

Supplementary Information

Exploiting rice industry wastewater for a more sustainable sunlight-driven photocatalytic hydrogen production using a graphitic carbon nitride polymorph

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Table S1 Chemical and physical-chemical parameters of the rice industry wastewater.

pH	4.31
$\chi_{25^\circ\text{C}}$ ($\mu\text{S}/\text{cm}$)	392
Cl^- (mg/L)	3.5
NO_3^- (mg/L)	< 0.5
SO_4^{2-} (mg/L)	1.3
F^- (mg/L)	< 0.1
Ca^{2+} (mg/L)	37.7
Mg^{2+} (mg/L)	10.1
Sr^{2+} (mg/L)	0.14
Na^+ (mg/L)	14.6
K^+ (mg/L)	5.8
SiO_2 (mg/L)	29.1
Fe (mg/L)	0.16
Mn (mg/L)	0.02
COD (mg/L)	4650
Glucose (mg/L)	1540
Acetic acid (mg/L)	123
Formic acid (mg/L)	49
Suspended solids (g/L)	2.8

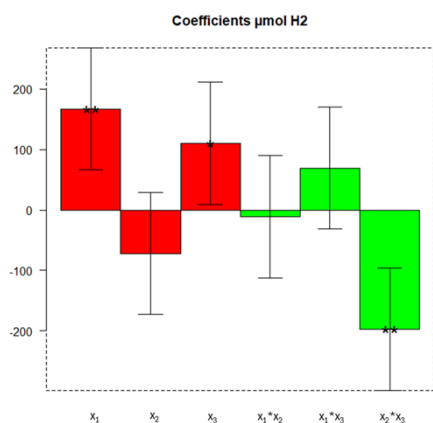
Table S2 Experimental domain for the 2³ factorial design in glucose standard solution.

	Levels	
	-1	+1
Glucose concentration (M), x_1	0.025	0.2
Catalyst concentration (g L ⁻¹), x_2	0.5	2
Pt loading (wt%), x_3	0.5	3

Exp.#	x_1 , glucose concentration (M)	x_2 , catalyst concentration (g/L)	x_3 , Pt loading (wt%)	HER
1	0.025	0.5	0.5	56
2	0.2	0.5	0.5	69
3	0.025	2	0.5	125
4	0.2	2	0.5	502
5	0.025	0.5	3	328
6	0.2	0.5	3	1028
7	0.025	2	3	16
8	0.2	2	3	263

Table S3 Experimental plan and mean HER ($n=2$) observed for each experiment in glucose standard solution.^a

^a the model, elaborated on these experimental data, is: $HER = 298 + 167x_1 - 72x_2 + 110x_3 - 11x_1x_2 + 70x_1x_3 - 197x_2x_3$; at the test point [$x_1 = 0$; $x_2 = 0$; $x_3 = 0$], which means 0.1125 M, 1.25 g L⁻¹ catalyst, 1.75 wt% Pt, a HER of $320 \pm 28 \mu\text{moles g}^{-1} \text{h}^{-1}$ ($p=0.05$, $n=4$) was experimentally obtained, not statistically different from the predicted value ($298 \mu\text{moles g}^{-1} \text{h}^{-1}$), therefore the model is validated.

**Fig. S1** Plots of the coefficients of the model where the stars indicate the significance of the coefficients (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$), while error bars indicate the confidence intervals ($p = 0.05$).

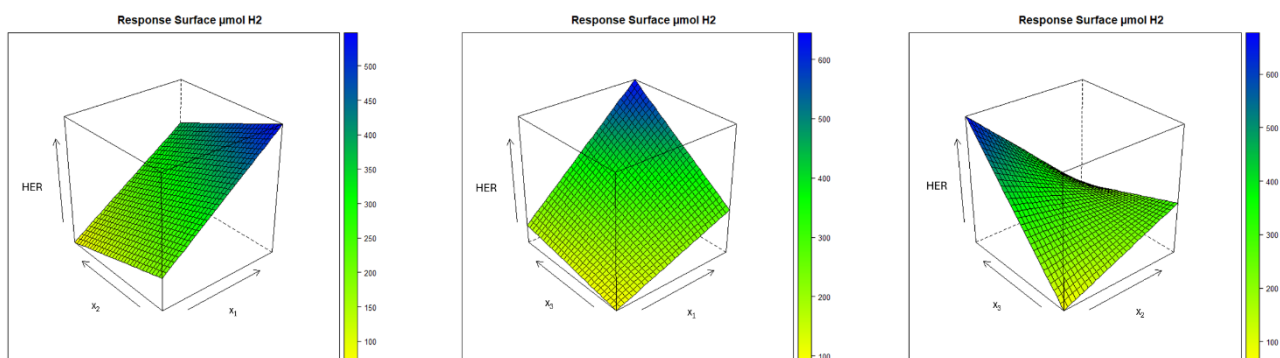


Fig. S2 Response surfaces obtained by CAT from the experimental results of the H₂ production from glucose aqueous solution.

