Structural Effects on the Incident Photon-to-Current Conversion Efficiency of Zn Porphyrin Dyes on the Low-Index Planes of TiO₂

Ryo Ide, Yamato Fujimori, Yukihito Tsuji, Tomohiro Higashino, Hiroshi Imahori, Hideki Ishikawa, Akihito Imanishi, Ken-ichi Fukui, Masashi Nakamura, and Nagahiro Hoshi

†Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
‡Department of Molecular Engineering, Graduate School of Engineering and §Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
¶Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

ABSTRACT: The structural effects of substrates on the incident photon-to-current conversion efficiency (IPCE) of Zn porphyrin (ZnP) dyes (ZnP-ref, YD2, and ZnPBAT) have been studied on well-defined single-crystal surfaces of rutile TiO₂ (TiO₂(111), TiO₂(100), and TiO₂(110)). IPCE of ZnP-ref depends on the structure of the substrates remarkably: TiO₂(100) < TiO₂(110) < TiO₂(111). IPCE of ZnP-ref/TiO₂(111) is 13 times as high as that of ZnP-ref/TiO₂(100) at 570 nm. YD2 and ZnPBAT also give the highest IPCE on TiO₂(111). The relative coverages of the porphyrin dyes give the following order: TiO₂(111) < TiO₂(110) < TiO₂(100). This order is opposite to that of IPCEs. The orientation of the dyes is predicted using density functional theory calculations on simplified models of TiO₂ surfaces. The highest IPCE on TiO₂(111) is attributed to the high rate of electron transfer through the space due to the fluctuation of the tilt angle of the adsorbed dyes.

INTRODUCTION

Power supply depends on fossil fuel at present, and emission of CO₂ causes global warming. A solar cell generates power using sunlight without any emission of CO₂; it is one of the most important technologies for building up a sustainable society.

Bell laboratories developed a Si solar cell in 1955. The power-conversion efficiency (η) of the Si solar cell is high; however, its production is expensive. TiO₂ also absorbs light and generates power. The cost of TiO₂ production is lower than that for Si. However, the band gap of TiO₂ is too large for solar cells based on a Ru complex dye-sensitized porous TiO₂ electrode with high values of η. Encouraged by these seminal studies, the DSSCs have attracted worldwide research interest in basic and practical aspects.

In recent years, the η-values of DSSCs based on push–pull-type porphyrin sensitizers have significantly increased and reached exceptionally high values of ca. 14%. However, the theoretical maximum η-value of DSSCs is predicted to be 25.6%, and the precise understanding of the relationships between the sensitizer and semiconductor is necessary to realize ideal photovoltaic performances. Imahori et al. previously reported that the rate of electron transfer depends on the orientation of the adsorbed Zn porphyrin (ZnP) dye on TiO₂ nanoparticles. Electron transfer between the porphyrin ring and TiO₂ occurs through the space, not through the spacer connecting the porphyrin ring to TiO₂. In fact, the orientation of the porphyrin sensitizer on the TiO₂ surface affects the electron injection and charge recombination processes and the resultant η-values. Accordingly, if the orientation of the dye molecule on the TiO₂ surface is suitably controlled, the η value may be enhanced dramatically. Well-defined single-crystal surfaces of TiO₂ are expected to control the orientation of adsorbed dyes. Previous papers report the shape effects on η, and electron transfer rates from dyes to the substrate using shape-controlled TiO₂ nanoparticles. However, a shape-controlled nanoparticle is composed of several kinds of faces, edges, and corners; it is difficult to determine the factors governing the structural effects clearly.
well-defined single-crystal surface is the best platform to study the structural effects precisely. Parkinson et al. reported pioneering studies using well-defined rutile and anatase TiO2 single-crystal surfaces. However, there has been no report on the structural effects on IPCE of ZnP dyes on single-crystal surfaces of TiO2.

In this article, the structural effects of the substrate on IPCE have been studied on the low-index planes of rutile TiO2 (TiO2(111), TiO2(100), and TiO2(110)). Although some papers reported basic study of DSSCs on natural anatase TiO2 single-crystal surfaces, we adopted rutile TiO2 single-crystal surfaces that can be obtained commercially. The adsorbed dye molecules are ZnP’s: 5,10,15,20-tetramesitylporphyrinatozinc(II) (ZnP-ref), ZnPBAT, and YD2. Molecular structures of these dyes are shown in Figure 1.

