Electronic Supplementary Information

Efficient charge storage in photoexcited TiO$_2$ nanorod-noble metal nanoparticle composite systems

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1. Synthesis of TiO$_2$ nanorod-stabilized metal nanoparticles

Materials. All chemicals were of the highest purity available and were used as received without further purification. Chloroauric acid trihydrate (HAuCl$_4$·3H$_2$O, 99.998%), silver nitrate (AgNO$_3$, 99.99%) titanium tetraisopropoxide (Ti(OPr^i)$_4$ or TTIP, 99.999%), trimethylamino-N-oxide dihydrate ((CH$_3$)$_3$NO·2H$_2$O or TMAO, 98%), oleic acid (C$_{18}$H$_{33}$CO$_2$H or OLEA, 90%), Uniblue A (UBA, sodium salt, M.W. 506.49; the molecular structure is reported in **Fig. 1S**) were purchased from Aldrich. All solvents used were of analytical grade and purchased from Aldrich.
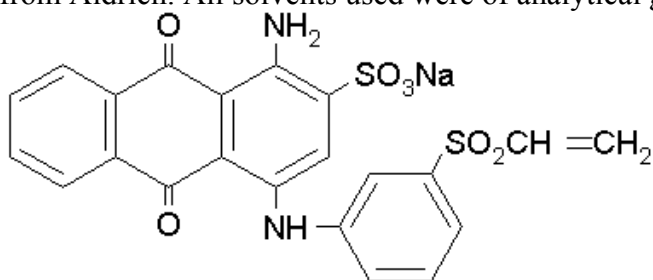

Figure 1S Molecular structure of Uniblue A

Synthesis of TiO$_2$ nanorods (NRs). Organic-capped anatase TiO$_2$ nanorods were synthesized by hydrolysis of TTIP using OLEA as the surfactant at low temperatures (80-100 °C), as reported in ref. 16 of the manuscript. Briefly, TTIP was hydrolyzed by reacting with an excess of aqueous TMAO solution (H$_2$O:TTIP molar ratio ranged from 40:1 to 150:1). Rod-like titania nanocrystals resulted from the direct injection of large aqueous base volumes into OLEA:TTIP mixtures. The as-prepared OLEA-coated TiO$_2$ NRs were easily re-dispersed in chloroform, without any further

growth or irreversible aggregation. In the photocatalytic experiments in this work, the native OLEA capping on the surface of the oxide nanocrystals was first removed by extensive washing, and then replaced by a fresh one, as described in ref. 16 of the manuscript.

Photocatalytic synthesis of TiO$_2$/metal nanocomposites. A quartz cuvette was filled with a solution containing the desired concentration of TiO$_2$ nanocrystals (expressed with reference to the parent species, TTIP) and either HAuCl$_4$ or AgNO$_3$ in a CHCl$_3$:EtOH=90:10 v/v mixture. The metal precursor concentration ranged between 10^{-5} M and 10^{-4} M, while TiO$_2$ concentration was between 10^{-3} M and 10^{-1} M. To obtain stable nanocomposites (i.e. to prevent the precipitation of the metallic particles), the TiO$_2$:metal precursor molar ratio should be kept in the range 100:1 to 20:1. The cuvette was sealed by a Teflon-faced rubber cap and the solution was subsequently deaerated by gently purging with nitrogen for 30 min. The mixture was UV-irradiated under stirring by using a High Pressure 200 W mercury lamp (λ > 300 nm). The lamp output was reduced to 10% of the original power by placing neutral density filters on the light path. This condition also ensured a minimal photo-oxidation of the TiO$_2$ organic capping, thereby prolonging the colloidal stability of the TiO$_2$ nanorods under illumination. Aliquots were withdrawn at scheduled time intervals via a syringe for TEM observations. Metal particle sizes in the 5-25 nm range with size variance of 10-20% were typically employed. Detailed structural and morphological characterization of the TiO$_2$ NR-metal NP composites has been reported previously in ref. 17-18.

In the case of silver, the mean Ag particle size and size distribution was modulated by varying the absolute AgNO$_3$ concentration and the irradiation time, as such metallic nanoparticles are susceptible to size modification based on light-induced fragmentation and/or ripening processes (see details in ref. 17 of the manuscript).

In the case of gold, the mean Au particle size and size distribution was modulated by varying the absolute HAuCl$_4$ concentration and the irradiation time. Irradiation was stopped at the desired particle growth stage before the metal NPs started to aggregate in chainlike assemblies (see ref. 18 in the manuscript).

