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Trapping dynamics of electrons and holes in a nanocrystalline TiO_2 film revealed by femtosecond visible/near-infrared transient absorption spectroscopy

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Abstract

The trapping dynamics of electrons and holes in TiO_2 nanocrystlline films excited by ultraviolet laser pulses (266-nm wavelength) were studied with femtosecond visible/near-infrared transient absorption spectroscopy. UV irradiations of the TiO_2 film generated hot carriers in the conduction and valence bands. The formation rate of deeply trapped holes was estimated to be 200 ± 50 fs. The rate was limited by intraband relaxation (cooling) of hot holes. The spectral shift of the transient absorption indicated that trapped holes relax from shallow sites to deep ones. This relaxation was occurring more than 100 ps after photoexcitation. ***To cite this article: Y. Tamaki et al., C. R. Chimie 9 (2006)***.

Résumé

La dynamique de piégeage des électrons et des trous dans des films de TiO_2 nanocristallins excités par des impulsions laser ultraviolettes (longueur d'onde : 266 nm) a été étudiée par la spectroscopie d'absorption transitoire femtoseconde dans le visible/proche infrarouge. Les irradiations par UV du film de TiO_2 ont généré des porteurs chauds dans les bandes de conduction et de valence. On a estimé que le taux de formation de trous profondément piégés est de l'ordre de 200 ± 50 fs. Le taux a été limité par la relaxation entre bandes (refroidissement) des trous chauds. Le décalage spectral de l'absorption transitoire révèle que les trous piégés quittent les emplacements peu profonds pour les plus profonds. Cette relaxation se produit pendant plus de 100 ps après la photoexcitation. ***Pour citer cet article : Y. Tamaki et al., C. R. Chimie 9 (2006)***.

Keywords: TiO_2; Hole, Electron; Trapping, Cooling; Transient absorption

Mots clés : TiO_2 ; Trou ; Électron ; Piégeage ; Refroidissement ; Absorption transitoire

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1. Introduction

Photocatalytic reactions on titanium dioxide (TiO_2) nanoparticles have attracted much interest because of their applications for water splitting, degradation of pollutants, wettability control, and so on [1,2]. The reaction is caused by electrons and holes generated in TiO_2 nanoparticles by UV-light irradiation. Upon photoexcitation, free electrons and free holes are generated in the particles. These free carriers can move in the particle very fast and then they are trapped efficiently because there are many traps in the particles, especially at the surface. After trapping the diffusion coefficient is decreased dramatically and therefore electron-hole recombination is suppressed effectively. These carriers have long lifetime and therefore they can effectively react with various molecules at the surface. These sequential primary processes are important to understand the reactivity of such materials.

The trapping dynamics of carriers photogenerated in TiO_2 nanoparticles can be divided into following three steps. Just after excitation by laser pulse, the photogenerated free electrons and holes having finite kinetic energy, i.e. hot carriers, relax within the conduction and valence bands, respectively (free carrier cooling). The free carriers relax into localized levels of defects or impurities (free carrier trapping), where the trapping process involves shallow and deep trapping sites. There is continuous energy level dispersion for the localized levels, so that the carriers in shallow trapping sites further relax into deep trapping sites by their migration (relaxation through trap sites) [3,4].

Since trapped electrons and holes in TiO_2 nanoparticles give rise to absorption bands, the trapping dynamics of the carriers can be investigated by transient absorption spectroscopy [5–17]. Trapping times of free carriers [6,8] have been estimated by analysis of rise profiles of transient absorption bands of TiO_2 colloidal solutions on the subpicosecond time range. Absorption bands in the transient absorption spectra of TiO_2 colloidal solutions [6,7,11,14] and powders [5] shift from red to blue in the pico- and subnanosecond domains as the carriers relax. This process is considered to be due to relaxation through trapping sites [5].

Transient absorption bands of TiO_2 nanoparticles are very broad and depend on the particle size and preparation conditions, making spectral assignments very difficult [5–7,11,15,18]. To study the trapping dynamics, transient absorption spectra of well characterized TiO_2 sample must be measured over wide spectral and temporal ranges. For this purpose, we chose to study a transparent nanocrystalline film of TiO_2. In our previous study using nanosecond transient absorption, we have successfully assigned the origin of a transient absorption spectrum of the TiO_2 film. Absorption bands of three carrier species, free electrons, trapped electrons, and trapped holes, in the wavelength range from 400 to 2500 nm were clarified [12]. The trapped electrons and holes are considered to be in deep trapping sites, because their spectral shape did not show temporal change after 50 ns.

