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## Sunlight-promoted photocatalytic hydrogen gas evolution from water-suspended cellulose: a systematic study†

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This work presents a systematic study of cellulose (CLS) as a sacrificial biomass for photocatalytic H<sub>2</sub> evolution from water. The idea is indeed to couple a largely available and not expensive biomass, and water, with a renewable energy like solar radiation. An aqueous CLS suspension irradiated either at 366 nm (UV-A) or under sunlight in the presence of Pt/TiO<sub>2</sub> behaves as a H<sub>2</sub> evolving system. The effects of irradiation time, catalyst and CLS concentrations, pH and water salinity are studied. Addition of CLS to the sample significantly improved H<sub>2</sub> evolution from water splitting, with yields up to ten fold higher than those observed in neat water. The mechanism of the photocatalytic process relies on the TiO<sub>2</sub>-mediated CLS hydrolysis, under irradiation. The polysaccharide depolymerisation generates water-soluble species and intermediates, among them 5-hydroxymethylfurfural (HMF) was identified. These intermediates are readily oxidized following the glucose photoreforming, thus enhancing water hydrogen ion reduction to give gas-phase H<sub>2</sub>. The formation of "colored" by-products from HMF self-polymerization involves a sort of "in situ dye sensitization" that allows an effective photoreaction even under solar light. The procedure is evaluated and successfully extended on cellulosic biomasses, *i.e.* rice husk and alfalfa (*Medicago sativa*) stems, not previously investigated for this application.

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## Introduction

Lignocellulosic biomass is the most abundant type of biomass on the Earth and its conversion and upgrading are expected to play a significant role in the production of future fuels.<sup>1</sup> Indeed, lignocellulosic materials represent the largest feedstock for renewable fuels and chemicals, in particular with regard to bioethanol and biodiesel, produced by hydrolysis and fermentation processes starting from sugar-rich and starch-rich feedstock biomass, respectively.<sup>2</sup>

Lignocellulose consists of three main polymers, namely lignin, hemicellulose and cellulose (CLS). The latter is a homopolymer consisting of D-glucose linked by β-1,4 bonds. Since CLS is particularly difficult to be hydrolyzed, its uses have been considered extremely limited so far.<sup>3</sup> However, as the most abundant biopolymer on the Earth, it is now attracting

the interest of the scientific community with regard to its conversion into biofuels.<sup>4</sup> Some recent studies<sup>1,5,6</sup> showed that CLS can be used also as feedstock to generate hydrogen gas (H<sub>2</sub>). This is presently produced almost entirely from fossil fuels, *i.e.* natural gas and petroleum, by not sustainable processes that are very expensive and involve the release of high amounts of carbon dioxide.<sup>7</sup> For these reasons, the development of new ways to obtain hydrogen gas from renewable resources, essentially water and biomass,<sup>7</sup> is of primary importance and requires intensive research study.<sup>8</sup> H<sub>2</sub> is an appealing energy carrier because only water is released from its combustion in fuel cells, thus it can be considered an environmentally friendly fuel; moreover H<sub>2</sub> shows an energy yield of 142 kJ g<sup>-1</sup>, 2.75 times higher than that of any hydrocarbon.<sup>9</sup>

H<sub>2</sub> can be obtained starting from CLS by supercritical water gasification,<sup>1</sup> dark fermentation<sup>6</sup> and enzymatic photoproduction.<sup>5</sup> However, to the best of our knowledge, no systematic studies on the use of CLS as a sacrificial agent for the photocatalytic H<sub>2</sub> gas production from water have been reported in the literature as yet.

Photocatalysis is becoming increasingly important due to its efficient role in the energy field<sup>10,11</sup> and also in environmental remediation, as well described in recent reviews;<sup>12,13</sup> also our research group focused on photocatalysis for

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abatement of water contaminants.<sup>14,15</sup> Indeed, this emerging technology is clean, effective, energy-saving, simple, eco-friendly and not expensive.<sup>2</sup> Photocatalysis appears as an attractive alternative to other methods of H<sub>2</sub> production such as steam reforming of biomass components and biomass gasification, which are relatively complex and energy intensive due to the requirement of high temperatures or pressures.<sup>16</sup> In fact, the photocatalytic production of H<sub>2</sub> from water is the most attractive and rewarding work because water is abundant and renewable, and because the process can take place under ambient conditions using only sunlight and a semiconductor catalyst.<sup>7</sup> In view of its chemical stability, low cost and non-toxicity, titanium dioxide (TiO<sub>2</sub>) is the most used photocatalyst.<sup>7</sup> Loading with metal particles (*e.g.* platinum) and modification with visible-light sensitizers (*e.g.* Eosin Y, CdS) have been practiced to improve hydrogen gas yields and to extend the activity of TiO<sub>2</sub> in the visible region.<sup>7,17–19</sup> Indeed, the main limitation of the TiO<sub>2</sub> semiconductor is that it absorbs only the UV component of solar light (<387 nm) that accounts for only 4–5% of the solar spectrum; for this, it is essential to shift the semiconductor light absorption to the visible region.<sup>7,17</sup>

Various systems based on aqueous electron donor substrates have been reported in the literature,<sup>20</sup> enabling the evolution of H<sub>2</sub> by oxygenate photoreforming of organic chemicals, such as alcohols and sugars. Since the photoreforming process is non-selective, theoretically a number of biomasses can be used, including polysaccharides.<sup>16</sup>

On the basis of the above considerations in this study we deemed necessary to explore the solar hydrogen gas photocatalytic production from water in the presence of fibrous CLS as the sacrificial biomass. The aim was to use an insoluble raw biomass, much less expensive and abundant with respect to the most famed fine chemicals (*e.g.* methanol, ethanol, glucose, and glycerol) to obtain gas-phase H<sub>2</sub> under UV-visible light, in the presence of platinised TiO<sub>2</sub> (Pt/TiO<sub>2</sub>), an efficient photocatalyst for H<sub>2</sub> evolution from water.<sup>7,11</sup> The effects of CLS concentration, catalyst amount, irradiation time, pH and water salinity have been investigated. Irradiation was carried out under UV-A, solar simulated light and natural sunlight outdoor conditions, at ambient temperature and pressure. The mechanism of the process has been proposed to describe the role of the sacrificial agent played by CLS, and to explain the behaviour of the system under solar radiation. The procedure was assessed on non-food waste cellulosic biomasses, not considered in the literature as yet, under simulated or natural solar light.

