

## Soft-chemistry assisted strong metal-Support interaction on designed plasmonic core-shell photocatalyst for enhanced photocatalytic hydrogen production

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### Experimental details

The UV–vis spectroscopy (model Cary 5000 series, Agilent Technologies) was used to analyze the optical properties of the hybrid films. The maximum reflectance was set to 100 % using tetrafluoroethylene as a reference in a wavelength range between 200 and 800 nm.

The X-ray photoelectron spectroscopies (XPS) of core-shell nanopartilces were obtained on Kratos Axis-Ultra spectrophometer irradiated with a monochromatic Al K $\alpha$  (1486.6 eV) radiation (10 kV; 22 mA). The analysis chamber was operated under ultrahigh vacuum conditions with an approximate pressure of  $5 \times 10^{-7}$  Pa. The sample was. The binding energies were calibrated using C1s at 284.6 eV.

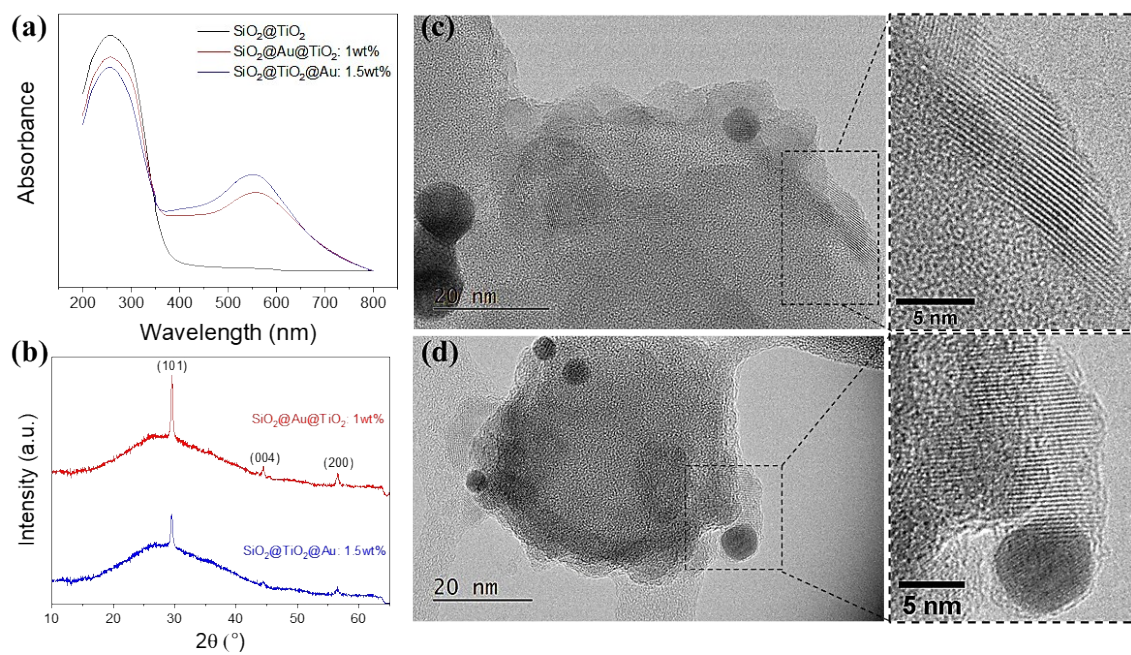
### Quantum efficiency

The so-called quantum efficiency is defined has been estimated according to the IUPAC recommendation as follows [1]:

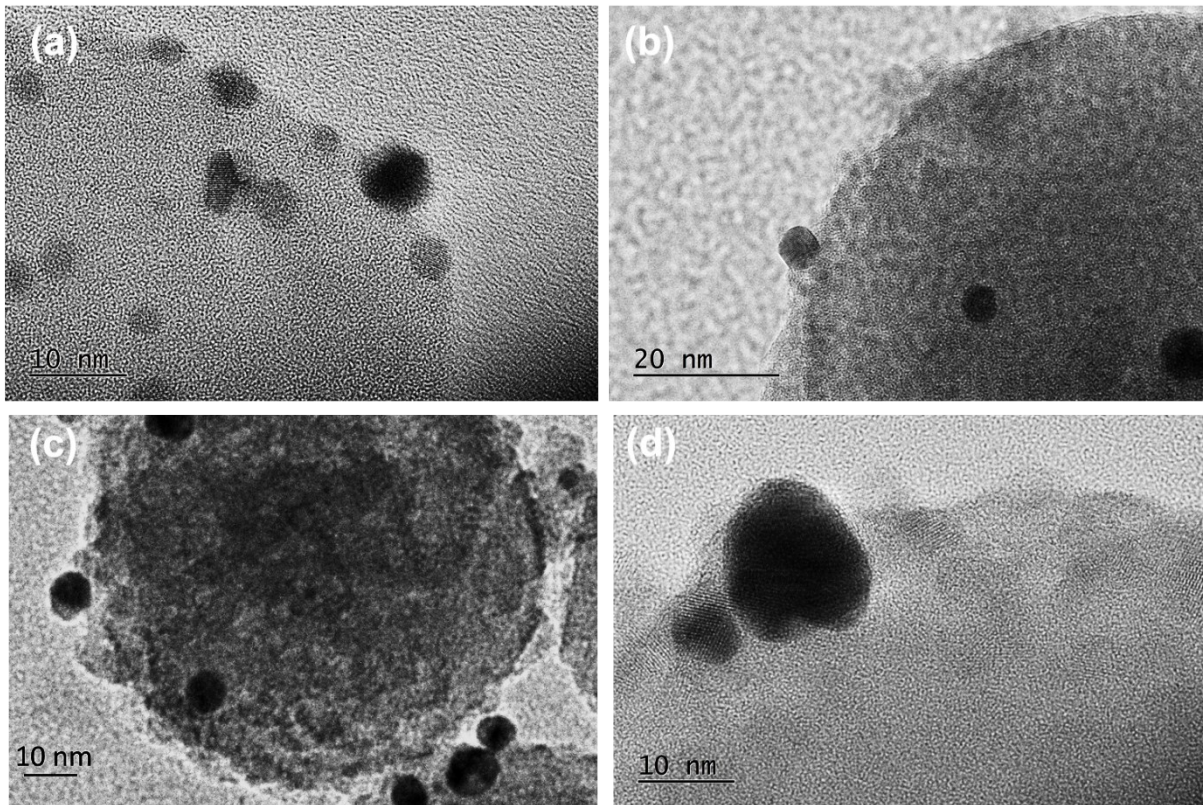
$$\eta_q(\%) = 100 \times \frac{2 \times r}{q} \quad (1)$$

where, the reaction rate  $r$  (mol.m<sup>-3</sup>.s<sup>-1</sup>) and  $q$  represents the incident radiation flux averaged in the illuminated reactor surface. A value of  $q$  equal to 1.2 mol.m<sup>-2</sup>.s<sup>-1</sup> at the sample average position was experimentally measured using a photoradiometer.

