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Infrared and Near-Infrared Spectrometry of Anatase and Rutile Particles Bandgap Excited in Liquid

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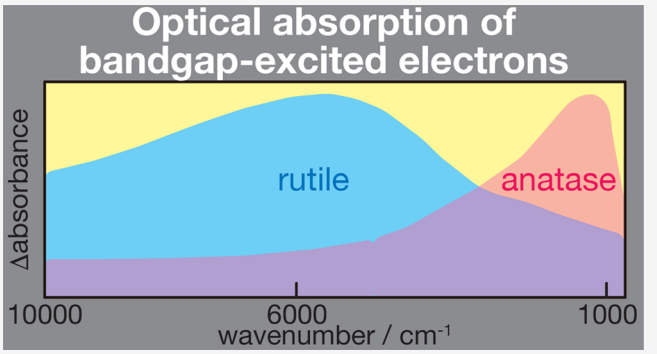
ABSTRACT: Chemical conversion of materials is completed in milliseconds or seconds by assembling atoms over semiconductor photocatalysts. Bandgap-excited electrons and holes reactive on this time scale are key to efficient atom assembly to yield the desired products. In this study, attenuated total reflection of infrared and near-infrared light was applied to characterize and quantify the electronic absorption of TiO_2 photocatalysts excited in liquid. Nanoparticles of rutile or anatase were placed on a diamond prism, covered with liquid, and irradiated by steady UV light through the prism. Electrons excited in rutile particles (JRC-TIO-6) formed small polarons characterized by a symmetric absorption band spread over 10000−700 cm^{-1} with a maximum at 6000 cm^{-1}. Electrons in anatase particles (JRC-TIO-7) created large polarons and produced an asymmetric absorption band that gradually strengthened at wavenumbers below 5000 cm^{-1} and sharply weakened at 1000 cm^{-1}. The absorption spectrum of large electron polarons in TIO-7 was compared with the absorption reported in a Sr-doped $NaTaO_3$ photocatalyst, and it was suggested that excited electrons were accommodated as large polarons in $NaTaO_3$ photocatalysts efficient for artificial photosynthesis. UV-light power dependence of the absorption bands was observed in N_2-exposed decane liquid to deduce electron−hole recombination kinetics. With light power density P > 200 W m^{-2} (TIO-6) and 2000 W m^{-2} (TIO-7), the polaron absorptions were enhanced with absorbance being proportional to $P^{1/2}$. The observed 1/2-order power law suggested recombination of multiple electrons and holes randomly moving in each particle. Upon excitation with smaller P, the power-law order increased to unity. The unity-order power law was interpreted with recombination of an electron and a hole that were excited by the same photon. In addition, an average lifetime of 1 ms was estimated with electron polarons in TIO-6 when weakly excited at P = 20 W m^{-2} to simulate solar-light irradiation.



1. INTRODUCTION

Chemical conversion over semiconductor photocatalysts has been extensively investigated but not yet understood completely. Transient absorption spectroscopy (TAS) determines the initial fate of the electrons and holes excited in photocatalysts. Photon absorption and electronic excitation are followed by exciton formation or separation and subsequent charge carrier transport from the bulk to the surface.[1−3] The electron-based steps are initiated in femtoseconds and completed in microseconds, whereas reaction products are formed in milliseconds or even seconds via the assembly of atoms on the surface.[4,5] TAS with short light pulses for photocatalyst excitation is not always suitable for characterizing excited charge carries reactive on the time scale of atom assembly. Short-life charge carriers detected in TAS may or may not contribute atom assembly in their limited lifetimes.

In this study, Fourier transform (FT) spectroscopy in a wavenumber range of 10000−700 cm^{-1} is applied to characterize and quantify electrons excited in two TiO_2 polymorphs, namely, rutile and anatase, irradiated with steady ultraviolet (UV) light. Excited electrons absorb infrared (IR), near-IR, or visible light according to the host semiconductors in which they are created. A number of earlier studies[6−12] reported that electronic absorption appeared in the IR and near-IR regions when TiO_2 photocatalysts are excited in vacuum and vapor environments.

The other requirement in this study is operando characterization. Because most photocatalysts are operated in liquid environments, our spectrometry should be conducted in liquid. This is a difficult task because IR light used for probing is

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absorbed by the liquid, while UV light for excitation is absorbed by photocatalyst particles. The ordinary setup for attenuated total reflection (ATR) through a prism made of ZnSe, Si, etc. is convenient to guide probing light into photocatalyst particles in liquid but problematic for delivering light for excitation.