## Experimental

### Chemicals

Evonik P25 titanium dioxide (80% anatase, 20% rutile), with an average particle size of 30 nm and a reactive surface area of  $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ , was purchased from Evonik Industries AG (Hanau, Germany). H<sub>2</sub>PtCl<sub>6</sub> (~38% Pt basis), activated RANEY® Ni, 5-hydroxymethyl furfural (HMF, 99%), dinitrophenyl-

hydrazine (≥99%) and fibrous long CLS were supplied by Sigma Aldrich (Milan, Italy). HPLC gradient grade acetonitrile (ACN) was supplied by VWR (Milan, Italy). H<sub>2</sub>SO<sub>4</sub> (96% w/w), CH<sub>3</sub>COOH (99.9% w/w), glucose (>99% w/w) and NaOH anhydrous pellets (97% w/w) were purchased from Carlo Erba Reagenti (Milan, Italy). Ultrapure water (resistivity 18.2 MΩ cm<sup>-1</sup> at 25 °C) was produced in the laboratory by means of a Millipore (Milan, Italy) Milli-Q system. Argon (99.999%), nitrogen (99.999%), carbon dioxide (99.5%) and hydrogen (99.995%) were supplied by Sapio S.r.l. (Milan, Italy).

### Synthesis and characterization of the photocatalysts

Pt/TiO<sub>2</sub> (0.5 wt%) was prepared by a photochemical deposition procedure.<sup>21</sup> Briefly, 1.0 g of P25 TiO<sub>2</sub> was added to a solution made of 10 mL 0.1 M glacial acetic acid and containing 330 μL of 0.077 M H<sub>2</sub>PtCl<sub>6</sub> (pH 4.1); the suspension was irradiated (UV fluorescent lamps emitting at 366 nm, 30 W) under magnetic stirring for 24 h and then filtered. The grey powder obtained was washed with plenty of ultrapure water until neutrality of the eluate and dried at 100 °C for 4 h. The actual Pt amount was determined by scanning electron microscopy (SEM). This was performed using a Leo 1530 Gemini instrument, field emission gun (FEG); acceleration voltage V<sub>acc</sub> = 0.2–30 kV, resolution 1.0 nm at 20 kV, 2.5 nm at 1 kV, 5 nm at 0.2 kV; detectors: Inlens, conventional SE, BSE; methods: SEM, HRSEM; manufacturer: Zeiss, Oberkochen.

Brunauer–Emmett–Teller (BET) analyses were carried out using an ASAP 2010 physisorption analyzer (Micromeritics Instrument Corp). Before the measurements the samples were heat-treated at 200 °C under vacuum. The result was a full report on the isotherm and specific surface area. For SEM characterization, powders were inserted in special stubs and coated with gold under low vacuum to obtain a conductive material. UV-visible Diffuse Reflectance Spectroscopy (DRS) was performed using a JASCO V-570 UV-VIS-NIR spectrophotometer instrument. Samples were prepared in tablets (diameter 1 cm, weight *ca.* 400 mg) by pressing the powders at 4 atm. The analysis on samples was repeated several times (tablets were destroyed and freshly prepared) to verify the reliability of the results. The energy gap ( $E_{\text{gap}}$ ) value of the catalyst was calculated according to the equation  $E_{\text{gap}} = h\nu = hc\lambda^{-1}$ .<sup>22</sup>

### Sample preparation

The experiments under UV irradiation were conducted with 200 mg CLS suspended in 30 mL distilled water in glass vials (capacity 40 mL) equipped with silicon/PTFE septa, while in the case of solar light irradiation 140 mg of CLS were placed in 21 mL distilled water in Pyrex glass containers (28 mL capacity). After addition of the catalyst (2.0 g L<sup>-1</sup>), the suspension was deoxygenated by nitrogen bubbling for 20 min and irradiated for 4 h under magnetic stirring. The influence of pH was investigated by modifying the sample native pH (around neutrality) by addition of small volumes (50–400 μL) of NaOH or H<sub>2</sub>SO<sub>4</sub> aqueous solutions, negligible with respect to the final volume. An Orion 420A pH meter (Thermo Electron



Corporation, Rodano, Italy) was used. Seawater, collected in Sestri Levante (Italy), was also tested. Irradiation was performed under UV-A (366 nm,  $4 \times 15$  W), solar simulated and natural sunlight. A Solar Box 1500e (CO.FO.ME.GRA S.r.l., Milan, Italy) set at a power factor of  $250 \text{ W m}^{-2}$ , and equipped with a UV outdoor filter of soda lime glass IR treated, has been used as the solar light simulator. Irradiation under natural solar light was performed in Pavia ( $45^{\circ}11'N$ ,  $9^{\circ}09'E$ ) on the window ledge (July 2013, temperature  $29\text{--}32$  °C) during sunny days; the average solar power was  $450 \text{ W m}^{-2}$  in the visible range and  $25 \text{ W m}^{-2}$  in the UV, respectively. The flux was measured by means of a HD 9221 (Delta OHM) (450–950 nm) and of a Multimeter (CO.FO.ME.GRA) (295–400 nm) radiometer.

Rice husk and alfalfa stems were tested as actual cellulosic biomass under the experimental conditions reported above. These biomasses were air-dried at room temperature, milled and then sieved at 70 mesh (0.2 mm); rice husk was also used as received. All experiments were performed in triplicate.

