Exponential optical absorption edge in PbS quantum dot-ligand systems on single crystal rutile-TiO₂ revealed by photoacoustic and absorbance spectroscopies

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Abstract

The photovoltaic properties of quantum dot (QD) sensitized solar cells (QDSCs) depend significantly on the surface modification applied to the QDs and on the nanostructured interface between the QDs and the electrode surface. In the development of QDSCs with spatially ordered QD arrays, linking molecular ligands with the QDs (QD-ligands) can lead to the realization of novel QDSCs. The ligand shell around the QDs mediates the electron and energy transfer processes that underpin their use in QDSC applications. The dependence of the photovoltaic properties on the interparticle distance (QD spacing) can also be evaluated by applying different sizes of molecular ligands. The present study focuses on specific attention to the exponential optical absorption edge (often termed Urbach tail) in PbS QD-ligand systems with different QD spacing adsorbed on rutile-TiO₂ (R-TiO₂) substrates with different crystal orientations. It is essential to accurately characterize QD-ligands on electrode surfaces with different crystal orientations, not only for scientific studies, but to further optimize the growth conditions and processes in order to design and fabricate advanced QDSCs. Photoacoustic (PA) and conventional absorbance (Abs) spectroscopies were applied to determine the optical absorption and nonradiative relaxation properties. There is a discrepancy between the PA and Abs spectra especially in the Urbach tail region. As the Urbach tail states are related to the absorbed photon energy lost in the form of heat generated by nonradiative relaxation, therefore characterization of the Urbach tail is important and essential for QDSC applications. Characterization of the Urbach tail and the heat generated by nonradiative relaxation of PbS QD-ligand systems by combined PA and Abs spectroscopies showed that the characteristics depend strongly on the crystal orientation of the R-TiO₂ substrate, the QD spacing, and the free energy change.

1. Introduction

There has been a number of studies focusing on the nanoscale electronic and optical properties of materials and devices, which can provide major benefits to applications. For more than two decades, nanoscale semiconductor materials (quantum dots: QDs) have been applied for solar cells (QD sensitized solar cells: QDSCs) [1–10]. The interesting features of QDs are their size-dependent tunable energy-gap and the higher extinction coefficient than bulk material due to the quantum confinement effect. The electron injection process benefits from the large dipole moments in QDs, accelerating the separation of the electron-hole pairs [11, 12]. QDSCs have the
potential to increase the efficiency limit of single junction solar cells, with the possibilities of multiple exciton generation (MEG) and hot-electron extraction before thermalization of the photogenerated carriers. Even though QDs have been widely explored for solar cells and the efficiency of QDSCs has exceeded 11% (PbS-QDSC) [13], the mechanisms of exciton dissociation and subsequent charge-carrier transport for QDSC depend on their morphological and chemical attributes [14]. The photovoltaic properties of QDSCs significantly depend on the surface modification applied to the QDs and the interfaces. In the development of QDSCs with ordered QD arrays, molecular ligands linked with QDs (QD-ligands) have been expected to realize novel QDSCs [15]. Dependence of the interparticle distance (QD spacing) on the photovoltaic properties can be evaluated by applying different sizes of molecular ligands [15–17].

Although ligand exchange can change the carrier mobility, this has rarely been employed in investigations of the effect of the electrode surface onto which the QDs are adsorbed. Characterization of the substrate surface on performance is important, because there are differences in the density of states, the dielectric constant, and the thermodynamic stability depending on the crystal orientation of TiO2 electrode surface, due to the differences in the occupancies of the elements in the surface layers. In general, well studied surfaces are of great scientific and technological interest. On the other hand, polycrystalline nanoparticulate TiO2 used as electrodes play a role in QDSCs, as a result of the large surface area onto which a great number of QDs can be adsorbed [18]. However, heterogeneity is produced by the distribution of defects and the abundance of grain boundaries on the nanoparticulate TiO2 electrodes [19]. These complexities make it difficult to get a clear understanding of the electronic structure and the electron transfer mechanisms for QDs. There are reports that the morphology and structure of the electrode oxide has an influence on electron transfer due to changes in the dielectric constant and the different densities of the band-edge states [7, 20–23]. Also, there was a report that the optical absorption edge of Nb-doped TiO2 film depends on the different kind of the substrate [24]. Therefore, it is essential to characterize the QD-ligands on electrode surfaces with different crystal orientations to study the growth conditions and processes, thereby advancing the design of QDSCs. One of the most important step for understanding the electronic structure of QDs is to study the optical absorption of QDs and their dependencies on different well-characterized single crystal TiO2 surfaces [19]. Despite this being crucial for advanced QDSCs, detailed optical absorption studies of QDs looking at the influence of the electrode surface has seldom been done [25–33].

