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Excited states in the conduction band and long-lifetime hot electrons in TiO$_2$ nanoparticles observed with photoemission electron microscopy

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ABSTRACT

The authors propose that high catalysis of TiO$_2$ nanoparticles (NPs) originates in the generation of excited states in the conduction band, which realize a long lifetime of hot electrons. This paper confirms their claim by observing individual NPs in the femtosecond laser pump-and-probe technique using photoemission-electron-microscopy. The low slope of the power dependence of the brightness of NPs is attributed to thermionic electron emission from an excited state below the vacuum level. An intermediate excited state is required to explain the asymmetrical delay dependence of the brightness enhancement, and the energy position is assigned to 0.78 eV above the conduction band minimum from the laser wavelength for the longest decay time of the brightness enhancement. A lifetime as long as 4 ps for hot electrons of 0.8 eV kinetic energy is observed when resonantly excited by a 760 nm light. The observed lifetime in TiO$_2$ NPs is more than 10 times longer than those in previous papers using single crystals, which supports the authors’ claim.

I. INTRODUCTION

Titanium dioxide (TiO$_2$) is one of the most important materials and its properties were studied by many people. About 40 years ago, Fujishima et al. found the photo-induced water-splitting by TiO$_2$, and the number of papers discussing dye-sensitized nanocrystalline TiO$_2$ as a low-cost high-efficiency solar cell increased exponentially since 1990. Presently, the mainstream of solar cell research has shifted to perovskite-type solar cells (PSC), and most PSCs use TiO$_2$ as an electron transfer layer. Many studies revealed that defects play a decisive role in the catalysis of TiO$_2$. The defect is oxygen vacancy and the electronic states of defects are Ti3d t$_2$g states. The optical absorption of TiO$_2$ increasing from 600 nm to the maximum at about 2 μm is identified as transitions from Ti3d defect states in the bandgap. To deeply understand the carrier dynamics, time-resolved measurements were performed extensively and the lifetimes of carriers were reported. Yamada and Kanemitsu reported a lifetime of 18 ns for photoluminescence (PL), 24 ns for photoconductivity (PC), and 48 ns for transient absorption (TA). They attributed the PC decay to the electron decay and TA of 1.2 eV light to the optical absorption of holes excited by a 3.5 eV laser. Zhang et al. reported a lifetime of 80 ps observed at 780 nm illumination. They attributed the TA to the d-d transition of electrons trapped in the mid-gap states. Du et al. studied the lifetime of electrons transferred from Au nanoparticle (NP) attached to TiO$_2$ NP. They reported that the lifetime of electrons detected by 3,440 nm light was shorter for a smaller diameter TiO$_2$ NP; 100 ps for a 50 nm diameter and 10 ps for a 10 nm diameter.
Although so many papers have reported carrier lifetimes, most articles related to trapped holes and electrons “in the bandgap”. Yoshihara et al.\textsuperscript{21} reported that the absorption of trapped holes has a peak at about 500 nm, trapped electrons generate absorption between 500 nm and 1100 nm, and electrons in the CBM produce infrared absorption monotonically increasing with the wavelength. Katoh et al.\textsuperscript{22} reported that higher density UV irradiation produced larger trapped electrons than holes.

In chemical reactions, however, the relevant electrons are so-called “hot electrons” in the “conduction band”. Photochemical reactions, such as desorption and dissociation, are explained in the MGR model,\textsuperscript{23–25} in which a high energy electron transfers from a catalyst to an excited state of an adsorbed molecule, forming a transient negative ion (TNI) at high potential energy. TNI propages along the reaction coordinate toward the minimum potential energy and gains kinetic energy. Then, TNI makes the Franck-Condon transition to the ground state and dissociates or desorbs owing to the gained kinetic energy. Yang et al.\textsuperscript{26} observed velocity of CH$_3$Br photo-desorbed from GaAs was larger for higher photon energy; molecules with the kinetic energy of 2.5 eV were observed when excited by a 193 nm laser, and 1.1 eV molecules were observed when excited by a laser shorter than 355 nm. Buntin et al.\textsuperscript{27} reported that NO molecules desorbed from Pt had lower kinetic energy and 1/4 excited by a laser shorter than 355 nm. Weik et al.\textsuperscript{28} observed that cross-sections both for desorption and dissociation of O$_2$ adsorbed on Pd increased exponentially from 4 eV to 6 eV. Sun et al.\textsuperscript{29} reported an exponential decrease of the photo-desorption yield of SO$_2$ molecules from Ag with increasing the wavelength from 200 nm to 500 nm.