In the present study, we focused on charge-carrier trapping dynamics in nanocrystalline TiO_2 films before completion of the deeply trapping process. The trapping dynamics were investigated by means of femtosecond visible/near-infrared transient absorption spectroscopy. The observed charge-carrier dynamics are discussed in terms of free carrier cooling, free carrier trapping, and relaxation through trapping sites. Although the spectral analysis was difficult due to spectral overlap between the three species (free electrons, deeply trapped electrons, and deeply trapped holes) as well as additional species in shallow traps, we could elucidate the dynamics of deeply trapped holes whose absorption was very strong in the visible region.

2. Experimental section

Nanocrystalline TiO_2 films were prepared by a method reported [19]. The mean diameter of the constituent nanoparticles was about 20 nm. The crystal phase was found to be anatase. The film thickness was 2–5 μm.

Fig. 1 shows a schematic diagram of our femtosecond transient absorption spectrometer. The light source was a regenerative amplifier system of a Ti:sapphire laser (Hurricane, Spectra Physics; 800 nm wavelength, 130 fs FWHM pulse duration, 1.0 mJ per pulse intensity, 1 kHz repetition rate). Half of the fundamental output of the amplifier system was frequency tripled (266 nm) and used as an excitation light pulse. The energy of the excitation pulse was measured with a joule meter (A407, Spectra Physics). The residual of the fundamental output was focused into a sapphire crystal to generate a white-light continuum as a probe pulse. To

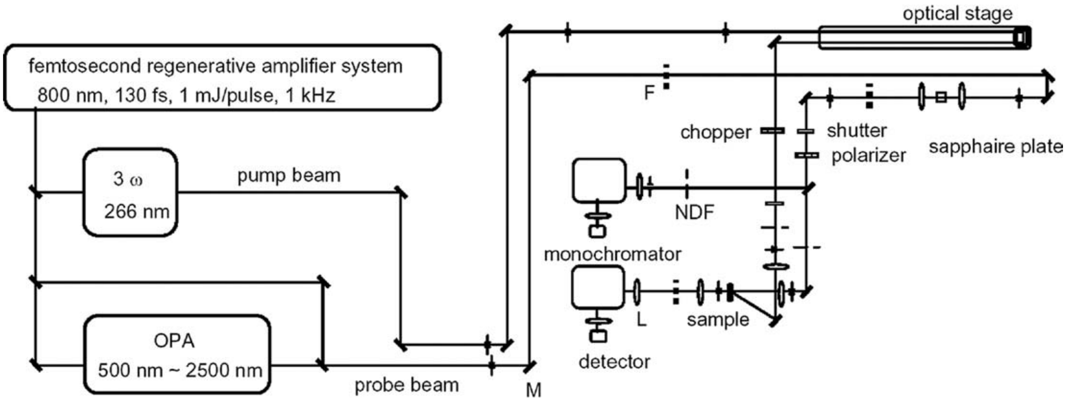

Fig. 1. Schematic diagram of the femtosecond visible/near-infrared transient absorption spectroscopic setup.
M, mirror; F, filter; NDF, neutral-density filter; L, lens.

obtain a probe pulse at 1100 nm, the fundamental output was introduced to an optical parametric amplifier (OPA; Topas, Quantronix) instead of the white-light generator, and the output of the OPA was used as the probe pulse. The probe beam was detected with a Si, InGaAs, or MCT photodetector after passing through a monochromator (Spectra Pro 150, Acton Research). Fluctuation of the probe pulse was monitored with another monochromator and detector. The two outputs of the detectors were analyzed with three boxcar integrators and an analog processor (SR 250 and SR235, Stanford Research) to obtain the transient absorption. All measurements were conducted at 295 K.

