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Supplementary Information

The critical role of intragap states in the energy transfer from gold nanoparticles to TiO_2

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Experimental Methods

Preparation of TiO_2-based materials. A commercial amorphous TiO_2 powder (NanoActive®, NanoScale Co., USA) was used as starting material to produce black TiO_2 nanocrystals. The amorphous powder was firstly kept at 200°C under pure O_2 flow for 1 h. After cooling down to room temperature, it underwent a reduction step under pure H_2 flow at 500°C for 1 h. P25 was supplied by Evonik-Degussa. P25 and black TiO_2 were loaded with Pt and Au nanoparticles as follows: 500 mg of TiO_2 were suspended in 40 mL of H_2O and sonicated for 20 min; then, a H_2PtCl_6 or $HAuCl_4$ water solution was added to the suspension and the so obtained mixture was stirred for 30 min. Finally, a $NaBH_4$ solution (10 mg of $NaBH_4$ dissolved in 10 mL of H_2O) was added drop wise under stirring and the suspension was allowed to undergo reaction for 10 min. The product was then centrifuged, washed 3 times with deionized H_2O and dried under vacuum (10^{-5} mbar). The nominal amount of metal loaded on TiO_2 samples was 1 wt.% in both cases (Au and Pt). The actual Pt and Au loadings were determined by ICP-OES (ICAP6300, Thermo Electron) after microwave digestion of samples in a 3:1 HCl/HNO_3 mixture. For both the supports the measured Au and Pt loadings were 0.80 and 0.70, respectively.

Characterization. Diffuse reflectance (DR) UV–Vis spectra of carefully ground powders were recorded with a Thermo Scientific Evolution 600 spectrophotometer, equipped with a diffuse reflectance accessory Praying–Mantis sampling kit (Harrick Scientific Products, USA). A Spectralon® disk was used as reference material. High resolution transmission electron microscopy (HRTEM) and High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis were carried out by using a Zeiss Libra 200FE instrument. The samples were finely ground using an agate mortar and then dispersed in isopropanol in an ultrasonic bath. A drop of the suspension was gently deposited on a holey-carbon film supported on a copper 300 mesh grid. After solvent evaporation, TEM micrographs were taken spanning wide regions of all examined samples in order to provide a truly representative statistical map of the powders. The size distribution of Au and Pt NPs deposited on TiO_2 was calculated by STEM measurements. Cathodoluminescence spectroscopy (CL) emission spectra were acquired by using a commercial GatanMONOCL2 system mounted on a S360 Cambridge Stereoscan scanning electron microscope. The system was equipped with a grating and a multi-alkali photomultiplier detector sensitive in the 350 – 830 nm range (3.6 - 1.5 eV). The spectra were collected with an accelerating voltage of 10 kV, a beam current of 75 nA and a spectral resolution of 9 nm (about 70 meV). The single peak parameters are evaluated by a deconvolution procedure using a standard Levenberg-Marquardt algorithm for the minimization of the Chi Square. In order to avoid any possible artefacts the fitting parameters peak position (x_C) and amplitude (A) were left free, while constraints were applied to the full width half maximum (w). We impose a w maximum equal to 0.5 eV. At the end, all the peak positions are affected by an error of 10 meV, which is less than the error due to the spectral resolution of the measurement. The amplitude and the full width half maximum have a relative error of 5%.