2. METHODS AND MATERIALS

This study used an ATR assembly with a diamond prism (Figure 1) constructed by Jasco in our earlier study.[13] The angle of

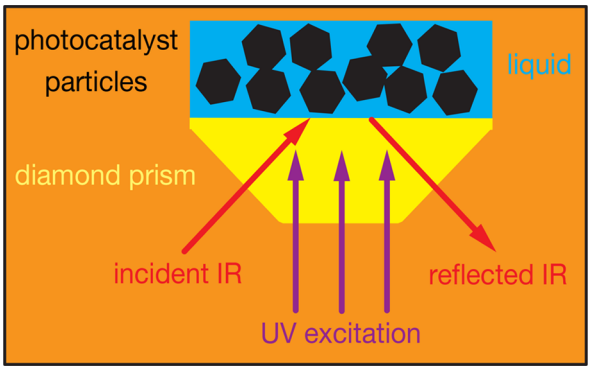

Figure 1. A prism assembly for ATR spectroscopy under UV light irradiation through the prism. An isosceles trapezoidal prism with a circular reflection plane of 1.8 mm in diameter is assembled with an LED or Hg−Xe lamp as the UV light source.

probe-light incidence was fixed at 45° from the normal of the reflection plane. The depths of IR (wavenumber: 1000 cm^{-1}) and near-IR (wavenumber: 10000 cm^{-1}) light penetration into water were estimated to be 1.5 and 0.15 μm with the refractive indexes of diamond and water, 2.38 and 1.32, respectively.[14] The refractive index of TiO_2 particles mixed with water should be greater than that of water to accordingly increase penetration depth. A light-emitting diode (LED; 365 nm center wavelength, M365L3, Thorlabs) provided UV light for bandgap excitation through the prism to the volume probed by IR light. The UV light power density on the reflection plane was calibrated using a photodiode sensor (PD-300, Ophir) and tuned in a range of 20−3600 W m^{-2}. A Hg−Xe lamp (200 W, UVF-204S, San-Ei Electric) was used instead of the LED when intense UV light (9.0 kW m^{-2} on the reflection plane) was necessary.

The prism assembly was set in a Fourier transform infrared spectrometer (FT/IR-6600, Jasco). The reflection plane was irradiated with He−Ne laser light (wavelength: 633 nm) for interferometer calibration, which was unable to excite TiO_2 particles across the bandgap. To measure IR absorption at 7000−700 cm^{-1}, a ceramic light source was used with a mercury−cadmium−telluride (MCT) detector, while a halogen lamp and an InGaAs detector were employed in near-IR spectrometry at 10000−4000 cm^{-1}. The acquisition time was 19 s per IR spectrum and 52 s per near-IR spectrum with a wavenumber resolution of 8 cm^{-1}. Figure S1 shows the near-IR transmittance spectrum of the prism assembly with a water droplet on the reflection plane. A corresponding spectrum in the IR region is available in the Supporting Information of ref 13. IR transmittance decreased to <30% at 2500−1800 cm^{-1} because of the absorption in the diamond prism. Hence, absorbance spectra of photocatalysts are shown herein in the wavenumber ranges of 10000−2500 and 1800−700 cm^{-1}. The absorbance change induced by UV light was observed and quantified in an absorbance range of 10^{-1}−10^{-3}.

TiO_2 photocatalyst particles were placed on the reflection plane of the prism and covered with a liquid droplet. The prism assembly inside the spectrometer was exposed to air or N_2 gas to make the droplet anaerobic when necessary. Figure S2 shows the near-IR absorbance spectra of water and other liquids observed on the prism assembly. Two TiO_2 photocatalysts provided by the Catalysis Society of Japan were used: rutile TiO_2 (JRC-TIO-6) and anatase TiO_2 (JRC-TIO-7). The nominal particle sizes of TIO-6 and TIO-7 were 15 and 8 nm, respectively. X-ray diffraction patterns of the photocatalysts are shown in Figure S3. The size of particles was much less than the penetration depth of probe light. Hence, probe-light absorption averaged over multiple particles was observed. The Supporting Information lists the reagents used in preparing liquid droplets.

