Role of Dissociatively Adsorbed Water on the Formation of Shallow Trapped Electrons in TiO₂ Photocatalysts

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ABSTRACT: The mismatch between short lifetimes of free charge carriers and slow kinetics of surface redox reactions substantially limits the efficiency of most photocatalytic systems. Hence, the knowledge of trapping and recombination of photogenerated electrons and holes at different time scales is key for a rational optimization of photocatalytic materials. In this study, we used subsecond time-resolved diffuse-reflectance FTIR spectroscopy to investigate how energy and intensity of the incident irradiation affect the dynamics of photogenerated charge carriers in TiO₂ P25 photocatalysts subjected to different pretreatments and how shallow trapped electrons (STE) are formed under these conditions. Intensity-dependent measurements demonstrated that electrons and holes generated by 325 and 409 nm irradiation undergo bimolecular and trap-assisted recombination, respectively. Analysis of characteristic times of photogenerated electron absorption rise and decay indicated that the apparent charge carrier dynamics at the time scale of seconds to minutes relate to chemical trapping of photogenerated electrons and holes. The presence of dissociatively adsorbed water on the oxide surface was required for efficient STE formation. This suggests that STE form at the seconds–minutes time scale upon surface-mediated self-trapping of electrons.

1. INTRODUCTION

One of the most desired and yet very challenging processes for sustainable energy conversion is the solar-light-driven production of chemical fuels from CO₂ and water. Photocatalysis is one of the main approaches explored to address this challenge. However, solar-to-chemical energy conversion efficiency of most photocatalytic systems remains low due to severe charge carrier recombination. Trapping of photogenerated electrons and holes plays an important role in this process. Trap states can either act as recombination centers increasing electron–hole recombination rates or aid charge carrier separation, increasing their lifetimes and enabling slow redox reactions.

Thus, understanding of charge carrier trapping and recombination at different time scales as well as the role of surface species in these processes is key for optimization of photocatalytic materials.

Dynamics of photogenerated electrons and holes can be accessed by means of different spectroscopic techniques such as electron paramagnetic resonance, time-resolved photoluminescence, microwave conductivity, and transient absorption spectroscopy. Often, a combination of several methods is needed to obtain information about the charge carrier lifetimes and the related interfacial chemical processes. In this regard, time-resolved mid-infrared spectroscopy (trIR) is a versatile tool that can access both the majority charge carriers through their characteristic absorption and interfacial chemical reactions via the changes of molecular vibrational bands. Temporal resolution of modern IR instruments ranges from picoseconds–nanoseconds to milliseconds–seconds, covering both fast transfer and trapping of photogenerated charge carrier as well as slow redox reactions facilitated by them.

Over the past decades, steady-state and time-resolved IR spectroscopies have been used to study trapping and recombination of photogenerated electron in TiO₂-based materials. This wide-bandgap n-type oxide semiconductor is used for photocatalytic degradation of pollutants, self-cleaning surfaces, and as the anode material in dye-sensitized solar cells. Photogenerated electrons exist in titania in the form of free conduction band (CBE) and shallow trapped electrons (STE). CBE species give rise to distinct exponential absorption features:

\[ A^{CBE}(\nu) = K\nu^{-n} \]  

where \( A^{CBE}(\nu) \) is the CBE absorbance at the frequency of the probing light \( \nu \), \( K \) the proportionality coefficient, and \( n \) an exponent with values between 1.5 and 3.5 depending on the electron scattering mode. In contrast to the featureless

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exponential CBE absorption, STE give rise to broad bands which can be described by optical excitation of electrons from shallow trap states into the conduction band:

\[
A^{\text{STE}}(E) = K \frac{(E - E_{\text{op}})^{3/2}}{E(E - E_{\text{op}} + E_{\text{thermal}})^3}
\]

where \( E \) is energy of IR irradiation in eV, \( K \) is the proportionality coefficient, and \( E_{\text{op}} \) and \( E_{\text{thermal}} \) are optical and thermal energy required to detrapping an electron from the shallow state into the conduction band continuum, respectively.\(^{18,30}\) Trapping of photogenerated electrons affects the efficiency of photocatalytic systems,\(^4,5,28\) but the mechanism of STE formation in TiO\(_2\) and the nature of the trap states remain unclear. Some works attributed these trap states to oxygen vacancies,\(^9\) while other studies advocate polaronic self-trapping effects the electron trapping of free charge carriers.\(^{16−19}\)