Photocatalytic tests – H_2 production by methanol photo-steam reforming. Methanol photo-steam reforming experiments were carried out to assess the photocatalytic H_2 production ability of the powders investigated in this work. The photoreactor set-up and the experimental conditions were nearly identical to those adopted in previous works (ref. 33 manuscript). The photocatalyst bed was prepared by mixing 14 mg of photocatalyst with 3 g of 20–40 mesh (0.42–0.85 mm) quartz beads and 1.2 mL of ultra-pure water. The solid mixture was then dried in oven at 70 ˚C for 2 h. The so obtained photocatalyst bed was inserted in the photo-reactor, consisting of a flat cylindrical Plexiglas cell frontally closed by a Pyrex glass optical window (surface *ca.* 20 cm^2). The photoreactor was connected to a recirculation, stainless steel apparatus, containing a N_2 gas bubbling system filled with a 20 vol% CH_3OH aqueous solution and kept at 30 ˚C (precisely, the methanol molar fraction in the liquid phase, x, was 0.10). The gas phase fed from the bubbling system to the photocatalyst bed within the reactor was therefore an N_2–saturated stream containing a constant concentration of CH_3OH and H_2O vapors. Prior to any run, the whole setup was thoroughly flushed with an inert gas, namely N_2, in the dark for 30 min, in order to remove any trace of oxygen. The photocatalyst bed was irradiated either for 6 h, when testing bare TiO_2 powders, or for 2 h, for noble metal-modified samples. In this case, three consecutive irradiation cycles were performed with each photocatalyst bed, with 30 min of N_2 purging (in the dark) between each irradiation cycle. All kinetic tests were repeated three times. The amount of hydrogen, CO_2 and CO produced under irradiation and accumulated at constant rate in the inert gas was determined by an on-line Agilent 6890 N gas-chromatograph, employing N_2 as carrier gas, equipped with two columns (HP-PlotU and Molesieve 5A), two detectors (thermo-conductivity and flame ionization) and a Ni-catalyst kit for CO and CO_2 methanation. The irradiation source, always switched on 30 min prior to the beginning of the run, was a Xenon arc lamp (LSH302 LOT Oriel, 300 W), emitting in the UV–Vis range with a full irradiation intensity of 6.0×10^{-8} Einstein s^{-1} cm^{-2} on the reactor. The catalytic runs under visible light were performed applying different cut-off filters (385, 400, 550 nm cut-off wavelength) to the Xenon arc lamp.

Figures

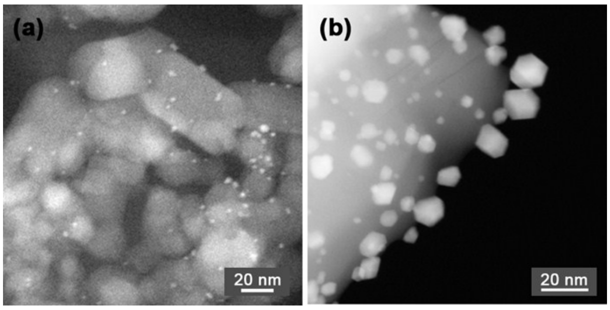

Figure S1 HAADF-STEM images of (a) Pt/P25 and Pt/black TiO_2.

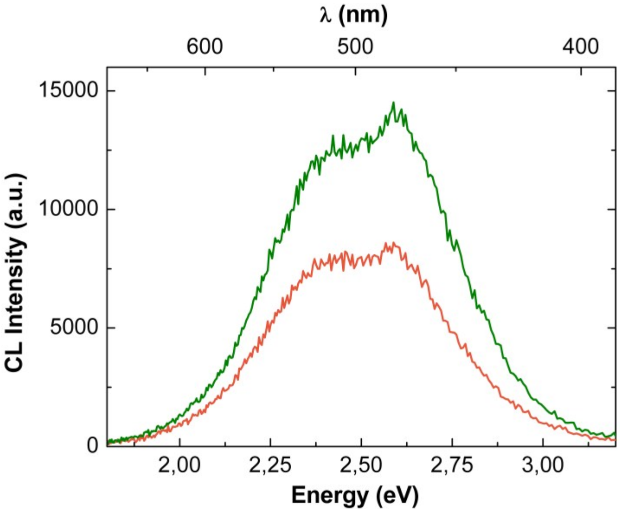

Figure S2 CL spectra of P25 (orange line) and black TiO_2 (green line).