### Analytical determination

The evolved gases ( $\text{H}_2$  and  $\text{CO}_2$ ) were determined by gas chromatography (GC) through injection of  $250 \mu\text{L}$  of the vial headspace in the GC system (splitless mode). A DANI 3600 gas chromatograph (DANI S.p.A., Cologno Monzese, Italy) equipped with a thermal conductivity detector (TCD) and interfaced with a C-R3A recorder (Shimadzu, Milan, Italy) was used. Separation was performed on a glass column ( $3 \times 250$  mm) packed with Carbosieve SII (60/80 mesh); high purity argon was the carrier gas, at a flow rate of  $12.4 \text{ mL min}^{-1}$ ; temperature program:  $70$  °C for 8 min, from  $70$  °C to  $230$  °C at  $15$  °C  $\text{min}^{-1}$ , and  $230$  °C for 16 min. The temperature of the injection port and the detector was  $100$  °C and  $200$  °C, respectively. The quantification was performed by external calibration. Three independent five points calibration curves were generated by injection of different volumes of pure gases ( $10\text{--}70 \mu\text{L}$  for  $\text{H}_2$  and  $50\text{--}400 \mu\text{L}$  for  $\text{CO}_2$ ), obtaining linear responses ( $r^2 > 0.999$ ) and suitable peak area precision (RSD  $< 6\%$ ,  $n = 3$ ).

A UV-Vis Cary 100 Scan spectrophotometer (Varian, Turin, Italy) was used to collect absorbance spectra on the aqueous fraction of the samples.

Aqueous HMF in the irradiated samples was detected in the native form by HPLC-UV and by UPLC-DAD after derivatization. In the first procedure, the sample was filtered and injected in the HPLC system before and after spike with known amounts of standard HMF. A Supelco C18 ( $5 \mu\text{m}$ ,  $4.6 \times 250$  mm) column was used with water-ACN (92:8) as the mobile phase, flow rate  $1 \text{ mL min}^{-1}$ , detection  $280 \text{ nm}$ .<sup>23</sup> For a more accurate detection, HMF was derivatized with dinitrophenylhydrazine to obtain the corresponding dinitrophenylhydrazone, according to the EPA standard method 1667.<sup>24</sup> The sample was analyzed using a 1290 Infinity UPLC-DAD system (Agilent, Cernusco sul Naviglio, Milan, Italy) using an Acquity UPLC BEH C18 column ( $1.7 \mu\text{m}$ ,  $2.1 \times 100$  mm) thermostated at  $20$  °C. The mobile phase was water-ACN at a flow rate of  $0.3 \text{ mL min}^{-1}$ , 30% ACN for 1 min, linear gradient to 70% ACN

in 9 min, to 100% ACN in 1 min, isocratic ACN 100% for 2 min; detection  $390 \text{ nm}$ . HPLC-ESI-MS/MS was finally adopted to confirm HMF. The LC-MS system consisted of a Waters MassLynx mass spectrometer equipped with a Phenomenex LUNA C18 column ( $3 \mu\text{m}$ ,  $2 \times 150$  mm) maintained at  $25$  °C; the mobile phase was 0.01% formic acid (A) and methanol-5 mM ammonium formate aqueous solution 90/10, flow rate  $0.3 \text{ mL min}^{-1}$ , gradient elution: 100% A for 1.5 min to 100% B until 6.5 min, 100% B until 15 min. For HMF identification, the parent ion  $m/z$  127.0 and the two ion product transitions with  $m/z$  109.1 and  $m/z$  81.3 were monitored (collision energy  $9.0 \text{ eV}$ ). The MS/MS chromatograms were recorded in multiple reaction monitoring (MRM) mode (see ESI†).

The concentration of the anions present in the seawater was determined by ion chromatography with a DX 500 Ion Chromatograph (Dionex, Milan, Italy) equipped with a GP40 gradient pump, CD20 conductivity detector and anion self-regenerating suppressor (ASRS 400, 4 mm);  $70 \mu\text{L}$  of each sample were injected into a  $250 \times 4$  mm IonPac AS23 coupled with a AG23  $50 \times 4$  mm guard-column. The eluent was  $8 \times 10^{-4} \text{ M NaHCO}_3\text{--}4.5 \times 10^{-4} \text{ M Na}_2\text{CO}_3$ , at a flow rate of  $1.0 \text{ mL min}^{-1}$ .

The cations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer (Milan, Italy) Optima 3300 DV instrument.

## Results

### Catalyst characterization

The specific surface area of  $\text{TiO}_2$  was preserved after platinum deposition (from  $56$  to  $54 \text{ m}^2 \text{ g}^{-1}$ ), as expected from literature data.<sup>25</sup> The actual platinum content, determined by SEM, resulted to be 0.32 wt%, the average of five scans acquired on five different regions of the sample.

The catalyst was characterized by SEM and DRS techniques. As reported in Fig. 1, SEM analysis showed the morphology of Pt/ $\text{TiO}_2$ .

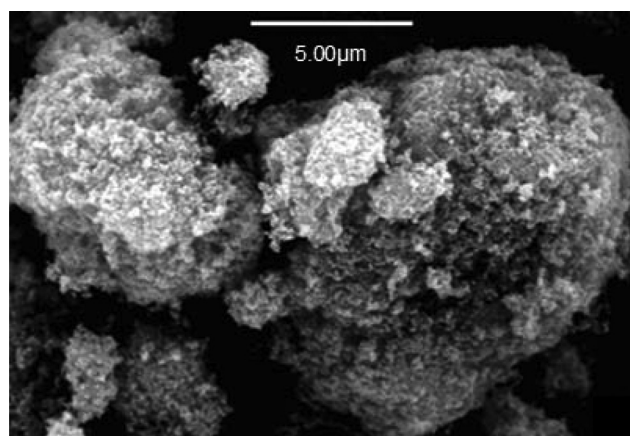


Fig. 1 SEM image acquired on Pt/ $\text{TiO}_2$  (ETH 20.0Kv, MAG.X6.00).



