Photochemical & Photobiological Sciences

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pps

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

Andrea Speltini[a,*], Michela Sturini[a,*], Daniele Dondi[a], Enrico Annovazzi[a], Federica Maraschi[a],
Valentina Caratto[b], Antonella Profumo[a], Armando Buttafava[a]

[a]*Department of Chemistry, University of Pavia, via Taramelli 12, 27100 Pavia, Italy*

[b]*Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, 16146 Genova, Italy*

[*]*Corresponding authors. Tel.: +39 0382-987347-9; fax: +39 0382-528544.*

E-mail addresses: andrea.speltini@unipv.it (A. Speltini), michela.sturini@unipv.it (M. Sturini)

Abstract

This work presents a systematic study of cellulose (CLS) as a sacrificial biomass for photocatalytic H_2 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. Aqueous CLS suspension irradiated under either at 366 nm (UV-A) or sunlight in the presence of Pt/TiO_2 behaves as a H_2 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_2 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_2-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 ions reduction to give gas-phase H_2. The formation of "colored" byproducts 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.

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.[1] 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.[2]

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.[3] However, as the most abundant biopolymer on Earth, it is now attracting the interest of the scientific community with regard to its conversion into biofuels.[4] Some recent studies[1,5,6] showed that CLS can be used also as feedstock to generate hydrogen gas (H_2). 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.[7] For these reasons, the development of new ways to obtain hydrogen gas from renewable resources, essentially water and biomass,[7] is of primary importance and requires intensive research study.[8] H_2 is an appealing energy carrier because only water is released from its combustion in fuels cells, thus it can be considered an environmentally friendly fuel; moreover H_2 shows an energy yield of 142 kJ g^{-1}, 2.75 times higher than that of any hydrocarbon.[9]

H_2 can be obtained starting from CLS by supercritical water gasification,[1] dark fermentation[6] and enzymatic photoproduction.[5] However, to the best of our knowledge, no systematic studies on the use of CLS as sacrificial agent for the photocatalytic H_2 gas production from water have been reported in literature as yet.

Photocatalysis is becoming increasingly important due to its efficient role in the energy field[10,11] and also in environmental remediation, as well described in recent reviews;[12,13] also our research group focused on photocatalysis for abatement of water contaminants.[14,15] Indeed, this emerging technology is clean, effective, energy-saving, simple, eco-friendly and not expensive.[2] Photocatalysis appears as an attractive alternative to other methods of H_2 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.[16] In fact, the photocatalytic production of H_2 from water is the most attractive and rewarding work because water is abundant and renewable, and because the process can take place at ambient conditions using only sunlight and a semiconductor catalyst.[7] In view of its chemical stability, low cost and non-toxicity, titanium dioxide (TiO_2) is the most used photocatalyst.[7] 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_2 in the visible region.[7,17-19] Indeed, the main limitation of TiO_2 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.[7,17]

Various systems based on aqueous electrondonor substrates have been reported in the literature,[20] enabling the evolution of H_2 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, polysaccharides included.[16]

On the basis of the above, in this study we deemed necessary to explore the solar hydrogen gas photocatalytic production from water in 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, glycerol) to obtain gas-phase H_2 under UV-visible light, in the presence of platinised TiO_2 (Pt/TiO_2), an efficient photocatalyst for H_2 evolution from water.[7,11] 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 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 ± 15 m^2 g^{-1}, was purchased from Evonik Industries AG (Hanau, Germany). H_2PtCl_6 (~ 38% Pt basis), activated Raney Ni, 5-hydroxymethyl furfural (HMF, 99%), dinitrophenylhydrazine (≥99%) and fibrous long CLS were supplied by Sigma Aldrich (Milan, Italy). HPLC gradient grade acetonitrile (ACN) was supplied by VWR (Milan, Italy). H_2SO_4 (96% w/w), CH_3COOH (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^{-1} at 25°C) was produced in 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_2 (0.5 wt%) was prepared by a photochemical deposition procedure.[21] Briefly, 1.0 g of P25 TiO_2 was added to a solution made of 10 mL 0.1 M glacial acetic acid and containing 330 μL of 0.077 M H_2PtCl_6 (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 by a Leo 1530 Gemini instrument, field emission gun (FEG); acceleration voltage Vacc= 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 isotherm and specific surface area. For SEM characterization, powders were inserted in special stubs and coated with gold in low vacuum to obtain a conductive material.

