Supporting Information

Facet-Dependent Photoelectrochemical Performance of TiO₂ Nanostructures: An Experimental and Computational Study

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1. Synthesis & characterization of {101}, {010}, and {001}-TiO$_2$ nanoparticles

**Synthesis of {101}-TiO$_2$:** Octahedral {101}-TiO$_2$ nanoparticles (NPs) were prepared by a previously reported two-step hydrothermal method.\(^1\) In the first step, titania NPs (1 g, P25, Sigma) were hydrothermally treated with 40 mL of KOH solution (17 M) made from solid KOH (Sigma, 99.99\%) in a Teflon autoclave with a capacity of 50 mL at 110 ºC for 20 h. The resulting precipitate was washed and neutralized using deionized water and an aqueous acetic acid solution, respectively. The white powder was dried at 80 ºC. Then, the prepared titanate nanowires (100 mg) were stirred in ultrapure water (30 mL) and heated in a Teflon-lined autoclave (100 mL) at 170 ºC for 24 h. The white precipitate was centrifuged and dried at 120 ºC.

**Synthesis of {010}-TiO$_2$:** Anatase TiO$_2$ nanobelts with selective exposure of the {010} facet were synthesized via a two-step hydrothermal method described by Wong and co-workers.\(^2\) In the first step, commercial anatase TiO$_2$ powder (978 mg, Alfa Aesar, 325 mesh, 99.6\%) was stirred in a solution of 10 M NaOH prepared from solid NaOH (Macron Chemicals, Reagent Grade) dissolved in ultrapure water ($R = 18$ MΩ·cm). The mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 180 ºC for 24 h. The resulting Na$_{1-x}$H$_x$TiO$_3$ nanostructures were isolated by filtration and washed with ultrapure water to remove all of the excess sodium hydride and then dried at 80 ºC. The powder was then dispersed in 80 mL of 1 M hydrochloric acid with sonication and stirred for 20 min to form HTiO$_3$ nanotubes. The powder was collected by filtration, washed with ultrapure water until all of the hydrochloric acid was removed and the white powder was dried at 80 ºC. The HTiO$_3$ nanotubes were converted to anatase TiO$_2$ nanobelts by dispersing 200 mg of the powder into ultrapure water in a Teflon lined autoclave and heating at 170 ºC for 16 h. The final product was collected by filtration as a white powder, which was washed with ultrapure water and dried at 120 ºC to remove excess water.

**Synthesis of {001}-TiO$_2$:** In a typical experimental procedure, 25 mL of Titanium(IV) butoxide (Sigma, \(\geq 97.0\%\)) and 3 mL of hydrofluoric acid solution (Sigma, \(\geq 48\%\)) were mixed in a dried Teflon autoclave with a capacity of 100 mL, and then held at 200 ºC for 24 h.\(^3\) The white powder was separated by high-speed centrifugation and washed with ethanol (Sigma, 99.5\%) and ultrapure water several times. The powders were soaked in a NaOH (0.1 M, 100 mL) solution overnight to remove fluorine ions, followed by rinsing with ultrapure water five times. The white precipitate was centrifuged and dried at 120 ºC.

**Characterization Methods:** Scanning electron microscopy (SEM) was conducted on a Hitachi SU-70 instrument at 10 kV. Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (Micrometrics ASAP 2010 BET Surface Area Analyzer). The band gaps of the materials were determined by diffuse reflectance UV-visible spectrophotometry performed with a Shimadzu UV-2600 UV-visible spectrophotometer and an ISR-2600Plus integrating sphere. Measurements were collected from 7 µm thick films of the facetted NPs deposited on TEC 15 FTO coated glass (Hartford Glass). UV-visible spectra were recorded on a Varian Cary 50 Bio Scan UV-visible system.
2. Time-resolved spectroscopy