Although higher energy hot electrons are more favorable for chemical reactions as explained above, the electron lifetime in solid is shorter for higher energy; inverse proportional to the square of the kinetic energy.\textsuperscript{30} Hot electrons generated deep in solid lose energy before reaching the surface to be transferred to adsorbed molecules. The number of hot electrons reaching the surface is proportional to the traveling distance which is proportional to the lifetime. Therefore, chemical activities are expected to be proportional to the lifetime of hot electrons. Based on these considerations, we propose that high catalysis of TiO$_2$ NPs originates in a long lifetime of hot electrons which is realized by the generation of the new excited states in the conduction band.

Thus, it is essentially important to study a lifetime of hot electrons for understanding photochemical reactions. However, only a few papers reported the lifetime of hot electrons. Observation of hot electrons is very difficult than detecting trapped carriers in the bandgap states due to the following reasons. First, a lifetime of hot electrons is usually tens femtosecond (fs) and shorter than 1 ps in most of the cases, far shorter than trapped carriers, and fs lasers are required for the measurement. Secondly, because of the extremely short lifetime, the signal is very small. Thirdly, in common methods such as light absorption and emission, the signal of hot electrons is completely overwhelmed by the signal of trapped charges, the detection of hot electrons in solid is performed the best by observing photoemission, and vacuum is required for the measurement. Because of these reasons, all measurement of the lifetime of hot electrons were performed by photoemission using fs lasers.

Onda et al.\textsuperscript{31} reported a lifetime of less than 15 fs for the so-called “wet electrons” at 2.4 eV above the Fermi level on an H$_2$O/TiO$_2$ (110) rutile surface. Argondizzo et al.\textsuperscript{32} observed several times enhancement of the photoemission for a 3.66 eV laser than for 3.22 eV and 3.95 eV laser illumination on a single rutile TiO$_2$ (111) crystal. They explained that the defect states lying 0.85 eV below the Fermi level were two-photon ionized with the help of the Ti3d $e_g$ state in the conduction band as an intermediate state. According to their claim, the energy position of the $e_g$ state was 2.81 eV above the conduction band minimum (CBM) if we assume the Fermi level coincides with the CBM. Because the two-pulse correlation profile was close to the pulse width of 20 fs, we deduce that a lifetime of electrons in the $e_g$ state was shorter than a few fs. Gundlach et al.\textsuperscript{33} reported a lifetime of 100 fs for electrons at 0.6 eV above the Fermi level in a 440 nm-pump and 480 nm-probe technique.

NPs is well known to have high catalysis\textsuperscript{34–37} and a study of lifetime of hot electrons is very important as described above. Although only a few but there are papers reporting a lifetime of hot electrons in a single crystal, there has been no study on these subjects in NPs because the measurement of the lifetime of hot electrons in NPs is extremely difficult than for crystals. This paper reports a study of electron lifetime in individual NPs. Using the fs laser pump-and-probe technique with photoemission-electron-microscopy (PEEM), we found that a slope of the power dependence of brightness was lower than expected and that the delay dependence of brightness enhancement was asymmetrical. The former is attributed to thermionic emission from an excited state at about 3 eV above the CBM and the latter is explained by introducing an intermediate excited state at 0.78 eV above the CBM. Electron lifetime as long as 4 ps was observed for 0.8 V electrons when resonantly excited by a 760 nm light, which is more than 10 times longer than those reported in single crystals. These observed results support our hypothesis.

