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Supplementary Data for

Making H_2 from light and biomass-derived alcohols: the outstanding activity of newly designed hierarchical MWCNTs/Pd@TiO_2 hybrid catalysts

A. Beltram, M. Melchionna, T. Montini, L. Nasi, M. Prato, and P. Fornasiero

Figure S1: HRTEM of the titania shell in CNTs/Pd@TiO_2-calc (left); FFT of a selected area showing the reflections of TiO_2 anatase phase (right).

Figure S2: Typical HAADF images of **10-CNT/Pd@TiO_2** (A) and **20-CNT/Pd@TiO_2** (B).

Figure S3: HRTEM of a CNT/Pd@TiO_2 where Pd nanoparticles can be observed; inset, zoom of a Pd NP showing the crystallographic facet and the size of approximately 3-5 nm range.

Figure S4: H_2 chemisorption measurements for **Pd@TiO_2** (A), **10-CNT/Pd@TiO_2** (B), **20-CNT/Pd@TiO_2** (C); insets: extrapolation of the linear part in the 10-20 mmHg range to evaluate contribution of H adsorbed on the surface.

Figure S5: Results from photocatalytic hydrogen production from methanol/water solutions under UV irradiation for the fresh and calcined catalysts. Activities are normalised by the grams of catalyst.

Figure S6: Results from photocatalytic hydrogen production from ethanol (left) and glycerol (right) water solutions under UV irradiation. Activities are normalised by the grams of catalyst.

Table S1: Comparison with the performance of some recent catalytic systems containing carbon supports and integrated metal phases.

Figure S7 Gaseous by-products formation during photocatalytic H_2 production from ethanol/water solutions under UV irradiation with **10-CNT/Pd@TiO_2** (left) and **20-CNT/Pd@TiO_2** (right).

Table S2: Results from semi-quantitative analysis (1-butanol was used as internal standard) of liquid solutions collected after photocatalytic H_2 production from ethanol/water solutions under UV irradiation.

Figure S8: Photocatalytic water splitting under UV irradiation. Methanol (10% v/v) was added after 19 h. Activities (H_2 on the left and CO_2 on the right) are normalised by the grams of catalyst.

Figure S9: Photocatalytic water splitting under UV irradiation. Acetaldehyde (4% v/v) was added after 3 h. Activities (H_2 on the left and byproducts on the right) are normalised by the grams of catalyst.

Figure S10: Results from photocatalytic by-products production from glycerol/water solutions under UV irradiation expressed in terms of production rate.

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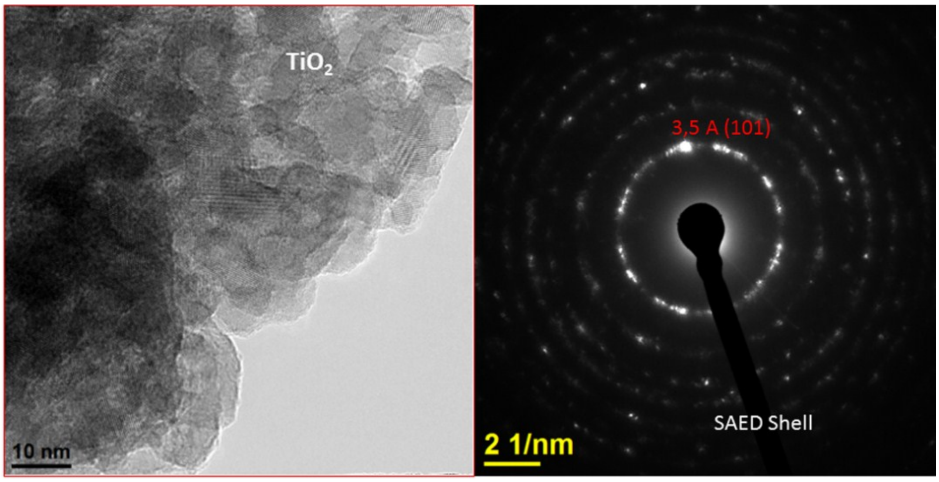

