Electronic Supplementary Information (ESI)

for

Bimetallic Au-Pt/TiO_2 photocatalysts active under UV-A and simulated sunlight for H_2 production from ethanol.

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PREPARATION OF THE CATALYSTS

Au, Pt and Au-Pt/TiO_2 systems were prepared by impregnation of commercial amorphous titania nanoparticles (Nanoactive TiO_2, Nanoscale – USA) with aqueous $HAuCl_4$ and/or $(NH_4)_2PtCl_6$ solutions, followed by drying, calcination at 200°C for 1 hour and reduction, under 1 bar H_2 flow, at 250 °C or 500 °C for 1 hour. Four samples were obtained (the number after the metal chemical symbol denotes the metal loading expressed in % wt.): Au1, Pt1, Au0.5-Pt0.5 and Au1-Pt1/TiO_2.

PHOTOCATALYTIC ACTIVITY EVALUATION

Photocatalytic tests were perfomed suspensing the powder photocalysts in a solution of EtOH/H_2O 1:1 by volume. For UV-A experiment, a suspension of 500 mg of photocatalyst in 240 mL of solution was irradiated using a 125W medium-pressure Hg lamp (Helios). For simulated sunlight experiments, a suspension of 125 mg of photocatalyst in 80 mL of solution was irradiated using a Solar Simulator (150 W Xe lamp mounting an Atmospheric Filter to simulate absorption from air). In the case of visible light experiment, a solution of MeOH/H_2O 1:1 by volume, a suspension of 250 mg of photocatalyst in 80 mL of solution was irradiated using a 125W medium-pressure Hg lamp (Helios) with a 400 nm cutoff filter. After degassing the reactor with Ar stream, lamp was switched on the effluent was analyzed to quantify H_2 using a Thermal Conductivity Detector (TCD, connected to a Molsieve 5A column) and the carbonaceous compounds using a Flame Ionization Detector (FID, connected to a PoraPLOT Q column and a methanator). Liquid phases after reaction were analyzed using a GC/MS mounting a DB-225ms column.

CHARACTERIZATION OF THE MATERIALS

Powder XRD diffractions were collected by a Rigaku D III-Max horizontal scan powder diffractometer with Cu-Kα and data were analyzed by Eva software/compared to database.

TPR measurements were conducted using a Micromeritics PulseChemisorb2700 instrument. Around 25 mg of each sample was loaded in a pyrex U-shaped reactor and calcined at 200°C under pure O2 flow. TPR was conducted under 15 mL min^{-1} H_2/Ar 8% mixture, heating rate 8°C min^{-1}.

CO adsorption tests were performed using a home-made DRIFTS reaction chamber. Apparatus details are described elsewhere [see ref. V. Dal Santo, C. Dossi, A. Fusi, R. Psaro, C. Mondelli, S. Recchia, Talanta 2005, 66(3), 674.]. Before chemisorption, the samples were reduced in-situ at 250°C for 60 min. CO chemisorption was performed in pure CO flow at RT until the saturation of carbonyl adsorbed on Pt bands was reached. Finally the DRIFT cell was purged with He until CO adsorption bands stabilized.

The morphology and distribution of the supported metal particles were evaluated by HRTEM. The powder samples were further ground and dispersed in toluene in an ultrasonic bath. A drop of the suspension was deposited on a perforated carbon film supported on a copper TEM grid. The specimen, after solvent evaporation under vacuum, was inserted in the column of a ZEISS LIBRA 200FE HRTEM. Pictures were taken spanning wide regions of several support grains in order to provide a truly representative map of the catalyst system. Distribution histograms of metal particle fraction versus diameter were evaluated from about 65 to 120 counts per sample.

DR-UV-Vis spectra were collected, from 200 to 800 nm, on pure samples using a Praying –Mantis Diffuse Reflectance Accessory (Harrick Sci, USA) mounted in a Evolution 600 spectrofotometer (Thermo). A Spectralon ® disk was used as reference material for background measurement. All the samples were measured under ambient conditions.