In this work, we used subsecond time-resolved diffuse-reflectance Fourier transform infrared spectroscopy (DRIFTS) to investigate CBE and STE formation in commercial TiO\(_2\) P25 (\( E_g = 3.2 \) eV), anatase (\( E_g = 3.2 \) eV), and rutile (\( E_g = 3.0 \) eV) titania. We used 409 nm (3.03 eV) and 325 nm (3.81 eV) laser irradiation to study how excitation energy and intensity influence the dynamics of mid-IR photogenerated electron absorption. Above-bandgap excitation (i.e., 325 nm) is expected to yield CBE which can then be trapped and form STE species, while sub-bandgap excitation with a 409 nm laser can lead to direct population of shallow trap states (Scheme 1). Formation of a prominent STE signal was observed in oxidized TiO\(_2\) P25 under both 325 and 409 nm excitation. In untreated titania, STE were formed under a broad range of 409 nm light intensities and under low-intensity 325 nm irradiation (\( \leq 3.0 \) mW/cm\(^2\)). Intensity-dependent measurements revealed that for 325 and 409 nm excitation the steady-state concentration of free photogenerated charge carriers is controlled by bimolecular and trap-assisted recombination, respectively. The apparent electron absorption rise and decay kinetics at the seconds–minutes time scale, on the other hand, relate to chemical trapping of free charge carriers and their concomitant recombination. The presence of dissociatively adsorbed water on the oxide was found to be crucial for the formation of STE. This suggests that STE form in a surface-mediated physicochemical process involving hydroxyl groups rather than upon trapping in the bulk of titania particles.

2. EXPERIMENTAL SECTION

2.1. Materials and Characterization. Commercial mixed phase Aerioxide P25 (Evonik Industries), anatase (Sigma-Aldrich), and rutile (Sigma-Aldrich) were used as TiO\(_2\) sources. The materials were characterized by bright-field transmission electron microscopy (FEI Tecnai G2 type Sphera operated at 200 kV), powder XRD (Bruker Endeavor D2 Bragg–Brentano diffractometer with Cu cathode and a 1D LYNXEYE detector), diffuse-reflectance UV–vis spectrometry (Shimadzu UV-2401PC), and liquid N\(_2\) physisorption (Tristar II, Micromeritics). More details about instrument configuration and experimental procedures can be found in the Supporting Information.

2.2. IR Spectroscopy. Time-resolved and steady-state DRIFT spectra of TiO\(_2\) samples were recorded in a low-temperature reaction chamber (Harrick Scientific) connected to a home-built gas delivery and vacuum system. The IR signal was coupled in and out through two polished KBr windows while the sample was irradiated with 409 or 325 nm light through a third fused-silica window. The cell exterior was thermostated at 293 K by cooling water during all experiments. A Bruker Vertex 70v FTIR spectrometer equipped with a Praying Mantis diffuse-reflectance accessory (Harrick Scientific) and a liquid-nitrogen-cooled MCT detector was used for the rapid scan and steady-state measurements. The sample compartment of the spectrometer was purged by dry nitrogen during the experiments, the interferometer, and IR optics were kept under vacuum (ca. 3 mbar). The spectra were recorded at 4 cm\(^{-1}\) resolution in the spectral range 3950–600 cm\(^{-1}\). 100

Scheme 1. Excitation of a semiconductor with the bandgap \( E_g \) by above-\( h\nu \)) and sub-bandgap (\( h\nu_2 \)) irradiation, free conduction band electrons (CBE), and shallow trapped electrons (STE) along with the characteristic IR spectra of these species\(^\text{a}\)

\(^\text{a}\)For \( h\nu_2 \) two possible situations are shown: valence band–donor STE states (left) and acceptor states–valence band (right) transition.
scans were averaged per steady-state spectrum. A low-pass IR filter (cutoff frequency 3950 cm\(^{-1}\)) was placed in front of the detector compartment to prevent aliasing and block UV/vis excitation stray light. Dry KBr (Sigma-Aldrich, IR grade) was used as the reference for the survey DRIFT spectra. The sample in the dark state was used as the reference for difference spectra and for the time-resolved measurements.