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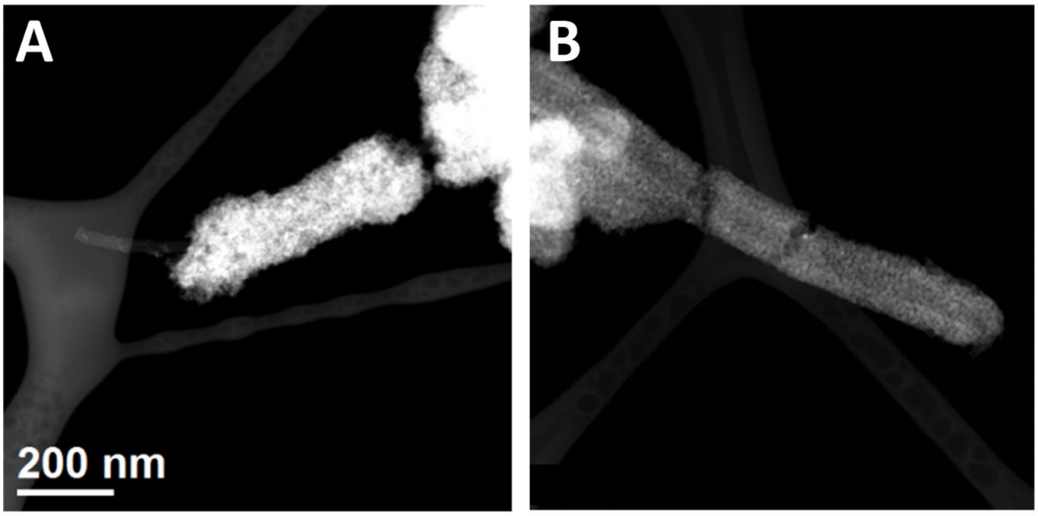

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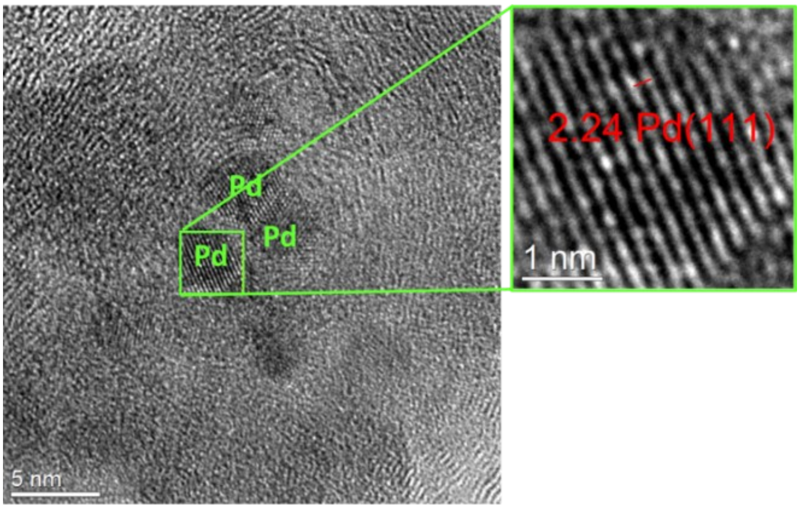