The EPR spectroscopic measurements were carried out on a Bruker Elexsys E500 CW-EPR equipped with a Super-X microwave bridge operating at 9.3–9.5 GHz and a standard Bruker X-band ER4119-SHQE cavity. Sample powder spectra were acquired at room temperature (23±1 °C) in a standard quartz tube with 4 mm I.D. using 5 mW incident microwave power, 10 G field modulation amplitude at 100 kHz, 80 Gauss sweep width.

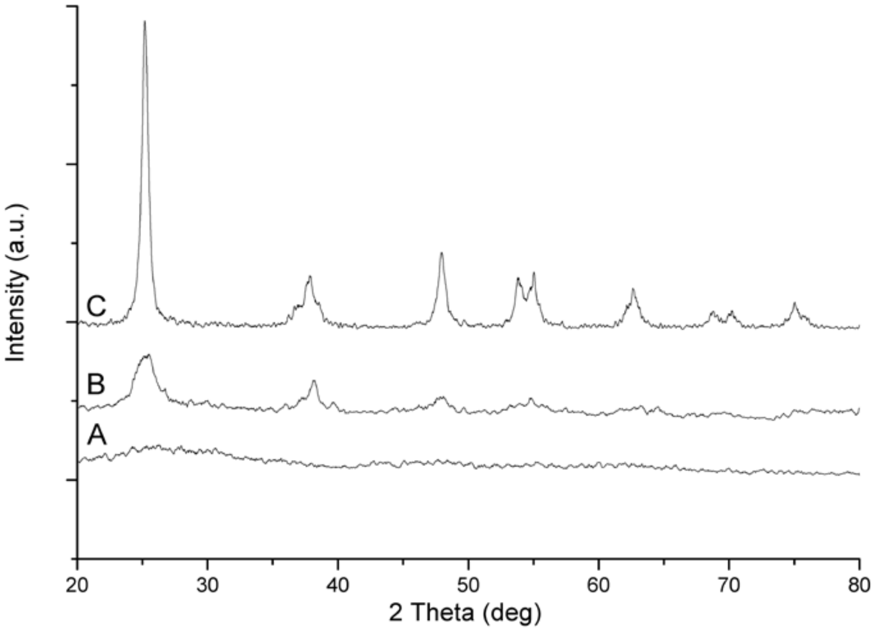

Figure S1. XRD patterns of original TiO_2 (trace A), TiO_2 calcined at 200°C and reduced at 250°C (trace B) and TiO_2 calcined at 200°C and reduced at 500°C (trace C).

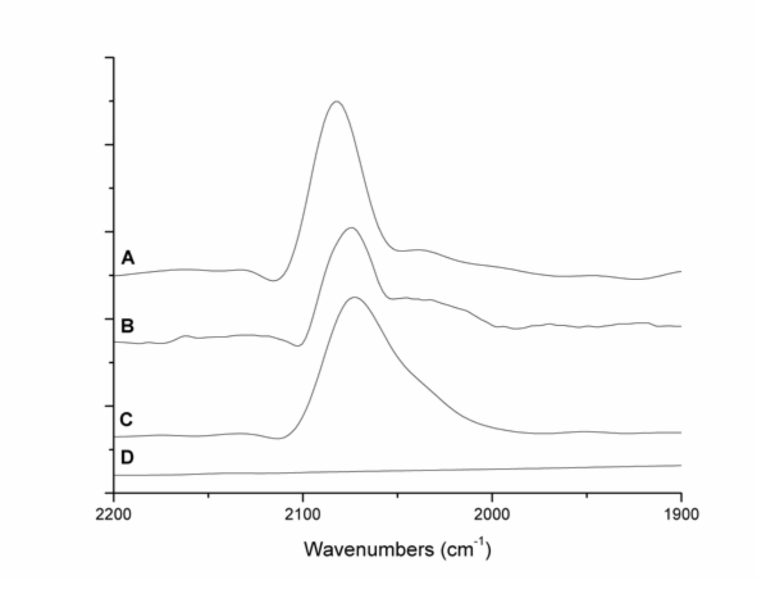

Figure S2. CO-DRIFT spectra of Pt1/TiO_2 (trace A), Au0.5-Pt0.5/TiO_2 (trace B) and Au1-Pt1/TiO_2 (trace C) Au1/TiO_2 (trace D), samples reduced at 500°C.

