limited use of the STH or other non-IUPAC parameters when methanol is utilized to generate hydrogen. In summary, it can be considered that the best systems could be close to a real efficiency of 10 % in the UV-visible range. Likely, the titania-based and other systems listed in Table 3 would not use efficiently the nearIR range, and thus there is room to improve and achieve efficient use of the sunlight full spectrum. A point to remark again is, however, that the energy release of all photons is not the same and although the nearIR range is very important, its energy content is significantly lower as well as more problematic to be used than the corresponding to visible counterpart, as already mentioned in the previous section.

Interestingly, measuring the hydrogen generation from methanol using the quantum efficiency cannot take into account explicitly the number of charge carrier species utilized. Neither can include chemical information. However, the photocatalytic reaction triggers the formation of a significant number of carbon, oxygen and hydrogen-containing molecules, with direct consequences in the production of hydrogen. This comes out for the presence of

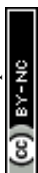


hydrogen in such molecules, limiting the production of molecular hydrogen. Table 4 captures the most relevant works where the selectivity of the reaction has been explored and reported. Such table contains information of the selectivity on carbon and hydrogen atomic bases. Due to the relative simplicity of the reactant(s), methanol and water, all potential products of the reactions have been reported if considered the works collectively. The summary of the evolution of the reactants and the concomitant production of hydrogen is presented in Figure 1. Under illumination, after charge separation and creation of electron-hole pairs, two different radicals would be formed from the hole-related species attack to the sacrificial molecule. The most typical products are related to the initial production of an oxygen-type radical generated by the mentioned hole-type attack to the OH moiety, leading to an oxygen-centered alkoxy-type radical. This radical is highlighted with a green colour in Figure 1. The subsequent (further) radical attack by hole-type species renders the carbon-containing oxidized species as well as protons. In a chain-type mechanism, formaldehyde, formic acid and carbon dioxide would be formed. Important to note, formaldehyde is formed in a dehydrogenation step while the formation of the next intermediate, formic acid, involves water in a reforming-type step. This point is highlighted using a magenta colour for an oxygen atom in Figure 1. In and after this intermediate, protons are extracted from the two reactant molecules (although we did not use the magenta colour in carbon dioxide and other molecules generated from the acid intermediate and included in Figure 1).^{37–39} Formation of carbon dioxide can be considered as a final step of the chain-type mechanism, but decarbonylation steps and production of carbon monoxide with subsequent triggering of the water gas shift reaction have been also shown to participate in the reaction. In addition, coupling of methanol molecules activated through the alkoxy route can lead to the formation of methyl formate species.^{37,40} As said, each step generates concomitantly hydrogen ions consuming the hole-type radicals in a one-by-one ratio. The number of hole-type charge



carrier / hydrogen ions is counted using the last observable in Figure 1. This information is key to obtaining the selectivity factor. In addition to this path, the formation of a carbon-centered radical (highlighted with an orange colour in Figure 1) can also take place, generating through a coupling step, as a first intermediate, ethylene glycol, a C_2 molecule. The further evolution of ethylene glycol leads to other C_2 molecules as well as C_3 molecules formed with methanol molecules activated using exclusively the carbon-centered route or, in specific C_{2+} cases, a mixture of the paths. In subsequent steps, it is obvious that this (carbon-centered radical) route can also lead to C_1 products including carbon dioxides.^{41,42} Again, we remark that formation of the (acetic) acid intermediate requires the use of water, as indicated in Figure 1. In all cases (see the upper part of Figure 1), the generation of the hydrogen molecule takes place from the hydrogen ions concomitantly originated with the carbon-containing intermediates and electrons, closing the catalytic cycle. Nevertheless, the presence of products which evidences a competence for the electrons (and holes through the consumption of hydrogen ions) is also encountered. This leads to the formation of hydrocarbon species, which are detected in a few studies when using methanol.^{37,40}

From Figure 1 we can progress in the utilization of adequate engineering efficiency factor(s) with the claimed dual aim of enclosing information concerning energy but also sustainability. In particular, we would discuss the consequences of using the selectivity factor and the potential of the “fraction of useful photons” factor, η_{θ} . For each molecule of hydrogen generated, essentially all steps of Figure 1 would use two hole-type radicals. Thus for a pure photocatalytic, radical-triggered mechanism, whatever the selectivity, the S factor takes a value of 1/2 in the denominator of the efficiency, or other words, the mentioned factor 2 multiplying the reaction rate in the numerator. This is true as far as thermal contributions to decarbonylation steps do not affect significantly the production of hydrogen. $\eta_{\theta}(H_2)$ has always a constant factor of 2 differing from the quantum efficiency. A different question is



the calculation of $\eta_{\Theta}(\text{H})$. If “electron-consuming” products like hydrocarbons are generated in the process, the (weighted) sum of the hydrogen and methane reaction rates should be considered in the calculation, and, critically important, the selectivity factor per H atom is different for these two products (Figure 1). Of course, all hydrogen containing products should be included in the calculation of $\eta_{\Theta}(\text{H})$ but carbon-containing molecules presented in Figure 1 and generated using hole-type species have a trivial treatment of the selectivity factor, as above discussed. Therefore, due to the inherent properties of the η_{Θ} parameter, a ratio of $\eta_{\Theta}(\text{H}_2)$ vs. $\eta_{\Theta}(\text{H})$ expresses the atom-efficiency for the generation of hydrogen (ions) in terms of the “fraction” of photons consumed in the generation of the hydrogen molecule vs. the total photons used in the process that consumes the “generation” of H atoms within the reactant molecules. The η_{Θ} parameter can thus braid energy and sustainability information. This $\eta_{\Theta}(\text{H}_2)$ observable is the most informative factor describing the (energy-related) efficiency of the reaction as it measures the fraction of initial photons used to generate hydrogen and can be used straightforwardly in the calculation of the global efficiency of the process. Besides that, the above mentioned $\eta_{\Theta}(\text{H}_2)$ vs. $\eta_{\Theta}(\text{H})$ ratio allows the inclusion of sustainability related to the atom-efficiency in the use of hydrogen atoms by the photocatalytic system. We again recall that depending on the reaction products encountered (Table 3/Figure 1), the hydrogen atoms come from the sacrificial molecules exclusively or also from water.

As discussed in the introduction, a parallel point is the selective formation of specific carbon-containing intermediates. This fact can contribute to making the process “fully” sustainable. Examples of catalysts having high selectivity on carbon-basis are presented in Table 3. Of course, we can delineate the $\eta_{\Theta}(\text{C}_p)$ vs. $\eta_{\Theta}(\text{C})$ ratio to analyze the carbon-based selectivity of the reaction on a photon basis. In this ratio, $\eta_{\Theta}(\text{C}_p)$ is the fraction of useful photons utilized to obtain the desired (carbon-containing) products. From Figure 1 and the procedures above



outlined, we can calculate easily the selectivity factors for the $\eta_{\Theta}(C_p)$ and $\eta_{\Theta}(C)$ parameters.

A simple inspection of the figure shows that the calculation of the selectivity factor corresponding to $\eta_{\Theta}(C_p)$ is not as simple as the case of $\eta_{\Theta}(H_2)$, that is, is not a constant.

