Supporting Information

High photocatalytic yield in the non-oxidative coupling of methane using a Pd-TiO_2 nanomembrane gas flow-through reactor

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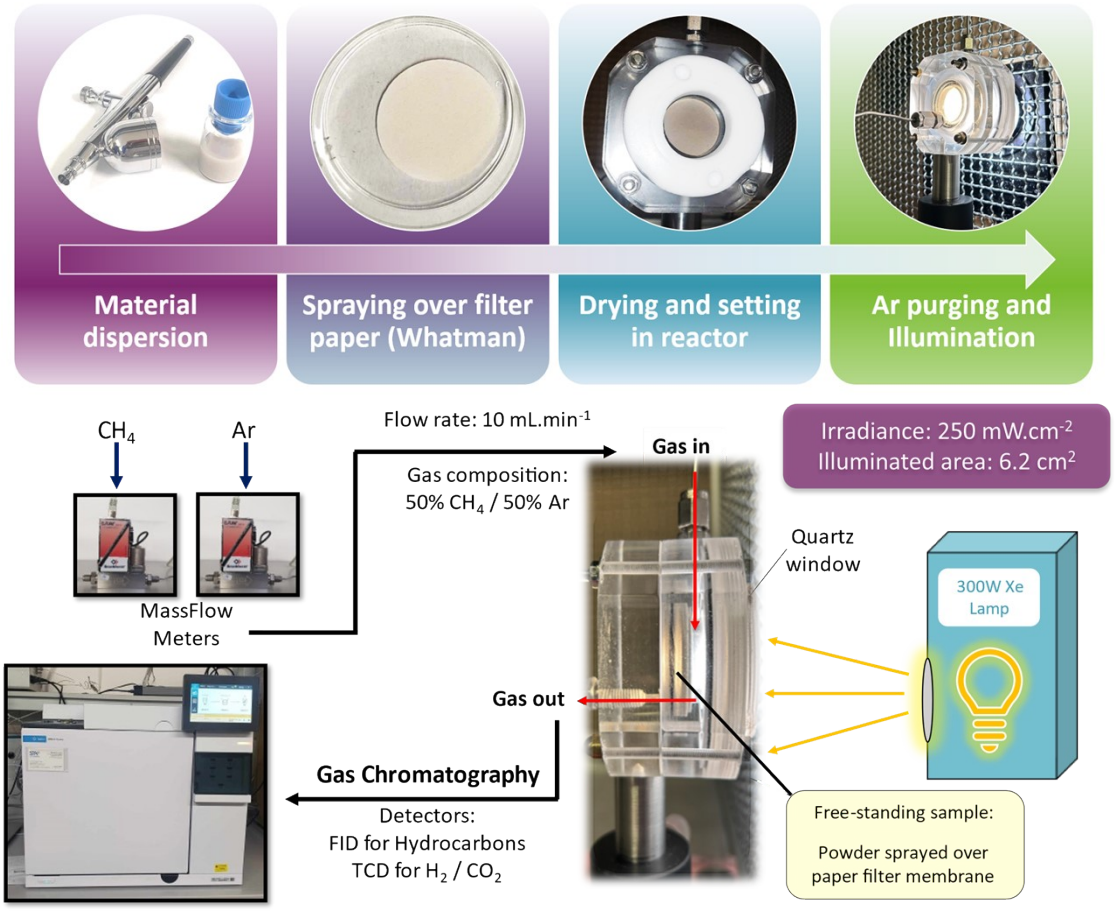

Figure S1. Scheme of photocatalytic membrane preparation and testing set-up.