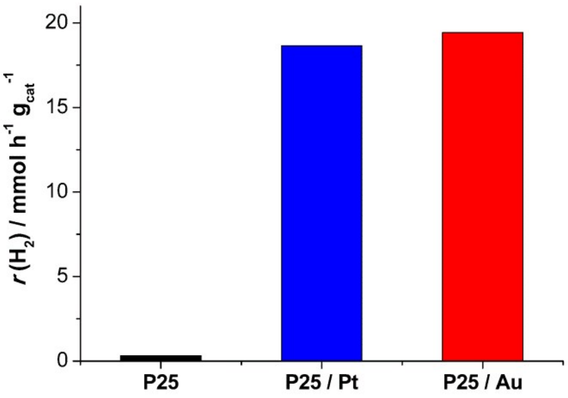

Figure S3 Photocatalytic hydrogen production from photocatalytic water splitting for P25, Pt/P25, and Au/P25 under full solar irradiation.

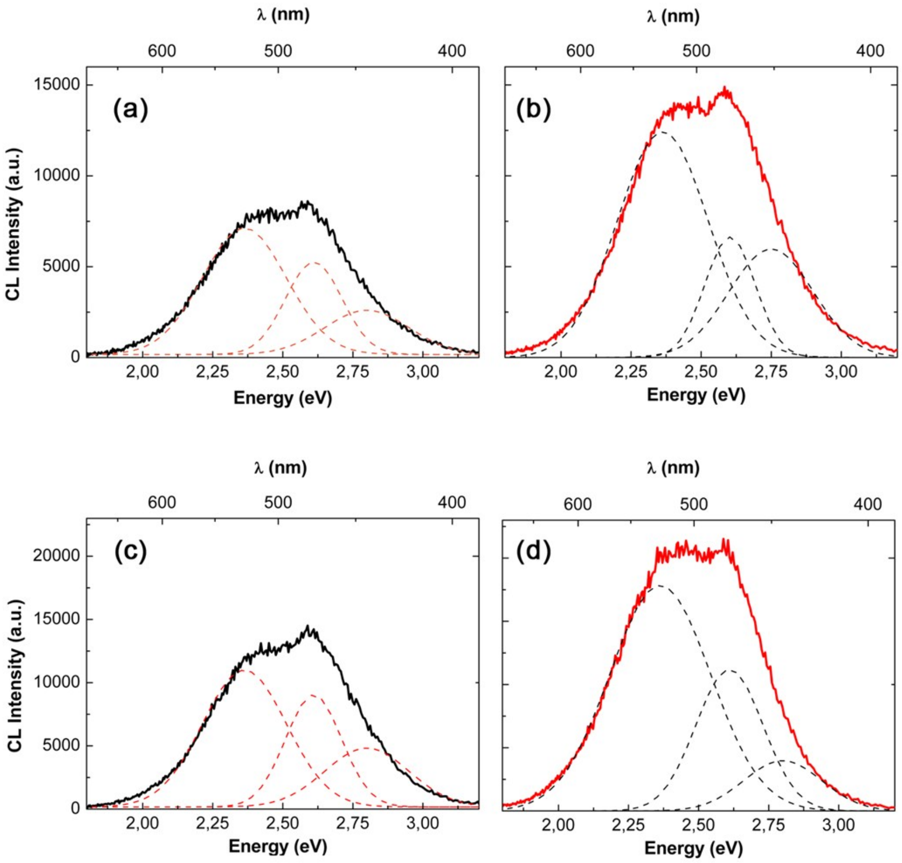

Figure S4 Gaussian deconvolution of the CL spectra reported in Fig. 4 in the manuscript, for the samples (a) P25; (b) Au/P25; (c) black TiO_2; (d) Au/black TiO_2.

Tables

Table S1 Photocatalytic H_2 production rates of the investigated photocatalysts in the methanol steam reforming, $r(H_2)$ (in mmol h^{-1} g^{-1}) under full solar irradiation.

Sample	***r*** **(H_2)**
Black TiO_2	0.061
Pt / Black TiO_2	1.44
Au / Black TiO_2	1.92
P25	0.32
Pt / P25	18.66
Au / P25	19.44