3.3.- Ethanol

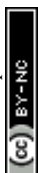
As it is obvious, in the case of ethanol, more intermediates could be formed but several potentially feasible paths are not supported by experimental evidence. In any case, Table 5 summarizes efficiency values for the production of hydrogen using this molecule. Results concerning efficiency parameters allowing quantitative measurement mainly concern titania-based systems, promoted with different noble metals and/or doped. A few non-titania systems are collected at the end of the table. From the inspection of Table 5, it is also plausible that a value of the true efficiency, as measured by the quantum efficiency, can reach a value of around 10 % using this molecule. The results concern the use of the UV-visible region although up to ca. 600 nm, but not the whole UV-Visible-nearIR range of the solar spectrum. Considering the evolution of the sacrificial molecule, Table 6 collects the reports with careful investigation of the selectivity and Figure 2 summarizes the results. We encountered relatively similar results to the more explored case of methanol. As can be seen in Figure 2, the hole-triggered radicals detected are two. One oxygen-centered alkoxy-type radical and one carbon-centered radical corresponding to the CH_3 moiety of the alcohol molecule. Other possible radicals are rather unlikely and unstable. Similarly to the methanol case, the alkoxy radical leads to the chain-type mechanism generating acetaldehyde, acetic acid and carbon dioxide. Decarbonilation reactions, the subsequent water gas shift equilibrium reaction, as well as “coupling” intermediates such as ethyl acetate can be also generated through this path. In addition, C_1 products generated from the rupture of the C-C bond are sometimes observed.^{38,43} From the carbon-centered radical, we are only aware of the selective generation (96.6 % selectivity on carbon basis) of 2,3-butanediol (Table 5/Figure 2).⁴⁴ In the case of



ethanol, the presence of hydrocarbons was again detected, but a higher number of such molecules can be formed (Figure 2).^{45,46} Being the reaction scheme rather parallel to the ethanol case, except for the C-C breaking products, the analysis above described essentially holds for the ethanol case. Thus, the mentioned possible achievement of a 10 % profit of sunlight appears feasible and supported by results of Table 5, although with the associated challenges just outlined for the methanol case. On the other hand, the generation of a significant number of products challenges the obtaining of high selectivity on carbon basis, although Table 6 includes some cases. It is also evident that both the frequent presence of hydrocarbons as products as well as the relatively lower selectivity to carbon dioxide (or, in other words, the higher number of products) observed in the majority of cases would lead to lower values of the $\eta_{\Theta}(\text{H}_2)$ vs. $\eta_{\Theta}(\text{H})$ ratio. Thus, the sustainability of ethanol as a sacrificial molecule for hydrogen generation would not reach values as in the case of methanol.

3.4.- Glycerol

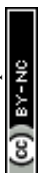
For glycerol, data concerning efficiency values are presented in Table 7. Although the results are encouraging, a complete lack of reports containing information extracted from the quantum efficiency parameter can be noticed. The STH parameter could render a value near 1 % under sunlight excitation. This indicates that glycerol would be a far more thought molecule to obtain a significant profit from sunlight. There are several studies analyzing qualitatively (e.g. detection of products) the evolution of the glycerol molecule in the reaction. These studies used titania-based materials and can be summarized in Figure 3, where we can see that only oxygen-centered radicals are considered for the formation of intermediates. The formation of electron-consuming products, competing with hydrogen, was also reported.⁴⁷⁻⁴⁹ As shown in Table 8, only a couple of contributions reported the full analysis of the selectivity,^{49,50} and thus there is limited information in this case to progress in the quantitative analysis of energy and sustainability issues.



3-5.- Other sacrificial molecules

We can briefly discuss the case of carbon-containing molecules using other (than those previously studied here) biomass-derived molecules which may strengthen the sustainability of the process. Table 9 summarizes results considering other alcohols such as ethylene glycol and 2-propanol, acids such as lactic and ascorbic, sugars as glucose, as well as more complex substrates such as 2,5-dimethylfuran, alpha-cellulose or lignocellulose. Catalysts utilized are oxides, nitrides, sulfides, MOFs, or carbon nitride sensitized with dyes, porphyrins or phthalocyanines. Similarly to the glycerol case, there is limited information although a couple of results using the photonic yield parameter suggest that glucose can be an ideal choice for generating hydrogen. The selectivity of the reaction is scarcely studied. Table 10 summarizes a couple of results encountered where the production of diesel precursors from 2,5-DMF⁵¹ or of pyruvic acid from lactic acid⁵² are achieved with high (carbon-basis) selectivity and concomitant production of hydrogen. It can be also mentioned that hydrogen generation from biomolecules for example, ethanol, can be used in a cascade-type process to trigger hydrogenation steps of other bio-molecules to render valuable products, such as benzimidazole derivatives.⁵³

Finally, for completeness, we collected selected results for efficiency calculations using other sacrificial molecules of use in the field such as TEOA. Results are compiled in Table 11. Catalysts employed with this sacrificial agent frequently utilized molecular-type catalysts such as carbon nitride but also composite systems with dyes such as erythrosine B and eosin Y, as well as porphyrins or phthalocyanines. High values of efficiency can be observed in several cases but using parameters having a limited confidence, as earlier discussed in this

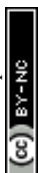


work using methanol, where a most complete database is available. Thus, their potential to achieve the 10 % profit from solar light is still to be ascertained.

Conclusions

Nowadays, the photocatalytic generation of hydrogen attempts to produce this energy vector using renewable energy sources and reactants. To reach a holistic approach towards the settlement of a clean, green hydrogen production and explore the future of the process, the setting up of parameters allowing a quantitative measurement of both the energetic and sustainability implications of the process appears as a must.

To this end, here we surveyed the literature available parameters primarily oriented to measuring efficiency. Efficiency parameters are defined by the IUPAC for photocatalytic processes, being quantum efficiency the one that allows a rigorous metrics to evaluate to global efficiency of a process. From this, we delineated the work aiming to progress further on the evaluation of both energetic and sustainability sides of the hydrogen photocatalytic process using a quantum efficiency related parameter, the so-called “fraction of useful photons”. This parameter allows the true calculation of the global efficiency, rendering a dimensionless parameter, but also expresses the hydrogen atom efficiency of hydrogen production in a photon-based metrics. In addition, up to four additional parameters, all of them demanding less experimental-computational effort in their calculation were considered. These go from the photonic yield parameter defined by the IUPAC, to other broadly used parameters such as the solar-to-hydrogen efficiency. These parameters focus on the energetic side of the problem but, unfortunately, would not inform straightforwardly about the possible energy-related losses and the ways to circumvent them. In spite of it, their simplicity compared with the quantum efficiency related parameters makes their use broad and



appealing. The article also described briefly the application of new tools based on artificial intelligence in the field. We stressed the point that results would indicate that the knowledge of the rate of photon absorption or simpler yet related parameters appears unavoidable to obtain useful information.

We utilized the set of six parameters (quantum efficiency, fraction of useful photon, photonic yield, apparent (photonic) yield, solar-to-hydrogen and photochemical thermodynamic efficiency factor) to evaluate the field of photocatalytic production of hydrogen. In parallel, the perspective article paid particular attention to the interpretation of physical basis of the quantum efficiency and the fraction of useful photon parameters. We sort out the research published in the field considering the different catalytic processes studied. Starting with the use of water in the splitting reaction, we analyzed the use of different sacrificial molecules, paying particular attention to the use of renewable sacrificial molecules, particularly alcohols which can come from fermentation and other bio-based processes.

