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Study of the Bulk Charge Carrier Dynamics in Anatase and Rutile TiO₂ Single Crystals by Femtosecond Time Resolved Spectroscopy

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Abstract:

Understanding of the fundamentals behind charge carriers dynamics of photocatalytic materials are still illusive, hindering progress in our quest for renewable energy. TiO₂ anatase and rutile are the most understood phases in photocatalysis and serve as the best model systems for fundamental studies. The ultrafast charge carrier dynamics especially on TiO₂ anatase single crystal (the most active phase) are unresolved. Here femtosecond time resolved spectroscopy (TRS) was carried out to explore the dynamics of photoexcited charge carriers' recombination in anatase single crystal, for the first time using pump fluence effects, and compares it to that of the rutile single crystal. A significant difference in charge carrier recombination rates between both crystals is recorded. More specifically, we found that the time constants for carrier recombination are two orders of magnitude slower for anatase (101) when compared to those of rutile (110). Moreover, bulk defects introduced by reduction of the samples via annealing in ultra-high vacuum resulted in faster recombination rates for both polymorphs. Both states (fresh and reduced) probed by pump fluence dependence measurements revealed that the major recombination channel in fresh and reduced anatase and reduced rutile is the first-order Shockley-Read-Hall mediated. However, for fresh rutile, third-body Auger recombination was observed and, attributed to the presence of higher density of intrinsic charge carriers. At all excitation wavelengths and fluence investigated, the anatase (101) single crystal shows longer charge carrier lifetimes when compared to the rutile (110) single crystal. This may explain the superiority of the anatase phase than the rutile phase in M/TiO₂ catalysts for molecular hydrogen production.

Introduction:

Photocatalytic reactions rely on the concentration and the dynamics of excited charge carriers of the absorber layers. Slow recombination rate of these excited carriers is therefore an important sought after characteristic needed for the design of a photocatalyst.¹⁻² In that regard, the morphology and crystallinity of the photoactive material play a key role.³⁻⁵ TiO_2 is one of the most extensively studied transition metal oxide semiconductors and probably the most understood at the fundamental level.^{6-7, 2, 8-11} It is also the only oxide semiconductor, which is used as a photoanode in third generation solar cells.¹²⁻¹³

Among the three polymorphs, anatase and rutile are the most common phases for photocatalysis¹⁴⁻¹⁵ and water oxidation.¹⁶⁻¹⁷ Both anatase and rutile form a tetragonal lattice structure, that can be described in terms of the repetition of TiO_6 octahedron units. The octahedral arrangement in anatase is distorted due to the four-edge sharing structure, while rutile has non-distorted two-edge sharing structure. However, anatase has a larger band gap (3.2 eV)¹⁸ compared to rutile (3 eV).¹⁹ The band structures of rutile^{20, 11} and anatase^{21, 11} have direct and indirect band gaps, respectively. Experimentally, transient photo-conductance study showed that $e-h$ recombination dynamics is slower in anatase (101) in contrast to rutile (110) which is in line with its indirect band gap electronic structure.¹¹ These together along with differences in crystal symmetry induce differences in their photophysical properties. Anatase TiO_2 nano- and micro-particles²² have been shown by many authors to outperform rutile TiO_2 in photocatalytic hydrogen ion reduction²³⁻²⁴, as well as photoanode in dye-sensitized solar cell (DSSC).^{9, 25-26} Moreover, it has been reported often that the presence of two phases at specific proportion leads to synergism (i.e., increasing of the catalytic activity more than the arithmetic sums of the individual components).^{9, 23, 27-28, 24} While many interpretations have been given, as of today, this phenomenon is still subject to studies and quantitative measures of the dynamics of charge carriers on model surfaces are still needed.

