Defect Density-Dependent Electron Injection from Excited-State Ru(II) Tris-Diimine Complexes into Defect-Controlled Oxide Semiconductors

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Supporting Information

ABSTRACT: Dye-sensitized solar cells and photocatalysts that consist of a light-absorbing dye and a wide gap oxide semiconductor substrate have been studied extensively as a means of solar energy conversion. Although defects existing at an oxide surface have a significant impact on the electron injection efficiency from the excited state dye-molecule into the oxide, the effects of defects on the electron injection process have not been fully understood in any dye-sensitized system. In this study, we present a systematic evaluation of electron injection into defects using emissive Ru(II) complexes adsorbed on oxide substrates $(HCa_2Nb_3O_{10} \text{ nanosheets and nonstoichiometric SrTiO}_{3-\delta})$, which had



different defect densities. Using these oxides, electron injection from adsorbed Ru(II) complexes was observed by time-resolved emission spectroscopy. It was shown that electron injection from the excited state Ru(II) complex into an oxide was influenced by the defect density of the oxide as well as by the excited state oxidation potential (E_{ox}^*) of the Ru(II) complex. Electron injection was clearly accelerated with increasing defect density of the oxide, and was inhibited with increasing electron density of the oxide because of a trap-filling effect. Even though the E_{ox}^* of the Ru(II) complex was more positive than the conduction band edge potential of the oxide, electron injection into defects could be identified when a defective oxide was employed. The electron injection event is discussed in detail, on the basis of the defect density and the energy levels of oxides as well as the E_{ox} * values of the Ru(II) complexes. Overall, the results suggest that it is possible to estimate the potential of surface defect states in oxide by changing E_{ox}^* of an emissive complex dye.

INTRODUCTION

Dye-sensitized solar cells (DSSC) and photocatalysts have been widely studied as a potential means of solar energy conversion.¹⁻¹⁰ Such dye-sensitization systems typically consist of a wide gap metal oxide material and dye molecules, which are adsorbed onto the oxide surface. The dye photosensitizers absorb visible light, and the excited electrons are transferred into the conduction band of the oxide material. The transferred electrons are consumed by (cathodic) reduction reactions, while the oxidized form of the photosensitizer is reduced by an electron donor to regenerate its original form.

It is well known that defects in metal oxides have a significant impact on dye-sensitized photocatalyst systems¹¹ as well as on the DSSC.^{9,10} Defects can work as traps for the injected electrons and reduce charge mobility significantly,⁸ thereby decreasing the efficiency of the desired process.¹⁰ Therefore, numerous efforts have been made to investigate the effects of defect formation on the efficiency, particularly in dyesensitized systems.^{9,10,12-17} For example, Dittrich and coworkers have shown that the energy conversion efficiency of a DSSC drops dramatically with increasing defect density of the TiO₂ substrate, which can be qualitatively controlled by heat treatment of TiO₂ under different oxygen partial pressures.¹⁰

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Some researchers have reported that electron injection from alizarin, C-343 dye or N3 dye into ZrO_2 could occur through the surface defect levels, even though the conduction band edge potential ($E_{\rm C}$) of ZrO_2 is significantly more negative than the excited state oxidation potential ($E_{\rm ox}^*$) of the dye molecule.^{18–20}

These early works about the influence of defects in oxide substrates on the electron injection process give rise to predictions of three different electron injection pathways, which depend on E_{ox}^* of the dye molecule and E_C of the oxide, as shown in Scheme 1. When E_{ox}^* of the dye molecule is more negative than $E_{\rm C}$ of the oxide, electron injection both into the conduction band and into defect levels can be observed (Scheme 1a). When E_{ox}^* of the dye molecule is more negative than the defect level but more positive than $E_{C_{r}}$ electron injection in principle occurs only into the defect level (Scheme 1b). When \hat{E}_{ox}^* of the dye molecule is more positive than the defect level, however, no electron injection from the dye molecule to the oxide is observed (Scheme 1c). These conjectures have not been quantitatively investigated so far, and the effects of defect density and the energy levels of electron-accepting defects on the electron injection efficiency have not been fully clarified.

The difficulty in examining this question is at least in part due to the lack of a methodology to quantitatively control the density of defects in an oxide. In principle, one should prepare an oxide without varying any other physicochemical properties (e.g., chemical composition, crystal structure, surface area, and surface electronic structure), because the excited electrons in dye molecules are quite sensitive to the character of the substrate, particularly the details of interactions to the surface.^{13-15,19,21} For example, it is well known that the pH of the solution affects the electron injection efficiency from Re complex dyes into TiO₂ or SnO₂ because the pH varies the band edge potentials of the oxide substrate surface.²¹ In addition, Katoh and coworkers found that decreasing the quantity of surface-adsorbed water molecules reduced the electron injection efficiency measured in a nonaqueous environment, and claimed that the cause was an increase in Gibbs energy for electron injection due to the presence of protons surrounding the dye molecules at the substrate surface.²² These observations reinforce the need for substrate materials to be prepared with care so as to avoid any unknown factors that might influence the surface conditions.