Being water a potentially optimal reactant, the results of the literature considering the whole use of the solar spectrum would indicate that research output is far from achieving the benchmark value of 10 %. For sacrificial molecules, analysis of the dual-aim “fraction of useful photons” parameter was carried out in terms of both the charge-carrier utilization as well as the molecules (and water) roles and evolution under reaction conditions, and the result utilized to interpret the capability of any catalytic system in terms of energy and sustainability and thus to serve as a firm ground to guide the future of the field. The survey of the sacrificial molecules studied in the literature would indicate that methanol and (to a somewhat lower extent) ethanol can be optimal choices. Glucose could be also a good choice in terms of energy related issues. For the cases of methanol and ethanol, it appears that titania-based composite systems are close to the 10 % cutoff value in the UV-visible range, but the efficient use of the complete solar spectrum is still challenging. In particular, the



nearIR region would need to be fruitfully utilized. According to the literature results, this would require a more intensive exploration of multicomponent composite systems, where, in addition to the co-catalyst presence, the (titania) oxide based systems would be doped and/or accompanied with lanthanide and/or carbon elements (doping) and semiconductors (composite). A more exhaustive analysis of other alternatives, such as the two photon technologies, awaits in the future in order to show potential in the field.

The analysis has been extended to other sacrificial molecules of interest, such as glycerol coming from the transesterification of fatty acids (triglycerides) and other processes, or less commonly tested molecules such as isopropanol, lignin acid, and others. Unfortunately, the limited and (relative) low quality of the information precludes any rigorous analysis, although in most cases, the benchmark value of 10 % of the solar spectrum light appears unattainable with current capabilities.

Acknowledgments

Authors acknowledge the financial support through grant and PID2022-136883OB-C21. The project is funded by MCIN/AEI/10.13039/501100011033. M.F.G. is fully indebted to multiple discussions with Prof. F. Fernández-Martín.

Conflict of interest

The authors declare no conflict of interest.

View Article Online
DOI: 10.1039/D4TA00361F



Table 1. Efficiency parameters defined for hydrogen-production photocatalytic processesView Article Online
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Parameter	Reference
<i>Efficiency: IUPAC definition</i> $\eta = \text{energy output} / \text{energy input}$	16
<i>Global Efficiency of the process</i> $\eta = \eta_{\text{Source}} \eta_{\text{reactor}} \eta_{\text{reaction}}$ $\eta_{\text{Source}} = \text{radiant energy (rate of photon generation)} / \text{energy input}$ $\eta_{\text{reactor}} = \text{rate of photon inside reactor} / \text{rate of photon generation}$ $\eta_{\text{reaction}} = \eta_{\text{Abs}} \eta_{\phi}$ $\eta_{\text{Abs}} = \text{rate of photon absorption} / \text{rate of photon inside reactor}$ $\eta_{\phi} = \text{rate of the target molecule} / \text{rate of photon absorption}$	13,14,16,17
<i>STH: Solar to hydrogen</i> $\text{STH} = [\text{rate of target molecule (mol s}^{-1}) \times 237 \times 10^3 \text{ (J mol}^{-1}) / \text{P (W m}^{-2}) \times \text{A (m}^{-2})]$	26–28
<i>PTEF: Photochemical thermodynamic efficiency factor</i> $\text{PTEF} = [\text{rate of the primary radical produced (OH}^{\bullet}) / \text{rate of photon absorption}]$	32,33



Table 2. Summary of efficiency values presented in the literature for the water splitting reaction.

Catalyst	Source and Radiation	Reaction conditions Reagent/ Catalyst concentration	QE, PY, APY, STH, PTEF / %	Reference
0.1 wt.% Ru-CrOx/SrTiO ₃ :Al	Sunlight	H ₂ O	0.76	35
1 wt.% Ru/SrTiO ₃ :Rh	Xe lamp (300 W) 420-440 nm	H ₂ O 0.42 g/L	5.9 0.10	54
Ru/SrTiO ₃ :La,Rh	Xe lamp (300 W) > 420 nm	H ₂ O 0.25 g/L	3.3 1.10	55
4 mol.% Ru/SrTiO ₃ :La, 4 mol.% Rh/C/BiVO ₄ : 0.05 mol.% Mo	Xe lamp (300 W) > 420 nm	H ₂ O 0.25 g/L	0.7 1.0	56
0.3 wt.% Pt/SrTiO ₃ : 1 mol.% Cr/1 mol.% Ta	Xe lamp (300 W) > 420 nm	H ₂ O 0.80 g/L	0.10	57
0.75 wt.% Ni-La ₂ Ti ₂ O ₇ :8 mol.% Ba	Hg lamp (450 W) > 420 nm	H ₂ O 2 g/L	50.0	58
Cr ₂ O ₃ /Rh/La ₅ Ti ₂ Cu _{0.9} Ag _{0.1} S ₅ O ₇ :Ga	Xe lamp 300 W 420 nm	H ₂ O 0.07 g/L	4.9 0.11	59
0.3 wt.% Pt/TaON	Xe lamp (300 W) > 420 nm	H ₂ O	0.4%	60



1.0 wt.% Pt/ZrO₂/TaON	Xe lamp (300 W) > 420 nm	H ₂ O 0.50 g/L	6.30	61
g-C₃N₄	Xe lamp 300 W > 420 nm	H ₂ O 0.50 g/L	1.4 0.06	62
Pt / g-C₃N₄	Xe lamp (300 W) 390-700 nm	H ₂ O 0.30 g/L	1.5	63
5 wt.% Pt@βKetone COF	Xe lamp (300 W) >420 nm	H ₂ O 0.30 g/L	2.8 23.0	34
0.1 wt.% Rh-0.1 wt.% CrO_x/ SrTiO₃:Al	Xe lamp (300 W) 365 nm	H ₂ O 0.20 g/L	65.0 10.0	64
0.1 wt.% Rh-0.05 wt.% Cr₂O₃/ 0.05 wt.% CoOOH/SrTiO₃Al	Xe lamp 300 W 365 nm	H ₂ O	91.6 0.065	65
0.05 wt.% NiO-NaTaO₃	Xe lamp (300 W) 270 nm	H ₂ O 2.9 g/L	20.0	66

Table 3. Summary of efficiency values presented in the literature for hydrogen production using methanol as a sacrificial agent.