3. RESULTS

3.1. Absorbance Change Induced by UV Light Irradiation. Absorbance change (Δabsorbance) was deduced from the absorbance spectra recorded in the presence and absence of UV light irradiation. We present in Figure 2 the

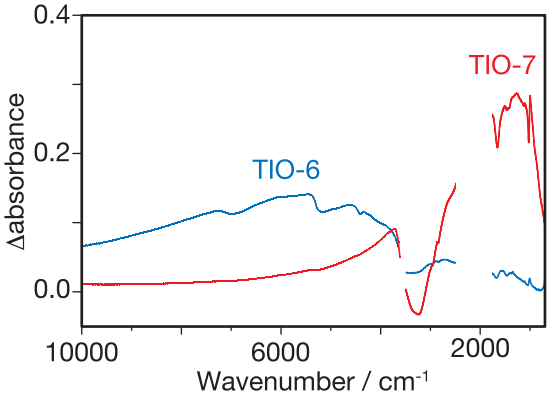

Figure 2. Absorbance change (Δabsorbance) spectra of TiO_2 particles. TIO-6 (blue spectrum) and TIO-7 (red spectrum) were irradiated in a methanol−water mixture (50 vol %) exposed to N_2. UV light source: Hg−Xe lamp. UV light power density on the reflection plane of the prism: 9.0 kW m^{-2}. Probe light source and detector for 10000−3800 cm^{-1}: halogen lamp and InGaAs detector. Probe light source and detector for 3800−700 cm^{-1}: ceramic source and MCT detector. The spectra are shown in the wavenumber ranges of 10000−2500 and 1800−700 cm^{-1} because IR transmittance through the prism decreased to <30% at 2500−1800 cm^{-1}.

Δabsorbance spectra of TIO-6 and TIO-7 in a methanol−water mixture (50 vol %) induced by intense irradiation (9.0 kW m^{-2}) with the Hg−Xe lamp because Δabsorbance of the two photocatalysts was not detectable in pure water. Methanol is a hole-scavenging reagent that increases the population of electrons that are excited and not yet recombined with holes, as demonstrated in a number of TiO_2 photocatalysts exposed to its vapor.[15]

On TIO-6 of rutile, a symmetric absorption band appeared in the full wavenumber window of 10000−700 cm^{-1} with a maximum at 6000 cm^{-1}. A narrower, asymmetric absorption band was recognized on TIO-7 of anatase; Δabsorbance gradually increased at wavenumbers below 5000 cm^{-1}, making a peak at 1300 cm^{-1} and rapidly decreasing at 1000 cm^{-1}. The two Δabsorbance bands were present in the methanol−water mixture whereas they were absent in pure water. This set of results allowed us to assign the two Δabsorbance bands to

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electrons excited in the TiO_2 photocatalysts. Photoexcited holes were rapidly consumed in methanol oxidation. Excited electrons complementary to the holes left in photocatalyst particles and slowly consumed in water reduction to produce H_2. In a steady state, a small number of holes and a large number of electrons are present in a particle. Hence, the particle should have been positively charged and neutralized with the anion atmosphere in the solution.

Negative Δabsorbance peaks superimposed at 3700−3000 and 1600 cm^{-1} on the spectra of TIO-6 and TIO-7 correspond to the vibrational absorption of water bleached by UV light irradiation. Bleached overtones of water vibration appeared at 7000 and 5200 cm^{-1} on the spectrum of TIO-6.

UV-light-induced Δabsorbance was further examined in the solutions of electron scavenging reagents $FeCl_3$ (50 mmol L^{-1})[16] and $NaIO_3$ (50 mmol L^{-1}).[17] As shown in Figure S4, absorbance change was not detectable; this supports our assignment of the bands present in Figure 2 to excited electrons. It is also suggested that holes in the TiO_2 particles presented optical absorption, if any, out of the wavenumber range examined in this study. Hole population should have been enhanced in the electron scavengers, but no additional band appeared in Δabsorbance.

The symmetric spectrum on TIO-6 and the asymmetric spectrum on TIO-7 suggested qualitatively different properties of the electrons excited in the two TiO_2 photocatalysts. The symmetric and asymmetric spectra are consistent with those reported in a transient absorption study by Yamakata et al.[11] They observed UV-light-induced transient Δabsorbance with rutile and anatase particles placed in a vacuum or vapor environment. Two different anatase particles (one 21 nm in diameter and the other 15 nm in diameter) presented a Δabsorbance band that monotonously strengthened at wavenumbers of 4000 to 1000 cm^{-1} in Figure 1 of ref 11. Rutile particles having diameters of 40 and 15 nm exhibited two bands that peaked at 22000 and 13000 cm^{-1} with a slight increment centered at 6000 cm^{-1} in Figure 3 of ref 11. They assigned the absorption increment at 6000 cm^{-1} to excited electrons according to the increment enhanced in the presence of methanol vapor. Shinoda and Murakami[12] also reported a Δabsorbance band at 3000−1000 cm^{-1} for anatase particles exposed to ethanol vapor, while rutile particles presented a broad band centered at 8000−7000 cm^{-1}. Savory and McQuillan[18] reported an absorbance change that peaked at 880 cm^{-1} for anatase particles 23 nm in diameter excited under water. Our findings in the methanol−water mixture are consistent with their reports in vacuum/vapor/water environments. The symmetric and asymmetric bands are intrinsic with electrons excited in rutile and anatase regardless of environments to suggest excited electrons accommodated in bulk particles.