UV-visible Diffuse Reflectance Spectroscopy (DRS) was performed by 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_{gap}) value of the catalyst was calculated according to the equation $E_{gap} = h\,\nu = h\,c\,\lambda^{-1}$.[22]

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^{-1}), 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_2SO_4 aqueous solutions, negligible with respect to the final volume. An Orion 420A pHmeter (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 × 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 250 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°11'N, 9°09'E) on the window ledge (July 2013, temperature 29-32°C) during sunny days; the average solar power was 450 W m^{-2} in the visible range and 25 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) radiometers.

Rice husk and alfalfa stems were tested as actual cellulosic biomass under the experimental conditions above reported. 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 determinations

The evolved gases (H_2 and CO_2) were determined by gas chromatography (GC) through injection of 250 μL 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 × 250 mm) packed with Carbosieve SII (60/80 mesh); high purity argon was the carrier gas, at a flow rate of 12.4 mL min^{-1}; temperature program: 70°C for 8 min, from 70°C to 230°C at 15°C min^{-1}, and 230°C for 16 min. The temperature of the injection port and 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 (10-70 μL for H_2 and 50-400 μL for 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 μm, 4.6 × 250 mm) column was used with water-ACN (92:8) as the mobile phase, flow rate 1 mL min^{-1}, detection 280 nm.[23] For a more accurate detection, HMF was derivatized with dinitrophenylhydrazine to obtain the corresponding dinitrophenylhydrazone, according to the EPA standard method 1667.[24] The sample was analyzed by a 1290 Infinity UPLC-DAD system (Agilent, Cernusco sul Naviglio, Milan, Italy) using a Acquity UPLC BEH C18 column (1.7 μm, 2.1 × 100 mm) thermostated at 20°C. The mobile phase was water-ACN at a flow rate of 0.3 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 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 μm, 2 × 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 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 products transitions with m/z 109.1 and m/z 81.3 were monitored (collision energy 9.0 eV). The MS/MS chromatograms were recorded in multiple reaction monitoring (MRM) mode (see Supplementary Data).

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 µL of each sample were injected into a 250 × 4 mm IonPac AS23 coupled with a AG23 50 × 4 mm guard-column. The eluent was 8×10^{-4} M $NaHCO_3$ - 4.5×10^{-4} M Na_2CO_3, at a flow rate of 1.0 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

Catalysts characterization

The specific surface area of TiO_2 was preserved after platinum deposition (from 56 to 54 m^2 g^{-1}), as expected from literature data.[25] The actual platinum content, determined by SEM, resulted to be 0.32 wt%, 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/TiO_2.

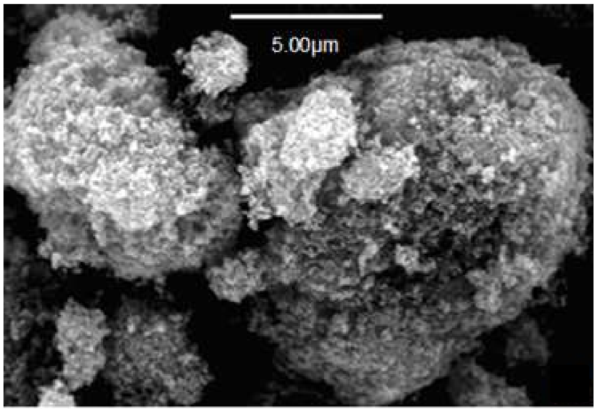

Fig. 1 SEM image acquired on Pt/TiO_2 (ETH 20.0Kv, MAG.X6.00).

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

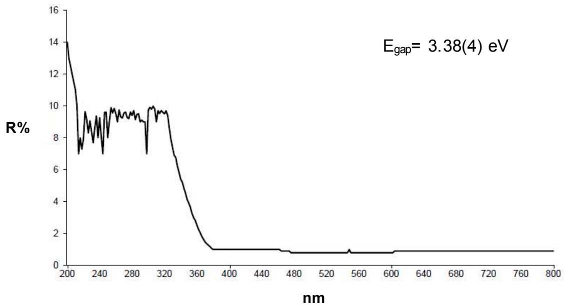

Fig. 2 DRS spectrum obtained on Pt/TiO_2.

Photocatalytic hydrogen gas evolution from water-suspended CLS

Preliminary experiments, carried out to investigate H_2 evolution from aqueous suspensions of fibrous CLS, proved that under UV-A radiation appreciable amounts of H_2 were generated in presence of Pt/TiO_2. 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).