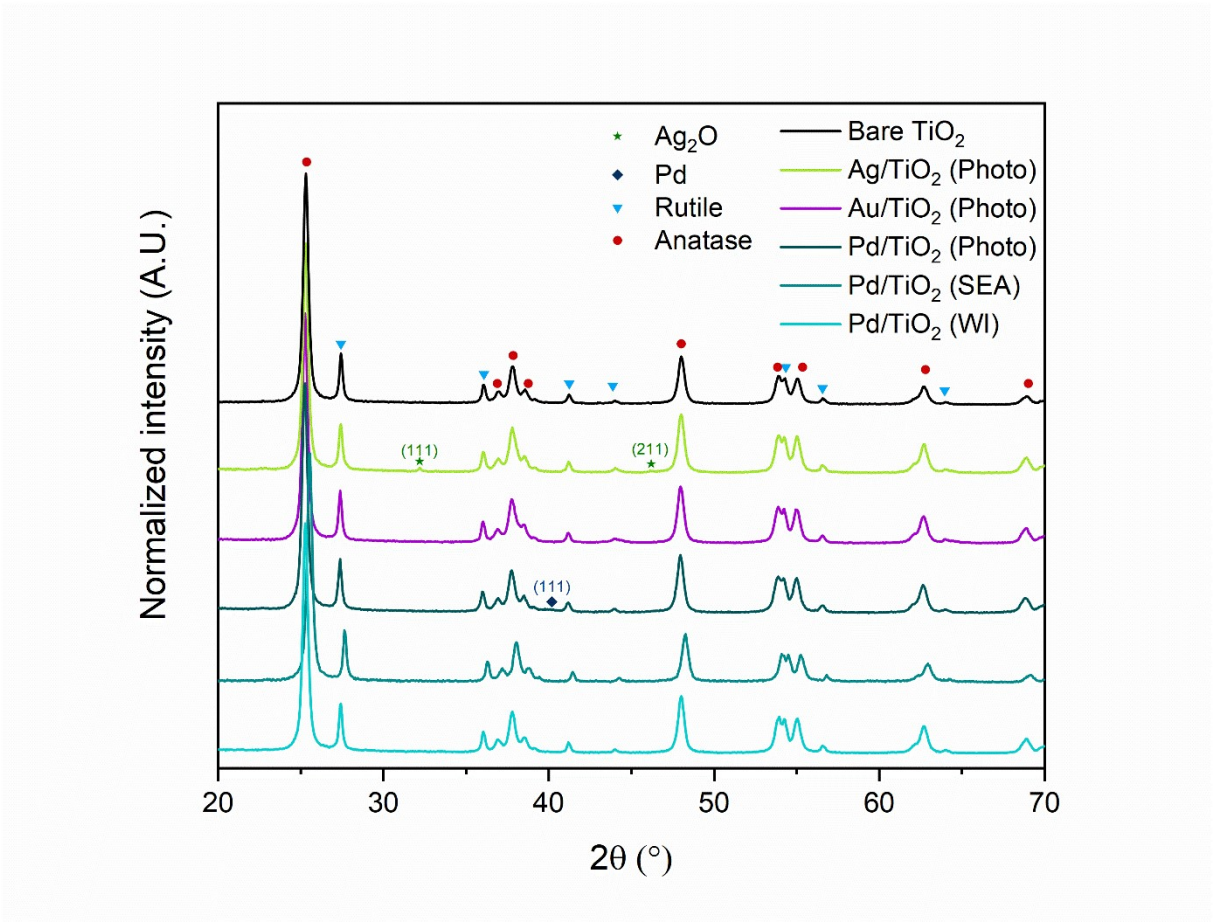

Figure S2. XRD patterns of all metal-loaded TiO_2 synthesised materials and bare TiO_2 P25 as reference.

The different peaks from the bare TiO_2 P25 support can be indexed to the rutile polymorph (JCDPS no 88-1175) for reflections at 27.42°, 36.08°, 41.25°,44.03°, 54.33°, 56.57° and 63.44° corresponding to planes of Miller indices of (110), (101), (111), (210), (211), (220) and (002), respectively, and to the anatase polymorph (JCPDS no. 84-1286) for reflections at 25.64°, 37.27°, 38.14°, 38.90°, 48.40°, 54.22°, 55.36°, 62.99° and 69.07° corresponding to planes of Miller indices (101), (103), (004), (112), (200), (105), (211), (204) and (116) [1]