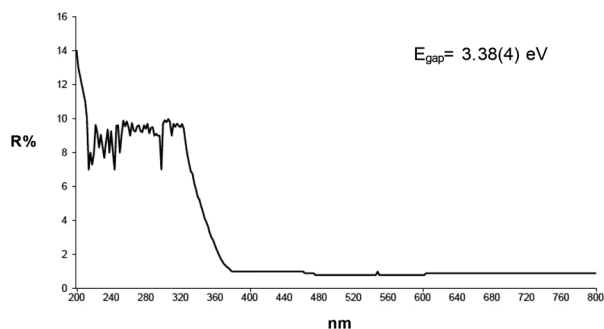


Fig. 2 DRS spectrum obtained on Pt/TiO<sub>2</sub>.

The sample is homogeneous and consists of round shaped grains that form sponge-like aggregates. The energy gap value, calculated from the DRS spectrum reported in Fig. 2, is 3.38(4) eV.

### Photocatalytic hydrogen gas evolution from water-suspended CLS

Preliminary experiments, carried out to investigate H<sub>2</sub> evolution from aqueous suspensions of fibrous CLS, proved that under UV-A radiation appreciable amounts of H<sub>2</sub> were generated in the presence of Pt/TiO<sub>2</sub>. The yields were up to tenfold higher than those observed by water splitting occurring in neat water, that is, in the absence of biomass (see Table 1).

The results obtained are consistent with the role of sacrificial agent played by CLS. Indeed, the presence of CLS enhances H<sub>2</sub> evolution from water, in particular the addition of CLS to the water samples largely accounts (*ca.* 90%) for the yields experimentally observed. Omitting the catalyst, no H<sub>2</sub> was detected (<limit of detection) from irradiated CLS aqueous suspensions, showing the key role of photocatalysis in the reaction. Similarly, no H<sub>2</sub> was detected in the presence of TiO<sub>2</sub> not loaded with platinum (see Table 1), confirming the role of the metal as the reduction site for hydrogen ions.<sup>26</sup> The inter-

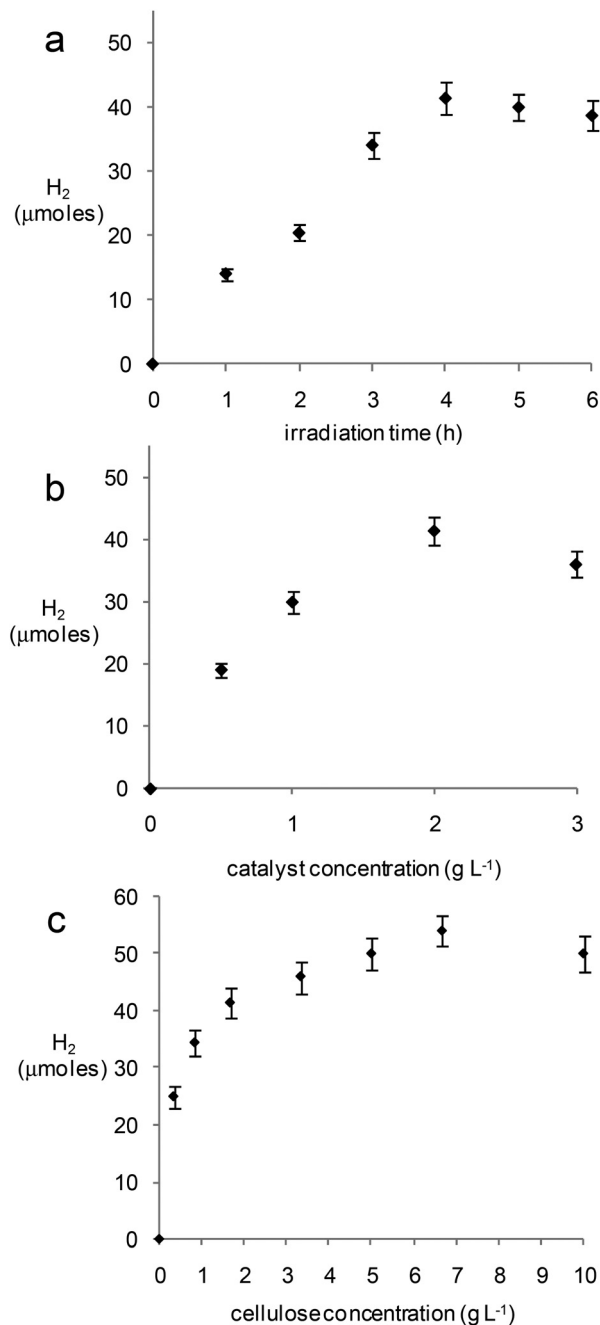


Fig. 3 H<sub>2</sub> yields as a function of (a) irradiation time, (b) catalyst amount and (c) CLS concentration. Conditions: (a) 50 mg CLS, 2 g L<sup>-1</sup> catalyst; (b) 50 mg CLS, 4 h UV-A; (c) 2 g L<sup>-1</sup> catalyst, 4 h UV-A; sample volume 30 mL. Error bars represent the standard deviation from three independent experiments (*n* = 3).