Catalyst	Source and Radiation	Reaction conditions Sacrificial Agent / Catalyst concentration	QE, PY, APY, STH, PTEF / %	Reference
TiO ₂	Two Solarium Philips HB 175 lamps. 4x15 W Philips CLEO Fluorescent lamps 300-400 nm (max. 365 nm)	Methanol:H ₂ O 1:4 1 g/L	2.18	67
TiO ₂ (P25)	8-W Hg UVA lamp 365 nm	Methanol:H ₂ O 1:1 0.25 g/L Opt.	1.0	68
0.5wt.%Pt/TiO ₂ (P25)	Hg-Xe lamp (500 W) 280–400 nm	Methanol:H ₂ O 1:1 0.50 g/L Opt.	28	69
2.1 wt.% Pt/TiO ₂	Philips CLEO 15W fluorescent lamps 300-400 nm (max.365 nm)	Methanol:H ₂ O 1:4 1 g/L	31.8	70
1 wt.% Pt/TiO ₂ nanotubes	High pressure Xe/Hg lamp 150 W 313 nm	Methanol:H ₂ O 1:3.5	16.0	71
0.64 wt.% Pt/TiO ₂	UV–vis 150W Xe lamp > 420 nm	Gas phase from a Methanol:H ₂ O liquid mixture 1:5	14.0	39

1 wt.% Cu/TiO₂	Xe lamp (300 W) 365 nm	Methanol:H ₂ O 1:1 1 g/L	10.0	72
0.5 wt.% PtCu/TiO₂	LED irradiation 365 nm (70 °C)	Methanol:H ₂ O 3:7 0.13 g/L	99.2	73
0.8 wt.% Au/TiO₂	3 Solarium Philips B175 lamps, each equipped with 4 15 W Philips CLEO fluorescent lamps 300-400 nm (max.365 nm)	Methanol:H ₂ O 1:4 1 g/L	17,5	74
1.5 wt.% Au/TiO₂	Two Solarium Philips HB 175 lamps. 4 x15W Philips CLEO Fluorescent Lamps 300-400 nm (max.365 nm)	Methanol:H ₂ O 1:4 1 g/L	2.6	75
1 wt.% Pt/0.5 mol.% SnS₂-TiO₂	Hg-Xe lamp (500 W) 280-400 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	4.3	76
1 wt.% Pt/(Nb)TiO₂	Hg-Xe lamp (500 W) 280–400nm 420–680 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	UV: 5.0 Visible: 2.5	38
1 wt.%Pt / 0.25 mol. % NbTiO₂	Hg-Xe lamp (500W) 280–400nm 420–680 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	UV: 6.5 Visible: 3.0	77



1Pt-Pd / (1:1)/(3mol.%Nb)TiO₂	Xe lamp (500 W) 280–400nm 420–680 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	UV: 2.7 Vis: 1.0	78
1 wt.% Au/1.75 mol.% Zr-TiO₂	Xe lamp (500 W) 280–400nm 420–680 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	UV: 3.3 Vis: 1.9	79
0.23 wt.% Ni(OH)₂ / TiO₂	Four low power UV-LEDs 3 W; 80.0 mW/cm ² 365 nm	Methanol:H ₂ O 1:3 0.63 g/L	12.4	80
2 wt.% NiO/TiO₂	8W Hg lamp 254 nm	Methanol:H ₂ O 1:1 1 g/L	2.9	81
0.25 wt.% NiO/TiO₂	Xe lamp (300 W), 25 mW/cm ² 365 nm	Methanol:H ₂ O 1:4 0.63 g/L	1.7	82
1 wt.% Pt/1.0 mol.% SnS_x - 2.5 mol.% Zr-TiO₂	500 W Xe arc lamp (Lot Oriel) 280-400 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	15.7	41
1 wt.% Pt/3-5 mol.%(CuGaS₂)- TiO₂	Hg–Xe lamp (500 W) 280–400nm 420–680 nm	Methanol:H ₂ O 3:7 0.50 g/L Opt.	UV: 5.1 Vis: 5.8	36





0.5 wt.% Cr₂O₃/ 1.0 wt.% Pt/ 0.5 wt.% IrO₂/STOS	Xe lamp 300W 420 nm	Methanol:H ₂ O 1:10 1.3 g/L Opt.	21.7 0.22	83
0.01 wt.% Pd/TiO₂-WO₃	Xe lamp (300 W) 300–800 nm 300–400 nm	Methanol:H ₂ O 1:1 0.17 g/L Opt.	2.3 7.7	84
Au@Cu₇S₄	Monochromatic Xe lamp (150 W) monochromator 500 - 2200 nm	Methanol:H ₂ O 1:20	9.4 7.3	85
ZnIn₂S₄	420 nm	Methanol:H ₂ O 1:4 0.7 g/L	5.8	86
MoS₂/CdS nanorods	Xe lamp (300 W)	Methanol:H ₂ O 4:1 2 g/L	5.0	42
ZnIn₂S₄/ZnWO_x	Xe lamp (300 W) > 420 nm	Methanol:H ₂ O	10.5	87
InGaN/GaN	Xe lamp (300 W) 395-405 nm 440-450 nm	Methanol:H ₂ O 1:10	1.9 13.0	88
GaN:ZnO	Xe lamp (300 W) > 420 nm	Methanol:H ₂ O 1:9 0.25 g/L	5.1	89

1 wt.% Pt/g-C₃N₄ nanotube	Xe lamp (300 W) > 420 nm	Methanol:H ₂ O 1:3 1.3 g/L	5.7	90
Graphene-like dot / N-defective g-C₃N₄	Xe lamp (300 W) 420-800 nm	Methanol:H ₂ O 1:3 1 g/L	13.0	40



Table 4. Summary of selectivity values presented in the literature for hydrogen production using methanol as a sacrificial agent.

Catalyst	Source and radiation	Reaction conditions Reagent/ Catalyst concentration	Product	Selectivity C basis / %	Selectivity H basis / %	Reference
TiO₂	Two Solarium Philips HB 175 lamps. 4x15 W Philips CLEO Fluorescent lamps 300-400 nm (max. 365 nm)	Methanol:H ₂ O 1:4 1 g/L	HCHO	100	100	67
TiO₂ 1 wt.% Au/TiO₂ 1 wt.% Pt/TiO₂	Xe lamp (300 W)	Gas phase from a Methanol:H ₂ O liquid mixture 1:5	TiO₂ H ₂ H ₂ CO CO CO ₂ Au/TiO₂ H ₂ H ₂ CO CO CO ₂ Pt/TiO₂ H ₂ H ₂ CO CO CO ₂	- 52.6 31.6 15.8 - 72.3 2.9 24.8 - 61.2 1.6 37.2	86.7 13.3 - - 72.8 27.2 - - 79.8 20.2 - -	39
1wt.%	Hg-Xe lamp	Methanol:H ₂ O	Pt/TiO₂			38

Pt/(Nb)TiO₂	(500 W) UV: 280–400nm Vis.: 420–680 nm	3:7 0.50 g/L Opt.	UV			
			H ₂	-	78.4	
			HCOOH	90	17.7	
			HCOOCH ₃	10	13.9	
			Vis			
			H ₂	-	79.7	
			HCOOH	98	17.6	
			HCOOCH ₃	2	0.8	
			Pt/(Nb)TiO₂			
			UV			
			H ₂	-	79.0	
			HCOOH	85	18.5	
HCHO	8	1.7				
HCOOCH ₃	7	0.8				
Vis						
H ₂	-	78.4				
HCOOH	90	17.6				
HCOOCH ₃	10	3.9				
2.1 wt.% Pt/TiO₂	Philips CLEO 15W fluorescent lamps 300-400 nm (max.365 nm)	Methanol:H ₂ O 1:4 1 g/L	H ₂	-	50.8	70
			HCHO	96.8	47.7	
			HCOOH	3.2	1.5	
0.5 wt.% Pt/TiO₂	Hg lamp (250 W) 350-450 nm	Gas phase from a Methanol:H ₂ O liquid mixture 1:5	H ₂	-	77.2	91
			HCHO	78.2	22.3	
			HCOOH	1.9	0.5	
			CO ₂	19.9	-	
10wt.% Pt/P25	Xe lamp (300 W)	Methanol:H ₂ O 1:5 15 g/L	H ₂	-	88.1	37
			HCHO	0.2	0.8	
			HCOOH	27.6	11.1	
			CH ₄	7.8	1.3	
			CO	6.2	-	
			CO ₂	56.2	-	