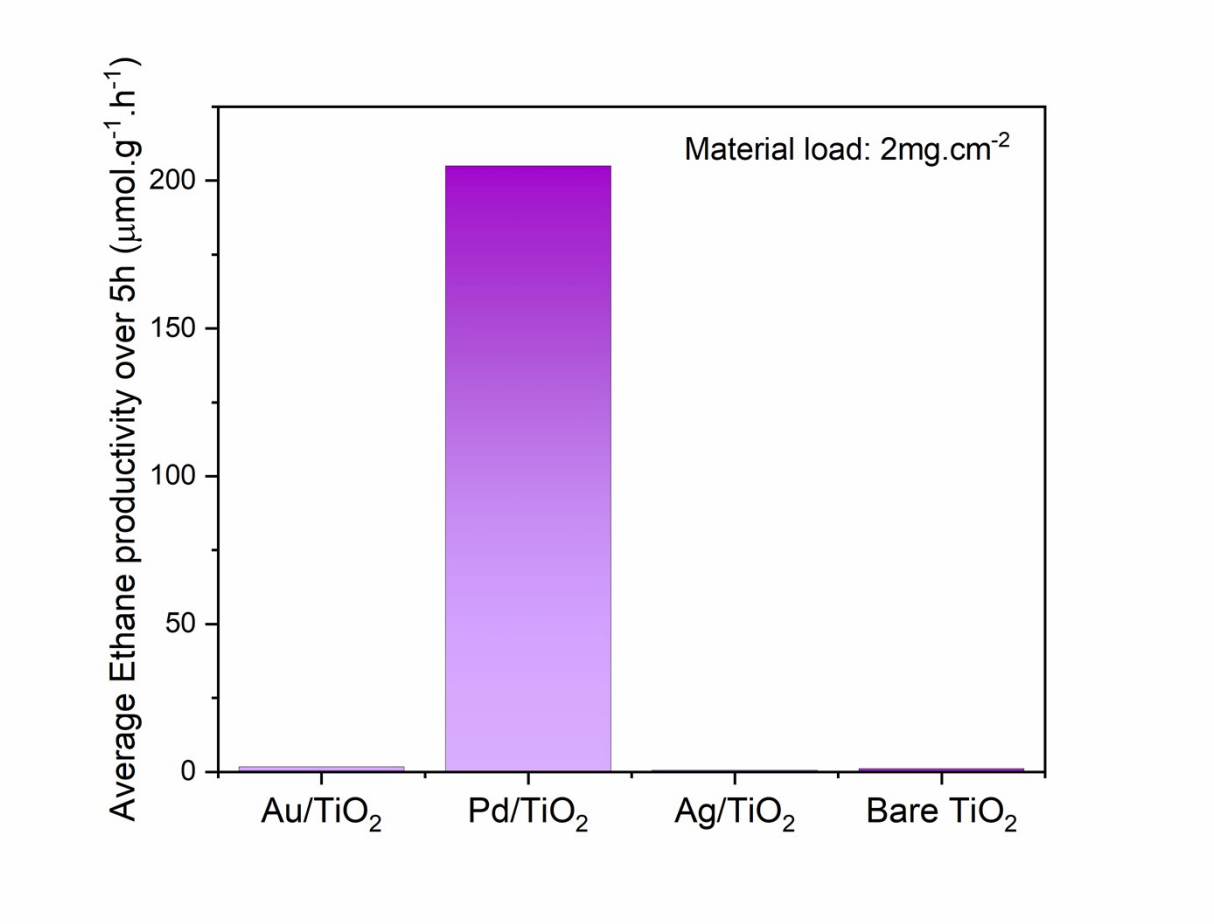

Figure S3. Ethane productivity for photocatalytic NOCM over Pd, Au and Ag on TiO_2 prepared by photo-deposition. Bare TiO_2 as reference. Reaction conditions: flow 0.6 $l \cdot h^{-1}$, CH_4 50% in Ar, light irradiation for 5 hours