Time-resolved experiments were conducted in rapid scan mode. Single-sided interferograms at forward and backward mirror movements were acquired at 4 cm\(^{-1}\) spectral resolution and 40 kHz scanner velocity. The backward and forward components of the interferograms were automatically split by Bruker OPUS 7.5 software. With these settings, a single scan took ca. 125 ms and the delay between consecutive mirror movements was ca. 40 ms. Temporal profiles of the IR signal at particular wavenumbers were extracted from the 3D data blocks consisting of individual transient spectra stacked against recording time with Bruker OPUS 7.5 and further processed toward lower wavenumbers emerged (Figure 1). The cutoff of the absorbance band at wavenumbers <1000 cm\(^{-1}\) and high noise level this spectral region are due to the high absorbance of the TiO\(_2\) lattice.\(^{35}\) The behavior of untreated and oxidized TiO\(_2\) P25 was very similar under ca. 0.5–3.0 mW/cm\(^2\) 325 nm irradiation except for the intensity of the photogenerated electron absorption feature, which was higher for the oxidized material (Figure 1). In both samples, 325 nm irradiation of intensities \(\leq\) 3.0 mW/cm\(^2\) generated very broad absorption bands with an absorbance onset in the 3500–3000 cm\(^{-1}\) region and intensities almost linearly increasing toward lower wavenumbers emerged (Figure 1). The cutoff of STE signal, while photogenerated electron absorption in untreated titania was dominated by CBE. The present study, we investigated the formation mechanism of STE by studying photogenerated electron absorption dynamics in untreated and oxidized mixed-phase TiO\(_2\) P25 as well as in commercial anatase and rutile under variable intensity of 325 nm (3.81 eV, above bandgap) and 409 nm (3.03 eV, below bandgap) excitation at different temperatures.

3.1. Above-Bandgap 325 nm Excitation of Untreated and Oxidized TiO\(_2\).

3.1.1. Intensity-Dependent Steady-State Difference Spectra. Survey DRIFT spectra of untreated and oxidized TiO\(_2\) P25 are shown in Figure S1 (Supporting Information). In oxidized titania, the 3693 cm\(^{-1}\) band of dissociatively adsorbed water\(^{32–34}\) was more prominent than in the untreated material, and so was the broad band of molecular associated water. When these samples were exposed to 325 nm light, a broad absorption feature with intensity increasing toward lower wavenumbers emerged (Figure 1). The cutoff of
The contribution of CBE and STE species. Differences between the photogenerated electron absorption bands developed in the untreated and oxidized samples became apparent. The onset of the absorption feature formed in the untreated material under 6.0–15.6 mW/cm² 325 nm occurred at lower wavenumber. The shift of the electron absorbance onset was partially due to bleaching of the associated water band which spans through the 3500–2500 cm⁻¹ spectral region. Besides this, the band formed under 6.0–15.6 mW/cm² 325 nm appeared narrower, compared with features observed under lower light intensities, and could be fit by exponential function (1) characteristic for CBE. Even though oxidized TiO₂ P25 developed more prominent bleaching of associated water bands than untreated material, the photogenerated electron absorption band formed under 325 nm irradiation was broader, and its signal almost linearly increased toward lower wavenumbers. This band and the bands formed under lower light intensities could be fit with a complex function consisting of a sum of function (1) and a number of components described by function (2) (for detailed fitting see Figure S2). Such a combined function has been previously used in the literature to fit similar broad absorption bands due to the contribution of CBE and STE species. Besides the different structures of the photogenerated electron absorption bands formed in untreated and oxidized TiO₂ P25 under higher UV light intensities, these samples showed different rearrangement of surface hydroxyls. In the untreated sample, the 3632 cm⁻¹ band was affected the most while in the oxidized titania the bands at 3695 and 3660 cm⁻¹ showed a more prominent intensity decrease. These surface hydroxyls form upon dissociative adsorption of water molecules. Reversible bleaching of these bands under 325 nm irradiation suggests either partial removal of these hydroxyls or dissociation of the O–H bonds. Addition of oxygen quenched intensities of the low-wavenumber absorption features developed under 325 nm excitation in both oxidized and untreated TiO₂ P25, thereby confirming their assignment to photogenerated electrons.

3.1.2. Intensity-Dependent Time-Resolved Measurements: Above-Bandgap Excitation. Temporal profiles of the photogenerated electrons absorbance rise and decay were found to be wavenumber-independent in the spectral ranges free from molecular vibrational bands which agrees well with results reported in the literature. In this work, temporal changes of the photogenerated electron signal were monitored at 1280 cm⁻¹ because there are no molecular bands, while the signal-to-noise ratio was found to be the highest. Experimental profiles of the electron absorption generated in the oxidized TiO₂ P25 under 325 nm irradiation of high and low intensity at 1280 cm⁻¹ are shown in Figure 2. From this figure one can see that the increase of the light intensity had a more prominent effect on the electron absorption signal rise than on its decay.