The purpose of this study is to focus on the impact the different crystal orientations of single crystal rutile-TiO2 (R-TiO2) substrates and the QD spacing have on the optical absorption of QD-ligands. We chose PbS QDs as these have been extensively studied and are candidate for high-efficiency and stability QDSCs [15, 16, 31, 34–38]. PbS QDs bear significant advantages due to the small effective masses of electrons (0.08 m0) and holes (0.075 m0) (m0: electron rest mass), high static dielectric constant (~181), and large exciton Bohr radius (~18 nm). The energy gap of PbS QDs can be adjusted by controlling the size of the QDs due to the quantum confinement effect. Advanced preparation in the form of PbS QD-ligands for surface passivation and control of the QD spacing would enable further improvements to the QDSC properties [17]. Three kinds of mercaptoalkanoic acids (MAAs, S–(CH2)n–1–COOH): 3-mercaptopropionic acid (n = 3, 3MPA), 6-mercaptophexanic acid (n = 6, 6MHA), and 16-mercaptophexadecanoic acid (n = 16, 16MHA) were applied as ligands. The QD spacing between the PbS QDs has been controlled by the different lengths of the MAAs [39].

In this work, we demonstrate the use of photoacoustic (PA) and absorbance (Abs) spectroscopies, which can be treated as complementary techniques for optical absorption measurements. Whilst there are many different mechanisms for optical absorption, many of the deexcitation processes eventually result in the absorbed optical energy being dissipated as heat (photothermal phenomena), and PA spectroscopy is a photothermal techniques. In the PA spectroscopy, optical absorption properties are determined from the acoustic signals generated by deexcitation processes, arising from the periodic heat flow from the sample to the surrounding gas as the sample is cyclically heated by the absorption of modulated light [40]. PA spectroscopy has a number of attractive features for (1) high scattering media; (2) a broad range of materials; (3) a wide range of absorption coefficient magnitudes; (4) an increase in S/N ratio with increasing in input light power [41]. The PA technique is a powerful tool and is used for many applications [40, 42–44] because of higher sensitivity than conventional optical absorption measurements [10, 45]. According to the Rosencwaig-Gersho (R-G) theory [40] in which the PA intensity is proportional to the product of optical absorption coefficient and probability for heat generation, it has been assumed that the probability for heat generation by nonradiative processes is 100% [40]. Therefore, PA spectra should be in agreement with Abs spectra; thus, PA spectroscopy has been applied as a complementary technique for the optical absorption properties of opaque and light scattering materials [46, 47]. However, there is a report that indicates the discrepancies between PA and Abs spectra [48]. In addition, there have been reports of discrepancies between the PA and Abs spectra of low-dimensional systems due to the nature of the lattice relaxation [49, 50] and the hard x-ray spectra in metals due to inelastic interactions [51, 52]. Thus, new insights into excitation and deexcitation processes can be gained by comparing PA and Abs spectra. To the best of our
knowledge, there have been few comparative studies using PA and Abs spectroscopies. Therefore, comparisons between the PA and Abs spectroscopies of PbS QD-ligands on single crystal R-TiO₂ with different crystal orientations and variable QD spacing was applied to obtain new data on the optical absorption (excitation) and nonradiative (deexcitation) processes. In addition, photoelectron yield (PY) spectroscopy was applied to determine the ground state energy levels of the PbS QD-ligands together with the valence-band maximum (VBM) of R-TiO₂ [10, 53–55]. The ground state energy level is related to open circuit voltage (Voc) of QDSCs. The free energy change related to the photoexcited electron transfer rate [28] is estimated by PY measurements so as to discuss the relationship between the electron transfer and the exponential optical absorption edge.

2. Experimental details

2.1. Materials and chemicals

Single-crystal R-TiO₂ wafers, (5 × 7 × 0.5 mm²), with (001)-, (110)-, and (111)-cuts were obtained (Furuuchi Chemical Co., Ltd) [27], and they showed the basic unit cell structure of R-TiO₂ with lattice constants of

\[ a = b = 0.4594 \text{ nm} \quad \text{and} \quad c = 0.2959 \text{ nm} \]  

(figure S1 (available online at stacks.iop.org/MRX/9/025005/mmedia)). The surface layers (light blue broken lines in figure S1) are anisotropic in these crystal orientations, especially the (111) orientation, indicating that the dielectric properties are different due to the different occupancies of the elements at the surface. The surface roughness of the (001)-, (110)-, and (111)-cuts were 0.322 nm, 0.356 nm, and 0.394 nm, respectively.

The syntheses of the colloidal PbS QDs and PbS QD-ligand layers were pursued similar to the references [15, 56]. The flat surfaces of the R-TiO₂ were treated by washing them in acetone for 30 min, immersing them in distilled water for 30 min, and exposing them to ozone for 10 min. A mixture of PbO, oleic acid (OA), and 1-octadecene (ODE) was degassed at 80 °C for 1 h. The solution obtained was heated to 115 °C for 2 h under N₂, and this was followed by addition of the hexamethyldisilathiane (TMS) solution. Then, the obtained colloid was cooled to 70 °C, and then a halide precursor was added. After cooling to room temperature, the QDs were isolated by adding acetone with centrifugation. The supernatant was discarded and the precipitate was purified by successive dispersion in toluene and precipitation with a mixture of acetone and methanol, and dispersed in octane.

