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Photocatalytic H_2 and Added-Value By-Products – The Role of Metal Oxide Systems in Their Synthesis from Oxygenates

Matteo Cargnello,[a] Alberto Gasparotto,[b] Valentina Gombac,[a] Tiziano Montini,[a] Davide Barreca,*[c] and Paolo Fornasiero*[a]

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The growing demand for hydrogen for industrial use and as a fuel pushes for innovative and sustainable production strategies, which can be applied both in centralized, large-scale plants and in delocalized small units. At present, hydrogen is mainly produced by steam reforming of natural gas or oil. Nevertheless, the shortage of fossil fuel reserves and the increasing concern regarding environmental pollution have stimulated the search for alternative production routes, among which photocatalysis over metal oxide semiconductors represents a strategically attractive solution. Whereas the direct splitting of water is still a challenging issue because of intrinsic process drawbacks, a valuable alternative for a sustainable photocatalytic H_2 production is the use of biomass-derived compounds as raw materials. Upon photoactivation in the presence of an appropriate semiconductor, such feedstocks can undergo oxidation to CO_2 with simultaneous H_2 production in the so-called photoreforming process. When the oxidation is selective rather than complete, the process might be of further interest due to the added value of the obtained carbon-containing by-products. This microreview focuses on recent developments in this field, with particular attention to the use of representative biomass-derived oxygenated compounds, such as methanol, ethanol, glycerol, and sugars.

1. Introduction

Over the last decade, the interest in the production of hydrogen, a key reactant for a variety of purposes, has registered a remarkable increase. In addition to being widely used in various industrial processes,[1,2] hydrogen has emerged as a strategic energy vector in view of the inevitable depletion of fossil fuels. It also offers advantages in curbing environmental pollution. In fact, its conversion in fuel cells efficiently generates energy, producing only water as a by-product.[2–4] However, although hydrogen is the most abundant element in the universe, it is not freely present on earth, and one of the main challenges is its viable production in appreciable amounts.

Nowadays, nearly 95% of the total hydrogen supply is produced from fossil fuels, mainly by methane steam reforming, an unsustainable process on a long-term scale. As a consequence, great efforts are currently devoted to hydrogen production starting from renewable resources,[5] for instance by biomass catalytic steam reforming/gasification and photoelectrochemical or enzymatic approaches.[6–14] Nevertheless, these methods suffer from severe limitations associated with low efficiency or high energy demand, since they require the use of harsh operating conditions. On the other hand, photoactivated routes, though at present far from large-scale industrial application, are extremely promising as alternative hydrogen preparation strategies. In fact, they can ultimately enable the exploitation of sunlight, an infinite energy source, and to obtain hydrogen from natural products, such as water or biomass.[15]

Photocatalytic reactions can be classified into "down-hill" and "up-hill" processes (Figure 1), the former category comprising photooxidation of organic compounds at the expense of oxygen.[16] In these irreversible reactions, a photocatalyst triggers the production of various active species ($O_2^{\cdot-}$, $OH^\cdot$, $HO_2^\cdot$, and H^+, among others), initiating the oxidation process. On the other hand, the "up-hill" water splitting into H_2 and O_2 is accompanied by a large positive change in the Gibbs free energy ($\Delta G^0 = 237\ \mathrm{kJ\,mol^{-1}}$).[17] In

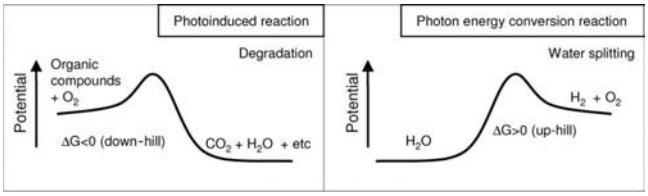

Figure 1. Types of photocatalytic reactions. Adapted with permission from ref.[16] Copyright 2003 Springer.

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[a] Department of Chemical and Pharmaceutical Sciences and ICCOM CNR Trieste Research Unit, Trieste University,
Via L. Giorgieri 1, 34127 Trieste, Italy
Fax: +39-040-5583903
E-mail: pfornasiero@units.it
[b] Department of Chemistry, Padova University and INSTM,
Via F. Marzolo 1, 35131 Padova, Italy
[c] CNR-ISTM and INSTM, Department of Chemistry, Padova University,
Via F. Marzolo 1, 35131 Padova, Italy
Fax: +39-049-8275161
E-mail: davide.barreca@unipd.it

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this reaction, photon energy is converted into chemical energy as in photosynthesis by green plants, so this process is also termed *artificial photosynthesis*.[18]

The key feature of a photocatalytic process is the presence of a semiconductor material, with a band gap E_g,[19] in which, upon illumination with radiation having an energy greater than or equal to E_g, the promotion of an electron (e^-) from the valence band (VB) to the conduction band (CB) takes place. Concomitantly, the formation of a positive hole (h^+) in the VB occurs. Photogenerated electrons and holes can either undergo undesired recombination or migrate to the surface of the system, where they can initiate reactions with adsorbed species. Whereas holes in the VB are powerful oxidizing species that can produce hydroxyl radicals ($OH^{\cdot}$) from the reaction with H_2O, photogenerated electrons in the CB are directly involved in H_2 production.

Matteo Cargnello graduated in Chemistry in 2008 at the University of Trieste. In 2008, he was a visiting graduate student at the University of Pennsylvania in the group of Prof. R. J. Gorte. He is currently a PhD candidate at the Graduate School of Nanotechnology (University of Trieste). His activity relates to the design of embedded Au and Pd catalysts for photocatalytic applications. He is coauthor of 10 ISI publications and 2 book chapters.

Alberto Gasparotto graduated in Chemistry in 2002 and received his PhD in Chemical Sciences in 2006. Since 2007 he is a Research Scientist at Padova University, and his research is mainly devoted to functional inorganic nanosystems synthesized by CVD, RF-sputtering, and sol–gel methods. For his scientific activity, documented to date by more than 100 papers in international journals, he has been awarded several prizes, among which are the "Eni Italgas Prize for Energy and Environment – Debut in Research" (2007), the "Prize for extraordinary innovation: answer to the challenges of the planet" (2008), and the Sapio Prize for Italian Research (2009).

Valentina Gombac graduated in Chemistry at the University of Trieste in 1992. From 1993 to 2001, she worked as a Researcher in the Area Science Park of Trieste. From 2002, she holds a research position at the University of Trieste. Her recent scientific interests are in the technological applications of materials science and photocatalysis to the solution of environmental problems. She is coauthor of 21 ISI publications and 3 patents.

Tiziano Montini obtained a PhD in heterogeneous catalysis in 2005. Since 2005, he holds a research position at the University of Trieste. His scientific interests lie in materials science and environmental heterogeneous catalysis, with particular attention to the use of photocatalysis in the valorization of renewable raw materials. He is coauthor of 52 ISI publications, 2 book chapters and 2 patents. In 2003 he was awarded the M. Forchiassin Prize for his undergraduate thesis.

Davide Barreca studied Chemistry and obtained his PhD at Padova University in 2000. From 2001 he is a Senior Research Scientist at the CNR-ISTM Institute in Padova. He is the European Editor of Nanoscience and Nanotechnology Letters and Associate Editor of Journal of Nanoscience and Nanotechnology. He is coauthor of over 190 scientific publications on multifunctional inorganic nanosystems based on metals, oxides, and sulfides. For the significant results achieved, Dr. Barreca has been awarded the Sapio Prize for Italian Research (2009), the Prize for Strategic/Excellence results for Italian CNR researchers and technologists (2009), and the "Vincenzo Caglioti" International Prize for Chemistry – Accademia Nazionale dei Lincei – Rome (2008).

Paolo Fornasiero obtained his PhD in heterogeneous catalysis in 1996. After his postdoctoral fellowship at the University of Reading in 1997, he became Assistant Professor in 1998 and Associate Professor of Inorganic Chemistry in 2006 at the University of Trieste. His scientific interests are in the technological applications of materials science and environmental heterogeneous catalysis. He is coauthor of 130 ISI publications, 10 book chapters and 3 patents. He was awarded the National Stampacchia Prize in 1994 and the Nasini Gold Medal (Italian Chemical Society) in 2005 for his contributions to the research in the field of inorganic chemistry.

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For this process to occur, the semiconductor CB edge must be more negative than the $H^+ \rightarrow H_2$ reduction potential [$E(H^+/H_2) = 0.00$ V with respect to the normal hydrogen electrode (NHE) at pH = 0]. In addition, oxygen evolution from water requires a VB edge that is more positive than the oxidation potential of H_2O [$E(O_2/H_2O) = 1.23$ V with respect to NHE at pH = 0].

