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Hydrogen Production by Photo-Induced Reforming of Biomass Components and Derivatives at Ambient Conditions

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Abstract Hydrogen can be produced at ambient conditions via an efficient, technologically simple, ecologically benign, and potentially very low-cost process, with the use of a Pt/TiO_2 photocatalyst and three abundant and renewable sources: biomass, solar light, and water. The method combines photocatalytic splitting of water and light-induced oxidation of biomass compounds into a single process, able to produce hydrogen at room temperature and atmospheric pressure.

Keywords Hydrogen production · Reforming · Biomass · Water splitting · Photocatalysis · Platinum · Titanium dioxide · Glycerol

1 Introduction

The demand for hydrogen as an energy carrier is expected to increase significantly in the near future as a result of the envisaged transition from a fossil-fuel-powered economy toward a hydrogen-powered one [1, 2]. Hydrogen is a storable, clean, and environmentally friendly fuel, the combustion of which results in the generation of water only, with no emissions of atmospheric pollutants, greenhouse gases or particulates. However, about 95% of hydrogen is currently derived from fossil fuels, mainly by steam reforming of natural gas and petroleum [3] and, therefore, it is clearly not sustainable. Consequently, there have been intensive efforts toward the development of novel technologies for the production of hydrogen from renewable resources, mainly water and biomass [4]. These include photoelectrochemical [5–9], photocatalytic [10–13], photobiological [14], and enzymatic [15] approaches, which are characterized by relatively low efficiencies, as well as steam reforming of biomass components in the gas [16] or liquid [17, 18] phase and biomass gasification [19], which are relatively complex and energy intensive due to the requirement for application of high temperatures or pressures.

In our previous work it was shown that photocatalytic degradation of organic pollutants such as azodyes [20], alcohols and organic acids [21] can take place with simultaneous production of hydrogen over irradiated Pt/TiO_2 photocatalyst suspensions [20, 21] and immobilized films [22]. In the present study we further investigate this issue to show that, in general, hydrogen can be produced in an efficient manner via aqueous, photocatalytic reforming of biomass components and derivatives at ambient conditions.

Photocatalytic processes over irradiated semiconductor surfaces, mainly titanium dioxide (TiO_2), have received particular attention during the past three decades as environmentally friendly and low cost methods for water [23, 24] and air [25] purification as well as for the production of hydrogen by splitting of water [5–13, 26, 27]. Photocatalytic reactions are initiated by excitation of the semiconductor with light energy ($h\nu$) equal to or greater than its band gap energy (E_{bg}) (Fig. 1). This results in the promotion of an electron (e^-) from the valence band (VB) to the conduction band (CB) of TiO_2, which leaves a hole (h^+) behind. As schematically shown in Fig. 1, production of hydrogen (I) and oxygen (II) from water cleavage takes place under anaerated conditions and is achieved by photogenerated electrons and holes, respectively, provided that

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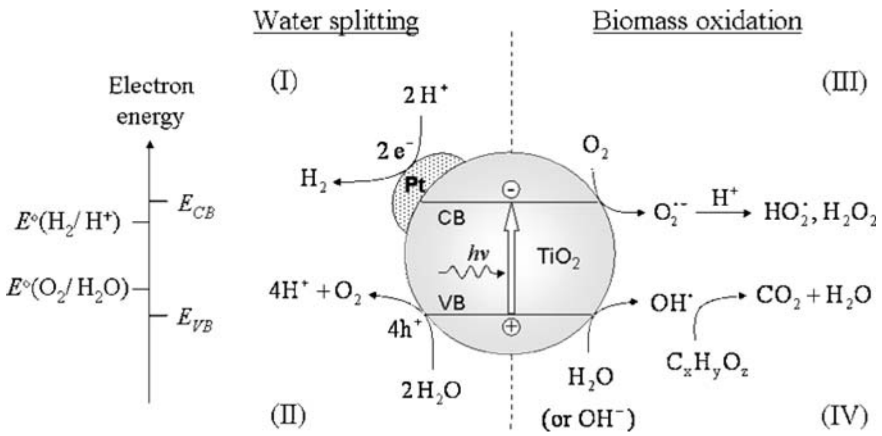