PbS QD-ligand layers were deposited on R-TiO₂ surfaces using a layer-by-layer method. For each layer, the colloidal QDs was spun-cast onto the R-TiO₂ substrate at 2500 rpm for 15 s. Then, a ligand solution in methanol was dropped onto the substrate. Finally, the substrate was rinsed three times with methanol, followed by baking distilled water for 30 min, and exposing them to ozone for 10 min. A mixture of PbO, oleic acid

1-octadecene (ODE) was degassed at 80 °C for 1 h. The solution obtained was heated to 115 °C for 2 h under N₂, and this was followed by addition of the hexamethyldisilathiane (TMS) solution. Then, the obtained colloid was cooled to 70 °C, and then a halide precursor was added. After cooling to room temperature, the QDs were isolated by adding acetone with centrifugation. The supernatant was discarded and the precipitate was purified by successive dispersion in toluene and precipitation with a mixture of acetone and methanol, and dispersed in octane.

PbS QD-ligand layers were deposited on R-TiO₂ surfaces using a layer-by-layer method. For each layer, the colloidal QDs was spun-cast onto the R-TiO₂ substrate at 2500 rpm for 15 s. Then, a ligand solution in methanol was dropped onto the substrate. Finally, the substrate was rinsed three times with methanol, followed by baking at 100 °C for 30 s. This process was repeated 5 times. To compare the effect the different substrate have on the PbS QD-ligand layers, these were also deposited on a glass substrate (insulator) in the same way. Fourier transform infrared (FTIR) spectra (Nicolet 6700, FT-IR spectrometer) of the PbS QD solid films were measured before and after MAI ligand exchanges. The FTIR spectra confirmed that the QD surfaces were covered with the MAI ligand after ligand exchange, similar to previous references [15, 16]. To estimate the diameter and the distance between adjacent PbS QD-ligands (QD spacing), monolayer PbS QDs were deposited on an ultrathin carbon foil and characterized using transmission electron microscopy (TEM) (JEM-2100F, JEOL), indicating that the diameter of the PbS QDs was ~2.0 nm. The average QD spacings were estimated to be 0.3, 0.8, and 2.1 nm for the 3MPA, 6MHA, and 16MHD ligands, respectively, from the TEM images together with the statistical data of the QD spacings (figure S2). The QD spacing increases linearly with the number of carbon atoms in the corresponding ligand (n = 3, 6, and 16) [15, 16].

2.2. Characterization by PA and Abs spectroscopies

The PA spectra were obtained using a gas-microphone detection configuration (figure S3). Monochromatic light (resolution: ±6 nm) from a 300 W xenon arc lamp was modulated with a mechanical chopper at 77 Hz and focused onto the sample surface in the sealed aluminum PA cell with a quartz transmission window. Surface temperature changes due to the photothermal effect cause pressure changes (acoustic wave) in the PA cell, and the acoustic wave is detected by an electret microphone. The amplitude and phase components of the PA signal were measured with a lock-in amplifier (time constant, 10 s). The spectra were taken at room temperature in the wavelength range of 400–800 nm, using the air as the medium for propagation of the acoustic waves. The spectra were calibrated by PA signals from a carbon black sheet for normalization [40]. The data were averaged to improve the S/N ratio. For the Abs spectra, we used a UV-vis spectrometer (JASCO V-670 spectrometer) to quantitatively estimate the optical absorption.

2.3. Characterization by PY Spectroscopy

The PY spectra were obtained using an ionization system (BIP-KV201, Bunkoukeiki Co., Ltd) [10]. The ionization energy was chosen to be the minimum energy (threshold) required to remove an electron from the
and the photoemission yield was measured as a function of photon energy in the range of 131–310 nm with a deuterium lamp (30 W) as the light source. The number of photoelectrons was obtained using an ammeter to measure the current needed to compensate for the photoexcited holes in the sample. A voltage of −50 V was applied to the base plate to prevent carrier recombination of the photoelectrons emitted from the sample surface with photogenerated holes. All the measurements were carried out in a vacuum chamber (∼4 × 10⁻³ Pa) at room temperature.