II. EXPERIMENTAL SETUP

The experimental setup for the pump-probe measurement is shown in Fig. 1. A beam from the femtosecond laser (80MHz, 150 fs, Mira 900, Coherent, Santa Clara) separated by a beam splitter was focused to a BBO crystal by a lens of 125 mm focal length to generate the second harmonic (SH) with a maximum conversion efficiency of 7.5%. The maximum laser power was 1 W. The optical path length of the fundamental (F) wavelength beam reflected by the beam splitter was varied by sending to a corner cube mounted on a translator (GCD-302002M, Daheng Optics, Beijing) of 600 mm length. The position of the corner cube was electrically controlled by an electronic controller (GCD-0401M) with a 1.25 μm temporal accuracy. Two beams were combined by a beam combiner and focused on a sample in the vacuum chamber of PEEM with a focal length of 200 mm. The vacuum pressure was about 10$^{-7}$ Pa. The incident angle of the beams was 25 degrees from the sample surface. The power of the F and SH lasers was varied by attenuators at each beam before combining. Measurement was performed at powers of about 160 mW for F and 1.6 mW for SH. Thus, the pulse energies were about 2 nJ and 20 pJ with a peak power of 13 kW and 130 W, respectively. The focused beam diameter on the sample was about 100 μm, hence, the power density was of the order of 100 MW/cm$^2$ and 1 MW/cm$^2$ for F and SH, respectively. The laser wavelength was tunable from 700 nm to 900 nm and monitored by observing a spectrum of the F beam leaking behind...
the beam-combiner with a spectrometer (Ocean Optics 4000). An F laser component remaining in the path of the SH beam was transmitted through the combiner mirror. The interference between this F component leaking from the mirror for the SH and the F beams reflected by the corner cube at the combiner helped finely adjust the path lengths of the F and SH beams.

Anatase type TiO$_2$ NPs with a nominal diameter of 100 nm (Beijing DK nanotechnology, Beijing) diluted in distilled water was ultrasonically cleaned, one drop was dropped on an n-type Si wafer and blown off by an air current within seconds to leave a thin layer of TiO$_2$ on the Si substrate. The prepared sample with sparsely distributed TiO$_2$ NPs was baked for 1 hour in the air at 500 °C before being mounted on the sample holder of PEEM.

The intensity of the electron image was enhanced by a microchannel plate (MCP), and the converted fluorescent image on a phosphor after the MCP was recorded by a charge-coupled-device (CCD) camera. The dynamic range of the MCP spanned about four orders of magnitude. To observe the brightness variation over several orders of magnitude, the voltage applied to the MCP, $V_{\text{MCP}}$, was changed to avoid saturation. A calibration measurement was performed multiple times and we found that the brightness recorded by the CCD camera increased 10 times by increasing $V_{\text{MCP}}$ by 110 V. In the data analysis, the image brightness was normalized to that at 1 kV, denoted $B_N$, using the equation $B_N = \left(\frac{B_M - B_G}{110}\right) \times 10^{\left(\frac{1000V_{\text{MCP}}}{\text{MCP}}\right)}$, where $B_M$ depicts the raw reading of the brightness before normalization.

Figure 2 shows an example of PEEM images. We selected 95 particles as shown by the circles in Fig. 2(a). Figure 2(b) shows an enlarged display of the square region shown in Fig. 2(a), where the sizes of particles spanned a few pixels. In the experiments reported here, the images were observed with a field of view of 64 μm to observe many NPs in a single frame. There are 560 x 560 pixels in one frame. Then, the one-pixel size was about 120 nm. Therefore, the size of the particles was about 400 nm. Hence, strictly speaking, particles were clusters of NPs, but we call them simply NPs in this paper.

In the results reported later, we refer to the brightness of the brightest pixel in each NP as the brightness of each NP. The averaged background of PEEM images was about 110, and the brightness after subtracting the background is referred. Mainly owing to shot noise, the brightness below 10 can be unreliable.