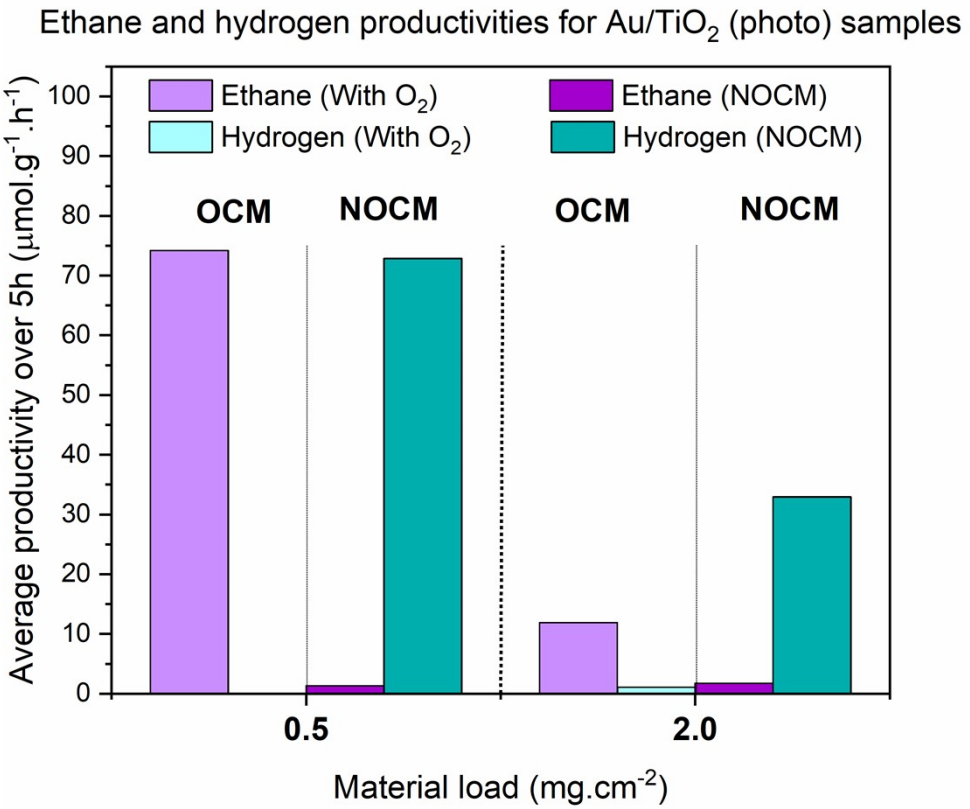

Figure S4. Average ethane and hydrogen productivity for aerobic and anaerobic photocatalytic reaction over Au/TiO_2 (photo) -0.5 and 2.0 mg cm^{-2} loadings. Reaction conditions: flow 0.6 $l \cdot h^{-1}$, CH_4 50% in Ar, light irradiation for 5 hours, for OCM 5000 ppm of O_2, ratio $CH_4:O_2$ = 100)

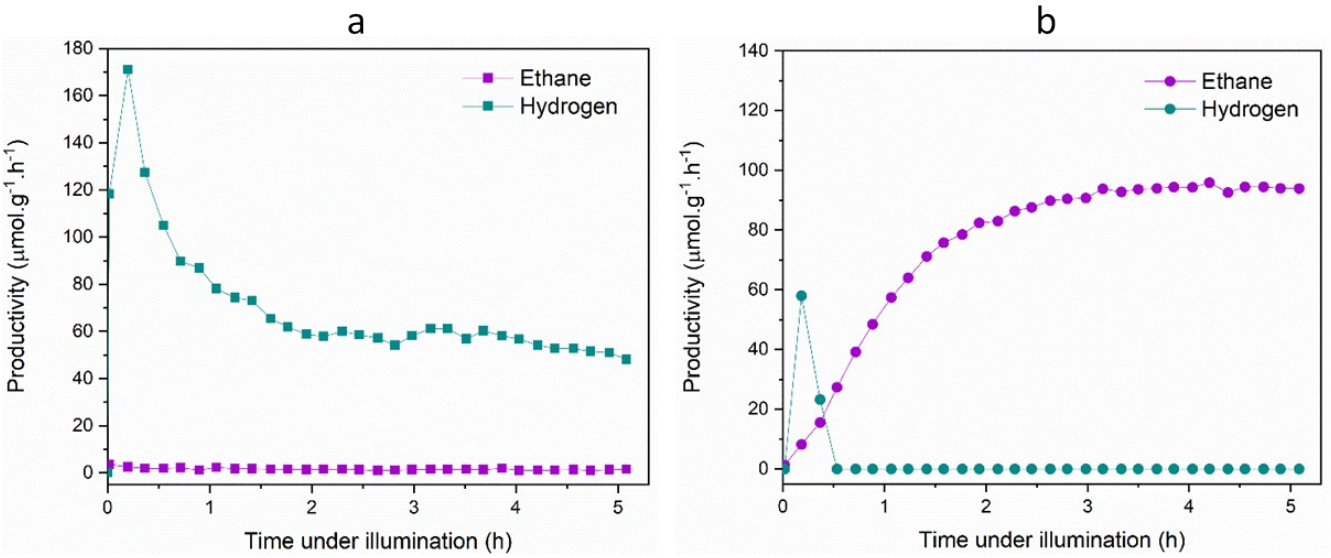

Figure S5 Trends of ethane and hydrogen productivity for the sample Au/TiO_2 (photo) (loading 0.5mg. cm^{-2}) in anaerobic (a) and aerobic (b) (5000ppm of O_2, ratio CH_4:O_2 = 100) conditions.