1.0 wt.% Pt / TiO₂	Xe lamp (1000 W)	Methanol:H ₂ O 1:10 0.5 g/L	H ₂ HCHO HCOOH CO CO ₂	- 63.9 13.6 7.4 15.1	66.9 27.3 5.8 - -	92
0.8 wt.% Au/TiO₂	3 Solarium Philips B175 lamps, each equipped with 4 15 W Philips CLEO fluorescent lamps 300-400 nm (max.365 nm)	Methanol:H ₂ O 1:4 1 g/L	H ₂ HCHO HCOOH	- 58.1 41.9	58.7 24.0 17.3	74
0.5 wt.% PtCu/TiO₂	LED irradiation 365 nm (70 °C)	Methanol:H ₂ O 3:7 0.13 g/L	H ₂ HCHO CO	98.6 0.06	66.7 33.3 0	73
5 wt.% Cu/CeO₂	Xe lamp (300 W)	Methanol/H ₂ O 1:1	H ₂ CO CO ₂	100 0 100	100 0 100	93
Graphene-like dot / N-defective g-C₃N₄	Xe lamp (300 W) 420-800 nm	Methanol:H ₂ O 1:3 1 g/L	H ₂ CO CO ₂ CH ₄	0 2.7 96.5 0.2	99.7 0 0 0.3	40

Table 5. Summary of efficiency values presented in the literature for hydrogen production using ethanol as a sacrificial agent.

Catalyst	Source and Radiation	Reaction conditions Reagent/ Catalyst concentration	QE, PY, AQY, STH, PTEF / %	Reference
1 wt.% Pt/TiO ₂	Black Light Blue (BLB)Lamp 15W 340–410 nm	Ethanol:H ₂ O 1:50 0.50 g/L	4.6	94
0.5 wt.% Pt/TiO ₂	Xe-lamp (300 or 450 W) Solar light-simulating light source	Ethanol:H ₂ O 0.04:1 1.3 g/L	50.0	95
0.25 wt.% Pd/TiO ₂	15 W BLB UV-Lamp 15 W fluorescent visible light lamp UV-Vis	Ethanol:H ₂ O 1:50 0.15 g/L	UV: 34.8 UV-Vis: 8.8	45
0.25 wt.% Pd/TiO ₂	BLB near-UV lamp 15 W fluorescent visible light lamp UV-Vis	Ethanol:H ₂ O 1:50 0.15 g/L	13.7	46
0.25 wt.% Pd/ TiO ₂	BLB near-UV lamp 15 W fluorescent visible light lamp UV-Vis	Ethanol:H ₂ O 1:50 0.15 g/L	13.7	96
2 wt.% Au/TiO ₂	UV visible light (176 W) 0.24 mW/cm ² 254 nm	Ethanol:H ₂ O 1:3 1.3 g/L Opt.	61.2	97



1wt.%Pt/(Nb)TiO₂	Hg-Xe lamp (500 W) 280–400nm 420–680 nm	Ethanol:H ₂ O 3:7 0.50 g/L Opt.	UV: 4.0 Vis.: 1.0	38
1 wt.% Au /NaYF₄(Er³⁺, Yb³⁺) - CdS	Xe lamp (300W) NIR (> 700 nm)	Ethanol:H ₂ O 0.12:0.88 1.5 g/L	9x10 ⁻⁴	98
7.4 wt.% Ni/ g-C₃N₄	20W fluorescent lamps Simulated sunlight	Ethanol:H ₂ O 1:9	1.7	99

Table 6. Summary of selectivity values presented in the literature for hydrogen production using ethanol as a sacrificial agent.

Catalyst	Source and radiation	Reaction conditions Reagent/ Catalyst concentration	Product	Selectivity C basis / %	Selectivity H basis / %	Reference	
1wt.% Pt/TiO ₂ 1wt.% Pt/(Nb)TiO ₂	Hg-Xe lamp (500 W) 280–400nm 420–680 nm	Ethanol:H ₂ O 3:7 0.50 g/L Opt.	Pt/TiO ₂ UV	H ₂	-	29.6	38
			CH ₃ CHO	81	47.9		
			CH ₃ CH ₂ COOCH ₃	19	22.5		
			Vis	H ₂	-	27.9	
			CH ₃ CHO	71	39.7		
			CH ₃ CH ₂ COOCH ₃	29	32.4		
			Pt/(Nb)TiO ₂ UV	H ₂	-	31.0	
			CH ₃ CHO	89	55.3		
			CH ₃ CH ₂ COOCH ₃	11	13.7		
			Vis	H ₂	-	32.7	
			CH ₃ CHO	97	63.4		
			CH ₃ CH ₂ COOCH ₃	3	3.9		
1 wt.% Pt/TiO ₂	Xe lamp (300 W)	Ethanol:H ₂ O 3:7 5 g/L	H ₂ CH ₃ CHO CH ₃ CHOHCHOHCH ₃	- 96.6 3.4	50.0 40.3 9.7	44	
3.8 wt.%Pt / 3 wt.% rGO-TiO ₂	Hg lamp (450 W)	Ethanol:H ₂ O 2:8 0.50 g/L	H ₂ CO ₂	- 100	100 -	100	
0.25 wt.% Pd/TiO ₂	BLB near-UV lamp 15 W fluorescent visible light lamp UV-Vis	Ethanol:H ₂ O 1:3 0.15 g/L	H ₂ CH ₃ CHO CO CO ₂ CH ₄	- 34.8 7.0 0.9 1.7	12.5 31.2 - - 1.6	46	



			CH ₃ CH ₃	10.4	14.1	
			CH ₂ CH ₂	45.2	40.6	
0.25 wt.% Pd/TiO₂	15 W BLB UV-Lamp 15 W fluorescent visible light lamp UV-Vis	Ethanol:H ₂ O 1:50 0.15 g/L	H ₂	-	14.4	⁴⁵
			CH ₃ CHO	1.8	28.8	
			CH ₄	35.5	1.4	
			CH ₃ CH ₃	10.6	13.0	
			CH ₂ CH ₂	52.1	42.4	
7.4 wt.% Ni/ g-C₃N₄	20W fluorescent lamps Simulated sunlight	Ethanol:H ₂ O 1:9	H ₂	-	31.3	⁹⁹
			CH ₃ CHO	100	68.7	

Table 7. Summary of efficiency values presented in the literature for hydrogen production using glycerol as a sacrificial agent.

