Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO₂ films

Tim Luttrell¹, Sandamali Halpegamage¹, Junguang Tao¹*, Alan Kramer¹, Eli Sutter² & Matthias Batzill¹

¹Department of Physics, University of South Florida, Tampa, FL 33620, USA, ²Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton New York, 11973, USA.

The prototypical photocatalyst TiO₂ exists in different polymorphs, the most common forms are the anatase- and rutile-crystal structures. Generally, anatase is more active than rutile, but no consensus exists to explain this difference. Here we demonstrate that it is the bulk transport of excitons to the surface that contributes to this difference. Utilizing high-quality epitaxial TiO₂ films of the two polymorphs we evaluate the photocatalytic activity as a function of TiO₂-film thickness. For anatase the activity increases for films up to ~5 nm thick, while rutile films reach their maximum activity for ~2.5 nm films already. This shows that charge carriers excited deeper in the bulk contribute to surface reactions in anatase than in rutile. Furthermore, we measure surface orientation dependent activity on rutile single crystals. The pronounced orientation-dependent activity can also be correlated to anisotropic bulk charge carrier mobility, suggesting general importance of bulk charge diffusion for explaining photocatalytic anisotropies.

Titania (TiO₂) is the most widely used photocatalyst¹–³ for decomposition of organic pollutants because it is chemically stable and biologically benign. The band gap of TiO₂ is larger than 3 eV (~3.0 for rutile and ~3.2 for anatase), thus making pure TiO₂ primarily active for UV light. The most common commercial photocatalyst is the Degussa P-25, a powder consisting of both rutile and anatase crystallites⁴. The phase mixture of different polymorphs is known to have synergistic effects and an increased photocatalytic activity is observed compared to pure phases⁵. However, for pure phases it is generally accepted that anatase exhibits a higher photocatalytic activity compared to rutile TiO₂⁶. Furthermore, not only do the two polymorphs show varying photoactivity, but the different crystallographic orientations of the same material may exhibit different activities⁷–¹². Despite the intensive study of TiO₂ there is no generally accepted explanation for the differences of photocatalytic activity of different polymorphs or surface orientations. Possible explanations may be categorized as follows:

• Anatase has a larger band gap than rutile TiO₂. While this reduces the light that can be absorbed, it may raise the valence band maximum to higher energy levels relative to redox potentials of adsorbed molecules. This increases the oxidation ‘power’ of electrons and facilitates electron transfer from the TiO₂ to adsorbed molecules⁴. This explanation has also been expanded to explain surface orientation dependent activities by suggesting that different surfaces exhibit different band gaps⁴.

• Surface properties may play a role in the adsorption of molecules and subsequent charge transfer to the molecule. The surface properties may not just be polymorph dependent but may differ largely for the same material for different surface orientations or reconstructions⁴⁵–⁴⁶ and consequently may contribute to the observation of pronounced surface effects in photocatalytic activities. Surface properties may again be subdivided into (i) chemical effects, e.g. coordination structure of surfaces that controls adsorption of molecules⁷, (ii) electronic structure of the clean surface⁴⁸ or defects and adsorbate (e.g. hydroxyl)-induced states that may be crucial for charge trapping and separation at the surface⁹, (iii) interaction of molecules with surface defects⁶,⁹, and (iv) surface potential differences (such as work function differences measured in vacuum or flat band potentials in aqueous solution)¹¹,¹² may affect charge transfer from the photocatalyst to molecules. It should be mentioned that the relative position of the conduction band minimum (CBM) in rutile and anatase is still controversial, while the large band gap of anatase might suggest the CBM in anatase to be higher than that of rutile⁶.
Anatase exhibits an indirect band gap that is smaller than its direct band gap. For rutile, on the other hand, its fundamental band gap is either direct or its indirect band gap is very similar to its direct band gap. Semiconductors with indirect band gap generally exhibit longer charge carrier lifetime compared to direct band gap materials. A longer electron-hole pair life in anatase than in rutile would make it more likely for charge carriers to participate in surface reactions. One evidence for longer charge carrier lifetime in anatase than in rutile comes from transient photocconductivity measurements on single crystalline samples.

