Photoinduced Charge Carrier Dynamics of Metal Chalcogenide Semiconductor Quantum Dot Sensitized TiO₂ Film for Photovoltaic Application

Safna Ravindi Padmaperuma¹, Maning Liu¹, Ryosuke Nakamura², and Yasuhiro Tachibana¹,²

¹ School of Engineering, RMIT University, Bundoora, VIC 3083, Australia
² Project Research Center for Fundamental Sciences, Faculty of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan
*yasuhiro.tachibana@rmit.edu.au; y.tachibana@uic.osaka-u.ac.jp

Semiconductor quantum dot (QD) sensitization is one of the most attractive structures to employ QDs for photovoltaic application. The function of QD sensitized solar cells (QDSSC) is controlled by the interfacial charge transfer dynamics. Here we employ transient absorption spectroscopy (TAS) to assess charge transfer dynamics at CdS QD/TiO₂ interface, and correlate their dynamics with their solar cell performance. An electron injection occurs from CdS QD conduction band to TiO₂ on ultrafast time scales, and the time constant decreases from ~10 ps to 1 ps, as the QD size decreases from 4 nm to 1.6 nm. Also, the charge recombination lifetime at the QD/TiO₂ interface increases, as the QD size increases. An absorbed photon to current conversion efficiency (APCE) of the QDSSC increases, as the QD size increases. Therefore, we conclude that the APCE of the CdS QDSSC is controlled by the interfacial charge recombination dynamics competing with dynamics of the hole transfer from the QD valence band to the reduced electrolyte. The optimum CdS QD size is close to or larger than 4 nm, as long as the light harvesting efficiency of the CdS QD sensitized film is sufficiently high.

Keywords: Electron injection, Charge recombination, CdS quantum dot sensitized TiO₂, Solar cells, Quantum dot size, Photocurrent generation efficiency

1. Introduction

Semiconductor quantum dot (QD) is one of the most attractive photoactive nanomaterials to be applied to optoelectronic devices such as light emitting diodes, lasers, optical sensors and solar cells.[1-7] For photovoltaics application, QDs are generally employed as a light absorber owing to their band gap tunability with their size, excellent photostability and their relatively high extinction coefficient.[8-12] Once QDs are assembled to form a QD solid film, it can also be employed as a charge transporting layer.

To design efficient QD based devices, it is extremely important to control charge carrier transfer dynamics at a QD/charge transport layer interface. To function as a solar cell, such an interface is designed to induce fast interfacial charge separation following light absorption by the QDs and subsequently to retard interfacial charge recombination (ICR), while the dissociated charge carriers are transported away from the interface. QD sensitization is the most suitable structure to understand a mechanism of their interfacial charge transfer dynamics and to identify an underlying key parameter to control and optimize the charge separation and recombination dynamics.

Metal chalcogenide QD sensitized solar cells (QDSSCs) have widely been developed over the last decade. A solar energy conversion efficiency of 5.4% was achieved by Kamat and coworkers by doping optically active transition metal ion (Mn²⁺) into CdS QDs to suppress interfacial charge recombination.[13] This metal ion (Mn²⁺) creates mid band gap states where the light generated electrons are trapped, but screened to prevent recombination with the generated holes in the QDs.
or reaction with the oxidized species in the electrolyte.[13, 14] Intensive studies have been conducted to develop highly efficient QDSSCs with a solar energy conversion efficiency of 12%[15], and recently, a significant improvement has been made with an efficiency of 15.3% by introducing a novel secondary deposition method resulting in MgCl2 solution treated Zn-Cu-In-S-Se QD sensitized TiO2 electrodes.[16]

