Supplementary Info

Experimental Section

All chemicals were used as received, unless stated otherwise. TiO_2 p25 powder (Sigma-Aldrich) was used as semiconductor in all the reported experiments. The purity was 99.8% and the particle size less than 5 micron. The particles were annealed by heating them to a temperature of 475°C for 2 hours.

Adsorption of solvents on TiO₂ anatase particles

A stock solution of 5 g/l TiO₂ was made in Milli-Q distilled water, ethanol (Uvasol Spectroscopic, Merck) and ethylene glycol (99% purity, Sigma-Aldric), respectively. The solutions were sonicated for 30 minutes to ensure full mixture and were subsequently stored in a dark environment for at least 24 hours. This time period is necessary to obtain an equilibrium for the adsorbed organic molecules on the TiO_2 surface.

Photo-deposition of Gold particles

Two gold loading amounts, 0.4 wt% and 1.0 wt%, were photo-deposited on the stored TiO₂. For this 0.6 ml of the TiO₂ solutions was diluted with 2.4 - x ml of the respective solvent (being H₂O, EtOH or EG solution) in a cylindrical teflon reactor with vigorous stirring. x is 1.5 μ l for 0.4 wt% and 3.8 μ l for 1.0 wt% 20 mM HAuCl₄·3H₂O (Acros Chem.) solution in the corresponding solvents. The gold salt solution was added just prior to irradiation with UV. The solutions were irradiated from the top for 4 minutes under vigorous stirring with UV light from 300 W Xenon light source (Asahi-Max 303) and a 300 nm SP filter. Sunlight grafting was done by irradiation with a solar simulator (LOT Quantum Design) at 1 sun. Irradiation with visible light was done with the same solar simulator (LOT Quantum Design) at 1 sun and a 400 nm LP filter. The resulting grafted particles were thoroughly washed twice by centrifugation and stored in Milli-Q water. Total number of TiO2 particles present

	H2O		EtOH		EG	
	1 wt%	0,4 wt%	1 wt%	0,4 wt%	1 wt%	0,4 wt%
Total number of TiO2 particles	23	26	71	14	75	20
TiO2 particles with Au NP	8	13	11	2	49	17
Fraction Au/TiO ₂ systems	34,78	50,00	15,49	14,29	65,33	85,00

SI Table 1: Statistical analysis of TEM images of photo-deposited Au NP on TiO_2 . The fraction represents the fraction of TiO_2 particles with Au NPs.

Control experiment Au NP formation without TiO₂

Gold loading amount, similar to 1.0 wt% loading was mimicked for the control experiment. For this 3.8 μ l pf a 20 mM HAuCl₄·3H₂O (Acros Chem.) was diluted in 2.9962 ml of the respective solvents (being H₂O, EtOH or EG solution) in a cylindrical teflon reactor with vigorous stirring. The solutions were irradiated from the top for 4 minutes under vigorous stirring with UV light from 300 W Xenon

light source (Asahi-Max 303) and a 300 nm SP filter. To mimic the sunlight photo-deposition, the solutions were irradiated with the same solar simulator (LOT Quantum Design) at 1 sun and a 400 nm LP filter.

Control experiment possible dark reaction after NP photo-deposition on TiO_2

A gold loading amount of 1.0 wt%, was photo-deposited on the stored TiO₂. For this 0.6 ml of the TiO₂ solutions was diluted with 2.3962 ml of the respective solvent (being H₂O, EtOH or EG solution) in a cylindrical teflon reactor with vigorous stirring. 3.8 μ l 20 mM HAuCl₄·3H₂O (Acros Chem.) solution was added just prior to irradiation with UV. The solutions were irradiated from the top for 30 seconds under vigorous stirring with UV light from 300 W Xenon light source (Asahi-Max 303) and a 300 nm SP filter. The particles were then stored in a dark sealed container, to investigate any ongoing reaction, for 30 minutes. The resulting particles were washed twice by centrifugation and stored in Milli-Q water.