### RESULTS AND DISCUSSION

Figure 2 shows topographic scanning tunneling microscopy (STM) images (upper panels) and cross-sectional profiles (lower panels) of TiO2 in air. TiO2(100): I, (tunneling current) = 1.00 nA, Eb (bias voltage) = −159.5 mV; TiO2(110): I, = 0.84 nA, Eb = −518.7 mV; TiO2(111): I, = 0.83 nA, Eb = −451.0 mV.

The values of IPCE for ZnP-ref dye, IPCE increases in...
accord with the absorption spectrum of the dye on TiO$_2$(111) and TiO$_2$(110): ZnP-ref on TiO$_2$(111) and TiO$_2$(110) gives maximum of IPCE at 570 nm. However, IPCE on TiO$_2$(100) does not correlate with the absorption spectrum, giving the lower value than that on other surfaces between 450 and 650 nm. IPCE on ZnP-ref/TiO$_2$ (111) is 13 times as high as that on TiO$_2$ (100) at 570 nm.

In the cases of YD2 and ZnPBAT dyes, IPCE increases below 500 nm according to the increase of the absorbance of the dye molecules between 450 and 500 nm. IPCE is nearly 0.00% above 500 nm, although the absorbances of YD2 and ZnPBAT give maxima around 650 nm in the absorption spectra. These results differ from those of ZnP-ref. The coverages of YD2 and ZnPBAT may be lower than those of ZnP-ref on well-defined TiO$_2$ surfaces because of the large steric hindrance, resulting in zero IPCE, at which the absorbance of the dyes is lower.
The structural effects of the substrate on IPCE are summarized as follows:

ZnP-ref/TiO₂(hkl): TiO₂(100) < TiO₂(110) < TiO₂(111)

YD2/TiO₂(hkl): TiO₂(110) < TiO₂(100) < TiO₂(111)

ZnPBAT/TiO₂(hkl): TiO₂(110) < TiO₂(100) < TiO₂(111)

All of the ZnP’s examined give the highest IPCE on the TiO₂(111) surface. IPCE depends on the coverage as well as orientation of the dye molecules remarkably; we estimated the relative coverage of the dye molecules using X-ray photo-electron spectroscopy (XPS). We tried to determine the orientation of the dye molecules using STM; however, the dye molecules could not be imaged clearly. We could not find the height difference of the surface before and after the dye adsorption either. This fact indicates that the dyes may be adsorbed uniformly on well-defined TiO₂ surfaces without the formation of island-like structures. Thus, we predict the orientation of dye molecules using DFT calculations.

The relative coverages of ZnP’s on TiO₂(hkl) are estimated using the ratio of integrated XPS peak intensity of Zn 2p 3/2 to that of Ti 2p 3/2 (I(Zn 2p 3/2)/I(Ti 2p 3/2)). Neither the absolute coverages nor the amount of the dyes can be obtained using XPS because XPS signals from Zn and Ti are attenuated by carbon atoms in the dyes. The dye molecules examined contain different number of carbon atoms; thus, the degree of the attenuation of XPS signals cannot be estimated exactly. That is why we calculated relative coverages. Figure 7 shows the value of I(Zn 2p 3/2)/I(Ti 2p 3/2) normalized to that on TiO₂(100). All of the dyes give the following order of relative coverages: TiO₂(111) < TiO₂(110) < TiO₂(100). This tendency agrees with the previous reports that the (100) facet of the anatase TiO₂ nanoparticle adsorbs more dyes because the (100) facet has higher density of adsorption sites (5-coordinated Ti atom). Hard sphere models of rutile TiO₂ single-crystal surfaces (Figure 8) show that the density of 5-coordinated Ti atoms increases in the following order: TiO₂(111) < TiO₂(110) < TiO₂(100). Rutile TiO₂(100) surface uptakes more ZnP dyes as is the case of the anatase TiO₂(100) facet. However, the order of the relative coverage of ZnP dyes is completely opposite to that of IPCE. Aggregation of ZnP dyes quenches the excited state, giving lower η and IPCE on TiO₂ nanoparticles with irregular shapes. Lower IPCE on ZnP-ref/TiO₂(100) might be due to the higher coverage of the dye on TiO₂(100). However, in the cases of YD2 and ZnPBAT, the values of IPCE on TiO₂(100) are higher than those on TiO₂(110), although the coverages on TiO₂(110) are higher than those on TiO₂(111). These facts indicate that the other factors, such as orientation of the dye, may affect the IPCE remarkably.