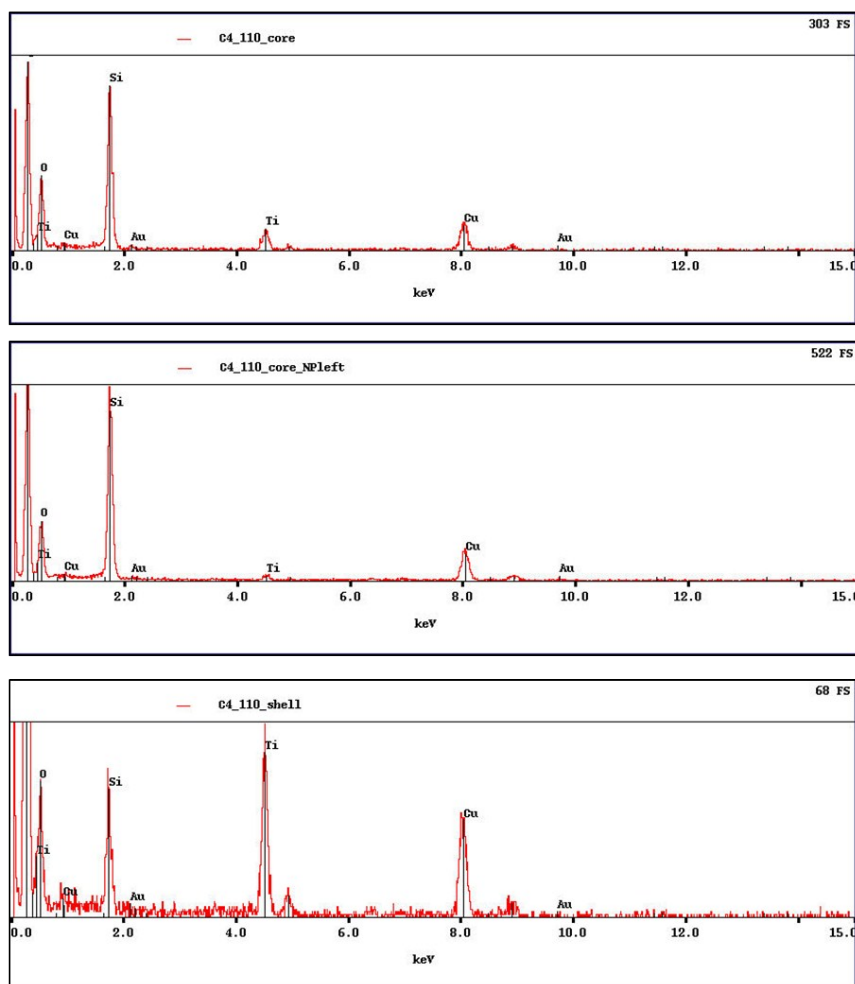
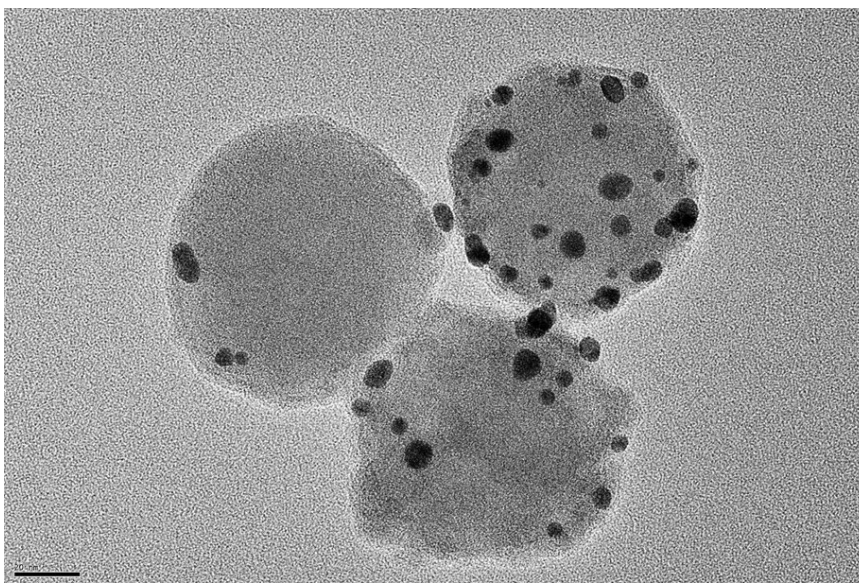
[1] Fontelles-Carceller ; O., Muñoz-Batista ; M. J., Rodríguez-Castellón ; E., Conesa ; J.C., Fernández-García; M., Kubacka; A. Journal of Catalysis 347, **2017**, 157–169.