3. Results and discussion

3.1. Estimated average diameter of PbS QDs by PA and Abs spectroscopies

Figures 1 and 2 show examples of the ln(PA) and ln(Abs) spectra for PbS QDs-3MPA on (a) (001), (b) (110), and (c) (111) single crystal R-TiO₂, respectively. To compare the effect the surface orientation has on the PbS QD-ligand layer, ln(PA) and ln(Abs) spectra on a glass substrate are shown in figure 2(d) (PA) and 3(d) (Abs), respectively. Similar ln(PA) and ln(Abs) spectra were obtained for PbS QDs-6MHA and PbS QDs-16MHDA on R-TiO₂ and glass. The arrows ↓ in the ln(PA) and ln(Abs) spectra show the first transition energy peak position (E₁) between the ground state and the first excitation state of the PbS QDs [31]. The E₁ value is determined from the intersection between the straight line in the lower photon region (less than 1.9 eV) and that in the higher photon energy region (above 1.9 eV). Both lines were determined by least-square method. The E₁ values in the ln(PA) spectra are in agreement with those obtained in the ln(Abs) spectra.

The E₁ values in the ln(PA) spectra of bulk semiconducting materials give a clear indication of the fundamental absorption edges which are in good agreement with published values. Relative to the band gap energy of 0.40 eV for bulk PbS, the E₁ value for PbS QDs on R-TiO₂ exhibits a blue shift due to the quantum confinement effect. Higher transition energy peaks, assigned to 1Sₓ-1Pₓ (or 1Pₓ-1Sₓ) and 1Pₓ-1Pₓ [31, 58], are not obvious in figures 1 and 2. Using the optical absorption spectra and the TEM analysis, the average diameter, R, of the QDs can be estimated from the phenomenological relationship between E₁ and R given by the following.
Also, equation (1) agrees well with the theoretical tight-binding calculations for diameters less than 3 nm [60]. There is a possibility of a distribution in the size of the PbS QDs. In the case of a large size distribution, the value of $E_1$ depends on the modulation frequency of the irradiated light because of the different saturation effect on size in PA spectroscopy [40]. However, the PA measurements suggest that there is not much of a distribution in size because the position of $E_1$ is independent of the modulation frequency (30 ~ 430 Hz). The value of $E_1$, both in the ln(PA) and ln(Abs) spectra, was found to be independent of the different kinds of MAA ligands and the crystal orientation of the R-TiO$_2$ substrate, and was $E_1 \sim 1.8$ eV. The calculated value of $R$ was approximately 2.1 nm, which is in good agreement with our TEM observations (figure S2), which allows us to determine $R$ directly avoiding lengthy TEM analysis of each synthesized sample. The $E_1$ values in the ln(PA) spectra for PbS-QDs on glass are in agreement with those in the ln(Abs) spectra ($\sim 1.8$ eV; $R \sim 2.1$ nm) independent of the MAA ligands, and similar to the results for PbS QD-ligands on R-TiO$_2$.

3.2. Urbach tail characterization in PA and Abs spectroscopies

The next target of the PA and Abs characterization was to obtain information on the optical absorption and nonradiative deexcitation processes of PbS QD-ligands on R-TiO$_2$ related to the QDSC properties [14, 45]. These occur just below the fundamental absorption edge correspond to a linear exponential tail called Urbach tail [61–63]. Regarding QDSC studies, characterization of the Urbach tail region is important, since it limits the value of $V_{oc}$ in QDSCs [14, 45]. The dependence of $V_{oc}$ on the bandgap correlates with the Urbach tail slope (figure S4), indicating that $V_{oc}$ increases as the Urbach tail slope increases [14, 45]. The Urbach tail states in QDs result in losses in $V_{oc}$ and inhibit carrier transport in QDSCs. Hence, the Urbach tail in the absorption edge is a major factor with regard to the limitations in QDSC applications [14, 45]. In general, studies of the Urbach tail give basic information on the disorder and electron-phonon interactions [64, 65]. A variety of Urbach tails has been demonstrated with many semiconductors with a number of external parameters affecting the Urbach tail. In QDs, however, there may not only be random distributions on the substrate but also additional sources of
disorder that produce Urbach tail. Significant thermal disorder may arise from the abundance of QD surfaces
[35]. The mechanically soft surfaces of PbS QDs enable large atomic displacements and strong electron–phonon
interactions [66]. Linked ligands may also induce disorder and the formation of sub-bandgap states [67].
Excitonic generation in QDs affects the electronic energy levels in a different way to conventional disorder.
Hence, studies of the Urbach tail for QDs adsorbed on different surface orientation substrates provide us with
comprehensive understanding of the optical absorption of QDs. The optical absorption intensity (P) in the
Urbach tail region is given by [27, 61]:

\[ P = P_0 \exp \left( \frac{h\nu - h\nu_0}{k_B T} \right) \]  