The study of charge carrier recombination processes in TiO_2 is mainly conducted experimentally although some computational work is also pursued. Most theoretical work addresses simulation of reaction kinetics using non ab initio based methods²⁹⁻³⁰, a few using Hybrid Density Functional Theory (such as DFT HSE06)³¹⁻³² and a handful using a full ab initio time dependent DFT for small clusters.³³⁻³⁷ None of the theoretical work provides deep insight for accurate comparison with transient absorption at the pico- and nanosecond time scales over

solid semiconductors at present. Femtosecond transient absorption spectroscopy (TAS) is one of the most powerful techniques to directly investigate charge carrier dynamics in semiconductors.³⁸⁻³⁹ For example, the kinetics of de-excitation processes that may follow first, second, or third order mechanism can be determined through pump fluence dependent measurements.^{40-41,42-43} Photo-generated charge carriers recombination in TiO₂ anatase and rutile nanoparticles, mesoporous and microparticles have been studied previously through transient absorption spectroscopy,^{44-50, 5} however, the exact mechanism of charge recombination in TiO₂ is still under debate.⁵¹⁻⁵³ Recently, Durrant *et al.*, have reported that, unlike II-VI chalcogenides, charge recombination processes in TiO₂ mesoporous, dense anatase and rutile films do not take place through surface defect states.⁴ In their report, the role of defects was explored by conducting a comparative study of the dense thin films that possessed less defects as compared to the mesoporous ones.

Single crystals, having no grain boundaries compared to polycrystalline materials, are more suitable to study the influence of morphology and bulk defects on charge carrier recombination processes. Photoexcited charge recombination kinetics in TiO₂ single crystal has not been studied except for rutile single crystal by Katoh *et al.*,⁵⁴ using sub-nanosecond transient absorption spectroscopy. In their study, the measured electron-hole recombination rate ($k_{\text{rec}} = 5 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$) was found to be about four orders of magnitudes smaller than the diffusion-controlled reaction rate ($k_{\text{rec}}^{\text{diff}} = 1.4 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$). The smaller *e-h* recombination rate in bulk rutile TiO₂ is due to the low reactivity of electron and hole inside the crystals. No such studies on anatase single crystals have been reported to date. Equally important, the charge recombination over subpicosecond timescale using single crystals of anatase and rutile, and the effect of pump fluence, has not been explored.

The low index anatase (101) and rutile (110) single crystals represent the most thermodynamically stable surfaces of these polymorphs. In this work, we are addressing three questions by studying these two crystals. 1. We investigate the carrier dynamics of both their reduced and “near” stoichiometric forms in order to gauge the kinetic effect of bulk defects. 2. De-excitation of the charge carriers is studied as a function of pump fluence to extract their reaction order. 3. We also probe the intraband electron “cooling” process at different excitation energies (band edge and above band edge excitation).

Results:

The rutile (110) and anatase (101) single crystals are obtained from MTI Corporation and MaTech, respectively. Reduction was conducted by heating the crystals at 600 °C each in Ultra High Vacuum (UHV; base pressure in the low 10^{-10} torr) for extended periods (hours). The crystals were characterized by XPS and STM as reported previously.⁵⁵⁻⁵⁶ To study their bulk properties, we have further characterized them, in this work, by Raman spectroscopy.