III. EXPERIMENTAL RESULTS

A. Power dependence of brightness

We wanted to observe a variation of electronic states among individual NPs. One theory predicted the ionization energy, $E_i$, of 8.3 eV. Two experimental observations reported two different values of $E_i$ of 7.5 eV and 7.25 eV. From this variation of results among papers, we expect $E_i$ exhibits different values among NPs. Because PEEM can help observe individual NPs, we can thus evaluate $E_i$ of an individual particle from the power dependence of particle brightness. For example, if $E_i$ is 8 eV, five photons of 770 nm (1.61 eV) are enough but at 780 nm (1.59 eV), six photons are required for ionization. Hence, the slope of the power dependence...
dependence of the brightness jumps from 5 to 6 between 770 nm and 780 nm. The wavelength, at which a jump in the slope of power dependence is observed, is used to specify the ionization energy.

Figure 3 shows the brightness when the laser power was varied in a log-log plot at various F wavelengths for four TiO$_2$ NPs. As stated in Section II, values of normalized brightness below 10 can be unreliable, however, data points can be connected by lines of a slope of 4-photon absorption for most of NPs, as represented by NP #78 and #80 in Fig. 3. For the other NPs, data points can be connected by lines of a slope of 3-photon absorption, as represented by NP #24 and #65. We chose two particles each having near one order of magnitude difference in brightness as representatives of 3-photon and 4-photon NPs to show a variety of behavior among NPs having different brightness. This result was contrary to our expectation. First, the slope was the same at all wavelengths and no jump was observed in the slope. Secondly, the slope was smaller than expected. As discussed above, a slope of five was expected at 800 nm, whereas a slope of four was observed. A larger surprise was that some NPs even exhibited a smaller three-photon slope. The total photon energy of three photons at 800 nm light amounts to a mere 4.65 eV. According to a theory, the electron affinity (i.e., the energy between the CBM and the vacuum level) is 5.1 eV, and three photons of 800 nm wavelength are not sufficient to even ionize electrons at the CBM.

B. Multi-photon excitation spectrum

In Fig. 3, we notice that the brightness strongly depended on the wavelength. Figure 4 shows the brightness at 200 mW laser power shown in Fig. 4 as a function of photon energy. The brightness at 1.75 eV (710 nm) was more than 10 times of that at 1.55 eV (800 nm). This wavelength dependence cannot be explained by the absorption spectrum of reduced TiO$_2$. As explained in the Introduction, the absorption in reduced TiO$_2$ increases at a longer wavelength becomes nearly flat between 1.5 μm and 2 μm, and then decreases slightly up to 5 μm. In the report by Yoshihara et al., the absorption by trapped electrons has a broad peak around 800 nm. Thus, the wavelength dependence of the absorption in reduced TiO$_2$ is opposite to the wavelength dependence in Fig. 4. Hence, the observed wavelength dependence will be the characteristic of multiphoton excitation. Presently, however, we do not...
have a good explanation of the wavelength dependence shown in Fig. 4.

One interpretation of this structure seen in Fig. 4 is the presence of two sharp absorptions at 1.72 eV and 1.63 eV. However, this interpretation is not persuasive. In photoemission, electrons are emitted from a region thinner than a few nanometers, and an extremely large absorption coefficient, which is not acceptable, is required to form a dip. One might assume that the structure reflects a potential barrier such as a Schottky barrier, for example at the interface between the substrate. When the electron energy is higher than the barrier height, a larger electron flux flows out of NPs. However, this explanation is neither persuasive, because the electron flux will be larger at higher photon energy and hence no dip will be formed.

Another interpretation is that there are two broad enhancement peaks; the first between 1.65 eV and 170 eV, and the other between 1.57 eV and 1.61 eV. Enhancement can occur if there exist intermediate states in the conduction band, which assist multi-photon excitation. This interpretation looks plausible because intermediate states are also required for explaining the asymmetry in the delay dependence of the brightness enhancement observed in the pump-probe measurements, as reported next.