Fig. 1 Schematic representation of water splitting, biomass ($C_xH_yO_z$) oxidation and photo-reforming reactions over an irradiated Pt/TiO_2 photocatalyst. Production of hydrogen (I) and oxygen (II) from water cleavage takes place under anaerated conditions and is achieved by photo-generated electrons and holes, respectively. Oxidation of organic compounds takes place in the presence of oxygen (air) with the participation of photo-generated holes, and ultimately lead to the production of CO_2 and H_2O (IV). This is accompanied by consumption of photo-generated electrons by chemisorbed oxygen (III). The proposed photo-reforming process takes place in a manner which combines photo-induced production of hydrogen (I) and oxidation of organic components and derivatives (IV) under anaerated conditions

their energy is sufficient to reduce protons toward hydrogen molecules [$E_{CB} < E^{o}(H_2/H^+)$] and to oxidize water toward oxygen [$E_{VB} > E^{o}(O_2/H_2O)$]. On the other hand, oxidation of organic compounds takes place in the presence of oxygen (air) with the participation of photo-generated holes, which act either directly or indirectly via generation of hydroxyl radicals ($OH^{\bullet}$), and ultimately lead to the production of CO_2 and H_2O (IV). In this case, photo-generated electrons are consumed by chemisorbed oxygen (III). In the proposed photo-reforming process, the two reactions are combined, i.e., photocatalytic treatment of aqueous solutions of biomass components and derivatives (denoted here as $C_xH_yO_z$) takes place under anaerated conditions. This results in oxidation of the organic substrate by water toward CO_2 (IV), which is accompanied by production of gas-phase hydrogen (I) (Fig. 1). The rate of hydrogen evolution is much higher, compared to that obtained in the absence of biomass in the irradiated photocatalyst suspension, due to the irreversible reaction of $C_xH_yO_z$ with photo-generated holes and/or oxygen originating from water splitting and the concomitant suppression of electron-hole recombination and H_2–O_2 back reaction, i.e., the most important reactions for decreasing the light-to-hydrogen conversion efficiency.

2 Experimental

The 0.5 wt.% Pt/TiO_2 catalyst was prepared by impregnation of TiO_2 powder (Degussa P25) with an aqueous solution of $(NH_3)_2Pt(NO_2)_2$ (Alfa). The catalyst was characterized with respect to its specific surface area (41 m^2/g), metal dispersion (87%) and anatase-to-rutile content (75–25%), employing nitrogen physisorption at the temperature of liquid nitrogen, selective chemisorption of H_2 at 25 °C and X-ray diffraction (XRD), respectively. Details on the equipment and procedures used for catalyst preparation and characterization can be found elsewhere [20, 21, 28].

Two similar apparatuses were used for the photocatalytic experiments, each one consisting of a solar light-simulating light source (Oriel), a quartz photoreactor and an on-line analysis system [20, 21]. Illumination is carried out with a Xe-arc lamp (300 or 450 W) equipped with a water filter to remove infrared radiation. The reactor is placed on a heating plate/magnetic stirrer and has provisions for measurements of solution pH and temperature, and connections for inlet/outlet of argon gas (Ar), which serves as a means of collection and transfer of gaseous products to the analysis system. The analysis system consists of a gas chromatograph (SRI-8610C) equipped with a molecular sieve 5 A column and a TCD detector, and a CO_2 analyzer (Binos) connected on line at the exit of the photo-reactor. The carrier gas is high purity Ar (99.999%). The photon flow entering the reactor was measured by chemical actinometry [29] under conditions similar to those used for the photocatalytic experiments, thereby eliminating the need of making corrections for the reflectance and non-uniformity of the incident light beam [20, 21].

In a typical experiment, known amounts of a biomass compound and the photocatalyst (80 mg) are added in triply distilled water (60 mL) under continuous stirring. The system is then purged with flowing Ar (20 cm^3/min) to remove atmospheric oxygen from the reactor and tubing, heated to the desired temperature (40 °C, unless otherwise indicated) and then exposed to light (at $t = 0$). Samples are periodically collected via an automatic gas sampling valve and the concentrations of H_2 and CO_2 present at the reactor effluent are determined as functions of time of irradiation with the use of the on-line analysis system described above.