Figure 1 depicts the Raman spectra of fresh and reduced anatase (101) and rutile (110) single crystals. Anatase TiO_2 has a distorted tetragonal crystal structure (D_{4h}^{19} -I $_4$ /amd)⁵⁷, with six symmetry-allowed Raman active modes of transition. The Raman spectra of both fresh and reduced anatase samples exhibit major peaks at 141, 197, 399, 515, and 639 cm^{-1} . The Raman peak at 515 cm^{-1} splits into two bands, 513 and 519 cm^{-1} at 73 K.⁵⁸ These bands are assigned to E_{1g} , E_{2g} , B_{1g} , A_{1g} , B_{1g} , and E_{3g} , respectively for the symmetry-allowed transitions, obtained from group theory calculations. The rutile polymorph also retains a tetragonal lattice with D_{4h}^{14} -P 4_2 /mm⁵⁷ space group which has four Raman active modes. The Raman bands at 143, 235, 447 and 612 cm^{-1} can be attributed to B_{1g} (two phonon scattering), E_g , and A_{1g} active mode transitions.⁵⁹ The band intensity at 143 cm^{-1} for rutile phase is substantially weaker when compared to that of the anatase phase. In addition, a weak band at 826 cm^{-1} is seen and can be ascribed to the B_{2g} transition mode. The intensity of the 612 cm^{-1} band due to A_{1g} symmetric stretching depends on the excitation laser power.⁶⁰ As the excitation power increases, the Ti–O bond strength decreases (due to local heating effect), resulting in increase of probability of symmetric stretching. In the case of anatase, a broadening of the E_{1g} at ca. 144 cm^{-1} has been reported by others and was attributed to oxygen-defects when TiO_2 samples were reduced with hydrogen at a pressure of 10^{-2} torr at 300°C for prolonged time.⁶¹ Moreover, also for anatase, the relative intensity of the B_{1g} , A_{1g} and E_{3g} is sensitive to chemical treatment. Treatment of nanosheets of TiO_2 anatase with HF has resulted in the increase of the B_{1g} and A_{1g} and a decrease of the E_{3g} .⁶² Since the B_{1g} and A_{1g} of TiO_2 anatase (figure 1) are for symmetric and asymmetric bending modes of O–Ti–O, they are affected together. Structural arguments have been invoked for the change in the relative intensities of these three bands.⁶² Our results show the same trend for reduced anatase TiO_2 (101) single crystal with a slight broadening of the E_{1g} and an increase in the relative intensity of the bending/stretching modes as shown in figure 1B. Since Ti cations in the bulk are 6-fold coordinated in an octahedral arrangement, the creation of oxygen vacancies

would affect more the stretching mode (affected by both axial in in-plane vibrations) than the bending modes (affected more by in plane vibrations). The rutile TiO_2 (110) single crystal shows an attenuation of the E_{1g} mode upon reduction (figure 1A). It has been reported by others that the broadening of E_{1g} and A_{1g} modes is due to non-stoichiometry (oxygen vacancies).⁶³⁻⁶⁴

Figure 1:

Raman shift (532 nm excitation wavelength) of fresh and reduced anatase (101) and rutile (110) TiO_2 single crystals.

The charge carrier lifetime of different TiO_2 polymorphs have been previously reported^{44, 48, 4, 65}, however, comparison of their depopulation in rutile and anatase TiO_2 single crystals has not been explored. Earlier work by Katoh and coworkers have studied the $e-h$ recombination dynamics in the bulk rutile TiO_2 single crystals using sub-ns transient absorption spectroscopy.⁵⁴ They have concluded that long $e-h$ recombination time in bulk rutile single crystals is due to low reactivity, which is unlike the case of nanoparticles. The transient signal due to photo-excited electrons was identified in NIR and IR spectral regions,⁶⁶⁻⁶⁷ while the UV and near visible region (~ 500 nm) are ascribed to holes.^{68, 67} It should be pointed out that electrons and holes transient absorption signals strongly overlap in the visible region.

To monitor the $e-h$ recombination dynamics in both, fresh and reduced single crystals, the samples were excited at 320 nm laser light i.e. above the band edge excitation. The TA spectra of

all single crystals at different time delays are shown in Figure 2. All samples show a broad photo-induced absorption in the 400 to 900 nm spectral region. However, the signal intensity below 600 nm is significantly lower compared to NIR region (Figure S1). The TA spectra of all samples exhibit several features at 765, 775, 825, 845, and 870 nm (± 5 nm) for all time delays, although the fresh TiO_2 (110) rutile showed the least pronounced distinct features.

Figure 2:

Transient absorption (TA) spectra of (A) fresh anatase (101), (B) reduced anatase (101), (C) fresh rutile (110), and (D) reduced rutile (110) TiO_2 single crystals at different time delay following 320-nm laser excitation with 13 mJ cm^{-2} pump fluence. The corresponding spectra in the visible region are presented in Figure S1.