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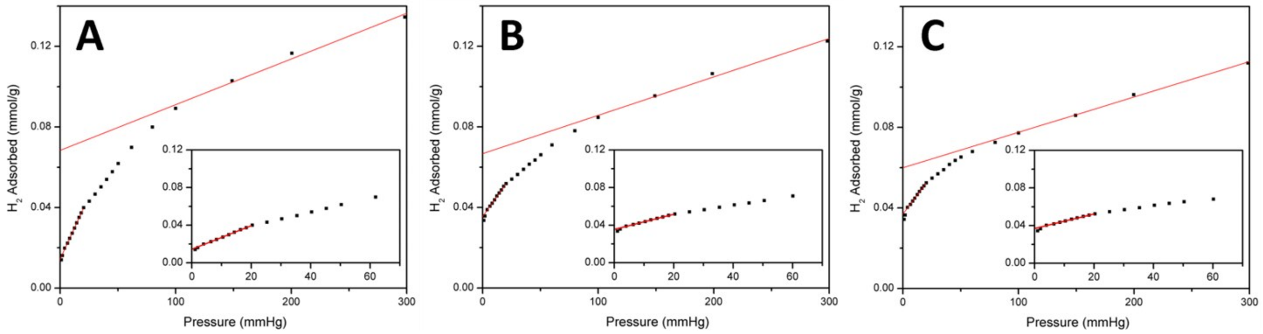

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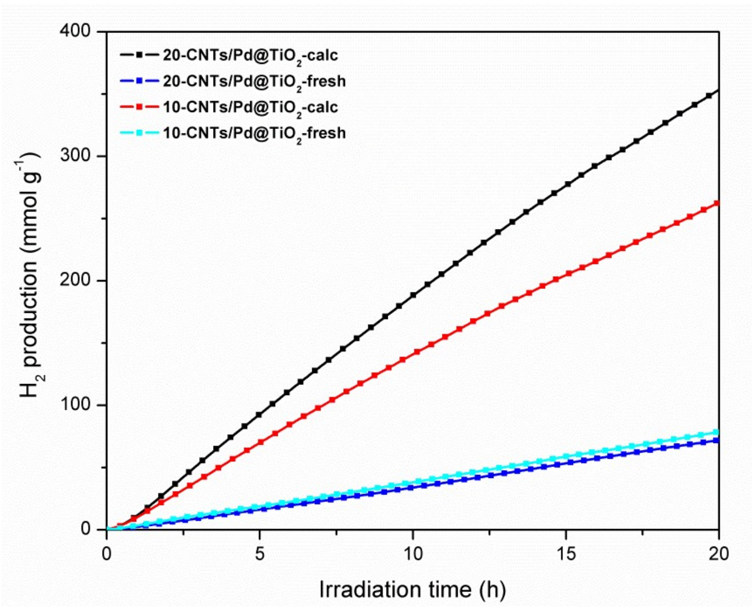

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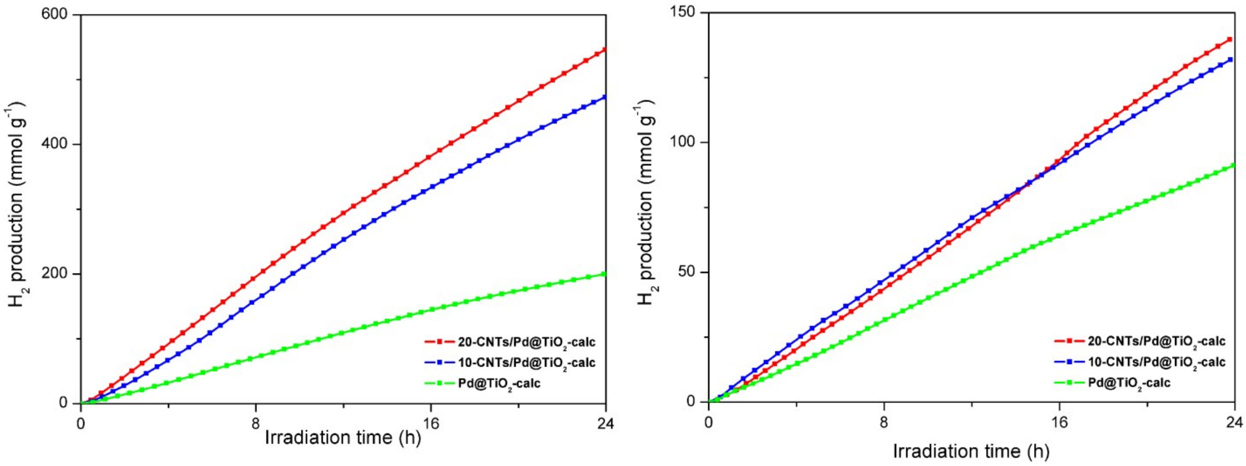