3 Results and Discussion

Typical results obtained in the absence and in the presence of a small concentration of glycerol ($C_3H_8O_3$) in solution are shown in Fig. 2. It is observed that when pure water is used the rate of hydrogen production (r_{H2}) initially increases with time of illumination and goes though a weak maximum of 0.05 μmol min^{-1} after ca 35 min. Prolonged exposure to irradiation results in a progressive decrease of r_{H2}, which eventually reaches a pseudo-steady value of ca 0.02 μmol/min. It is of interest to note that, under the present experimental conditions, no oxygen was detected in the gas phase. The same is true for all experiments conducted in this study. In fact, direct oxygen evolution has been rarely reported to take place over irradiated TiO_2 or Pt/TiO_2 suspensions, and the possibility for achieving this at ambient conditions remains doubtful [30]. As discussed in detail in our previous studies [20, 21], photogenerated oxygen either remains adsorbed on the TiO_2 surface and/or further reacts to form peroxotitanate complexes at the surface of TiO_2 particles [31] and H_2O_2 in solution [31, 32]. It is also possible that the photogenerated holes may cause oxidation of the semiconductor surface, in which case TiO_2 itself acts as an electron donor [33].

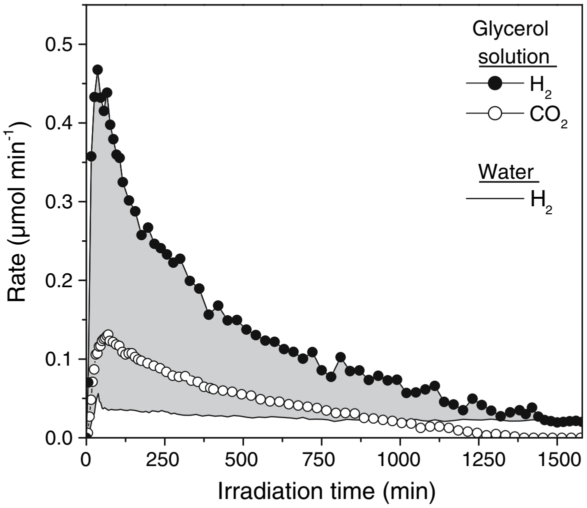

Fig. 2 Rates of H_2 and CO_2 evolution as functions of time of irradiation obtained from Pt/TiO_2 photocatalyst suspensions in the presence of glycerol (0.368 mM). With *solid line* is shown the hydrogen production curve obtained from pure water. The amount of "additional" hydrogen ($H_{2,add.}$) produced due to the presence of glycerol in solution is estimated by the difference between curve of *closed circles* and *solid line*. Incident light intensity: 3.79×10^{-7} Einstein s^{-1}

The presence of glycerol in solution results, initially, in a significant enhancement of the hydrogen production rate, the maximum of which (0.47 μmol min^{-1}) is approximately one order of magnitude higher than that obtained from pure water (Fig. 2). Prolonged exposure to light results in a progressive decrease of r_{H2}, which eventually drops to values similar to those obtained in the absence of glycerol in solution. The total amount of hydrogen produced in the presence of glycerol, over and above the amount produced by pure water splitting, can been calculated by the area difference between the corresponding H_2-production curves, as schematically shown in Fig. 2 (shadowed area). This amount, denoted in the following as "additional" hydrogen ($H_{2,add.}$) is in the present case equal to 155.9 μmol. Production of hydrogen is accompanied by evolution of 63.6 μmol of CO_2, the rate of which goes through a maximum after *ca*. 70 min and finally diminishes after *ca*. 1,300 min under irradiation (Fig. 2).

Similar experiments were conducted with the use of variable initial concentrations of glycerol (C_{glyc}) in solution and results are summarized in Fig. 3, where the total amounts of $H_{2,add}$ and CO_2 produced are plotted as functions of C_{glyc}. It is observed that the amounts of hydrogen and CO_2 produced increase linearly with increasing $C_3H_8O_3$ concentration, with the molar ratio $H_{2,add} : CO_2$ being practically constant at 7:3.

