Supporting Information for
“Water-assisted hole trapping at highly curved surface of nano-TiO₂ photocatalyst”

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Sec. 1. Characterization of TiO$_2$ nanoparticles

1-1. X-ray diffraction (XRD) patterns

CuKα-XRD patterns were observed with an X-ray diffractometer (miniflex600/Rigaku). The angle resolution of the diffractometer is 0.05 degree. Figure S1 shows the XRD patterns of three kinds of nanoparticles. Prominent peaks at $2\theta = 25.6^\circ$, 38.1°, and 48.3° correspond to the reflections of (101), (004), and (200) planes, respectively, characteristic to the anatase phase of TiO$_2$ (Ref. 1). No peaks at $2\theta = 27.7^\circ$, 36.3°, and 41.5° corresponding to the reflections of (110), (101), and (111) planes of the rutile phase were observed. Therefore, all samples are composed of pure anatase TiO$_2$.

Reflection peaks of OAP and ST-01 are much broader than those of DAP, indicating that these particles are smaller than DAP. We estimated the average particle sizes of OAP and ST-01 from the widths of XRD peaks. The reflection peak around 38° shown in Fig. S1 is composed of three peaks, which are assigned to (103), (004), and (112). Fitting the peak of OAP with three Gaussian functions determines a width of (004) peak to be 0.79°, while the reflection peaks of (200) and (101) have widths of 0.96° and 0.73°, respectively. The angle resolution of the diffractometer, 0.05°, is negligibly smaller than those values. Thus, we estimated the crystal lengths along [001], [100] and [101] directions to be 13, 12 and 12 nm, respectively, from the widths of these peaks using the Scherrer equation. Similarly we also estimated the crystal lengths of ST-01 along [001], [100] and [101] directions to be 5.3, 8.3, and 6.4 nm from the width of (103), (004), (112) peaks (1.91°, 1.43°, 1.38°), respectively. The peak widths of DAP are too sharp to estimate the particle size.

![Figure S1. XRD patterns of DAP, OAP, and ST-01 nanoparticles.](image)

Figure S1. XRD patterns of DAP, OAP, and ST-01 nanoparticles.
1-2. Diffuse reflectance infrared Fourier transform (DRIFT) spectra

Figure S2a and S2e show the temperature dependence of DRIFT spectra of OAP and ST-01, respectively, at 0.01 Pa. The bending (1500-1700 cm\(^{-1}\)) and OH stretching bands (2600-3750 cm\(^{-1}\)) of water adsorbates clearly appear at room temperature. Figure S2b and S2f show that the intensities of the bending and OH stretching bands decrease with increasing temperature, indicating that water adsorbates desorb thermally. The intensity ratio between the OH stretching and bending bands in Figure S2c and S2g drastically changes at about 500 K. This indicates associative desorption of dissociatively adsorbed species (surface OH) occurs above 500 K. Because the OH stretching band is contributed by both molecularly adsorbed water and surface OH species while the bending band is contributed only by molecularly adsorbed water, we estimated the ratio of contributions to the OH stretching band intensity at room temperature between the two species by extrapolating the plots in Fig. S2c and S2g below 500 K to the point with the intensity of the bending band to be 0; about 50% of the OH stretching band intensity is contributed by surface OH.