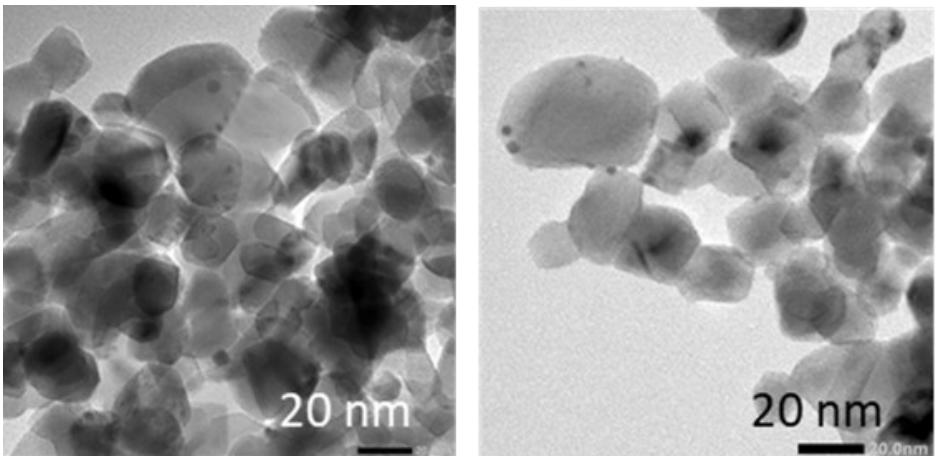

Figure S6. TEM images of Pd/TiO_2 sample prepared by photo deposition.

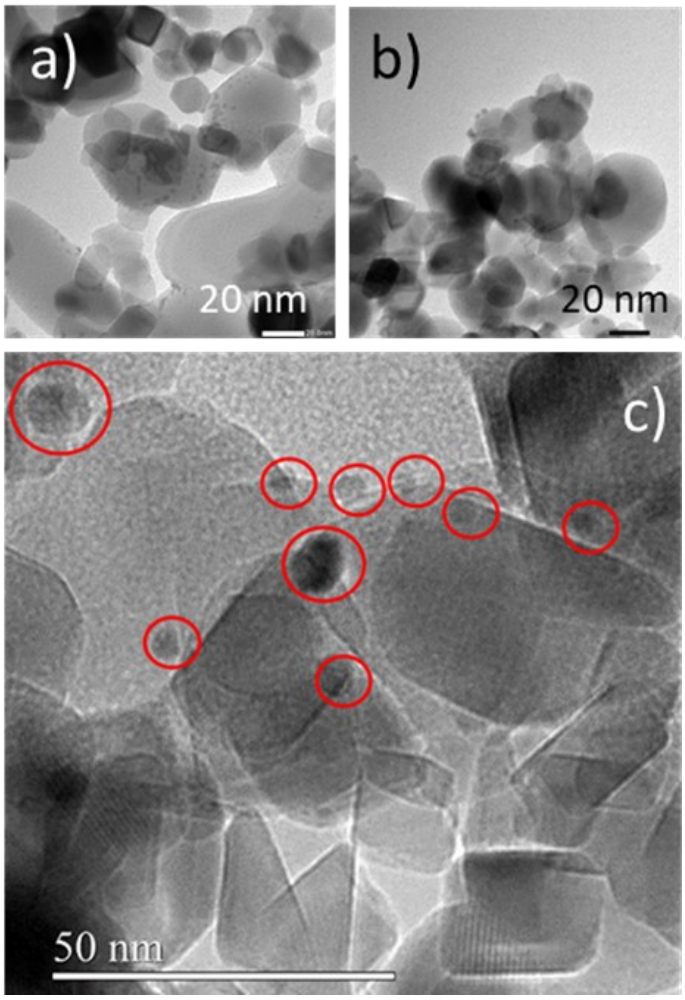

Figure S7. a, b) TEM **c)** HR-TEM image of Pd/TiO_2 sample prepared by impregnation (WI)