As an example, **Fig. 2S** shows a typical TEM overview of the bare TiO$_2$ NRs and of the metal-TiO$_2$ nanorod composite photocatalysts used for the experiments reported in Fig. 1-3 in the manuscript.
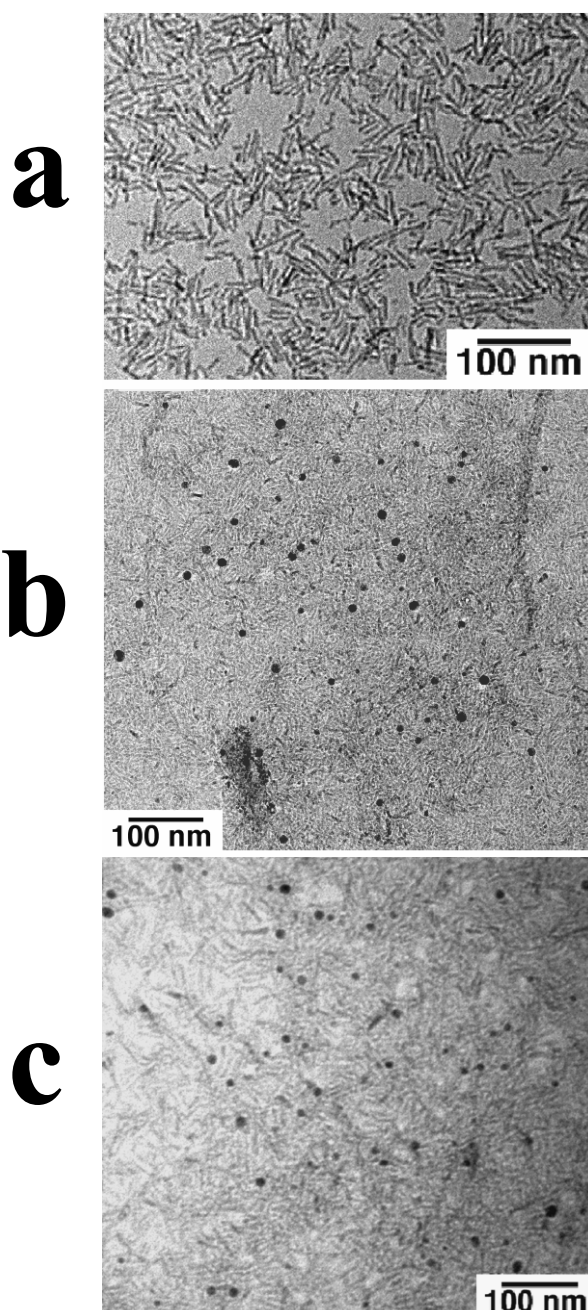
Figure 2S: Representative low resolution TEM images of the TiO_2 nanorods (a), and of the TiO_2 NR-stabilized Ag (b) and Au nanoparticles (c) employed for the present study. Note that in (a) the titania NRs appear well separated on the carbon grid due to the very low NR concentration in the solution used for TEM analysis. As opposed, in (b-c) the NRs can not be individually discerned as they form a compact layer because higher particle concentration had to be generally used in order to

show an extensive grid coverage by the metal NPs. Thus, in (b-c), the significantly different image contrast characterizing TiO_2 when compared to the metal makes the Au and Ag nanoparticles easily identifiable as dark spots superimposed on an underlying titania background, as confirmed by energy dispersive analysis of X-rays (EDAX). Electron diffraction pattern analysis also reveals that the samples contain both the metallic particles and anatase titania.

2. Photoinduced charge storage experiments.

The TiO_2/metal nanocomposite solutions were always freshly prepared. The composite photocatalyst was co-precipitated from the original growth solution upon addition of excess methanol (10 times the volume of the starting solution), then it was washed twice with methanol before being re-dissolved completely in anhydrous $CHCl_3$ under the inert atmosphere of a glove-box. Such a procedure served to eliminate unreacted metal precursor ions, that could be further reduced in the subsequent irradiation step.

A quartz cuvette was filled with a solution containing the desired amount of the purified TiO_2/metal stock solution in $CHCl_3$ and diluted with a concentrated TiO_2 nanorod solution in deaerated $CHCl_3$: EtOH mixture. The final solvent composition was typically $CHCl_3$:EtOH=60:40 v/v. The concentration of the nanocrystal species is always expressed with reference to the parent species, TTIP and either $HAuCl_4$ or $AgNO_3$ in a $CHCl_3$:EtOH=90:10 v/v mixture. The metal precursor concentration ranged between 10^{-5} M and 10^{-4} M, while TiO_2 concentration was between 10^{-3} M and 10^{-1} M.