C. Pump-probe measurement

Now, we report the results of pump-probe measurements using F and SH beams. Among the selected 95 NPs shown in Fig. 2, the brightness differed across two orders of magnitude. Figure 5 shows the brightness of four particles; NPs #24 and #65 are 3-photon slope NPs and NPs #78 and #80 are 4-photon slope NPs. The wavelengths of the irradiating lasers were 800 nm (F) and 400 nm (SH). Laser powers of 168 mW for F and 1.8 mW for SH were chosen such that the image brightness was similar for the F irradiation only and the SH irradiation only. The horizontal axis in the figure is the position of the corner cube for varying the delay time of F pulses. From the increase of the brightness at around 482.37 mm, we know that both F and SH pulses reached the sample at the same time. We call this position as the t=0 position.

Hereafter, we call the increase of brightness of images around t=0 as brightness “enhancement” and the dependence on the position of the corner cube as “delay dependence”. We can estimate the lifetime of electrons from the delay dependence of the enhancement.

In order to compare the delay dependence of enhancement of particles with largely different brightness values, as seen in Fig. 5(a), the brightness enhancement was normalized by setting the smallest value of the brightness of each particle to 0 and the largest value to 1. The delay dependence of the “normalized enhancement” is shown in Fig. 5(b). Although the brightness of the selected four NPs was different by one-orders-of-magnitude as seen in Fig. 5(a), there was no large difference in the delay dependence of enhancement among NPs except for NP #65. As depicted by the dashed curve in Fig. 5(b), the delay dependence of NP #65 was fitted considerably well with a single Gaussian. For the other three NPs, the delay dependence was not fully fitted by a Gaussian, as seen in Fig. 5(b), and there was a component remaining long after t=0. We call the brightness-enhancement fitted by the dotted Gaussian curve seen for #65 as the “fast decay component” and the signal remaining after the fast component is called as the “slow decay component”.

D. Asymmetrical delay dependence of brightness enhancement

When the position of the corner cube is larger, the F pulse arrives at the sample earlier. Interestingly, as seen in Fig. 6, the slow component was observed only when the F pulse arrived first and the SH arrived later. This asymmetry of the delay dependence was also contrary to our initial expectation. We expected symmetrical delay time dependence also for the slow component, as it was observed for the fast component. The asymmetry in the delay dependence of the slow component implies that an intermediate state can be excited by one photon of the F laser and that electrons in the intermediate states are not easily excited to the final state by the F excitation. We will discuss this in detail later in section IV, Discussions.

E. Wavelength-dependent slow decay component

We compare the delay dependence of the brightness enhancement at various wavelengths. As shown in Fig. 6(b), the delay dependence of the enhancement in NP #80, a 4-photon slope NP, was similar all at 740 nm, 760 nm, 780 nm, and 800 nm. On the other hand, as seen in Fig. 6(a), NP #65, a 3-photon slope NP, showed only a fast component when excited at 800 nm, as already shown in Fig. 5(b), whereas a slow component was observed at 740 nm, 760 nm, and 780 nm. Figures 6(c) and (d) show that, at 750 nm, 770 nm, and 790 nm, the delay dependence of the enhancement was the same for NPs #65 and #80. Hence, the difference between NPs #65 and #80 was clear when NPs were excited at 800 nm. In NP #80, the delay dependence at 770 nm was different from that at other wavelengths.