Since the pioneering work of Fujishima and Honda,[20] who first demonstrated water splitting into H_2 and O_2 by a photoinduced process, enormous research efforts have been devoted to the design of active and stable photocatalysts capable of producing hydrogen under activation by UV and, ultimately, by visible light.[21] In this regard, various semiconducting systems, such as sulfides, oxysulfides, oxynitrides, have been considered.[22,23] Nevertheless, metal oxide semiconductors show superior long-term stability and corrosion resistance, and, as a result, they have been investigated much more.[16,21,24] Among them, the most popular is undoubtedly titania (TiO_2), which has been the object of intensive studies.[25]

An open problem for such systems is related to the fact that they generally absorb in the UV spectral range, which accounts for only 3–4% of the incident solar radiation. As a consequence, great attention has been devoted to the development of suitable semiconducting systems absorbing light in the visible range, in view of a really sustainable H_2 production.[26,27]

In spite of the intense research activities registered in the last decades, pure water splitting is still far from any technological application,[28,29] because of the complexity of the process and its inherent drawbacks.[17,30] In particular, the main problems are the fast recombination between H_2 and O_2 (the reverse reaction is thermodynamically favorable) and between photogenerated electrons and holes. In order to minimize the former, the production of the two gases in separate chambers, connected through photocatalyst thin films, has been proposed (Figure 2).[31,32]

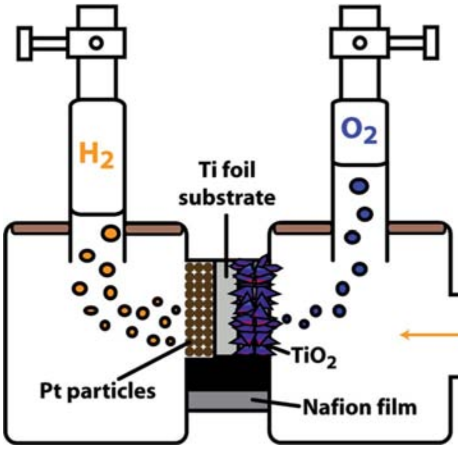

Figure 2. Schematic representation of a two-compartment photochemical cell for the evolution of H_2 and O_2 separated by a TiO_2 thin film. Adapted with permission from ref.[20] Copyright 1972 Nature Publishing Group.

To prevent the e^-/h^+ recombination processes, the use of cocatalysts, such as noble metals (NM; Pt, Pd, and Au, among others), transition metal oxides (RuO_2, IrO_2, and NiO, among others), sulfides (MoS_2 among others), which are able to act as electron or hole traps, has been proposed.[26] The presence of supported metal nanoparticles that have surface plasmon resonance bands can further enhance the photoreactivity under visible irradiation as a result of increased light absorption.[33–35] Nishijima et al.[35] reported surface-plasmon-assisted photocurrent generation by near-infrared radiation with use of Au nanorods and TiO_2 systems. Similarly, photosensitization of titania by small gold nanoparticles was reported by Corma et al.[33] An alternative attractive approach is the addition of sacrificial agents to water.[15,31] Such species can irreversibly react with photogenerated holes (or $OH^·$ radicals derived from the reaction of h^+ with H_2O), undergoing an easier oxidation than that of water, with concomitant H_2 production by photogenerated electrons, which is much higher than that for pure water splitting.

To date, many sacrificial reactants, both inorganic, such as H_2S, S^{2-}/SO_3^{2-}, Br^-, I^-, CN^-, Fe^{2+}, and Ce^{3+}, among others, and organic, such as alcohols, acids, aldehydes, sugars, have been proposed for hydrogen generation.[26,36] In particular, the use of largely available organic species in the so-called photoreforming processes (Figure 3) has been increasingly considered. Such routes, which are other examples of an "up-hill process" (Figure 4), can be expressed by the following general equation:[15,37]

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + (2x + y/2 - z)H_2$$

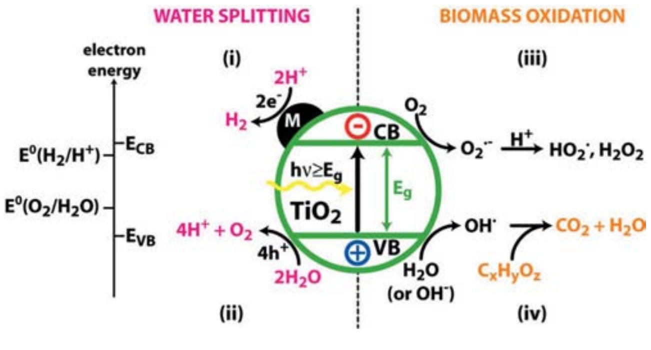

Figure 3. Schematic representation of water splitting, biomass ($C_xH_yO_z$) oxidation and photoreforming reactions over an irradiated M-TiO_2 photocatalyst. Production of hydrogen (i) and oxygen (ii) from water cleavage is triggered by photogenerated electrons and holes, respectively. Oxidation of organic compounds takes place in the presence of oxygen (air) with the participation of photogenerated holes and ultimately leads to the production of CO_2 and H_2O (iv). This process is accompanied by consumption of photogenerated electrons by chemisorbed oxygen (iii). The overall photoreforming process combines photoinduced hydrogen production (i) and oxidation of organic derivatives (iv). Adapted with permission from ref.[41] Copyright 2008 Springer.

Many oxygenate molecules, mostly derived from biomass (sugar, starch, vegetable oils, lignocellulosic crops, and algae fuels, among others), have been tested for H_2 production by these routes.[21] Among them, the species obtained by the hydrolysis of lignocellulosic materials are particularly im-

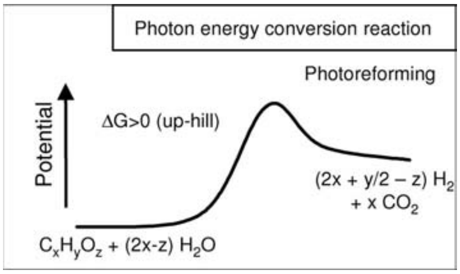

Figure 4. "Up-hill" process representing the photoreforming of biomass-derived feedstock.

portant. In these cases, a significant fraction of the generated CO_2 can be taken up by plants during their growth. One additional key advantage is the possibility to interrupt the process at the desired stage, with the selective production of important chemicals through clean and sustainable routes.[38–40]

An aspect of great importance for technological applications, which has not been adequately considered in the scientific literature up to date, concerns photocatalyst deactivation. At variance with traditional heterogeneous catalysts operating under conditions of medium to high temperature, photocatalysts work close to room temperature, making sintering phenomena generally negligible. On the other hand, surface poisoning is a frequent reason for the observed deactivation. In particular, photocatalysts that do not completely oxidize sacrificial agents to CO_2 can lead to the production of nonvolatile intermediates that accumulate on the active sites, thus causing detrimental poisoning phenomena. In addition, undesired leaching effects of the active phase can be favored by a progressive pH variation during the process and by the capability of reaction intermediates (e.g., carboxylic acids) to coordinate metal ions on the catalyst surface.[42,43]

For photocatalytic processes, a set of key parameters is usually employed to quantitatively characterize the efficiency in substrate conversion.[44] Such efficiency, defined in photochemistry by the quantum yield, Φ,[45] is based on the knowledge of the number of photons with a particular wavelength absorbed by the system. Whereas this quantity can be measured with great accuracy in homogeneous processes,[46] in heterogeneous ones only the number of photons incident onto the photocatalyst surface, representing the upper limit of the photons that can be absorbed, can be estimated. As a consequence, the concept of photonic yield, based on the number of incident photons arriving at the internal surface of the irradiation window, has been introduced in heterogeneous photocatalysis. In addition, whereas the term "yield" can only be used for excitation with monochromatic photons (i.e., with energy in the wavelength range between λ and $\lambda + d\lambda$),[45] it is convenient to adopt the generalized definition of "efficiency" when a polychromatic source is used.

In general, the following considerations on the evaluation of quantum yields for heterogeneous photocatalysis must be taken into proper account.

(1) It is of fundamental importance to monitor the initial rates of reactant consumption and product formation. Under these conditions, products do not interfere with the measurements, and possible catalyst deactivation is minimized. In fact, the quantum yield of substrate consumption, as well as that of product formation, generally varies with the irradiation time, especially upon prolonged illumination.

(2) The catalyst concentration should not affect the reaction rate.