Table 1 H<sub>2</sub> yields (μmoles) observed for CLS and cellulosic biomass aqueous suspensions under UV-A, solar simulated light and natural sunlight (*n* = 3, RSDs < 8%). Conditions: 4 h irradiation, 2 g L<sup>-1</sup> catalyst, 6.7 g L<sup>-1</sup> biomass

Sample	H <sub>2</sub> yields (μmoles)		
	UV-A <sup>a</sup>	Solar simulated light <sup>b</sup>	Natural sunlight <sup>b</sup>
Water cellulose suspension <sup>c</sup>	n.d.	n.d.	n.d.
Water (no biomass) + TiO <sub>2</sub>	n.d.	n.d.	n.d.
Water cellulose suspension + TiO <sub>2</sub>	n.d.	n.d.	n.d.
Water (no biomass) + Pt/TiO <sub>2</sub>	6	3	4
Water cellulose suspension + Pt/TiO <sub>2</sub>	54	31	33
Water rice husk suspension + Pt/TiO <sub>2</sub>	24	15	16
Water Alfalfa stems suspension + Pt/TiO <sub>2</sub>	24	—	—

<sup>a</sup> 30 mL sample. <sup>b</sup> 21 mL sample. <sup>c</sup> No catalyst. n.d., not detected.

day precision for all measurements showed residual standard deviations (RSDs) lower than 8% (*n* = 3).

The effects of irradiation time, catalyst amount and biomass concentration, key factors in heterogeneous photocatalytic systems,<sup>26–29</sup> were investigated to characterize the behaviour of the system in terms of H<sub>2</sub> yield. The influence of irradiation time is clearly shown in Fig. 3a.



The hydrogen gas yield considerably increased in going from 1 to 4 h, almost reaching a plateau for longer irradiation times (not convenient to be applied). As expected, upon increasing the catalyst concentration the reaction was strongly favored. As apparent from Fig. 3b, H<sub>2</sub> evolution was enhanced for concentrations up to 2 g L<sup>-1</sup>; higher catalyst concentrations did not further improve the yields. The reaction was dependent on the amount of the sacrificial agent. Fig. 3c provides evidence that H<sub>2</sub> evolved by the system gradually increased as a function of the CLS amount, reaching a plateau above 6.7 g L<sup>-1</sup>.

The pH of the water solution was investigated in the range 2–10. The highest yield was observed at the native pH (around neutrality), with addition of acids or bases suppressing H<sub>2</sub> evolution (up to ca. 60%, data not shown).

Additionally, the salinity of the aqueous solution was investigated by comparing the reaction yields obtained in distilled and seawater. Under the same experimental conditions (2 g L<sup>-1</sup> catalyst, 6.7 g L<sup>-1</sup> biomass, 4 h UV-A irradiation), it was observed that inorganic ionic species present in the seawater sample (pH 7.7 ± 0.1, conductivity 49 mS cm<sup>-1</sup>, Cl<sup>-</sup> 5.65 × 10<sup>-1</sup> M, SO<sub>4</sub><sup>2-</sup> 2.75 × 10<sup>-2</sup> M, HCO<sub>3</sub><sup>-</sup> 2.4 × 10<sup>-3</sup> M, Na<sup>+</sup> 4.70 × 10<sup>-1</sup> M, K<sup>+</sup> 10<sup>-2</sup> M, Ca<sup>2+</sup> 10<sup>-2</sup> M, Mg<sup>2+</sup> 5.5 × 10<sup>-2</sup> M) did not affect the reaction in a significant manner. Indeed, the comparable yields experimentally found in the two matrices (difference <10%) indicate that natural waters of various compositions could be used.

### Irradiation under solar light

In view of the findings obtained with UV-A radiation, we further investigated the reaction yields under solar simulated light, with the aim to exploit natural sunlight (see Table 1). High H<sub>2</sub> yields were obtained using the UV-Vis source compared to UV-A. In particular, the production was ca. 85% with respect to that observed under 366 nm-radiation.

As it is apparent, the results obtained with the solar light simulator in the presence of Pt/TiO<sub>2</sub> are in excellent agreement with those observed by experiments performed on the window ledge under natural solar light. The UV-Vis spectra collected on the irradiated sample and on the control sample (4 h stirring in the dark, 2 g L<sup>-1</sup> catalyst) are reported in Fig. 4.

### Photocatalytic tests in the presence of raw biomasses

The encouraging results obtained by fibrous CLS prompted us to explore the possibility to directly use raw cellulosic biomasses. In particular, rice husk and alfalfa stems were chosen in view of the appreciable content of CLS<sup>30,31</sup> and large availability since they are waste materials.

As reported in Table 1, under UV-A radiation significant production was attained also in the presence of these actual substrates, with reaction yields threefold higher than those from water splitting occurring in pure water. The homogenization of the vegetal tissues, mandatory in the case of alfalfa stems, was not convenient for rice husk; indeed it was observed that the use of milled/sieved rice husk suppressed H<sub>2</sub>

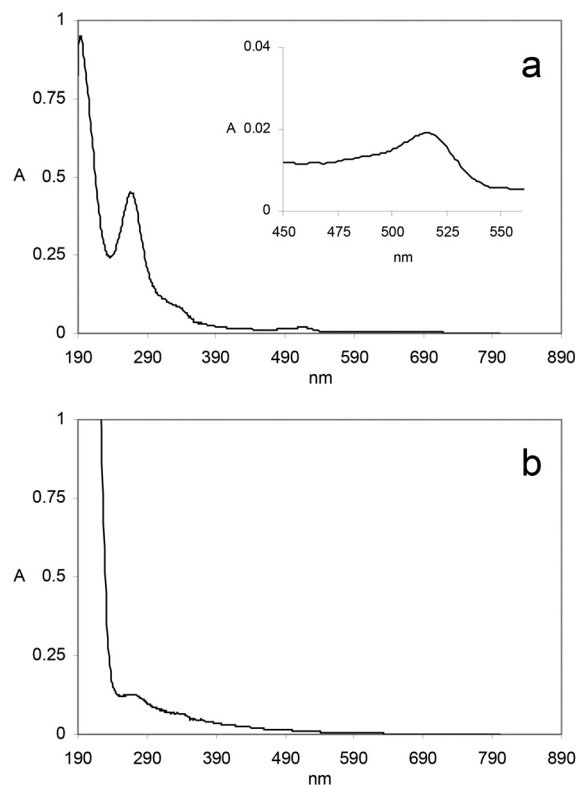


Fig. 4 UV-Vis spectra collected on the aqueous fraction from (a) the CLS suspension after irradiation (2 g L<sup>-1</sup> catalyst, 4 h UV-A) and from (b) the control sample (2 g L<sup>-1</sup> catalyst, 4 h dark).

evolution (up to ca. 60%), likely due to the saturation of radiation absorption and/or light scattering phenomena.<sup>28</sup> Therefore, untreated rice husk was tested also under simulated and natural solar light reaching a fivefold improvement of the water splitting yield (see Table 1).