**FIG. 5.** (a) The delay dependence of the brightness of NPs #24, #65, #78 and #80 shown in Fig. 4 when both F (800nm) and SH (400 nm) beams irradiated the sample. The brightness was enhanced when the corner cube for varying the delay time of F beam was moved to 482.37 mm on the translator. (b) The brightness enhancement was normalized as explained in the text to compare delay time dependence of NPs having largely different brightness. Brightness enhancement of NP #65 was fitted well by a single Gaussian (dotted curve). In other NPs, a slow decay component was noticed when F pulse arrived earlier than SH, the larger number in position.
To observe the wavelength dependence of the slow component in further detail, the delay dependence of all 95 NPs were averaged to reduce the fluctuation of data points. The results are shown in Fig. 7(a), in which the abscissa is converted to time in ps. At all wavelengths, the shape at the rising part was the same, that is, the same Gaussian can fit the rising part before $t=0$, as shown by the dotted curves. In Figs. 5, 6, and 7, we used the same parameter for the Gaussian with a full width at half maximum (FWHM) of 150 fs for the fast component. Figure 7(b) shows the slow component calculated by subtracting the fast component shown by the dotted curves from the brightness enhancement shown in Fig. 7(a). From the observed decay time shown in Fig. 7(b), we found wavelengths are separated into three groups. We call wavelengths 740 nm, 790 nm, and 800 nm as Group 1; wavelengths 750 nm and 780 nm as Group 2; and wavelengths 760 nm and 770 nm as Group 3. The decay constant in Group 1 and Group 2 was 0.23 ps and 0.33 ps, respectively. The lifetime was the longest in Group 3. The delay dependence can be fitted with the decay...
constant of 0.47 ps when excited at 770 nm and 4 ps when excited at 760 nm.

IV. DISCUSSIONS

A. Thermionic electron emission

The low magnitude of the slope of the power dependence of the brightness observed in Fig. 4 implies that the observed electrons were photoexcited to an excited state in the conduction band, but not excited directly into the vacuum. We can explain the low slope in Fig. 4 by assuming that electrons are thermionically emitted from excited states. In a previous study, we observed thermionic emission from gold NPs of nominal size of 10 nm. In papers by other groups, photoemission spectra having the Boltzmann distribution were reported, and we can attribute them to thermionic emission. Thus, it is reasonably expected that thermionic emission is observable in TiO$_2$ NPs as well. In thermionic emission, electrons are multiphoton excited to an excited state below the vacuum level, and electrons excited to the excited state are thermally emitted to the vacuum.

The Ti 3d $3e_g$ state observed by Argondizzo et al., which was referred to in the Introduction, is one of the candidates for the excited states for thermionic emission observed in the present study. As was explained in Introduction, they claimed that the defect state lying at 0.85 eV below the Fermi level, annotated as “def” in Fig. 8, was resonantly excited to the $e_g$ state by a 3.66 eV photon. The $e_g$ state lies at 2.81 eV above the CBM when the Fermi level is assumed to be very close to the CBM. Then, the $e_g$ state lies at 6.01 eV above the valence band top when the bandgap energy is 3.2 eV. Then, electrons even in the valence band can be excited to the $e_g$ state by four photons of 800 nm.

The total photon energy of 4.65 eV for three photons of 800 nm is not large enough to excite valence electrons to the $e_g$ state. Therefore, in the case of NPs showing a three-photon slope, another excited state is required below the $e_g$ state, as shown by “Int” in Fig. 8. Otherwise, we need to assume that the states observed by Zhang et al. with a lifetime of 80 ps were excited to the $e_g$ state. The state observed by Zhang et al. can be the same as the “def” state from which electrons were resonantly excited to the $e_g$ state by a 3.66 eV photon in Argondizzo et al. In our experiment, the “def” state in the bandgap might have been fully filled because pulses from the 80 MHz laser irradiated the sample every 12.5 ns. The energy between “def” and the $e_g$ state is 3.66 eV and three photons of 800 nm are enough to populate the $e_g$ state.

In the case of thermionic emission in Au NPs observed in our previous study, the brightness of the NPs increased steeply at a laser power higher than 200 mW, which meant that the temperature of the electrons in the excited state was determined by the power of the irradiating laser. In the present study, no steep increase of the brightness at a high laser power was observed in Fig. 4. So, the electron temperature was independent of laser power. Presently, it is not clear what determined the electron temperature.