(3) Non-uniform catalyst distribution and mass-transfer limitations must be carefully avoided by effective stirring.

(4) The adsorption of reactants on the catalyst surface should have reached a steady-state regime before starting irradiation.

(5) The reaction rate should linearly depend on the spectral radiance, a requisite which is rigorously fulfilled only at moderate radiation intensities.

(6) The emission spectrum of the adopted polychromatic source and the absorption spectrum of the substrate must be taken into account. In addition, the contribution of the absorbed radiation should be properly determined.

Hereafter, the following general definitions will be used, in accordance with IUPAC rules.[44]

Photocatalytic efficiency: amount of product formed (alternatively, of reactant consumed) divided by the number of photons incident on the system.

Quantum efficiency: rate of a given photophysical/photochemical process divided by the total absorbed photon flux. In heterogeneous photocatalysis, *photonic efficiency* is commonly used.

Photonic efficiency: ratio of the photoreaction rate measured for a specified time interval to the rate of incident photons within a defined wavelength interval inside the reactor irradiation window.

Quantum yield, Φ: number of defined events occurring per photon absorbed by the system at a specified wavelength. The integral quantum yield is:

$$\Phi(\lambda) = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

For a photochemical reaction:

$$\Phi(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}}$$

Although these parameters do not depend on the irradiation angle, a correlation between the quantum or photocatalytic efficiency and the specific irradiation conditions (such as the standard Air Mass 1.5 or Air Mass 0) might offer additional interesting information on the performance of the system.

In the literature, various excellent reviews on photocatalytic hydrogen generation are available.[26,47,48] Recently, we have dealt with the innovative use of supported oxide nanosystems for photoactivated H_2 production.[15,49–51] In this microreview, we mainly focus our attention on the photoreforming of biomass-derived oxygenates over powdered metal oxide photocatalysts, an alternative and less studied

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process with respect to water splitting. Far from offering a comprehensive overview, we will discuss the use of selected representative oxygenates, that is, methanol, ethanol, glycerol, and sugars. As a matter of fact, methanol is largely used as sacrificial agent in photocatalysis, being an attractive model compound for its high reactivity, structural simplicity, and absence of C–C bonds. These aspects enable an easier investigation of reaction pathways and limit photocatalyst deactivation phenomena due to surface adsorption of partial oxidation by-products. Nevertheless, methanol is not a preferred choice in terms of sustainability. In fact, although methanol can be obtained from bio-syngas, produced, for instance, during biomass gasification, its production is still largely accomplished from fossil fuels, in particular, methane. As a consequence, in this microreview, attention will also be dedicated to other compounds, which are already largely produced from biomass. For instance, ethanol can be obtained from the fermentation of sugars, as well as from the enzymatic or thermochemical degradation of cellulose.[52,53] Similarly, glycerol is nowadays the major by-product in the *trans*-esterification of vegetable oils to biodiesel.[54] Finally, degradation of cellulose-derived compounds and lignin can lead to large quantities of sugars.[55] The mechanisms involved in the decomposition of the substrate to hydrogen will be briefly discussed, together with some selected literature examples highlighting the main achievements in the chemistry of H_2 and added-value by-product formation.

2. General Mechanisms for Hydrogen Production

In spite of extensive studies involving the design of active oxide photocatalysts, limited attention has been dedicated to photodegradation mechanisms of oxygenates over oxide semiconductors, which are still subject of debate. In the case of TiO_2, the most studied semiconductor, the main oxidizing species are reported to be free or trapped holes, $OH^{\cdot}$ radicals, $O_2^{\cdot-}$ and $^1O_2$, as well as H_2O_2 and O_2.[25,56] While in some cases the reaction pathway involves direct oxidation by holes, in others the process is reported to be mediated by highly oxidizing species. Among them, $OH^{\cdot}$ radicals, derived by the reaction of photogenerated holes with water molecules, are generally considered responsible for initiating the oxidation process.[56,57]

Several studies highlight the presence of both shallowly and deeply trapped holes on the photocatalyst surface.[58,59] Their mutual content directly depends both on the nature of the catalyst and the adopted experimental conditions. Shallowly trapped holes show reactivity and mobility comparable to free ones, reacting thus very rapidly with chemisorbed species. In this case, oxidation processes might even be competitive with ultrafast charge-trapping events. On the other hand, deeply trapped holes, which exhibit lower oxidizing potentials, preferentially react with more mobile physisorbed substances, and the corresponding reaction rates are lower.[58–60]

For a given molecule, the predominance of physisorption vs. chemisorption is significantly affected by the environment and, in particular, by the presence of water or oxidation by-products. In this regard, Nosaka et al. demonstrated the competitive adsorption between CH_3CH_2OH and H_2O on TiO_2 photocatalysts by NMR analysis.[61] In a similar way, Wang et al. investigated the interaction of methanol and water with TiO_2 by means of in situ sum frequency generation (SFG), a highly sensitive surface characterization technique.[62] Upon using pure methanol vapor in contact with TiO_2, both molecular methanol and methoxide were detected. The former one was still present after the addition of water, whereas chemisorbed methoxide signals disappeared and were reversibly recovered upon removal of H_2O. These data indicate that the methanol oxidation pathway is directly dependent on the H_2O/CH_3OH ratio. In addition, the predominance of physisorption/chemisorption influences the oxidation rate. For instance, NMR studies showed that, during the oxidation of ethanol and 2-propanol, the chemisorbed species, that is, ethoxide or propoxide, are oxidized much more rapidly than the corresponding H-bonded ones.[63,64]

In spite of the extensive use of methanol as electron donor for photocatalytic H_2 production, only few studies have discussed the underlying process in detail. Chen et al. investigated the photoelectrochemical oxidation of alcohols and organochlorides on the surfaces of Pt- or Pd-loaded TiO_2[65,66] and proposed a mechanism for the oxidation of both methanol and ethanol. Specifically, in the case of suspended powders, the oxidation of the organic compound and the concomitant reduction (of oxygen or protons in aerated or deaerated systems, respectively) take place on different areas of the photocatalyst surface. In particular, two mechanisms were proposed for the anodic oxidation of methanol. The first one consists of the direct oxidation by holes of adsorbed methanol, up to its complete conversion into CO_2. The second one involves an indirect oxidation mediated by $OH^{\cdot}$ species (either adsorbed or in solution). In these situations, both CH_3OH and its oxidation products are adsorbed on the photocatalyst surface. Alternatively, methanol can be oxidized without being adsorbed on the catalyst surface, and, correspondingly, its partial oxidation intermediates, such as formaldehyde or formic acid, can be identified and isolated in the reaction medium.

Notably, whereas some reports describe the photocatalytic production of H_2 from aqueous solutions as water splitting,[67–71] others classify the process as CH_3OH dehydrogenation to formaldehyde, or CH_3OH reforming to CO_2.[72,73]

The mechanism for hydrogen evolution with use of metal oxide semiconductors and alcohols includes the release of H^+ from the sacrificial agent and the formation of different oxygenated radicals, which are powerful oxidizing species. The result is the reduction of protons to H_2 and the concomitant full oxidation of the organic compounds to CO_2 through various intermediates, including aldehydes and carboxylates.[26]

A direct correlation between the yield of H_2 and the polarity of the different alcohols (methanol, ethanol, propanol, and butanol) used as sacrificial agents was evidenced over TiO_2-based photocatalysts by taking into consideration the first reaction step, that is, dissociative alcohol adsorption on the TiO_2 surface to form alkoxide and surface OH groups. Nevertheless, the limited process efficiency (< 10 %) under UV light means that this approach is still far from a practical technological application.[74]

Bowker and co-workers[75] concluded that the presence of hydroxy groups in the sacrificial agent was essential for the photoreforming process to occur, since chemicals like alkanes and alkenes were revealed to be inactive under the same experimental conditions.

Bahruji et al. studied hydrogen production using Pd-TiO_2 photocatalysts,[76] obtaining similar H_2 evolution rates from primary/secondary alcohols and observing the formation of the alkane derivatives of the parent alcohols (e.g. propane and butane from 1-propanol and 1-butanol, respectively). This phenomenon suggested that metal particles dehydrogenate alcohols, and the obtained alkenes are subsequently hydrogenated by the photocatalytically produced H_2. In the case of methanol, the dehydrogenation step is accompanied by the formation of CO, which, in turn, is oxidized by titania. The authors also found that, in general, a higher number of hydrogen atoms in the α-position with respect to the OH group led to improved catalyst activity in H_2 generation. The use of compounds with different chain lengths (methanol, ethanol, propanol, butanol, glycerol, sugars) resulted in similar hydrogen production rates, which was related to the inability of the catalyst to promote the process after the first dehydrogenation steps, even if C–C bond breaking occurred. Different mechanisms for H_2 production were thus proposed, α-hydrogen dissociation and β-hydride elimination to a ketone intermediate being suggested as the rate-determining steps for primary and secondary alcohols, respectively. In the case of tertiary alcohols, where no α-hydrogen atoms are present, H_2 production was not observed.