(2)

where \( h \) is Planck’s constant, \( \nu \) is the incident light frequency, \( k_B \) is Boltzmann’s constant, \( T \) is absolute
temperature, and \( P_0, \nu_0, \) and \( \sigma \) are fitting parameters. \( \sigma \) is an essential characteristic of the Urbach tail
corresponding to the slope of the exponential optical absorption and is called the steepness parameter [10,
27–31]. As one possibility, the value of \( \sigma \) is thought to arise from lattice termination effects at interfaces and/or
potential fluctuations due to trapped charge at the PbS QD surfaces [68]. Although, the physical origin of
absorption edge may differ between materials, any linear exponential absorption tail can be characterized by the
steepness parameter [65, 69]. The steepness parameters, \( \sigma_{PA} \) for PA spectra and \( \sigma_{Abs} \) for Abs spectra, are defined
by equation (2) with \( P = PA \) and \( P = Abs \) intensities, respectively. We fitted the Urbach tails in the logarithmic
spectra in figures 1 and 2 (PbS QD-3MPA) to equation (2), covering photon energy region of 0.3 eV (fixed
between 1.5 and 1.8 eV) at absorption edge, using the most probable values of \( \sigma_{PA} \) and probable errors by least-
square method (table S1). The values of the optical absorption coefficient, \( \alpha \), for these photons, range between
800 and 10 000 cm\(^{-1}\). The \( \alpha \) values mentioned above were estimated from the Abs spectrum assuming that \( \alpha \) is
\( 1 \times 10^5 \text{ cm}^{-1} \) at 1.8 eV [35]. We note that absorption below 800 cm\(^{-1}\) was rather complex and noisy and
was not included in the analysis. We applied the above fixed photon energy region in all cases to compare \( \sigma_{PA} \)
and \( \sigma_{Abs} \). Similarly, the most probable values of \( \sigma_{PA} \) and probable errors were also obtained for PbS QDs-6MHA and
PbS QDs-16MHDAs on R-TiO\(_2\) and glass (table S1). The average value of the ratio, (probable error)/ (most
probable value), for \( \sigma_{PA} \) is \( \sim 0.05 \) (5%), indicating that the measurement conditions were satisfactory. That for
\( \sigma_{Abs} \) is \( \sim –0.02 \) (2%), also showing satisfactory measurement conditions. Our results for the ln(PA) spectra are
different from the reported photothermal deflection (PD) spectra [35] which have higher S/N ratios and higher
dynamic ranges covering 3 orders between \( \alpha = 10 \) and 10 000 cm\(^{-1}\). In our case, the ln(PA) spectra have lower
S/N ratios and dynamic range of, at most, 2 orders. It is likely that the substrate in the PD spectra is fused quartz
[35] which has a lower thermal conductivity (\( \sim 0.55 \text{ W m}^{-1} \text{K}^{-1} \)) than R-TiO\(_2\) (\( \sim 5.5 \text{ W m}^{-1} \text{K}^{-1} \)). The
photothermal intensity in both PA and PD spectra is proportional to the inverse of the thermal conductivity of
the substrate [40]. As a result, a higher signal intensity and higher S/N ratio were obtained for fused quartz
substrate in the PD spectra [35]. In our case, similar results can be obtained for the higher PA signal intensity and
the smaller probable errors of \( \sigma_{PA} \) and \( \sigma_{Abs} \) on glass substrates than those on R-TiO\(_2\) (table S1). Another problem
for PD spectroscopy is sample immersion in a perfluorohexan (FC-72). It may change the surface states of PbS
QDs in FC-72 from those obtained under real QDSC conditions.

Figure 3 shows \( \sigma_{PA} \) (left side) and \( \sigma_{Abs} \) (right side) of PbS QDs as functions of QD spacing on (a), (e) (001);
(b), (f) (110); (c), (g) (111) single crystal R-TiO\(_2\); and (d), (h) glass, respectively. Figure 3 shows that the values of
\( \sigma_{PA} \) on (a) (001) and (b) (110) surface are independent of QD spacing and have similar values to each other
(\( \sim 0.035 \)) although that on the (c) (111) surface decreases (\( \sim 0.06 \rightarrow \sim 0.04 \)) with increasing QD spacing,
indicating the peculiarity of the (111) surface. Figure 3 shows that \( \sigma_{Abs} \) on (e) (001) and (f) (110) surfaces
decreases (\( \sim 0.06 \rightarrow \sim 0.04 \)) although that on the (g) (111) surface increases (\( \sim 0.03 \rightarrow \sim 0.05 \)) with increasing
QD spacing, also indicating the peculiarity of the (111) surface. Figure 3(d) (on glass) shows that \( \sigma_{PA} \) is
independent of the QD-spacing (\( \sim 0.10 \)), a similar tendency to that obtained on (001) and (110) surfaces
although \( \sigma_{Abs} \) decreases (\( \sim 0.30 \rightarrow \sim 0.10 \)). The absolute values of \( \sigma_{PA} \) and \( \sigma_{Abs} \) on glass are higher than those of
R-TiO\(_2\), indicating the contribution from the different kinds of substrate are not only due to the difference in
thermal conductivity, but also the substrate is insulating (glass) or conductive (R-TiO\(_2\), in other words, without
or with electron transfer. These discrepancies between \( \sigma_{PA} \) and \( \sigma_{Abs} \) are even more striking due to the fact that
the PA spectra and Abs spectra are identical according to the R-G theory [40]. The discrepancies with respect to
QD spacing suggest that new insights into excitation and nonradiative processes can be obtained from PbS QD-
MAA ligands on R-TiO\(_2\) with different crystal orientations. The decreasing \( \sigma_{Abs} \) on (e) (001) and (f) (110)
surfaces, and (h) glass indicates the possibility of an increase in the orientational/positional disorder with
increasing QD spacing. The increasing \( \sigma_{Abs} \) on the (111) surface with increasing QD spacing suggests a decrease
in structural disorder on this surface due to the different occupancies of the elements at the surface (figure S1(c)).
For reference, the Urbach energy, \( E_U \) (defined as \( k_B T/\sigma \)), which indicates the width of the exponential tail in the
spectra [35], is provided (figure S5). If the temperature dependence of \( E_U \) can be measured, it is possible to
characterize the effects of the structural disorder and the thermal effect separately [65].
To discuss the difference between the absolute values and the dependences of $\sigma_{PA}$ and $\sigma_{Abs}$ on QD spacing, we assume the following relationship between $\sigma_{PA}$ and $\sigma_{Abs}$:

$$\sigma_{PA} = \frac{1}{\eta'} \sigma_{Abs}$$

(3)

where $\eta'$ is related to the parameter for heat generation by nonradiative processes. In the case of R-G theory, $\eta'$ is equal to 1 (that is, $\sigma_{PA} = \sigma_{Abs}$; standard case). To illustrate the meaning of $\eta'$, figures 3(a)–(c) show schematic
graphs of the ln(PA) and ln(Abs) intensities versus photon energy for the cases of (a) $\sigma_{PA} < \sigma_{Abs}$, (b) $\sigma_{PA} \approx \sigma_{Abs}$, and (c) $\sigma_{PA} > \sigma_{Abs}$, respectively. Figures 4(a)–(c) show that the parameter $\eta'$ corresponds to the cases, (a) $\eta' > 1$: higher heat generation, (b) $\eta' \approx 1$: standard case, and (c) $\eta' < 1$: lower heat generation, respectively.

Figures 4(d)–(g) show $\eta'$ for PbS QD-ligands as functions of QD spacing on (d) (001), (e) (110), (f) (111) surfaces, and (g) glass, respectively. The broken red lines in figures 4(d)–(g) correspond to $\eta' = 1$ (standard case). Figures 4(d)–(e) show that $\eta'$ on (d) (001) and (e) (110) surfaces decreases ($\sim 2.0 \rightarrow \sim 1.0$) with increasing QD spacing although that on (f) (111) surface increases ($\sim 0.5 \rightarrow \sim 1.1$), again indicating the peculiarity of the (111) surface. Figure 4(g) (on glass) shows that $\eta'$ decreases ($\sim 2.5 \rightarrow \sim 1.0$) with increasing QD spacing which indicates a similar tendency to the (001) and (110) surfaces. These results show that $\eta'$ depends on the crystal orientation of R-TiO$_2$ and the QD spacing. The reason why $\sigma_{PA}$ is constant on (001) and (110) surfaces, and glass (figure 3) is because $\eta'$ decreases with increasing QD spacing, $\sigma_{Abs}$ on (001) and (110) surfaces, and glass decreases with increasing QD spacing (figures 3(e), (f), (b)) which signifies the possibility of increasing structural disorder. However, a noteworthy point of these results is that the values of $\eta'$ on (001) and (110) surfaces, and glass are lower with higher QD spacing in spite of the lower $\sigma_{Abs}$. At higher QD spacing, the lower $\eta'$ corresponds to an increase in radiative processes with increasing QD spacing. In this respect, there is a report on the complementarity of the photoluminescence (PL) spectra of PbS QD-ligands on ZnO nanowires, in that the PL intensity increases monotonically with increasing QD spacing [15]. On the other hand, the reason why $\sigma_{PA}$ on the (111) surface decreases with increasing QD spacing (figure 3(c)) is the increase in $\eta'$. These results also indicate the distinctiveness of the (111) surface.
3.3. Relationship between free energy change and Urbach tail
In the next section, we discuss the relationship between the free energy change ($-\Delta G$) and the steepness parameter in Urbach tail. $-\Delta G$ is important for characterizing the electron transfer from the donor species (PbS QDs) to the acceptor species (R-TiO$_2$). To discuss the relationship between the electron transfer and the Urbach tail, the free energy change, $-\Delta G$, was estimated. In general, the electron transfer rate constant is proportional to the increase in $-\Delta G$ [28, 70]. There are multiple factors that can contribute to the overall change in $-\Delta G$, the free energy change for charging ($-\Delta G_{charge}$), that for Coulomb interactions ($-\Delta G_{Coulomb}$), and the change in electronic energy ($-\Delta G_{el}$) which accounts for the difference in energy between the initial and final electronic states ($-\Delta G = -\Delta G_{charge} + \Delta G_{Coulomb} + \Delta G_{el}$) [28, 70]. Of these three terms, only $\Delta G_{el}$ can be measured experimentally [70]. $\Delta G_{el}$ is defined to be the energy gap $\Delta E$ between the conduction band minimum (CBM) of R-TiO$_2$ and the first transition energy level of the PbS QD-ligands. It is thought that $\Delta G_{el}$ is influenced with the Coulomb interaction. For that purpose, PY spectroscopy was applied to determine the absolute values of the ground state energies of the PbS QD-ligands. The positions of these can be regarded as ionization energies on the basis of the intersection of the