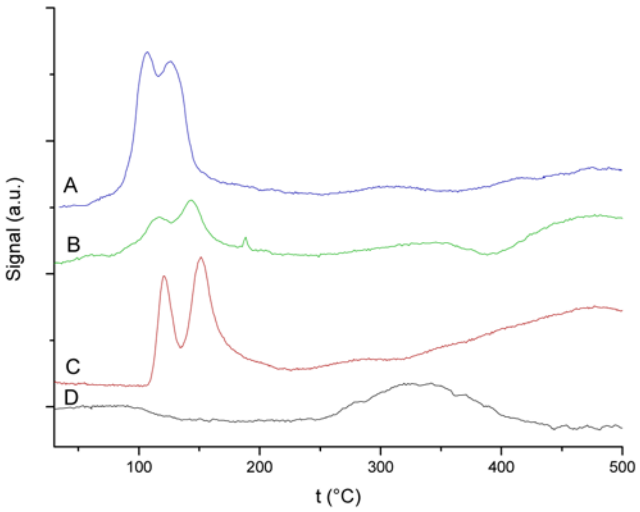

Figure S3. TPR profiles of Pt1/TiO_2 (blue trace A), Au0.5-Pt0.5/TiO_2 (green trace B), Au1-Pt1/TiO_2 (red trace C), and Au1/TiO_2 (black trace D) samples calcined at 200°C.

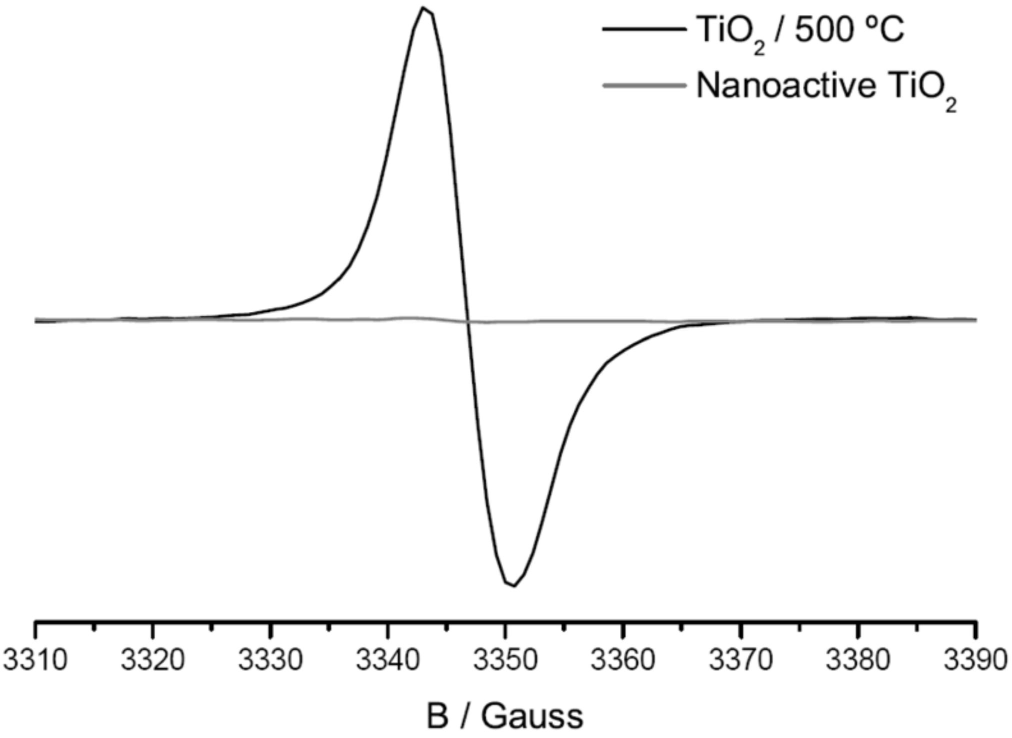

Figure S4. EPR spectra for TiO_2 after oxidation at 200°C and reduction at 500 ºC (dark line) and commercial Nanoactive TiO_2 calcined at 500°C (gray line).