Results of Figs. 2 and 3 can be understood by considering that the role of glycerol, which acts as a sacrificial electron donor, is to rapidly remove the photo-generated holes (hydroxyl radicals) and/or photo-generated oxygen in an irreversible fashion, thereby suppressing electron-hole recombination and/or H_2–O_2 back reaction. By doing so, glycerol is progressively oxidized toward CO_2, with

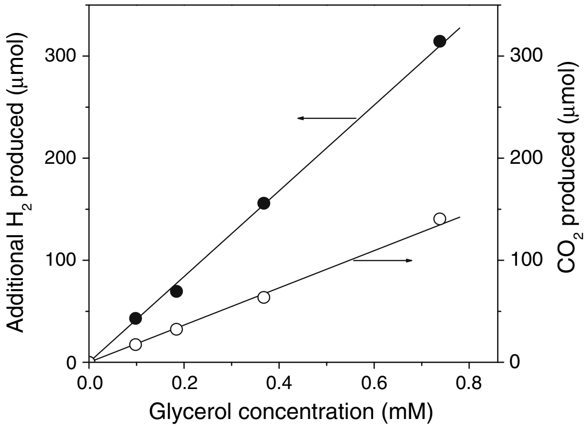

Fig. 3 Amounts of "additional" hydrogen and CO_2 produced as functions of initial glycerol concentration in solution. *Straight lines* correspond to the amounts of $H_{2,add}$ and CO_2 predicted from the stoichiometry of Eq. 1

intermediate formation of partially oxidized products. When complete oxidation of glycerol (and reaction intermediates) is achieved, oxygen can no longer be removed from the photocatalyst surface and the rate of hydrogen production drops to steady-state values comparable to those obtained in the absence of glycerol in solution. The overall process, which may be described as photo-induced reforming of glycerol at room temperature, can be expressed by the following equation, which predicts the observed $H_{2,add}$: CO_2 = 7:3 molar ratio of products formed:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \qquad (1)$$

Reaction (1) may also predict the absolute amounts of $H_{2,add}$ and CO_2 evolved. For example, for the experiment shown in Fig. 2, where the amount of glycerol initially added in the photo-reactor was 22.1 μmol, stoichiometry of glycerol reforming reaction predicts production of 154.7 μmol H_2 and 66.3 μmol CO_2, in excellent agreement with the experiment (155.9 μmol H_2 and 63.6 μmol CO_2, respectively).

It should be noted that the photo-reforming reaction rate is very small in the absence of platinum dispersed on the semiconductor surface. It is well known that noble metals, including Pt, Au, Pd, Rh, Ni, Cu, and Ag, enhance photocatalytic properties of TiO_2 by "pumping" photogenerated electrons and, therefore, decreasing the electron-hole recombination rate [13]. Furthermore, evolution of H_2 and CO_2 stops when light is turned off, showing that the reaction is induced by absorption of light by the photocatalyst. In addition, blank experiments conducted in the absence of light and/or photocatalyst under otherwise the same experimental conditions did not lead to evolution of either H_2 or CO_2, verifying that the presence of both light and the photocatalyst is required for the photo-reforming reaction to proceed.

Results similar to those presented in Fig. 2 were obtained with the use of a variety of biomass-derived components and derivatives, including monosaccharides, such as pentoses (ribose, arabinose) and hexoses (glucose, calactose, fructose, and mannose), alcohols (methanol, ethanol, propanol, and butanol) and organic acids (acetic acid, formic acid). In all cases, the amounts of $H_{2,add}$ and CO_2 produced were found to be in accordance to the stoichiometry of the following general reforming reaction:

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

Results obtained are summarized in Fig. 4, in which the amounts of "additional" H_2 and CO_2 produced are plotted against those predicted by the stoichiometry of reaction (2). It is observed that the experimentally measured amounts of $H_{2,add}$ and CO_2 evolved are in very good agreement with those predicted from the stoichiometry of the reforming reaction. This is true for all organic compounds investigated, at various initial concentrations, solution pH (2–10) and temperature (40–80 °C).