ZnP dyes are known to be adsorbed on the TiO₂ surface via carboxyl group (−COO⁻). The ZnP dyes examined have one carboxyl group; thus, it is probable that the tilt angle of ZnP dyes changes on the TiO₂ surface easily.

Figure 9a shows the stabilization energy of ZnP-ref on TiO₂ single-crystal surface plotted against the tilt angle, which is defined as the angle between the surface and molecular axis, as shown in Figure 10. ZnP-ref has minimum stabilization energy at tilt angles of 110° and 90° on TiO₂(100) and TiO₂(110), respectively. However, the energy curve on TiO₂(111) gives a shallow potential minimum, showing that the molecular axis of ZnP-ref can be fluctuated between 70° and 110° almost freely, as shown in Figure 10. The vertical adsorption geometry of the dye on TiO₂(110) contrasts the report that the adsorbed dye molecules are tilted on TiO₂ nanoparticles, the shapes of which are not controlled. However, the geometry and the adsorption sites of adsorbates strongly depend on the structures of well-defined surfaces. For example, the sulfate/bisulphate anion is adsorbed in three-fold geometry on Pt(111), whereas the anion is adsorbed in two-fold geometry on Pt(100) and Pt(110). The surface structure of Pt affects the superstructure and adsorption site of CO remarkably. Cobalt(II) phthalocyanine gives an ordered layer on the unreconstructed Au(100) (1 × 1) structure; however, the ordered structure is not found on the reconstructed Au(100)-hex structure. It is probable that the adsorption angles of ZnP dyes on a well-defined TiO₂ surface differ from those on TiO₂ nanoparticles, the shapes of which are uncontrolled. We did not take interaction between dye molecules because the models are too large to be calculated using Gaussian 09. However, the results will indicate the tendency of the orientation of an adsorbed dye.

The porphyrin ring of ZnP-ref approaches the TiO₂(111) surface when it is tilted, enhancing the rate of electron transfer from the porphyrin ring to the TiO₂ surface through space.

![Figure 7. Relative intensity ratio of the XPS peak (Zn/Ti) in ZnP’s/TiO₂(hkl).](image-url)
Figure 8. Hard sphere models of the low-index planes of TiO\textsubscript{2} (top view).

Figure 9. Energy change in the adsorption orientation of TiO\textsubscript{2}.

Figure 10. Adsorption models of ZnP on the low-index planes of TiO\textsubscript{2}.
porphyrin ring and the TiO₂(110) surface, accelerating the rate of coverage of ZnP-ref on TiO₂(111) is 2.5 times as high as that on TiO₂(110). On the other hand, a slower injection rate decreases the coupling between the ZnP-ref cation and the injected electron; the rate of charge recombination gets lower, enhancing IPCE on TiO₂(110). Lower IPCE on TiO₂(110) indicates that decrease of IPCE due to the slower injection rate overwhelm the enhancement of IPCE by the slow charge recombination. The difference between the IPCEs of TiO₂(111) and TiO₂(110) can be attributed to the distance between the porphyrin ring and the surface.

The tilt angle of ZnP-ref is 110° on TiO₂(100) according to DFT calculations. IPCE on TiO₂(100) should be as high as that on TiO₂(111) because the distance between the porphyrin ring and the surface on TiO₂(100) is as long as that on TiO₂(111) (Figure 10). However, IPCE of ZnP-ref/TiO₂(100) is 1 order of magnitude lower than that of ZnP-ref/TiO₂(111). The coverage of ZnP-ref on TiO₂(100) is 2.5 times as high as that on TiO₂(111). ZnP-ref molecules may be aggregated due to the high coverage. The excited state of ZnP-ref is quenched, giving lower IPCE on TiO₂(100).