B. Long lifetime of hot electrons

Figure 9 shows a comparison of the observed lifetime with those reported in the literature. The values obtained in this work, shown in Fig. 7(b), are displayed by solid squares. Horizontal value is the kinetic energy of electrons above the Fermi level, which is the CBM in the case of TiO$_2$. We assumed that the initial state of the electrons observed in our work was 0.85 eV below the CBM. The solid curve
shows the lifetime observed for Cu (111) single crystal reported by Knoesel et al.,\textsuperscript{17} which scaled roughly as the inverse square root of the kinetic energy above the Fermi level, as predicted by theory.\textsuperscript{19} The experimentally observed lifetime in Ag (110) and Ta (poly) was lower than the curve.\textsuperscript{20} Link and El-Sayed,\textsuperscript{21} Zhukov et al.,\textsuperscript{22} and Bauer and Aeshlimann,\textsuperscript{23} reported similar values for metals. The value observed in TiO$_2$ reported by Gundlach et al.,\textsuperscript{24} shown by an open triangle, was close to those in metals. Compared with these values, the lifetime observed in the present work is 10 times longer. As discussed above, the lifetime at 760 nm observed in the present study was much longer. Argondizzo et al.,\textsuperscript{25} did not explicitly discuss the electron lifetime, which is much shorter than the pulse width of their 20-fs laser and may lie close to the solid curve by Knoesel et al.\textsuperscript{17} The lifetime of the so-called “wet electrons” at 2.4 eV above the Fermi level reported by Onda et al.,\textsuperscript{26} shown by the red closed circle, was a little longer than that in Argondizzo et al.\textsuperscript{17}

The significantly extended lifetime observed in our work is attributed to the sample being in the NP form. Gundlach et al.,\textsuperscript{24} and Argondizzo et al.,\textsuperscript{25} used a single crystal as the sample. NPs have an extremely high density of defects and defects will have excited states where electrons are trapped for an extended amount of time. Generally, it is important to keep hot electrons at a high energy state for a longer time to achieve high catalytic activity. We presume that the high catalytic activity of TiO$_2$ originates in high-density excited states with a long lifetime. In the study of Onda et al.,\textsuperscript{26} water molecules attached to the rutile TiO$_2$ single crystal may have increased the lifetime of hot electrons in comparison to a clean crystal used in the study of Argondizzo et al.\textsuperscript{17}

C. Asymmetric delay dependence

Here, the asymmetrical delay dependence of the brightness enhancement is discussed. A brightness enhancement was observed when F pulse arrived first at the sample. This asymmetry can take place under two conditions. The first condition is that one photon energy of the F laser is not sufficient to excite the intermediate state to the final excited state. The second condition is that one photon of the F laser excites electrons in the initial state to the intermediate state.

The electronic structure proposed in Fig. 8 satisfies the above two conditions. We assume the $e_g$ state to be the final state. The initial state is the state lying at 0.85 eV below the CBM, as assumed by Argondizzo et al.\textsuperscript{17} Because the longest lifetime was observed at 760 nm, as seen in Fig. 7(b), we can say that the intermediate state in our measurement was the “Int” state at 1.63 eV above the initial state, the “def” state. The energy separation between the “Int” and the $e_g$ state is about 2 eV. Hence, for exciting electrons in the “Int” to the final state, the $e_g$ state, two-photons are required at 740 nm (1.68eV) to 800 nm (1.55 eV) and SH excitation is required. To explain the brightness enhancement observed at 800 nm, we need another intermediate state below the “Int” state.

The above electronic structure and interpretations are tentative and should be confirmed by future studies.

D. Long lifetime of hot electrons and catalytic activities

Here, we emphasize the importance of the excited states which serve as a stage for hot electrons to stay for a while. For efficient catalysis, hot electrons transferred from an attached molecule to the catalyst must remain at a high energy state before the next molecule arrives at the active site. At one atmospheric pressure, molecule arrives at the active site every 0.5 ns. Thus, when the lifetime of hot electrons is shorter than 0.5 ns, the chemical activity is proportional to the lifetime of hot electrons. This consideration agrees with the result observed by Xu et al.\textsuperscript{27} stating that the lifetime of anatase, which has one-order-of-magnitude higher activity compared to rutile, was one-order-of-magnitude longer. Our claim that high catalysis in NPs originates in the long lifetime of hot electrons is confirmed by Fig. 9, which shows that the lifetime in TiO$_2$ NP was more than ten times those for single crystals.