Figure S3a, S3c, and S3e show the IR spectra of three samples under different water vapour pressures. In these spectra, two absorption bands at 1500-1700 and 2600-3650 cm\(^{-1}\), which are assignable to H-O-H bending and hydrogen-bonded OH-stretching, monotonically increase with water vapour pressure. At 1000 Pa, the centre frequencies of OH stretching bands of multi-layered adsorbed water are about 3400 cm\(^{-1}\) in all the samples. But at 0.01 or 0.1 Pa, the peak frequency of OH stretching band of ST-01 (~3050 cm\(^{-1}\)) is much lower than those of DAP or OAP (~3200 cm\(^{-1}\)). This indicates that water molecules adsorbed at low pressure have specific adsorption structures influenced by local structures of TiO\(_2\) nano-particle surface, while they have the common liquid-like adsorption structure not influenced by its surface at high pressure. In Figure S3b, S3d, and S3f we compare the intensities of the bending and OH stretching bands with the adsorption density per unit surface area estimated by the adsorption amount and the surface area measured from volumetric analysis for each sample as a function of water vapour pressure. The intensities of the bending band correlate well with the adsorption densities in all the samples. This indicates that the oscillator strength of the bending band of water is less affected by interactions with surface in contrast to the OH-stretching band\(^3\). In the main text, the amount of adsorbed water molecules is expressed in the monolayer unit (ML), where 1 ML is defined by the amount of water molecules in a layer of bulk liquid water (~6 × 10\(^{14}\) cm\(^{-2}\)).
Figure S2. Temperature dependence of DRIFT spectra. The left column is for OAP and the right column is for ST-01. a and e, Temperature dependence of DRIFT spectra at 0.01 Pa. b and f, Peak intensities of bending and OH stretching bands as a function of temperature. The intensities are normalized at 300 K for OAP and 401 K for ST-01. c and g, Correlation between normalized intensities of bending and OH stretching bands at different temperatures. d and h, Distribution of heat of adsorption of adsorbed species contributing to Component A₀.
Figure S3. Water-vapour pressure dependence of DRIFT spectra. The left column is the pressure dependence of IR spectra and the right column is the comparison of the intensities of OH stretching and bending bands with the amount of water adsorbate obtained from volumetric analysis. a and b, for DAP, c and d, for OAP and e and f, for ST-01.
Figure S4 shows the DRIFT spectra in the free-OH stretching band (3600-3750 cm\(^{-1}\)) region as a function of water-vapour pressure. Although the spectral intensities of ST-01 at ~3680 and 3720 cm\(^{-1}\) decrease with vapour pressure, those of DAP or OAP increase monotonically. The depletion in the ST-01 spectra is confirmed in the difference spectra between 10\(^2\) and 10\(^{-2}\) Pa shown in the inset of Fig. 2b in the main text.

**Figure S4.** Pressure dependence of DRIFT spectra in the free-OH stretching band region of a, DAP, b, OAP and c, ST-01.
Sec. 2. Computational details

2-1. Electronic structure calculations

In the present work we have performed calculations with the CRYSTAL14\textsuperscript{4} code where the Kohn–Sham orbitals are expanded in Gaussian type orbitals (the all-electron basis sets are O 8-411(d1), Ti 86-411 (d41) and H 511(p1)). The B3LYP\textsuperscript{5,6} hybrid functional has been used for all the calculations.

The calculated lattice constants of bulk anatase are 3.789 for $a$ and 9.777 Å for $c$, in good agreement with the experimental values.\textsuperscript{7}

The faceted nanoparticle or nanocrystal (NC) has been carved from a bulk anatase supercell following the methodology already employed in a previous work by some of us.\textsuperscript{8} The stoichiometric nanocrystal (TiO\textsubscript{2})\textsubscript{260} · 6 H\textsubscript{2}O was cut according to the minimum energy decahedral shape,\textsuperscript{9} where the two most stable anatase surfaces, (101) and (001), are exposed. The average size of this nanocrystal is 2.2 nm and 32.8% of the titanium or oxygen atoms are on the surface. Specifically, 106 out of 260 titanium atoms are five-fold coordinated, 12 are four-fold coordinated with terminal OH and only 4 titanium atoms are four-fold coordinated (Fig. 3a).