The stabilization energies of the YD2 and ZnPBAT dyes give a shallow potential curve between 70 and 100° on TiO₂(111) as is the case of ZnP-ref (Figure 9b,c). Thus, the highest IPCE of ZnP’s on TiO₂(111) is attributed to the free fluctuation of the porphyrin ring. The order of IPCEs of YD2 and ZnPBAT is TiO₂(111) < TiO₂(100), whereas ZnP-ref gives the opposite order: TiO₂(100) < TiO₂(111). On TiO₂(100), the tilt angles of YD2 and ZnPBAT (120°) are larger than that of ZnP-ref (110°). This larger tilt angle shortens the distance between the porphyrin ring and the TiO₂ surface, accelerating the rate of electron injection through space compared with that for ZnP-ref. Although absolute coverage of ZnP’s cannot be obtained using XPS, the higher IPCE of YD2 and ZnPBAT compared with that of ZnP-ref on TiO₂(100) may show that the coverages of ZnP-ref and YD2 are lower than those of ZnP-ref on TiO₂(100), leading to smaller aggregation tendency. On TiO₂(111), the stabilization energies of YD2 and ZnPBAT give minima around 80 and 100°, respectively; YD2 and ZnPBAT are adsorbed almost vertically as is the case of ZnP. Although we do not know the angle that changes the route of electron injection from space to spacer, the electrons of YD2 and ZnPBAT are assumed to be injected via the spacer to TiO₂(110). The spacers connecting the porphyrin ring and the carboxyl group of YD2 and ZnPBAT are longer than those of ZnP; the rates of electron injection of YD2 and ZnPBAT are lower than those of ZnP. Overlapping of the orbitals between LUMO on the carboxyl group and TiO₂ also affects the rate of charge recombination. DFT calculations show that the density of LUMO on the carboxyl group of ZnP-ref is lower than that of YD2 and ZnPBAT; the rate of charge recombination of ZnP-ref is lower than that of the other dyes. The lower rate of charge recombination also enhances the IPCE of ZnP-ref on TiO₂(110). The different order of IPCEs of YD2 and ZnPBAT compared with that of ZnP may be attributed to a larger tilt angle on TiO₂(100), smaller surface coverage, longer spacer distance, and difference in overlapping of orbitals.

Determination of the orientation of the adsorbed dye molecules is necessary for the elucidation of the origin of the structural effects of the IPCE as the discussion above is based on the calculations using simple models. We will carry out high-resolution STM and vibrational spectroscopy measurements of the adsorbed dyes on TiO₂ single-crystal surfaces in future.

### CONCLUSIONS

The IPCE of ZnP dyes depends on the surface structure of rutile TiO₂ remarkably as follows.

\[
\text{ZnP/TiO}_2(hkl): \quad \text{TiO}_2(100) < \text{TiO}_2(110) < \text{TiO}_2(111)
\]

\[
\text{YD2/TiO}_2(hkl): \quad \text{TiO}_2(110) < \text{TiO}_2(100) < \text{TiO}_2(111)
\]

\[
\text{ZnTBAT/TiO}_2(hkl): \quad \text{TiO}_2(110) < \text{TiO}_2(100) < \text{TiO}_2(111)
\]

All of the dyes give the highest IPCE on TiO₂(111). The order of relative coverages of the dyes is as follows: TiO₂(111) < TiO₂(110) < TiO₂(100), showing that the highest IPCE is not attributed to the coverage. DFT calculations indicate that the tilt angle of porphyrin dyes fluctuates almost freely on TiO₂(111). The highest IPCE on TiO₂(111) is ascribed to the short distance between the porphyrin ring and the TiO₂ surface when the dye is tilted: electron transfer between the porphyrin ring and the TiO₂ surface through space is enhanced due to the short distance.

### EXPERIMENTAL SECTION

Single-crystal wafers of rutile TiO₂ (10 mm × 10 mm, 1 mm thickness) doped with 0.05 wt % Nb were purchased from Furuchi Kagaku. These wafers were cut to (100), (110), and (111) orientations within an error of 0.5°. We prepared atomically flat TiO₂(hkl) surfaces using the method reported by Imanishi et al. Single-crystal wafers were chemically polished in 30 wt % HF solution for 10 h. Then, they were annealed at 600 °C for 10 h to obtain atomically flat surfaces. TiO₂ wafer was attached to a Pt plate using indium–gallium alloy to make an electric contact. The resistance of Nb-doped TiO₂ single crystal was lower than 20 Ω after annealing. We can image the surface structures of TiO₂ using STM, as shown below. Nb-doped TiO₂(100) and TiO₂(110) give clear (1 × 1) low-energy electron diffraction spots after the procedure, as shown in Figure S1.

