

Supporting Information

Visible-light Photodecomposition of Acetaldehyde by TiO₂-coated Gold Nanocages: Plasmon-mediated Hot Electron Transport via Defect States

*Rajesh Kodyath, * Maidhily Manikandan, Lequan LiU, Gubbala V. Ramesh, Satoshi Koyasu, Masahiro Miyauchi, Yoshiki Sakuma, Toyokazu Tanabe, Takao Gunji, Dao Duy Thang, Shigenori Ueda, Tadaaki Nagao, Jinhua Ye and Hideki Abe **

Experimental

Silver Nitrate (AgNO₃, ACS reagent, ≥99.0%, Sigma Aldrich), Ethylene Glycol (HOCH₂CH₂OH, Sigma Aldrich), Polyvinyl Pyrrolidone (PVP, Mw=55000, Sigma Aldrich), Sodium Sulfide (Na₂S, Sigma Aldrich), Gold Chloride Solution (HAuCl₄, 200 mg/dL in deionized water, Sigma Aldrich), TiCl₃ and Sodium hydrogen carbonate (NaHCO₃, Sigma Aldrich) were used as received.

Synthesis of Silver Nanocubes (Ag NCs): In a typical synthesis, a round bottom flask contained 70 ml ethylene glycol was stirred at 400 rpm and heated at 140 °C for 1h in an oil bath in order to remove residual water in the EG. After 1 h, 0.8 g of PVP dissolved in 5 ml of ethylene glycol was added to the reaction mixture. Temperature of the reaction mixture was gradually raised to 155 °C. At this temperature, 0.4 ml of 3 mM sodium sulfide in EG was added. 0.25 g of AgNO₃ dissolved in 5 ml of EG at 200 rpm was then added to the reaction mixture. The reaction mixture was turned dark brownish yellow after 10 minutes and the stirring was stopped when the solution turned opaque. The reaction mixture was immediately cooled down to room temperature in order to control the growth of the Ag NCs. The Ag NC solution was diluted with distilled water and then centrifuged at 13 000 rpm for 5 -10 minutes to separate the Ag NCs.

Synthesis of Gold Nanocages (Au NCs)¹⁻³ Gold Nanocages were synthesized using prepared Ag NCs as the template. An aliquot of 10-20 mg of Ag nanocubes was dispersed in distilled water and brought to boiling. An aliquot of 0.5 mM of HAuCl₄ was then added drop wise to the solution of the Ag nanocubes at an injection rate of 45 ml/h until the absorption reaches to 750 nm, corresponding to the LSPR of the desired Au NCs. The solution was cooled down to room temperature and centrifuged at 13000 rpm for 10 minutes to separate the Au NCs.

TiO₂ deposition onto the Au NCs⁴: An aliquot of 1 ml of deionized water was added to 1 ml of aqueous solution of TiCl₃. The pH of this solution was adjusted to 2.5 by adding 1 M solution of sodium hydrogen carbonate. An aliquot of 0.1 g of Au NCs was dispersed in 2 ml of distilled water, added to the prepared TiCl₃ solution and stirred for 20 minutes. The solution was centrifuged to obtain the final product, TiO₂/Au NCs.

TiO₂/Au NPs: TiO₂ deposition was carried out following the same method described as above. Au NPs were synthesized by following a reported method.⁵

Crystalline TiO₂/Au NCs: This sample was prepared by dispersing 50 mg of Au NCs and 70 mg of anatase-type TiO₂ (Wako, 96 %) in isopropanol for 30 min. The mixture was then separated by centrifugation and dried under vacuum for 2 h.

Photocurrent measurements: Mesoporous TiO₂ films (10 μm thickness; 5 × 5 mm²) were prepared as photoanodes by pasting a slurry of TiO₂ nanoparticles (P-25, Degussa) over fluorinated tin oxide (FTO) glass, followed by annealing at 450 °C for 1 h. The prepared photoanode was dipped in aqueous solution of the Au NCs, dried in air and cleaned by UV-ozone treatment for 1 h. This dip- and UV-ozone treatment was repeated ten times to disperse and immobilize the Au NCs over the pore surface of the TiO₂ film. The photoanodes was assembled with a 30 μm-thick spacer, and a Pt-coated FTO glass as the counter electrode. The gap between the electrodes was filled with aqueous solution of 0.2 M FeCl₃, 0.2 M FeCl₂ and 0.1 M HCl. The photon-to-current conversion efficiency (IPCE) was measured as a function of the wavelength of the incident monochromatic light, using a CEP-99W system (BUNKOH-KEIKI Co., Ltd.).