To gain insight into the nature of charge recombination in both crystals, we have compared the kinetics profiles of the four samples at 860 nm (the other regions 765, 775, 825, 845 nm were also monitored and their decay is given in the supplementary information, Figures S2 and S3 and

tables S1 and S2). It should be noted that the five regions indicated above gave the same quantitative signal decay so it is safe to only use one region for the study, the 860 nm.

Figures 3A and 3B depict the normalized kinetics traces of fresh and reduced anatase and rutile single crystals, following the 320-nm laser excitation with 13 mJ cm^{-2} pump fluence. For all samples, the data were fit with two exponential decays: t_1 and t_2 . In the case of rutile single crystals, we observed a very fast decay ($t_1 = \sim 0.5 \text{ ps}$) when compared to anatase single crystals. This fast decay ($t_1 = \sim 0.5 \pm 0.05 \text{ ps}$) component did not change for the monitored wavelengths for both fresh and reduced samples. However, for fresh and reduced anatase (101) single crystals, t_1 varied. In addition, we have performed similar analysis of charge recombination in all four samples with 5 mJ cm^{-2} pump fluence (see the Supporting Information for details, Figure S4, Table S3). At lower pump fluences, the first decay components (t_1) of both fresh and reduced rutile changed from $0.5 \pm 0.05 \text{ ps}$ to $0.72 \pm 0.07 \text{ ps}$. However, for fresh and reduced anatase it varied significantly (for anatase fresh it changes from $30 \pm 2.2 \text{ ps}$ to 106 ± 5.8 while for reduced anatase it varies from 20 ± 1.6 to $74 \pm 3.5 \text{ ps}$). As annealing in a high vacuum does not induce a significant change in the rutile single crystal, we attribute the faster decay found in rutile (110), when compared with anatase (101), to an innately higher density of oxygen vacancies found in the rutile single crystal. Others have investigated similar decays in anatase and rutile phases but using powder of different sizes and packing. In particular, a study that compared dense layers to mesoporous layers of powder TiO_2 anatase and rutile⁴ has shown that time decay in the anatase phase is slower than that of rutile and that increasing the surface to bulk ratios did not change the decay kinetics. Working on powder materials while important has its own limitation and may be considered as guideline in particular when dealing with phases and orientation. For example, it is difficult to analyze the inevitable amorphous layers when TiO_2 anatase is synthesized at temperatures below 500°C . Also, the presence of minor phases, such as the brookite phase, is often seen upon refinement of XRD data TiO_2 anatase prepared by the solgel method.²⁴ Other factors include changes in degrees of crystallinity with particle size, changes in lattice dimension especially for nanoparticle of TiO_2 , as well as the presence of multiple crystallographic directions in any 3D particle make. It is worth stressing that the stoichiometric single crystal has the lowest possible surface to bulk ratio and the highest possible degree of crystallinity.

Before proceeding to investigate the modes of $e-h$ recombination in the two single crystals, we have studied the charge carrier density and mobility by Hall effects measurements. It

was not possible to measure the charge carrier density and mobility of the (110) fresh rutile TiO_2 single crystal due to its very high resistivity ($>M\Omega$). Hall measurements data indicated that the (110) reduced rutile and both fresh and reduced (101) anatase TiO_2 single crystals are n-type semiconductors. The charge carrier density is found to be maximum for the (110) reduced rutile TiO_2 . The measured charge carrier densities were 5.5×10^{18} , 4.4×10^{16} , and $7.3 \times 10^{15} \text{ cm}^{-3}$ for reduced rutile, fresh anatase, then reduced anatase single crystals, respectively. Moreover, the Hall mobility were 2.7, 127, and $175 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively for reduced rutile (110), fresh, and reduced anatase (101) TiO_2 single crystals at room temperature. Mobility of the charge carrier in TiO_2 varies depending on morphology. Anatase shows higher mobility when compared to the rutile.⁶⁹ The Hall mobility of pure rutile and anatase TiO_2 single crystal has been reported by others and are 1^{19} and $>>1^{70} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. An overview of Hall mobility of TiO_2 has been reported by Poumellec et al.⁷¹ Low Hall mobility of the reduced rutile single crystal, in spite of its high charge carrier density suggests that electrons are strongly scattered due to high concentration of bulk defects. Since the anatase single crystal has been grown naturally, it possesses impurities that are responsible for a high Hall mobility value.

