Assessment of photocatalytic production of hydrogen from biomass or wastewaters depending on the metal co-catalyst and its deposition method on TiO_2

Mikel Imizcoz, Alberto V. Puga*[‡]

Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos, s/n, 46022 Valencia, Spain.

[‡] Current address: Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. dels Països Catalans, 26, 43007 Tarragona, Spain

alberto.puga@urv.cat

Supporting Information

Table S1. Product yields for the photocatalytic reforming of glucose under simulated solar light on *M*/TiO_2.[a,b]

Photocatalyst	Production rate/μmol g_{cat}^{-1} h^{-1}		TOF[c]/s^{-1}
	H_2	CO_2	H_2
$^{H,DP}Au/TiO_2$	993.8	73.8	1171
$^{H,DP}Ag/TiO_2$	320.2	17.0	298
$^{H,DP}Cu/TiO_2$	560.4	59.0	44
$^{H,DP}Pt/TiO_2$	1706.9	250.3	306
$^{PD}Au/TiO_2$	905.6	83.8	2169
$^{PD}Ag/TiO_2$	402.4	30.7	796
$^{PD}Cu/TiO_2$	904.3	56.3	134
$^{PD}Pt/TiO_2$	1912.7	158.2	1353
$^{IM}Au/TiO_2$	298.3	10.3	5993
$^{IM}Ag/TiO_2$	203.8	13.2	1099
$^{IM}Cu/TiO_2$	259.3	23.0	27
$^{IM}Pt/TiO_2$	157.1	29.6	52

[a] Stirred suspensions of the photocatalyst (25 mg) in aqueous glucose (5% *w*/*v*, 25 mL) were irradiated under simulated solar light (AM1.5G, 1.0 kW m^{-2}) under Ar atmosphere (1.4 bar) at 25 °C for 2 h. [b] Estimated standard deviations for H_2 production rates lie within a ± 5% error bar, as determined by independent results. [c] The activities per active site (TOF) were calculated according to the average co-catalyst particle size as listed in Table 1, assuming semi-spherical morphology and {111} facet surface atom densities.

Table S2. Hydrolysis of α-cellulose in acidic aqueous media in short thermal cycles at different temperatures.[a]

T/°C	cycle	yield/%[b]				global saccharide yield/%[c]	conversion/%[d]	molar balance/%[d]
		glucose	xylose	HMF	furfural			
160	#1	7.6	67.4	-	-	18.3	21.5	96.8
	#2	4.8	18.4	-	-	7.2	30.6	94.9
	#3	3.7	7.8	-	-	4.5	35.0	95.0
	overall	*16.2*	*93.6*	-	-	*29.9*	*35.0*	*95.0*
180	#1	9.1	22.2	4.3	23.9	11.5	41.3	77.9
	#2	4.9	10.0	2.6	2.1	6.5	59.2	69.0
	#3	3.0	7.0	2.0	0.5	4.2	70.3	63.8
	overall	*17.1*	*39.2*	*8.9*	*26.6*	*22.1*	*70.3*	*63.8*

concentrations of biomass-derived oxygenated substances in the hydrolysate used for photocatalytic H_2 production experiments

		c/%(*w*/*v*)			
160	#1	0.53	0.85	-	-
		c/%(mM)			
160	#1	29.5	56.5	-	-

[a] Reaction conditions: α-cellulose (6.00 g) in aqueous HCl (1% *w*/*v*, 60 mL), N_2 atmosphere, heated to the specified temperature (ramp ≈ 10 °C min^{-1}) and then, allowed to cool down naturally to room temperature. [b] Yields relative to the expected amounts of either glucose or xylose (≈ 85:15 *w*/*w*) units in the starting α-cellulose, as determined by HPLC using an Aminex® HPX-87H column. [c] Global yields relative to the total amount of saccharide units in the starting α-cellulose. [d] Conversions and molar balances are cumulative.

Table S3. Product yields for the photocatalytic reforming of the α-cellulose hydrolysate obtained after a first hydrolysis cycle at 160 °C[a] under simulated solar light[b] either directly or after UV pre-treatment[c] on *M*/TiO_2

Photocatalyst	Production rate/µmol g_{cat}^{-1} h^{-1}	
	H_2	CO_2
simulated sunlight irradiation on raw hydrolysate		
$^{H,DP}Au/TiO_2$	< 0.1	64.1
$^{PD}Pt/TiO_2$	0.2	75.8
$^{H,DP}Cu/TiO_2$	0.1	129.3
UV pre-treatment on raw hydrolysate		
$^{H,DP}Cu/TiO_2$	17.3	125.8
simulated sunlight irradiation on after UV pre-treatment		
$^{H,DP}Cu/TiO_2$	2.9	93.4

[a] Hydrolysis conditions at 160 °C (cycle #1) as described in Table S2. [b] Stirred suspensions of the photocatalyst (25 mg) in α-cellulose hydrolysate (25 mL) were irradiated under simulated solar light (AM1.5G, 1.0 kW m^{-2}) under Ar atmosphere (1.4 bar) at 25 °C for 2 h. [c] Irradiated by a similar procedure as described in [b] for simulated sunlight, but using an Hg lamp (125 W, ≈ 1.5 kW m^{-2}). [e] Determined by HPLC using an Aminex® HPX-87H column.