The presence of hydroxy groups in the structure of the sacrificial agent is therefore a significant benefit for increased hydrogen production.[77] It is also worthwhile noting that, when photocatalysts yield a modest amount of H_2 and CO_2, the selective preparation of added-value intermediate oxidation products can be fruitfully exploited.

3. Methanol

Methanol is one of the most popular sacrificial agents used in the photocatalytic evolution of H_2 from water, since its hydroxy group captures photogenerated holes and minimizes the probability of e^-/h^+ recombination. Yet, CH_3OH can only be partially considered as a renewable source (see Section 1), and bio-methanol obtained from biomass gasification might be of higher interest as a sustainable sacrificial agent in photoreforming.

In this context, systems based on Pt-TiO_2 were extensively investigated since 1980, when Kawai and Sakata[78] reported on the efficient production of hydrogen from liquid CH_3OH and H_2O at room temperature under Xe-lamp irradiation. In general, the NM-TiO_2 system (NM = Rh, Pd, Pt) can be regarded as a photoelectrochemical cell in which a TiO_2 semiconductor electrode and a metal counter-electrode are brought into contact. In fact, well-dispersed metal nanoparticles act as mini-photocathodes, trapping electrons, which, in turn, reduce water to hydrogen. In this regard, Chiarello et al.[79] studied methanol photoreforming over metal-containing TiO_2 both in aqueous solution and in the vapor phase, observing a 30-fold enhancement of the H_2 production rate upon the addition of 1 % gold to TiO_2. Thanks to the absence of mass transfer limitations, a further rate increase was obtained in a vapor-phase photoreactor (up to a hydrogen yield greater than 10 $\text{mmol}\,\text{h}^{-1}\,\text{g}_{\text{cat}}{}^{-1}$, or 70 $\text{mmol}\,\text{h}^{-1}\,\text{m}^{-2}$, corresponding to an apparent photon efficiency higher than 6 %). Identification of the main reaction products demonstrated that the first step of methanol photoreforming on Au-TiO_2 consisted of its photocatalytic dehydrogenation to formaldehyde, the only intermediate species detected in the gas phase. Moreover, isotope exchange photocatalytic tests demonstrated that a complex network of steps is involved in the photoreforming of methanol, comprising (1) an indirect pathway mediated by the $OH^{\cdot}$ radical; (2) a direct path, implying the reaction of valence band holes with adsorbed methanol at the titania–NM interface; (3) a water-assisted direct path, involving the reaction of valence band holes with methanol molecules adsorbed far from the interface between titania and the noble metal.[80] A general scheme of the reaction involved in the gas-phase photoreforming of methanol over TiO_2 is presented in Figure 5.

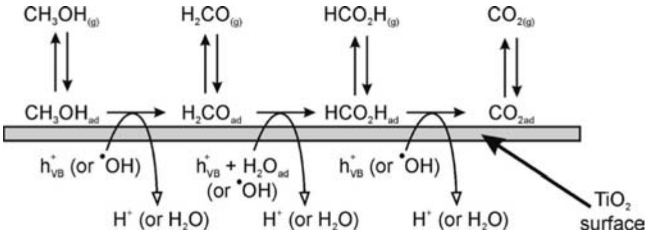

Figure 5. Reaction scheme of the photocatalytic gas-phase oxidation of methanol on the TiO_2 surface. Adapted from ref.[80] with permission from Elsevier.

A similar reaction pathway can be proposed for the liquid-phase photoreforming of methanol. In this case, multiple equilibria are established, leading to a repartition of each oxidation intermediate between the surface of the catalyst, the liquid, and the gaseous phases.

Subsequently, the photocatalytic reforming of methanol over a series of NM-based (NM = Rh, Pt, Ag, Au, and so on) TiO_2 photocatalysts was attempted; this resulted in a high yield of hydrogen, thanks to the reduced NM particle size and the high dispersion of NM on a high-surface-area oxide (Figure 6).[81]

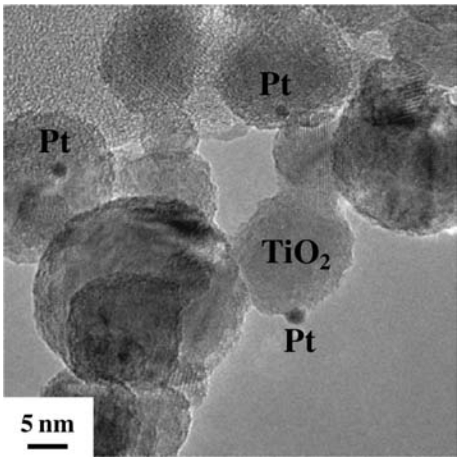

Figure 6. HRTEM micrograph of a 0.5% Pt-TiO_2 photocatalyst prepared by flame spray pyrolysis (surface area = 70 $m^2 g^{-1}$). Adapted from ref.[81] with permission from Elsevier.

In another study by Bahnemann et al.,[82] H_2 production with ultra-low CO concentration (< 10 ppm) was achieved via photoreforming of aqueous CH_3OH solutions on Pt-TiO_2 catalysts containing adsorbed sulfate/phosphate ions. The role of Pt nanoparticles was reported to be twofold, that is, enhancement of H_2 generation and suppression of CO formation. Sulfate and phosphate ions adsorbed on TiO_2 were found to further inhibit CO production, without appreciably decreasing H_2 evolution.[83]

Further interesting results were achieved by tailoring TiO_2 morphology, focusing in particular on titania nanowires obtained by a hydrothermal route. Upon annealing at suitable temperatures, photocatalytic H_2 evolution from CH_3OH/H_2O solutions over such systems was even higher than that exhibited by Degussa P-25, the benchmark TiO_2 standard for powdered materials.[69]

Recent attempts to increase H_2 production from methanol solutions under visible light irradiation included N-doping of titania by using urea[84] or codoping with Ce and N.[85] In the same context, a series of Pt- and Au-TiO_2 photocatalysts were also employed, examining different TiO_2 materials with variable anatase/rutile contents.

Under optimized conditions, a significant H_2 production efficiency (120 $\mu mol\,min^{-1}$) was obtained with very low amounts of methanol over days of irradiation, without any significant deactivation.[71]

Finally, the research efforts devoted to materials different from TiO_2 are also worth mentioning. Recently, a tin(II) tungstosilicate derivative, $K_{11}H[Sn_4(SiW_9O_{34})_2]\cdot 25H_2O$, with four sandwiched Sn^{2+} cations, was prepared by reaction of $SnCl_2$, KCl, and $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot xH_2O$. Good visible-light photocatalytic H_2 evolution was observed with Pt nanoparticles as cocatalysts and methanol as sacrificial agent.[86]

4. Ethanol

Ethanol is an attractive renewable source for hydrogen production via photoreforming, since it can be obtained in large amounts by fermentation processes starting from second-generation biomass, as well as from steam reforming of cellulose and lignocellulose.[87]

As with methanol, various studies on H_2 photoproduction with ethanol have been devoted to NM-TiO_2 systems, such as that of Mizukoshi et al. reporting on the use of a sonochemical synthesis.[88] In this case, among Pd, Pt, and Au, Pt was found to be the best choice in terms of functional performance, because of the lower dimensions of the nanoparticles obtained.

Yang et al. studied hydrogen production from CH_3CH_2OH over TiO_2 doped with Pd, Pt, or Rh obtained by flame spray pyrolysis.[74] They found a good H_2 yield under UV light for 1 wt.-% Pd/Pt-TiO_2 samples, whereas the use of Rh led to an inferior activity due to Rh oxidation, as confirmed by ex situ X-ray photoelectron spectroscopy (XPS) analyses. The process was mainly governed by the formation of surface ethoxide and OH groups by dissociative adsorption at the interface between metal particles and TiO_2:

$$CH_3CH_2O\text{–}H_{(a)} + Ti_{(s)}\text{–}O_{(s)} \rightarrow CH_3CH_2O\text{–}Ti_{(s)} + H\text{–}O_{(s)}$$

where (a) and (s) stand for adsorbed and surface, respectively (see Figure 7 for Pt). Upon illumination with UV light, at the Pt-TiO_2 interface hydrogen atoms of hydroxy groups are readily reduced by electrons from Pt particles, whereas chemisorbed ethoxide species act as hole traps.