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Table S1: Comparison with the performance of some recent catalytic systems containing carbon supports and integrated metal phases.

Entry	Carbon Support	Metal phase	Maximum Rate of H_2 evolution ($mmol \cdot g^{-1} \cdot h^{-1}$)	Hole scavenger	Quantum efficiency	Power of irradiating lamp	Reference
1.	Ox-MWCNT	Pt/TiO_2	40	Methanol	Not reported	200W (240-500 nm range)	1
2.	Ox-MWCNTs	Pt/TiO_2	10	Methanol	Not reported	125W (λ>365)	2
3.	GO	TiO_2	0.4	Methanol	Not reported	300W (λ>320nm)	3
4.	GO	Cu/TiO_2	19	Methanol	Not reported	300W (λ>365)	4
5.	g-C_3N_4	Pt	0.15	Triethanolamine	Not reported	300W (λ>420)	5
6.	Ox-CNTs	TiO_2	2	Glycerol	Not reported	Not specified	6
7.	Ox-MWCNTs	Pt/TiO_2	8	Triethanolamine	Not reported	250W (λ>320)	7
8.	GO	TiO_2	0.7	Methanol	QE = 3.1%	350W (λ>320)	8
9.	GO	Pt/CdS	55	Lactic Acid	QE = 22%	350W (λ>420)	9
10.	C_{60}-SWCNTs	TiO_2	3.2	Triethanolamine	Not reported	300W (λ>320)	10
11.	GO	Pt/$Sr_2Ta_2O_{7-x}N_x$	3	Methanol	QE = 6.5%	300W (λ>420)	11
12.	MWCNTs	Pt/Ta_2O_5	32	Methanol	Not reported	450W (λ>365)	12

13.	RGO	TiO_2	1	Ethanol	Not reported	300W (λ>320)	[13]
14.	RGO	V-TiO_2	0.12	Methanol	Not reported	300W λ not specified	[14]
15.	RGO	Pt/TiO_2	14	Methanol	Not reported	300W λ not specified	[15]
16.	**f-MWCNTs (20%)**	**Pd/TiO_2**	**21**	**Methanol**	**Not reported**	**125W (λ>365)**	**This work**
17.	**f-MWCNTs (20%)**	**Pd/TiO_2**	**6**	**Glycerol**	**Not reported**	**125W (λ>365)**	**This work**
18.	**f-MWCNTs (20%)**	**Pd/TiO_2**	**26**	**Ethanol**	**QE = 21%**	**125W (λ>365)**	**This work**