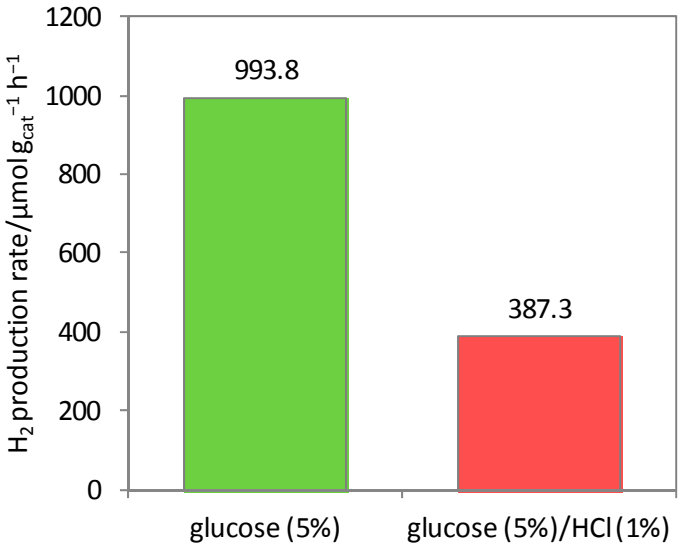

Figure S1. Photocatalytic H_2 yields from aqueous glucose at either natural pH or in an HCl-acidified medium on $^{H,DP}Au/TiO_2$. Stirred suspensions of the photocatalyst (25 mg) in aqueous glucose (5% *w*/*v*, 25 mL, without or with HCl, 1% *w*/*v*) irradiated under simulated solar light (AM1.5G, 1.0 kW m^{-2}) under Ar atmosphere (1.4 bar) at 25 °C for 2 h.

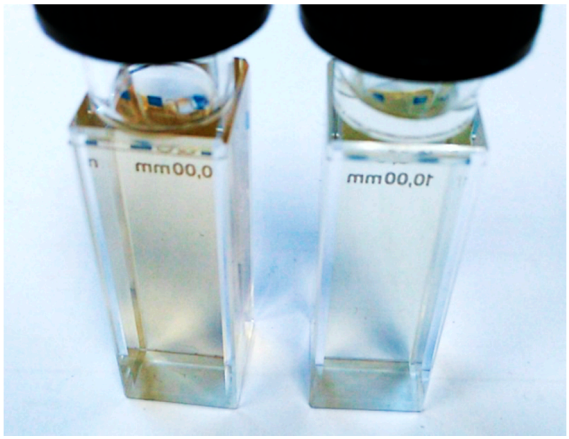

Figure S2. Picture showing the amber colour of the α-cellulose hydrolysate (left) obtained at 160 °C (cycle #1, see Table S2 footnote), and the bleaching effect caused by the UV photocatalytic treatment leading to an almost colourless solution (right).

Table S4. Chemical characteristics of the rice husks hydrolysate,[a] and wastewaters used in photocatalytic experiments.

biomass hydrolysate or wastewaters	*c*/%(*w*/*v*)[b]					COD[c]/ mg L^{-1}	[N][d]/ mg L^{-1}	σ[e]/ µS cm^{-1}
	sucrose	glucose	xylose	HMF	furfural			
rice husks hydrolysate	-	0.27	0.88	< 0.01	0.02	≈ 10^3 [f]	-	-
municipal wastewater	-	< 0.01	-	-	-	389	25	2130
juice production wastewater	0.02	0.04	0.03	-	-	≈ 10^2 [f]	-	2850

[a] Reaction conditions: milled rice husks (6.00 g) in an aqueous solution of concentrated HCl (1% *w*/*v*, 60 mL), N_2 atmosphere, heated to the specified temperature (ramp ≈ 10 °C min^{-1}) and then, allowed to cool down naturally to room temperature. [b] Determined by HPLC using an Aminex® HPX-87H column. [c] COD: Chemical Oxygen Demand. [d] The major N species was $[NH_4]^+$. [e] Conductivity (σ) measured using a Crison CM 35 device and a Crison + Pt 1000 Conductivity Cell. [f] Estimated from HPLC data.

Table S5. Product yields for the photocatalytic reforming of wastewaters under simulated solar light[a] on *M*/TiO_2

Photocatalyst	Production rate/µmol g_{cat}^{-1} h^{-1}	
	H_2	CO_2
municipal wastewater		
^{H,DP}Au/TiO_2	< 0.1	15.8
^{H,DP}Cu/TiO_2	0.1	18.2
juice production wastewater		
^{H,DP}Au/TiO_2	115.1	306.9
^{H,DP}Cu/TiO_2	10.7	291.2

[a] Stirred suspensions of the photocatalyst (25 mg) in the corresponding wastewater (25 mL) were irradiated under simulated solar light (AM1.5G, 1.0 kW m^{-2}) under Ar atmosphere (1.4 bar) at 25 °C for 2 h.