The function of the QDSSC is initiated by an electron injection (EI) from a QD to the conduction band (CB) of n-type nanocrystalline metal oxide such as TiO2, following light absorption by the QD.[17] Upon light excitation, i.e. when the absorbed photon energy exceeds the band gap energy of the QD, an electron-hole pair (exciton state) is formed inside the QD, and then the EI reaction occurs from the QD CB to the TiO2 CB, before the electron-hole recombination occurs inside the QD. The injected electrons are readily transported inside TiO2 (n-type semiconductor) and collected by the FTO before recombined with the generated holes inside the QD or the oxidized electrolyte. Also before the ICR, the generated holes inside the QD are reduced by the electrolyte, and transported to the counter electrode.[18]

Extensive studies have been performed to investigate interfacial charge transfer processes, in particular EI[19, 20] and ICR[21] between a QD and TiO2 using transient absorption spectroscopy (TAS). The dynamics results confirm that the EI occurs on ultrafast time scales (typically on sub-picosecond to 100 ps),[20, 22-25] while ICR occurs on nanosecond to microsecond time scale.[23, 26, 27] However, despite these ample kinetic results and investigation to control the interfacial charge transfer reactions, no study has so far been conducted to correlate the interfacial charge transfer dynamics with the solar cell performance. Therefore, no study was reported to design interfacial structures to optimize QD size and solar cell performance.

In this paper, we employ CdS QD sensitized TiO2 films to investigate photo-induced charge transfer dynamics at the CdS QD/TiO2 interface, and to assemble and characterize a CdS QDSSC. The resultant dynamics will be correlated with the solar cell performance to identify an underlying key parameter to control a solar cell performance. The most suitable CdS QD size will be proposed to design an optimal solar cell structure.

2. Experimental

2.1. Materials

TiO2 paste (Solaronix SA, Ti-Nanoxide HT/SP) was purchased from Solaronix SA, Switzerland. Sulfur powder (99.98%), lithium perchlorate (LiClO4) (99.99%), Na2S·9H2O (≥98%), Cd(ClO4)2·xH2O, were purchased from Sigma-Aldrich, Australia, and ethanol (99.5%) was from ChemSupply, Australia, Al2O3 powder (Aeroxide Alu C, particle diameter: approximately 13 nm) was provided by Evonik Degussa GmbH, Australia. All chemicals were used without further purification.

2.2. Preparation of CdS QD attached nanoporous metal oxide films

A fluorine doped tin oxide (FTO) glass plate (15 × 25 mm2, 9 - 11 Ω/sq., Asahi Glass, type-U) was sonicated for 15 min in acetone. A transparent TiO2 nanocrystalline film (printed area: 0.25 cm2, film thickness: 6 µm) was prepared by screen-printing the TiO2 paste (Solaronix SA, Ti-Nanoxide HT/SP) on the FTO substrate. Al2O3 nanocrystalline films (thickness: 3.0 µm) were prepared by the same screen printer, but with a different printing mask, following the previously reported method.[26, 28] A CdS QD attached nanocrystalline film was prepared by using the “successive ionic layer adsorption and reaction” (SILAR) technique.[17, 29] One cycle was completed by dipping the film in 0.1 M Cd(ClO4)2 aqueous solution for 1 min, followed by rinsing in water and drying, and then dipping the film in 0.1 M Na2S aqueous solution for 1 min, followed by rinsing in water and drying. This sequential coating was repeated 5~25 cycles for the TiO2 film (CdS-5~25/TiO2) and 18 cycles for the Al2O3 film (CdS/Al2O3).

2.3. Solar cell fabrication

The sandwich cell was fabricated by binding a polysulfide electrolyte in a PET spacer (thickness 25 µm) with the QD sensitized TiO2 electrode and the Pt counter electrode.[17, 29] The polysulfide electrolyte was prepared by dissolving 3 M S, 2 M Na2S·9H2O, and 0.1 M LiClO4 in an ethanol/water mixture at a ratio of 1:4, and purged with N2 gas. All the steps involved in the solar cell fabrication were conducted under ambient conditions. The QDs in the solar cell are stable at least for several hours under the light irradiation in the laboratory.