This is in contrast to observation on $NaTaO_3$ photocatalyst particles doped with Sr cations. UV-light-induced Δabsorbance of the $NaTaO_3$ photocatalyst presented qualitatively different spectra when excited in a vacuum[19] and in liquid.[13] The absorption quenched in liquid was assigned to electronic states localized on the surface.

One note here is about UV-light-induced Δabsorbance reported on P25 (Degussa), one of the most well-known commercial TiO_2 photocatalysts. The asymmetric absorption band that monotonously strengthened from 4000 to 1000 cm^{-1} has been frequently reported and assigned to excited electrons.[8−10,20] The reported spectra are identical with those of TIO-7 shown in Figure 2. Because P25 contains more than 70% anatase with a minor amount of rutile and a small amount of amorphous TiO_2,[21] the Δabsorbance band upon excitation is dominated by that of anatase. A minor contribution of rutile should have appeared at 6000 cm^{-1}, which is outside the wavenumber ranges considered in the earlier studies of P25.

Under steady irradiation of UV light in the methanol−water mixture, methanol oxidation and water reduction should have occurred simultaneously on the photocatalysts. Infrared absorption assignable to molecular vibration of the oxidation products was not recognized, probably because their limited concentration.

The TiO_2 particles might be reduced during UV irradiation in the mixture. However, ex-situ characterization of the irradiated particles to detect reduced Ti cations by using XPS was difficult. The penetration depth of UV light used in our measurements into TiO_2 particles was on the order of 10 nm.[22] The small amount irradiated particles should be mixed with other particles when transferred for ex-situ characterization.

3.2. UV-Light Power Dependence. Excited electrons recombine with complementary holes in the TiO_2 particles. Recombination always competes with photocatalytic reactions and hence determines the quantum yield of desired reaction products. In this section, the recombination kinetics is examined in terms of UV-light power dependence of Δabsorbance.

TIO-6 and TIO-7 particles were placed on the prism and covered with an *n*-decane droplet. The spectrometer was then purged with N_2 to provide a less-reactive liquid environment to excited photocatalysts. Electrons and holes were not transferrable to anaerobic decane and thus exclusively recombined in the TiO_2 particles.

Figure 3a shows Δabsorbance spectra of TIO-7 recorded at 7000−700 cm^{-1}. The power density of UV light for bandgap excitation was tuned in the range of 22−3600 W m^{-2}, which corresponded to 39−6400 photons s^{-1} nm^{-2}. A power range 2 or more orders of magnitude wide was suitable to characterize the recombination kinetics. An asymmetric band peaked at 1300 cm^{-1} appeared, as found for the methanol−water mixture. Bleached bands at 1600 and 1500−1400 cm^{-1} are attributed to vibrations of water and decane. TIO-7 particles are small enough to be moist even when dried in air at room temperature. Water that remained on the particle surface induced the water-related bleached band under irradiation in decane. The strength of the electron-induced absorption was quantified with Δabsorbance at 1267 cm^{-1} and shown in Figure 3c as a function of UV light power density *P*.

A straight line representing $P^{0.50}$ fitted the results (red dots) observed with $P > 2000$ W m^{-2}. The 1/2-order power law suggests recombination of multiple electrons and holes randomly moving in each anatase particle. The rate of excitation per second is proportional to *P*, while the recombination rate is expressed in terms of the number of electron−hole collisions per second. The rates of excitation and recombination are balanced in the steady state:

$$P \propto \text{electron excitation rate} = \text{recombination rate} = k[\text{electron}][\text{hole}] \quad (1)$$

with electron population [electron], hole population [hole], and a second-order rate constant *k*. In the absence of a redox reaction on the decane−particle interface, an equivalent number of electrons and holes are present in a particle, leading to the 1/2-order power law:

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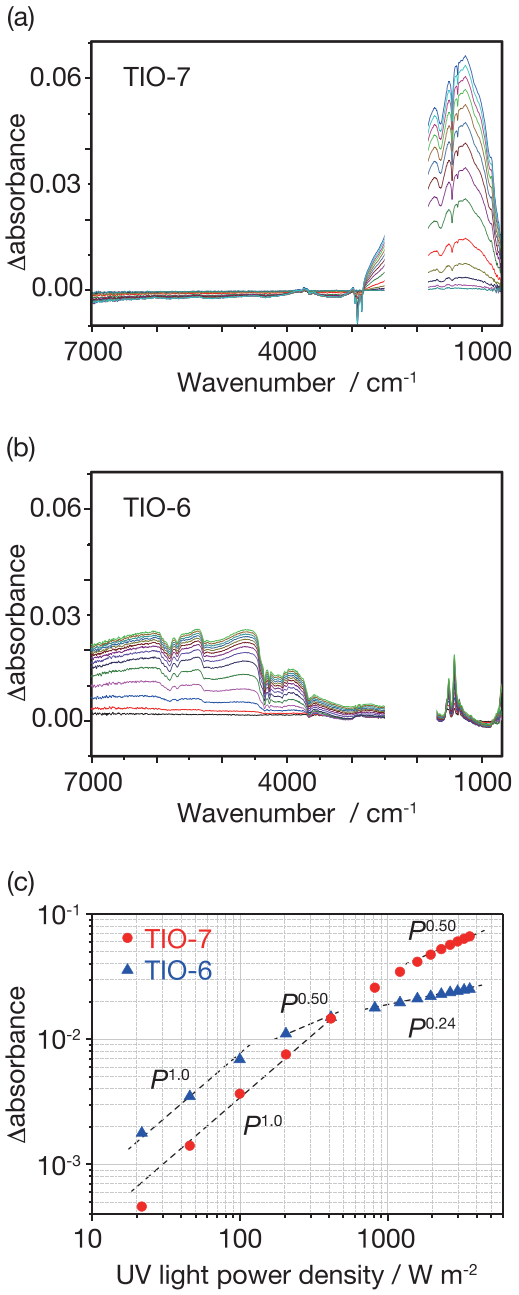

Figure 3. UV-light-induced Δabsorbance spectra of (a) TIO-7 and (b) TIO-6 in anaerobic *n*-decane. UV light power density: 22, 46, 100, 200, 410, 820, 1200, 1600, 2000, 2300, 2600, 3000, 3300, and 3600 W m^{-2}. (c) A log−log plot of Δabsorbance on TIO-7 (red dots) and TIO-6 (blue triangles) as a function of light power density, *P*. Broken lines show $P^{1.0}$, $P^{0.50}$, and $P^{0.24}$ laws fitted to the observations. Δabsorbance is quantified at 1267 cm^{-1} for TIO-7 and at 6000 cm^{-1} for TIO-6. UV light source: LED (M365L3). Probe light source and detector: ceramic source and MCT. The spectra are shown in the wavenumber ranges of 7000−2500 and 1800−700 cm^{-1} because IR transmittance through the prism decreased to <30% at 2500−1800 cm^{-1}.

$$P \propto k[\text{electron}]^2 \propto \Delta\text{absorbance}^2 \quad (2)$$

As *P* decreased to 400 W m^{-2}, the power-law order gradually increased to unity. The unity order claims full contribution of weak excitation, where a limited number of UV photons are absorbed in a particle. When neighboring places of UV-photon absorption are separated in space, recombination requires collision of an electron and a hole that were created by the same photon. The electron−hole collision rate is proportional to the number of electron−hole pairs created by the same photon [electron−hole pair], leading to the first-order power law with a rate constant k':

$$P \propto k'[\text{electron–hole pair}] \propto \Delta\text{absorbance} \quad (3)$$

The power-law order shifted to unity with $P < 400$ W m^{-2}. The intensity of natural solar light on the surface of Earth's atmosphere is 1.4 kW m^{-2}.[23] When the fraction of UV light for bandgap excitation is 5% of the total solar irradiation, electrons and holes recombine according to eq 3 in TIO-7 particles under solar light on the ground. This indicates the dominant role of weak excitation in real TiO_2 photocatalysts. Because excitation and decay dynamics are often traced in TAS with highly intense light pulses, we should be careful to transfer knowledge reported in TAS to reaction kinetics on real photocatalysts. A light pulse of 10 ns in time width and 1 mJ cm^{-2} in power density, which numbers are typical for excitation in TAS, provide a peak light power density of 1 GW m^{-2}.

Δabsorbance spectra of TIO-6 are shown in Figure 3b. The symmetric band maximized at 6000−5000 cm^{-1} appeared as was observed in the methanol−water mixture. The strength of the electron-induced absorption was quantified with Δabsorbance at 6000 cm^{-1} and is indicated with blue triangles in Figure 3c. Water overtones bleached on moist TIO-6 particles produced negative peaks at 5300−4700 cm^{-1}. Bleaching at 5900−5600 and 4400−3900 cm^{-1} was ascribed to overtones of decane vibrations. The fundamental tone of decane vibration produced positive peaks at 1600−1300 cm^{-1}. The unusual behaviors, bleached overtones accompanied by enhanced fundamental tones, may be ascribed different depths of probing in the photocatalyst−decane suspension. Probing depth on the prism should be proportional to the wavelength of the probe light.