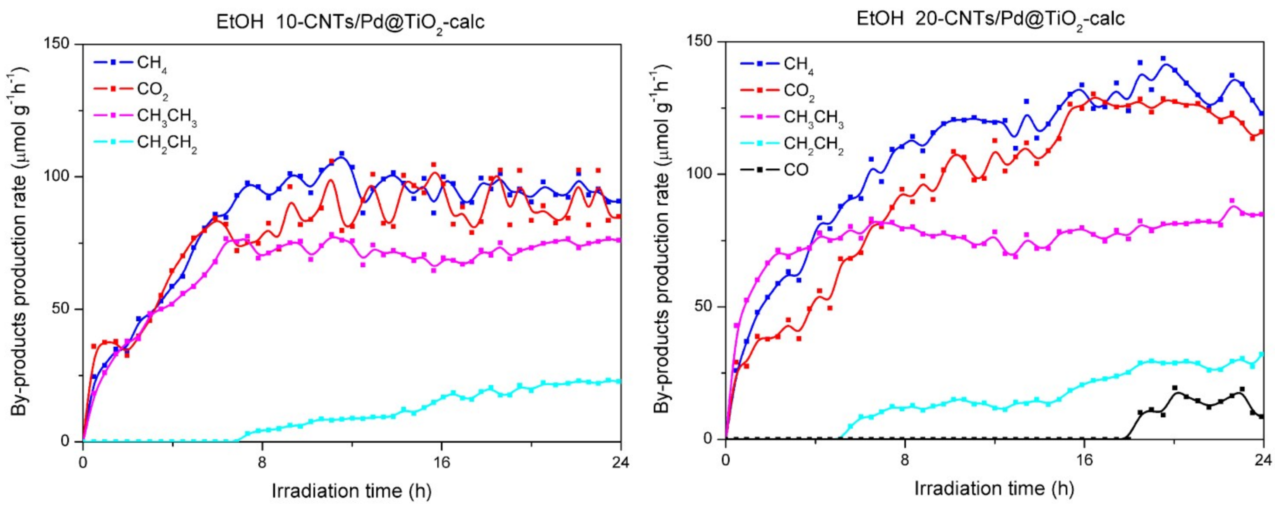

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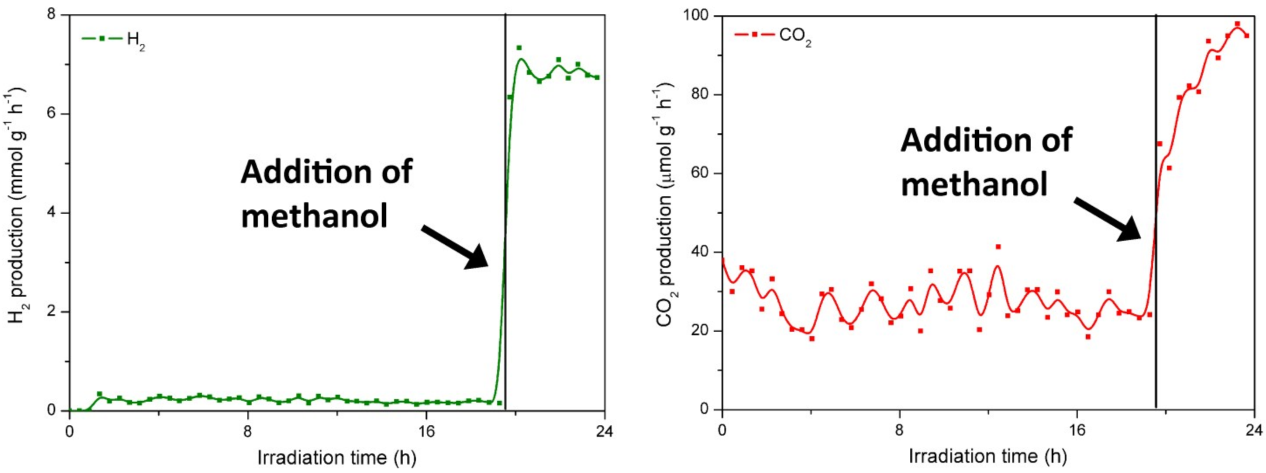
Table S2: Results from semi-quantitative analysis (1-butanol was used as internal standard) of liquid solutions collected after photocatalytic H_2 production from ethanol/water solutions under UV irradiation.