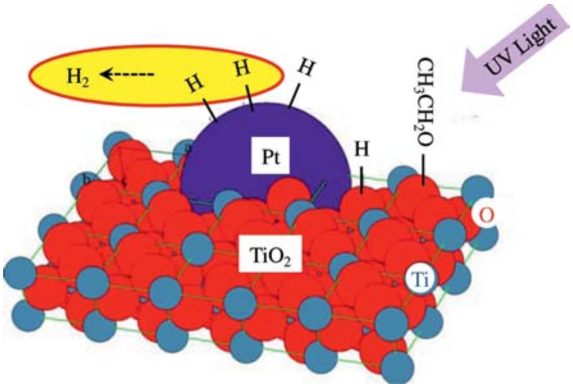

Figure 7. Schematic representation of ethanol photodecomposition on Pt-TiO_2 photocatalysts. Adapted from ref.[74] with permission from Elsevier.

Kondarides et al. performed various studies on photocatalytic hydrogen production, mainly using Pt-TiO_2 materials, from biomass-derived sacrificial molecules, such as acids, aldehydes, and alcohols.[37] Among the latter, ethanol was one of the easiest to be fully converted into CO_2 as a result of its simpler structure, leading to the limited formation of intermediate C-containing products. Interestingly, with acetaldehyde the hydrogen yield was lower than the predicted stoichiometric one, an unexpected phenomenon, considering that acetaldehyde is an intermediate product of ethanol oxidation. In all cases, photocatalyst deactivation was observed and attributed to the formation of photogenerated species poisoning the Pt surface.

Another work reported on the use of metal-doped nanocrystalline titania for ethanol photoreforming.[89] Under the

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best conditions, over Pt-TiO_2, an overall quantum efficiency as high as 74% was obtained. These systems were used to assemble a two-compartment chemically biased photoelectrochemical cell to produce H_2 and/or electricity from aqueous CH_3CH_2OH.[90,91] Yet, the measured cell activity showed a marked deactivation after 20 h due to the formation of several by-products, including acetaldehyde, acetone, and 2-butenal, produced by the partial oxidation and UV decomposition of ethanol.

Yu et al. prepared TiO_2 nanosheets with exposed (001) facets by a hydrothermal process involving the use of HF and resulting in F-doped titania.[92] The material showed very good hydrogen production rates from ethanol solutions after deposition of 2 wt.-% Pt. The same photocatalyst was also appreciably active when more complex oxygenates, such as glycerol or glucose, were used.

Recently, Pt/CdS/TiO_2 nanocomposites[36] were used under simulated solar light for photoelectrochemical H_2 production from ethanol. High hydrogen yields were obtained when the CdS/TiO_2 photoanode was separated, but short-circuited, from a Pt cathode. The effect of spatial separation on the effectiveness of the sacrificial agent as hole scavenger was explained through a favorable cascade of energy states, enabling electron accumulation on Pt and favoring hydrogen production. The presence of OH^- ions, acting as hole traps at the CdS/TiO_2 anode, was also found to play a key role for the observed activity. This study highlights how the matching of component energy states in composite systems is of great importance to optimize hydrogen production.

Due to the high cost and toxicity of Pt and noble metals, recent efforts have been devoted to the development of systems alternative to the widely investigated NM-TiO_2 ones. Among these, Cu_2O or CuO nanomaterials have received great attention. Recently, some of us[50] reported hydrogen photogeneration by using methanol as organic oxygenate from such systems and found an appreciably higher activity for copper(II) oxide, which was mainly attributed to its higher active area. Further attention was also devoted to Cu_xO-TiO_2 (x = 1,2) nanocomposites, which have been found to be active for H_2 photoproduction from aqueous ethanol.[93] In this study, the authors correlated the photocatalytic activity with the copper content, observing the maximum-like behavior reported in Figure 8. As can be observed, the hydrogen production rate increased rapidly and reached a maximum value (ca. 54 μmol h^{-1}) at 1.0 wt.-% Cu. More detailed studies revealed that the best performance could be related to the content of Cu^I centers, recognized as active sites for the transfer of photogenerated electrons, whereas Cu^{II} species were found to promote detrimental electron–hole recombination. Some of us also reported on the preparation of Cu_xO species embedded in titania as photocatalysts, with H_2 production rates higher than 1000 μmol g^{-1} h^{-1}.[43] One of the main problems of these photocatalysts is their deactivation, for two main reasons: besides the accumulation of by-products, in line with other reports,[94] photoreduction of copper to Cu^0 may limit electron transfer to TiO_2, thus decreasing the hydrogen evolution rate.

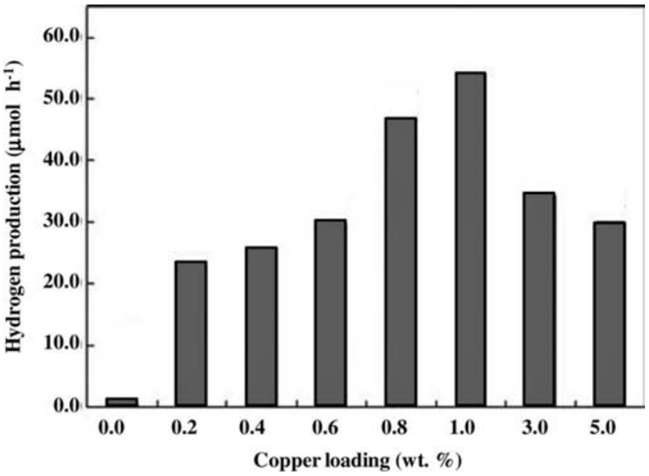

Figure 8. Dependence of the H_2 production rate on copper loading for Cu_xO/TiO_2 photocatalysts synthesized by wet impregnation. Adapted with permission from ref.[93] Copyright 2009 Springer.

As in the case of methanol photoreforming over TiO_2-based materials (see above), ethanol photoreforming proceeds trough a progressive oxidation coupled with acetal formation promoted by the presence of surface acidic sites and accompanied by dehydration and water gas shift reactions (Figure 9).[42]

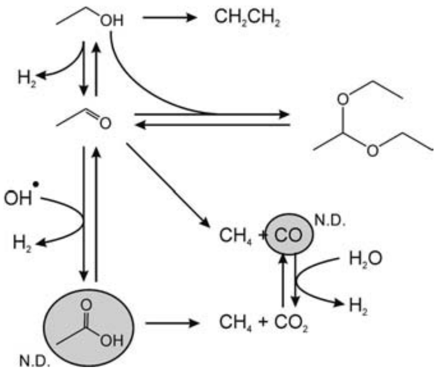

Figure 9. Reaction pathway involved in the photoreforming of ethanol over Cu_xO/TiO_2. N.D.: not detected. Adapted with permission from ref.[42] Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA.

Another interesting alternative to TiO_2-based materials has been proposed by Wang et al.,[95] who prepared VO_2 nanorods in a novel body-centered cubic phase. This phase was found to have a much larger band gap (2.7 eV) with respect to the previously known monoclinic one (0.7 eV). When these materials were used for H_2 production from water/ethanol solutions, a production rate of 800 mmol h^{-1} m^{-2} was observed, with a quantum efficiency as high as approximately 40% even in the absence of noble metals.

To date, some studies on more complex photocatalysts for CH_3CH_2OH photoreforming are also available. Various factors yielding improved functional performance in H_2 generation were considered, though their nature and impact depended both on the target systems and on the adopted processing conditions. Dubey and co-workers[96] incorporated titania, phosphomolybdic acid, and cobalt into zeolite-Y, and the resulting composites showed good H_2 generation rates, though long-term stability tests were not reported. Hoffmann et al. showed that Ni/NiO/$KNbO_3$/CdS composites were active in hydrogen production from ethanol, though the use of 2-propanol yielded improved results.[97] The same group also used CdS/zeolite and CdS/silica nanosystems for the same reaction under simple visible irradiation, an important technological issue.[98]

Other studies were devoted to perovskite-like materials. Mesoporous $SrTiO_3$ with the addition of small amounts of Pt demonstrated good UV or visible H_2 photoproduction from both ethanol and methanol,[99] a result that was directly related to the peculiar system morphology. In a different way, in the case of S-doped $La_{0.8}Ga_{0.2}InO_3$, a significant synergistic effect between photocatalytic performance and ultrasonic irradiation was reported.[100] The promise of mixed perovskites in this field was also evidenced by results obtained on $CaTi_{1-x}Zr_xO_3$ materials ($x = 0$–0.15) prepared by a polymerized complex method.[101] In this case, the substitution of small amounts of Ti^{IV} with Zr^{IV} resulted in larger surface areas, reduced crystallite sizes and enhanced H_2 production from aqueous CH_3CH_2OH solutions, after addition of small quantities of Pt. A maximum of approximately 9000 $\mu mol\, g^{-1} h^{-1}$ of H_2 under UV irradiation (500 W high-pressure Hg lamp) was obtained for $x = 0.07$, corresponding to a quantum yield higher than 13%.