With $P < 100$ W m^{-2}, Δabsorbance of TIO-6 was proportional to *P*, indicating pair recombination formulated in eq 3. When *P* was increased to 200−400 W m^{-2}, the power-law order decreased to 1/2, suggesting random-walk recombination of multiple electrons and holes in this power density range. When power density was increased to 800−3600 W m^{-2}, an even flatter power law, $P^{0.24}$, fitted the results. It is not easy to physically interpret a 0.24-order power law. We hypothesize that the power-law order decreases to zero under greater UV-light intensity. The observed $P^{0.24}$ law indicates a transition from the 1/2-order law to the zero-order law. The zero-order law suggests the number of excited electrons saturated in a particle. When the number of electrons and holes exceeds the saturation limit, a quick recombination path may open in addition to the ordinary random-walk recombination. Another hypothesis can be proposed when the $P^{0.24}$ law is recognized as a 1/4-order law. A redox reaction requiring four electrons to complete presents a 1/4-order law. Four-electron reduction of molecular oxygen, resident in the decane droplet or the moist surface of particles, is taken into consideration. The hypotheses for the $P^{0.24}$ law are to be tested further.

The probing depth of 6000 cm^{-1} light was estimated to be 0.25 μm over the prism. Multiple layers of TIO-6 particles were present in the probed volume. If UV absorption of particles in contact with the prism was bleached under intense UV irradiation, particles deposited on the bleached particles and not yet bleached would absorb UV light penetrating through the bleached particles. Hence, bleaching of bandgap absorption is not a reason for the saturated Δabsorbance.

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4. DISCUSSION

4.1. Number of Electrons Excited in a TIO-6 Particle. Bogomolev and Mirlin[7] observed near-IR absorption in rutile single crystals doped with lithium cations. The embedded Li atoms became completely ionized in the host lattice at 300 K, donating one electron per atom. They observed a symmetric spectrum with a peak at 6600 cm^{-1} (Figure 3 of ref 7) and assigned the absorption to electrons donated to the host lattice. The spectrum reported in Li-doped crystals was similar to that observed in TIO-6. Here, we estimated the electron population in a TIO-6 particle by assuming that the molar absorption coefficients of electrons donated in Li-doped crystals and electrons excited in TIO-6 are the same.

With a Li concentration of 8.6×10^{16} atoms cm^{-3}, which corresponds to the same number of donated electrons, the absorption coefficient was 1 cm^{-1}.[7] Suppose that the volume probed by 6000 cm^{-1} light was filled with TIO-6 particles. Because the probing depth was 0.25 μm, TIO-6 particles with 8.6×10^{16} excited electrons cm^{-3} present a Δabsorbance of 2.5×10^{-5}. In the results shown in Figure 3c, Δabsorbance was 0.023 with P = 2000 W m^{-2}. Hence, the number density of excited electrons at this light power density was estimated to be 8×10^{19} electrons cm^{-3} = 0.08 electron nm^{-3}.

Although it is difficult to precisely determine the probing depth as well as the fraction of the probed volume filled with particles, estimating the order of magnitude is still meaningful. The number density of excited electrons estimated in the preceding paragraph indicates that a TIO-6 particle having a spherical diameter of 15 nm steadily contained 140 electrons under UV irradiation of P = 2000 W m^{-2}. When decreasing P to 20 W m^{-2}, 9 electrons are present in a particle to produce the Δabsorbance of 0.0015 as shown in Figure 3c. A significant number of excited electrons and holes remain active in TIO-6 particles excited with LED light in decane. The estimated number of excited electrons provides an insight of rutile photocatalyst particles. Although optical absorption of electrons excited in TiO_2 particles has been observed in a number of earlier studies,[1,8−12,18,19,22,24,25] the number of the excited electrons was difficult to be evaluated.

A spherical TIO-6 particle received 6.5×10^3 photons s^{-1} per particle under 365 nm light of P = 20 W m^{-2}. When received photons are fully absorbed in the particle to present 9 electrons in a steady state, the average lifetime of excited electrons defined by eq 4 should be 1 ms.

$$\text{average lifetime} = \frac{\text{steady number of excited electrons}}{\text{number of electrons excited per second}} \quad (4)$$

The 365 nm light of 20 W m^{-2} simulated UV light in solar irradiation. Excited electronic states active for milliseconds were quantified as supposed in the Introduction.