Photocatalytic tests: An aliquot of 0.1 g of the TiO₂/Au NCs, Crystalline TiO₂/Au NCs and TiO₂/Au NPs was spread uniformly in a quartz reaction vessel with an irradiation area of 9.0 cm². An aliquote of 50 mg of Au NCs were used for the photocatalytic study. The reaction vessel was evacuated and backfilled with 1 atm of a mixture gas (O₂:N₂=1:9). Vaporous acetaldehyde was injected into the vessel

while the vessel was kept in a room-temperature water bath. Prior to visible-light irradiation, the reaction vessel was kept in dark for 2 h until an adsorption–desorption equilibrium was established. The light source was a 300 W Xe lamp. Visible light was obtained by combining Y44, R900 and water filters ($420 < \lambda < 910$ nm). The atmospheric composition in the reaction vessel was analyzed with a gas chromatograph system (GC-2014, Shimadzu, Japan) which was equipped with a flame ionization detector (FID).

Characterization

Powder X-ray diffractometry (pXRD): The pXRD measurements were performed using Cu K α radiation ($\lambda = 0.15418$ nm) with an increment of 0.02 degrees in a range of diffraction angles from 20 to 100 degrees. An obliquely finished Si crystal (non-reflection Si plate) was used as a sample holder to minimize the background.

Hard X-ray photoemission spectroscopy (HX-PES): The HX-PES measurements were performed using X-rays with photon energy of 5.95 keV, at the undulator beam line BL15XU of SPring-8, Japan. Samples for HX-PES measurements were prepared by mixing the sample solution (in THF) with carbon black (Vulcan XC-72, Cabot Co. Ltd.) to avoid charging effects. 10 μ l of the sample was dropped onto carbon substrates (Nilaco Co., Ltd.) and dried under vacuum. The core-level states of the samples were examined at room temperature in UHV using a hemispherical electron energy analyzer (VG SCIENTA R4000). The total energy resolution was set to 240 meV. The binding energy was referenced to the Fermi edge of an Au thin film.

Transmission electron Microscopy: We used a 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (JED-2300T, JEOL) for elemental mapping. The samples for TEM were prepared by dropping a ethanol suspension of the sample powder onto a commercial TEM grid coated with a collodion film. The sample was thoroughly dried in vacuum prior to observation.

UV-vis absorption Spectroscopy: UV-vis absorption spectra of Ag NCs, Au NCs and TiO₂/ Au NCs were recorded on a Shimadzu UV-2600 spectrometer. Suspension of nanostructures in water was used to record the extinction spectra.

Photoluminescence (PL) Spectroscopy: PL spectra from the TiO_2 electrode and the fluorine-doped SnO_2 ($\text{SnO}_2:\text{F}$) substrate were measured at 10 K and 300 K by using a 32 cm-length monochromator (Jobin Yvon HR320) equipped with a liquid-nitrogen (LN_2) cooled Si-CCD detector. The samples were placed in an optical cryostat and excited with a 325 nm He-Cd laser source of 1.4 mW output power.