From the asymmetry of the delay dependence of brightness enhancement and the wavelength-dependent lifetime, we can say that the long lifetime of hot electrons is realized by the generation of new excited states in the conduction band such as shown by “Int” in Fig. 9.

Our claim can explain high catalysis of Au NPs. Gold (Au) is chemically the most inert element. But, in 1987, Haruta et al.\textsuperscript{28} discovered that Au NPs showed a quite high catalytic activity. Understanding the mechanism of changing the chemically inert material to the highly active catalyst has been one of the hottest topics in nanoscience. In most of the applications, Au NPs are supported on reducible oxides. Therefore, metal-oxide interaction can be the origin; charge transfer between Au and oxides, strain in the Au NPs due to the mismatch of the lattices at the interface, and so on. However, Nørskov et al.\textsuperscript{29} concluded that low-coordinated Au atom is the origin of the extraordinary catalytic activity. They plotted CO oxidation activities reported by many groups as a function of diameter, $d$, of Au NPs. The reactivity increased steeply below 5 nm and the effect of supporting material was smaller compared to the size effect. From the observed scaling of the activity of $1/d^3$, they concluded that a corner atom is the activity site.

However, we claim that the essence of high catalysis of Au NPs originates in a long lifetime of hot electrons. When the size of materials becomes smaller, the electronic state becomes quantized, and there appears an energy gap between electronic states. When the energy separation between electronic levels is larger than the phonon energy, energy relaxation time becomes long, which is called “phonon bottleneck.”\textsuperscript{30} In our case shown in Fig. 8, there will exist phonon bottleneck effect between the $e_g$ state and the “Int” state and between the “Int” state and the CBM.

Fang et al. reported the data supporting our claim. They are studying MoS$_2$ as a photocatalyst in hydrogen evolution.\textsuperscript{31,32} When graphene nanodots were deposited on MoS$_2$, the reflection of a 650 nm probe laser by photo-carriers in MoS$_2$ pumped by a 400 nm laser decreased rapidly within 1 ps.\textsuperscript{33} They concluded that the decrease was brought about by the generation of trions, i.e., two electrons and one hole, caused by the injection of slow electrons from graphene nanodots to MoS$_2$. By solving rate equations, they estimated that the cooling lifetime increased from 3 ps for 10 nm NP to 30 ps for 5 nm. Their method was in-direct but supports our claim.

In our next work, we will try to directly observe energy levels of discrete electronic states and a long lifetime of hot electrons in individual Au NPs.
E. Fast decay component

Finally, we comment on the fast decay component. The fast decay component is considered as electrons not trapped by the “Int” state. Because they are not trapped by the “Int” state, the delay dependence is symmetrical. Since the Gaussian curve fitted to the fast component in F-SH was almost the same with the pulse width, the electron lifetime was far shorter than the laser pulse width of 150 fs, which lies on the curve by Knoesel et al. in Fig. 9.

V. CONCLUSION

We are proposing that high catalysis of TiO₂ NPs originates in the generation of excited states in the conduction band, which realizes a long lifetime of hot electrons. The slope of power dependence of NP brightness was lower than expected from the reported ionization energy. This phenomenon was attributed to the thermionic emission from an excited state. The qₑ state at 2.8 eV above the CBM is the most plausible candidate. Electron lifetime as long as 4 ps at 0.8 eV kinetic energy was observed when resonantly excited by a 760 nm light, which was more than 10 times longer than those reported in previous works for single crystals. Our expectation of a 760 nm light, which was more than 10 times longer than those reported in previous works for single crystals. The asymmetry was explained by an intermediate excited state at 0.78 eV above the CBM. Because they are not trapped by the “Int” state, the delay dependence is symmetrical; a slow decay component is considered as electrons not trapped by the “Int” state. The asymmetry was explained by an intermediate excited state at 0.78 eV above the CBM.

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