Reflection measurements Au/TiO2 particles

The samples were exchanged from water to ethanol as a solvent. By centrifugation the concentration was increased to 3 g/l TiO₂. Thick non-transparent particle films were created by dropcasting 200 μ l of the new Au/TiO₂ solution on clean coverslides every hour. The films were dried at room temperature. The reflectance spectrum was measured with a Perkin-Elmer Lambda 950 spectrometer. The absorbance was derived from the reflectance following the Kubelka-Munk theory.



SI Figure 1: Colour change during UV grafting of Au 1.0 wt% on anatase TiO₂ particles. A sample was taken every 15 seconds during 4 minutes of grafting. After 4 minutes no further colour changes are observed. In H₂O, 4 minutes was necessary for the reaction to finish. The grafting takes place slowly, but the particles are small and the solution changes colour to pink/purple. In EtOH, less particles were formed and the particles that were formed are large. The colour changed to light grey-blue

(nearly indistinguishable from the original colour) after less than a minute. The fastest grafting was done in EG. After 1 minute the colour became stable. The particles are small and well-distributed over the TiO_2 particles.



SI Figure 2: Colour change during sunlight grafting of Au 1.0 wt% on anatase TiO_2 particles. A sample was taken every 30 seconds during 5 minutes of grafting. After 5 minutes no further colour changes are observed. In H₂O, minimum 5 minutes was necessary for the reaction to finish. The grafting takes place slowly, but the particles are small and the solution changes colour to pink/purple. In EtOH, less particles were formed and the particles that were formed are large. The colour changed to light greyblue after a minute. The fastest grafting was done in EG with a colour change already after 1 minute. After 3 minutes the colour became stable. The particles are small and well-distributed over the TiO_2 . particles.



SI Figure 3: Colour change after 30 seconds of UV irradiation and 30 minutes of Visible light grafting of Au 1.0 wt% on anatase TiO₂ particles. 30 minutes was used since there was no visible colour change after 25 minutes for EG. No colour change was visible when H₂O was used as a solvent. Using EtOH, no clear colour is visible after 30 seconds. After 30 minutes a very faint pinkish colour was visible, indicating the growth of Au NP. In EG already after 30 seconds of UV, a pinkish colouring was visible indicating many small seeds. When irradiating with 30 minutes of visible light, a strong colouring was visible, suggesting a strong Au NP growth.



SI Figure 4: UV-Vis spectra of a 25μ M HAuCl₄ solution (mimicking 1.0 wt%) in H₂O. Time periods were chosen to mimic the experiments as close as possible. Without the presents of TiO₂ no signs of NP formation are seen.



SI Figure 5: UV-Vis spectra of a 25μ M HAuCl₄ solution (mimicking 1.0 wt%) in ethanol. Time periods were chosen to mimic the experiments as close as possible. Without the presents of TiO₂ no signs of NP formation are seen.



SI Figure 6: UV-Vis spectra of a 25μ M HAuCl₄ solution (mimicking 1.0 wt%) in EG. Time periods were chosen to mimic the experiments as close as possible. Without the presents of TiO₂ no signs of NP formation are seen.



SI Figure 7: Absorbance of Au/TiO2 (1 wt% Au) particles made by photo-deposition using 30s of UV (dotted line) and 30s UV followed by 30 minutes stored in a closed dark container (full line). No Au NP growth can be seen when the TiO_2 particles are stored in the dark.

Photocatalytic Activity on 4-chlorophenol

An aqueous stock solution of a 40 ppm 4-chlorophenol (4-CP, >99%, Sigma-Aldrich) is made and used for further experiments.