2.4. Characterization of CdS QD sensitized films

Absorption spectra were measured by a UV/Vis absorption spectrometer (JASCO, V-670).
Morphology of the CdS QD sensitized film was observed by FE-SEM (Hitachi, S-5200).

2.5. Photovoltaic measurements

Performance of the solar cell was assessed by observing incident photon-to-current conversion efficiency (IPCE) spectra under the light irradiation with an irradiation aperture area of $4.8 \times 4.8 \text{ mm}^2$ using a photomask.[17, 29] The IPCE spectra were obtained by a monochromatic light source (Bunko-Keiki, SM-100) and a source meter (Keithley Instruments Inc.: 2400). A 0.5 cm$^2$ silicon photodiode was used to calibrate the monochromatic light intensity.

2.6. Transient absorption spectroscopy (TAS)

Femtosecond TAS measurements were conducted by an amplified mode-locked Ti:sapphire laser system operating at 1 kHz.[22] Pump pulses at 400 nm (3.1 eV) were generated by frequency doubling fundamental pulses in BBO crystal, while the femtosecond supercontinuum generated in a sapphire plate was used as broadband probe pulses. The spot sizes at sample position were 200 and 100 μm in diameter for pump and probe pulses, respectively. The pump pulse energy was adjusted to 40 nJ/pulse, which corresponds to about 100 μJ/cm$^2$ per pulse. The polarization of the pump pulse was set at the magic angle (54.7°) with respect to the probe pulse. The probe pulse after the sample was dispersed onto a diode array detector with a spectrometer. The output signals were digitized and collected at the repetition rate of the laser system (1 kHz). The pump beam was modulated at 500 Hz by a mechanical chopper, frequency locked to the laser pulse train. The group velocity dispersion (GVD) of the broadband probe pulse was estimated from the measurement of the cross-phase modulation in 1.0 mm quartz glass, and then, the data were corrected for GVD. The full width at half-maximum of the cross-correlation traces between the pump and probe pulses was 0.15 ps.

Sub-microsecond to millisecond transient absorption studies were conducted by a home-built transient absorption spectrometer with a Nd/YAG laser (Spectra Physics, QuantaRay GCR-11) pumped dye laser (Usho Optical Systems, DL100, ~10 ns pulse duration) as a pump pulse source, a 100 W tungsten lamp as a probe light source, a photodiode-based detection system (Cotronics Electronics), and a TDS-2022 Tektronix oscilloscope.[26] All transient data were collected by confirming identical excitation homogeneity and density of absorbed photons for all samples. An excitation wavelength was selected to 425, 480, 500, 515, and 520 nm for CdS-5, -10, -15, -20, and -25/TiO$_2$, respectively. The CdS/Al$_2$O$_3$ film was excited at 480 nm. The measurements were conducted with low pulse excitation energy densities (120–150 μJ/cm$^2$), corresponding to about 2 absorbed photons per TiO$_2$ nanoparticle, with a repetition rate of 1 Hz at 25 °C. This excitation energy adjustment was confirmed by setting ~2 mΔOD at 800 nm for the TiO$_2$ film sensitized by (tetrahydrofurazolium)$_2$cis-(2,2′-bipyridyl-4,-COOH,4′-COO⁻)-(NCS)$_2$-ruthenium (II), N719 (Solaronix), for each excitation wavelength.[30, 31] No change in the steady state absorption spectra before and after the transient experiments was observed, suggesting that the samples are stable during the optical experiments.

3. Results and discussion

3.1. Influence of CdS coating cycles on QD sizes

Fig. 1 shows absorption spectra of CdS QD sensitized TiO$_2$ films at different coating cycles. A shift of the absorption onset to a longer wavelength was observed with the increase of the coating cycle, indicative of “quantum size effect”, suggesting that the QD size increases with the increase of the coating cycle. An absorbance also linearly increases with the number of the coating cycles, suggesting that the amount of CdS inside the TiO$_2$ nanoporous structure increases almost linearly with the number of the coating cycle.