In order to ensure the chemical stability of the spherical nanoparticle or nanosphere (NS), we set for the titanium and oxygen atoms a minimum of four-fold and two-fold coordination, respectively. Therefore, after carving a sphere of radius $R$ from the bulk anatase supercell, all the two-fold Ti atoms on the surface were removed, whereas three- and, when necessary, four-fold Ti atoms were coordinated by at the most one hydroxyl group. A hydrogen atom has been added in order to saturate monocoordinated oxygen atoms. We carved a stoichiometric nanosphere with a radius $R$ of 1.22 nm (TiO\textsubscript{2})\textsubscript{223} · 18 H\textsubscript{2}O (Fig. 3b).

No periodic boundary conditions have been imposed for the calculations of nanoparticles, which are thus considered as isolated molecules in the vacuum. Consequently, when a positive charge is introduced in the system, no background of charge is necessary. In the case of open-shell systems, we took into account the spin polarisation. Geometry relaxation runs were performed without any symmetry constraint.

As commonly done, flat anatase facets were modelled with a three triatomic layers slab with 108 atoms and a $1 \times 3$ periodicity along the [10-1] and [010] directions for the (101) surface and a four triatomic layers with 96 atoms and a $4 \times 2$ periodicity along the [100] and [010] directions for the (001) surface; no periodic boundary condition was imposed in the direction perpendicular to the surface. The slab models have been used only to calculate the vibrational frequencies of water adsorbates on the (101) and (001) and hole states on the (001), whereas we have employed the
faceted nanoparticle model (NC) for all the other calculations. For the surface geometry optimisations we used a Monkhorst-Pack k-point sampling of the Brillouin zone: $2 \times 2 \times 1$ and $1 \times 2 \times 1$ meshes ensured convergence of the electronic structure for the (101) and (001) slabs, respectively.

Cut-off thresholds in the calculation of Coulomb and exchange sums (or series), which appear in the SCF equation, were set to $10^{-7}$ for Coulomb overlap tolerance, $10^{-7}$ for Coulomb penetration tolerance, $10^{-7}$ for exchange overlap tolerance, $10^{-7}$ for exchange pseudo-overlap in the direct space, and $10^{-14}$ for exchange pseudo-overlap in the reciprocal space. The SCF convergence criteria was defined on the total energy difference between two subsequent cycles, which has to be lower than $10^{-6}$ a.u.

The forces with respect to atomic coordinates are computed analytically. Equilibrium geometries are determined by using a quasi-Newton algorithm with a BFGS Hessian updating scheme. Convergence of the relaxation process is tested on the root mean square (RMS) and on the absolute value of the largest component of both the forces and atomic displacements. We made use of the default thresholds for geometry optimisation within the CRYSTAL14 code: the limits for the maximum and the RMS of forces have been set to 0.000450 and 0.000300 a.u., and for the maximum and the RMS of atomic displacements to 0.001800 and 0.001200 a.u., respectively.

Total densities of states (DOS) of the nanoparticles have been simulated through the convolution of Gaussian functions, with a $\sigma$ equal to 0.005 eV, localised at the Kohn-Sham eigenvalue of each molecular orbital. Projections onto different atoms of the density of states (PDOS) have been determined by using the coefficients in the linear combination of atomic orbitals (LCAO) of each molecular orbital: the normalised sum of the squares of the coefficients of all the atomic basis functions localised on a certain atomic species results in the relative contribution of each atomic species to a specific eigenstate. Then, the different projections have been obtained from the convolution of Gaussian functions, which have heights proportional to their relative contribution to a specific eigenstate. For spin polarised systems, total and projected densities of states are computed separately using the Kohn-Sham eigenvalues of alpha or beta population. The zero energy level for all the densities of states is set to the vacuum, which corresponds to the energy of an electron at an infinite distance with respect to the surface (Figs. 4b,c,d).

The binding energies for water molecules on the nanoparticles are computed as the difference between the total energy of the final product of the adsorption and the total energy of the isolated systems, i.e. an isolated water molecule and the isolated nanoparticle.
The stability of a hole trap on the surface of the nanoparticles has been evaluated as the total energy difference between the system with a hole localised on the surface site and the same system with a hole localised on the innermost O\(_{3c}\) atom of the nanoparticle, which has been considered as the reference hole trapping site.