3. Results and discussion

3.1. Transient absorption spectra from femto- to nanosecond range

The transient absorption spectrum of a TiO_2 nanocrystalline film has been assigned in a spectral range from 400 to 2500 nm in our previous study [12]. Fig. 2a shows the spectrum measured at 1 μs after excitation by a 355-nm nanosecond laser pulse. The observed transient absorption spectrum was separated into three species, free electrons, trapped electrons, and trapped holes. The trapped electrons and holes exhibited broad bands in the visible range with maxima at 770 and 530 nm, respectively. Free electrons showed a broad absorption band whose intensity increased with wavelength, and the tail of the band overlapped with the bands of the trapped electrons and holes. It should be pointed out that in the visible range the absorption intensity of trapped holes is very large relative to that of free and trapped electrons. The spectral shape of the film did not change in a time range from 50 ns to 1 μs, indicating that the spectrum shown in Fig. 2a is attributed to carriers in the equilibrium state. Therefore, the trapped electrons and holes should be in deep trapping sites after relaxation through trapping sites. We call them 'deeply trapped electrons' and 'deeply trapped holes' in this paper.

Transient absorption spectra of the film excited by a femtosecond laser at 266 nm were measured on the femto- and picosecond time range. Fig. 2b shows the transient absorption spectra of delay times from 200 fs to 100 ps in the wavelength range from 550 to 1000 nm. The transient absorption spectra are very broad, and the absorption intensity decreases gradually with time after 450 fs.

To confirm that nonlinear excitation did not occur in the femtosecond experiment, transient absorption of the TiO_2 film was measured at different excitation intensity. Fig. 3 shows temporal profiles of the transient absorption at 1100 nm. The peak intensity of the transient absorption at just after excitation is plotted as a function of the excitation power in the inset of Fig. 3. The absorbance is proportional to the excitation power, indicating that the carriers were formed through one-photon excitation process and nonlinear excitation process was not involved. The absorption decay in the picosecond range became faster when increasing the excitation power. This indicates that the number of electrons and holes in a single TiO_2 particle is large enough to cause bulk recombination.

