Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Photocatalytic Hydrogen Evolution by Co-Catalyst-Free TiO_2/C Bulk Heterostructures Synthesized under Mild Conditions

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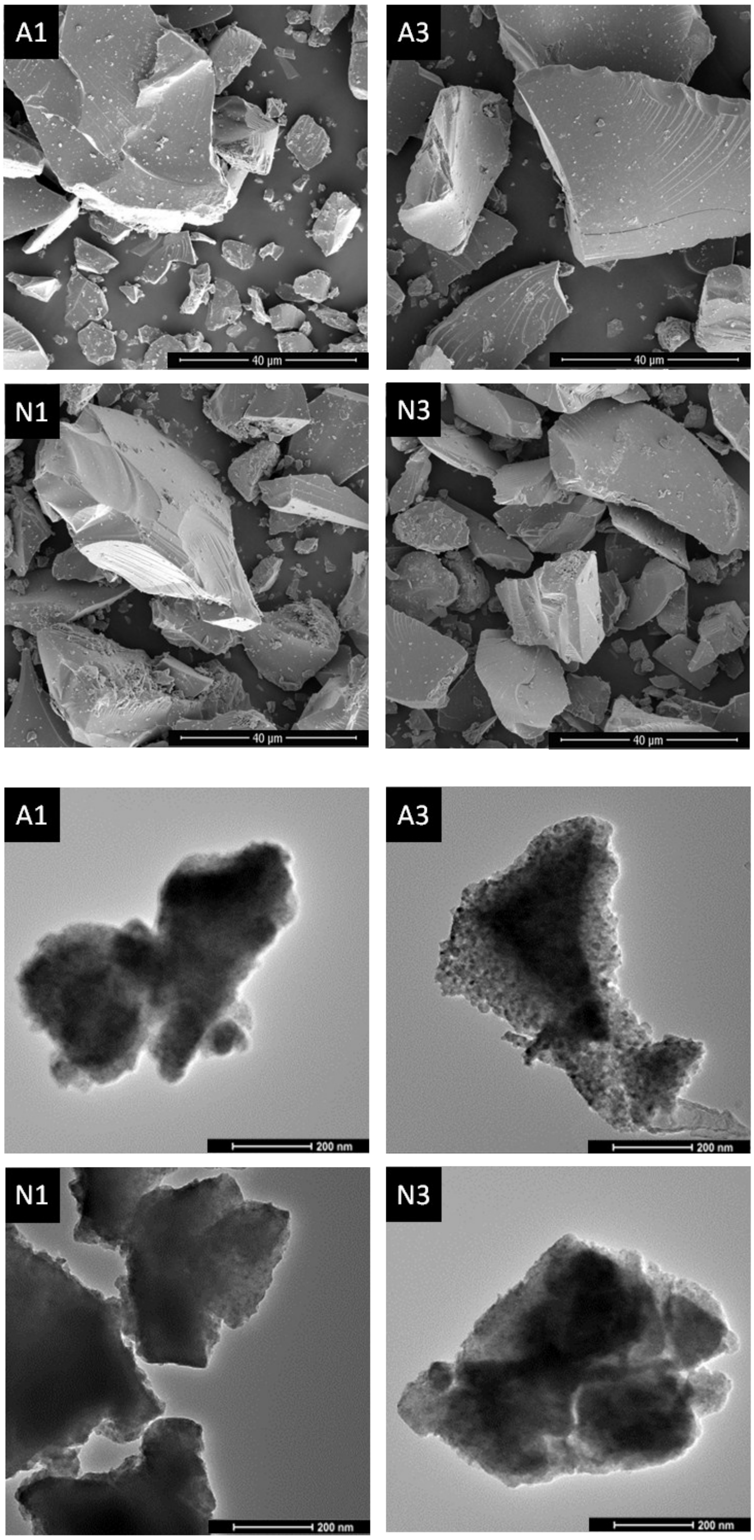

Figure S1. SEM images (top, scale bar = 40 µm) and TEM images (bottom, scale bar = 200 nm) of samples derived from HSGT-v dried gel annealed at 400 °C in air or nitrogen for 1 h or 3 h.