Charge transport may differ for different polymorphs. In addition to the exciton lifetime the exciton mobility needs to be taken into account. Only excitons that efficiently diffuse can reach the surface within their lifetime. Preferential diffusion of excitons along certain crystallographic directions has been proposed for other photocatalysts to be important to explain surface orientation dependencies in their oxidation/reduction behavior. One measure for exciton mobility is the polaron effective mass. Although contradicting values for effective masses are reported, generally a higher effective mass is reported for rutile than for anatase. The polaron effective mass for rutile is ~7–8 m₀ (where m₀ is the electron mass) while anatase exhibits a polaron effective mass of ~m₀. In addition, in rutile a strong anisotropy for the effective electron masses exists and consequently, its charge mobility is reported, with values ~2–4 m₀ along the <001> direction and ~10–15 m₀ along the <100> direction. No values are reported for other crystallographic directions. Here we demonstrate that bulk charge carrier transport indeed explains the difference between rutile and anatase and furthermore is consistent with orientation dependent activity variations in rutile.

One main obstacle that has prevented a better fundamental description of titania photocatalysis is the masking of bulk properties by complex surface effects. Here we describe a new approach that enables separating surface from bulk effects in describing the photocatalytic activity and to compare photocatalytic activity on rutile and anatase TiO₂.

Utilizing thin epitaxial films of anatase and rutile we evaluate the photocatalytic activity as a function of film thickness. Since the surface properties are the same for any film thickness of the same material any change in the photocatalytic reaction can be solely ascribed to the increased bulk volume. The increase in the photocatalytic activity with film thickness is thus a consequence of more excitons, generated by photo-absorption in the bulk, reaching the surface. In this case the photocatalytic activity increases saturates for TiO₂-films that are thicker than ~50–100 nm. While anatase TiO₂(001) has been synthesized on SrTiO₃ or LaAlO₃ films, rutile TiO₂(101) has been previously synthesized on SrTiO₃ or LaAlO₃ substrates. For anatase TiO₂ on LaAlO₃ the crystallographic relationship is (001)[-110]anatase//([110]LaAlO₃ and for rutile TiO₂ on sapphire the crystallographic relationship is (101)[-111]rutile//(-1102)20–21. For rutile TiO₂(101) grown on LaAlO₃ rutile, it is known that it forms twin domain structures with coherent boundaries in [101] planes. In the studies reported here mainly LaAlO₃ and Al₂O₃ are used, because these substrates (contrast to SrTiO₃) are wide band gap materials and do not exhibit any photocatalytic properties by themselves. Furthermore, the large band-gap of the substrate prevents charges to be transferred to the substrate.

Central to the success of measuring photocatalytic activity as a function of film thickness is the growth of well-defined TiO₂-films and thus we briefly present key characterizations of the prepared films. Fig. 1 shows characterization of anatase and rutile films. Reflection high energy electron diffraction (RHEED) patterns of the as prepared films are shown in Fig. 1(a) and 2(a) for the anatase (001) and rutile (101) samples, respectively. For the anatase sample a 4 × 1 superstructure is observed in the RHEED pattern. This is the typical surface reconstruction for the anatase (001) surface in vacuum and the fairly sharp diffraction pattern confirms a good surface quality of the film. For the rutile (101) surface no superstructure spots are observed despite the fact that the rutile (101) surface is known to reconstruct into a 3 × 1 superstructure. Absence of surface superstructure spots is consistent with the diffraction pattern exhibiting bulk-like diffraction and thus may indicate a somewhat larger surface roughness.

Surface roughness has been characterized by atomic force microscopy (AFM) for every sample. Fig. 1(b) and 2(b) show typical images for anatase and rutile films, respectively. On the anatase films, flat terraces with mono-atomic steps are observed indicating a well-defined crystalline surface quality in agreement with the RHEED pattern. The rutile samples exhibits slightly higher surface roughness, with some ~40 nm wide ‘grains’ with roughness ~2 nm for a 12 nm thick film. The ‘grains’ have a slightly rectangular shape and two kinds of rectangular grains oriented 90° to each other are observed. These are due to the before mentioned twinning of the film. As the zoomed-in image in Fig. 2(b) shows the individual ‘grains’ are flat and atomic-height step edges can be imaged.