Catalyst	Source and Radiation	Reaction conditions Reagent/ Catalyst concentration	QE, PY, AQY, STH, PTEF / %	Reference
1 wt.% Pt/TiO ₂	8 W black lamps Max. at. 365 nm	C ₃ H ₈ O ₃ :H ₂ O 0.03:1	10.2	101
1 wt.% Pt/TiO ₂	Hg lamp (1000 W) 313-366 nm	C ₃ H ₈ O ₃ :H ₂ O 0.03:1 0.67 g/L	0.08	102
1 wt.% Pt / N-TiO ₂ (nanotubes)	Fluo (Philips HPL-N 250 W/542 E40 HG 1SL) 17% UV + 83% Vis	C ₃ H ₈ O ₃ :H ₂ O 1:9 1 g/L	37.4	103
2.8 wt.% Ag ₂ O /TiO ₂	Xe lamp (300 W) 320–780 nm	C ₃ H ₈ O ₃ :H ₂ O 0.07:1 2 g/L	10.9	104
2.5 wt.% CuO _x /TiO ₂	Hg lamp (125 W)	C ₃ H ₈ O ₃ :H ₂ O 0.07:1 0.50 g/L	29.0	105
1:10 w/w CuO-TiO ₂	Sunlight Compound Parabolic Collector	C ₃ H ₈ O ₃ :H ₂ O 0.005:1 2.1 g/L Opt.	1,4	106

Table 8. Summary of selectivity values presented in the literature for hydrogen production using glycerol as a sacrificial agent.

Catalyst	Source and radiation	Reaction conditions Reagent/ Catalyst concentration	Product	Selectivity C basis / %	Selectivity H basis / %	Reference
1%wt Rh / TiO ₂	300 W Xe lamp	C ₃ H ₈ O ₃ :H ₂ O 0.75 g/L	H ₂ C ₂ H ₄ O ₂ CO ₂	- 61.2 38.8	70.8 29.2 -	49
0.1wt.% Ag - 0.3wt.% Pd /TiO ₂	100 W UV lamp ≥360 nm	C ₃ H ₈ O ₃ :H ₂ O 1:20 0.25 g/L	H ₂ CO CO ₂ HCHO C ₂ H ₆ O ₂ C ₃ H ₆ O ₂	- 0.08 2.4 21.0 7.4 69.1	2.2 - - 20.3 10.7 66.8	50

Table 9. Summary of efficiency values presented in the literature for hydrogen production using biomass as a sacrificial agent.

Catalyst	Source and Radiation	Reaction conditions Reagent/ Catalyst concentration	QE, PY, AQY, STH, PTEF / %	Reference
1.5 wt.% P, 3 wt.% Ni-doped TiO ₂	Two solar simulator bulbs (300 W) > 420 nm	Ethylene Glycol:H ₂ O 1:10 1 g/L	34.9	107
1 wt.% Pt / (Nb)TiO ₂	Hg-Xe lamp (500 W) 280-400 nm 420-680 nm	2-propanol:H ₂ O 1:10 0.50 g/L Opt.	UV: 1.8 Vis: 0.8	38
5 wt.% Pt CdS	Xe lamp (1000 W) 430- 520 nm	Lactic acid:H ₂ O 1:10 6 g/L	0.71	52
0.8 wt.% NiB/CdS	Xe lamp (300 W) 420 nm	Lactic acid:H ₂ O 1:10 0.66 g/L	21	108
0.79 wt.% NiS/CdS	Xenon lamp (300 W) > 420 nm	Lactic acid:H ₂ O 30:70 3 g/L	51.3	109



0.2 wt.% MoS₂/CdS	Xe Lamp (300 W) > 420 nm	Lactic acid:H ₂ O 10:90 0.50 g/L	7.3	110
20 wt.% NiS/CdS	300 W Xe lamp λ >400 nm	Lactic acid Lactic and lignin acid 1 g/L	29.3 44.9	111
GaN:ZnO	Xe lamp (300 W) λ >420 nm	Ascorbic acid (10 mM) 0.25 g/L	5.1	89
Zn-tri-PcNc-g-C₃N₄	300 W Xe lamp ≥ 500 nm	H ₂ O Ascorbic acid (8.8 g/L) 1 g/L Opt	1.85	112
0.5 wt.% Pt /Zn-tri-PcNc-2/g-C₃N₄	300 W Xe lamp 700 nm	H ₂ O Ascorbic acid (8.8 g/L) 1 g/L	1.07	113
ZnPyd/C₃N₄	300 W Xe Lamp ≥420 nm	H ₂ O Ascorbic acid (8.8 g/L) 1.5 g/L	32.3	114
1.5 wt.% Pt/ZnMT3PyP/g-C₃N₄	300 W Xe Lamp ≥420 nm	H ₂ O Ascorbic acid (8.8 g/L) 1.5 g/L	25.1	115
0.5 wt.% Pt/TiO₂	Xe-arc lamp (450 W) 365 nm	Glucose:H ₂ O 7:60 1,33 g/L	63	95

0.1 wt.% Ru/ZnIn₂S₄	LED irradiation (9.6 W) 455 nm	CH ₃ CN:2,5-DMF 1:1 10 g/L	15.2	51
0.3 wt.% Pt/TiO₂	4 x UV-A lamp (15 w) 366 nm	Swine sewage:H ₂ O 1.7:100 2 g/L Opt.	0,0052	116
1.0 wt.% Pt/ TiO₂	300 W Xe Lamp 380 nm	alpha cellulose:H ₂ O 3.1:1000 0.40 g/L	1.84	117
2 wt.% TiO₂/MoS₂	300 W Xe Lamp 380 nm	alpha cellulose:H ₂ O 3.1:1000 0.40 g/L	1.45	118
0.5 wt.% Pt NCs/TiO₂	300 W Xe Lamp 380 nm	Lignocellulose:H ₂ O 0.18:1000 0.25 g/L	4.1	119



Table 10. Summary of selectivity values presented in the literature for hydrogen production using biomass as a sacrificial agent.

Catalyst	Source and radiation	Reaction conditions Reagent/ Catalyst concentration	Product	Selectivity C basis / %	Selectivity H basis / %	Reference
0.1 wt.% Ru / ZnIn₂S₄	LED irradiation (9.6 W) 455 nm	CH ₃ CN:2,5- DMF 1:1 10 g/L	H ₂ Dimers (C12) Trimers(C18) Tetramers(C24)	- 68.3 28.3 3.3	63.3 17.8 4.0 14.8	⁵¹
5 wt.% Pt / CdS	1000 W Xe Lamp 430 - 520 nm	Lactic acid:H ₂ O 1:10 6 g/L	H ₂ CO ₂ CH ₃ COCOOH	- 2.1 97.9	45.1 - 54.9	⁵²

Table 11. Summary of efficiency values presented in the literature for hydrogen production using several sacrificial molecules as a sacrificial agent.