Finally, it is worth mentioning a study by Liu et al. on the preparation of mixed lanthanum–tantalum oxynitrides as visible-active photocatalysts for hydrogen production from water/ethanol solutions.[102] A synergistic effect of small amounts of Pt and Ru added as cocatalysts was observed, producing up to approximately 130 $\mu mol\, g^{-1} h^{-1}$ of H_2.

5. Glycerol

Glycerol is an attractive candidate for hydrogen production for different reasons. In addition to being renewable, it is a biodegradable, nontoxic, nonflammable molecule, which, despite having poor properties as a fuel, does not swell the Nafion in proton exchange membrane (PEM) fuel cells used for electricity production from hydrogen.[103] Glycerol can be prepared in a variety of processes, such as sorbitol hydrogenolysis or glucose fermentation, but one of its most important sources is biodiesel. In fact, in biodiesel plants, around 10% of the vegetable oil or animal fat is converted to glycerol, thus contributing to approximately 100 kg for every ton of biodiesel obtained.[54] The huge overproduction of glycerol has a negative impact on the global biodiesel economy, since the processes for the economical valorization of glycerol are still limited.[104,105] In addition, glycerol as a by-product comprises a mixture of several other constituents, such as methanol, water, inorganic salts, free fatty acids, triglycerides, and methyl esters. This mixture as such has a low commercial value and further refining processes are not economically viable. As a consequence, great efforts are being devoted to the search of more convenient alternatives for the utilization of glycerol. Though conventional steam reforming routes for its conversion to hydrogen and CO_2 are available, for example, with Ni, Pt, or Ru catalysts,[106–108] the high temperatures (800 °C) required and problems related to catalyst poisoning make the process hardly sustainable. Recently, aqueous-phase reforming of glycerol was proposed as an alternative less energy-demanding technology.[7] In a different way, glycerol photoreforming is an appealing route for its conversion not only into H_2, but also into other added-value chemicals.

Kondarides et al.[41] described the photoreforming of glycerol to H_2 and CO_2 (and other biomass-derived compounds, such as saccharides and organic acids) over Pt(0.5%)-TiO_2 materials under nonaerated conditions and with UV irradiation (Figure 10). The presence of glycerol in aqueous solution resulted in an initial enhancement of the H_2 production rate of one order of magnitude with respect to pure water. The extra amount of hydrogen produced upon the introduction of glycerol into pure H_2O can be estimated from the difference in area under the corresponding H_2 evolution curves shown in Figure 10 and equals 156 μmol under the adopted conditions. Production of hydrogen is also accompanied by the evolution of CO_2, the rate of which goes through a maximum at 70 min of illumination and subsequently decreases, reaching a value of zero after approximately 1300 min of irradiation. The photocatalysts used were very active even for cellulose-derived materials, but their main disadvantages were progress-

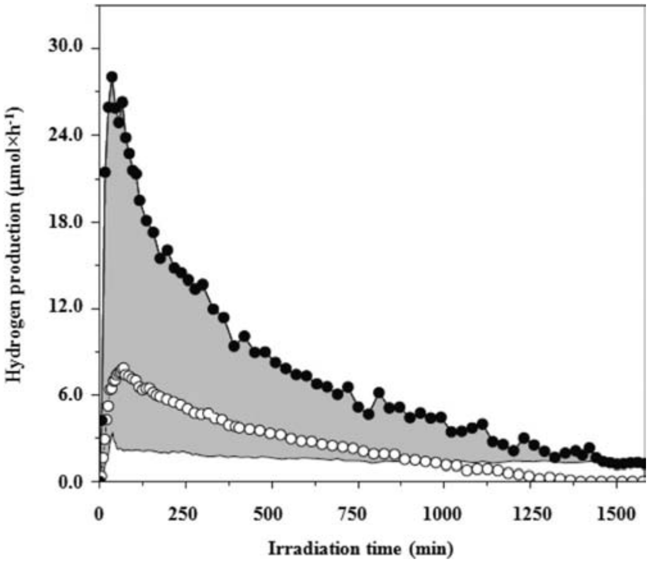

Figure 10. H_2 (filled circles and solid line) and CO_2 (open circles) production rates vs. irradiation time for Pt-TiO_2 photocatalysts. Filled and open circles show data obtained with a 0.368 mM glycerol solution, whereas the solid line represents data obtained with pure water. The area marked in gray highlights the extra hydrogen produced thanks to the presence of glycerol in solution. Incident light intensity: 3.8×10^{-7} Einstein s^{-1}. Adapted with permission from ref.[41] Copyright 2008 Springer.

ive deactivation and the requirement of UV excitation. In comparison, Bowker and co-workers used Pd and Au-TiO_2 systems for the same process.[75] They found that a Pd(0.5%)-TiO_2 catalyst was as active as Pt under similar conditions, whereas a Au(2%)-TiO_2 catalyst presented an inferior hydrogen yield with respect to the Pd-containing catalyst, in spite of the higher metal loading. Yet, the main limitation was the use of UV light also in this case.

In an attempt to move towards the use of activation by visible light, Fu and Lu[109] employed heteropolytungstate-sensitized TiO_2 materials. Upon UV illumination in the presence of an electron donor, heteropolytungstate yields dark blue heteropoly blue (HPB), which absorbs light in the visible spectral range. The authors prepared a Pt(0.5%)-TiO_2 catalysts and deposited heteropoly blue on its surface by UV irradiation in the presence of glycerol as electron donor. HPB was capable of absorbing energy in the visible range and, subsequently, to activate an interfacial electron transfer to TiO_2. Interestingly, the composite was effective for H_2 production under visible light, but a dramatic system deactivation, mainly due to the light-induced decomposition of HPB, took place.

Another interesting attempt to use visible light was proposed by Luo et al.[110] on B,N-codoped TiO_2 systems. After Pt deposition, the materials showed good results in hydrogen photoproduction. In a similar way, Lalitha and coworkers demonstrated the activity of mixed copper and titanium oxide photocatalysts under visible light.[111] After Cu deposition by impregnation, the materials were calcined ex situ at different temperatures, resulting in the copresence of CuO/Cu_2O species. A continuous and stable photocatalytic hydrogen production under visible light was observed for Cu^I-containing samples.

Finally, TiO_2-embedded Cu_xO photocatalysts were prepared by an innovative approach through a water-in-oil microemulsion synthesis. Briefly, copper-based nanoparticles protected in water droplets in an inverse microemulsion were covered by a layer of TiO_2 produced by hydrolysis of

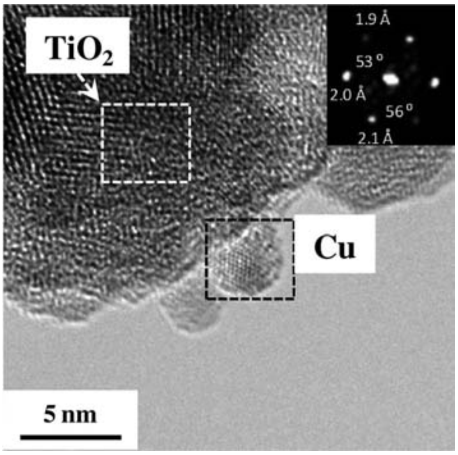

Figure 11. HR-TEM micrograph of TiO_2-embedded Cu_xO photocatalysts. The digital diffraction pattern (DDP) of the particle in the black square can be assigned to metallic copper. The amorphous shell surrounding the Cu nanoparticle may consist of either titania or Cu_xO phases resulting from the partial oxidation of the particle itself. Adapted with permission from ref.[43] Copyright 2010 American Chemical Society.