The dependencies of the electron absorption rise and decay times from the 325 nm light intensity are shown in Figure 3. Both the untreated and oxidized TiO₂ P25 demonstrated a linear correlation between characteristic times of the electron absorption rise and decay and the square root of the UV light intensity. Besides this, the decay was significantly slower than the rise. Intensity-dependent plots obtained for untreated TiO₂ P25 exhibited two distinct linear regions intersecting at ca. 3.0 mW/cm². Up until this value, the electron absorption rise and decay rates increased with increasing 325 nm light intensity but showed much weaker intensity dependence at higher intensities.

![Figure 2](image-url) **Figure 2.** Experimental kinetic curves of photogenerated electron absorption rise (a) and decay (b) at 1280 cm⁻¹ normalized to OD = 1. Oxidized sample, 293 K, static vacuum, 325 nm excitation. The dashed blue line shows the time when the exposure to UV light started (a) and ended (b).

![Figure 3](image-url) **Figure 3.** Dependence of the half-life rise (left) and decay (right) times of photogenerated electron absorption in the untreated (a, b) and oxidized (c, d) TiO₂ P25 from the square root of 325 nm light intensity measured at 293 K under static vacuum. (Figure 3a,b). On the other hand, the oxidized sample showed no such behavior, and the electron absorption rise and decay rates decreased with increasing UV light intensity throughout the entire range (Figure 3c,d). Besides this, the electron absorption dynamics were slower in the oxidized material than in untreated TiO₂ P25.

The substantial difference between the electron absorption rise and decay rates (Figure 3) suggests that accumulation and recombination of photogenerated charge carriers in TiO₂ P25 at the seconds–minutes time scale did not reflect the dynamics of free photogenerated charge carriers directly. This can be understood by considering a simple kinetic model describing generation and recombination of free electrons and holes in a semiconductor under above-bandgap excitation:

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2^* + e^- + h^+
\] (3)
\[ \text{TiO}_2^\ast + e^- + h^+ \xrightarrow{k_i} \text{TiO}_2 + h\nu \text{ or } kT \]  

(4)

When process (4) is the primary pathway of charge carrier recombination, the concentrations of electrons and holes in the system under irradiation are determined by the charge carriers generation (i.e., light intensity \( I \)) and recombination rates, while relaxation of the system to the ground state in the dark (\( I = 0 \)) is described solely by the latter process:

\[
\frac{d[h^+]}{dt} = \frac{d[e^-]}{dt} = aI - k_i[e^-][h^+] 
\]

(5)

where \( a \) is the effective absorption coefficient, \( I \) is the incident light flux in photons/s, and \( k_i \) is the rate constant of electron–hole recombination. For such a system, steady state concentrations of photogenerated charge carriers \( \{[e^-]_0, [h^+]_0\} \) under irradiation, and characteristic times of their accumulation and recombination (i.e., signal rise and decay half-life times) are

\[
[e^-]_0 = [h^+]_0 = \sqrt{aI/k_i} 
\]

(6)

\[
\tau_{\text{rise}} = \frac{\ln 3}{2\sqrt{aI/k_i}} \approx \frac{0.5S}{\sqrt{aI}} 
\]

(7)

\[
\tau_{\text{decay}} = \frac{1}{k_i[e^-]_0} = \frac{1}{\sqrt{aI/k_i}} 
\]

(8)

From expressions 7 and 8, one can see that for each light intensity \( I \) the rise half-life time should be about half of the decay half-life time, while we observed a 3–10× difference (Figure 3). Therefore, the photogenerated electron absorption dynamics at the seconds–minutes time scale could relate to the following interfacial processes instead:

\[
h^+ + H_2O_{ad}/OH_{ad} \xrightarrow{k_i} H_2O_{ad}/OH_{ad}^\ast \approx HO_{ad}^\ast/O^\ast_{ad} + H^+ 
\]

(9)

\[
e^- + H^+ \xrightarrow{k_i} H^* 
\]

(10)

\[
H^* + HO_{ad}^\ast/O^\ast_{ad} \xrightarrow{k_i} H_2O_{ad}/OH_{ad} 
\]

(11)

\[
e^- + H_2O_{ad}^\ast/OH_{ad}^\ast \xrightarrow{k_i} H_2O_{ad}/OH 
\]

(12)

Reactions 9 and 10 represent trapping of photogenerated electrons and holes by adsorbed water and/or surface hydroxyls, respectively. Processes 11 and 12 exemplify the recombination of trapped species. The rates of reactions 9 and 10 are proportional to the concentrations of free charge carriers which increase with the square root of light intensity for systems with predominant bimolecular recombination (cf. eq 6). This manifests itself in the linear correlation between \( \tau_{\text{rise}} \) and \( I^{0.5} \) as observed for above-bandgap excitation (Figure 3).