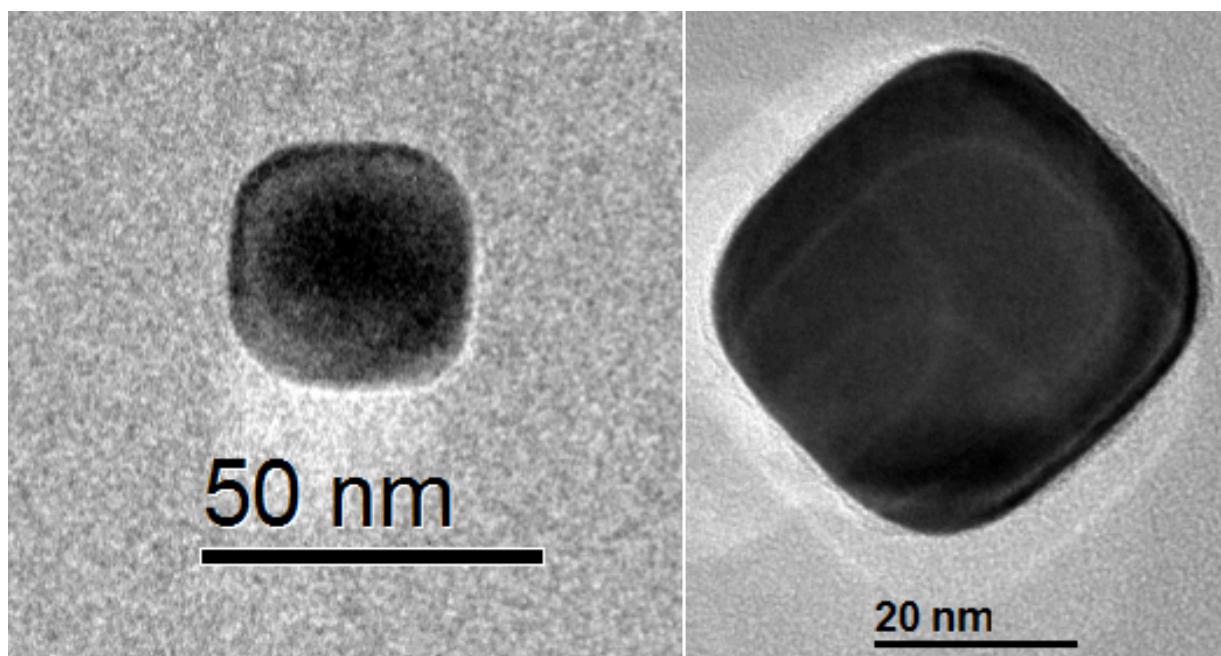


Figure S1 . TEM images of one of the prepared silver nanocubes.