## Discussion

Dispersion of CLS, completely water-insoluble with no chemical modification or derivatization, is hard to achieve because of the rigid long-chain and strongly inter-molecular and intra-molecular hydrogen-bonded structure.<sup>32</sup> Indeed, the photocatalytic conversion of CLS into HMF requires a solubilisation step in concentrated ZnCl<sub>2</sub> aqueous solution to take place gradually.<sup>32</sup>

In the present work it has been experimentally observed that CLS can be step-by-step solubilised (depolymerised) in aqueous Pt/TiO<sub>2</sub> suspension under both UV-A and solar light radiation, giving rise to water-soluble by-products characterized by reducing properties. The process is accompanied by the simultaneous evolution of the gas phase H<sub>2</sub> from the water sample. Because of the necessity to work under anaerobic conditions, as photogenerated electrons would be otherwise consumed by oxygen chemisorbed on the catalyst,<sup>16</sup> the degradation is obviously not quantitative but nonetheless sufficient



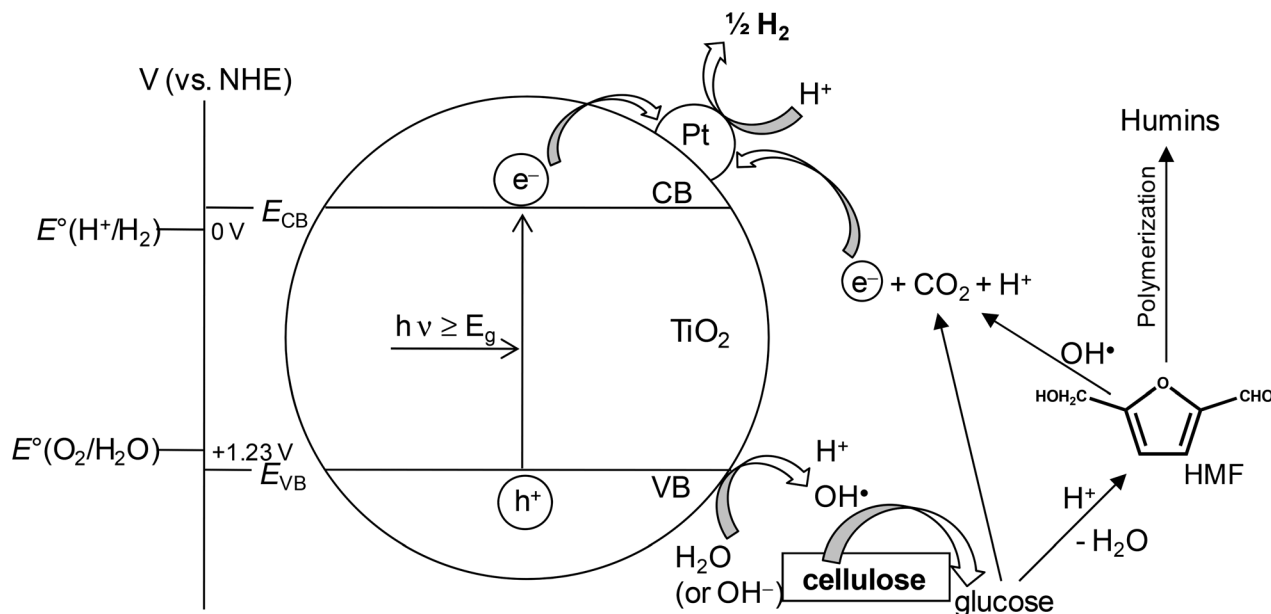


Fig. 5 Schematic representation of the photocatalytic system for the  $\text{H}_2$  evolution by water splitting over irradiated Pt/TiO<sub>2</sub> in the presence of cellulose as the sacrificial agent.

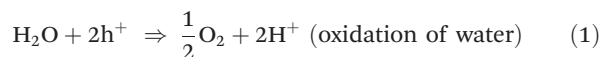
to sustain the process. Indeed, it is documented that CLS degradation in the presence of the TiO<sub>2</sub> photocatalyst is favored in aerobic media due to the key role played by O<sub>2</sub><sup>-</sup>.<sup>32</sup> The results reported above clearly indicate that CLS behaves as sacrificial agent, appreciably increasing the H<sub>2</sub> yield with respect to that observed in neat water.

The influences of the variables investigated are typical of heterogeneous photocatalysis, with the substrate concentration, catalyst amount and irradiation time having a large effect on the overall yield. This was lowered by addition of acids or bases (H<sub>2</sub>SO<sub>4</sub> or NaOH) in the water sample. The interference of co-added sulphate and/or sodium ions is excluded on the basis of the high H<sub>2</sub> yield observed in seawater (see characterization in “Photocatalytic hydrogen gas evolution from water-suspended CLS”), not significantly different from that attained in distilled water.

The general scheme of the photocatalytic system here studied, combining water splitting and light-induced oxidation of biomass (CLS), which sustain the former process, is reported in Fig. 5.