Although, rutile is the most stable polymorph, the surface energy of anatase (101) is lower than that of the rutile (110) surface. The lower density of bulk defects in anatase (101) single crystal when compared to that in rutile (110) single crystal, decreases the charge carrier recombination rates, which in turn may enhance its photocatalytic performance. Moreover, the fresh anatase (101) has slower charge carriers recombination rates than the reduced one. It is worth noting that the penetration depth of the UV laser light (for 320 and 350 nm) in TiO_2 single crystal and nanoparticles film varies from 50-500 nm.⁷² Therefore, charge carrier lifetimes are largely those of the bulk single crystals. In the case of rutile samples, both fresh and reduced rutile show similar fast decay (0.5 ps) which can be attributed to inherent bulk defects. However, the overall charge recombination of the fresh rutile is slower than the reduced one. All the relevant fitting parameters are summarized in Table 1.

Table 1:

Transient absorption fitting parameters of fresh reduced anatase (101) and rutile (110) single crystals. Parentheses refer to the contribution of the corresponding decay components.

Systems (λ , nm)	t_1 (ps)	t_2 (ps)
Anatase fresh-101-860 nm	32.3 ± 2.5 (51%)	472.3 ± 27 (49%)
Anatase reduced-101-860 nm	24.6 ± 1.7 (58%)	306 ± 20 (42%)
Rutile fresh-110-860 nm	0.5 ± 0.07 (33%)	257 ± 17 (67%)
Rutile reduced-110-860 nm	0.5 ± 0.05 (35%)	108.9 ± 14 (65%)

Figure 3: Normalized transient absorption decay kinetics probed at 860 nm after 320- nm excitation of fresh (A) and reduced (B) anatase (101) and rutile (110) single crystals, respectively.

In order to determine the charge de-excitation channel(s), we have performed excitation pump fluence dependence TA measurements for all samples. Figure 4 illustrates changes in absorption as a function of pump fluence of the rutile and anatase single crystals. It is clear that with increasing pump fluences the intensity of the TA increases, while accelerating the charge recombination. To explore the recombination mechanism of each single crystal, following varying excitation intensities, the decay pattern can be fitted with a simple charge carrier de-excitation rate equation:

$$-\frac{dn}{dt} = An + Bn^2 + Cn^3 \tag{Equation 1}$$

Where the depopulation ($-\frac{dn}{dt}$) of the charge carriers is expressed in three terms: linear (An), square (Bn^2), and a cubic one (Cn^3), which are ascribed to trap-state-assisted (or Shockley-Read-Hall), free charge carriers mediated non-geminate (radiative), and three-body Auger type

recombination, respectively.⁴⁰ Utilizing this approach, we fitted the decay patterns with the three-term polynomial (fitted curves are indicated with red solid lines in Figure 4), the coefficients of the fitting curves are listed in Table 2. For all samples, the coefficient of the non-geminate recombination term of free electrons and holes has a negative sign. This resonates well with the fact that titania single crystals has considerably weak PL signal at room temperature when compared to those collected at liquid nitrogen or liquid helium temperatures.⁷³ Therefore, the second order non-geminate radiative recombination process can be excluded from the depopulation rate equation in the case of TiO₂ single crystals. Moreover, the coefficient of the cubic term (Auger type) has much lower weight (contribution) except for the fresh rutile sample. Taking this into account, we conclude that the major channel of charge recombination in TiO₂ single crystals is first order, trap states mediated (Shockley-Reed). Interestingly, the maximum value of the coefficient of the trap-mediated decay is in the case of fresh rutile (110) sample. It is also noticed from the pump fluence measurements that the fast decay component of the fresh rutile single crystal is independent of pump intensity, which can be attributed to inhomogeneous distribution of charge carriers. This effect is less pronounced for the reduced rutile sample. Also, the significant contribution of the cubic coefficient in fresh rutile suggests the possibility of three body annihilation during the charge recombination process. This can be possible due to inhomogeneous distribution of intrinsic charge carriers.