2-2. Simulated annealing procedure

Starting from the geometrical constructed “as-cut” structure, we performed a simulated annealing simulation in order to find a global potential energy minimum for the nanosphere considered. At this stage, we made use of the self-consistent charge density functional tight-binding (SCC-DFTB) approach.\(^\text{11}\) This method has been used successfully to calculate, at an extremely reduced computational cost, properties of periodic systems such as bulk TiO\(_2\) and TiO\(_2\) surfaces as well as TiO\(_2\) small clusters, giving results in good agreement with ab initio (DFT) references.\(^\text{12,13}\) Since we are in vacuum, we have employed of the well-suited “matsci-0-3” set of tight-binding parameter as reported in Ref. 14. All the DFTB calculations have been performed with the open-source simulation package DFTB+.\(^\text{15}\)

For the simulated annealing calculations Born-Oppenheimer DFTB molecular dynamics was performed within the canonical ensemble (NVT). The Newton’s equations of motion were integrated with the Velocity Verlet algorithm and a relative small time step of 0.5 fs was used to ensure reversibility. A Nosé-Hoover thermostat allows for targeting the desire temperatures of 300 K, 500 K and 700 K. From a technical point of view, the simulated annealing calculation consists of three different steps. i) Starting from a Boltzmann’s distribution of the initial velocities at 150 K, the system is rapidly heated up to the target temperature (this process lasts for 0.25 to 0.925 ps depending on the target temperature). ii) Successively, the system is equilibrated to the desired temperature for 5 ps, until the temperature profile results flat. iii) Finally, the cooling process brings the system close to 0 K into a deep potential energy basin, ideally a global minimum. This process lasts for 12.75 ps to 18.96 ps depending on the initial target temperature.

A final DFTB conjugate-gradient geometry optimisation gave us the final annealed structure. For these calculations, the convergence threshold on the self-consistent charge (SCC) procedure was kept to \(10^{-6}\) a.u. and forces were relaxed to less than \(10^{-4}\) a.u.. Among the nanospheres obtained from different target temperatures the most stable one, the one coming from the 700 K simulated annealing simulation, was chosen for all further DFT calculations. To this end, the structure has been optimised again with the B3LYP functional.
2-3 Vibrational frequencies calculations

For molecular systems, harmonic frequencies for a potential energy minimum have been computed by numerical differentiation of the gradient vector.\textsuperscript{16,17} A “two point” formula have been used with 0.003 Å as step. For periodic systems, second-order energy derivatives are evaluated at $\Gamma$ point. Additionally, only for frequency calculations, the SCF convergence threshold has been lowered to $10^{-9}$ a.u., in order to increase numerical accuracy. All the calculated frequencies have been scaled with a scale factor obtained as the ratio between the experimental\textsuperscript{18} and computed value for the symmetric stretching mode of gas phase water.
Sec. 3 Binding energy and vibration frequency of water adsorbates on nanosphere

The binding energies of water adsorbates at different sites on the nanosphere model surface and their local structures are depicted in Fig. S5 and Fig. S6, respectively, by ball-and-stick models. Figure S7 shows how the torsional angle between OH and Ti d orbitals influences the stretching frequency of free OH even at the same three-coordinated site. Figure S8 shows the correlation between OH stretching frequency and OH···O distance of various surface OHs and water adsorbates on the nanosphere model surface.