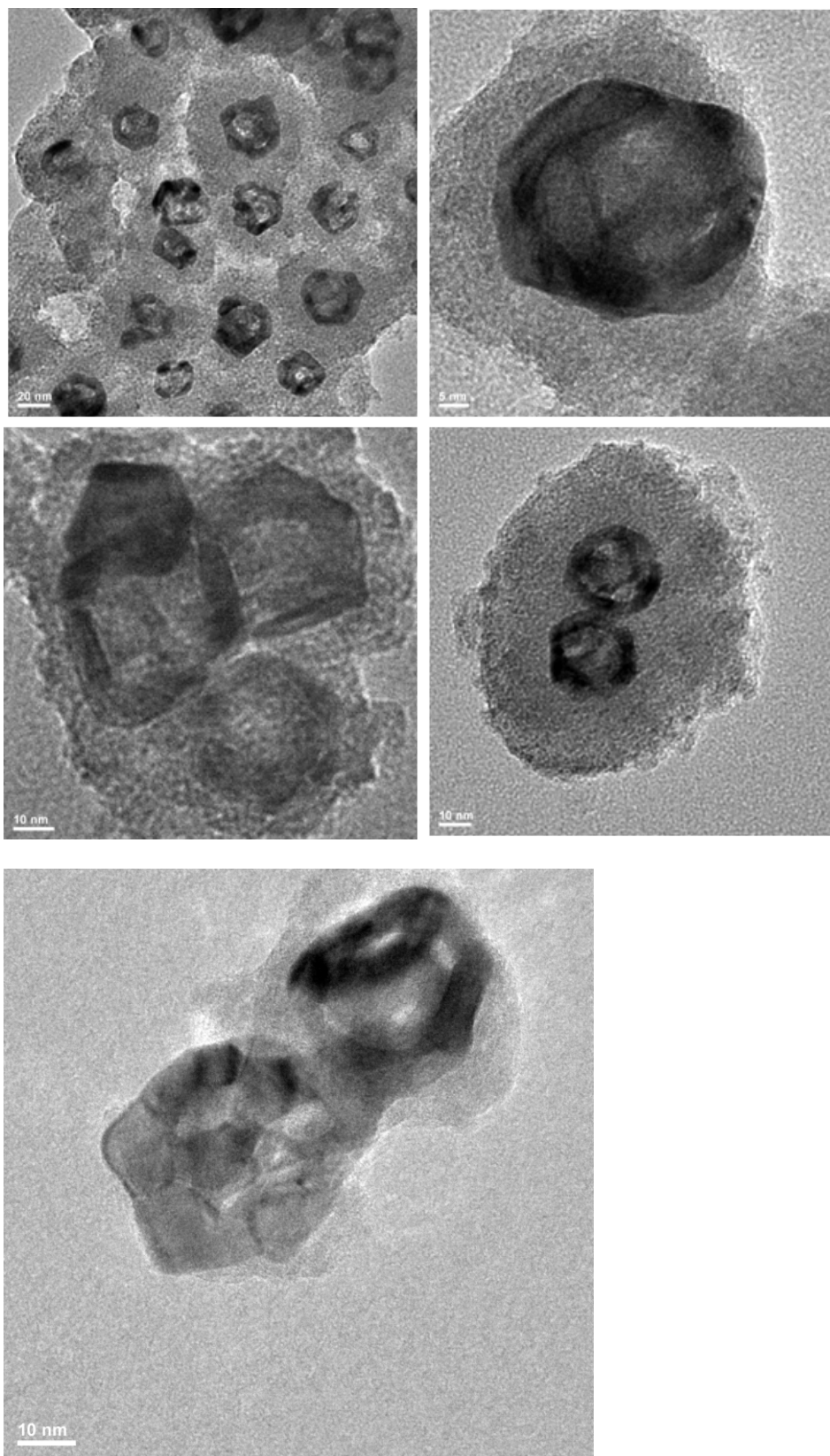


Figure S2. TEM images of the TiO₂/Au NCs.

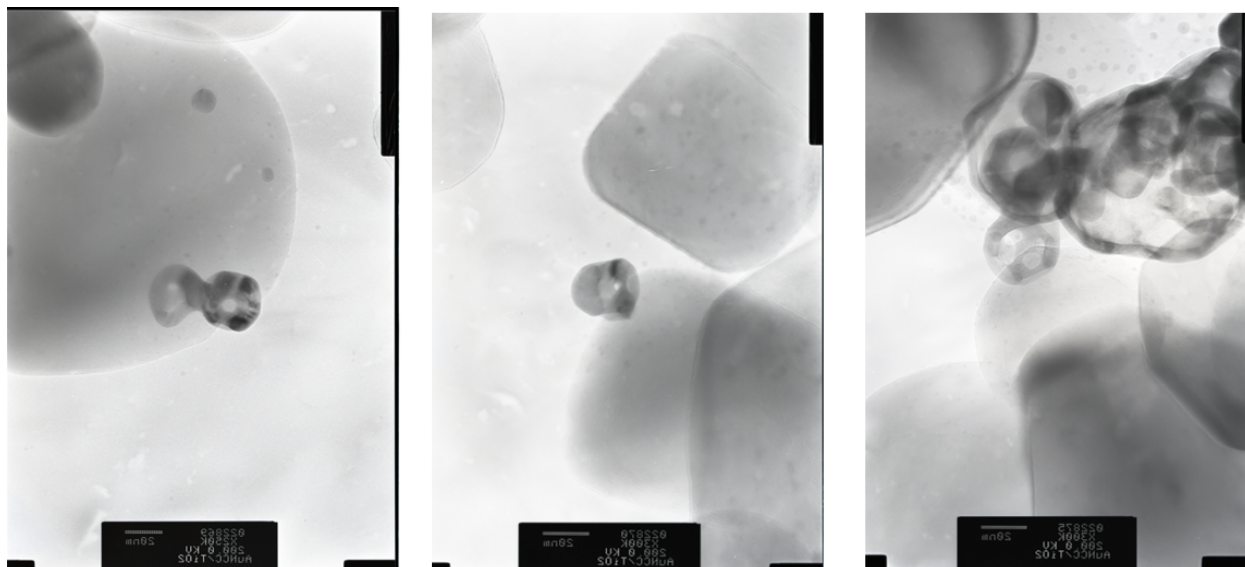


Figure S3. TEM images of the Crystalline TiO₂/Au NCs.