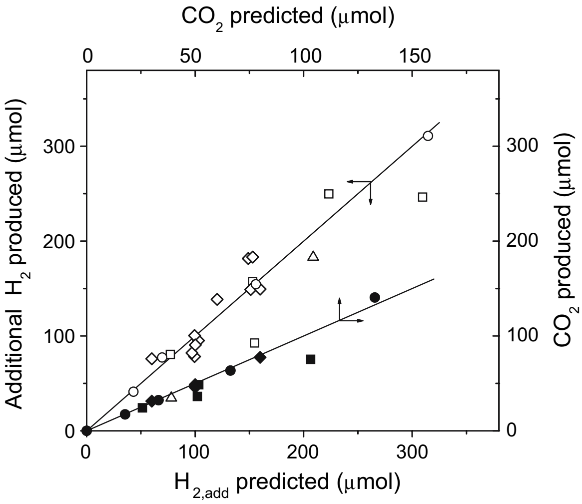

Fig. 4 Amounts of "additional" hydrogen and CO_2 produced from irradiated photocatalyst suspensions containing different biomass components against the corresponding amounts predicted by the stoichiometry of the reforming reaction (Eq. 2). *Open* and *filled symbols* refer to hydrogen and carbon dioxide, respectively. *Circles*: glycerol (0.1–1.36 mM); *diamonds*: saccharides (glucose, fructose, lactose; 0.07–0.22 mM, pH2-pH10, 40–80 °C); *squares*: alcohols (methanol, ethanol); *up triangles*: organic acids (formic, acetic acid). The light intensity was 1.30×10^{-6} Einsteins s^{-1} for all experiments, except for those obtained with glycerol, where intensity was 3.79×10^{-7} Einsteins s^{-1}

The rate of hydrogen production depends strongly on the nature and concentration of the organic substrate employed and, to a lesser extent, on solution pH and temperature. Results presented in Figs. 5 and 6 show that increasing

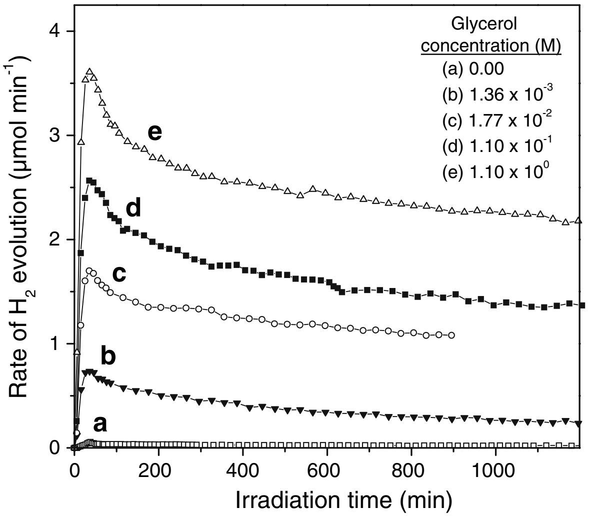

Fig. 5 Rates of hydrogen evolution as functions of irradiation time obtained from aqueous photocatalyst suspensions containing variable glycerol concentrations

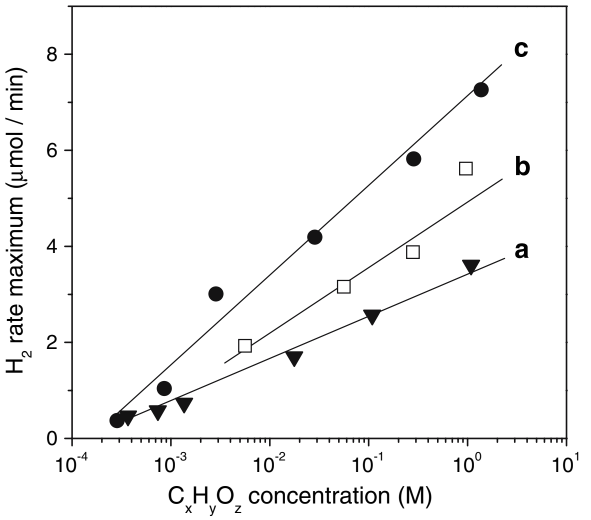

Fig. 6 Effect of **a** glycerol, **b** galactose or **c** ethanol concentration in solution on the maximum rate of hydrogen evolution. The incident light energy was 3.79×10^{-7} Einstein s^{-1} for the experiments conducted with glycerol and 1.30×10^{-6} Einstein s^{-1} for those obtained with galactose and glycerol

concentration (*C*) of biomass compounds in solution in the range of 10^{-3} to 10^{0} mol L^{-1} results in a monotonous increase of the H_2-rate maximum, which increases almost linearly with increasing log*C* (Fig. 6). The hydrogen production rate is further increased (by *ca.* 10–20%) with increasing temperature in the range of 60–80 °C and/or by using alkaline solutions (pH 8–10). Depending on experimental conditions employed, the rate of hydrogen production in the presence of organic compounds in solution has been measured to be more than two orders of magnitude higher than that obtained from photocatalytic cleavage of water, rendering the process suitable for practical application.