**THz-Spectroscopy:** Time-resolved THz spectroscopy (TRTS) measurements were performed following established experimental procedures.\(^4\)\(^5\) Approximately one quarter of the output of an 4 W amplified Ti:Sapphire laser system (Spectra Physics: Mai Tai SP, Empower 30, Spitfire Ace) with a 35 fs pulse duration, 800 nm center frequency, and 1 kHz repetition rate was used for THz generation via optical rectification in a ZnTe(110) crystal and THz detection via free-space electro-optic sampling in an additional ZnTe(110) crystal. Another quarter of the power was frequency doubled to 400 nm in a $\beta$-barium borate (BBO) crystal and used to photoexcite the sample. The change in peak amplitude of the time-domain THz pulse was monitored as a function of its delay with respect to the optical pump pulse to measure the time and efficiency of electron injection. 1 cm $\times$ 1 cm fused silica plates (commonly referred to as quartz) with a thickness of 1 mm were pre-treated to improve the adhesion of the 7 µm thick films of facetted TiO$_2$ NPs: First, the quartz plates were immersed into a mixture of 75% concentrated sulfuric acid (Fisher Scientific) and 25% hydrogen peroxide (30 vol% in water, Fisher Scientific) for a period of 30 min. A compact 100 nm thick layer of TiO$_2$ was then deposited by spin coating a titanium i-propoxide precursor sol onto them at 1000 rpm and annealing the substrate at 500ºC for 15 minutes. The titanium precursor sol consisted of 10 mL isopropanol (JT Baker, anhydrous), 0.17 mL glacial acetic acid (JT Baker), 0.86 mL of titanium i-propoxide (Strem, 98%). After annealing, the facetted TiO$_2$ NP films were deposited and sensitized in a fashion analogous to the method employed for preparing films for DSSC devices.

**Transient Absorption:** Transient absorption measurements were performed with a commercial LP920 laser flash photolysis spectrometer (Edinburgh Instruments). Sample excitation was achieved using an optical parametric oscillator (Spectra-Physics basiScan-M, 1 cm beam diameter, 200 mJ per pulse), pumped by the third harmonic of a Nd:YAG laser (Spectra-Physics Quanta-Ray INDI 40-10, 5 – 8 ns pulses, operated at 1 Hz). A pulsed 450 W Xe arc lamp provided a white light probe. Transmitted light was focused into a 0.3 m focal length monochromator and detected with a photomultiplier tube (PMT, Hamamatsu LP920-K Near IR detector). The PMT current was amplified and recorded with a transient digitizer (Tektronix TDS 3032C). A combination of short- and long-pass filters was employed to remove scattered light. Transient absorption measurements were carried out on sensitized TiO$_2$ films that were placed at a 45º angle in a 1 cm $\times$ 1 cm quartz cuvette containing acetonitrile. Samples were excited at 560 nm, and single wavelength transient absorption curves were collected at 800 nm.

3. Computational methods

The structure of the MK-2 molecule was optimized in gas phase using the B3LYP functional,\(^6\) a pruned integration grid of 75 radial shells and 302 angular points per shell, and the 6-31G(d,p) basis set\(^7\)\(^8\) as implemented in the Gaussian 09 software package.\(^9\) The surface of each TiO$_2$ facet was modeled with a TiO$_2$ slab consisting of four layers of Ti and O atoms arranged according to the crystalline structure of the facet considered. The structures of the pure TiO$_2$ slabs as well those with water or benzoic acid bound to the surface were obtained using periodic boundary conditions with constraints on the coordinates of the bottom two
layers of TiO$_2$ slab. Specifically, we employed the generalized gradient approximation (GGA-PBE) exchange functional$^{10}$ and the split double-$\zeta$ basis set$^{11}$ as executed by SIESTA 3.1.$^{12}$ The Monkhorst-Pack $k$-point grid for the Brillouin zone was $1 \times 1 \times 1$ for all structures ($\Gamma$). The real space grid energy cutoff and the electronic temperature used was 200 Ry. The pseudo-potential files used are those from the GGA Pseudo-Potential Database$^{13}$ and structures were optimized with a force tolerance on atoms of 0.04 eV·Å$^{-1}$.

Injection calculations were performed on models made by attaching an MK-2 molecule to the TiO$_2$ slabs. The geometry of the anchoring carboxylic group determined from energy optimizations of the benzoic acid molecule was employed to simulate the binding geometry for the carboxylate group of the MK-2.$^4$ Then, a code previously developed by Batista and co-workers for interfacial electron transfer simulation (IET)$^{14,15}$ was used to compute the time-dependent electron injection results for each structure. An absorbing potential was applied to the Ti atoms on bottom layer of the TiO$_2$ slabs, to simulate the effect of diffusion of electrons into bulk TiO$_2$ crystals. This absorbing potential was used only to damp the oscillations of the wave-packet and is not expected to affect the initial injection rate.