Catalyst	Source and Radiation	Reaction conditions Reagent/ Catalyst concentration	QE, PY, APY, STH, PTEF / %	Reference
CdS	300 W Xe Lamp 430 nm	Na ₂ S 1.6 g/L Na ₂ SO ₃ 6.3 g/L 0.56 g/L Opt.	0.47	120
Cd _{0.5} Zn _{0.5} S	300 W Xe Lamp 300–760 nm	Na ₂ S (0.35M) Na ₂ SO ₃ (0.25 M) 0.56 g/L	43.0	121
0.9 wt.% Pt/33% mol CdS-TiO ₂	Solar light-simulating source (Osram XBO 450W) 470 nm	Na ₂ S / Na ₂ SO ₃ and ethanol 1.3 g/L	20.0	122
0.3 wt.% Pt–0.13 wt.% PdS/CdS	300 W Xe Lamp > 420 nm	Na ₂ S (0.5 M) and Na ₂ SO ₃ (0.5 M) 1.5 g/L	93.0	123
7.5 wt.% Single-atom Ni / TiO ₂ - g-C ₃ N ₄	300 W Xe Lamp 420 nm, 500 nm, 550 nm	TEOA:H ₂ O 1:9 0.33 g/L	15.0	124
CdLa ₂ S ₄ /15 wt.% Ni ₂ P	300 W Xe Lamp > 420 nm	TEOA:H ₂ O 1:9 0.90 g/L	1.4	125
S-doped g-C ₃ N ₄	300 W Xe Lamp > 420 nm	TEOA:H ₂ O 1:9 0.50 g/L	13.7	126
g-C ₃ N ₄	300 W Xe Lamp	TEOA:H ₂ O	10.9	127





	> 420 nm	1:9 g/L		
g-C₃N₄	300 W Xe Lamp 400 nm	TEOA:H ₂ O 1:9 0.50 g/L	13.5	128
1 wt. % Pt / N-defective g-C₃N₄	300 W Hg lamp 420 nm	TEOA:H ₂ O 7:93 0.3 g/L	27.1	129
1 wt. % Pt /g-C₃N₄/PHI	300 W Hg lamp 420, 450,475, 500 nm	TEOA:H ₂ O 1:9 1 g/L	1.7, 1.5, 0.8, 0.4	130
MgPc/3%Pt/g-C₃N₄	300 W Xe lamp 420 nm	TEOA:H ₂ O 1:10 1 g/L	5.6	131
EY-g-C₃N₄-7%Pt	300 W Hg lamp ≥ 420 nm	TEOA:H ₂ O 1.25 g/L	18.8	132
N-annulated perylene-g-C₃N₄	300 W Xe lamp 520 nm	TEOA:H ₂ O 1:5 0.83	27.32	133
EB-MoSx-g-C₃N₄	400 W Hg lamp ≥420 nm	TEOA:H ₂ O 1.25 g/L	8.3	134
ZnPc-1.5%Pt/K⁺-g-C₃N₄	300 W Xe lamp ≥ 420 nm	TEOA:H ₂ O 1:9 1.5 g/L	2.74	135
P-CTFs	300 W Xe lamp ≥420 nm	TEOA:H ₂ O 1:10 0.4 g/L	4.65	136

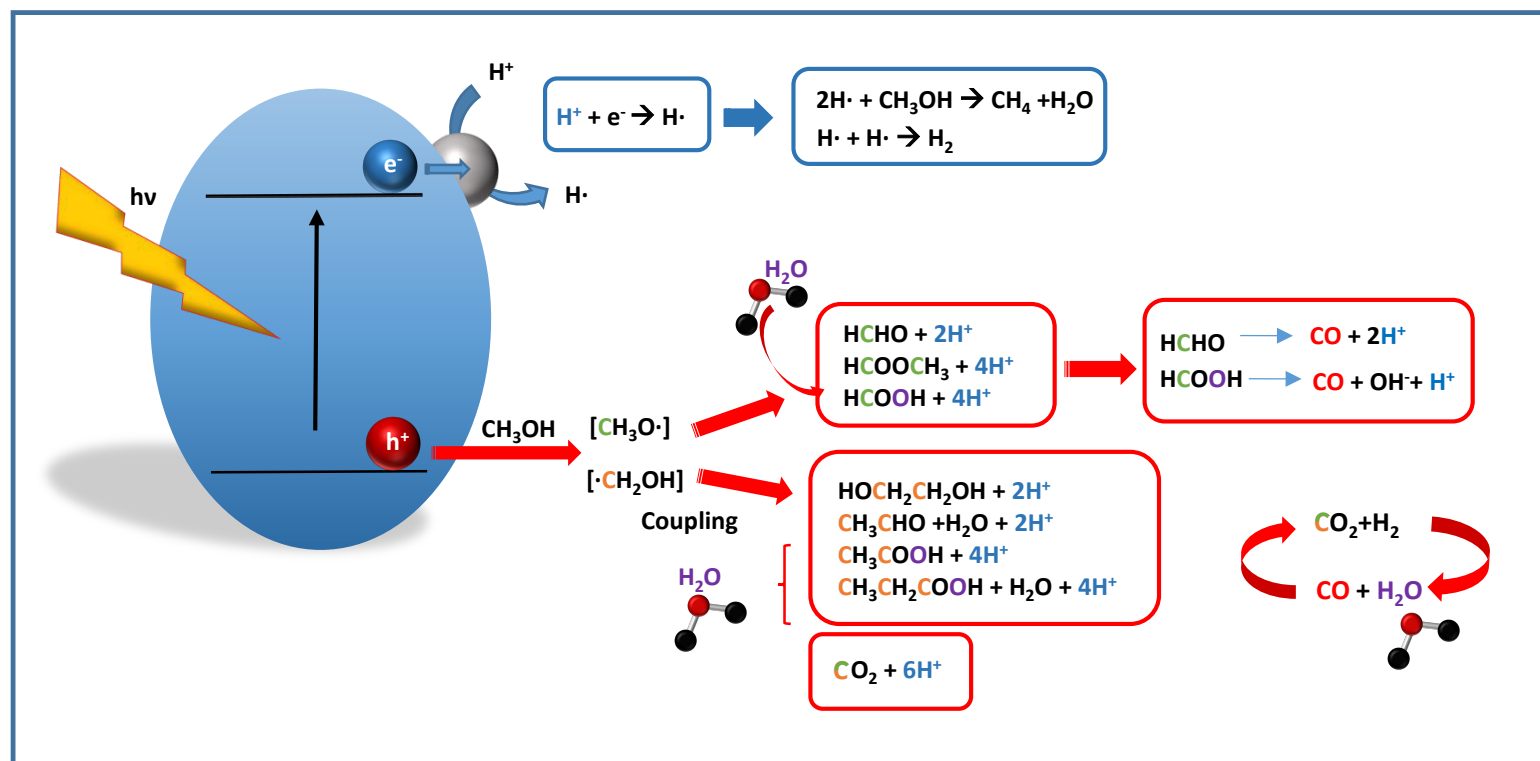


Figure 1. Schematic representation of the radical species and intermediates detected in the photocatalytic production using methanol as a sacrificial molecule. Colour codes are explained in the text.