Under the present experimental conditions, the maximum rates of hydrogen evolution obtained under photo-reforming using a solar light-simulating source and biomass concentrations around 1 mol L^{-1} are about 5 μmol min^{-1} (Fig. 6), which corresponds to 3.75×10^{3} μmol H_2 h^{-1} per gram of photocatalyst used (0.5%Pt/TiO_2). Experiments conducted with the use of photocatalysts of variable platinum loading showed that these rates do not practically change with decreasing Pt content to 0.1 wt.% and decrease by *ca.* 25% for catalysts containing only 0.05 wt.% Pt. These rates are significantly higher, compared to those obtained from enzymatic hydrolysis of glucose [15] (7×10^{2} μmol g^{-1} h^{-1}), and comparable to those obtained from aqueous-phase reforming of biomass-derived hydrocarbons (3–40×10^{3} μmol g_{cat}^{-1} h^{-1}) at elevated temperatures (230–270 °C) and high pressures (27–54 bar), where a catalyst with much higher Pt loading (3%Pt/Al_2O_3) was used [17, 18].

The photo-reforming process is non-selective and practically all biomass compounds and derivatives investigated so far may be used for the production of hydrogen. For example, results obtained from aqueous solutions containing 1.0% w/v of di- or poly saccharides (Fig. 7) show that the hydrogen production rate is 1–2 orders of magnitude higher, compared to that obtained from pure water. It is of special interest to note that significant amounts of hydrogen are produced with the use of polysaccharides, such as starch or cellulose, although these compounds are practically insoluble in water under the present experimental conditions. This indicates that the reaction involves in situ hydrolysis of polysaccharides under the influence of irradiation. In addition, the initial rate of hydrogen production was found to increase substantially when the cellulose suspension was pretreated with HCl prior to exposure to light. The possibility of direct production of solar hydrogen from illuminated polysaccharide suspensions at ambient conditions may be of immense practical importance, because of significant cost savings resulting from reduction of the required steps for production of hydrogen, compared to existing technologies (e.g., no need for hydrolysis, fermentation, etc.).

Regarding the thermodynamics of reaction (2), it is of interest to note that the heat content of hydrogen fuel produced (lower heating value, $\Delta H_{c,H2} = 285.8$ kJ mol^{-1}) is higher, compared to that of the corresponding photo-reformed biomass compound. For example, in the case of glycerol (reaction 1), the heat content of hydrogen produced ($7 \times \Delta H_{c,H2} = 2{,}000$ kJ mol^{-1}) is about 20% higher, compared to that of the heat content of reactant glycerol ($\Delta H_{c,glycerol} = 1{,}660$ J mol^{-1}). The same is true

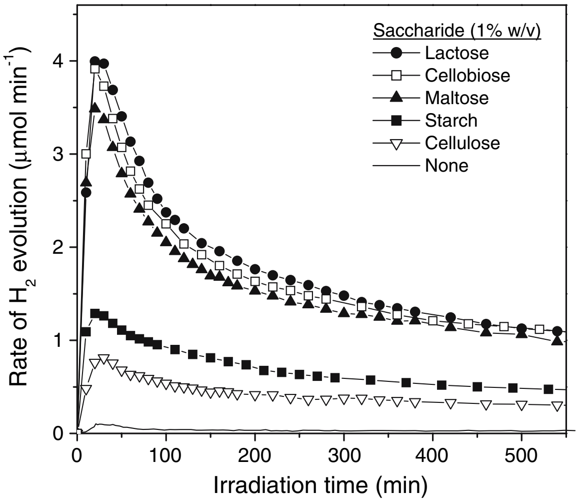

Fig. 7 Hydrogen production curves obtained in the presence of the indicated di- or poly saccharides of the same initial concentration (1% w/v) in solution. Incident light intensity: 1.30×10^{-6} Einsteins s^{-1}

for the reformation of saccharides and alcohols. In addition, for certain biomass compounds, the standard Gibbs free energy (ΔG^o) for the reforming reaction is positive (e.g., $\Delta G^o = 4$ kJ mol^{-1} for glycerol reforming and $\Delta G^o = 97$ kJ mol^{-1} for ethanol reforming) indicating that (a small) part of photon energy is stored as chemical energy. This is not the case for, for example, mono-saccharides, where ΔG^o is negative.