![Absorption spectra of CdS QD sensitized TiO$_2$ films](image_url)

**Fig. 1.** Absorption spectra of CdS QD sensitized TiO$_2$ films. The number in the figure indicates a coating cycle of the SILAR method to prepare in-situ CdS QDs inside the TiO$_2$ nanoporous structure.
Table 1. CdS QD size and electron transfer dynamics.

| Coating cycle | QD diameter / nm | QD surface coverage | EI time constant / ps | EI yield / % | ICR half lifetimes / µs | APCE at 400 nm / % |
|---------------|------------------|---------------------|-----------------------|-------------|------------------------|-------------------|
| 5             | 1.6              | 0.97                | 1.2                   | 96          | 0.5                    | 38                |
| 10            | 3.0              | 0.20                | 3.2                   | 90          | 4                      | 65                |
| 15            | 4.0              | 0.22                | 9.5                   | 80          | 25                     | 75                |
| 20            | 4.1              | 0.30                |                       |             | 40                     | 74                |
| 25            | 4.2              | 0.38                | 8.2                   | 81          | 50                     | 82                |

Fig. 2 shows FE-SEM images of a TiO$_2$ nanocrystalline film and a CdS QD sensitized TiO$_2$ film with 5 CdS coating cycles. The comparison clearly indicates the formation of CdS QDs on the TiO$_2$ surface (Fig. 2b). Although the QD can be recognized in the figure, it is not easy to estimate the average QD size formed on the TiO$_2$ surface. We therefore estimated average QD size in each film with XRD measurements.[26] The QD size was estimated by fitting the line widths ((111), (220) and (311) faces) of the CdS XRD spectra with Gaussian function, using the Debye-Scherrer formula. The results are summarized in Table 1. The results indicate that the CdS crystal size increases to about 4 nm with the number of coating cycles up to 15 cycles, and does not increase further with the extended coating cycles.[26]

Based on the reported relationship of the extinction coefficient with the CdS QD size,[12] using the absorption data shown in Fig. 1 and the average QD size summarized in Table 1, we estimated the coverage of the QDs on the TiO$_2$ nanoporous surface, assuming that the TiO$_2$ film is formed with close packing of the TiO$_2$ nanoparticles with the diameter of 20 nm, and all TiO$_2$ surface area is available for QDs to be occupied. The results are summarized in Table 1. In all films, less than 1 mono-particle layer of CdS QDs is formed on the TiO$_2$ nanoporous film.

3.2 Photo-induced charge transfer dynamics

We conducted TAS measurements for CdS sensitized TiO$_2$ films with the coating cycles ranging from 5 to 25 cycles, to observe influence of the coating cycles on interfacial charge transfer dynamics.

Fig. 3 shows transient absorption spectra of CdS QD sensitized TiO$_2$ films, observed at 0.2 and 100 ps, and 2 µs after the excitation. The spectrum of CdS QD attached Al$_2$O$_3$ film, observed at 2 µs after the excitation is included in Fig. 3c. The CdS/Al$_2$O$_3$ was used as a reference sample, as Al$_2$O$_3$ doesn’t thermodynamically accept an electron from the CdS QD CB. A weak positive absorption difference was observed for CdS QD attached Al$_2$O$_3$ film, attributed to the tail of the exciton states of CdS QDs. In contrast, a clear positive absorption difference with the maximum at 600-650 nm was observed at the excitation. The number indicates a coating cycle to prepare CdS QDs. Transient absorption spectrum of CdS QD attached Al$_2$O$_3$ is also shown as a reference in Fig. 2c.
100 ps and 2 µs after the excitation for the CdS/TiO$_2$ films. This positive broad absorption is assigned to absorption by trapped holes or S$^\cdot$ radical states in CdS QDs, thereby indicating a charge separated state (an electron in TiO$_2$ and a hole in CdS QD). The larger absorption difference was observed in the wavelength range of 800–950 nm, compared to the range of 550–720 nm in Fig. 3a, indicating that the charge separation at the CdS/TiO$_2$ interface occurs after 0.2 ps, but prior to 100 ps.