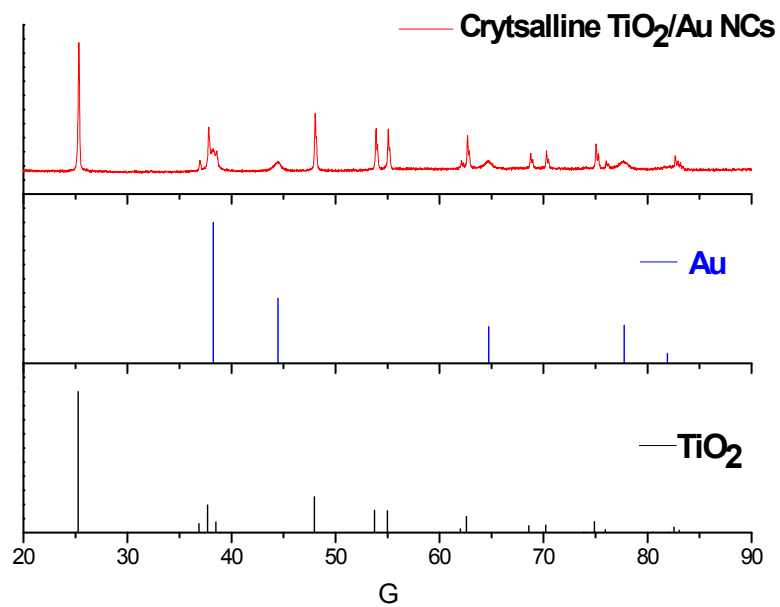
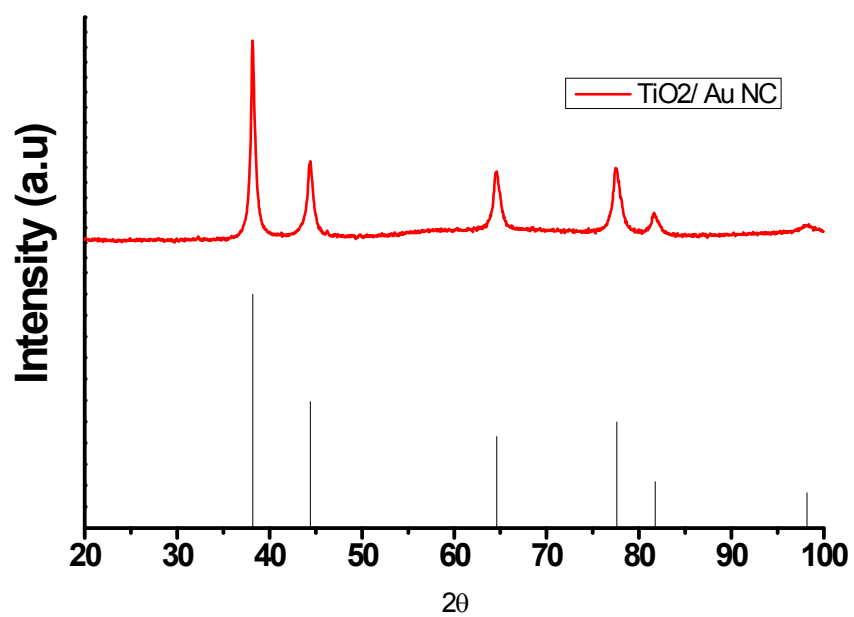


Figure S4. (a) *p*XRD profile of the (a) TiO₂/Au NCs (amorphous). (b) *p*XRD profile of the Crystalline TiO₂/Au NCs. The simulated *p*XRD patterns for Au and anatase-type TiO₂ are also presented.

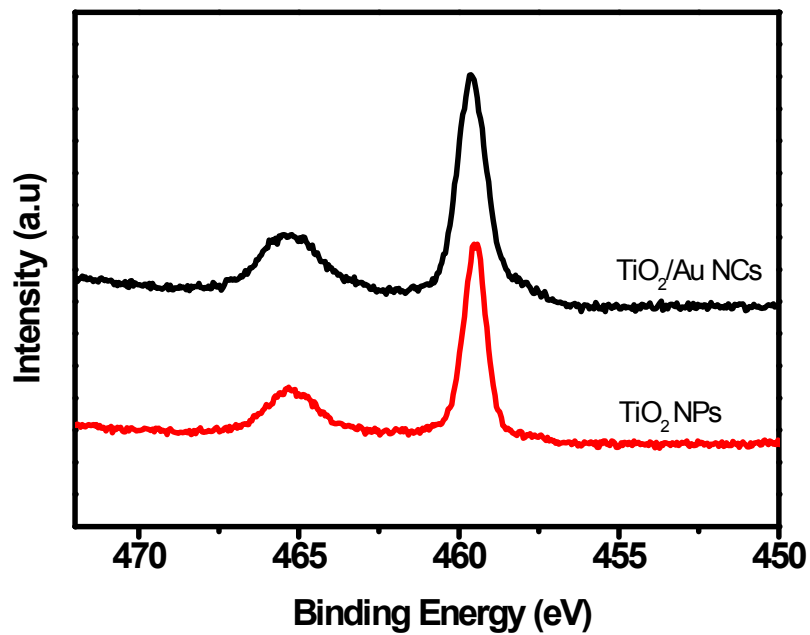


Figure S5 . Ti 2*p* core-level HX-PES spectra of TiO₂ NPs and the TiO₂/Au NCs.