tangent to the spectra with the baseline (figure S6). Figures 5(a)--(c) show examples of the alignment of the ground state energy levels of PbS QD-3MPA, -6MHA, and -1MMDA on the (111) surface, together with the position of the valence band maximum (VBM) of R-TiO$_2$ (111). A similar alignment of the ground state energy levels of PbS QD-ligands on (001) and (110) surfaces can be obtained. The first transition energy levels of PbS QD-ligands were deduced from the PA/Abs characterizations of $E_i$. The QD spacing dependences of the ground state energy levels of PbS QD-ligands on (001), (110), and (111) surfaces are shown in figures 5(d)--(f). Figure 5(d) (001) and 5(e) (110) show that the ground state energy levels of PbS QD-ligands are independent of QD spacing within the limits of the experimental accuracy. In figure 5(f) (111), there is a shift upward to the vacuum level (positive polarization) with increasing QD spacing. The ground state energy level on the (111) surface is lower than those on the (001) and (110) surfaces, indicating more negative polarization due to the possibility of a higher proximity effect and stronger Coulomb interactions when the QD spacing decreases. These results also indicate the peculiarity of the (111) surface. The ground state energy levels of PbS QD-ligands on glass are independent of the QD spacing and they have a constant value ($\sim 5.7$ eV), similar to those on (001) and (110) surfaces, within the experimental accuracy. Toyoda et al. reported on DFT calculations for R-TiO$_2$ [28] with periodic boundary conditions which were carried out using a plane wave-based program, Castep [71, 72] (figure S7). The partial density of states (PDOS) of Ti 3d states (mainly occupying the conduction band) in R-TiO$_2$ (001) and (110) shows a broad structure between 1.6 and 6 eV. However, PDOS of Ti 3d states in R-TiO$_2$ (111) has a somewhat localized structure between 1.6 and 3.6 eV, indicating the possibility that the PDOS in R-TiO$_2$ (111) is higher than in the other crystal orientations ((001) and (110)). For that reason, there is a possibility of an enhancement in the overlap of the wavefunctions between the PbS-QDs and R-TiO$_2$ (111) which gives a higher proximity effect and stronger Coulomb interactions.

To determine $-\Delta G_{el}$ values for PbS QD-ligands on R-TiO$_2$ with different crystal orientations, the bandgap value of R-TiO$_2$ was set to 3.0 eV and the VBM values derived from the PY measurements were used to determine the CBM position for R-TiO$_2$ [27]. The QD spacing dependence of $-\Delta G_{el}$ for PbS QD-ligands on (001), (110), and (111) surfaces are shown in figures 5(g)--(i). Figure 5 shows that the values of $-\Delta G_{el}$ for PbS QD-ligands on (g) (001) and (h) (110) surfaces are independent of the spacing and are constant at around 1.0 eV, within the limits of experimental accuracy. On the other hand, that on the (i) (111) increases ($\sim 0.5 \rightarrow \sim 1.0$ eV) with increasing QD spacing. The absolute values of $-\Delta G_{el}$ on the (111) surface are lower than those on the (001) and (110) surfaces, indicating the possibility of a higher proximity effect and stronger Coulomb interactions. To study the correlation between the electron transfer processes and the Urbach tail, $\sigma_{PA}$ for (111) (●) is plotted as a function of $-\Delta G_{el}$ in figure 6(a). Also, $\sigma_{PA}$ for (001) (■) and (110) (■), both of which correspond to the nearly constant values of $-\Delta G_{el}$ shown in figures 5(g)--(h), and $\sigma_{PA}$ for glass (◆) are plotted in figure 6(a). Figure 6(a) shows that $\sigma_{PA}$ for the (111) surface decreases with increasing $-\Delta G_{el}$, indicating a correlation between the electron transfer processes [28, 70] and the Urbach tail. There is further evidence for the correlation between the electron transfer processes and the Urbach tail. That is, the values of $\sigma_{PA}$ for the (001) ($-\Delta G_{el} \sim 1.07$ eV) and (110) surfaces ($-\Delta G_{el} \sim 0.97$ eV) agree with that on the $\sigma_{PA}$ (111) line, indicating that there is a correlation between $\sigma_{PA}$ and $-\Delta G_{el}$.