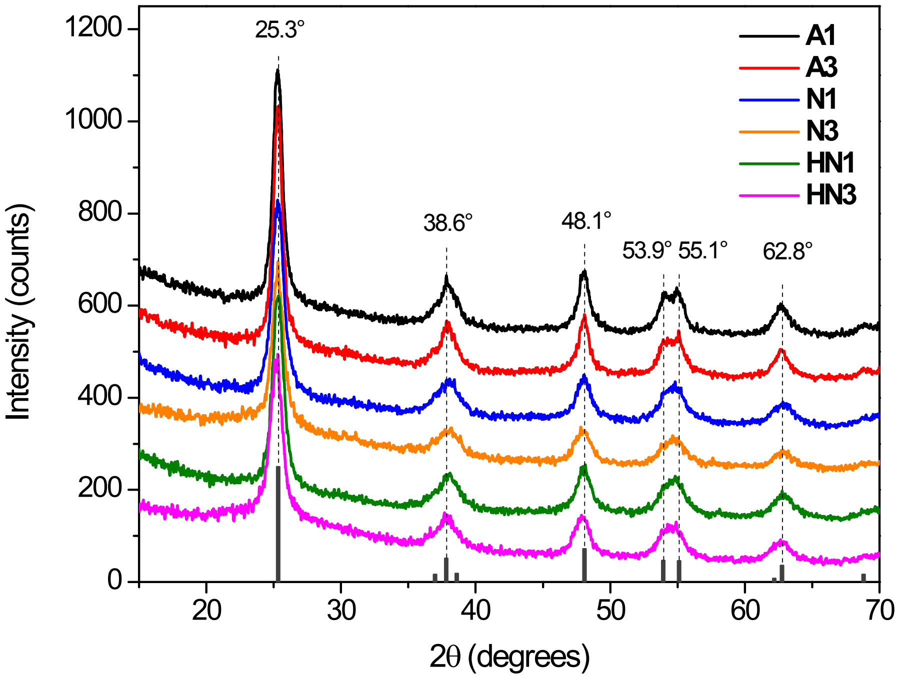

Figure S2. XRD profiles of the TiO_2 samples derived from HSGT-v dried gel annealed at 400 °C in different conditions. The XRD peaks of an anatase TiO_2 reference are shown as bars (from Howard et al., Acta Crystallographica B47 (1991) 462-468, in the American Mineralogist Crystal Structure Database, code amcsd 0019093).

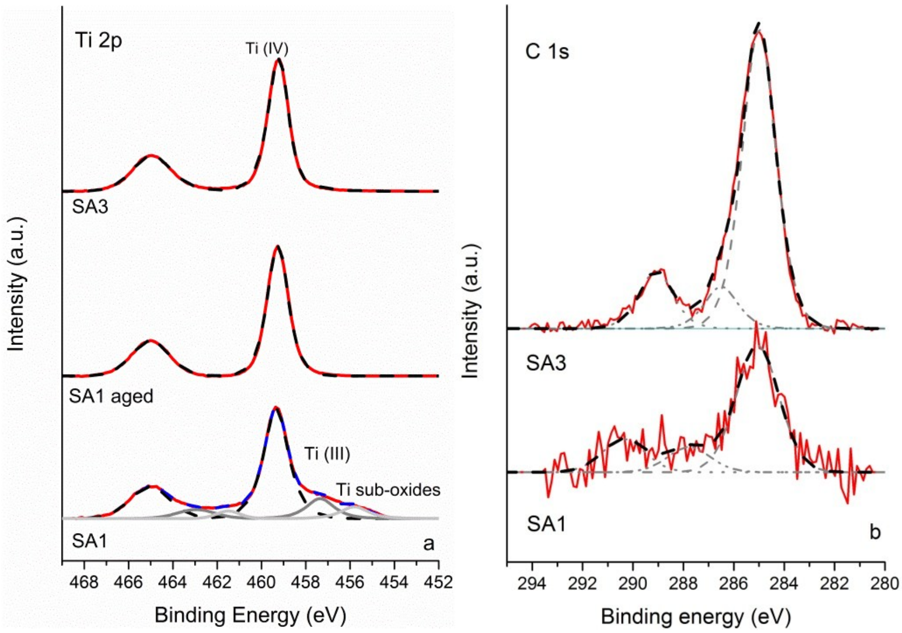

Figure S3. a) Ti 2p X-ray photoelectron spectra of HSGT samples annealed in air at 400 °C for 1 (SA1) and 3 h (SA3), and of SA1 sample after storage for about 2 years (SA1 aged); b) C 1s X-ray photoelectron spectra of HSGT samples annealed in air at 400°C for 1 (SA1) and 3 h (SA3).

