coatings

Supplementary Materials

Additional Structural and Morphologic Characterization

In the present work, we have prepared and used AuNRs colloidal solution as nucleation seeds for the growth of TiO_2 NPs. In particular, the spectrum of this solution is characterized by the transversal and the longitudinal, plasmon bands, respectively at 530 and 780 nm (Figure S1A). Moreover, TEM micrograph indicates that the particle population of Au colloidal solution consists mainly of Au NRs (Figure S1B).

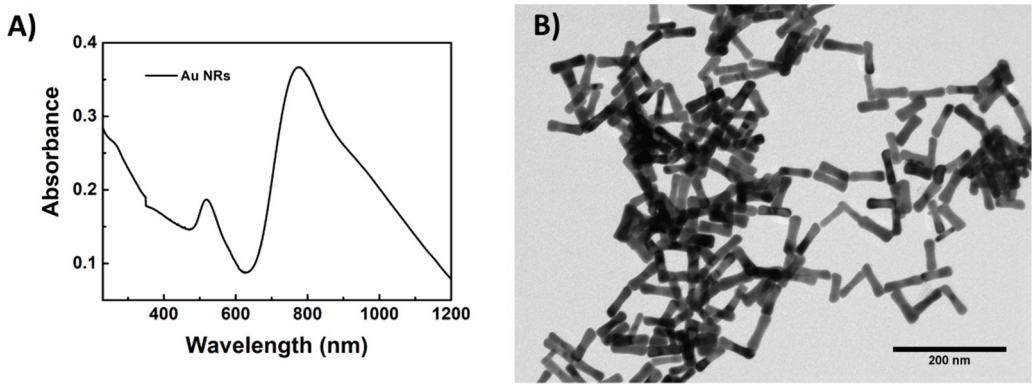

Figure S1. (**A**) UV-Vis absorption spectra of Au NRs solution, after purification in order to remove excess of CTAB; (**B**) Transmission electron microscopy image of the Au NRs.

TEM micrographs (Figure S2) confirms that AuNPs are mostly embedded in submicrometric aggregates composed of TiO_2NPs. As an evident feature, the TiO_2 NPs appeared in close contact with Au NRs and closely arranged around the Au NRs.

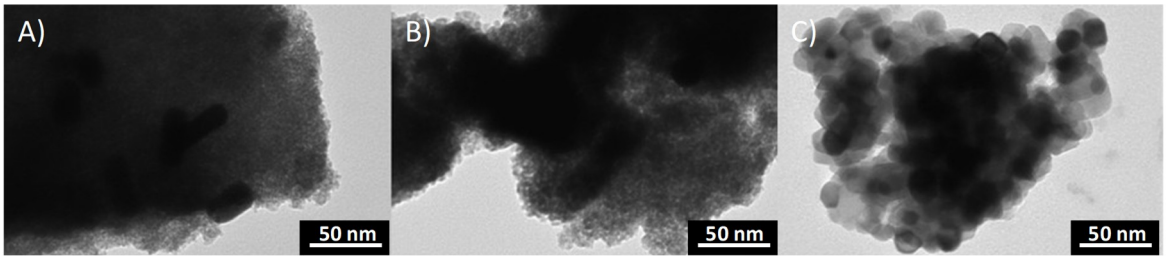

Figure S2. TEM micrograph of TiO_2/AuNRs photocatalysts for different synthesis conditions: TiO_2/AuNRs 250°C (**A**); TiO_2/AuNRs 450°C (**B**); TiO_2/AuNRs 650°C (**C**).

Moreover, it was observed that the shape and the size of Au NRs can be affected by the calcination temperatures. Indeed, the detected Au NPs underwent a reshaping in samples calcined at 650°C. In particular, in the case of TiO_2/AuNRs 650 °C the anisotropic shape seems to be lost leading to nearly spherical NPs.

Accordingly, DRS show a blue-shift and a broadening of longitudinal plasmon band (LPB) absorption as a function of calcination temperature (Figure S3). More in depth, the spectra of samples calcined at 250°C and 450°C clearly shows the two plasmon band typical of AuNRs, corresponding to the collective oscillations of the free conduction band electrons along the longitudinal and transverse axes of the NRs, respectively.

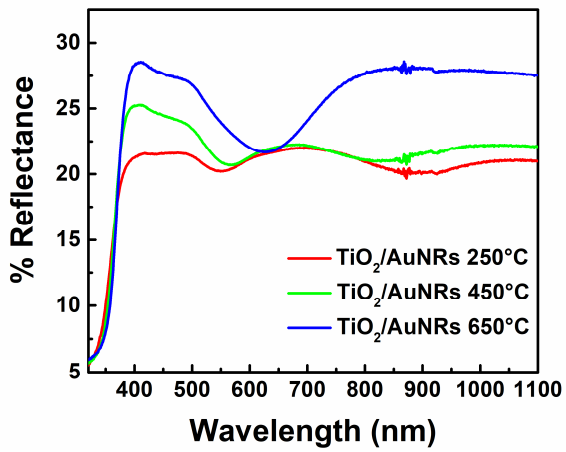

Figure S3. Diffuse reflectance spectra (DRS) of TiO_2/Au NRs nanocomposites deposited onto quartz slides, recorded in absorption mode.