Sample	H_2 yields (μmoles)		
	UV-A[a]	Solar simulated light[b]	Natural sunlight[b]
Water cellulose suspension[c]	n.d.	n.d.	n.d.
Water (no biomass) + TiO_2	n.d.	n.d.	n.d.
Water cellulose suspension + TiO_2	n.d.	n.d.	n.d.
Water (no biomass) + Pt/TiO_2	6	3	4
Water cellulose suspension + Pt/TiO_2	54	31	33
Water rice husk suspension + Pt/TiO_2	24	15	16
Water Alfalfa stems suspension + Pt/TiO_2	24	-	-

[a] 30 mL sample
[b] 21 mL sample
[c] no catalyst

n.d. not detected

Table 1 H_2 yields (μmoles) observed for CLS and cellulosic biomasses aqueous suspensions under UV-A, solar simulated light and natural sunlight (n=3, RSDs<8%). Conditions: 4 h irradiation, 2 g L^{-1} catalyst, 6.7 g L^{-1} biomass.

The results obtained are consistent with the role of sacrificial agent played by CLS. Indeed, the presence of CLS enhances H_2 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_2 was detected (< limit of detection) from irradiated CLS aqueous suspensions, showing the key role of photocatalysis in the reaction. Similarly, no H_2 was detected in the presence of TiO_2 not loaded with platinum (see Table 1), confirming the role of the metal as the reduction site for hydrogen ions.[26] The inter-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,[26-29] were investigated to characterize the behaviour of the system in terms of H_2 yield. The influence of irradiation time is clearly shown in Fig. 3a.

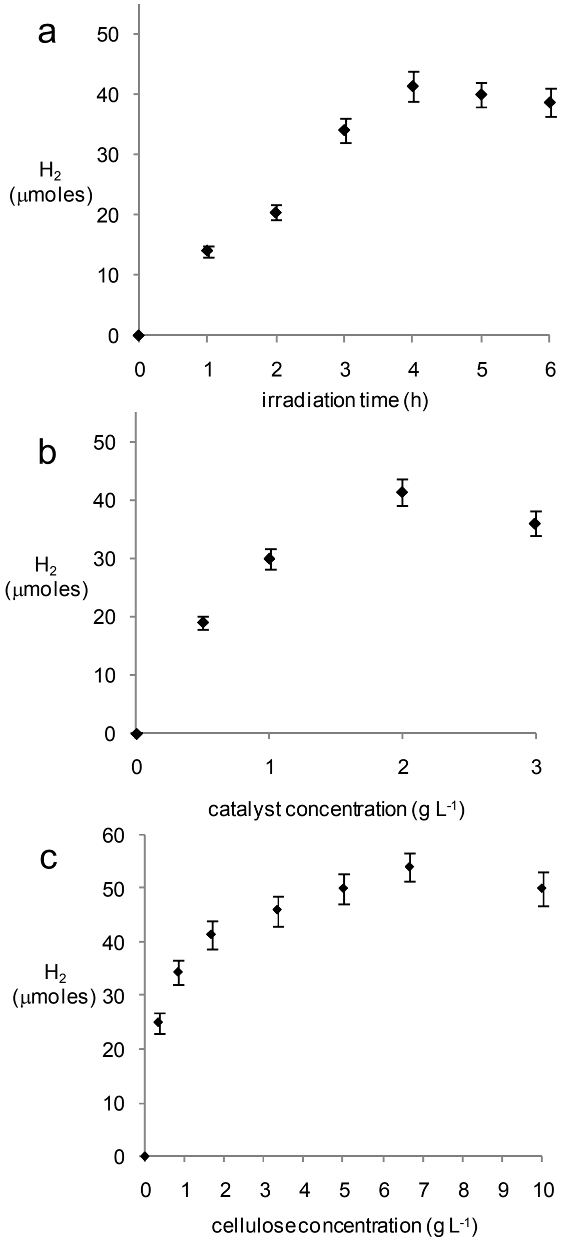

Fig. 3 H_2 yields as function of (a) irradiation time, (b) catalyst amount and (c) CLS concentration. Conditions: (a) 50 mg CLS, 2 g L^{-1} catalyst; (b) 50 mg CLS, 4 h UV-A; (c) 2 g L^{-1} catalyst, 4 h UV-A; sample volume 30 mL. Error bars represent the standard deviation from three independent experiments (*n*=3).

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, increasing the catalyst concentration the reaction was strongly favored. As apparent from Fig. 3b, H_2 evolution was enhanced for concentrations up to 2 g L^{-1}; higher catalyst concentrations did not further improve the yields. The reaction resulted dependent on the amount of sacrificial agent. Fig. 3c evidences that H_2 evolved by the system gradually increased as function of the CLS amount, reaching a plateau above 6.7 g L^{-1}.