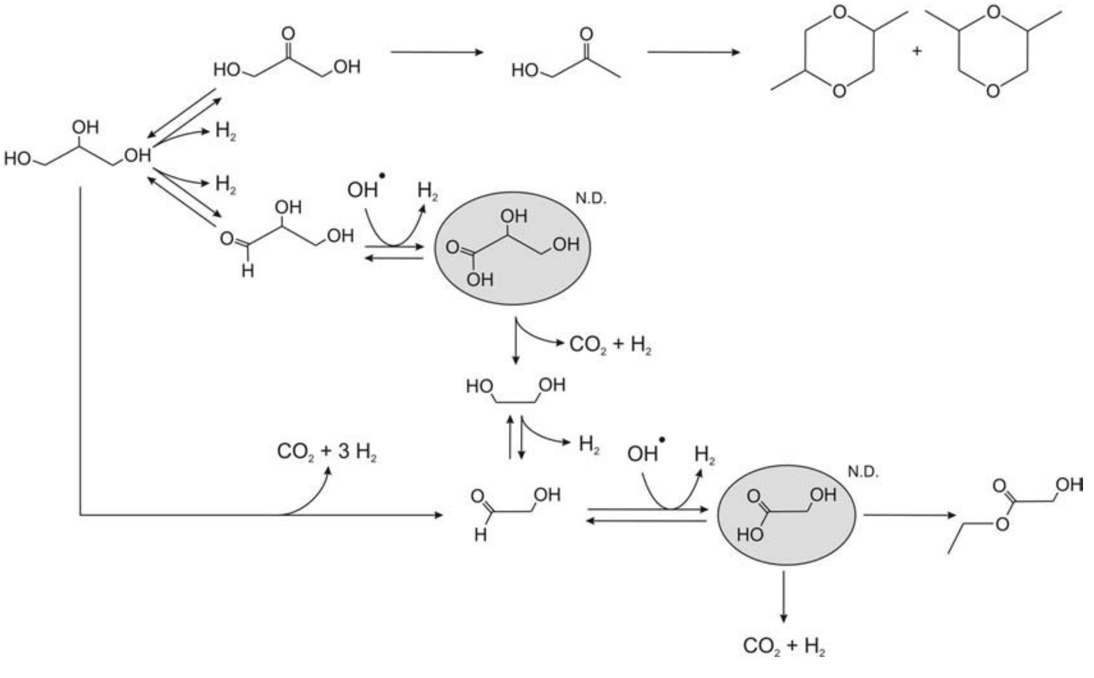

Figure 12. Reaction pathway in the photoreforming of glycerol over Cu_xO/TiO_2. N.D.: not detected. Adapted with permission from ref.[42] Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA.

titanium alkoxide. These systems demonstrated superior performance in glycerol photoreforming with respect to conventional Cu-TiO_2 materials prepared by impregnation.[43] The higher H_2 production could be related to the good dispersion of Cu_xO-containing species on TiO_2, as shown in Figure 11. Copper dissolution in the titania lattice, favorably influencing the system band gap, could also beneficially affect the observed performance. A further enhancement of Cu dispersion was subsequently obtained by photodeposition, leading to an improved H_2 production.[42]

The proposed reaction pathway (Figure 12) involves the progressive oxidation of the hydroxy groups of the glycerol, leading to the formation of various intermediates, some of which are of commercial interest.[42]

Surprisingly, copper leaching phenomena were observed under visible irradiation, whereas the use of UV light ensured a high system stability.[42] This phenomenon was associated with the regeneration of the Cu metal nanoparticles by a continuous UV-driven photodeposition process that limited the presence of Cu ions in solution.

6. Glucose and Sugars

Glucose and other sugars can be obtained from the degradation of cellulosic materials, and they are therefore very promising feedstock for hydrogen production under solar irradiation. In addition, sugars are also studied for H_2 generation from biological sources.[112] The feasibility of hydrogen evolution from carbohydrates, such as sugars, starches, and/or cellulose, on $RuO_2/TiO_2/Pt$ materials under light irradiation was demonstrated in 1980 in a pioneering work by Kawai and Sakata.[113] As previously mentioned (Section 2), the presence of many hydroxy groups in sugars enables their easy activation on semiconductor surfaces, though the complex skeleton is responsible for a lower H_2 yield than that from simpler alcohols.

The photoreforming of glucose and sucrose over B,N-codoped TiO_2 has been reported to occur even with visible light.[110] A possible mechanism for H_2 production from glucose, proposed in a detailed work by Fu et al. in 2008 for a Pt-TiO_2 photocatalyst, is sketched in Figure 13.[114] The initial step was suggested to be the coordination of one glucose OH group to an under-coordinated Ti^{IV} surface site. Subsequently, H^+ and an alkoxide anion (RCH_2O^-) are formed, and the latter reacts with a photogenerated hole to give the $RCH_2O^{\cdot}$ radical as oxidation product (process *a*). Subsequently, this species attacks another glucose molecule, transferring the electron to yield an $R'C^{\cdot}HOH$ radical. The latter undergoes process *a* again to give rise to aldehyde (process *b*) and carboxylic acid derivatives, which are ultimately converted to CO_2 (process *c*). Before being oxidized to CO_2, these products can undergo other deprotonation/decarboxylation cycles, whereas the obtained H^+ can be reduced to hydrogen on Pt sites by using photogenerated electrons. Although this scheme is complex, it provides only a rough picture of the occurring process, and the exact chemical identification of reaction intermediates is still an open challenge.

The same authors then studied the reactivity of NM-loaded TiO_2 catalysts for the photoreforming of glucose, sucrose, and starch.[114] An increased hydrogen production over Pt-TiO_2 was found in the order starch < sucrose < glucose, which is clearly related with the progressively decreasing complexity of the carbon skeleton. A further synergistic contribution to this activity is the faster dif-

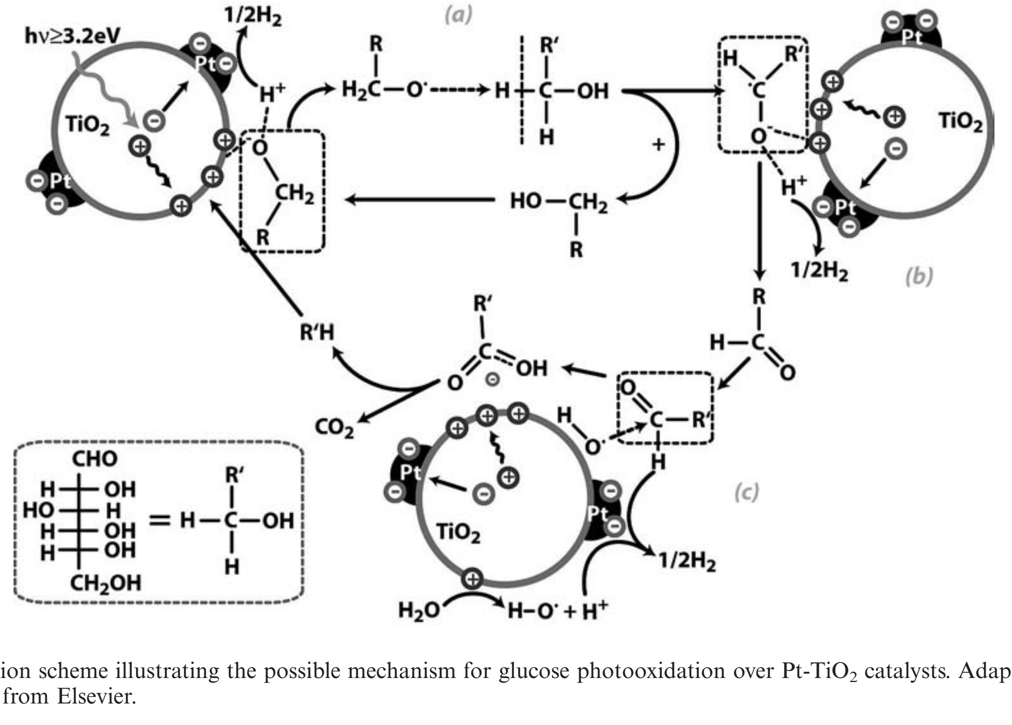

Figure 13. Reaction scheme illustrating the possible mechanism for glucose photooxidation over Pt-TiO_2 catalysts. Adapted from ref.[114] with permission from Elsevier.

fusion of smaller molecules to the active sites of the photocatalyst.

The dependence of the activity on glucose concentration provided evidence for a Langmuir-type catalytic behavior, and the photocatalytic performance followed the order Ag, Ru < Pd, Au, Rh < Pt. The latter effect can be explained in terms of the interaction between the titania energy levels and the metal work functions (WFs), Pt showing the highest WF and, hence, an improved possibility of storing photogenerated electrons.