Hence, the intensity-dependent plots provide information about faster dynamics of photogenerated charge carriers even though individual measurements performed at the seconds–minutes time scale reflect rather slow chemical reaction.40 Besides this, the decrease of hydroxyl group intensities observed under UV irradiation (Figure 1, insets) may evidence the hole trapping process 9. This is because a decrease of the hydroxyl band intensities can indicate either removal of these groups from the TiO \(_2\) surface or a dissociation of the O–H bond. The former usually happens at higher temperatures than one can expect for UV-induced sample heating.46 On the other hand, trapping of photogenerated holes on surface hydroxyls can induce dissociation of some groups, which would lead to a decrease of the O–H band intensity as well.

Slower electron absorption rise and decay rates have been observed for the oxidized TiO \(_2\) P25 and could be due to different charge recombination pathways reactions 11 and 12 as compared to untreated TiO \(_2\) P25. The electron absorption bands formed under 6.0–15.6 mW/cm\(^2\) 325 nm in these samples had a different spectral shape (Figure 1). While the absorption in the untreated sample had a prominent CBE character and the charge carriers recombine with trapped holes via process 12, the absorption in the oxidized material was dominated by STE, which can form upon interaction of photogenerated electrons with hydroxyls and/or protons as described by reaction 10.17,42 Recombination of such species (i.e., H\(^\ast\)) with trapped holes can then be represented by process 11. The rate constant \( k_i \) is expected to be lower than \( k_i \) due to a lower reactivity of trapped in comparison with free charge carriers.14 This results in different apparent rise and decay rates for untreated and oxidized TiO \(_2\) P25.

3.2. Sub-Bandgap 409 nm Excitation of Untreated and Oxidized TiO \(_2\) P25. Although the concept of STE has been put forward in a number of publications,17–19 the mechanism of their formation in TiO \(_2\) still remains unclear. The STE species observed in this study are unlikely to originate from in-gap states due to oxygen vacancies19 because a stronger STE absorbance was observed in the oxidized sample. On the other hand, some works attributed STE to polaronic self-trapping of photogenerated electrons in TiO \(_2\).16–18 However, it is unclear whether an electron polaron forms in the bulk or at the surface of titania particles. Hence, we studied photogenerated electron absorption dynamics under 409 nm sub-bandgap excitation in untreated and oxidized TiO \(_2\) at the seconds–minutes time scale. The energy of this light is 3.02 eV, which is ca. 0.2 eV lower than the apparent bandgap of TiO \(_2\) P25 (Figure S3) and matches the depth of STE states (0.05–0.2 eV).

3.2.1. Intensity-Dependent Steady-State Difference Spectra. The difference spectra developed in untreated and oxidized TiO \(_2\) P25 under 409 nm light of various intensities are shown in Figure 4. For low light intensities (<6.0 mW/cm\(^2\)) difference spectra were dominated by a broad STE absorption. When 409 nm light intensity was increased, the STE band became more prominent, while stretching (3400 cm\(^{-1}\)) and bending (1622 cm\(^{-1}\)) vibrational bands of adsorbed water decreased in intensity. Similar to the above-bandgap excitation (Figure 1), the photogenerated electron absorption signal was stronger in the oxidized material than in untreated TiO \(_2\) P25. For both samples, the photogenerated electron absorption band was dominated by STE for the broad range of studied 409 nm light intensities (2.0–128.0 mW/cm\(^2\)). Besides the structure of the photogenerated electron absorbance feature, light-induced rearrangement of the surface hydroxyls was similar for both untreated and oxidized TiO \(_2\) P25 under sub-bandgap irradiation. The main difference between these samples was a more prominent bleaching of the O–H bands in the oxidized material, which correlated well with the presence of a stronger STE signal.

These results suggest that sub-bandgap irradiation favors formation of trapped electrons in TiO \(_2\) P25. However, this material is composed of ca. 84 wt % anatase and 16 wt % rutile phases (Figure S3a). Hence, the spectral changes shown in Figure 4 may arise from the excitation of the rutile phase (\( E_g = \))
3.0 eV) by 409 nm light (3.03 eV) and not from the sub-bandgap excitation of anatase ($E_g = 3.2$ eV). In order to evaluate this hypothesis, we studied commercial anatase (>98 wt %) and rutile (>96 wt %) TiO$_2$ under 409 nm light. The difference spectra formed in these materials under 409 nm excitation were substantially different (Figure S4). Anatase developed a prominent broad absorption feature in the 2500–1000 cm$^{-1}$ region already at 4.0 mW/cm$^2$ 409 nm light, and its intensity increased with increasing light intensity (Figure S4a). In contrast to this, rutile TiO$_2$ developed a prominent photogenerated electron absorption band only at light intensities $\geq$16.0 mW/cm$^2$. Moreover, the bands formed in anatase and rutile polymorphs under 409 nm excitation had different spectroscopic signatures. The electron absorption formed in rutile TiO$_2$ could be fit with exponential function (1) characteristic for CBE, while the band observed in anatase TiO$_2$ was similar to the STE absorption observed in TiO$_2$ P25 (Figure 4). Therefore, we conclude that the spectral changes induced in untreated and oxidized TiO$_2$ P25 by 409 nm irradiation arise from the sub-bandgap excitation of the major anatase TiO$_2$ phase.