Figure S5 Binding energy of water adsorbates on different sites on the NS model surface. The superscripts “ax” and “eq” stand for axial and equatorial, respectively, and they are related to the missing atoms in the coordination shell. The superscript “OH” is related to the presence on the Ti site of a hydroxyl group from intrinsic water. The labels “a” and “b” indicate atoms with a different second coordination shell when the first is equal. Coordination number of each site is given by color coding.
Figure S6 a, Ball-and-stick models and wavenumber of OH stretching and bending mode for water adsorbates on the different titanium sites of the spherical anatase nanoparticle model. The comparison between the experimental infrared spectrum of ST-01 at 0.01 and 100 Pa and the theoretical scaled frequencies of H-bonded OH stretching (b), free OH stretching (c) and H$_2$O bending (d) is also given. Numbers in bold refer to the free OH frequencies (1-6) that are significantly redshifted after H-bonding with additional water molecules (1’-6’). Ti atoms are coloured according to the given color coding, H atoms are shown in white and O atoms in red.
Figure S7. Dependence with the H-O-Ti-Osurf torsional angle of the orbital overlap between hydroxyl bonding orbital (σ_{OH}) and titanium 3d states. The free OH stretching frequency is influenced by this torsional angle: the rotation around the Ti-O bond changes the overlap of the Ti d-orbitals (especially the d_{xy}) with the OH bonding state. When the dihedral favors the overlap, there is a small but significant charge transfer from the occupied σ_{OH} orbital to the empty d_{xy} of the titanium, resulting in a slight weakening of the O-H bond strength and, consequently, in a small decrease of the OH stretching wavenumber.
**Figure S8.** Correlation between the lowest scaled stretching frequency of various water adsorbates on the nanosphere model and the shortest H-bond length the adsorbed water molecule (or OH) makes with vicinal oxygen atoms from the surface (O$_{2c}$ or OH) or additional H$_2$O molecules. The atoms on which the vibrational mode is located are in bold in the legend. The identification numbers depicted in the figure corresponds to those in Fig. S6.
Sec. 4 Binding energy and vibration frequency of water adsorbates on nanocrystal

Figure S9. a. Comparison between experimental IR spectrum of OAP at 100 Pa and calculated scaled frequencies of the water adsorbates on a (101) anatase surface model. This is the most exposed surface on these anatase faceted nanoparticles. The frequencies have been assigned to stretching modes of the water monolayer (1 ML) or the first (1st) or the second (2nd) layer of the bilayer (2 ML). In bottom panels are reported the side and top view of the anatase (101) slab with a water monolayer (b and d) and bilayer (c and e) adsorbed on top. Absorption energies of the first and second water layer per water molecule are also given. Ti atoms are coloured in cyan, H atoms are shown in white and O atoms in red. Distances in Å.
Sec. 5 Hole trapping ability of molecularly adsorbed water on Ti cation

**Figure S10.** Hole-induced water dissociation on a Ti$_{5c}$ site on the (101) surface of the anatase TiO$_2$ nanocrystal (OAP in a, b) and nanosphere (ST-01 in c, d) models. In panels a and c are represented the systems before dissociation, in which the central water molecule adsorbed on the Ti$_{5c}$ site is undissociated and the electronic hole is trapped on the best trapping O$_{2c}$ site of the nanoparticle, which has been determined in our previous work. In panels b and d the electronic hole is trapped on the hydroxyl group which results from the dissociation of water. The total energy difference for the whole process in the two cases is given. 3D spin density plots of the nanoparticles are reported with an isovalue of 0.01 a.u. Ti atoms are coloured in cyan, H atoms are shown in white and O atoms in red or in blue, in the case they belongs to adsorbed water molecules. Relevant H-bonds are depicted with black dashed lines and their bond lengths are in Å.
Sec. 6 Hole trapping ability of terminal hydroxyls on Ti cation

**Figure S11.** (a) Ball-and-stick representation of the bare (001) surface, as obtained with DFT-B3LYP. (b) Structure of dissociated water on the anatase (001) surface. 3D spin density plot (isovalue = 0.01 a.u.) of the hole on anatase (001) surface, in the presence of only dissociated water (c) and with also an additional H-bonded water molecule (d). Relevant hydrogen bonds are given in blue and distances are given in Å. The percentage values in italics are the atomic spins of the atoms which carry the hole. Red, cyan and white spheres indicate oxygen, titanium and hydrogen atoms, respectively.
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