Fig. 4 shows ultrafast EI dynamics from the CB of CdS QD to that of the TiO$_2$, monitored at 650 nm, for the CdS QD sensitized films with different coating cycles ranging from 5 to 25 cycles. Note that such dynamics was not observed for the CdS/Al$_2$O$_3$ films. The EI time constant was evaluated by fitting all decay data with a global analysis, and the fitted result was summarized in Table 1. The results indicate that the EI occurs on <10 ps, but is faster with the smaller QD size. These observations are reasonable, since the thermodynamic driving force for the EI reaction, i.e. Gibbs free energy difference between the QD CB edge and the TiO$_2$ CB edge becomes larger, and the electronic coupling between the CdS QD CB edge and the TiO$_2$ CB edge also becomes larger with the decrease of the QD size.

The EI yield was calculated using Equation 1 by comparing the electron injection rate with the rate of the electron trapping in CdS QDs, assuming that the trapped electrons are not injected into TiO$_2$.

\[
EI \text{ yield} = \frac{1}{1 + \frac{\tau_{EI}}{\tau_{Trap}}}
\]  

where \(\tau_{EI}\) is the EI time constant, and \(\tau_{Trap}\) is the time constant of an electron trapped in the CdS QD. The results are shown in Table 1. The yield decreases with the increase of the coating cycle or the QD size, but the yield exceeds 80% at any QD size.

Fig. 5 shows transient decay dynamics measured at 650 nm for CdS QD/TiO$_2$ films ranging from 5 to 25 coating cycles. These multi-exponential kinetics indicate the ICR between the electron in TiO$_2$ and the hole in CdS QD. Since the identical number of photons is absorbed by CdS QDs for any film with different coating cycles upon the excitation, the difference in the decay dynamics must originate from the difference of the CdS QD size.

These decays were analyzed by fitting them with a stretched exponential function $\Delta OD(t) = \Delta OD_0 \cdot e^{-(t/\tau)^\alpha}$ and the half lifetimes (time taken for 50% of charge separated states to recombine) are included in Table 1. It is clear that the ICR occurs on nanosecond to microsecond time scales. The ICR was retarded by increasing the number of the coating cycles. These observations are reasonable, since the electronic coupling between the CdS QD valence band edge and TiO$_2$ CB edge becomes larger with the decrease of the CdS QD size (from 1.6 nm to 4 nm). Note that influence of the hole mobility between the CdS QDs on the ICR rate is...
negligible, as all films show less than 1 monoparticle layer coverage of CdS QDs on the TiO$_2$ surface.

3.3. Correlation of charge transfer dynamics with photocurrent generation efficiency

To investigate the influence of the coating cycle on the solar cell performance, we have fabricated a solar cell with CdS QD/TiO$_2$ films ranging from 5 to 25 coating cycles, Pt counter electrode and a polysulfide electrolyte (see Experimental for the details of the cell fabrication), and measured photocurrent generation under monochromatic light irradiation.

Fig. 6a shows their IPCE spectra. The IPCE increases with the number of the CdS coating cycles owing to increase of light harvesting efficiency (LHE). The highest IPCE of 65% at 400 nm was achieved with 25 coating cycles. Moreover, with the number of the coating cycles the IPCE onset shifted to longer wavelengths. This may be due to the band gap decrease resulting from QD size increase (quantum size effect), in agreement with the absorption onset shift to a longer wavelength, shown in Fig. 1.