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_2 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^{-1} catalyst, 6.7 g L^{-1} 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^{-1}, Cl^- 5.65×10^{-1} M, SO_4^{2-} 2.75×10^{-2} M, HCO_3^- 2.4×10^{-3} M, Na^+ 4.70×10^{-1} M, K^+ 10^{-2} M, Ca^{2+} 10^{-2} M, Mg^{2+} 5.5×10^{-2} 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 composition 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_2 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_2 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^{-1} catalyst) are reported in Fig. 4.

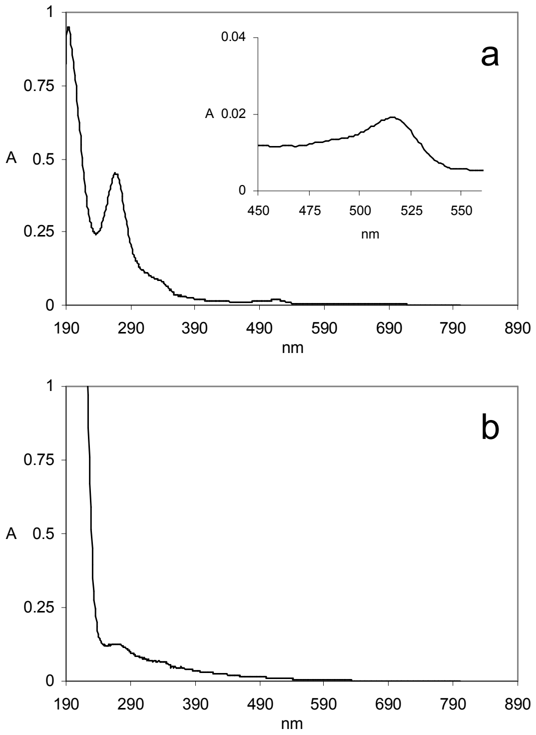

Fig. 4 UV-Vis spectra collected on the aqueous fraction from (a) the CLS suspension after irradiation (2 g L^{-1} catalyst, 4 h UV-A) and from (b) the control sample (2 g L^{-1} catalyst, 4 h dark).

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 their appreciable content of CLS[30,31] 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 with respect to 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 use of milled/sieved rice husk suppressed H_2 evolution (up to ca. 60%), likely due to the saturation of radiation absorption and/or light scattering phenomena.[28] 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.[32] Indeed, the photocatalytic conversion of CLS into HMF requires a solubilisation step in concentrated $ZnCl_2$ aqueous solution to take place gradually.[32]

In the present work it has been experimentally observed that CLS can be step-by-step solubilised (depolymerised) in aqueous Pt/TiO_2 suspension under both UV-A and solar light radiation, giving rise to water-soluble byproducts characterized by reducing properties. The process is accompanied by the simultaneous evolution of gas phase H_2 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,[16] the degradation is obviously not quantitative but nonetheless sufficient to sustain the process. Indeed, it is documented that CLS degradation in presence of TiO_2 photocatalyst is favored in aerobic media due to the key role played by $O_2^{-\cdot}$.[32] The results above reported clearly indicate that CLS behaves as sacrificial agent, appreciably increasing the H_2 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_2SO_4 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_2 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.