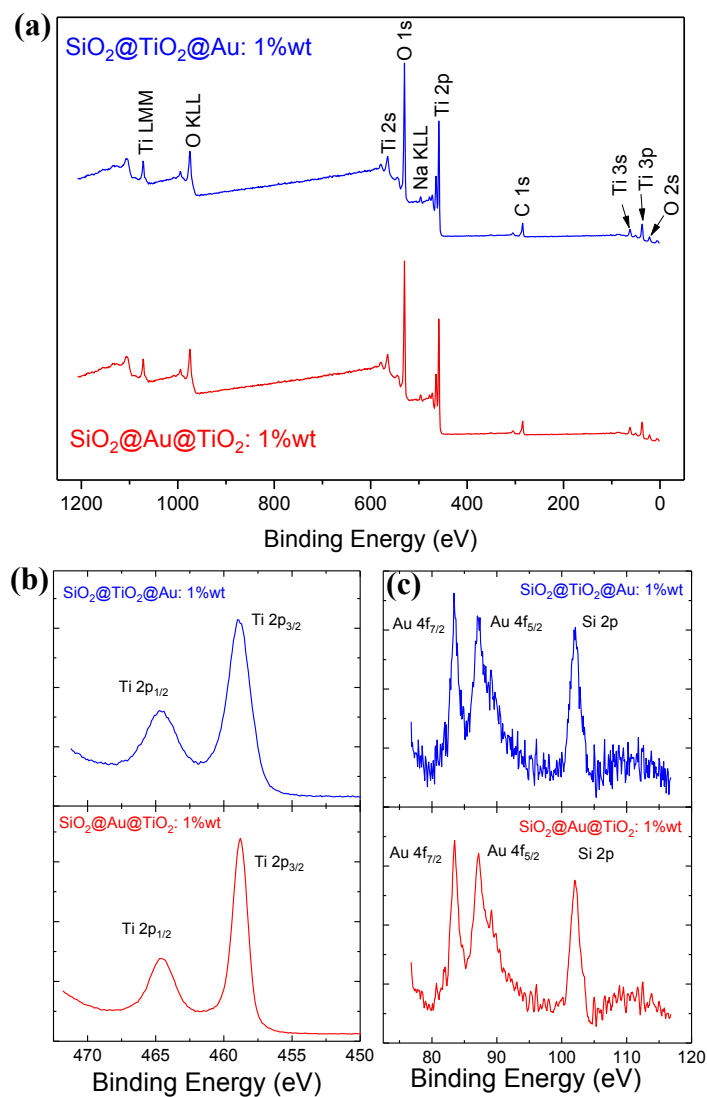
**Figure S1:** (a) UV-visible spectra, (b) X-ray diffraction pattern and HR-TEM of  $\text{SiO}_2@\text{TiO}_2@\text{Au}$ :1.5wt% and (d)  $\text{SiO}_2@\text{Au}@\text{TiO}_2$ :1wt% core-shell nanostructure.



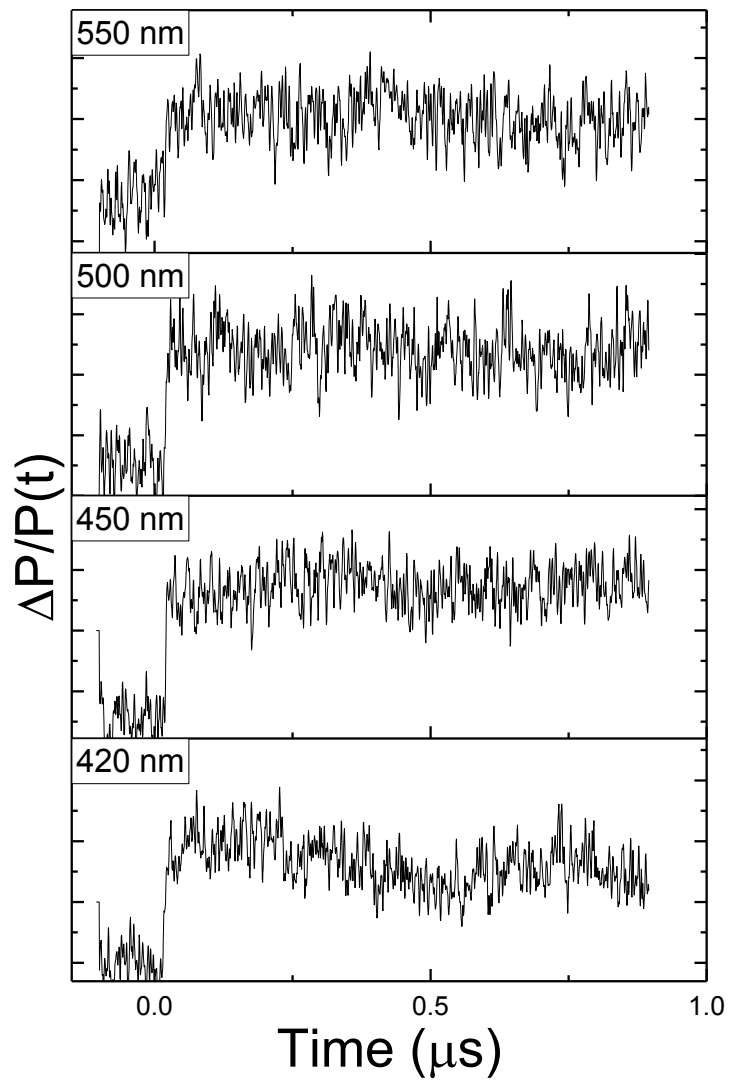
**Figure S2 :** TEM images of SiO<sub>2</sub>@ TiO<sub>2</sub>@Au system with increasing gold ratio : (a) 0.25 wt%, (b) 0.5 wt%, (c) 1 wt% and (d) 1.5 wt%.