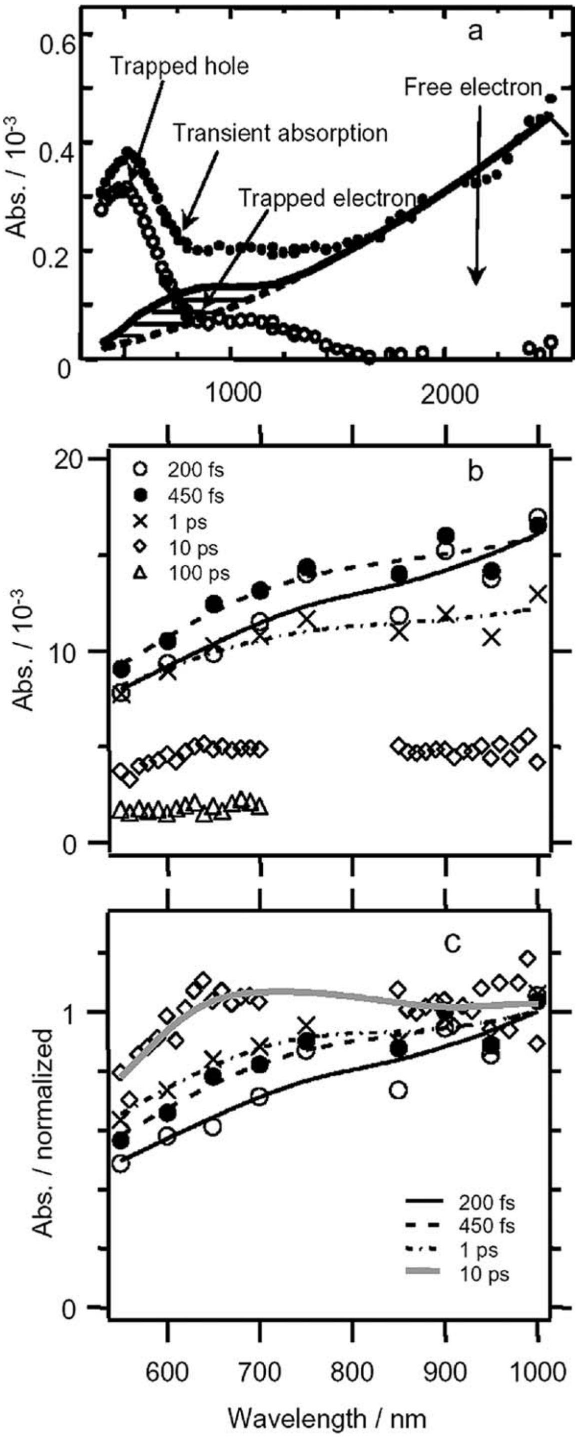

Fig. 2. (a) Transient absorption spectra of the nanocrystalline TiO_2 film at 1 µs after excitation by a 355 nm nanosecond laser pulse (solid circles): deduced absorption spectra of free electrons (dashed line, which overlaps the solid line at wavelengths above 1200 nm), trapped electrons (horizontal stripes), and trapped holes (open circles). (b) Transient absorption spectra of a nanocrystalline TiO_2 film in air after excitation by a 266 nm femtosecond laser pulse (excitation intensity, 20 µJ per pulse). (c) The same spectra normalized at 1000 nm.

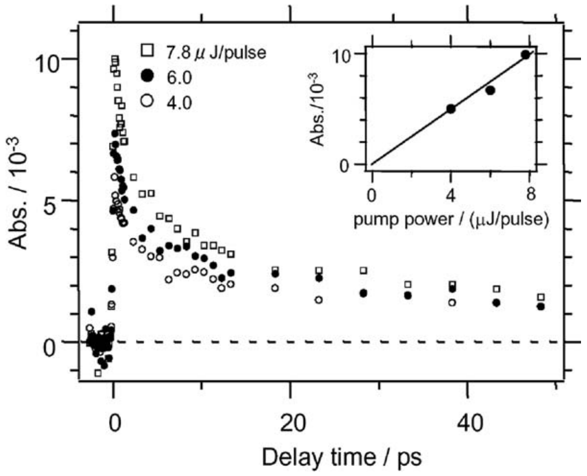

Fig. 3. Temporal profiles of the transient absorption at 1100 nm of a nanocrystalline TiO_2 film after excitation by a 266-nm femtosecond laser pulse. The peak intensity of the transient absorption at just after excitation is plotted as a function of the excitation power in the inset.

In order to exclude the contribution of the absorption decay due to electron-hole recombination, the spectra in Fig. 3b were normalized at 1000 nm. Normalized spectra are shown in Fig. 2c. It is obvious that the spectra are shifting to blue with time as a general trend. The spectrum immediately after excitation (at 200 fs) has increasing intensity with wavelength, indicating that free carriers are not trapped yet at this time. Free carrier cooling and trapping processes will be discussed in detail in 3.2. At 10 ps, a spectral shoulder around 650 nm can be seen in the visible region, representing that trapped species are observed; however, the spectral shape is different from that of the deeply trapped species (Fig. 2a). Therefore, the 10 ps spectrum includes contribution of shallowly trapped species. It is seen that relaxation through trapping sites proceeds on the picosecond time range. The details will be discussed in Section 3.3.

It should be noted that the observed spectral blueshift is similar to previous reports as for TiO_2 colloidal solutions [6] or powders [5]. Various types of trap sites are known to exist in semiconductor nanoparticles, and these sites are distributed over a wide range of energies. Previous experimental results suggest that electrons and holes are trapped quickly at shallow trapping sites, at which these charge carriers are bound loosely; and thermal fluctuations allow the carriers to migrate to deep trapping sites, where they are bound more tightly [4–6,8]. Consequently, the populations of electrons and holes in deep trapping sites will increase with time by carrier migration between trapping sites. As a general trend, transient absorption spectra of TiO_2 shift from red to blue with increasing delay times in the picosecond time range. This shift is considered to be due to relaxation of trapped electrons [5] and holes [6] to deeper trapping sites. Hence, shallowly trapped carriers tend to absorb photons of longer wavelengths, and deeply trapped carriers photons of shorter wavelengths.

In the present TiO_2 nanocrystalline film, deeply trapped holes have strong absorption in the visible region with a peak at 530 nm. Therefore, it is expected that shallowly trapped holes would give absorption with a peak at longer than 530 nm. Absorption of shallowly trapped electron would be hardly observable in the visible region, because deeply trapped electrons have an absorption peak at 770 nm and its intensity is weak. Therefore, the observed spectral change in Fig. 2c is considered to reflect mainly hole trapping dynamics.