This schematically shows the main steps involved in the reaction that leads to H<sub>2</sub> evolution from water, carried out over Pt/TiO<sub>2</sub> at room temperature and atmospheric pressure, in the presence of cellulose as the sacrificial agent. The mechanism of the photocatalytic process on the TiO<sub>2</sub> semiconductor is activated by absorption of a photon with an energy equal to or greater than the semiconductor band gap ( $E_g$ ); this promotes an electron ( $e^-$ ) from the valence band (VB) to the conduction band (CB), thus generating an electron ( $e^-$ )-hole ( $h^+$ ) pair. These charge carriers are able to promote redox reactions involving acceptor or donor species, in the

case of water splitting according to the following equations:<sup>7,20</sup>



Using the TiO<sub>2</sub> semiconductor, these reactions are possible because the CB potential is more negative than the H<sup>+</sup> reduction potential, that is 0.0 V vs. the normal hydrogen electrode (NHE); the reduction is strongly favored by Pt because, through the formation of a Schottky barrier, it makes electrons in the CB more readily available.<sup>7</sup>

Since the overall water splitting reaction is thermodynamically extremely difficult because it is highly endergonic, addition of sacrificial agents (able to combine with  $h^+$  more efficiently than water) is required to enhance H<sub>2</sub> evolution.<sup>20</sup> As shown in Fig. 5, CLS acts as a scavenger for the VB holes and/or the HO<sup>•</sup> (generated by reaction of water with the holes) undergoing oxidative degradation. Indeed, as in the case of other sacrificial agents, for instance glucose<sup>27</sup> or glycerol,<sup>33</sup> organic substrates act as sacrificial agents by removing rapidly and irreversibly  $h^+$ , oxidant species (e.g. HO<sup>•</sup>) and/or O<sub>2</sub> produced by cleavage of water. This results in suppression of charge carrier recombination and/or O<sub>2</sub>-H<sub>2</sub> back reaction,<sup>20,33</sup> providing at the same time electrons to the TiO<sub>2</sub> CB or directly to the Pt islands deposited on the catalyst surface (current doubling effect<sup>26</sup>) that are the active sites for the reduction of water hydrogen ions;<sup>7,16,26</sup> in fact, among all the metals, Pt is



the most widely used because it has the lowest overpotential and the highest activity for hydrogen generation.<sup>7</sup> As expected,<sup>7,27</sup> no detectable amounts of H<sub>2</sub> were generated in the presence of bare TiO<sub>2</sub> (see Table 1).

In order to assess the potential contribution of CLS aqueous phase reforming (APR) to the H<sub>2</sub> evolution from the present system, further experiments were conducted in the presence of RANEY® Ni instead of Pt, as the former is known to be an excellent C–C cleavage catalyst used for APR.<sup>34</sup> The evolved H<sub>2</sub> was around 1 micromole (RSD < 10%, *n* = 3) in the presence of TiO<sub>2</sub> and RANEY® Ni, while no H<sub>2</sub> was detected using RANEY® Ni, omitting TiO<sub>2</sub>. Under the same experimental conditions, 54 micromoles of H<sub>2</sub> were obtained over Pt/TiO<sub>2</sub> (see Table 1). It is evident that RANEY® Ni and, more generally, other C–C cleavage catalysts, under the present experimental conditions (ambient temperature and pressure), are not able to induce an efficient C–C cleavage of CLS, thus H<sub>2</sub> evolution from the biomass APR can be considered negligible. This confirms that water splitting over Pt/TiO<sub>2</sub> in the presence of CLS as the sacrificial agent is the main pathway for H<sub>2</sub> evolution from water, which involves reduction of water hydrogen ions on Pt.

Along with the O<sub>2</sub> expectable to be evolved by water splitting (but not detected in the headspace after sample irradiation, due to its reaction with the sacrificial biomass<sup>20</sup>), the HO· and h<sup>+</sup> can be assumed as the main oxidant agents of the system. These begin CLS degradation to form water-soluble organic intermediates, such as glucose and HMF. As observed in the analytical reports, the latter was found in the aqueous solution after irradiation and was confirmed by HPLC-ESI-MS/MS analysis (see ESI†). Indeed, the acidic sites of TiO<sub>2</sub> are able to catalyze dehydration of glucose to give HMF and the corresponding oligomers, *viz.* humins.<sup>35</sup> The photo-generated soluble species have higher effective molarity and quicker diffusion in the solution.<sup>27</sup> This means that CLS by-products can come into close contact with the catalyst surface, thus behaving as an electron donor more efficiently than the parent biomass. In fact HMF, having a molecular structure similar to glucose (HMF is its dehydrated product), performs as an excellent electron donor; being readily oxidized to CO<sub>2</sub> it favors the reduction of the water hydrogen ions.

The mean H<sub>2</sub>/CO<sub>2</sub> molar ratio experimentally found was 2.1 (RSD 4.8%, *n* = 3), which is very near to the theoretical value of glucose photoreforming,<sup>27</sup> according to eqn (4):



This further demonstrates that CLS undergoes depolymerisation, being converted into glucose, which is one of the most efficient sacrificial agents for H<sub>2</sub> photocatalytic production from water.<sup>20</sup> Comparison with the results obtained under the same conditions on aqueous glucose (3.5 × 10<sup>-3</sup> M) allowed us to evaluate the degree of conversion of the biopolymer. Similar yields were obtained with 10 mg glucose and 200 mg CLS (49 μmoles and 54 μmoles H<sub>2</sub>, respectively). In the reasonable hypothesis that the H<sub>2</sub> from the CLS water sample derives

from hydrogen ion reduction promoted by oxidation of glucose as the reaction intermediate, the conversion of CLS results to be around 5%. The partial conversion is mainly due to the water insolubility of the polysaccharide and to the anoxic conditions, in fact the photocatalytic depolymerization of other polysaccharides, *i.e.* pectin, was proved to proceed efficiently in aqueous solution under aerobic conditions.<sup>36</sup> The partial CLS depolymerization here observed is anyway noteworthy in terms of the H<sub>2</sub> yield. In this context, it should be considered that the rate of hydrogen evolution from water decreases with increasing molecular weights of carbohydrates.<sup>7</sup> In fact, Fu *et al.*<sup>27</sup> reported H<sub>2</sub> yields in the soluble order starch < sucrose < glucose, and showed that microwave-assisted hydroxylation of the soluble starch prior to the photocatalytic step enhances the overall yield. Though with yields lower than those from ethanol or glucose, it should be remarked that H<sub>2</sub> is here obtained using a raw biomass, which is the precursor of those fine sacrificial agents, *viz.* CLS ⇒ glucose ⇒ ethanol. In this context, the possibility of direct production of solar hydrogen from polysaccharide suspensions under ambient conditions is of tremendous practical importance, because of significant cost savings resulting from the decrease of the required steps compared to existing technologies (*e.g.* no need for hydrolysis, fermentation, *etc.*).<sup>16</sup>