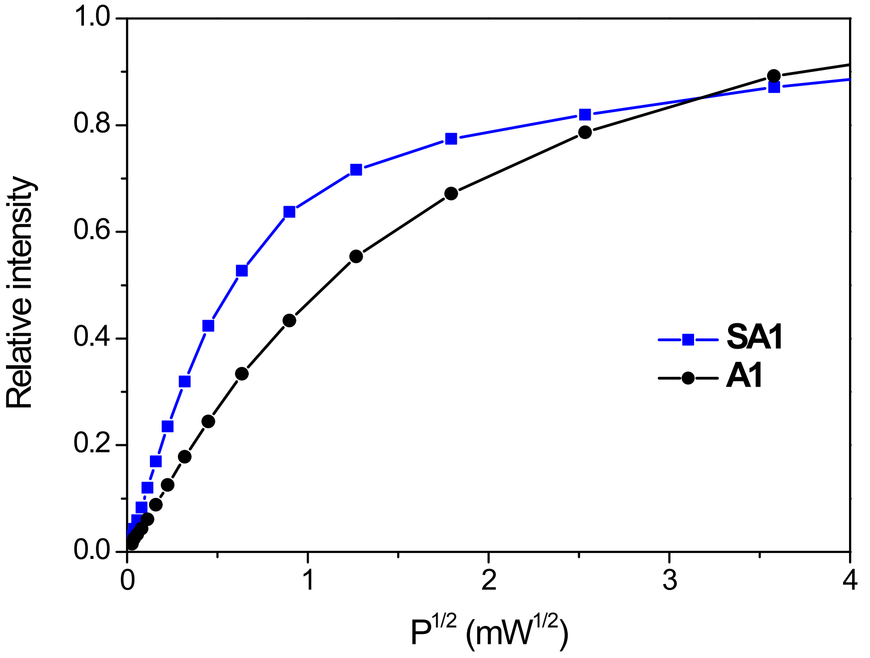

Figure S4. EPR microwave power saturation measurements on SA1 and A1 samples: relative intensity of the EPR signal as a function of the square root of the microwave power.

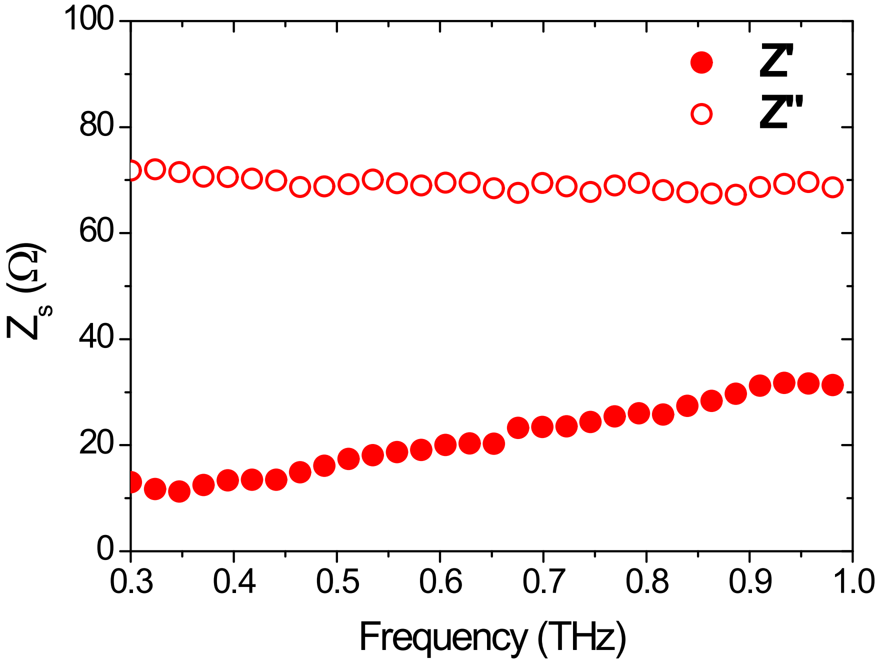

Figure S5. Real (Z') and imaginary (Z'') part of the surface impedance for the N3 sample as a function of frequency.

