Electronic Supplementary Information for the paper

From *trash* to *resource*: recovered-Pd from spent Three-Way Catalysts as precursor of an effective photo-catalyst for H_2 production

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Characterization of catalysts

Sample digestion and ICP-AES measurements

Samples were digested by using a Milestone (Sorisole, Bergamo, Italy) Ethos 1 Microwave digestor, equipped with a HPR1000/10S high pressure segmented rotor, ATC-400CE automatic temperature control and Terminal 640 with easyCONTROL software.
0.124 g of sample were introduced in a TFM (copolymer of PTFE, Polymer of TetraFluoroEthylene, with about 0.1% of PPVE, PerfuoroPropylene-VinylEther) vessel and treated with acid mixtures through a two-steps procedure as summarized in Table 2:

Table 2:

Step	Acid mixture	Microwave digesting conditions
1	H_2SO_4 (98%, 2 mL), HNO_3 (65%, 2mL), H_2O (bidistilled, 4mL)	t=10'; T=220°C; Power= up to 1000W
2	HBF_4 (48%, 0.5 mL), HCl (37%, 0.5mL), H_2O (bidistilled, 7mL)	t=20'; T=220°C; Power= up to 1000W

Samples were prepared for analysis by filtering the small white solid residue and diluting the digested solutions with 1% HCl/HNO_3 blank. Then, the metals were determined using a ICP-AES Varian (Palo Alto, USA) Lyberty 200 Spectrometer, with respect to 5 point calibration plots in the 0.5–10 ppm range.

DR UV Visible Spectra

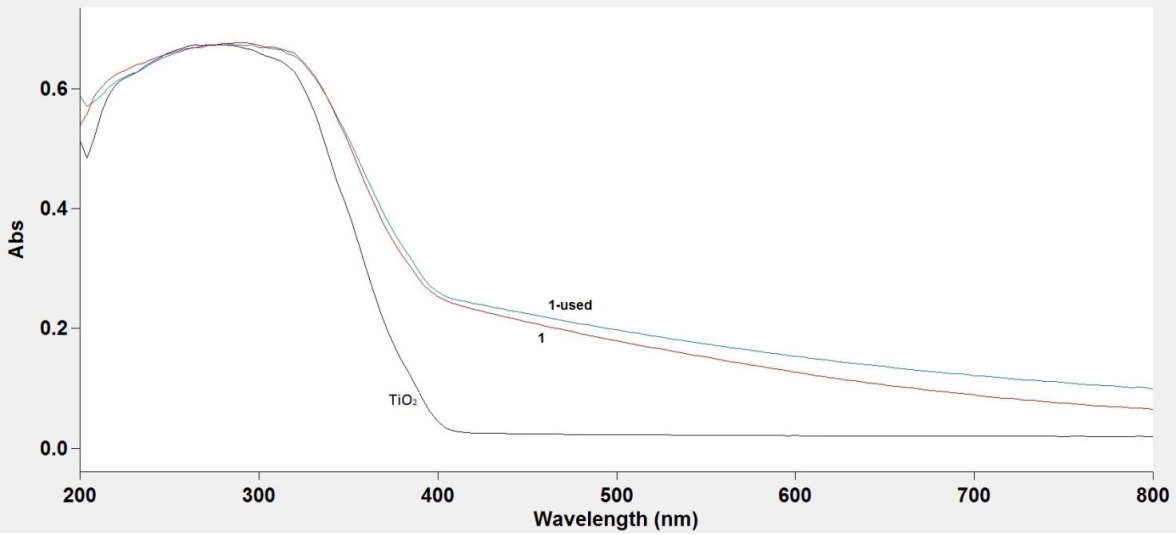

Fig. S1 DR-spectra of samples **1** and **1-used** *vs* TiO_2.