The cuvette was sealed by a Teflon-faced rubber cap and brought out of the glove box to be illuminated with a 254 nm He:Hg lamp ($400\mu W/cm^2$) for 30 min. The choice of this low-power monocromatic irradiation source ensured that the initial metal nanoparticle size, size-distribution were kept unchanged throughout the illumination period necessary to observe e_{CB} accumulation. It is, in fact, known that Ag NPs can photofragment and/or photofuse, while Au NPs can aggregate significantly upon illumination with much more intense and polycromatic UV sources (e.g. by a high Pressure 200 W mercury lamp, $\lambda > 300$ nm, as described in ref. 15, 17-18). The metal nanoparticle size, size-distribution were confirmed by TEM analysis.

The charging-discharging cycle could be repeated several times (up to about 30-40 times) with high reproducibility before observing incipient photocatalyst precipitation (likely due to photodegradation of the TiO_2 organic capping layer)

3. Titration of the trapped CB electrons

To titrate CB electrons stored on the photocatalysts, a concentrated UBA solution in CHCl$_3$:EtOH=60:40 v/v was prepared in the glove box and then syringed through the septum of the cuvette under strict exclusion of air. In **Table 1S** the results of several experiments are reported which show that the degree of e$_{CB}$ accumulation increased with increasing the metal NP concentration and/or decreasing the mean metal NP size. Such an effect appearing more pronounced for TiO$_2$ coupled with Au than with Ag at constant metal concentration Notably, at metal concentration significantly higher than $1*10^{-5}$ M, the amount of stored e$_{CB}$ did not increase appreciably.

| | **TiO$_2$/Ag** | | | **TiO$_2$/Au** | | |
| | **Ag particle size** | | | **Au particle size** | | |
[metal]	**10 ± 2nm**	**15 ± 3nm**	**25 ± 5nm**	**10± 2nm**	**15 ± 3nm**	**25 ± 5nm**
$5*10^{-7}$ M	71	60	45	102	84	59
$8*10^{-7}$ M	85	68	57	118	99	84
$2*10^{-6}$ M	98	77	62	133	114	92
$1*10^{-5}$ M	115	105	88	145	135	105

Table 1S In the table, the values of UBA concentration (μM, with accuracy of ± 2 μM) required to titrate e$_{CB}$ electrons stored in TiO$_2$ nanorod-metal composite solutions are reported as a function of the total metal concentration and/or of the metal mean particle size (constant conditions: [TiO$_2$]=0.1 M, irradiation time = 30 min). To titrate the sole TiO$_2$, about 50 μM UBA was required The corresponding concentration of trapped CB electrons can be calculated as: *[e$_{CB}$]= n*[UBA]*, where *n = 2* is the number of electrons involved in the reduction of one dye molecule.

In a first approximation, the conversion efficiency, Φ, of the excitation process, i.e. the number of generated electrons trapped in the TiO$_2$ conduction band (e$_{cb}$) per photon of UV incident radiation can be expressed as:

$$\Phi = [e_{CB}]/ D_{ph} \quad \text{(with } D_{ph} = \text{density of emitted photons)}$$

For a strictly monochromatic source at λ =254 nm, the energy carried by one photon will be about $7.818*10^{-19}$ J. As the light power incident to the cuvette wall is 400 μW/cm^2, the photon intensity

will be about $I_{ph}= 51*10^{13} \, sec^{-1} \, cm^{-3}$, in the approximation of an isotropic point source. I_{ph} can be converted into I_{ph}', the number of incident photons per second and per liter:

$$I_{ph}' = 51*10^{13} \, sec^{-1} \, cm^{-3} *1000 \, cm^3/L=51*10^{16} \, sec^{-1} \, L^{-1}$$

From the data of the experiments in Fig. 3 for the various photocatalyst systems (see also table 1), Φ can be calculated as:

$$\Phi = [e_{CB}]/ D_{ph} =2* [UBA] / (I_{ph}' *\Delta t / N_A)$$

where Δt is the irradiation time and N_A is the Avogadro number. For example, in the case of irradiation of TiO$_2$ 0.1 M with metal particle size of 15 ± 3cm carried out at [metal]= $5*10^{-7}$ M for $\Delta t=30 \, min$, it can be calculated:

$\Phi_{TiO2} =0.033$

$\Phi_{Ag-TiO2} =0.039$

$\Phi_{Au-TiO2} =0.055$

By increasing the metal concentration to $1*10^{-5}$ M (see table 1), the conversion efficiency becomes:

$\Phi_{Ag-TiO2} =0.069$

$\Phi_{Au-TiO2} =0.088$

3. Characterization techniques

UV-vis Absorption spectroscopy. UV-vis absorption spectra were recorded with Cary 5 Varian UV-vis near-IR spectrophotometer.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) images were obtained using Philips EM 430 microscope (TEM) operating at 300 kV. The samples for the analysis were prepared by dropping dilute solutions of TiO$_2$/metal nanocomposite onto 400-mesh carbon-coated copper grids and leaving the solvent to dry. The samples were stable under the electron beam and did not degrade within the typical observation times.