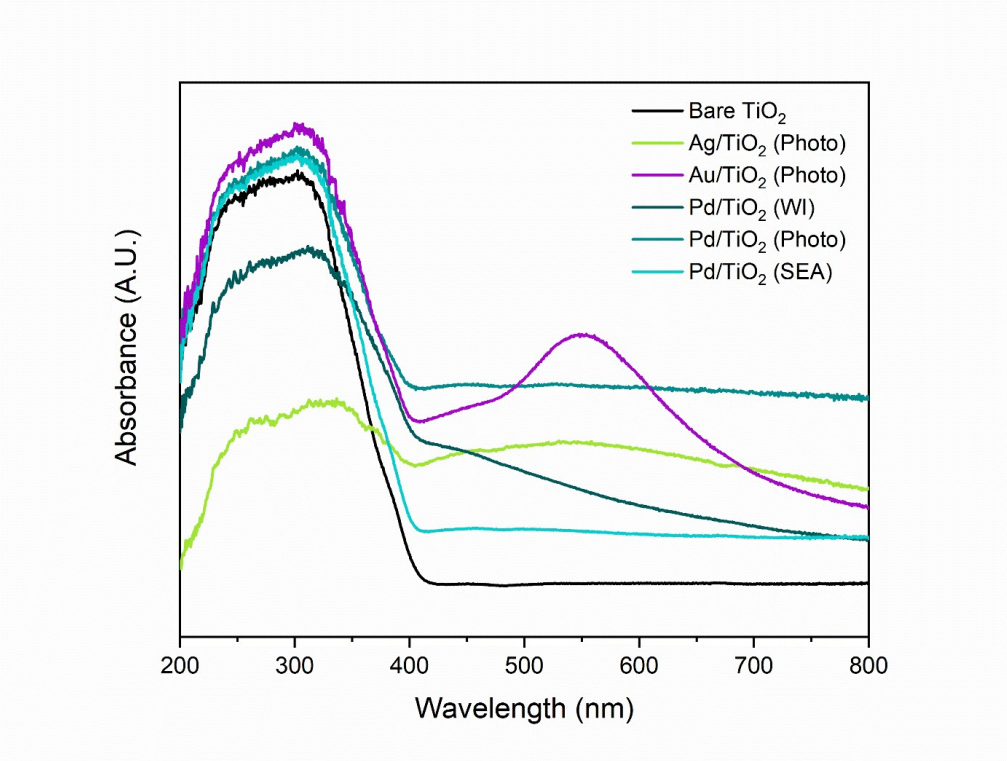

Figure S8. UV-vis spectra of metal loaded-TiO_2 samples and bare TiO_2 as reference

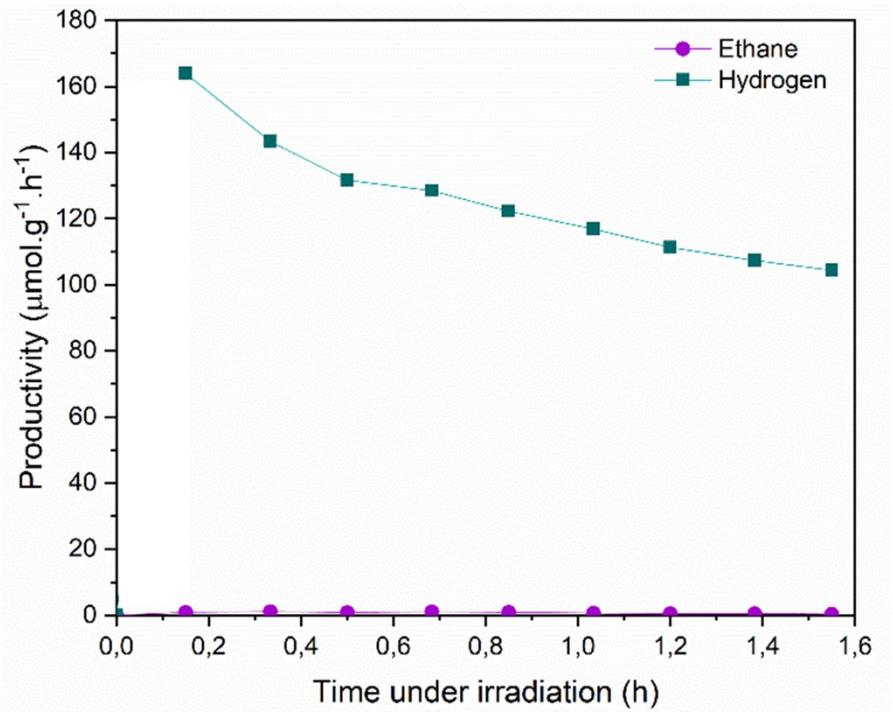

Figure S9. Blank test with Pd/TiO_2 (SEA) sample. Conditions: material loading: 1.0 $mg.cm^{-2}$, Flow: 100% Ar, 5 $ml.min^{-1}$ for 5 hours of irradiation