Photocatalytic activity

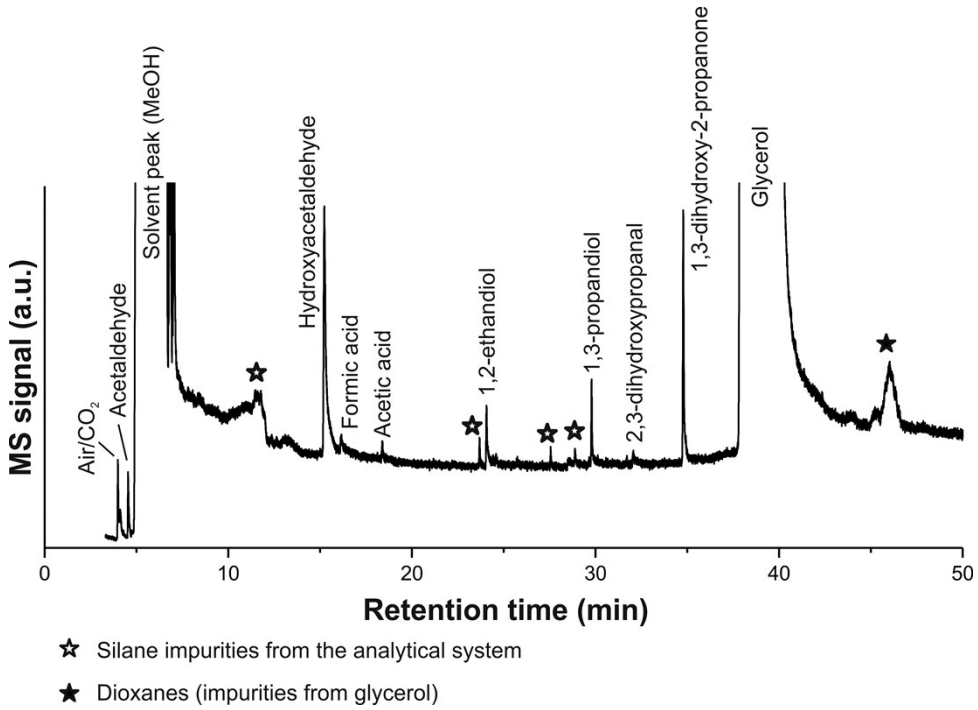

Fig. S2 GC-MS analysis of liquid phase recovered from glycerol photo-reforming using sample **1**, at the end of experiment of Fig. 2 (diluted with methanol 1 to 10).

XRD and TEM Characterization

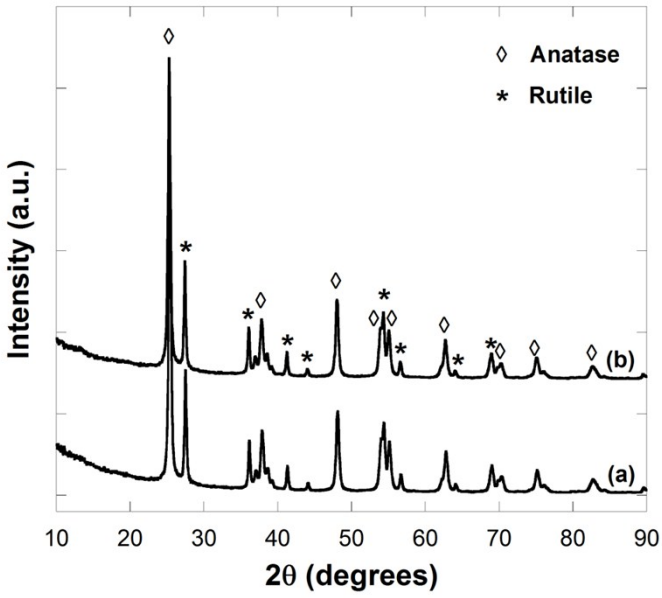

Fig. S3 XRD patterns of (a) sample **1** and (b) sample **1-used** (Anatase PDF card 21-1272, Rutile PDF card 21-1276).