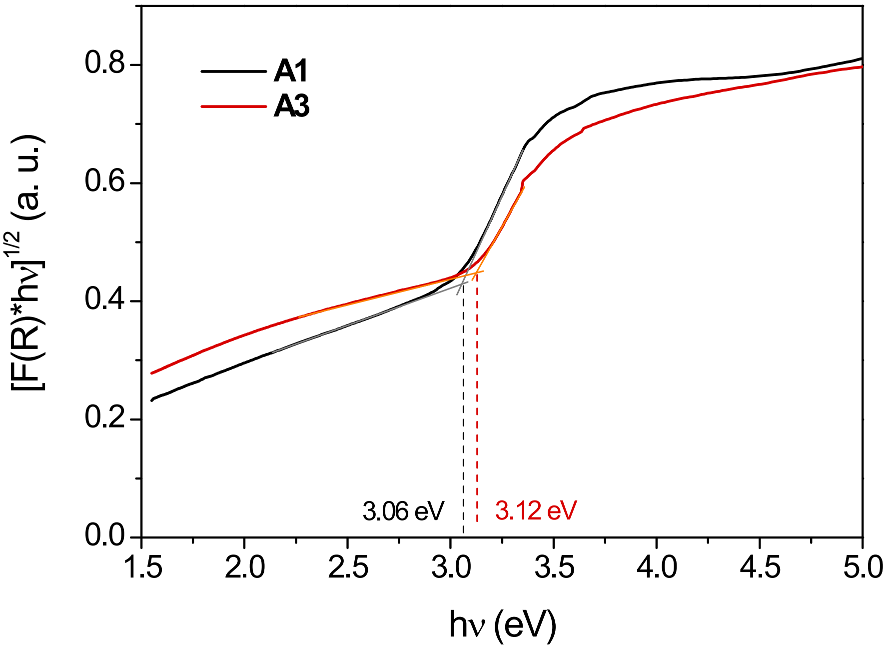

Figure S6. Tauc plot elaboration of UV-vis DRS spectra of A1 and A3 samples with band gap energy estimated values (indirect band gap).

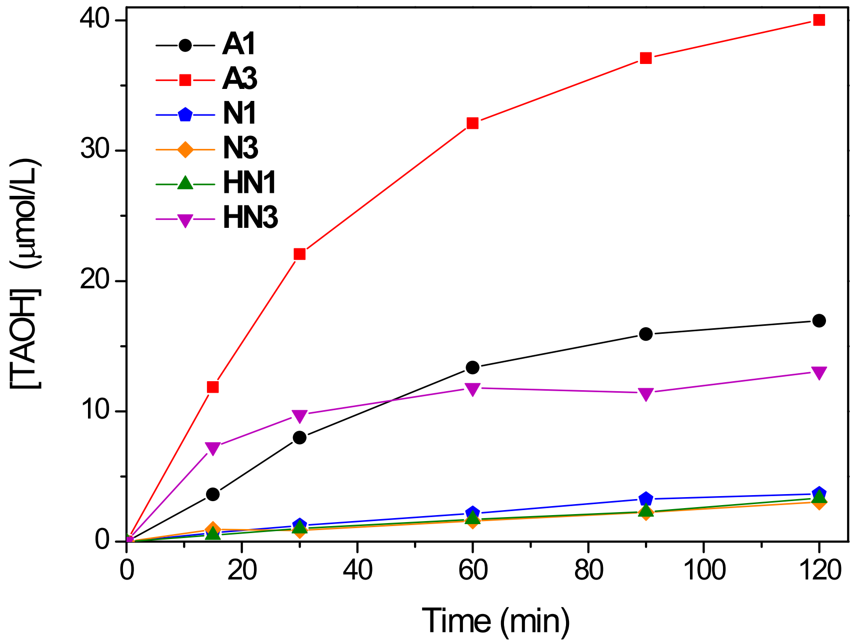

Figure S7. Concentration of hydroxyterephthalic acid (TAOH) produced during terephthalic acid (TA) photoxidation under UV/visible light irradiation (λ > 320 nm): $[TA]_0$ = 0.3 mmol/L; catalyst loading = 1 g/L.

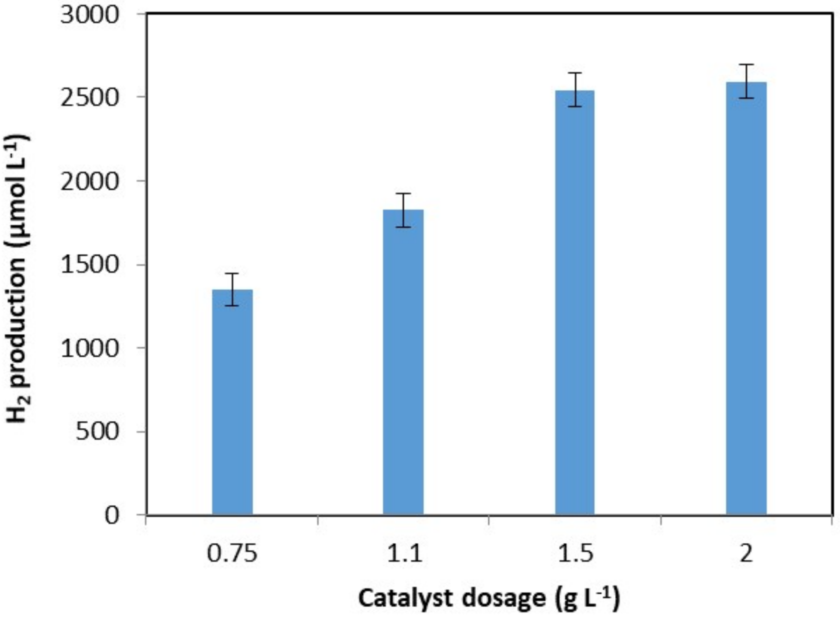

Figure S8. Photocatalytic H_2 production after 4 hours of UV irradiation at different catalyst dosages for N3 photocatalyst; initial glycerol concentration: 5 wt%; pH = 6.