The quantum yield (QY) of hydrogen evolution was measured in separate experiments with the use of a "black light" lamp emitting at 365 nm. The rate of incident photons has been measured with chemical actinometry and was found to be 16.5×10^{-6} Einstein min^{-1}, which is equivalent to an irradiation power of 90 mW. Since production of hydrogen ($2H^+ + 2e^- \rightarrow H_2$) is a two electron process, QY is defined as twice the number of hydrogen molecules produced divided by the number of incident photons. For pure water, the maximum rate of hydrogen production (r_{max}) is 1.51×10^{-7} mol min^{-1}, which corresponds to a QY of 1.8%. In the presence of a small glycerol concentration (0.738 mM) in solution, QY increases to 14% ($r_{max} = 1.12 \times 10^{-6}$ mol H_2 min^{-1}), while for higher glycerol concentrations (1 M) QY exceeds 70% ($r_{max} = 5.85 \times 10^{-6}$ mol H_2 min^{-1}). Under these conditions, the efficiency of light-to-chemical energy conversion, defined as the energy stored as hydrogen ($r_{max} \times \Delta H_{c,H2}$) divided by the incident photon energy (90 mW), is 31%. The significant enhancement of QY with increasing glycerol concentration is attributed to the more efficient suppression of the H_2–O_2 back reaction, which is a result of the faster scavenging of photogenerated oxygen, and the concomitant increase in electron-hole separation efficiency at the metal-semiconductor interface. The QY measured in similar experiments conducted with the use of aqueous solutions (1 M) of ethanol or glucose was 50 and 63%, respectively.

Our findings suggest that production of solar hydrogen by photo-induced reforming of biomass components and derivatives at ambient conditions is entirely feasible. An important characteristic of the process is that no heat input is required to balance the endothermic reforming reaction. In this respect, photo-reforming offers significant advantages over other, recently proposed, biomass reforming technologies in the gas [16] or liquid [17, 18] phase, which are relatively complex and energy intensive due to the requirement for application of high temperatures or pressures. The process can be applied for the production of hydrogen from raw biomass (e.g., cellulose, starch), surplus or waste materials from biomass processing industries, practical feedstocks (e.g., sugar containing hydrolysates) or glycerol containing liquors derived from biodiesel plants, with minimum purification. It could also provide an efficient and cost effective method for cleaning up waste streams originating from, for example, biomass processing industries, with simultaneous production of hydrogen [20, 21].

It should be noted however that, because of the relatively high band gap energy of TiO_2 ($E_{bg,TiO_2} = 3.2\,\text{eV}$), the photocatalyst used in the present study is activated by photons in the near UV region ($\lambda < 400$ nm), which accounts for <5% of the solar energy on the earth's surface. The solar light efficiency of the process may be improved significantly if efficient photocatalytic materials, capable of harvesting visible light [34, 35], are used.

4 Conclusions

Hydrogen can be produced at ambient conditions via an efficient, technologically simple, ecologically benign and potentially very low-cost process, with the use of a Pt/TiO_2 photocatalyst and three abundant and renewable sources: biomass, solar light and water. The method combines photocatalytic splitting of water and light-induced oxidation of biomass compounds into a single process, able to produce hydrogen at room temperature and atmospheric pressure. The overall reaction is non-selective with respect to the organic substrate employed and, therefore, practically all biomass-derived compounds in solution or in suspension may be used as feedstock. These include liquid bio-fuels (e.g., bio-ethanol), waste by-products of biodiesel production (e.g., glycerol), components of biomass processing (e.g., saccharides, alcohols and organic acids) as well as raw biomass (e.g., starch and cellulose). The photo-induced reforming of biomass components and derivatives at ambient conditions may provide a viable source of renewable hydrogen.

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