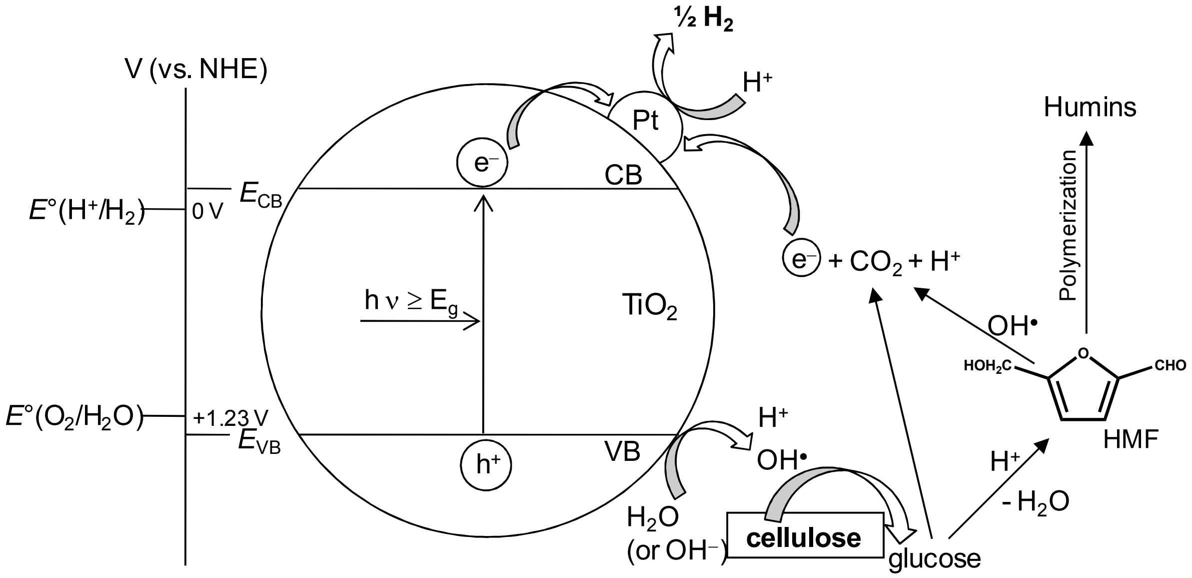

Fig. 5 Schematic representation of the photocatalytic system for the H_2 evolution by water splitting over irradiated Pt/TiO_2 in the presence of cellulose as the sacrificial agent.

This schematically shows the main steps involved in the reaction that leads to H_2 evolution from water, carried out over Pt/TiO_2 at room temperature and atmospheric pressure, in the presence of cellulose as the sacrificial agent. The mechanism of the photocatalytic process on TiO_2 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:[7,20]

$H_2O + 2\ h^+ \Rightarrow \frac{1}{2}\ O_2 + 2\ H^+$ (oxidation of water) (1)

$2\ H^+ + 2\ e^- \Rightarrow H_2$ (hydrogen ion reduction) (2)

$H_2O \Rightarrow H_2 + \frac{1}{2}\ O_2$ (overall reaction) (3)

Using TiO_2 semiconductor, these reactions are possible because the CB potential is more negative than the H^+ 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.[7]

Since the overall water splitting reaction is thermodynamically extremely difficult because is highly endergonic, addition of sacrificial agents (able to combine with h^+ more efficiently than water) is required to enhance H_2 evolution.[20] As shown in Fig. 5, CLS acts as scavenger for the VB holes and/or the HO• (generated by reaction of water with the holes) undergoing oxidative degradation. Indeed, as in the case of other sacrificial agents, for instance glucose[27] or glycerol,[33] organic substrates act as sacrificial agent by removing rapidly and irreversibly h^+, oxidant species (e.g. HO•) and/or O_2 produced by cleavage of water. This results in suppression of charge carriers recombination and/or O_2-H_2 back reaction,[20,33] providing at the same time electrons to the TiO_2 CB or directly to the Pt islands deposited on the catalyst surface (current doubling effect[26]) that are the active sites for the reduction of water hydrogen ions;[7,16,26] 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.[7] As expectable,[7,27] no detectable amounts of H_2 were generated in the presence of bare TiO_2 (see Table 1).

In order to assess the potential contribution of CLS aqueous phase reforming (APR) to the H_2 evolution from the present system, further experiments were conducted in presence on Raney Ni instead of Pt, as the former is known to be an excellent C-C cleavage catalyst used for APR.[34] The evolved H_2 was around 1 micromole (RSD <10%, *n*=3) in presence of TiO_2 and Raney Ni, while no H_2 was detected using Raney Ni, omitting TiO_2. Under the same experimental conditions, 54 micromoles of H_2 were obtained over Pt/TiO_2 (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_2 evolution from the biomass APR can be considered negligible. This confirms that water splitting over Pt/TiO_2 in presence of CLS as the sacrificial agent is the main pathway for H_2 evolution from water, that involves reduction of water hydrogen ions on Pt.

Along with the O_2 expectable to be evolved by water splitting (but not detected in the headspace after sample irradiation, due to its reaction with the sacrificial biomass[20]), the HO• and h^+ 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 resulted from the analytical reports, the latter was found in the aqueous solution after irradiation and was confirmed by HPLC-ESI-MS/MS analysis (see Supplementary Data). Indeed, the acidic sites of TiO_2 are able to catalyze dehydration of glucose to give HMF and the corresponding oligomers, viz. humins.[35] The photogenerated soluble species have higher effective molarity and quicker diffusion in the solution.[27] This means that CLS byproducts can enter in intimate contact with the catalyst surface, thus behaving as electrondonor 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 electrondonor; being readily oxidized to CO_2 it favors the reduction of the water hydrogen ions.