Ungrafted particles

0.6 ml of the ungrafted particles was diluted to 3 ml with their respective solvents and subsequently irradiated with UV for 4 minutes under vigorous stirring with UV light from a 300 W Xenon light source and a 300 nm SP filter in order to mimic the UV irradiation during the Au grafting. These particles were washed by centrifugation and stored in Milli-Q water. 1 ml of the 4-CP solution was mixed with 1 ml of the ungrafted particles. The solutions were kept for 24 hour in dark to assure the adsorption/desorption equilibrium. 4-CP was degraded by 20 minutes of irradiation with 70% of the 300 W Xenon light source with a 300nm SP filter. The progress of the reaction was followed by measuring the disappearance of 4-CP as a function of time with a Perkin-Elmer Lambda 40 spectrophotometer.



SI Figure 8: Photocatalytic degradation of 4-CP in aqueous solution under UV-light irradiation with TiO_2 pre-treated with water (circle), ethanol (square), and ethylene glycol (triangle).

Regenerating Ungrafted Particles

The ungrafted particles were washed twice by centrifugation and stored in Milli-Q water. The concentration was kept at 5g/l. 0.6 ml of the TiO_2 solutions was diluted to 3 ml and irradiated with UV for 20 minutes under vigorous stirring with UV light from 300 W Xenon light source and a 300 nm SP filter. The regenerated particles were washed by centrifugation and stored in Milli-Q water. 1 ml of the 4-CP solution was mixed with 1 ml of the regenerated ungrafted particles. The solutions were kept for 24 hour in the dark to assure the adsorption/desorption equilibrium. 4-CP was degraded by

20 minutes of irradiation with 70% of the 300 W Xenon light source with a 300nm SP filter. The progress of the reaction was followed by measuring the disappearance of 4-CP as a function of time with a Perkin-Elmer Lambda 40 spectrophotometer.



SI Figure 9: Photo-catalytic degradation of 4-CP in aqueous solution under simulated sunlight irradiation with TiO2 pre-treated with water, ethanol, and ethylene glycol. The pre-treated particles were first illuminated with 20 min UV, to restore their original activity. The EG pre-treated particles now show the same activity as the H_2O and EtOH pre-treated particles, indicating the degradation of EG with UV light.

Grafted Particles

1 ml of the 4-CP solution was mixed with 1 ml of the thoroughly washed Au grafted particles. The solutions were kept for 24 hours in dark to assure the adsorption/desorption equilibrium. 4-CP was degraded by 50 minutes of irradiation with a solar simulator (LOT Quantum Design) at 1 sun. The progress of the reaction was followed by measuring the disappearance of 4-CP as a function of time with a Perkin-Elmer Lambda 40 spectrophotometer.

Reflection measurements Au/TiO2 particle after 4-chlorophenol degradation

The degradation of 4-chlorophenol was now done for 4 hours to ensure full degradation of all organic compounds present. The particles were thoroughly washed after the degradation experiments to remove all excess of 4-chlorophenol residues. 4 identical experiments were combined to ensure a high enough concentration of TiO_2/Au . By centrifugation the concentration was even increased to 3 g/l TiO_2 . Thick non-transparent particle films were created by dropcasting 200 µl of the new Au/TiO_2 solution on clean coverslides every hour. The films were dried at room temperature. The reflectance spectrum was measured with a Perkin-Elmer Lambda 950 spectrometer. The absorbance was derived from the reflectance following the Kubelka-Munk theory.



SI Figure 10: Spectrum of the solar simulator. The red line marks the wavelength corresponding with 3.0 eV. This is the band gap of bulk TiO₂ and thus photon energy needed to excite an electron.



SI Figure 11: Absorbance of Au/TiO2 (1 wt% Au) particles made by photo-deposition using 4 minutes UV (full line) and after 4 hours 4-chlorophenol degradation with sunlight (dotted line). No Au NP size change can be seen.



SI Figure 12: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation with unmodified anatase TiO_2 particles under solar light illumination.



SI Figure 13: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation under solar light illumination with anatase TiO_2 particles grafted in H₂O with 0.4 wt% Au.