3.2.2. Intensity-Dependent Time-Resolved Measurements: Sub-Bandgap Excitation. The dependencies of electron absorption rise and decay times in untreated and oxidized TiO$_2$ P25 from the 409 nm light intensity are shown in Figure S5. The electron absorption rise was slower in the oxidized TiO$_2$ P25 in comparison with the untreated sample, while the decay rates were comparable. The latter suggests that recombination of trapped charged carriers in both samples involved similar processes such as reactions 9–11. The main difference between above- (Figure 3) and sub-bandgap (Figure 5) excitation was the linear correlation between characteristic times of photogenerated electron absorption rise and decay with square root of the incident light intensity, respectively. Hence, the steady-state concentration of the charge carriers generated by sub-bandgap excitation was governed by processes different from bimolecular recombination (4). The linear correlation between characteristic times of the electron absorption rise and decay and intensity of the sub-bandgap excitation can be described by the Shockley–Read–Hall model.1,2,40 This model describes systems in which charge carrier recombination is dominated by a trap-assisted process:

$$h^+e^- \rightarrow t \rightarrow t^*$$

$$e^-h^+ + t^* \rightarrow t + h\nu_2 + kT$$

where $t$ and $t^*$ are empty and filled traps, and $[t]$ and $[t^*]$ are their concentrations, respectively. In such a system, steady-state concentrations of photogenerated charge carriers ($[e^-]_0$, $[h^+]_0$) linearly increase with the light intensity, which results in the apparent intensity dependencies shown in Figure 5.

The distinct behavior of TiO$_2$ P25 under above- and sub-bandgap excitation can be due to several reasons. First of all, absorbance of this material at 409 nm is much lower than at 325 nm (Figure S5). This means that charge carrier generation under 409 nm irradiation is less efficient than under UV light. Therefore, the concentration of the charge carriers generated under 409 nm light can be comparable with that of the trap states, which enables the Shockley–Read–Hall recombination mechanism. On the other hand, even rather low intensities of 325 nm light can generate amounts of electron–hole pairs substantially exceeding the number of available trap states. This would lead to different recombination pathways and distinct apparent intensity dependencies in these cases. On the other hand, electronic transitions induced by UV and visible light can proceed via different initial and/or final states (Scheme 1). For instance, excitation of anatase TiO$_2$ ($E_g = 3.2$ eV) by 409 nm light can involve surface states as has been previously shown for the rutile phase active under visible light.43 This, arguably, would lead to different energetics and spatial distribution of charge carriers generated by 325 and 409 nm light.

3.3. On the Mechanism of STE Formation. Experiments performed with TiO$_2$ P25 (Figures 1 and 4), anatase, and rutile TiO$_2$ (Figure S4) at room temperature indicate that the STE
signal arises from photogenerated electron trapped in the anatase phase. Stronger STE absorption observed in the oxidized TiO₂ P25 suggests that this trapping involves adsorbed water and/or surface hydroxyls rather than crystal defects such as oxygen vacancies. This is due to several reasons. First of all, dark DRIFT spectra of oxidized titania showed stronger bands of molecularly and dissociatively adsorbed water in comparison with untreated material (Figure S1). Second, the amount of oxygen vacancies in the oxidized material should be lower or at least the same in comparison with the untreated titania. Thus, the signal of the charge carriers trapped by crystal defects should become weaker after the oxidative treatment which contradicts our observations. On the other hand, STE absorption can arise from large polarons formed upon self-trapping of photogenerated electrons in semiconducting materials. The observed correlation between hydration of TiO₂ P25 and the STE signal intensity favors the surface-mediated mechanism. In order to verify this hypothesis and to better understand the role of surface species (i.e., adsorbed water, terminal hydroxyls) in the STE formation, we studied oxidized and untreated TiO₂ P25 at 163 K and temperatures above 373 K. The results obtained with both samples were similar and, therefore we discuss here only oxidized titania.