3.2. Ultrafast relaxation of photogenerated hot holes by cooling and trapping

As discussed above, in general spectral overlap between many species (deeply and shallowly trapped carriers and free carriers) in TiO_2 over wide spectral range makes it difficult to analyze the observed transient absorption. However, we have demonstrated that trapped holes are dominant in the visible region, and especially at shorter wavelength deeply trapped holes are responsible for observable absorption. Here, we discuss formation dynamics of the deeply trapped holes in the early stage by analysis of femtosecond transient absorption rise at 550 nm. The temporal profile at 550 nm is potted against delay time together with calculated curves in Fig. 4. For comparison temporal profiles at 1000 and 700 nm are also shown. The calculated profiles were obtained by convoluting the instrument response function with several exponential rise functions. The instrument response function was determined by a two-photon absorption cross-correlation method, and could be fitted using a Gaussian function with a FWHM of 170 fs for all probe wavelengths. The rise times estimated from the transient absorptions at 1000, 700, and 550 nm were 100 ± 50, 150 ± 50, and 200 ± 50 fs, respectively.

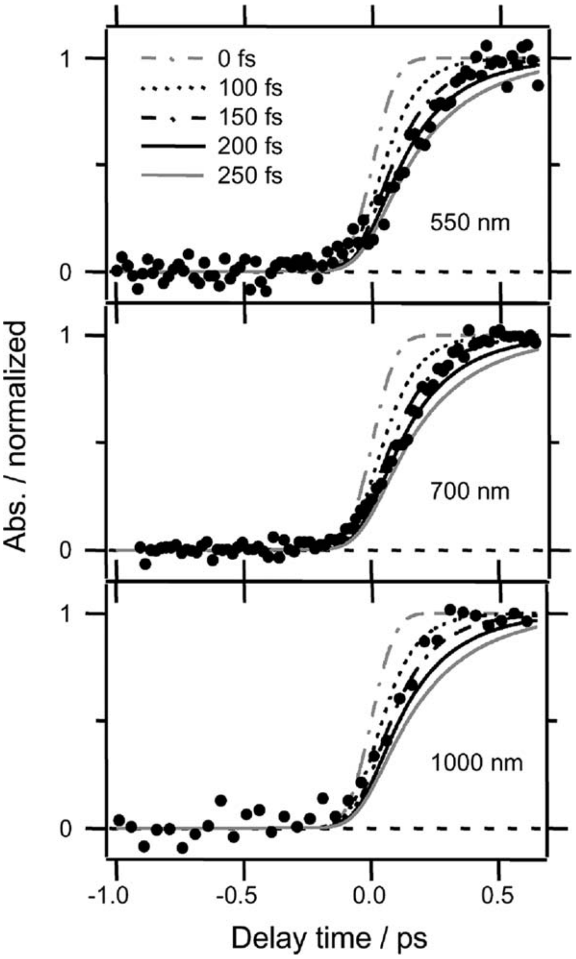

Fig. 4. The rise profiles of the transient absorption of a TiO_2 film after excitation by a 266-nm femtosecond laser pulse (excitation intensity, 20 μJ per pulse) measured at 1000, 700, and 550 nm (solid circles). The figure also shows simulated rise profiles obtained by convolution of the response function (170 fs FWHM) with exponential rise functions with rise times of 0, 100, 150, 200, and 250 fs.

In the obtained rise time of 200 fs at 550 nm for deeply trapped holes, the free carrier cooling and the free carrier trapping are considered to take place. From our experiment, separation of these two processes is difficult. Yang and Tamai [6] previously estimated hole trapping time in anatase TiO_2 colloidal particles excited at 360 nm (close to the band-gap), where the free carrier cooling would be neglected since excess excitation energy is small. The trapping time in the colloid was very rapid and less than 50 fs. The formation rate of the trapped holes in present study is slower than this trapping time. The difference of the rate can be explained by carrier cooling times. In present experimental condition the excitation photonic energy (4.7 eV) is much larger than the bang gap of anatase TiO_2 (3.2 eV). The hot carriers should dissipate excess photonic energy before free carrier trapping. Carrier cooling is responsible for slowing the formation of trapped holes in the TiO_2 film.