	10-CNTs/Pd@TiO$_2$-calc	**20-CNTs/Pd@TiO$_2$-calc**	**Pd@TiO$_2$**
Acetaldehyde	2.235	2.895	1.102
1,1-diethoxyethane	5.424	6.812	2.533
2,4,5-trimethyl-1,3-dioxolane	0.012	0.092	0
Acetic acid	0.026	0.145	0.003
3-hydroxy-2-butanone	0.026	0.045	0.006
2,3-butandiol	1.613	4.297	1.326



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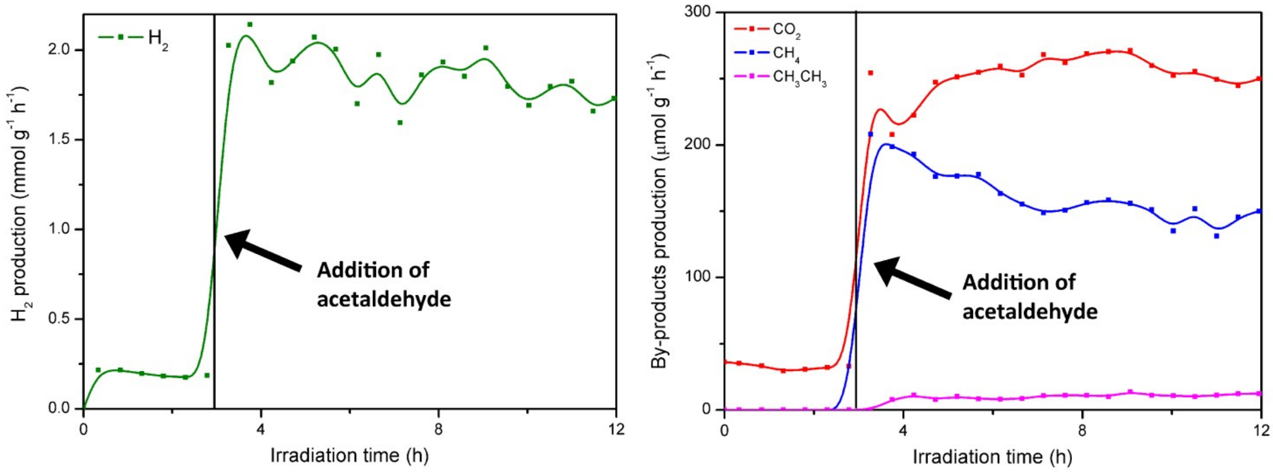

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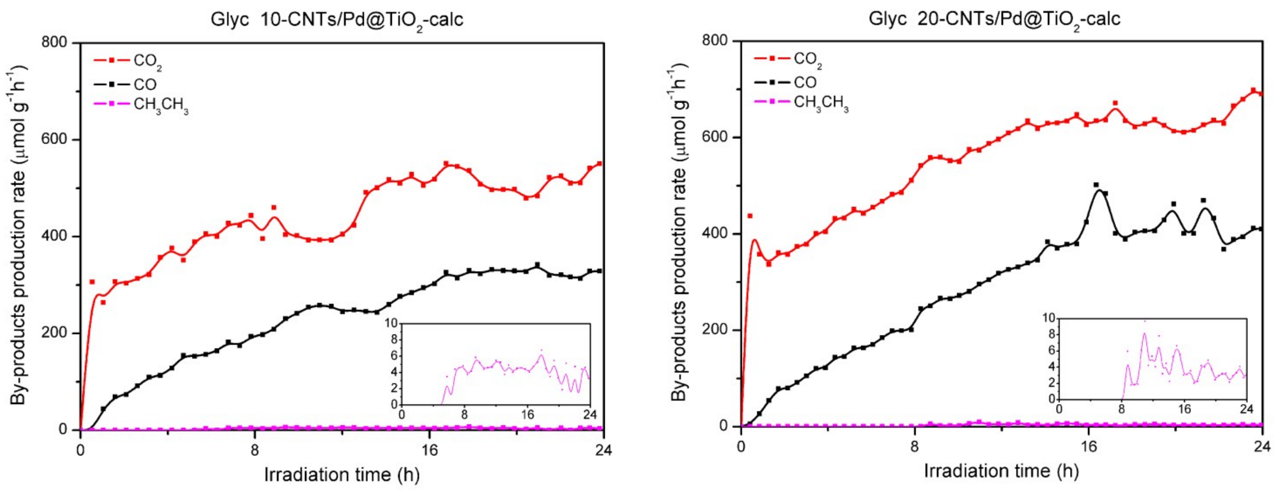