3.3.1. STE Formation in Oxidized TiO₂ P25 at 163 K. Survey DRIFT spectra of the oxidized TiO₂ P25 at 293 and 163 K are shown in Figure S6. Cooling of the material below 273 K decreased intensity of dissociatively (3693 cm⁻¹) and molecularly (3400, 1624 cm⁻¹) adsorbed water bands. Exposure of this sample to 325 or 409 nm light at 163 K led to the formation of the difference spectra shown in Figure 6. Absorption features developed under above- and sub-bandgap excitation in the low-wavenumber region had different spectroscopic signatures. In the case of 325 nm excitation, they could be described by function (1) characteristic for CBE.

The CBE absorbance increased with increasing light intensities, while the bands of associated adsorbed water became weaker (Figure 6a). In contrast to 325 nm light, photogenerated electron absorption produced by 409 nm irradiation was dominated by STE for light intensities ≤320 mW/cm² (Figure 6b). At higher 409 nm light intensities, the low-wavenumber region of the difference IR spectra developed a prominent CBE signal similar to that formed under 325 nm irradiation (Figure 6).

Spectral changes developed under 0.5–15.6 mW/cm² 325 nm or 4.0–50 mW/cm² 409 nm irradiation relaxed within several minutes in the dark and could be reproduced upon repeated exposure to the same light intensities. Contrary to this, when the oxidized TiO₂ P25 was exposed to 64.0–128 mW/cm² 409 nm light at 163 K, we observed some permanent spectral changes. First of all, the intensity loss of associated adsorbed water bands and surface hydroxyls (3700–2400, 1623 cm⁻¹) did not recover in the dark at 163 K (Figure S7). The intensity loss in the 3700–2400 cm⁻¹ region was attributed to perturbed hydrogen bonding among adsorbed water molecules and between adsorbed water and oxide as well as to partial removal of dissociatively adsorbed water. The minimum of the intensity loss in the O–H stretching region (Figure 6) shifted to lower wavenumber as compared to the measurement performed at room temperature (Figure 4), which can be attributed to the formation of ice-like structures on TiO₂ at 163 K. Second, when a sample, exhibiting the above-described permanent spectral changes, was irradiated with 409 nm light of intensities ≤320 mW/cm², we observed a weak photogenerated electron absorption signal dominated by CBE (Figure S7) and not prominent STE bands (Figure 6b). This effect of high intensity 409 nm irradiation could be partially recovered by heating the sample to 233 K, but overnight storing at room temperature in Ar or O₂ was needed to fully restore its properties. This suggests that association of the oxide with adsorbed water and/or the presence of dissociatively adsorbed water on titania play an important role in STE formation at low temperatures.

3.3.2. STE Formation at Elevated Temperatures. The role of surface hydroxyls as well as molecularly and dissociatively adsorbed water in STE formation was further investigated by exposing oxidized TiO₂ P25 to 325 and 409 nm irradiation at temperatures above 373 K. For both wavelengths, the STE signal was observed in a broad temperature range, but it disappeared completely when the bands of dissociatively adsorbed water substantially decreased in intensity. In the case of above-bandgap excitation, the STE signal intensity rapidly decreased with increasing temperature and desorption of molecular water. Almost no detectable STE signal was observed under 325 nm irradiation at T > 523 K. On the other hand, 409 nm light produced a rather strong STE signal (ca. 0.05 au) up to 573 K, but no STE absorbance was observed at 623 K. At this temperature, most of the molecularly and dissociatively adsorbed water desorbed from the oxide as was evident from the intensity losses at 3693, 3632, 3400, and 1624 cm⁻¹. When such a dehydrated sample was cooled to 293 K, no STE signal was produced by 409 nm light for several hours even though molecularly adsorbed water reappeared on titania upon cooling down. Only when the bands of surface hydroxyls formed upon dissociative water adsorption (i.e., 3693 and 3632 cm⁻¹) emerged in the survey DRIFT spectra, the STE signal emerged under sub-bandgap excitation again. This correlation between the STE formation and the presence of

Figure 6. Difference DRIFT spectra of oxidized TiO₂ P25 in static vacuum at 163 K under 325 nm (a) and 409 nm (b) irradiation of different intensity. Note: the spectra are vertically offset to match the baseline at 3800–3900 cm⁻¹.
3693 and 3632 cm\(^{-1}\) hydroxyl bands on TiO\(_2\) P25 further confirms that these surface species are involved in trapping of photogenerated electron in titania. The absence of the STE signal in dehydrated TiO\(_2\) P25 suggests that bulk electron trapping (i.e., by the crystal defects) did not have any significant contribution to the apparent STE absorbance.