To achieve the best correlation with the experimental TRTS results, the IET simulations were performed with equivalent contributions of the LUMO and LUMO+1 orbitals of the MK-2 dye. In the TRTS experiment, the MK-2 dye was excited with 400 nm light, which was equivalent to 3.1 eV. The HOMO-LUMO gap of the commercial MK-2 dye has been previously determined by our group to be ~2.16 eV.$^4$ Time-dependent DFT (TD-DFT) calculations were performed to determine the energy level diagram (Figure S1) of the MK-2 dye, which was corrected to reproduce the experimentally determined HOMO-LUMO gap. On this basis, the 400 nm pump light can populate both the LUMO and LUMO+1 orbitals, which can both contribute to the electron injection into the conduction band of TiO$_2$. Accordingly, we used equal contributions of LUMO and LUMO+1 in our injection simulations.

![Figure S1. Energy diagram of MK-2 dye. The red dashed line indicates the energy of the excitation pump beam used in the TRTS experiment.](image)
4. Determination of percentage of the predominant facet

The \{101\}-TiO$_2$ NPs have an octahedral geometry with nearly 100% exposure of the \{101\} facet of TiO$_2$ (Figure 1A). The schematic structure is shown below.

So $S_{101} \approx 100\%$

As shown in Figure 1B, the \{010\}-TiO$_2$ submicron-wires are composed of many smaller nanorods. As reported the predominant facet is \{010\}.$^{2,16}$ The nanobelts have an average length of 1.6 $\mu$m, width of 200 nm and thickness of 50 nm. The schematic structure is shown below along with the calculation for the percentage of \{010\} facets ($S_{010}$) exposed.

$$S_{010} = \frac{\text{Area of \{010\} Facets}}{\text{Total Surface Area}} = \frac{(1600 \text{ nm} \cdot 200 \text{ nm} \cdot 2) + (1600 \text{ nm} \cdot 50 \text{ nm} \cdot 2)}{2[(200 \text{ nm} \cdot 1600 \text{ nm}) + (50 \text{ nm} \cdot 1600 \text{ nm}) + (200 \text{ nm} \cdot 50 \text{ nm})]} = 97.5\%$$

The \{001\}-TiO$_2$ NPs (Figure 1C) have a plate-like morphology with an average edge length of 80 nm and thickness of 6 nm and the schematic structure is shown below. On the basis of a previous report, the percentage of the predominant \{001\} facet is given according to equation shown below, where $\theta$, $a$, $h$ represents the angle between the \{101\} and \{001\} facets of anatase ($68.3^\circ$), the length of \{001\} facet, and the thickness of nanoplate, respectively.$^{17,18}$

$$S_{001} = \frac{\cos(\theta)}{\cos(\theta) + \left(\frac{a}{a + \frac{h}{\tan(\theta)}}\right)^{-2} - 1}$$

$$S_{001} = \frac{\cos(68.3^\circ)}{\cos(68.3^\circ) + \left(\frac{80 \text{ nm}}{80 \text{ nm} + \frac{6 \text{ nm}}{\tan(68.3^\circ)}}\right)^{-2} - 1} = 85.9\%$$
5. Determination of bandgap from diffuse reflectance spectroscopy

Figure S2. Diffuse reflectance spectroscopy of faceted TiO$_2$ NPs.
6. Normalization of photodegradation reaction constant by surface area

Figure S3. UV-visible spectra collected at various times during the photodegradation reaction for the various TiO$_2$ NP samples (A-D) and a plot of the C/C$_0$ ratio measured from the absorption at 460 nm as a function of time (E).

Calculation of Surface Area Normalized Rate Constants: The measured rate constants were normalized to the BET surface area measured for each sample to determine the intrinsic photocatalytic performance of the TiO$_2$ nanostructures. The results summarized in Table S1 demonstrate that the trend in facet-dependent photocatalytic performance is $\{001\} > \{010\} > \{101\}$.

Table S1. Summary of photocatalysis results.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Percentage of predominant facet (%)</th>
<th>Measured rate constant (min$^{-1}$)</th>
<th>Surface area normalized rate constant (min$^{-1}$·m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>${101}$</td>
<td>99</td>
<td>$3.95 \times 10^3$</td>
<td>$7.31 \times 10^3$</td>
</tr>
<tr>
<td>${010}$</td>
<td>98</td>
<td>$7.20 \times 10^3$</td>
<td>$1.17 \times 10^4$</td>
</tr>
<tr>
<td>${001}$</td>
<td>86</td>
<td>$1.29 \times 10^2$</td>
<td>$1.84 \times 10^2$</td>
</tr>
</tbody>
</table>
7. Molecular structure and absorption spectrum of MK-2

Scheme 1 Molecular structure of MK-2.