Figure 4:
Pump fluence dependent charge carriers’ recombination pattern of anatase (101) and rutile (110) fresh and reduced single crystals. ΔA values are taken from the 860 nm decay kinetics at the highest magnitude of the transient signal.

Table 2:
Extracted parameters for equation 1 upon fitting of pump fluence results presented in Figure 4, for anatase (101) and rutile (110) fresh and reduced single crystals.

Samples	A	B	C
Anatase fresh-101	0.013	-0.0012	3.45×10^{-5}
Anatase reduced-101	0.018	-0.0014	3.62×10^{-5}
Rutile fresh-110	10.75	-0.67	0.015
Rutile reduced-110	0.007	-4.92×10^{-4}	1.18×10^{-5}

To investigate hot charge carrier relaxation in anatase and rutile single crystals, we performed a comparative study of the change in absorption following the band edge vs above-band edge excitation. Figure 5 shows the comparison of the decay traces of anatase and rutile single crystals. As the band gap of anatase (3.2 eV) is larger than that of rutile (3 eV), the excitation wavelengths of 365 and 350 nm were used for band edge and above-band edge excitations of rutile samples, while 320 and 300 nm excitation wavelengths were utilized for the anatase single crystal.

Both fresh and reduced anatase samples reveal rise in the dynamics profile (~ 1 ps time scale) after excitation above the bad gap, which is ascribed to intra-band relaxation (Figure 5). This closely resembles the intra-band relaxation process observed in II - VI semiconductors,⁷⁴⁻⁷⁵ where an additional time is needed to “cool” the photo-excited charge carriers to the conduction band edge. For the band edge excitation, “conventional” inter-band charge carrier decay is observed for the fresh and reduced anatase samples. Interestingly, the recombination dynamics of anatase upon band edge and above-band edge excitation follow exactly the same trend beyond the ten-picosecond time scale. In the case of rutile single crystals, the initial rise of the signal which is associated with the intra-band relaxation after above-band edge excitation is not observed. A sharp drop and a very similar decay dynamics was observed instead.

Fast decay of charge carriers can be due to trapping and/or to multiple carrier annihilation. Since the excitation energy is higher than the band gap energy, the involvement of the trapping process during de-excitation may be excluded. Thus, the faster drop in the TA decay

signal of rutile can be ascribed to inhomogeneous distribution of intrinsic charge carriers.⁷⁶⁻⁷⁸ The carrier recombination rates at longer delay times are slower upon above-band edge excitations. As deduced from Figure 3 the rutile has more bulk defects than anatase, so the slow recombination time of rutile upon above band edge excitation might be attributed to trapping of the charge carrier into deeper trap states.

Table 3.

Extracted time constants from the data presented in figure 5 upon band edge and above-band edge excitations. For rutile (110) the band edge and above band edge excitation wavelengths are 365 and 320nm (-35 and -80 nm; with a band gap at 400nm). For anatase (101) the band edge and above-band edge excitation wavelengths are 350 and 300 nm (-30 and -80 nm; with a band gap at 380 nm).