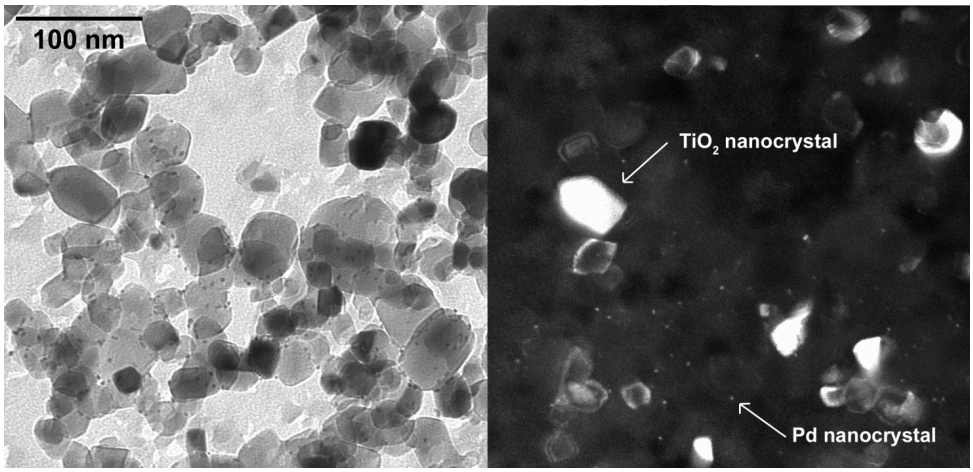

Fig. S4 Bright Field (left) and Dark Field (right) TEM images of the sample **4**.

XPS spectra

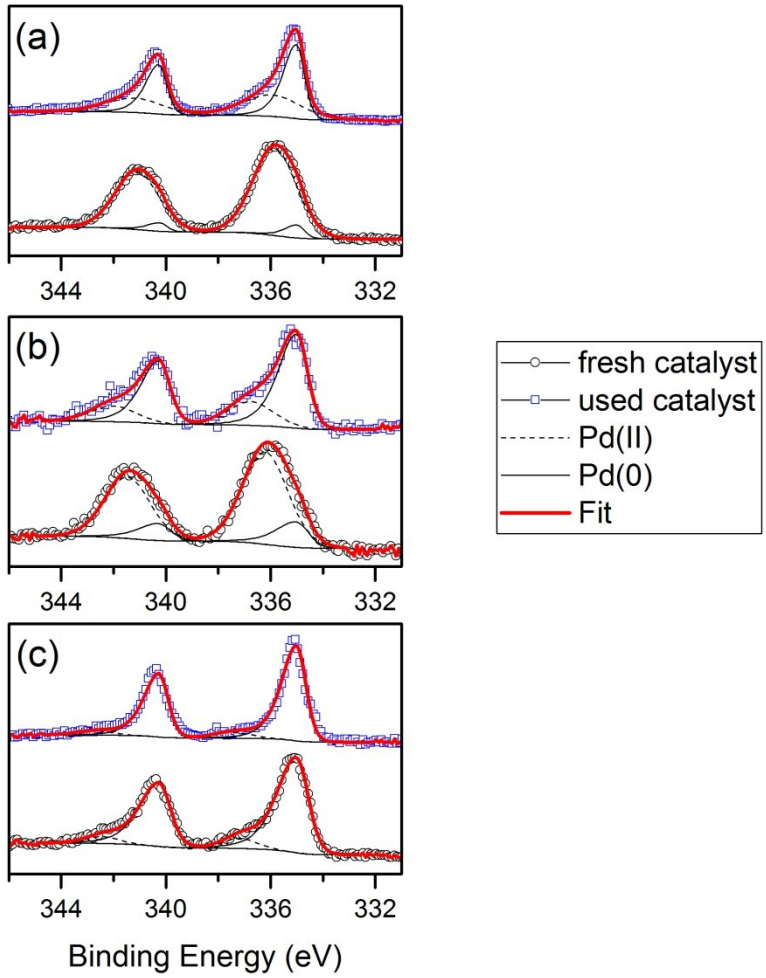

Fig. S5 Pd 3d XPS spectra collected on fresh and used photo-catalysts. (a) catalyst **2**, prepared from $[Pd(Me_2dazdt)_2](BF_4)_2$; (b) catalyst **3**, prepared from $PdCl_2$; (c) catalyst **4**, prepared from $Pd(NO_3)_2$. All the spectra have been deconvoluted to determine the Pd(0)/Pd(II) atomic ratio, as reported in Table 2 of the main text.