Table S1. Curve-fitting parameters of the D and G signals of Raman spectra of HSGT-v annealed samples. Raman shift (Rs, cm^{-1}), full width at half maximum (FWHM, cm^{-1}) and integrated intensity (I, %). For Rs, FWHM and I standard errors are: ± 10 cm^{-1}, ± 8% and ± 1%, respectively.

	Peak 1			*Peak 2*			*Peak 3*			*Peak 4*			*Peak 5*		
	Rs	FWHM	I	Rs	FWHM	I	Rs	FWHM	I	Rs	FWHM	I	Rs	FWHM	I
A1	1260	67	1	1386	199	52	1497	89	7	1590	86	38	1630	110	1
N1	1212	127	12	1368	184	44	1552	146	19	1593	56	21	1605	117	4
N3	1220	131	13	1368	164	38	1547	180	26	1597	56	21	1610	120	2
HN1	1210	122	10	1370	192	46	1538	144	16	1596	58	22	1605	120	6
HN3	1190	108	4	1382	270	66	1539	74	7	1595	64	21	1650	87	3

Table S2. Binding energy values (eV ± 0.1) of the main photoelectron signals and binding energy of the valence band maxima (eV ± 0.2). Surface O/Ti atomic ratio estimated by XPS results (expected ratio: O/Ti = 2). Elemental carbon content (at%).

	SA3	**A1**	**A3**	**N1**	**N3**	**HN1**	**HN3**
Elemental C	-	284.2	284.2	284.2	284.2	284.2	284.2
C1s aliphatic	285.0	285.0	285.0	285.0	285.0	285.0	285.0
C-OH/C-OC	286.6	286.5	286.5	286.6	286.6	286.5	286.6
$R_2C=O$	-	288.2	288.2	288.0	288.1	288.3	288.2
-COO and/or carbonate	289.1	289.0	289.4	289.3	289.3	289.4	289.2
Ti $2p_{3/2}$ – Ti (IV)	458.9	458.9	459.0	459.0	459.2	459.2	459.1
O 1s – TiO_2	530.2	530.3	530.3	530.3	530.5	530.5	530.4
O 1s – -OH	531.4	531.5	531.3	531.3	531.5	531.3	531.3
O 1s – water	532.5	532.6	532.5	532.6	532.5	532.5	532.5
*Valence band edge**	3.0	3.0	3.1	3.2	3.3	3.3	3.1
O/Ti^{4+} atomic ratio	2.1 (0.1)	1.8 (0.2)	1.8 (0.2)	1.6 (0.2)	1.8 (0.1)	1.8 (0.1)	1.8 (0.1)
$C_{elemental}$ at%	-	1.5 %	1.5–1.8 %	2.6 %	3.9–4.0 %	3.4–4.0 %	4.0–4.1 %

**Edge: Binding energy value determined using the linear extraction method.*

Table S3. Lineshape analysis parameters of the EPR spectra of the studied samples: g tensor, concentration of paramagnetic centers (spin density), peak-to-peak width (ΔH_{pp}), full width at half maximum (FWHM) of the integral curve and Gaussian percentage calculated by fitting the derivative signals by means of Xepr software.

	g factor (± 0.002)	**Spin density (10^{17} spin/g)**	**ΔH_{pp} (G)**	**FWHM (G)**	**FWHM/ΔH**	**Gaussian character**
SA1	2.0024	3 ± 1	5.5	8	1.45	44 %
SA3	2.0015	0.3 ± 0.1	4.3	7.3	1.70	17 %
A1	2.0024	4 ± 1	4.3	6.7	1.56	14 %
A3	2.0023	8 ± 1	4.7	7.3	1.55	15 %
N1	2.0029	45 ± 5	6.2	9.7	1.56	23 %
N3	2.0025	60 ± 5	5.3	9	1.70	0
HN1	2.0025	45 ± 5	4.9	8.1	1.65	0
HN3	2.0024	50 ± 5	3.6	7	1.94	0