Systems (λ , nm)	t_1 (ps)	t_2 (ps)	t_3 (ps)
Anatase fresh-101-860 nm-350 ex	32.27 ± 2.5 (-51%)	472.3 ± 27 (-49%)	
Anatase reduced-101-860 nm-350 ex	24.57 ± 1.7 (-58%)	306 ± 20 (-42%)	
Anatase fresh-101-860 nm-300 ex	1 (27%)	33.11 ± 1.26 (-33%)	476 ± 13.15 (-40%)
Anatase reduced-101-860 nm-300 ex	1 (27%)	23.25 ± 1.4 (-33%)	305.6 ± 10.1 (-40%)
Rutile fresh-110-860 nm-365 ex	0.15 ± 0.01 (-44%)	10 ± 1 (-30%)	217.2 ± 21 (-26%)
Rutile reduced-110-860 nm-365 ex	0.15 ± 0.01 (49%)	25 ± 1.4 (33%)	193.4 ± 20 (18%)
Rutile fresh-110-860 nm-320 ex	0.5 ± 0.07 (-33%)	257 ± 17 (-67%)	
Rutile reduced-110-860 nm-320 ex	0.5 ± 0.05 (-35%)	108.9 ± 14 (-65%)	

Figure 5:

Normalized charge recombination dynamics of anatase and rutile single crystals following band edge and above band edge excitation (probe wavelength is 860 nm in all cases). Solid lines represent exponential fit of the experimental data.

There first clear difference between both phases is related to t_1 . Its very short lifetime in rutile may not allow for excited electrons to migrate to the surface in order to make the reduction of hydrogen ions (of surface hydroxyls) to atomic hydrogen that can then recombine to make molecular hydrogen. Atomic hydrogen coupling to molecular hydrogen has been detected over TiO_2 (110) rutile single crystal with an estimated energy barrier of 1.6 eV⁷⁹. Femtosecond pump probe measurements of Pt/ TiO_2 when compared to TiO_2 have been measured by others.⁸⁰⁻⁸¹ The estimated trapping time using a simple diffusion equation ($\tau = \frac{r_0^2}{\pi^2 D}$) was found to be between a fraction of a ps and few ps; where τ is the transit time, D is the diffusion coefficient ($1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for TiO_2 anatase and r_0 is the radius of a particle. Similar experiments were conducted by us over Au/ TiO_2 ⁸² and Pt/ C_3N_4 ⁸³ (and similar observations were found). So it is clear that noble metals on top of TiO_2 and C_3N_4 pump away these excited electrons in line with many reported EPR measurements (where the population of radical species attributed to Ti^{3+} , upon UV excitation, decreases considerably in the presence of a metal). Because hydrogen ion reduction is much slower than the investigated time scale by the pump probe technique in this work, the surface must accumulate long-lived excited electrons for the reaction to take place. Such charge accumulation has been observed by EPR⁸⁴ and IR⁸⁵ by other researchers and is then thought to scale up with the trend observed and computed in table 1. t_2 is also shorter for rutile when compared to anatase single crystals, but the effect is less pronounced. Yet, the overall reaction rate in the absence of a metal might be affected by both time constants t_1 and t_2 .

In summary, we provide, for the first time, new insights into the charge carrier recombination for the two most thermodynamically stable TiO_2 anatase (101) and rutile (110) single crystal surfaces. The fresh and reduced forms of these single crystals have been used to elucidate the role of bulk defects on charge carrier dynamics and the photocatalytic activity. Although anatase and rutile have very close conduction and valence band alignment, we find that their charge carrier recombination dynamics vary significantly. Both fresh and reduced anatase single crystals show slow recombination rates compared to the rutile counterparts. This is due to the presence of higher density of bulk defects in rutile single crystal when compared to the

anatase one. Pump fluence dependence study reveals that the major de-excitation channel in both fresh and reduced anatase (101) and reduced rutile (110) is a first-order Shockley–Read–Hall (bulk defects) mediated. However, significant contribution of cubic term in de-excitation due to third-body Auger recombination in (110) rutile fresh is found and assigned to the presence of higher density of intrinsic charge carriers. The decay in anatase single crystal after above-band edge excitation show ~1 ps cooling time due to intra-band electron relaxation. However, due to higher density of intrinsic charge carriers in rutile single crystals no changes in the decay dynamics following above-band edge excitation are seen. The less bulk defected anatase single crystals increase the lifetime of charge carriers, which can be linked to the higher photocatalytic activity of anatase in general.

Supporting Information. Supporting information contains more details about the methodology conducted, figures and tables.

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