Transmission electron microscopy (TEM) imaging and selected area electron diffraction (SAED) of 25 nm thick films further corroborate the high crystalline order and epitaxial relationship between substrate and film. Fig. 1(e), (f) and 2(e), (f) show TEM images and corresponding diffraction patterns (DPs) for electron beam along the <0–10>LaAlO₃//<100>TiO₂ and <110>LaAlO₃//<010>TiO₂ for the anatase and rutile films, respectively. The SAED were taken with a ~500 nm aperture at several points along the film. In addition a 20 nm diameter electron beam was scanned along the film and the diffraction pattern monitored. No other phases were detected in the diffraction patterns, in particular the anatase films were phase-pure and formation of any rutile inclusions can be excluded. X-ray photo-emission spectra (XPS) of the films are compared to those of rutile single crystal samples and no discernible difference is observed indicating the formation of stoichiometric TiO₂ within the sensitivity of XPS.

Photocatalytic activity of rutile(101) and anatase(001) films. The photocatalytic activity of the films is measured by photocatalytic decomposition of an organic dye (methyl orange). Fig. 3(a) and (b) illustrate a typical measurement of the methyl orange
concentration versus reaction time for a TiO$_2$ film. From the rate of methyl orange decomposition the photocatalytic activity for different TiO$_2$ films is determined and this information is plotted in Fig. 3 (c) as a function of the film thickness. For thick films, it is apparent that the photoactivity for the anatase films is about twice the activity of rutile in agreement with the general notion that anatase is the photocatalytically more active material. Important for this study is, however, the dependence of the photoactivity with film thickness. For the rutile films, the photocatalytic activity does not change significantly for films thicker than $\approx 2.5$ nm. Only for the very thinnest films the activity drops. This suggests that for thick films excitons generated deeper than $\approx 2.5$ nm from the surface do not reach the surface, i.e. they recombine before reaching the surface, and thus do not contribute to photoreactions. For anatase films, on the other hand, the photocatalytic activity increases to film thickness larger than 5 nm. This indicates that in anatase charge carriers from deeper in the bulk reach the surface compared to rutile.

Dependence of photocatalytic activity on surface orientation and sample preparation conditions of rutile single crystals. High quality epitaxial thin films may only be grown with a few surface orientations. Thus, in order to investigate the variation of the photocatalytic activity as a function of surface orientation, we resort to studies of single crystal rutile TiO$_2$. No anatase single crystals of large-enough size are available to investigate surface dependence of the photocatalytic activity on anatase with our approach. However, it should be mentioned that there does exist some interesting investigations on surface engineered powder samples that exhibit preferential surface orientations.$^{44-52}$

Figure 1 | Characterization of anatase (001) films. (a) and (b) RHEED pattern along the $<101>$ and $<110>$ azimuths, respectively. Note the superstructure streaks in (a) indicating the 4 × 1 surface reconstruction. (b) and (c) show ambient AFM images, indicating atomically flat terraces. (e) cross-sectional TEM of the LAO/anatase interface, with (f) showing the diffraction pattern of the interface indicating the epitaxial alignment of the anatase film.

Figure 2 | Characterization of rutile (101) films. (a) and (b) RHEED pattern along the $<010>$ and $<−101>$ azimuths, respectively. (b) and (c) show ambient AFM images, indicating two crystal orientations due to twinning in the film. (e) cross-sectional TEM of the Al$_2$O$_3$/rutile interface, with (f) showing the diffraction pattern of the interface indicating the epitaxial alignment of the rutile film.

Figure 4 (a), shows the measured photocatalytic activity for rutile samples with different surface orientations for different surface preparation methods. For all sample preparation procedures, with exception of HF-etched and tube furnace annealed samples, the activity follows the order (101) > (110) > (001) > (100) for photocatalytic degradation of organics. For HF etched and tube furnace annealed samples the (001) orientation exhibited a slightly higher activity than the (110) sample. Remarkably, the photoactivity of the ’as-received’ samples are as much as 30% higher than the samples after HF-etching and tube furnace annealing, which results in a much better defined surface as indicated in the AFM images shown in Fig. 4(b) and (c). Formation of surface defects has been discussed in several publications to affect surface charge trapping and charge transfer to adsorbates and/or water.$^{53-57}$ Our observation of a variation of the overall activity of the single crystals on the surface preparation is in agreement with such an influence of the surface morphology. This further underlines the challenge in separating bulk from surface effects for photocatalytic activities and illustrates the need of identical sample preparation to enable quantative comparisons.