The position of the LPB is almost retained in the TiO_2/AuNRs 250 °C sample, while the TiO_2/Au NRs 450 °C sample show a slight blue shift (850 nm) of the LPB indicative of a slight reduction of the AuNRs aspect ratio. Conversely, the sample treated at higher calcinations temperature (TiO_2/Au NRs 650 °C) shows a strong modification of the line profile of the DRS spectrum being transversal and longitudinal plasmon bands merged in one broad band centred at 680 nm, due to a strong modification of NR size/shape. Indeed, nearly spherical and ellipsoidal NPs were detected during TEM investigation.

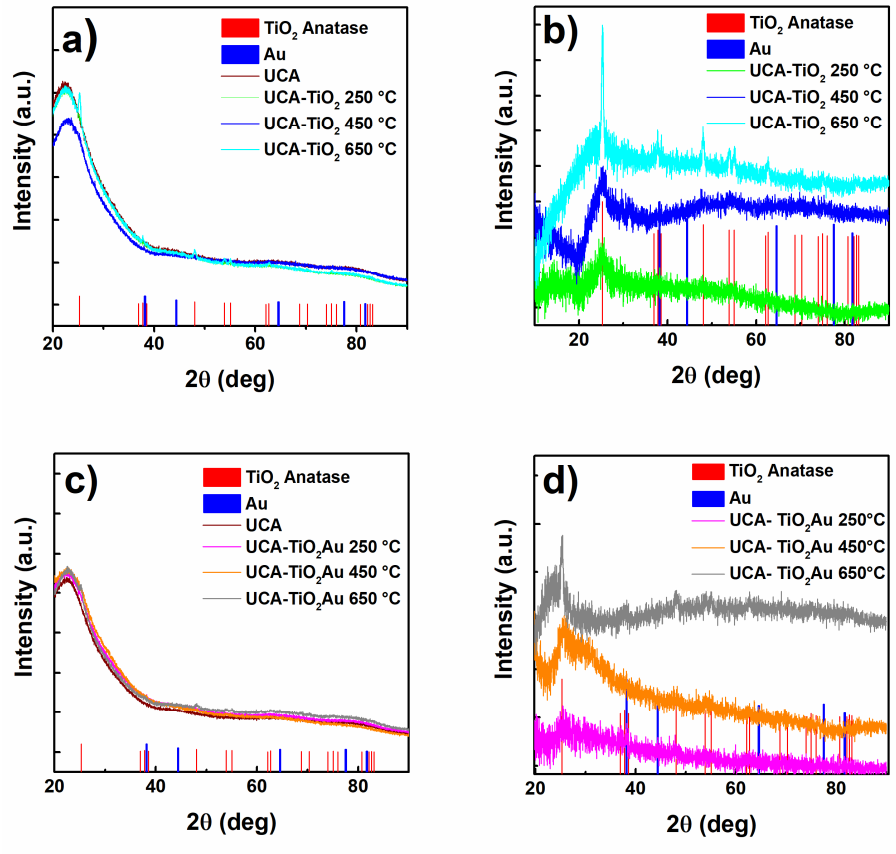

Figure S4. XPD patterns of the UCA-TiO_2 and UCA-TiO_2Au nanocomposites under study. (**a**,**c**) Original data of compounds; (**b**,**d**) Data corrected by subtracting the contribution of UCA component to enhance the contribution of the TiO_2 nanocrystals and Au NRs.

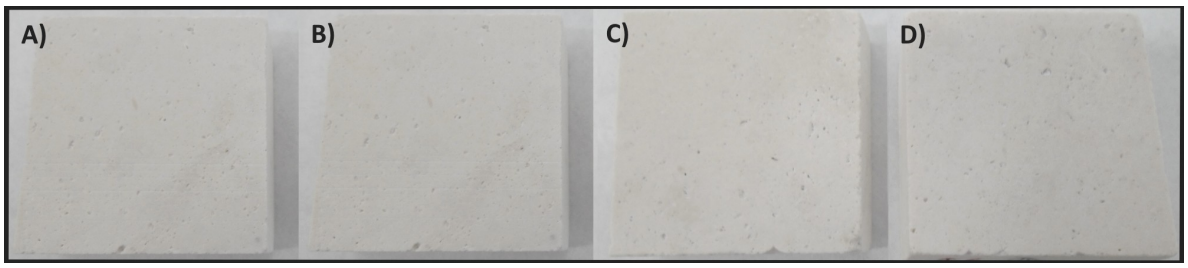

Figure S5. Representative pictures of the stones before and after coating: (**A**) untreated; (**B**) UCA-TiO_2 P25; (**C**) UCA-TiO_2 450 °C; (**D**) UCA-TiO_2/Au NRs 450 °C.