SI Figure 14: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation under solar light illumination with anatase TiO_2 particles grafted in H₂O with 1.0 wt% Au.



SI Figure 15: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation under solar light illumination with anatase TiO_2 particles grafted in ethanol with 0.4 wt% Au.



SI Figure 16: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation under solar light illumination with anatase TiO_2 particles grafted in ethanol with 1.0 wt% Au.



SI Figure 17: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation under solar light illumination with anatase TiO_2 particles grafted in ethylene glycol with 0.4 wt% Au.



SI Figure 18: Absorption spectrum of 4-chlorophenol ranging from 0 to 50 minutes after degradation under solar light illumination with anatase TiO_2 particles grafted in ethylene glycol with 1.0 wt% Au.



SI Figure 19: Absorption spectrum of 4-chlorophenol after 0 hours and 24 hours visible light illumination (>430 nm) in the presence of unmodified or modified anatase TiO_2 particles. No degradation was visible after 24 hours of illumination.

Theoretical Details

The Ab initio calculations were performed based on the density functional theory (DFT) within the Generalized Gradient Approximation (GGA) as implemented in the SIESTA computational code [1] within the Perdew-Burke-Ernzerhof (PBE) form [2]. The core electrons were replaced by Troulier-Martins pseudopotentials [3]. A double- ζ basis set of localized atomic orbitals was used for the valence electrons. Sampling of the Brillouin zone was restricted to the Γ point, upon relaxation and a (10 x 10 x 1) Monkhorst-Pack grid was used for DOS calculations [4]. A mesh cutoff energy of 300 Ry has been imposed for real-space integration. All structures have been relaxed until forces were less than 0.05 eV/Å. In the calculations, a vacuum interval of more than 10 Å was used to avoid the interaction between the periodic slabs. The surface areas are 7.57 Å x 7.57 Å and 10.24 Å x 11.35 Å for anatase TiO₂ (001) and (101) respectively. The BSSE corrected [5] adsorption energy E_{ads} is calculated using the formula:

 $E_{ads} = E (TiO_2/X) - E (TiO_2) - E (X)$

Where E (TiO₂/X) is the total energy calculated after geometry relaxation of the surface with one adsorbed molecule X which is H_2O (SI Figure 15), Ethanol (SI Figure S16) or Ethylene Glycol (Figure 4 in the main text) present and E (TiO₂) and E (X) are the total energies of the clean TiO₂ surface and isolated X molecule respectively.

References:

[1] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, Journal of Physics: Condensed Matter 14, 2745 (2002).

[2] J. P. Perdew, K. Burke and M. Ernzerhof, Physical Review Letters 77, 3865 (1996).

- [3] N. Troullier and J. L. Martins, Physical Review B, 43, 1993 (1991).
- [4] H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13, 5188 (1976)
- [5] S. F. Boys and F. Bernardi, Molecular Physics, 19, 553 (1970).



SI Figure 20: DFT calculations of 1 molecule H_2O adsorbing on the two most prevalent TiO_2 facets. On the more active <001> facet, H_2O undergoes a dissociative adsorption, while on the <101> facet the adsorption is molecular. Red: O, grey: Ti, and blue: H



SI Figure 21: DFT calculations of 1 molecule EtOH adsorbing on the two most prevalent TiO_2 facets. On the more active <001> facet, EtOH undergoes a dissociative adsorption, while on the <101> facet the adsorption is molecular. Red: O, grey: Ti, green: C, and blue: H



SI Figure 22: DFT calculations of 1 molecule EG adsorbing on the two most prevalent TiO_2 facets. On the more active <001> facet, EG undergoes a dissociative adsorption, while on the <101> facet the adsorption is molecular. Red: O, grey: Ti, green: C, and blue: H



SI Figure 23: DFT calculations of the DOS of <101> TiO₂ with adsorption of H₂O (red), EtOH (blue) and EG (black). The energy is relative to the Fermi level energy.