Also for glucose and sugars, research efforts have been devoted to photocatalysts different from TiO_2. Among the various systems, it is worth citing the case of $Bi_xY_{1-x}VO_4$ materials prepared by solid-state synthesis. The as-prepared particles had a relative uniform shape and were aggregated into large bundles with lengths in the μm range (Figure 14a). These materials were reported to be active under visible light for the photoreforming of glucose to H_2.[115] The highest H_2 production rate was obtained for a Bi/Y ratio of 1:1 (Figure 14b). In fact, this ratio influences the photocatalyst band positions, and at such a particular value, the resulting solid solution has a beneficial effect on charge transport and separation phenomena. Nevertheless, the maintenance of the observed activity required the photodeposition of Pt and the removal of gaseous products. These observations highlight that material properties useful for preparing active photocatalysts must be well tuned in terms of band positions, solid phases, and operational conditions.

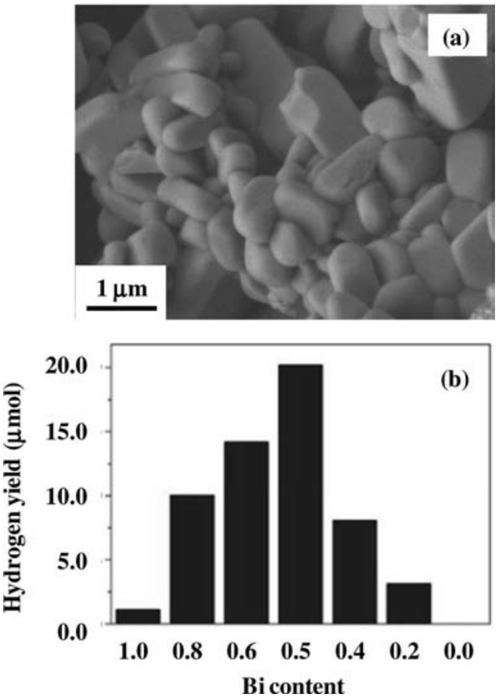

Figure 14. (a) Representative SEM image of $Bi_{0.5}Y_{0.5}VO_4$ photocatalysts. (b) Amount of H_2 produced after 2 h of illumination at pH = 3. Samples were loaded with 1% Pt. Illumination: Xe lamp (350 W) with a 430 nm cut-off filter for the removal of UV light. Adapted from ref.[115] with permission from Elsevier.

7. Other Biomass-Derived Sacrificial Reagents

Other biomass-derived oxygenates or organic wastewater pollutants have been investigated as sustainable sacrificial agents for photocatalytic hydrogen production.[41] These include various alcohols, for example, 2-propanol,[116] acids, including oxalic, formic, and acetic,[116–122] and aldehydes, such as formaldehyde and acetaldehyde.[37,123]

Very recently, reforming of 2-propanol over Pt(1%)-TiO_2 photocatalysts was investigated by means of FTIR spectroscopy.[124] The results indicated that both chemisorbed and physisorbed propanol were present on the catalyst surface. Under UV irradiation, an initial rapid deprotonation of chemisorbed 2-propoxide occurs (Figure 15, step 1). Acetone is subsequently produced on the surface of the catalyst and can either be desorbed into the gas phase or slowly oxidized by holes or hydroxy radicals to carboxylates (mainly acetate and formate species, step 2). Finally, these intermediates are decarboxylated over Pt nanoparticles, resulting in the evolution of CO_2 and CH_4 (step 3). The OH groups of 2-propanol and its intermediates serve as anchoring sites for the adsorption and are involved in charge transport processes, facilitating oxidation by valence band holes.

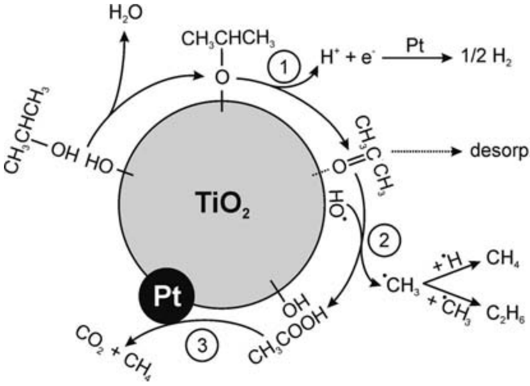

Figure 15. Schematic representation of the mechanism proposed for the photoreforming of 2-propanol over Pt-TiO_2. Adapted from ref.[124] with permission from Elsevier.

Notably, some of the above-mentioned aldehydes and acids are the products of the partial mineralization of the already discussed oxygenates (methanol, ethanol, glycerol). Interesting results were obtained on $LaNiO_3$-based catalysts by simple visible-light activation, with formaldehyde as sacrificial agent (Figure 16). The rate of H_2 evolution in the second and subsequent runs was almost constant, indicating that the photocatalyst had a good reproducibility and could be used repeatedly in practical technological applications. Notably, some of the above studies were aimed at developing efficient and sustainable technologies for wastewater purification with the concomitant production of hydrogen.[37] This latter "green" approach was also proposed for the degradation of azo dyes, with the simultaneous generation of H_2 from irradiated Pt-TiO_2 suspensions.[125] Further studies in this direction are needed to extend the validity of this methodology and to evaluate the actual sustainability of the process.

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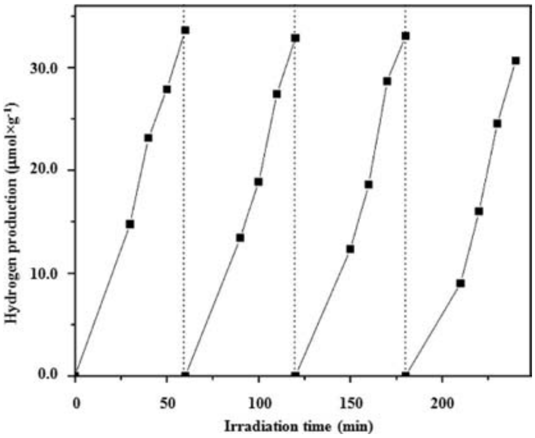

Figure 16. Effect of consecutive photocatalyst recycling: hydrogen production from aqueous formaldehyde solution under visible irradiation on Ni/$LaNiO_3$-based photocatalysts. Illumination: Xe lamp (125 W) with a 400 nm cut-off filter for the removal of UV light. Vertical dotted lines mark the evacuation of the reaction system. Adapted from ref.[123] with permission from Elsevier.

8. Conclusions and Perspectives

This microreview has focused on the use of sustainable liquid oxygenates for the production of H_2 by photoreforming processes. As an alternative to the pure water splitting, which has been much more investigated up to date, such routes are of strategic interest, since they join in a single process photocatalytic H_2O decomposition and photoinduced oxidation of organic compounds in the presence of suitably active catalysts. Such processes require an inferior energy input and less harsh conditions than conventional catalytic reforming, thus presenting themselves as amenable and eco-friendly routes for the simultaneous production of energy and decomposition of pollutants.

This microreview has tried to summarize the most important advances to date in this rather uncovered research field, presenting the main issues and open challenges that still have to be met for the development of active and stable catalysts capable of producing hydrogen by visible-light activation. Among the various target chemicals, in this work the main attention has been devoted to selected oxygenates, that is, simple alcohols, glycerol, glucose, and sugars, and a brief survey has been presented on the mechanisms of hydrogen production and the parallel obtainment of added-value carbon-containing by-products. The design of various oxide catalysts, either used as such or functionalized with metal particles, has been discussed with an assessment of the yield in hydrogen and the possible technological impact of the related production processes. Yet, this review reveals that the research activities in these fields are still at the starting line rather than at the winning post, which seems indeed still far to be reached. In fact, most of the studies to date have been dedicated to titania-based materials, whereas the extension of such tests to other oxides, or even to non-oxide systems, appears quite limited. In addition, the large-scale diffusion and technological transfer of the present results are still hindered by the concomitance of various issues, such as the real sustainability and production routes of the starting oxygenates, as well as the long-term stability and environmental impact of the used photocatalysts. Finally, although the use of solar radiation, a largely available and intrinsically renewable source, is an extremely attractive option for the photoreforming of oxygenates to H_2, its technological viability is still far from being demonstrated.

A deeper insight into such issues undoubtedly requires further research on the synthesis of nanostructured composite photocatalysts, exploiting the synergistic combination of the properties of the single components, and a detailed investigation of the underlying reaction mechanisms, enabling an unambiguous identification of the various chemical intermediates. The development of the pertaining investigations will surely represent one of the most intriguing perspectives in the field, from both a fundamental and an applicative point of view.

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