Figure S4. UV-visible spectrum of MK-2 dye in toluene.
8. Determination of dye loading and desorption kinetics

The relevant kinetic parameters for desorption were determined from fits of the desorbed dye concentration \([Dye]_{\text{des}}\) with respect to time (Figure S5) assuming a first-order process described by Equation 1. According to Equation 2, the total MK-2 dye loading on the surface of TiO$_2$ \([Dye]_{\text{total}}\) consists of a mixture of covalently bound dye \([Dye]_{cb}\) and dye in the form of non-specifically bound aggregates \([Dye]_{ag}\). Prior reports have shown that the dye aggregates desorb within the first few seconds of immersion.$^{19}$ The fraction of non-specifically bound aggregates \(\chi_{ag}\) for each surface was estimated using Equation 3 to be 0.369, 0.253 and 0.431 for the \{101\}, \{010\}, and \{001\} surfaces. To account for the essentially instantaneous desorption of dye aggregates, each point in the desorption curve was offset by subtracting the fraction of aggregated dye (Equation 4) before fitting the data. The \([Dye]_{\text{total}}\) was determined from the sum of the dye desorbed during the 90 min desorption experiment and the remaining dye that was desorbed by placing the electrode into a solution of tetrabutylammonium hydroxide dissolved in tetrahydrofuran.

\[
[Dye]_{\text{des}} = [Dye]_{cb} \left(1 - e^{-kt}\right) \quad (1)
\]
\[
[Dye]_{\text{total}} = [Dye]_{cb} + [Dye]_{ag} \quad (2)
\]
\[
\chi_{ag} = \frac{\delta_{\text{MK-2}} - \delta_{\text{BA}}}{\delta_{\text{BA}}} \quad (3)
\]
\[
[Dye]_{\text{des}} = [Dye]_{\text{total}} - ([Dye]_{\text{total}} \chi_{ag}) \quad (4)
\]

In Equation 3, the percentage of non-specifically bound aggregates is calculated from the surface coverage of MK-2 \(\delta_{\text{MK-2}}\) and the surface coverage of benzoic acid \(\delta_{\text{BA}}\). In this case, the surface coverage of benzoic acid serves as an estimate of the surface coverage of adsorption sites for carboxylate anchoring groups, since it is known that benzoic acid does not aggregate upon adsorption to the surface of TiO$_2$ NPs. Given the different sizes of the MK-2 and benzoic acid molecules, it is important to consider if the area occupied by a benzoic acid is suitably large to be occupied by an MK-2 molecule. On the basis of the surface coverages, we calculate that an average benzoic acid molecule occupies an area of 1.9 nm$^2$, 1.5 nm$^2$ and 3.5 nm$^2$ on the \{101\}, \{010\}, and \{001\} surfaces, respectively. All of these areas are larger than the calculated area of 1.2 nm$^2$ for an average MK-2 molecule and, thus, the projected adsorption sites can fully accommodate the MK-2 adsorbate.
**Figure S5.** Desorption data with associated fits of Equation 1 denoted by the green lines overlaying the data.
9. Computational models of water and benzoic acid adsorption onto TiO$_2$ surfaces

The structures for the anhydrous and hydrated surfaces with a monolayer of water atoms adsorbed to the anatase TiO$_2$ \{101\}, \{010\}, and \{001\} surfaces are shown in Figure S6. In the case of the \{101\} surface, water molecules are adsorbed molecularly to the coordinatively unsaturated Ti$^{4+}$ atoms forming a hydrogen-bonding network on the surface bridged by oxygen atoms. The O–H bond distance was calculated to be approximately 1.77 Å. By contrast, it was energetically favorable for the water molecules on the \{010\} surface to dissociate into protons and hydroxide ions. The dissociation of water on the \{010\} surface has been observed previously and is likely a result of the higher surface energy.\[^{20}\] Observation of the structure reveals that the hydroxide anions coordinate to the Ti$^{4+}$ atoms and the protons bond to adjacent bridging O atoms. As expected, the Ti–O bond lengths of 1.88 Å are slightly shorter, when compared with the Ti–O bond lengths of 2.23 Å on the hydrated \{101\} facet. In both cases, the overall structure of the TiO$_2$ surface remains largely the same in terms of the Ti–O frameworks’ bond lengths and angles.