3.4. Relationship between free energy change and parameter for heat generation
To study the correlation between the electron transfer processes and the parameter for heat generation, $\eta'$ for the (111) surface (●) is plotted as a function of $-\Delta G_{el}$ in figure 6(b). Also, $\eta'$ for the (001) (■), (110) (■) surfaces, and glass (◆) are plotted together in figure 6(b). The broken red line in figure 6(b) corresponds to $\eta' = 1$ ($\sigma_{PA} = \sigma_{Abs}$; standard case). Figure 6(b) shows that $\eta'$ increases with increasing $-\Delta G_{el}$, indicating a correlation between the electron transfer processes and $\eta'$. Here we assume that $\eta'$ is involved in two nonradiative processes: [1] deexcitation processes from the first transition energy levels of the PbS QD-ligands to the ground state.
energy levels via the CBM of R-TiO$_2$ (back electron transfer restoring the donor (PbS QDs) and acceptor (R-TiO$_2$) in their original level), and dec excitation processes from the first transition energy levels to the ground state energy levels directly. Figure 7 shows the energy diagrams of PbS QD-ligands on (001), (110), and (111) surfaces with increasing QD spacing $d$ (1) (0.3 nm), (2) (0.8 nm), (3) (2.1 nm) together with $\eta'$. In figure 7, $\eta'_1$ and $\eta'_2$ show the contributions from nonradiative processes [1] and [2], respectively, described above. We assume that $\eta'$ is the sum of $\eta'_1$ and $\eta'_2$ and is functions of $-\Delta G_{el}$ and $d$ as follows:

$$
\eta'(m) = \eta'_1(m) + \eta'_2(m) = \eta'_1(-\Delta G_{el}(m), d(m)) + \eta'_2(-\Delta G_{el}(m), d(m)), \quad (m = 1, 2, 3)
$$

where the symbol $m$ corresponds to the QD spacing ((1), (2), (3)). In the case of PbS-ligands on (001) and (110) surfaces, $-\Delta G_{el}$ is independent of the QD spacing (figures 5(g), (h)). Therefore, $\eta'$ in nonradiative processes [1] for different QD spacing are approximately equal: $\eta'_1(1) \approx \eta'_1(2) \approx \eta'_1(3)$. In contrast, from the experimental results in figures 4(d)–(e), $\eta'_2(m)$ depends on the QD spacing. Therefore, $\eta'$ in nonradiative processes [2] have the following relationship: $\eta'_2(1) > \eta'_2(2) > \eta'_2(3)$ with increasing QD spacing (figures 4(d)–(e)). In the case of PbS QD-ligands on the (111) surface, $-\Delta G_{el}$ increases with increasing QD spacing (figure 5(i)). Therefore, $\eta'$ in nonradiative processes [1] have the relationship $\eta'_1(1) < \eta'_1(2) < \eta'_1(3)$ with increasing $-\Delta G_{el}$. Also, the

**Figure 5.** Alignment of the energy levels of the PbS QD-ligands, (a) 3MPA, (b) 6MHA, and (c) 16MHDA on the (111) surface of R-TiO$_2$. QD spacing dependence of the ground state energy levels ((d)–(f)) and the free energy change $-\Delta G_{el}$((g)–(i)) on (d), (g)(001); (e), (h)(110); and (f), (i) (111) surfaces of R-TiO$_2$. 
possibility of smaller constant value in $\eta'_2(n)$ are conceivable for heat generation in nonradiative processes \{2\} with the increasing QD spacing. Although $\eta'_1$ on (001) and (110) surfaces are influenced only by the increase in QD spacing, that on the (111) surface is mainly influenced by the increases in $-\Delta G_{el}$. These results also indicate the distinctiveness of the (111) surface of R-TiO$_2$.

### 4. Conclusion

PA and Abs spectroscopies were used to characterize the overall optical absorption (excitation) and nonradiative (deexcitation) processes of ligand-linked PbS QDs adsorbed on R-TiO$_2$ substrates with different crystal orientations. A discrepancy between the PA and Abs spectra arises due to the fact that the heat generation probability is not constant but depends on the characteristics of the nonradiative processes which are different to those according to PA theory. Comparison between the Urbach tails in the PA and Abs spectra suggest that there are new insights to be gained.

Furthermore, the heat generation probability for the (111) surface is smaller than those for the (001) and (110) surfaces, indicating the peculiarity of the (111) surface of R-TiO$_2$, which arises because of the occupancies of the elements (Ti and O) at the surface being different to those at the (001) and (110) surfaces. This approach to the optical characterization of PbS QDs paves the way for further studies of other systems with different photoanodes, such as anatase-TiO$_2$ and ZnO. Characterization by ultrafast photoexcited carrier dynamics (by transient absorption and transient grating techniques) is desirable in order to understand the effect of the different crystal orientations on electron transfer and the electronic structure.
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Data availability statement

No new data were created or analysed in this study.

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