The mean H_2/CO_2 molar ratio experimentally found was 2.1 (RSD 4.8%, n=3), that is very near to the theoretical value of glucose photoreforming,[27] according to equation (4):

$$C_6H_{12}O_6 + 6\ H_2O \Rightarrow 6\ CO_2 + 12\ H_2 \qquad (4)$$

This further demonstrates that CLS undergoes depolymerisation, being converted into glucose, which is one of the most efficient sacrificial agents for H_2 photocatalytic production from water.[20] Comparison with the results obtained under the same conditions on aqueous glucose (3.5×10^{-3} M) allowed to evaluate the degree of conversion of the biopolymer. Similar yields were obtained with 10 mg of glucose and 200 mg CLS (49 µmoles and 54 µmoles H_2, respectively). In the reasonable hypothesis that the H_2 from the CLS water sample derives from hydrogen ions 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 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.[36]

The partial CLS depolymerization here observed is anyway noteworthy in terms of H_2 yield. In this context, it should be considered that the rate of hydrogen evolution from water decreases with increasing molecular weights of carbohydrates.[7] In fact, Fu et al.[27] reported H_2 yields in the soluble order starch < sucrose < glucose, and showed that microwave-assisted hydroxylation of the soluble starch prior the photocatalytic step enhances the overall yield. Though with yields lower than those from ethanol or glucose, it should be remarked that H_2 is here obtained using a raw biomass, that 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 at ambient conditions is of tremendous practical importance, because of significant cost savings resulting from decrease of the required steps compared to existing technologies (e.g. no need for hydrolysis, fermentation etc.).[16]

As above reported, the reaction proceeds also under solar light, with yields up to 87% with respect to UV radiation (see Table 1). The consistent H_2 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 water turns yellow-colored). The absorbance of the solution is ascribable to the spontaneous generation of HMF oligomers,[35,37,38] as shown in Fig. 5. It is reasonable to hypothesize a sort of "in situ dye-sensitization" that expands the activity of Pt/TiO_2 in the visible region. The photogenerated byproducts are water-soluble and therefore can easily adsorb to the catalyst surface, thus promoting a charge transfer to the TiO_2 conduction band and/or to the platinum islands.[17] In fact, dye-sensitized photocatalytic systems require the dye molecules to be linked/adsorbed to the catalyst surface to effectively inject electrons into the semiconductor conduction band for water reduction.[7,17] Evidently, the CLS-oxidation byproducts have suitable ground (HOMO) and excited (LUMO) states for the efficient electron transfer.[39]

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^{-2} 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^{-1} catalyst), further supporting the degradation pathway shown in Fig. 5.

The amount of evolved H_2 in 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 contain lignin (ca. 22%) and an inorganic fraction (silicates, ca. 14%).[30] 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%, inorganics 0.3%.[31]

The results suggest that lignin does not interfere in the process. Moreover, since lignin is highly recalcitrant towards TiO_2 degradation, requiring oxygen-saturated media to be decomposed,[40] it is reasonable to assume that under the applied conditions cannot behave as an efficient HO• scavenger; therefore the H_2 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_2 (RSD<8%, *n*=3), therefore a H_2 evolution of ca. 40 L could be obtained from 1 m^3 water. Considering the actual Pt content of the catalyst (0.32 wt%), 6.4 g Pt should be used to process 1 m^3 water sample, thus 1.8 g Pt would be necessary to obtain 1 g H_2. Irradiation under natural solar light would provide ca. 33 L H_2 per m^3 water, requiring ca. 2 g Pt. These values are very significant if compared to the H_2 production yield achievable through enzymatic conversion of CLS for hydrogen photoproduction,[5] where 8.1 g Pt are estimated to be required to attain 1 g H_2.

The use of vegetal tissues, rice husk in particular, could provide 18 and 15 L H_2 per m^3 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 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_2 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 costless polysaccharide, is photocatalytically solubilised (depolymerised) forming water-soluble products that have good reducing properties and undergo the typical photoreforming of glucose, promoting water hydrogen ions 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_2 evolved by the system does not contribute to the greenhouse effect because is part of a natural cycle (in nature CLS is built up by using atmospheric carbon dioxide);

7. H_2 is also evolved under solar radiation in the presence of waste cellulosic biomasses (i.e. rice husk).

Acknowledgement

The authors are indebted to Dr. Alessandro Granata (LabAnalysis S.r.l, Casanova Lonati, Pavia, Italy) for the HPLC-ESI-MS/MS measurements.

References

1 P. Azadi, S. Khan, F. Strobel, F. Azadi and R. Farnood, Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts, *Appl. Cat. B: Environ.*, 2012, **117-118**, 330.

2 Y. Lu, X. Y. Wei, Z. Wen, H. B. Chen, Y. C. Lu, Z. M. Zong, J. P. Cao, S. C. Qi, S. Z. Wang, L. C. Yu, W. Zhao, X. Fan and Y. P. Zhao, Photocatalytic depolymerization of rice husk over TiO_2 with H_2O_2, *Fuel Process. Technol.*, 2014, **117**, 8.