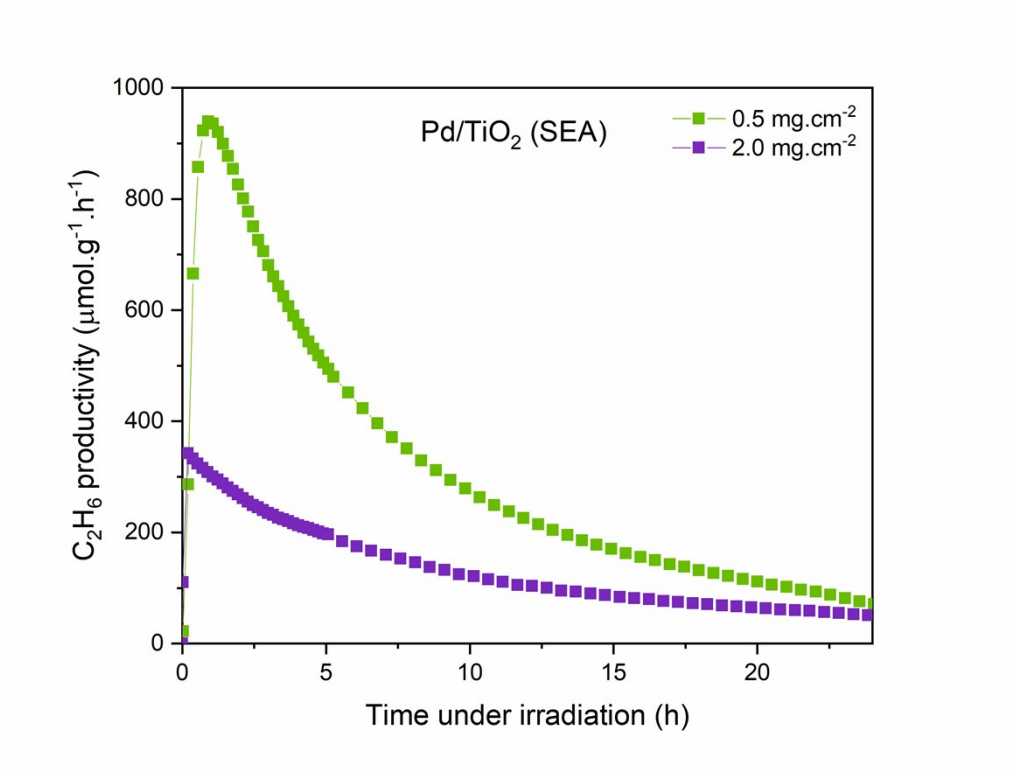

Figure S10. Ethane productivity for 24h of continuous NOCM photocatalytic test over Pd/TiO_2 (SEA) with loading of 0.5 and 2.0 $mg.cm^{-2}$.