4.2. Polaronic Character of Electrons Probed by IR and Near-IR Absorption. Here, we discuss the identity of the electrons excited in rutile and anatase particles following earlier studies.[24] When an electron is excited across the bandgap in rutile, the ionic lattice is deformed around the excited electron, creating a small polaron. A polaron is defined as the excess electron self-trapped in a Coulombic potential well, produced by the shifting of ions from their equilibrium positions.[25] When the wave function of the self-trapped electron collapses on one Ti cation, which was originally Ti^{4+}, it is recognized as a small electron polaron, as illustrated in Figure 4a.

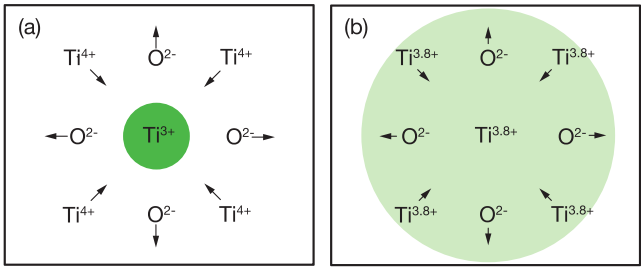

Figure 4. Illustration of electron polarons in TiO_2. (a) Small and (b) large polarons are illustrated in a virtual, square lattice of titanium cations and oxygen anions. An excess electron distributes in the green area. Arrows indicate displacement of cations and anions from the carrier-free positions. In (b), the excess electron shared by five cations is displayed in order to depict the definition of a large polaron and not to suggest that an electron excited in TIO-7 is shared by five cations.

The optical transition of a small polaron is energetically resonant to its hopping from the low-energy state of one cation to the high-energy state of a neighboring cation. The absorption spectrum is symmetric because of resonance with a state-to-state transition. In fact, optical absorption studies[6,7,11] reported a symmetric absorption peak at around 6000 cm^{-1} (0.7 eV). A valence-band photoemission study[26] accordingly found symmetric emission bands at 1.0 eV below the Fermi level on single-crystalline rutile wafers modified by Na adatoms. The Na adatoms are supposed to produce small polarons in rutile by donating electrons. Our absorption spectra shown in Figures 2 and 3 are consistent with the reported results and indicate that bandgap-excited electrons are accommodated as small polarons in rutile particles in liquid. The steady number of electron polarons was estimated 140 per TIO-6 particle irradiated with P = 2000 W m^{-2} in Section 4.1. Because a rutile particle having a spherical diameter of 15 nm includes 5.8×10^3 Ti cations, 0.2% of Ti cations were reduced to the 3+ state during irradiation.

In contrast to rutile, anatase is a host of large electron polarons, while the formation of small polarons in this polymorph is debated.[24] Figure 4b depicts the excess electron distributed over multiple Ti cations in a large polaron. When the electron is photoexcited from the ground state of the self-trapping potential well to unbound continuum states, optical absorption of an asymmetric spectrum appears.[25] The low-energy threshold of the absorption is determined by the energy gap between the self-trapped state and the bottom of the continuum states. The absorption coefficient decreases when the photon energy is above the threshold, generating a peak close to the threshold. This is because the initial state is confined in real space and limited in momentum. The probability of optical transition decreases with the electron momentum required in the final state, i.e., the electron energy in the final state. The required momentum is provided by phonons in the host lattice.[27] Δabsorbance spectra of anatase particles reported in this study and earlier studies[11,12,18] accurately followed the characteristics of large-polaron photoexcitation.

Finally, the UV-light-induced Δabsorbance spectrum of TIO-7 is compared with that of a $NaTaO_3$ photocatalyst doped with Sr cations reported in our earlier study.[13] Strontium-doped $NaTaO_3$ is one of the most efficient photocatalysts for realizing the overall water-splitting reaction.[28,29] The Δabsorbance spectra of TIO-7 and Sr-doped $NaTaO_3$ were observed in anaerobic decane by using the common set of prism assembly, spectrometer, and MCT detector. The two spectra, which are normalized at each Δabsorbance maximum and shown in Figure

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5, bear a striking resemblance: a gradual increase from 3000 cm^{-1} (TIO-7) or 5000 cm^{-1} (Sr-doped $NaTaO_3$) with