3 L. R. Lynd, P. J. Weimer, W. H. Zyl and I. S. Pretorius, Microbial cellulose utilization: fundamentals and biotechnology, *Microbiol. Mol. Biol. Rev.*, 2002, **66**, 506.

4 S. Xiao, B. Liu, Y. Wang, Z. Fang and Z. Zhang, Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide-ionic liquid mixtures, *Biores. Technol.*, 2014, **151**, 361.

5 N. Himeshima and Y. Amao, Green process for hydrogen production from cellulose derivative using visible light-harvesting function of Mg chlorophyll-*a*, *Green Chem.*, 2005, **7**, 742.

6 S. I. Gadow, Y. Y. Li and Y. Liu, Effect of temperature on continuous hydrogen production of cellulose, *Int. J. Hydrogen Energy*, 2012, **37**, 15465.

7 D. Y. C. Leung, X. Fu, C. Wang, M. Ni, M. K. H. Leung, X. Wang and X. Fu, Hydrogen production over titania-based photocatalysts, *ChemSusChem*, 2010, **3** 681.

8 A. Melis, Green alga hydrogen production: progress, challenges and prospects, *Int. J. Hydrogen Energy*, 2002, **27**, 1217.

9 M. L. Cai, J. X. Liu and Y. S. Wei, Enhanced biohydrogen production from sewage sludge with alkaline pretreatment, *Environ. Sci. Technol.*, 2004, **38**, 3195.

10 N. Serpone, A. V. Emeline and S. Horikoshi, in *Photochemistry*, ed. A. Albini, RSC, London, 2009, pp. 300-361.

11 M. Cargnello, A. Gasparotto, V. Gombac, T. Montini, D. Barreca and P. Fornasiero, Photocatalytic H_2 and added-value by-products – The role of metal oxide systems in their synthesis from oxygenates, *Eur. J. Inorg. Chem.*, 2011, **2011**, 4309.

12 M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, *Appl. Cat. B: Environ.,* 2012, **125**, 331.

13 G. Rammohan and M. N. Nadagouda, Green photocatalysis for degradation of organic contaminants: a review, *Curr. Org. Chem.*, 2013, **17**, 2338.

14 M. Sturini, A. Speltini, F. Maraschi, A. Profumo, L. Pretali, E. A. Irastorza, E. Fasani and A. Albini,Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight, *Appl. Cat. B: Environ.*, 2012, **119-120**, 32.

15 M. Sturini, E. Rivagli, F. Maraschi, A. Speltini, A. Profumo and A. Albini, Photocatalytic reduction of vanadium(V) in TiO_2 suspension: chemometric optimization and application to wastewaters, *J. Hazard. Mater.*, 2013, **254-255**, 179.

16 D. I. Kondarides, V. M. Daskalaki, A. Patsoura and X. E. Verykios, Hydrogen production by photo-induced reforming of biomass components and derivatives at ambient conditions, *Catal. Lett.*, 2008, **122**, 26.

17 Y. Li, C. Xie, S. Peng, G. Lu and S. Li, Eosin Y-sensitized nitrogen-doped TiO_2 for efficient visible light photocatalytic hydrogen evolution, *J. Mol. Catal. A: Chem.*, 2008, **282**, 117.

18 M. de Oliveira Melo and L. Almeida Silva, Visible light-induced hydrogen production from glycerol aqueous solution on hybrid Pt-CdS-TiO_2 photocatalysts, *J. Photochem. Photobiol. A: Chem.*, 2011, **226**, 36.

19 D. Chatterjee, Effect of excited state redox properties of dye sensitizers on hydrogen production through photo-splitting of water over TiO_2 photocatalyst, *Catal. Commun.*, 2010, **11**, 336.

20 M. Bowker, Photocatalytic hydrogen production and oxygenate photoreforming, *Catal. Lett.*, 2012, **142**, 923.

21 A. V. Vorontsov, I. V. Stoyanova, D. V. Kozlov, V. I. Simagina and E. N. Savinov, Kinetics of the photocatalytic oxidation of gaseous acetone over platinized titanium dioxide, *J. Catal.*, 2000, **189**, 360.

22 L. Kavan, T. Stoto, M. Gratzel, D. Fitzmaurice and V. Shklover, Quantum size effects in nanocrystalline semiconducting TiO_2 layers prepared by anodic oxidative hydrolysis of $TIC1_3$, *J. Phys. Chem.*, 1993, **97**, 9493.