Fig. 6b shows the absorbed photon to current conversion efficiency (APCE) at 400nm as a function of CdS QD size. The APCE was calculated with IPCE and LHE at the specified wavelength. The LHE of the cell was determined from the absorbance at the specified wavelength using Equation 2.

\[
LHE(\lambda) = 1 - 10^{-Absorbance(\lambda)} \quad (2)
\]

The APCE was then calculated with Equation 3, and the results are summarized in Table 1.

\[
APCE(\lambda) = IPCE(\lambda)/LHE(\lambda) \quad (3)
\]

The APCE value clearly increases with the increase of the QD size, however it reaches the maximum as the QD size increases to about 4 nm.

In Fig. 4 and Table 1, the EI completes in <10 ps, and the EI efficiency is greater than 80% at any QD size. These results suggest that the APCE is not limited by the EI process. In contrast, the ICR is retarded with the QD size increase (Fig. 5), and this retardation appears to influence the APCE value. Thus, it is reasonable to consider that the hole transfer from the QD valence band to the reduced electrolyte (S$_2^-$) competes with the ICR reaction at the CdS QD/TiO$_2$ interface, thereby determining the APCE.

From the current study, we have identified that controlling the ICR rate at the CdS QD/TiO$_2$ interface is the underlying key parameter to maximize the photocurrent generation, i.e. short circuit photocurrent density, $J_{SC}$. Since the CB edge of the bulk CdS is more negative by at least 200 mV than the TiO$_2$ CB edge,[26] the efficient EI is expected at the bulk CdS/TiO$_2$. The optimum CdS QD size is therefore close to or larger than 4 nm, as long as the LHE of the CdS QD sensitized film is sufficiently high.
4. Conclusion
We have employed transient absorption spectroscopy (TAS) to measure charge transfer reactions of CdS sensitized TiO2 films prepared by the SILAR method. We have investigated the influence of the coating cycles on electron injection (EI) rate, EI yield, interfacial charge recombination (ICR) rate, IPCE and APCE. The EI rate increased with the decreased QD size while the ICR was retarded with the increase of the CdS QD size. The APCE is mainly influenced by the ICR rate which competes with the transfer of the hole in CdS QD to the electrolyte. These observations suggest that the ICR process at the CdS QD/TiO2 interface is the most important factor determining the CdS QDSSC performance. Therefore, the optimum CdS QD size is close to or larger than 4 nm, as long as the LHE of the CdS QD sensitized film is sufficiently high.

Acknowledgement
This work was partly supported by JSPS KAKENHI Grants (JP16K05885) and (JP19H02813) and the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant number 2021-78), Japan. We also acknowledge supports from ARC DP fund (DP180103815), ARC LIEF fund (LE200100051) and ARC LIEF fund (LE170100235), Australia, and Project Research Center for Fundamental Sciences, Faculty of Science at Osaka University.