The estimated rise times at 1000 and 700 nm (100 ± 50 and 150 ± 50 fs, respectively) are shorter than the rise time at 550 nm (200 ± 50 fs). As mentioned above, many transient species can be observed in the spectral range from 700 to 1000 nm, such as shallowly trapped holes, deeply and shallowly trapped electrons, and free electrons. Absorption of free holes might appear in this range. Due to this spectral overlap, detailed analysis is very difficult; however, possible explanations may be raised as follows. Free carrier absorption is expected to give instantaneous response, so that this contribution could make the apparent profile to glow faster. Shallowly trapped holes may be dominantly observed. They, indeed, would be spread over the bulk of TiO_2 particles, in contrast with the deeply trapped holes that are likely to be trapped at surface. Then, the free carrier cooling time in the bulk might be decreased.

3.3. Relaxation through tapping sites in the time picosecond scale

Free carriers in TiO_2 nanocrystalline films were trapped into various sites, and then the trapped carriers relaxed into lower energy sites. The relaxations of trapped carriers are considered to be due to carrier migrations between traps. The spectral shift as shown in Fig. 2 indicates that the trapped carriers are relaxing over the time range longer than 10 ps after laser excitation.

To examine the relaxation dynamics of trapped carriers up to about 100 ps, the decay profiles of transient absorption for the TiO_2 film at 550, 700, and 1000 nm are plotted from 20 to 94 ps in Fig. 5. Since the 550 nm absorption is dominated by deeply trapped holes and 700 and 1000 nm include many contributions such as shallowly trapped holes, deeply trapped electrons, and shallowly trapped electrons, comparing the 550 nm decay with others will give information about population distribution change for the deeply trapped holes.

To smooth the scattered data points, the profiles were normalized at a delay time of 20 ps after being fitted to a double-exponential function with a constant component. The difference in the three curves is clear, though the decay rates of the absorbance are on the same order of magnitude, 10 ps, because of the recombination of the trapped electrons and holes. The longer the probe wavelength is, the faster the decay of the absorption is; that is, shallowly trapped carriers decay faster than deeply trapped ones in the picosecond time domain. This result can be explained in terms of relaxation through trapping sites, as discussed above. Thermal fluctuation allowed the carriers in shallow trapping sites to detrap more frequently than those in deeper trapping sites, and consequently the former easily underwent migration between the trapping sites. This is the reason that absorption of shallowly trapped carriers decreased rapidly. In contrast, once carriers were trapped at deep trapping sites, detrapping from the sites was difficult owing to the necessarily large activation energy. The large activation energy slowed the absorption decay at shorter wavelengths.

4. Summary

The trapping dynamics of holes in TiO_2 nanocrystlline films excited by ultraviolet laser pulses were

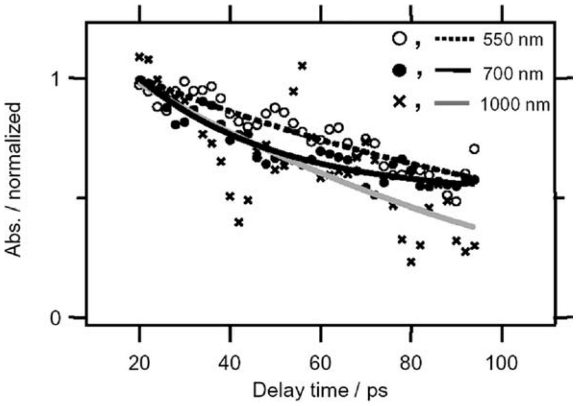

Fig. 5. Decay profiles of the transient absorption of a TiO_2 film at 550, 700, and 1000 nm in the picosecond time domain, normalized at a delay time of 20 ps after excitation. The curves indicate the results of fitting.

studied with femtosecond transient absorption spectroscopy in the spectral range from 550 to 1100 nm. UV irradiations of the TiO_2 film generated hot carriers in the conduction and valence bands. Formation of deeply trapped holes could be monitored by measuring the transient absorption at 550 nm without interference of other carrier species. The formation rate of deeply trapped holes was estimated to be 200 ± 50 fs. The rate was limited by intraband relaxation (cooling) of hot holes. Spectral blue-shift of transient absorption was observed on the time range from subpicoseconds to picoseconds. The spectral shift indicated that trapped holes relax through trapping sites. This relaxation was occurring longer than 100 ps after photoexcitation.

Acknowledgements

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