These facts suggest that formation of an insulating Nb oxide layer is negligible. Although the preparation and cleaning procedures of TiO₂ surfaces differ from those reported previously, our procedure also gives reproducible results.

The surface structures of TiO₂ were imaged with a scanning tunneling microscope (STM) (Digital Instruments, NanoScope E) in air. A tungsten probe was prepared by electrochemical polishing of tungsten wire.

The relative coverages of the adsorbed dye molecules were investigated by XPS. The binding energies of the XPS peaks were calibrated using the C 1 s peak at 285.0 eV from residual carbon remained on TiO₂ surface. XPS spectra were obtained with a Kratos Axis Ultra spectrometer, with an Al Kα line (1486.6 eV) as the X-ray source. The emission current and anode voltage are 10 mA and 15.0 kV, respectively. All of the spectra were measured in 0° (normal) emission geometry.

The ZnP dyes, ZnP-ref, ZnPBAT, and YD2 were synthesized according to the literature. A single crystal of TiO₂ was heated at 100 °C for 30 min in air to dry the surface and...
immersed into ethanol solution of the dye for 12 h. The concentrations of ZnP-ref, YD2, and ZnPBAT in ethanol were 0.25, 0.20, and 0.20 mM, respectively.

The dye-modified single-crystal wafer of TiO2 with a Pt plate was mounted in a holder made of poly-(chlorotrifluoroethylene), with a hole for light irradiation. The counter electrode was a Pt plate. The structures of the cell and the holder are shown in Figure S2. The electrolyte solution was acetonitrile containing 0.15 M Lil. Light was irradiated to the dye-modified single-crystal surface of TiO2 using a Xe lamp (150 W) combined with a monochromator. IPCE was calculated according to the following formula

IPCE = \frac{\text{number of electrons of photocurrent}}{\text{number of photons of incident light}} = \frac{e I}{h c} \times 100

where I is the photocurrent, e is the elementary charge, W is the energy of incident light, h is the Planck constant, and ν is the frequency of incident light.

The energy of incident light was measured using a power meter (OPHIR PD300-UV-ROHS).

Density functional theory (DFT) calculations were carried out using Gaussian 09. The basis functions were 6-31G** for H, O, N, and C atoms and LANL2DZ for Zn and Ti atoms. The B3LYP hybrid function was used for exchange-correlational functionals. The molecular weights of the dyes examined are too large to perform DFT calculations using personal computer; we calculated the stabilization energy of the dye on TiO2 single-crystal surfaces using a simplified model as follows:

1. First, the structure of the dye is optimized using Gaussian 09.
2. The surface model is a cluster composed of the first layer of TiO2.
3. The structure-optimized dye is adsorbed on the surface model. The stabilization energy is calculated by changing the tilt angle of the dye.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00013.

AFM images and LEED patterns of Nb-doped TiO2 single crystal surfaces after chemical etching in HF and annealing at 600℃ in air (Figure S1); illustration of the cell and the holder of TiO2 single crystal (Figure S2) (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: hoshi@faculty.chiba-u.jp. Phone: +81-(43) 290-3384.

ORCID®

Yukihiro Tsuji: 0000-0002-0130-3471

Tomohiro Higashino: 0000-0002-9511-8569

Hirosi Imahori: 0000-0003-3506-5608

Nagahiro Hoshi: 0000-0001-5808-580X

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

**REFERENCES**

(1) Miyasaka, T., Ed. Photovoltaic Cells of New Concepts and Manufacturing Processes (in Japanese); CMC Publishing Co., Ltd: Tokyo, 2009.

(2) Prince, M. B. Silicon Solar Energy Converters. J. Appl. Phys. 1955, 26, 534–539.

(3) Li, L.-L.; Diau, E. W.-G. Porphyrin-Sensitized Solar Cells. Chem. Soc. Rev. 2013, 42, 291–304.