Conversely, the hydration of the \{001\} facet leads to significant restructuring of the framework of the TiO$_2$ surface and is distinctive from the \{010\} and \{101\} surfaces. In this case, one-half of the adsorbed water molecules are dissociated and the Ti–O–Ti bridge is broken leading to coordination of the surface Ti$^{4+}$ atoms by two hydroxide anions. The second half of the adsorbed water forms a bridging hydrogen-bonding network above the reconstructed TiO$_2$ framework. This is consistent with prior experimental and computational work.\[^{21}\] On this basis, the decrease in the adsorption of carboxylate adsorbates on the \{001\} surface can be readily explained by the fact that the bridging hydrogen-bonding network serves to sterically hinder adsorption onto one-half of the Ti$^{4+}$ atoms, which lie underneath the bridges.
Figure S6. Optimized structures of the anhydrous (left) and hydrated (right) surfaces of the \{101\} (top), \{010\} (middle) and \{001\} surfaces (bottom) with one-monolayer of water. The green, red and blue spheres denote titanium, oxygen and hydrogen atoms, respectively.
Figure S7. Optimized structures of benzoic acid adsorbed to the hydrated {101} (A & B), {010} (C & D), and {001} (E & F) TiO$_2$ facets in the bridging bidentate (A, C, & E) and monodentate (B, D, & F) binding geometries. The green, red, blue and yellow spheres denote titanium, oxygen, hydrogen and carbon atoms, respectively.
10. Analysis of time-resolved THz transients

The efficiency of electron injection was determined by fitting the THz transients (Figure S8) to determine the maximum attenuation ($\Delta THz_{\text{max}}$) of the THz signal. The electron injection in the {010}- and {101}-TiO$_2$ films occurred within the ~300 fs instrument response time. For this case, the $\Delta THz_{\text{max}}$ was determined as the sum of the amplitudes ($A_1$ and $A_2$) and y-offset ($y_0$) of a double exponential fit (Equation 5) of the recovery of THz signal ($\Delta THz$) as a function of time ($t$). The fit parameters are summarized in Table S2.

$$\Delta THz = -y_0 - A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2}$$ \hspace{1cm} (5)

Table S2. Summary of fit parameters for the double exponential fit of the recovery of the THz signal in the {101} and {001} films. The uncertainties for each value are shown in the parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$y_0$ (%)</th>
<th>$A_1$ (%)</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$ (%)</th>
<th>$\tau_2$ (ps)</th>
<th>$\Delta THz_{\text{max}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>0.0452(4)</td>
<td>0.110(2)</td>
<td>27.5(5)</td>
<td>0.142(1)</td>
<td>172(3)</td>
<td>0.297(5)</td>
</tr>
<tr>
<td>010</td>
<td>0.139(1)</td>
<td>0.103(2)</td>
<td>32.1(7)</td>
<td>0.156(1)</td>
<td>269(6)</td>
<td>0.398(6)</td>
</tr>
</tbody>
</table>

In the case of the {001}-TiO$_2$ film, the attenuation of the THz signal continued beyond the instrument response time. The attenuation transient was fit with a single exponential with an offset (Equation 6), which was employed to determine the $\Delta THz$ and electron injection kinetics. The the attenuation of the signal after the instrument response time and the maximum attenuation of the THz signal ($\Delta THz_{\text{max}}$) were determined to be 0.03% and 0.13%, from the y-offset ($y_0$) and amplitude ($A$), respectively. Thus, the attenuation of the signal after the instrument response time represents 20% of the total injection. The time constant ($\tau$) for the injection after the instrument response time was determined to be 32 ps.

$$\Delta THz = -y_0 + Ae^{-t/\tau}$$ \hspace{1cm} (6)
Figure S8. Time-resolved THz transients with associated fits denoted by green lines overlaying the data.
11. Interfacial electron-transfer simulations

**Figure S9.** Injection simulation results for the MK-2 dye bound to the \{010\} (red), \{101\} (black), and \{001\} (blue) facets via a bridging bidentate interaction. The results are shown as survival probability of electron density on the MK-2 dye (solid lines) and the MK-2 dye and TiO$_2$ cluster (dashed lines) as a function of time.
12. References


(17) Xiang, Q.; Yu, J.; Jaroniec, M. Chemical Communications 2011, 47, 4532.