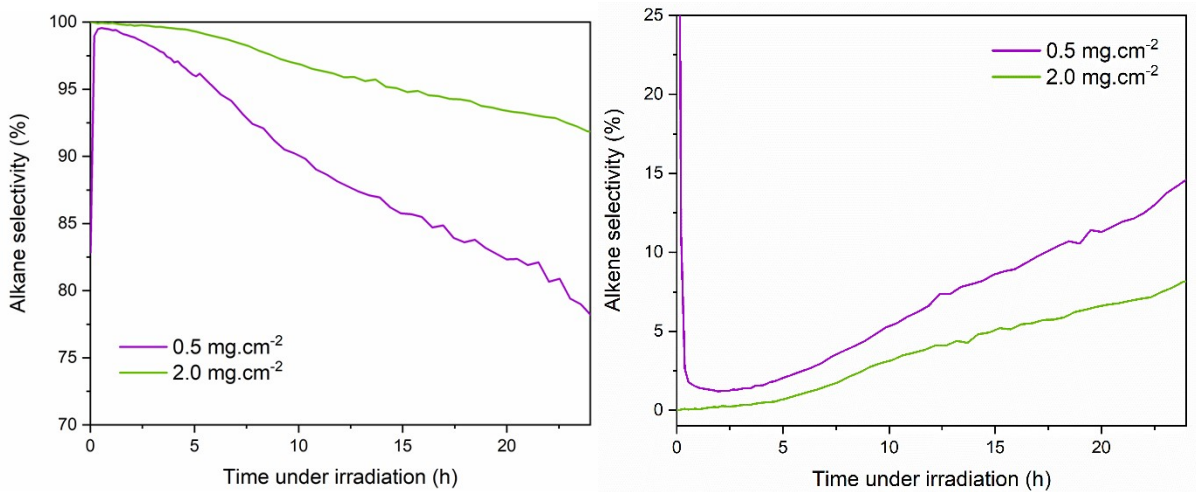

Figure S11. Alkane (ethane/propane) and alkene (ethylene/propylene) hydrocarbon selectivity for 24h of continuous NOCM photocatalytic test over Pd/TiO_2 (SEA) with loading of 0.5 and 2.0 $mg.cm^{-2}$.

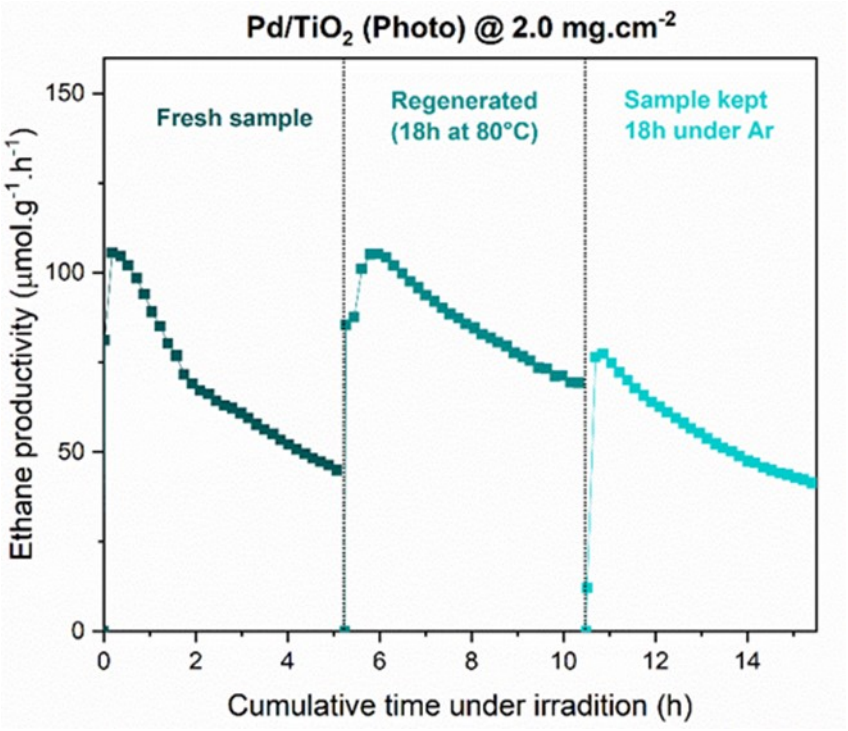

Figure S12. Regeneration cycles after 5h of photocatalytic test on samples Pd/TiO_2 (Photo) with 2.0 $mg.cm^{-2}$ in air at 80°C and Ar.

Pd/TiO_2 (SEA)	Products Yield (μmol·g-1)			
Time	Ethane	Ethylene	Propane	Propylene
5h	3539	55,4	9,8	3,9
24h	7382	290,1	25,5	31,3

Table S1. C-based products yield (μmol·g-1) for photocatalytic NOCM test over Pd/TiO_2 (SEA), 0.2% wt Pd loading. Reaction conditions: flow 0.6 L·h-1, CH_4 50% in Ar, light irradiation for 5 hours and 24 hours.

Calculation of selectivity.

Ethane selectivity was calculated according to Eq 1.

$$Ethane\ selectivity = \frac{2 \times [Ethane]}{2 \times [C_2] + 3 \times [C_3] + [CO_2]} \times 100\ \#(Eq.\ 1)$$

The alkane or alkene hydrocarbon selectivity was determined considering only the produced hydrocarbons as in Eq 2., and Eq 3.

$$Alkane\ Selectivity\ (\%) = \frac{2 \times [Ethane] + 3 \times [Propane]}{2 \times [Ethane + Ethylene] + 3 \times [Propane + Propylene]} \times 100\ \#(Eq.\ 2)$$

$$Alkene\ Selectivity\ (\%) = \frac{2 \times [Ethylene] + 3 \times [Propylene]}{2 \times [Ethane + Ethylene] + 3 \times [Propane + Propylene]} \times 100\ \#(Eq.\ 3)$$