23 D. Blanco Gomis, M. D. Gutiérrez Alvarez, L. Sopeña Naredo and J. J. Mangas Alonso, High-performance liquid chromatographic determination of furfural and hydroxymethylfurfural in apple juices and concentrates, *Chromatographia*, 1991, **32**, 45.

24 EPA method 1667, available at http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_1667.pdf

25 T. Chen, Z. Feng, G. Wu, J. Shi, G. Ma, P. Ying and C. Li, Mechanistic studies of photocatalytic reaction of methanol for hydrogen production on Pt/TiO_2 by in situ Fourier transform IR and time-resolved IR spectroscopy, *J. Phys. Chem. C*, 2007, **111**, 8005.

26 T. A. Kandiel, R. Dillert, L. Robben, D. W. Bahnemann, Photonic efficiency and mechanism of photocatalytic molecular hydrogen production over platinized titanium dioxide from aqueous methanol solutions, *Catal. Today*, 2011, **161**, 196.

27 X. Fu, J. Long, X. Wang, D. Y. C. Leung, Z. Ding, L. Wu, Z. Zhang, Z. Li and X. Fu, Photocatalytic reforming of biomass: a systematic study of hydrogen evolution from glucose solution, *Int. J. Hydrogen Energy*, 2008, **33**, 6484.

28 H. Kisch, On the problem of comparing rates or apparent quantum yields in heterogeneous photocatalysis, *Angew. Chem. Int. Ed.*, 2010, **49**, 9588.

29 A. Speltini, M. Sturini, F. Maraschi, D. Dondi, A. Serra, A. Profumo, A. Buttafava, A. Albini, Swine sewage as sacrificial biomass for photocatalytic hydrogen gas production: explorative study, *Int. J. Hydrogen Energy*, in press http://dx.doi.org/10.1016/j.ijhydene.2014.05.168.

30 P. S. Kumar, K. Ramakrishnan, S. D. Kirupha and S. Sivanesan, Thermodynamic and kinetic studies of cadmium adsorption from aqueous solution onto rice husk, *Braz. J. Chem. Eng.*, 2010, **27**, 347.

31 J. M. F. Johnson, N. W. Barbour and S. Lachnicht Weyers, Chemical composition of crop biomass impacts its decomposition, *Soil Sci. Soc. Am. J.*, 2007, **71**, 155.

32 H. Fan, G. Li, F. Yang, L. Yang and S. Zhang, Photodegradation of cellulose under UV light catalysed by TiO_2, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 1107.

33 V. M. Daskalaki and D. I. Kondarides, Efficient production of hydrogen by photo-induced reforming of glycerol at ambient conditions, *Catal. Today*, 2009, **144**, 75.

34 B. Meryemoglu, A. Hesenov, S. Irmak, O. M. Atanur, O. Erbatur, Aqueous-phase reforming of biomass using various types of supported precious metal and raney-nickel catalysts for hydrogen production, *Int. J. Hydrogen Energy*, 2010, **35**, 12580.

35 C. H. Kuo, A. S. Poyraz, L. Jin, Y. Meng, L. Pahalagedara, S. Y. Chen, D. A. Kriz, C. Guild, A. Gudz and S. L. Suib, Heterogeneous acidic TiO_2 nanoparticles for efficient conversion of biomass derived carbohydrates, *Green Chem.*, 2014, **16**, 785.

36 J. Burana-osot, N. Soonthornchareonnon, S. Hosoyama, R. J. Linhardt and T. Toida, Partial depolymerization of pectin by a photochemical reaction, *Carbohydr. Res.*, 2010, **345**, 1205.

37 F. Wang, A. W. Shi, X. X. Qin, C. L. Liu and W. S. Dong, Dehydration of fructose to 5-hydroxymethylfurfural by rare earth metal trifluoromethanesulfonates in organic solvents, *Carbohydr. Res.*, 2011, **346**, 982.

38 I. van Zandvoort, Y. Wang, C. B. Rasrendra, E. R. H. van Eck, P. C. A. Bruijnincx, H. J. Heeres and B. M. Weckhuysen, Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions, *ChemSusChem*, 2013, **6**, 1745.

39 R. Abe, K. Sayama and H. Arakawa, Dye-sensitized photocatalysts for efficient hydrogen production from aqueous I^- solution under visible light irradiation, *J. Photochem. Photobiol. A: Chem.*, 2004, **166**, 115.

40 H. Ohnishi, M. Matsumura, H. Tsubomura and M. Iwasaki, Bleaching of lignin solution by a photocatalyzed reaction on semiconductor photocatalysts, *Ind. Eng. Chem. Res.*, 1989, **28**, 719.