Importantly, the single crystal studies on rutile (101) show very similar photocatalytic activity as those of the rutile (101) films. The same photocatalytic activity of the films and the single crystal demonstrates that the films are of single-crystal quality in terms of photocatalytic activity. In particular, this implies that the twin-boundary structure and the slightly increased surface roughness of the rutile films compared to the single crystal surfaces does not adversely affect the photocatalytic activity of the films. We also point out that the (101) surface is the most photocatalytically active surface
of all the rutile surface orientations studied, in agreement with previous reports. This is important for comparing the overall photocatalytic activity of the rutile and anatase films. The fact that the most active rutile surface is significantly less active than the anatase (001) surface (which according to some reports is only the second most active anatase surface) further validates the fact that anatase is photocatalytically more active than rutile.

**Discussion**

The general perception that anatase has a higher photocatalytic activity compared to rutile TiO$_2$ is confirmed by our measurements on extended planar epitaxial thin films. The anatase (001) films (in the thick-limit: $\sim$20 nm) exhibit around twice the activity for photocatalytic decomposition of organic molecules than the rutile (101) films grown under identical conditions. Importantly, the film thickness-dependence of the photocatalytic activity demonstrates that this difference in the photocatalytic activity is at least partially a bulk property of the two forms of TiO$_2$. In particular the measurements show similar activity (or slightly higher activity for rutile) for very thin films (less than 2 nm) but while the activity for rutile films remains almost unchanged for films thicker than 2 nm the activity for anatase films keeps increasing and only saturates for films thicker than $\sim$5 nm. This behavior indicates that charge carriers for photocatalytic reactions can originate from much deeper in the bulk for

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**Figure 3** | Evaluation of photocatalytic activity of samples by decomposition of an organic dye (methyl orange). (a) shows the absorption spectra for the methyl orange solution for different irradiation times. The peak area of the absorption spectra is a direct measurement of the molecule concentration and thus its decrease with UV-irradiation time is a measure of the photocatalytic decomposition of the molecule. In (b) the absorption peak area is plotted versus irradiation time for anatase films with different film thicknesses. Fitting an exponential decay function gives the photocatalytic decomposition rate for the different samples. This measured rate is plotted in (c) as a function of film thickness for the rutile and anatase films. The anatase films reach a higher photocatalytic activity for thick films. However, the maximum activity is reached already for $\sim$2.5 nm thick films for rutile, while the maximum activity is only reached for $\sim$5 nm thick films for anatase.
anatase than for rutile. The film thicknesses are much smaller than the absorption depth of light and thus light absorption cannot be responsible for the saturation of the photocatalytic activity. Also, the film thickness is smaller than typical depletion regions in oxides, which excludes band-bending effects for charge separation. The studies reported here also compare favorably with previously reported work on photocatalytic activity as a function of film thickness for rutile films using photoreduction of Ag ions as a measure of the photoactivity. In these studies a sharp increase in the photoactivity for thin films up to less than 10 nm thickness was reported which then plateaued. This is very similar to the results presented here, however, different to the studies shown here a further increase in the activity at a lower rate has also been observed. The two different rates of increase in photoactivity suggest two different mechanisms at work. In studies reported here the increase for much thicker TiO2 samples could not be observed and the photocatalytic activity truly saturates at less than 10 nm. This difference in the two investigations is likely a consequence of the different photoreactions studied. In particular Ag-clusters that formed during photoreaction in previous work will modify the photocatalyst and this can give rise to additional phenomena.

In order to quantify the charge diffusion length normal to the surface of our macroscopically planar samples, we fit the increase in photocatalytic activity with increasing film thickness by an exponential dependence of the form: \( k = C \left[ 1 - \exp(-d/\ell) \right] \), where \( k \) is the photocatalytic activity of the films (equivalent to the measured decomposition rate constant) and \( d \) is the film thickness. \( C \) and \( \ell \) are fitting parameters, where \( C \) corresponds to the activity for very thick films (or bulk samples). The best fit parameters give a value of \( C_{\text{anatase}} = 0.0033 \pm 0.0003 \), \( \ell_{\text{anatase}} = 3.2 \pm 0.6 \text{ nm} \), and \( C_{\text{rutile}} = 0.0018 \pm 0.0001 \), \( \ell_{\text{rutile}} = 1.6 \pm 0.4 \text{ nm} \), for anatase and rutile respectively. The parameter \( \ell \) may be interpreted as the (surface-normal) charge diffusion length and its value indicates the distance from the surface at which a generated charge carrier has a probability of \( 1/e \) to reach the surface. The films studied here differ from pure TiO2 by the presence of an interface with a substrate. Consequently it may be important to consider how this interface may affect our observations. There are three main potential contributions by which the interface could distort the measured photocatalytic properties compared to a hypothetical ideal case of a ‘free’ TiO2 sheet. Firstly, charge carriers may be trapped and recombine at the interface and the rate of this process may be different for the LaAlO3 or Al2O3 substrates. Secondly, the lattice matching at the interface will induce some strain in the film that could affect the exciton diffusion to the surface. Thirdly, the lattice mismatch will facilitate point-defect formation in the film that varies with film thickness. All three of these effects are likely present.