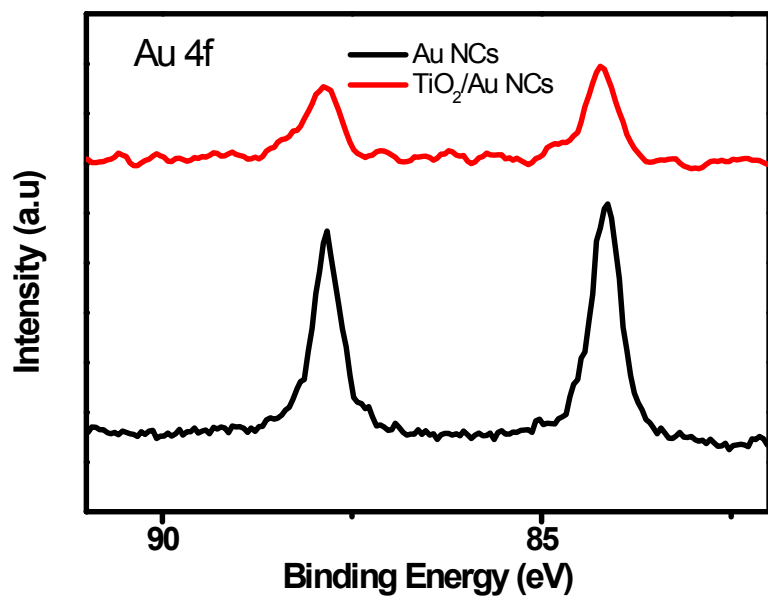


Figure S6 . Au 4*f* core-level HX-PES spectra of Au NCs and the TiO₂/Au NCs.

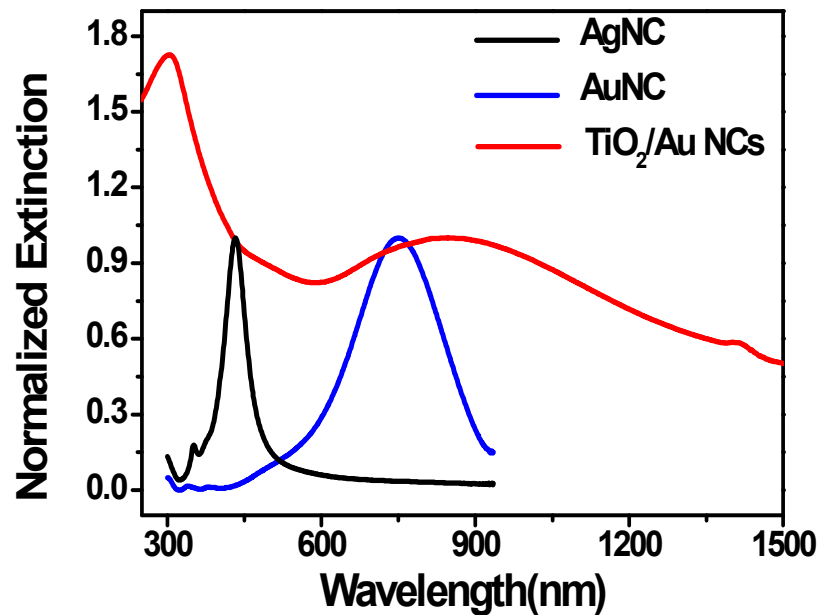


Figure S7. Extinction spectra of the Ag NCs, the Au NC and the TiO₂/Au NCs, acquired in water.

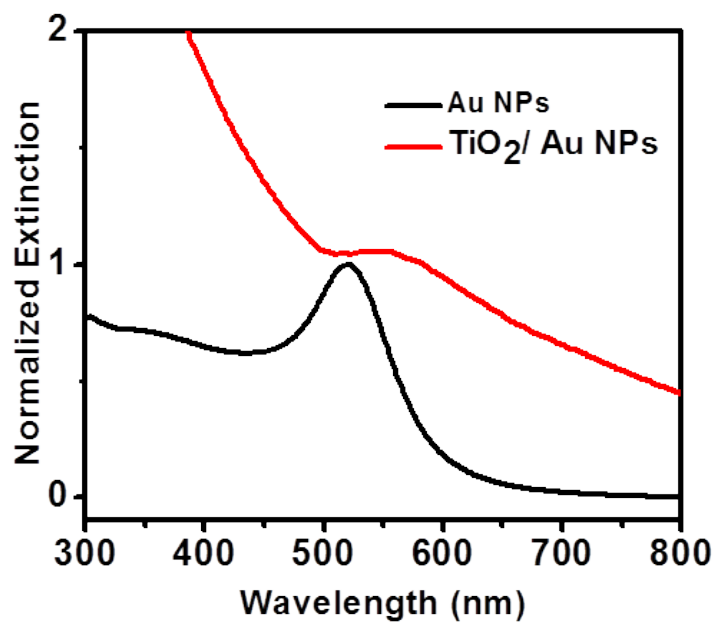


Figure S8. Extinction spectra of the Au NPs and TiO₂/Au NPs, acquired in water.