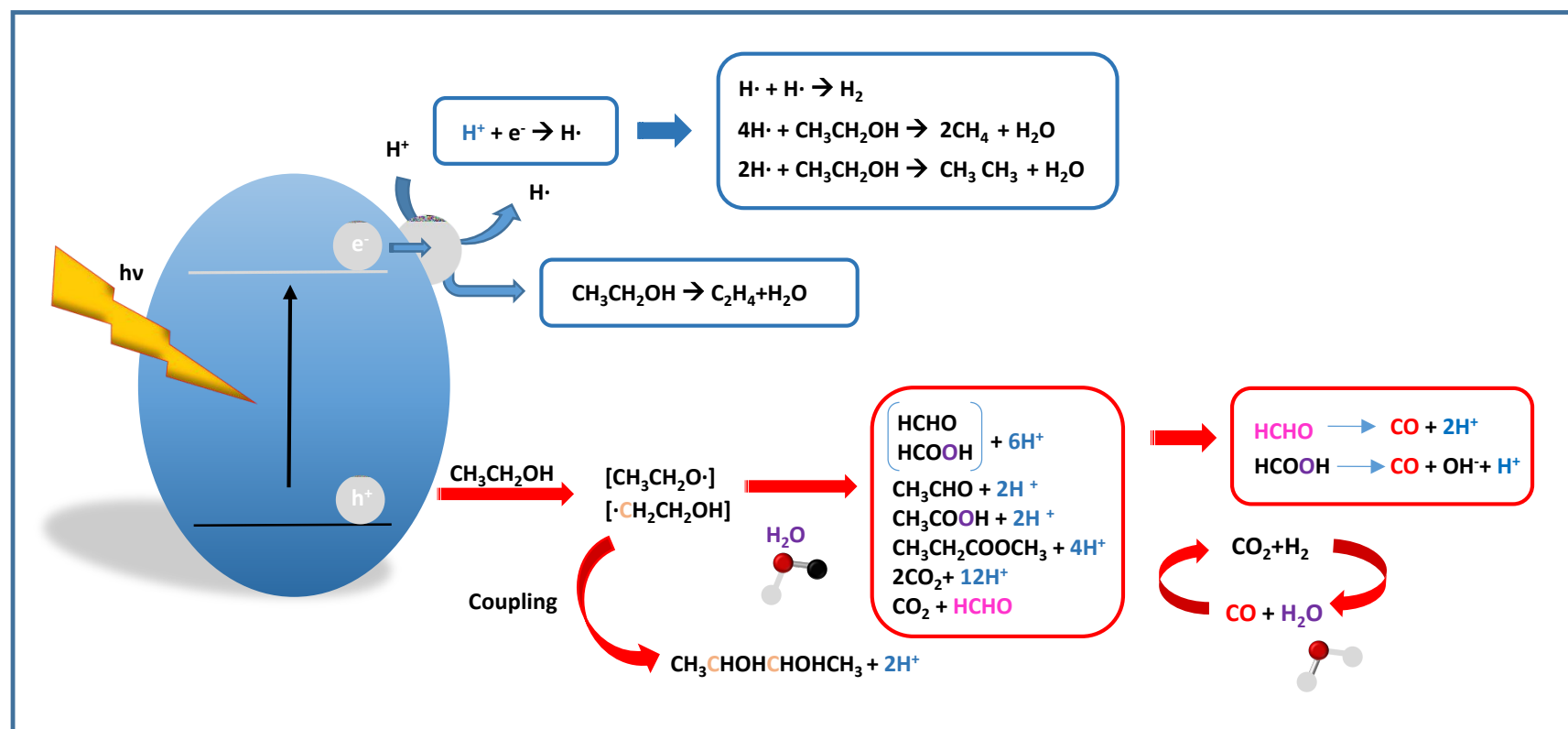


Figure 2. Schematic representation of the radical species and intermediates detected in the photocatalytic production using ethanol as a sacrificial molecule. Colour codes are explained in the text.

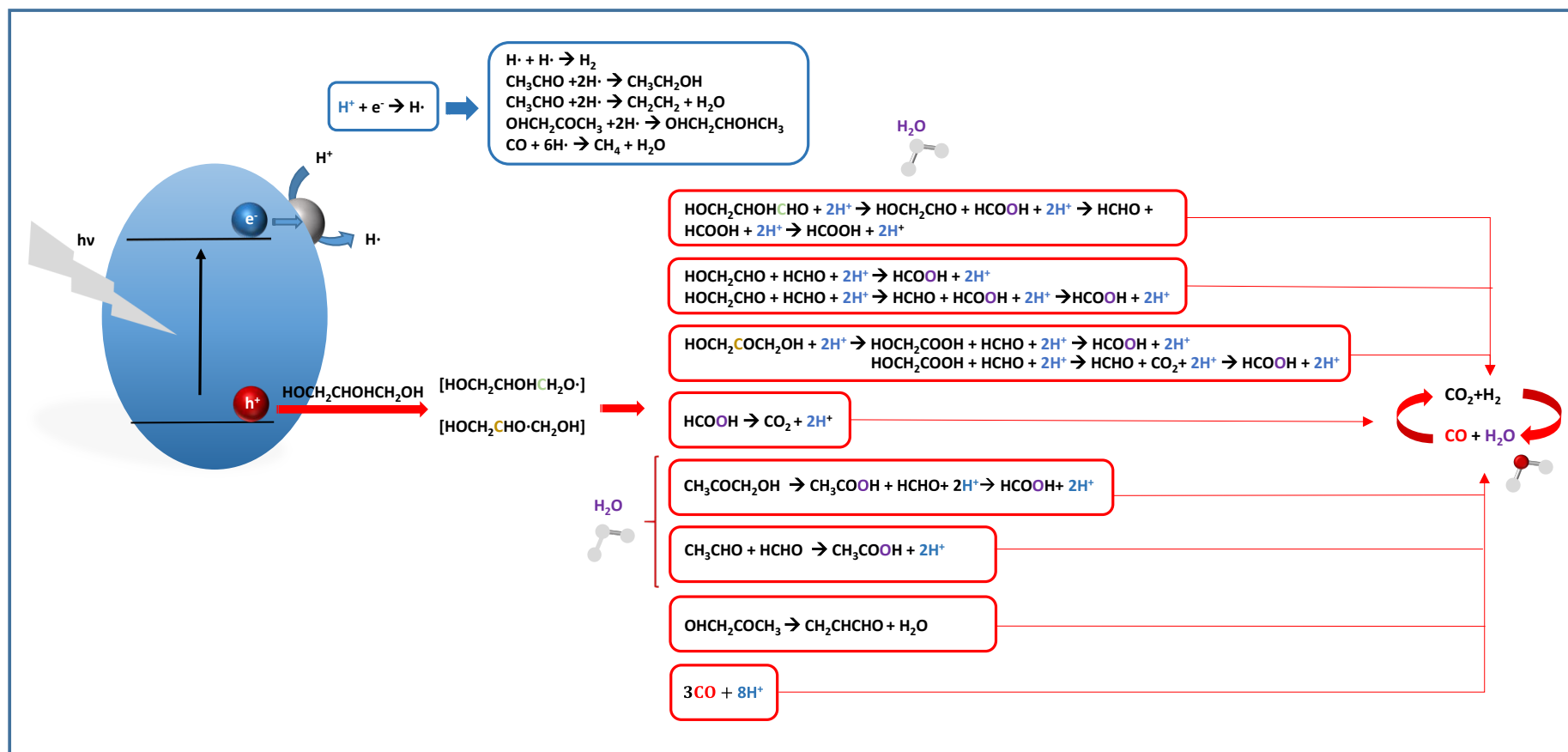
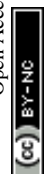


Figure 3. Schematic representation of the radical species and intermediates detected in the photocatalytic production using glycerol as a sacrificial molecule. Colour codes are explained in the text.



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View Article Online
DOI: 10.1039/D4YA00361F

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