Figure 4 | Photocatalytic activity measurements on rutile single crystals with four different surface orientations and three different sample preparation conditions. For all preparation conditions the (101) orientation is the most active surface. (b) and (c) shows AFM images for as-received and after HF and annealing treatment for all four sample orientations.
to some extent but we argue that they do not obscure the main conclusion of a twice longer exciton diffusion length in anatase compared to rutile. The observation that rutile films, only 5 nm thick (a thickness where substrate induced strain is expected to be still present), exhibit a photocatalytic activity that is identical as that for rutile single crystal samples, indicates that strain in the films does not significantly alter the photocatalytic properties. In terms of charge trapping and recombination at the interface, it is important to realize that this effect can only modify the photocatalytic activity for films appreciably thinner than the charge diffusion length (d < λ) and any influence from charge recombination at the interface diminishes as the film thickness approaches λ. Thus exciton recombination at the interface may only contribute to a deviation from the ideal exponential-functional dependence used to describe the behavior of the photocatalytic activity versus film thickness, but it will not change the film thickness at which the photocatalytic activity saturates. In order to assess the general possibility of lattice mismatch induced variation in the film properties, including formation of point defects, we compared the activity of anatase films grown on LaAlO3(001) with those grown on SrTiO3(001). These substrates exhibit largely varying lattice mismatch with respect to anatase films of 0.1% and 3.1%, respectively. Despite this large misfit for SrTiO3, we measure the same (within 5%) photocatalytic activity as for anatase films on LaAlO3 if the films thicker than 5 nm. For thinner films charge carriers generated in the photocatalytically active SrTiO3 substrate can contribute to the photocatalytic reactions and thus a slightly larger activity is measured compared to LaAlO3 substrates for very thin films. Thus from these arguments and test-studies we conclude that interface effects will not affect the key result of a larger λ for anatase than rutile and consequently our measurements show, for the first time conclusively, that the material-volume that contributes to the photocatalytic activity is significantly larger for anatase than for rutile.

The charge diffusion length λ is a convolution of charge carrier life time and charge carrier diffusivity. Arguably, it is the diffusion length λ that is the important property for characterizing the efficiency of a photocatalyst. The difference in the charge diffusion length between rutile and anatase may have its origin in the longer life-time of charge excitations and/or higher charge carrier mobilities in anatase than in rutile. Both properties have been previously reported1 but could not be unambiguously linked to photocatalytic activity differences between polymorphs.

Our determination that bulk properties are important to explain differences in the photocatalytic activity of different polymorphs of TiO2 can also be applied to the measured surface orientation dependence for the rutile samples. The known bulk anisotropy in the effective masses and charge mobility in rutile along and perpendicular to the c-axis, i.e. (001) and (100) surface orientations, respectively, correlates well with the observed photocatalytic activity measurements. Independently from the surface preparation, we consistently measure higher photocatalytic activity for the (001) direction than for the (100) direction for which room temperature mobilities of μ(001) = 8 cm2/V·s and μ(100) = 1.4 cm2/V·s are reported respectively10. Unfortunately, to the best of our knowledge, no charge mobility data for the (101) or (110) direction are known.

In conclusion, this investigation demonstrates the importance of bulk properties for the production of more efficient photocatalysts. For TiO2, it appears that a surface region of only a few nanometer depths contributes charge carriers to photoreactions. Higher activity in e.g. ZnO may be attributed to higher charge mobility in ZnO and thus the search for better photocatalysts should take charge mobilities and exciton life times into account. Finally, the approach described here for determining the active surface regions may not only be applied to pure materials but also to bulk dopant modified photocatalysts. This may enable future studies to extract information on the influence of dopants on the overall photocatalytic performance.