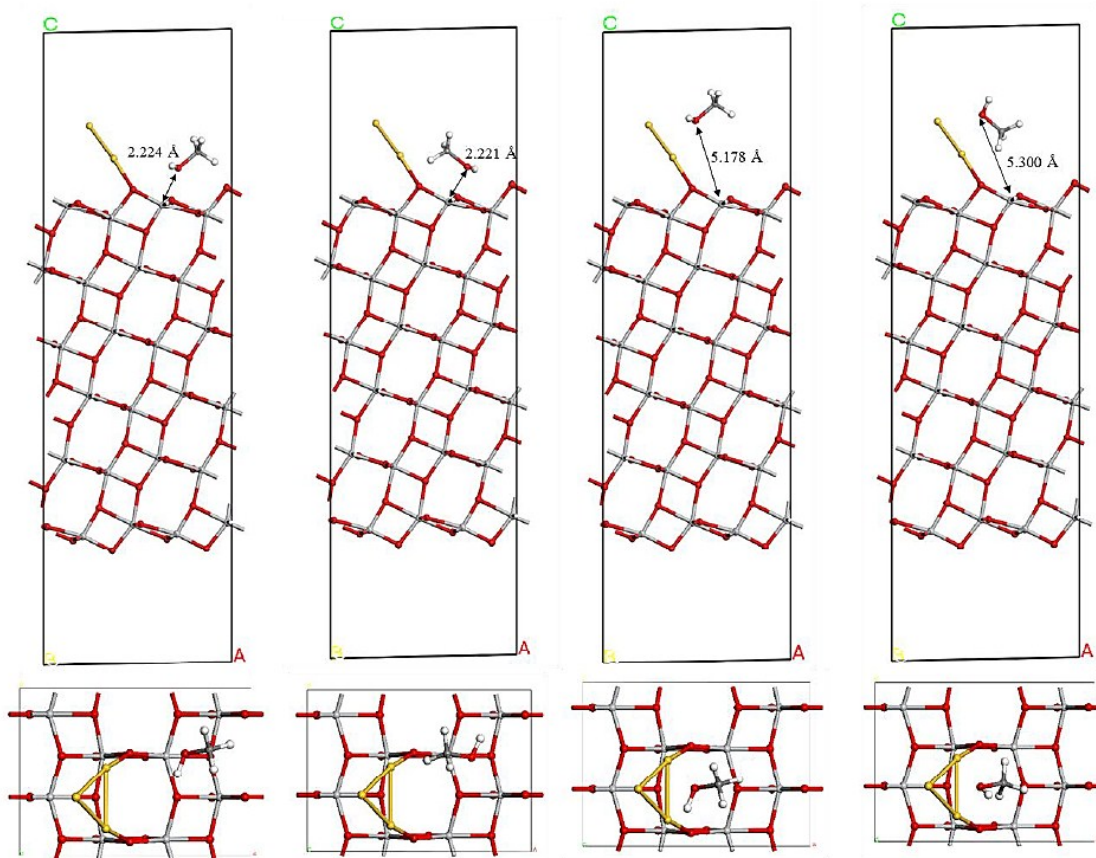
**Figure S3** : TEM image and EDS analysis of different region of the core-shell plasmonic  $\text{SiO}_2@Au@TiO_2$  with 1.5wt% of gold.