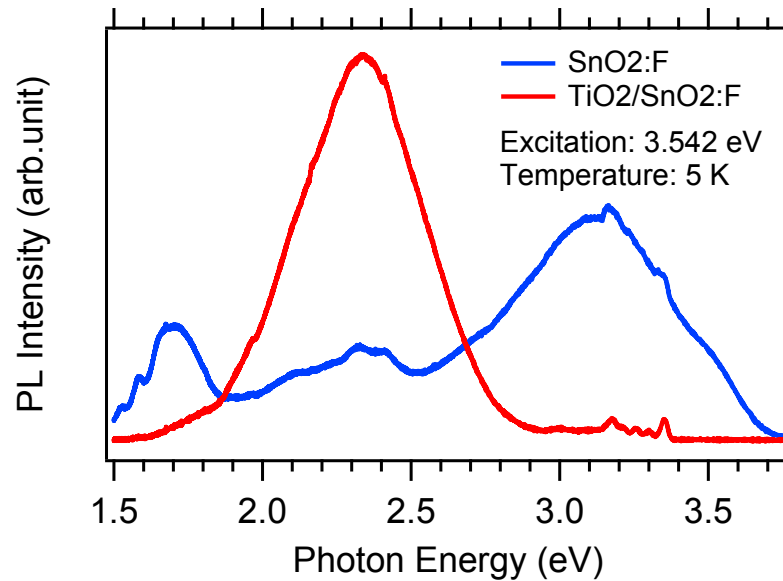


Figure S9. PL spectra of the TiO₂ photoelectrode (red) and of the fluorine-doped SnO₂ substrate (SnO₂:F; blue), on which the TiO₂ electrode was deposited. The spectra were acquired at 10 K in vacuum.

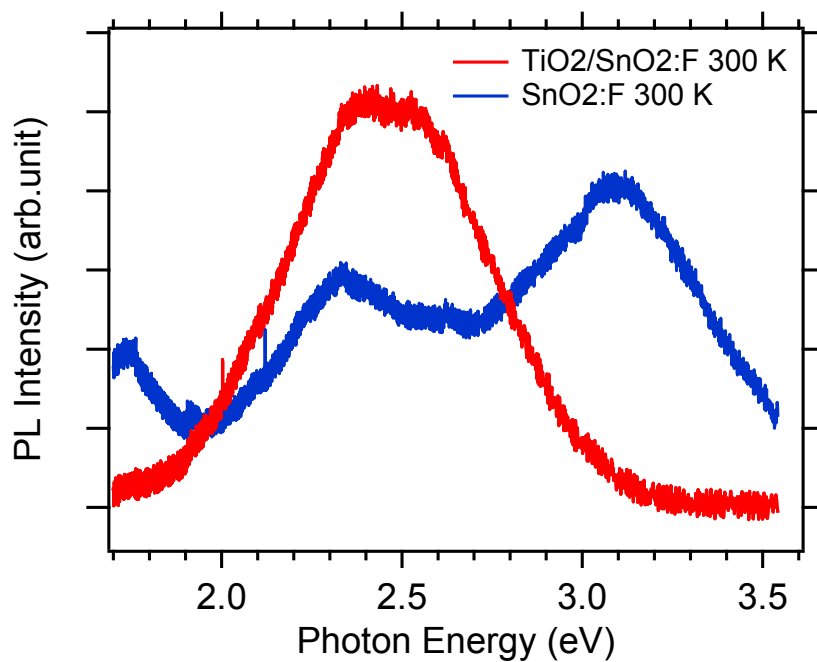


Figure S10. PL spectra at 300 K of the TiO₂ photoelectrode (red) and of the fluorine-doped SnO₂ substrate (SnO₂:F; blue).