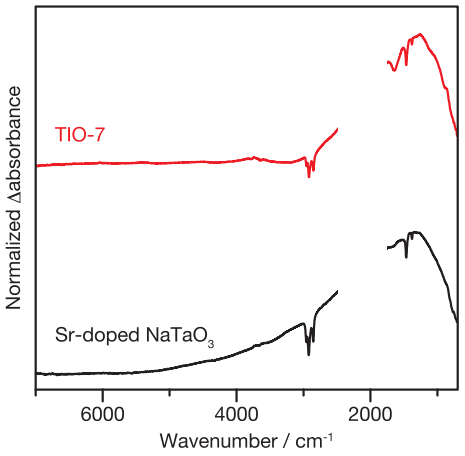

Figure 5. UV-light-induced Δabsorbance spectrum of TIO-7 compared with that of a $NaTaO_3$ photocatalyst doped with Sr cations (Sr concentration: 4 mol % relative to Ta cations). The black spectrum is adopted from Figure 1 of ref 13. The two Δabsorbance spectra are observed in anaerobic decane. UV wavelength and power density for excitation of TIO-7: 365 nm and 3600 W m^{-2}. UV wavelength and power density for excitation of Sr-doped $NaTaO_3$: 285 nm and 19 W m^{-2}. The two spectra are normalized at each Δabsorbance maximum and shown in the wavenumber ranges of 10000−2500 and 1800−700 cm^{-1} because IR transmittance through the prism decreased to <30% at 2500−1800 cm^{-1}.

absorption maxima at 1400−1300 cm^{-1} and cutoff at 1000 cm^{-1}. The analogous spectra suggest analogous identity of the initial and final states in the optical transition. We therefore propose here that bandgap-excited electrons created large polarons in the Sr-doped $NaTaO_3$ photocatalyst. Because the identity of electrons excited across the bandgap of $NaTaO_3$ is unknown, the assignment to large polarons proposed here delivers an insight of $NaTaO_3$ photocatalysts efficient for the overall water splitting reaction.

Theoretical[30−33] and experimental[34−37] studies have emphasized the role of polarons in the control of the carrier transport rate in metal oxides. Modification of the overpotentials of surface redox reactions is also predicted with polarons.[38−41] Methods, results, and interpretations delivered in this study provide easy access to electron polarons in semiconductor photocatalysts excited in liquid. Light-excited hole polarons are detectable with IR absorption, as was reported on a ZnO wafer placed in vacuum and probed with a reflection setup.[34] ATR-based spectroscopy has not yet been applied to holes in semiconductor photocatalysts in liquid.

5. CONCLUSIONS

The combination of the diamond prism assembly with the FT spectrometer enabled us to trace IR and near-IR absorption spectra of electrons excited across the bandgap of TiO_2 particles in liquid. Electrons excited in the rutile particles (TIO-6) formed small polarons characterized with a symmetric absorption band with a maximum at 6000 cm^{-1}. Electrons in anatase particles (TIO-7) formed large polarons, producing an asymmetric absorption band that gradually increased at wavenumbers below 5000 cm^{-1} and cutoff at 1000 cm^{-1}. The shapes of polaron-induced spectra were insensitive to the environment (liquid or vacuum), suggesting the electron polarons accommodated in bulk particles. The spectrum of large electron polarons in TIO-7 resembled the absorption reported for a Sr-doped $NaTaO_3$ photocatalyst, which suggests the presence of large polarons in $NaTaO_3$ photocatalysts.

The kinetics of electron−hole recombination was examined on UV-light power dependence of the polaron absorption in anaerobic decane. With light power density P greater than a threshold, 200 W m^{-2} on TIO-6 or 2000 W m^{-2} on TIO-7, the polaron absorption was enhanced with absorbance being proportional to $P^{1/2}$. The observed 1/2-order power law suggested recombination of multiple electrons and holes randomly moving in each particle. Upon excitation with smaller P, the power-law order increased to unity to indicate recombination of an electron and a hole that were excited by the same photon. An average polaron lifetime of 1 ms was estimated in TIO-6 particles irradiated at P = 20 W m^{-2}. Thus, this study demonstrated the feasibility of the diamond prism combined with the FT spectrometer for characterizing and quantifying electronically excited states active for milliseconds, which should play a major role in photocatalytic reactions under solar light. Applications to a broad range of photofunctional materials hybridized with quantum dots, plasmonic nanoparticles, or 2D materials are promising.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.2c07433.

Reagents; near-IR absorption spectra of the prism assembly (Figure S1) and liquid droplets (Figure S2); X-ray diffraction patterns (Figure S3) of TIO-6 and TIO-7 photocatalyst particles; UV-light-induced absorbance change in the hole scavengers (Figure S4) (PDF)

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Notes

The authors declare no competing financial interest.

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