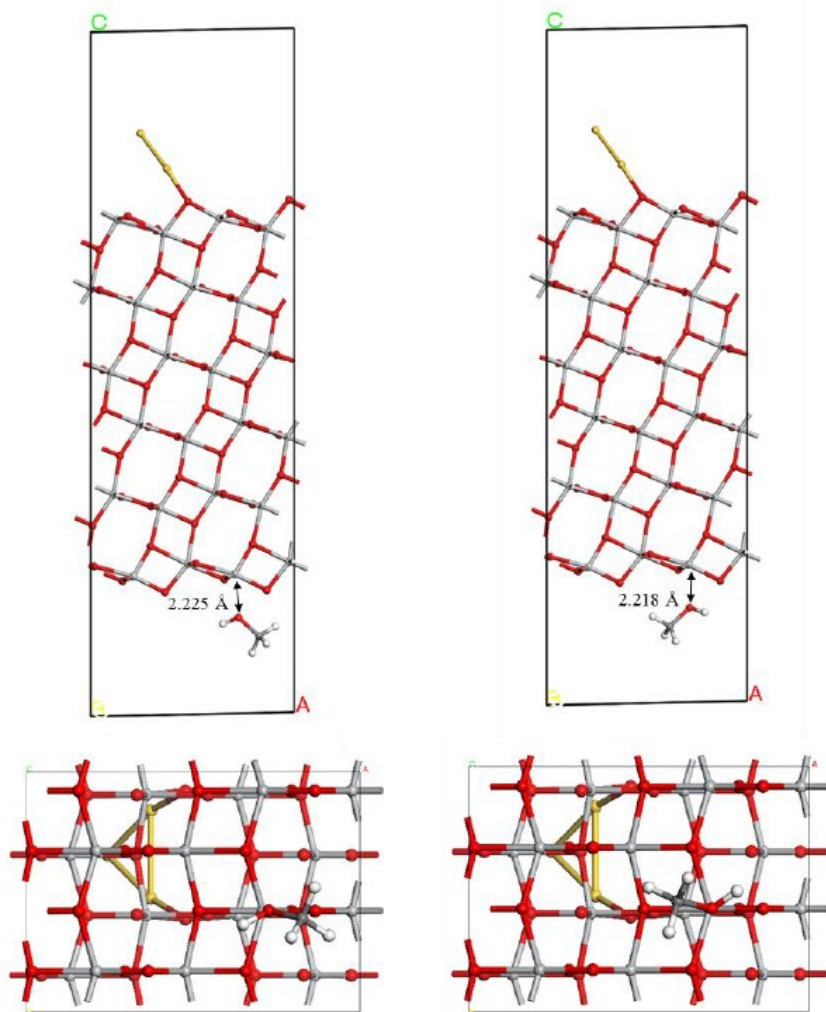
**Figure S4:** (a) XPS general spectra of plasmonic  $\text{SiO}_2@Au@TiO_2$  and  $\text{SiO}_2@TiO_2@Au$  containing 1%wt of gold. (b) Ti 2p, (c) Si 2p and Au 4f spectra for each nanostructure.



**Figure S5 :** TRMC signal for (a)  $\text{SiO}_2@Au@TiO_2$  system for variable wavelength excitation from 420 to 550 nm.



**Figure S6 :** Four initial adsorption locations of methanol on  $\text{TiO}_2@Au$ . Measurements are from oxygen in methanol to closest five-coordinated titanium site on the surface. Atom color schemes are the same as described in the caption of Figure 7.



**Figure S7 :** Two initial adsorption configurations of methanol on Au@TiO<sub>2</sub>. Measurements are from oxygen in methanol to closest five-coordinated titanium site on the surface. Atom color schemes are the same as described in the caption of Figure 7.