Formation of CBE and STE in TiO\(_2\)-based materials has been previously explored by different techniques.\(^{36,39} - 36,46\) For instance, Yates et al. used electron paramagnetic resonance (EPR) to study trapped electrons and holes in TiO\(_2\) under above-bandgap irradiation at 90 K.\(^{36,46}\) Comparison of the trapped electron and hole signals suggests that trapping of photogenerated holes is much more favorable than trapping of electrons. Hence, the major part of photogenerated electrons is present in the form of free conduction band electrons at 90 K. This agrees with our observation that electron absorbance formed under 325 nm at 163 K was dominated by the CBE component (Figure 6a). Interestingly, EPR signal of trapped electrons was not observed at temperatures higher than 90 K.\(^{46}\) While a rather strong STE absorbance formed in oxidized TiO\(_2\) P25 under 409 nm irradiation at 163 K (Figure 6b). This can be due to involvement of different processes in STE formation under sub-bandgap irradiation of titania at \(T \leq 163\) K or because of different nature of trapped electrons observed by EPR and IR spectroscopy. The fact that almost no STE signal was observed when water adsorption on TiO\(_2\) P25 was perturbed by high intensity 409 nm irradiation suggests that interaction between adsorbed and the oxide surface is crucial for photogenerated electron trapping in TiO\(_2\). This agrees with the fact that no STE signal was observed when hydroxyls formed upon dissociative water adsorption (i.e., bands at 3695 and 3632 cm\(^{-1}\)) were removed from TiO\(_2\) at elevated temperatures (see previous subsection).

The strong apparent STE signal formed in TiO\(_2\) P25 (Figure 4) and anatase (Figure S4a) under 409 nm irradiation may suggest that shallow trapped states can be directly populated by sub-bandgap excitation (Scheme 1). However, this conclusion contradicts the findings of Antila et al.,\(^{16}\) who observed no electron absorbance at delay times up to 1 ns for sub-bandgap excitation. Antila et al. proposed that STE states are not pre-existing features of the material (i.e., crystal defects) but form upon polaronic self-trapping of photogenerated electrons. Taking into account these findings and our experimental results, we surmise that STE form in a surface-mediated process which involves surface hydroxyls originating from dissociative water adsorption (i.e., 3693 and 3630 cm\(^{-1}\) bands). Involvement of a rather slow chemical process can then explain the absence of the STE signal at time scales up to 1 ns.\(^{16}\) The strong correlation between the presence of surface hydroxyls and STE formation is in line with a recent theoretical study which showed that an excess of electrons in anatase TiO\(_2\) can trigger water dissociation on (101) surface and form polarons with the resulting surface hydroxyls.\(^{42}\) This surface-mediated trapping of photogenerated electrons can play an important role in photocatalytic processes by slowing down charge carrier recombination and improving their accessibility to the reactants when photocatalytic reactions are carried out either on a hydrated oxide or on TiO\(_2\) particles suspended in aqueous media.

4. CONCLUSIONS

The seconds–minutes dynamics of photogenerated electron absorption in untreated and oxidized TiO\(_2\) P25 under 325 and 409 nm irradiation were investigated in detail in a broad range of temperatures. Intensity-dependent measurements evidenced that the steady-state concentrations of free charge carriers were governed by bimolecular and trap-assisted recombination in the case of above- and sub-bandgap excitation, respectively. STE formation in TiO\(_2\) P25 was observed in a broad range of temperatures under 325 and 409 nm irradiation in both mixed-phase TiO\(_2\) P25 and anatase titania but not in the rutile phase. At 163 K, the STE signal substantially decreased when high intensity 409 nm irradiation perturbed hydrogen bonding between the oxide and adsorbed water and decreased the intensity of surface hydroxyls formed upon dissociative water adsorption. In keeping with this, almost no STE signal was detected at room or elevated temperatures when 3695 and 3632 cm\(^{-1}\) hydroxyl bands were removed from titania. Characteristic rise and decay times of the STE signal suggest that formation of these species is coupled with a rather slow interfacial chemical process. The prominent correlation between the STE absorbance, crystal phase composition, and the presence of certain hydroxyls in the material showed that shallow trapping of photogenerated electrons is a surface-mediated process involving surface hydroxyls originating from dissociative water adsorption on anatase TiO\(_2\).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b01151.

TEM images, survey and difference DRIFT spectra, XRD patterns, UV–vis spectra, and detailed data processing (PDF)

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**Notes**

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