Table S4. Experimental plan and mean HER ($n=2$) observed for each experiment in the rice industry wastewater.

Exp.#	X ₁ , waste dilution (v/v)	X ₂ , catalyst concentration (g/L)	X ₃ , Pt loading (wt%)	HER
1	1:2	0.5	0.5	49
2	-	0.5	0.5	60
3	1:2	2	0.5	26
4	-	2	0.5	42
5	1:2	0.5	3	67
6	-	0.5	3	148
7	1:2	2	3	5
8	-	2	3	33

Table S5. Organic compounds determined in the sample solution before and after photocatalysis.

	Concentration	
	Before	After
Glucose	1540 mg/L	122 mg/L
Acetic acid	123 mg/L	82 mg/L
Formic acid	49 mg/L	32 mg/L
Furfural	< 10 μg/L	41 μg/L
Methylfurfural	< 10 μg/L	< 10 μg/L
Hydroxymethylfurfural	< 10 μg/L	13 μg/L

Material characterization

The crystal structure of the samples has been characterized by room temperature Cu-radiation XRD acquired with Bruker D2 diffractometer. DRS spectra were acquired in the wavelength range 300-800 nm directly on the powders by using a Jasco V-750 spectrophotometer, equipped with an integrating sphere (Jasco ISV-922). Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, TESCAN Mira 3) operated at 25 kV. Transmission electron microscopy (TEM) was performed on a ZEISS LIBRA200FE equipped with a high-angle annular dark-field (HAADF) detector for STEM (scanning TEM) mode. The determination of band gap energy by using TAUC PLOT was done by plotting the value of $(\alpha h\nu)^{1/2}(\text{eV}/\text{cm})^2$ with Energy ($h\nu$), then followed by taking the extrapolation in the linear area across the energy axis in the corresponding graph. The insertion with energy-axis is the estimation of the corresponding energy gap.

Analytical methods

The measurements of the parameters reported in Table S1 were done following the methods reported in "Standard Methods for the Examination of Water and Wastewaters" APHA Editor, 22nd Edition".

Briefly:

- Conductivity was measured by a classic conductivity cell whose constant cell is periodically verified by a standard solution of KCl.
- Cl^- , NO_3^- , SO_4^{2-} , acetic and formic acids (as acetate and formate) were determined by anion exchange chromatography and chemical suppression of eluent conductivity. A Metrohm ECO IC chromatograph equipped with a conductivity detector using a Metrosep A Supp 5-250/4.0 Metrohm column (20×2.1 mm, $5 \mu\text{m}$). The mobile phase was 3.2 mM Na_2CO_3 -1 mM NaHCO_3 aqueous solution, 0.7 mL/min flow rate.
- F^- was measured by Ion fluoride selective electrode equipped with a standard calomel reference electrode.
- Ca^{2+} , Sr^{2+} , Mg^{2+} , K^+ , Na^+ , Si, Fe, Mn were determined by ICP-OES following the conventional manufacturer instructions; quantification was obtained by the external standard calibration with four standards prepared daily in the in 0,5% HNO_3 suprapure water solution.
- COD was determined by the amount of dichromate consumed, expressed in terms of its oxygen equivalents, in controlled conditions (see method 5220 B of the Standard Methods for the Examination of Water and Wastewaters "APHA Editor, 22nd Edition) by a proper volume of sample.
- Total suspended solids: A well-mixed sample was filtered through a weighed glass-fiber filter and the residue retained on the filter dried to a constant weight at 105°C .

Glucose, furfural, methylfurfural were quantified by UPLC-MS/QTOF: Agilent Metacarb 87C $300 \times 7,8$ mm column (85°C), 0.6 mL/min, eluent H_2O ; hydroxymethylfurfural by HPLC-UV: 280 nm, Scharlab Kroma Phase 100 C18 (250×4.6 mm, $5 \mu\text{m}$) column, mobile phase was ACN- H_2O (10:90, v/v), 1 mL/min.

The GC-TCD analysis of the photoreactor headspace was carried out by an Agilent 8860 instrument (Agilent Technologies Italia S.p.a., Cernusco s/N, Milan, Italy) equipped with thermal conductivity detector, using a Carbosieve S-II (80/100 mesh) packed column (2 mm i.d., 510 mm length), high-purity argon as the carrier gas (10 mL/min). The temperature program was 35°C for 3 min, from 35°C to 200°C at $20^\circ\text{C}/\text{min}$. The temperature of the injection port and the detector was 100°C and 140°C , respectively.