(4) Anderson, S.; Constable, E. C.; Dare-Edwards, M. P.; Goodenough, J. B.; Hannett, A.; Seddon, K. R.; Wright, R. D. Chemical Modification of a Titanium(IV) Oxide Electrode to Give Stable Dye Sensitization without a Supersensitizer. Nature 1979, 280, 571–573.

(5) Deslverest, J.; Grätzel, M.; Kavan, J.; Moser, J.; Augustynski, J. Highly Efficient Sensitization of Titanium Dioxide. J. Am. Chem. Soc. 1985, 107, 2988–2990.

(6) O’Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal Titanium Dioxide Films. Nature 1991, 353, 737–740.

(7) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. Conversion of Light to Electricity by cis-X2bis(2,2′-bipyridyl-4,4′-dicarboxylate)- ruthenium(II) Charge-Transfer Sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on Nanocrystalline Titanium Dioxide Electrodes. J. Am. Chem. Soc. 1993, 115, 6382–6390.

(8) Grätzel, M. Recent Advances in Sensitized Mesoscopic Solar Cells. Acc. Chem. Res. 2009, 42, 1788–1798.

(9) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. Chem. Rev. 2010, 110, 6695–6663.

(10) Barea, E. M.; Zafer, C.; Gultekin, B.; Aydin, B.; Koyuncu, S.; Icli, S.; Santiago, F. F.; Bisquert, J. Quantification of the Effects of Recombination and Injection in the Performance of Dye-Sensitized Solar Cells Based on N-Substituted Carbazole Dyes. J. Phys. Chem. C 2010, 114, 19840–19848.

(11) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. Dye-Sensitized Solar Cells with 13% Efficiency Achieved through the Molecular Engineering of Porphyrin Sensitizers. Nat. Chem. 2014, 6, 242–247.

(12) Yella, A.; Mai, C.-L.; Zakeeruddin, S. M.; Chang, S.-N.; Hsieh, C.-H.; Yeh, C.-Y.; Grätzel, M. Molecular Engineering of Push-Pull Porphyrin Dyes for Highly Efficient Dye-Sensitized Solar Cells: the Role of Benzene Spacers. Angew. Chem., Int. Ed. 2014, 53, 2973–2977.

(13) Higashino, T.; Imahori, H. Porphyrins as Excellent Dyes for Dye-Sensitized Solar Cells: Recent Developments and Insights. Dalton Trans. 2015, 44, 448–463.

(14) Urbani, M.; Grätzel, M.; Nazeeruddin, M. K.; Torres, T. Meso-Substituted Porphyrins for Dye-Sensitized Solar Cells. Chem. Rev. 2014, 114, 12330–12396.

(15) Yao, Z.; Wu, H.; Li, Y.; Wang, J.; Zhang, J.; Zhang, M.; Guo, Y.; Wang, P. Dithienopicenocarbazole as the Kernel Module of Low-Energy-Gap Organic Dyes for Efficient Conversion of Sunlight to Electricity. Energy Environ. Sci. 2015, 8, 3192–3197.

(16) Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.; Hanaya, M. Highly-Efficient Dye-Sensitized Solar Cells with Collaborative Sensitization by Silyl-Anchor and Carboxy-Anchor Dyes. Chem. Commun. 2015, 51, 15894–15897.

(17) Henry, J. S. Estimating the Maximum Attainable Efficiency in Dye-Sensitized Solar Cells. Adv. Funct. Mater. 2010, 20, 13–19.

(18) Imahori, H.; Umezaya, T.; et al. Photoinduced Charge Carrier Dynamics of Zn-Porphyrin-TiO2 Electrodes: the Key Role of Charge Recombination for Solar Cell Performance. J. Phys. Chem. A 2011, 115, 3679–3690.