As reported above, the reaction also proceeds under solar light, with yields up to 87% with respect to UV radiation (see Table 1). The consistent H<sub>2</sub> evolution also under solar light can be explained considering that CLS conversion involves the formation of soluble species able to absorb light in the visible range. Indeed, from Fig. 4 it is apparent that after irradiation the filtered solution shows an appreciable absorbance (>0.015) above 400 nm (the color of water turns yellow). The absorbance of the solution is ascribable to the spontaneous generation of HMF oligomers,<sup>35,37,38</sup> as shown in Fig. 5. It is reasonable to hypothesize a sort of “*in situ* dye-sensitization” that expands the activity of Pt/TiO<sub>2</sub> in the visible region. The photogenerated by-products are water-soluble and therefore can easily adsorb onto the catalyst surface, thus promoting charge transfer to the TiO<sub>2</sub> conduction band and/or to the platinum islands.<sup>17</sup> In fact, dye-sensitized photocatalytic systems require the dye molecules to be linked/adsorbed onto the catalyst surface to effectively inject electrons into the semiconductor conduction band for water reduction.<sup>7,17</sup> Evidently, the CLS-oxidation by-products have suitable ground (HOMO) and excited (LUMO) states for the efficient electron transfer.<sup>39</sup>

The reaction mechanism has also been proposed on the basis of the results from further experiments carried out by irradiation of aqueous glucose (1.8 × 10<sup>-2</sup> M), claimed to be the intermediated product. As in the case of the CLS sample, HMF was found in the solution submitted to UV-A exposure (4 h, 2 g L<sup>-1</sup> catalyst), further supporting the degradation pathway shown in Fig. 5.

The amount of evolved H<sub>2</sub> in the presence of actual biomasses is about a half of that achieved with fibrous CLS (see Table 1). This can be explained considering that CLS accounts for about 54% of the total composition of rice husk, that in



fact also contains lignin (*ca.* 22%) and an inorganic fraction (silicates, *ca.* 14%).<sup>30</sup> Similarly, in alfalfa stems the cellulosic fraction can be estimated to be around 60% (insoluble polysaccharides); other constituents are lignin *ca.* 12%, sugars *ca.* 5%, starch 0.7%, and inorganics 0.3%.<sup>31</sup>

The results suggest that lignin does not interfere in the process. Moreover, since lignin is highly recalcitrant towards TiO<sub>2</sub> degradation, requiring oxygen-saturated media to be decomposed,<sup>40</sup> it is reasonable to assume that under the applied conditions it cannot behave as an efficient HO<sup>•</sup> scavenger; therefore the H<sub>2</sub> observed after irradiation is effectively generated from water reduction by oxidative degradation of the cellulosic fraction.

Along with the above discussion, it is also appropriate to comment on the reaction yields. UV-A irradiation of a 30 mL CLS water sample provides 54 μmoles H<sub>2</sub> (RSD < 8%, *n* = 3), therefore a H<sub>2</sub> evolution of *ca.* 40 L could be obtained from 1 m<sup>3</sup> water. Considering the actual Pt content of the catalyst (0.32 wt%), 6.4 g Pt should be used to process 1 m<sup>3</sup> water sample, thus 1.8 g Pt would be necessary to obtain 1 g H<sub>2</sub>. Irradiation under natural solar light would provide *ca.* 33 L H<sub>2</sub> per m<sup>3</sup> water, requiring *ca.* 2 g Pt. These values are very significant if compared to the H<sub>2</sub> production yield achievable through enzymatic conversion of CLS for hydrogen photoproduction,<sup>5</sup> where 8.1 g Pt are estimated to be required to attain 1 g H<sub>2</sub>.

The use of vegetal tissues, rice husk in particular, could provide 18 and 15 L H<sub>2</sub> per m<sup>3</sup> water under 366 nm-radiation and natural solar light, respectively. Thus, the use of CLS or CLS-containing biomasses appears as a sustainable route to be further investigated to obtain hydrogen gas from water, under solar light.

## Conclusions

The significance of this work can be enounced in the following key points:

1. A systematic study on the use of CLS as the sacrificial agent for the photocatalytic hydrogen gas evolution from water has been performed by investigating the reaction mechanism.
2. CLS suspended in water significantly improves the H<sub>2</sub> yields with respect to those observed by water splitting occurring in neat water.
3. The behaviour of the CLS-based photocatalytic system has been characterized by investigating the effects of irradiation time, catalyst amount, biomass concentration, along with pH and salinity.
4. CLS, a largely available and low cost polysaccharide, is photocatalytically solubilised (depolymerised) forming water-soluble products that have good reducing properties and undergo the typical photoreforming of glucose, promoting water hydrogen ion reduction.
5. With respect to UV radiation, the system performs efficiently also under natural solar light due to a sort of “*in situ*

dye-sensitization” promoted by the CLS products, in particular HMF oligomers.

6. The CO<sub>2</sub> evolved by the system does not contribute to the greenhouse effect because it is part of a natural cycle (in nature CLS is formed using atmospheric carbon dioxide).

7. H<sub>2</sub> is also evolved under solar radiation in the presence of waste cellulosic biomasses (*i.e.* rice husk).

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