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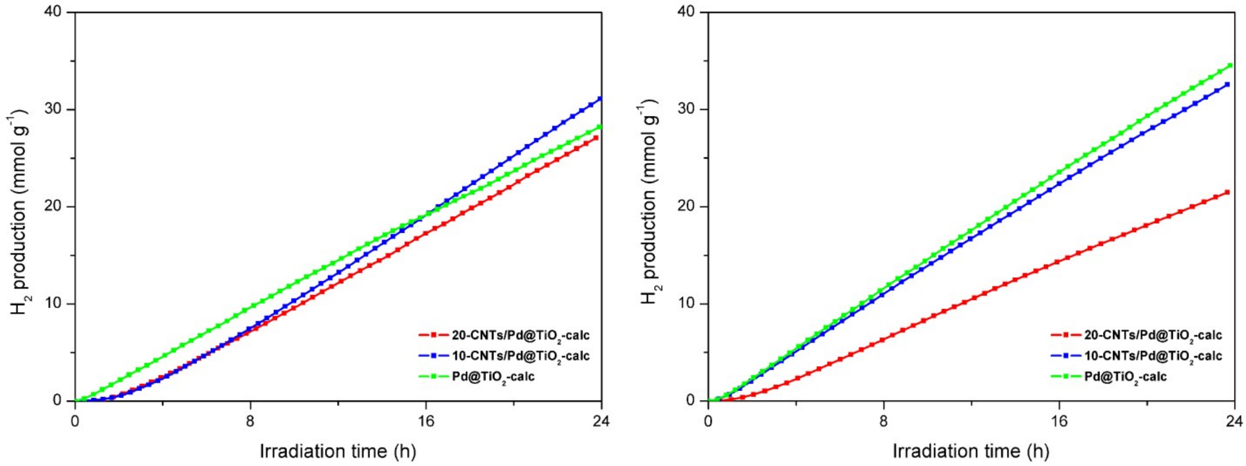
Table S3: Results from semi-quantitative analysis (1-hexanol was used as internal standard) of liquid solutions collected after photocatalytic H_2 production from glycerol / water solutions under UV irradiation.

	10-CNTs/Pd@TiO$_2$ - calc	**20-CNTs/Pd@TiO$_2$ - calc**	**Pd@TiO$_2$**
Hydroxy-acetaldehyde	2.34	3.03	1.65
Formic acid	0.37	0.26	0.22
Acetic acid	0.08	0.07	0.04
1-hydroxy-2-propanone	1.60	1.12	0.75
2,3-dihydroxypropanal	0.22	0.20	0.26
1,3-dihydroxy-2-propanone	1.62	2.05	1.13



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	10-CNTs/Pd@TiO_2-calc	**20-CNTs/Pd@TiO_2-calc**	**Pd@TiO_2**
Acetaldehyde	0.22	0.18	0.68
1,1-diethoxyethane	0.39	0.23	0.20

Table S5: Results from semi-quantitative analysis (1-hexanol was used as internal standard) of liquid solutions collected after photocatalytic H_2 production from glycerol / water solutions under simulated solar irradiation.

	10-CNTs/Pd@TiO_2 - calc	**20-CNTs/Pd@TiO_2 - calc**	**Pd@TiO_2**
Hydroxy-acetaldehyde	1.04	1.14	1.40
1-hydroxy-2-propanone	0.10	0.15	0.14
2,3-dihydroxypropanal	0.16	0.21	0.18
1,3-dihydroxy-2-propanone	1.18	1.30	1.53

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