(19) Ye, S.; Kathiravan, A.; Hayashi, H.; Tong, Y.; Infa saeng, Y.; Chabera, P.; Pascher, T.; Yartsev, A. P.; Isoda, S.; Imahori, H.; Sundström, V. Role of Adsorption Structures of Zn-Porphyrin on TiO2 in Dye-Sensitized Solar Cells Studied by Sun Frequency Generation Vibrational Spectroscopy and Ultrafast Spectroscopy. J. Phys. Chem. C 2013, 117, 6066–6080.
Formed by Self-Organized Photoetching. J. Phys. Chem. C 2007, 111, 3934–3937.
(38) Nakamura, R.; Ohashi, N.; Imanishi, A.; Osawa, T.; Matsumoto, Y.; Koimura, H.; Nakato, Y. Crystal-Face Dependences of Surface Band Edges and Hole Reactivity, Revealed by Preparation of Essentially Atomically Smooth and Stable (110) and (100) n-TiO2 (Rutile) Surfaces. J. Phys. Chem. B 2005, 109, 1648–1651.
(39) Hagfeldt, A.; Gratzel, M. Light-Induced Redox Reactions in Nanocrystalline Systems. Chem. Rev. 1995, 95, 49–68.
(40) SASAHARA, A.; TOMITOMI, M.; XPS and STM Study of Nb-Doped TiO2(110) (1 × 1) Surfaces. J. Phys. Chem. C 2013, 117, 17680–17686.
(41) YU, J. G.; Fan, J. J.; LV, K. L. Anatase TiO2 nanosheets with exposed (001) facets: improved photoelectric conversion efficiency in dye-sensitized solar cells. Nanoscale 2010, 2, 2144–2149.
(42) Hao, F.; Wang, X.; Zhou, C.; Jiao, X. J.; Li, X.; Li, J. B.; LIN, H. Efficient Light Harvesting and Charge Collection of Dye-Sensitized Solar Cells with (001) Faceted Single Crystalline Anatase Nanoparticles. J. Phys. Chem. C 2012, 116, 19164–19172.
(43) WENG, Y.-X.; LI, L.; LIU, Y.; Wang, L.; Yang, G.-Z. Surface-Binding Forms of Carboxylic Groups on Nanoparticulate TiO2 Surface Studied by the Interface-Sensitive Transient Triplet-State Molecular Probe. J. Phys. Chem. B 2003, 107, 4364–4363.
(44) Faguy, P. W.; Markovic, N.; Adzic, R. R.; Fierro, C. A.; Yeager, E. B. A Study of Bisulfate Adsorption on Pt(111) Single Crystal Electrodes Using In Situ Fourier Transform Infrared Spectroscopy. J. Electroanal. Chem. Interfacial Electrochem. 1990, 289, 245–262.
(45) Nart, F. C.; ISAWA, T.; WEBER, M. Vibrational Spectroscopy of Adsorbed Sulfate on Pt(111). Electrochim. Acta 1994, 39, 961–968.
(46) Nart, F. C.; ISAWA, T.; WEBER, M. Sulfate Adsorption on Well-Defined Pt(100) Electrodes. Electrochim. Acta 1994, 39, 2093–2096.
(47) ISAWA, T.; NART, F. C.; RODES, A.; Pastor, E.; WEBER, M. Vibrational Spectroscopy at the Electrochemical Interface. Electrochim. Acta 1995, 40, 53–59.
(48) Hoshiba, N.; Nakamura, A.; Yoneyama, T.; Uchida, H.; Watanabe, M. Structures of a CO Adlayer on a Pt(100) Electrode in HClO4 Solution Studied by In Situ STM. Chem. Commun. 2005, 2149–2152.
(49) Villegas, I.; Weaver, M. J. Carbon Monoxide Adlayer Structures on Platinum (111) Electrodes: A Synergy between In-Situ Scanning Tunneling Microscopy and Infrared Spectroscopy. J. Chem. Phys. 1994, 101, 1648–1660.
(50) Wakisaka, M.; Ohkanda, T.; Yoneyama, T.; Uchida, H.; Watanabe, M. Structures of a CO Adlayer on a Pt(100) Electrode in HClO4 Solution Studied by In Situ STM. Chem. Commun. 2005, 2149–2152.
(51) Wakisaka, M.; Ashizawa, S.; Yoneyama, T.; Uchida, H.; Watanabe, M. In Situ STM Observation of the CO Adlayer on a Pt(110) Electrode in 0.1 M HClO4 Solution. Langmuir 2010, 26, 9191–9194.
(52) Suto, K.; YOSHIMOTO, S.; Itaya, K. Electrochemical Control of the Structure of Two-Dimensional Supramolecular Organization Consisting of Phthalocyanine and Porphyrin on a Gold Single-Crystal Surface. Langmuir 2006, 22, 10766–10776.