References
1. H. Zhang, Q. Su, and S. Chen, Nat. Commun., 11 (2020) 2826.
2. T. Kim, K.-H. Kim, S. Kim, S.-M. Choi, H. Jang, H.-K. Seo, H. Lee, D.-Y. Chung, and E. Jang, Nature, 586 (2020) 385.
3. J. Roh, Y.-S. Park, J. Lim, and V. I. Klimov, Nat. Commun., 11 (2020) 271.
4. J. Lim, Y.-S. Park, and V. I. Klimov, Nat. Mater., 17 (2018) 42.
5. K.-S. Cho, C.-W. Baik, H. Jeong, S. Hwang, K.-S. Cho, K. Heo, C.-W. Baik, S. Hwang, K. Heo, Y. Choi Jun, H. Jeong, and Y. Lee Sang, Nat. Commun., 8 (2017) 840.
6. J. Du, R. Singh, I. Fedin, A. S. Fuhr, and V. I. Klimov, Nat. Energy, 5 (2020) 409.
7. M.-J. Choi, F. P. García de Arquer, A. H. Proppe, A. Seifitokaldani, J. Choi, J. Kim, S.-W. Baek, M. Liu, B. Sun, M. Biondi, B. Scheffel, G. Walters, D.-H. Nam, J. W. Jo, O. Ouellette, O. Voznyy, S. Hoogland, S. O. Kelley, Y. S. Jung, and E. H. Sargent, Nat. Commun., 11 (2020) 103.
8. P. V. Kamat, J. Phys. Chem. C, 112 (2008) 18737.
9. S. Rühle, M. Shalom, and A. Zaban, Chem. Phys. Chem., 11 (2010) 2290.
10. L. Cademartiri, E. Montanari, G. Calestani, A. Migliori, A. Guagliardi, and G. A. Ozin, J. Am. Chem. Soc., 128 (2006) 10337.
11. I. Mora-Seró, S. Giménez, T. Moehl, F. Fabregat-Santiago, T. Lana-Villareal, R. Gómez, and J. Bisquert, Nanotechnology, 19 (2008) 424007.
12. W. W. Yu, L. Qu, W. Guo, and X. Peng, Chem. Mater., 15 (2003) 2854.
13. P. K. Santra and P. V. Kamat, J. Am. Chem. Soc., 134 (2012) 2508.
14. K. Zhao, Z. Pan, and X. Zhong, J. Phys. Chem. Lett., 7 (2016) 406.
15. A. Sahu, A. Garg, and A. Dixit, Solar Energy, 203 (2020) 210.
16. H. Song, Y. Lin, Z. Zhang, H. Rao, W. Wang, Y. Fang, Z. Pan, and X. Zhong, J. Am. Chem. Soc., 143 (2021) 4790.
17. R. M. Evangelista, S. Makuta, S. Yonezu, J. Andrews, and Y. Tachibana, ACS Appl. Mater. Interfaces, 8 (2016) 13957.
18. H. K. Jun, Careem, and A. K. Arof, Renew. Sus. Energy Rev., 22 (2013) 148.
19. I. Robel, V. Subramanian, M. Kuno, and P. V. Kamat, J. Am. Chem. Soc., 128 (2006) 2385.
20. J. L. Blackburn, R. J. Ellingson, O. I. Mićić, and A. J. Nozik, J. Phys. Chem. B, 107 (2003) 102.
21. H. J. Lee, J.-H. Yum, H. C. Leventis, S. M. Zakeeruddin, S. A. Haque, P. Chen, S. I. Seok, M. Grätzsel, and M. K. Nazeeruddin, J. Phys. Chem. C, 112 (2008) 11600.
22. R. Nakamura, S. Makuta, and Y. Tachibana, J. Phys. Chem. C, 119 (2015) 20357.
23. J.-W. Lee, S. Makuta, S. Sukarasep, J. Bo, T. Suzuki, T. Nakayama, H. Suematsu, K. Niihara, and Y. Tachibana, J. Photopolym. Sci. Technol., 29 (2016) 357.
24. K. Gopidas, M. Bohorquez, and P. V. Kamat, J. Phys. Chem., 94 (1990) 6435.
25. J. E. Evans, K. W. Springer, and J. Z. Zhang, J. Chem. Phys., 101 (1994) 6222.
26. Y. Tachibana, K. Umekita, Y. Otsuka, and S. Kuwabata, J. Phys. Chem. C, 113 (2009) 6852.
27. R. S. Dibbeld and D. F. Watson, J. Phys. Chem. C, 113 (2009) 3139.
28. S. Makuta, M. Liu, M. Endo, H. Nishimura, A. Wakamiya, and Y. Tachibana, Chem. Commun., 52 (2016) 673.
29. Y. Tachibana, H. Y. Akiyama, Y. Ohtsuka, T. Torimoto, and S. Kuwabata, Chem. Lett., 36
30. M. Liu, M. Endo, A. Shimazaki, A. Wakamiya, and Y. Tachibana, *ACS Appl. Energy Mater.*, 1 (2018) 3722.

31. M. Liu, S. Makuta, S. Tsuda, S. Russo, S. Seki, J. Terao, and Y. Tachibana, *J. Phys. Chem. C*, 121 (2017) 25672.