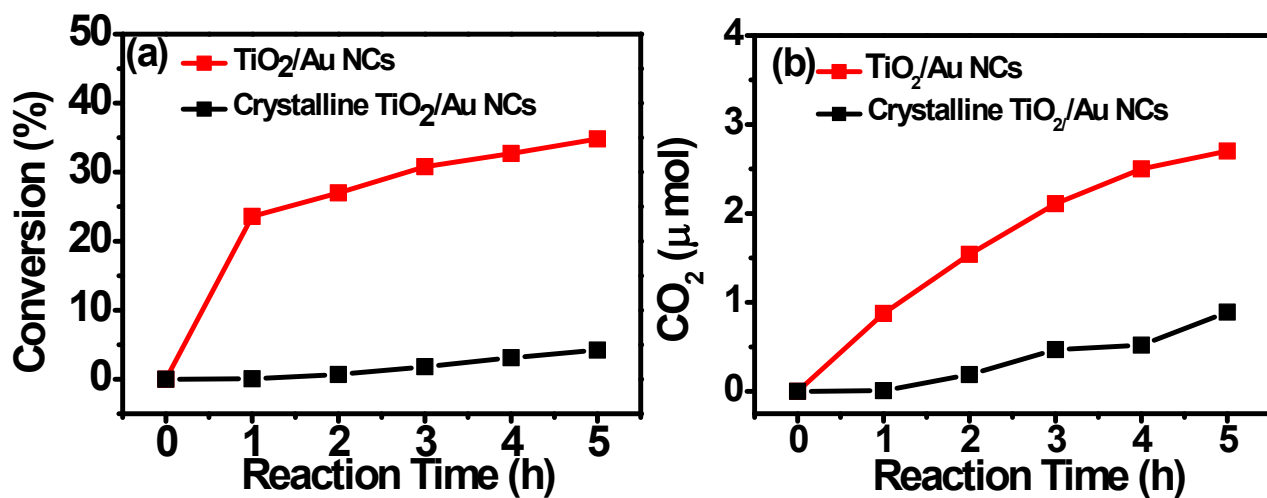


Figure S11. (a) Photocatalytic conversion of acetaldehyde under visible-light illumination ($420 < \lambda < 910$ nm) over the TiO₂/Au NCs and Crystalline TiO₂/Au NCs. (b) Production of CO₂ over the TiO₂/Au NCs and Crystalline TiO₂/Au NCs under visible-light illumination.

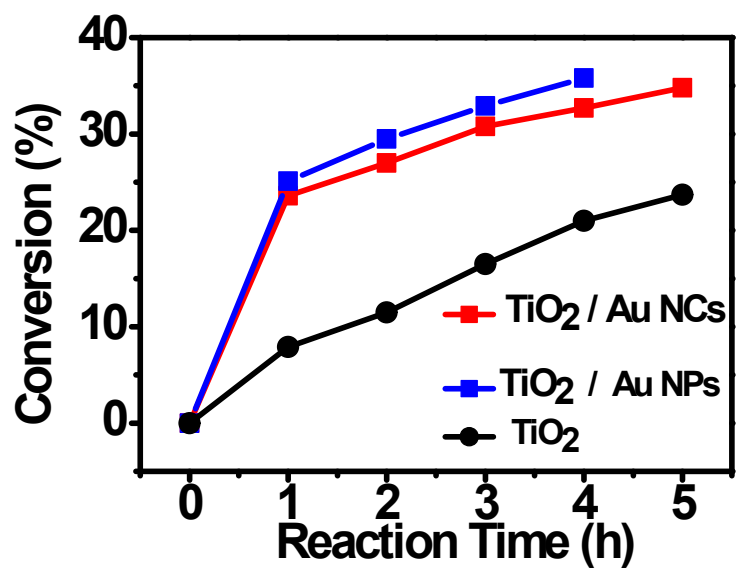


Figure S12. (a) Photocatalytic conversion of acetaldehyde under visible-light illumination ($420 < \lambda < 910$ nm) over the TiO₂/Au NCs, TiO₂/Au NPs and TiO₂.

References

- 1 D.Wan, X. Xia, Y. Wang and Y. Xia, *Small*, 2013, **9**, 3111-3117.
- 2 S. E. Skrabalak, L. Au, X. Li and Y. Xia, *Nat. Protoc.*, 2007, **9**, 2182-2190.
- 3 M. A. Mahmoud and M. A. El-Sayed, *J. Phys. Chem. C*, 2008, **112**, 14618-14625.
- 4 R. Liu and A. Sen, *J. Am. Chem. Soc.*, 2012, **134**, 17505-17512.
- 5 K. C. Grabar, R. G. Freeman, M. B Hommer and M. J. Natan, *Anal. Chem.* 1995, **67**, 735