In this study, we employed two oxide materials $(HCa_2Nb_3O_{10} \text{ nanosheets}^{11,23-26} \text{ and nonstoichiometric})$

+ V.B. SrTiO_{3-δ}²⁷) as substrates for evaluating electron injection from adsorbed Ru(II) tris-diimine type dyes into surface defects. The defect density of HCa₂Nb₃O₁₀ nanosheets can be controlled qualitatively by calcination of the host layered HCa₂Nb₃O₁₀ at different temperatures, while keeping an almost identical surface area.²⁶ The energy level of electronaccepting defects was evaluated by using three kinds of Ru(II) complexes on two different HCa₂Nb₃O₁₀ substrates synthe-

accepting defects was evaluated by using three kinds of Ru(II) complexes on two different HCa2Nb3O10 substrates synthesized at different temperatures. Our group recently reported that annealing a SrTiO₃ powder under oxygen partial pressurecontrolled atmosphere and subsequent quenching enabled the production of nonstoichiometric $SrTiO_{3-\delta}$ that had a controlled oxygen defect density while keeping other parameters such as crystallinity, (surface) chemical composition, morphology, and specific surface area unchanged.²⁷ Four kinds of $\text{SrTiO}_{3-\delta}$ substrates, which had different oxygen defect densities ranging from ~10¹⁵ to ~10¹⁹ cm⁻³, were used for evaluation of the effects of defect density on the electron injection by combining with two kinds of methylphosphonic acid-functionalized Ru(II) complexes. Using these two oxide materials and five Ru(II) complexes, electron injection from dye molecules into defects in the substrate was evaluated by means of time-resolved emission spectroscopy in a powder suspension system. Because time-resolved emission measurements with the time-correlated single-photon counting method is a powerful technique for observation of the first electron transfer after excitation,^{28,29} electron injection into defects can be observed. The overall effort makes it possible to evaluate the impact of defects on electron injection in terms of the density and energy levels of defects.

EXPERIMENTAL SECTION

Preparation of Oxide Materials. $HCa_2Nb_3O_{10}$ nanosheets were synthesized according to a procedure reported previously.²³ Briefly, a $KCa_2Nb_3O_{10}$ precursor was synthesized by the polymerized complex method³⁰ and subsequently annealed at different temperatures (1273 or 1673 K) for 2 h in air. The as-synthesized layered $KCa_2Nb_3O_{10}$ was subject to proton exchange with HNO_3 , followed by reaction with an aqueous TBA⁺OH⁻ solution (Aldrich Chemical Co., 40 wt % in H_2O) to exfoliate the layered structure. The resulting colloidal sheets were precipitated by adding HCl. Finally, the precipitates were dried in an oven at 343 K overnight.

The details of the synthesis of nonstoichiometric $\text{SrTiO}_{3-\delta}$ powder can be found in our previous paper, which includes the results of physicochemical characterization.²⁷ Briefly, an oxide

precursor of Sr and Ti was prepared by the polymerized complex method, followed by annealing at 1423 K for 2 h under controlled oxygen partial pressure. For precise control of the oxygen partial pressure, high-purity certified gases such as 10 ppm of O_2 balanced with Ar, dry air, dry H_2 , and humidified H_2 diluted with Ar were used.

Adsorption of Ru(II) Complexes. The Ru(II) complexes $[Ru(4,4'-X_2-bpy)_2(4,4'-(CH_2PO_3H_2)_2-bpy)](PF_6)_2$ (X = CH₃, CF₃; bpy = 2,2'-bipyridine) and $[Ru(4,4'-Y_2-bpy)_3](PF_6)_2$ (Y = H, CH₃, CF₃) were synthesized according to the previous literature methods with some modifications.³¹ It was confirmed by ¹H NMR spectroscopy, electrospray ionization mass-spectroscopy (ESI-MS), and UV–vis absorption spectroscopy that the complexes were successfully synthesized. Spectroscopic and electrochemical properties of the synthesized Ru(II) complexes are listed in Table 1 and Figure S1.

Table 1. Electrochemical Properties of Ru(II) Complexes

	potential/V	vs Ag/AgNO ₃	
Ru complex	E _{ox}	E_{ox}^{*a}	E_{00}/eV
Ru-CH ₃	0.78	-1.31	2.09
Ru-H	0.97 ^b	-1.13	2.10
Ru-CF ₃	1.34	-0.70	2.04
Ru-CH ₃ -P ^c	0.80	-1.18	1.98
Ru-CF ₃ -P ^c	1.21	-0.67	1.88

^{*a*}The oxidation potential of the excited state of a metal complex (E_{ox}^*) is calculated using the equation $E_{\text{ox}}^* = E_{\text{ox}} - E_{00}$ according to the Franck–Condon analysis.³² ^{*b*}From ref 33. ^{*c*}From ref 11.

The Ru(II) complexes without anchoring groups (Ru-CF₃, Ru-H, Ru-CH₃; see Chart 1) were adsorbed onto $HCa_2Nb_3O_{10}$ nanosheet by impregnation and the following stirring method. A substrate powder was dispersed by stirring in an acetonitrile or methanol (Kanto Chemical Co., >99.8%) solution containing the Ru(II) complex, followed by evaporation of the solvent. Acetonitrile was distilled over

Chart 1. Ru(II) Complexes Used as Photosensitizers in This Work

 P_2O_5 twice, and then distilled over CaH_2 prior to use. The resulting powder was stirred magnetically in water for one day. The suspension was filtered and the collected powder was dried in an oven at 343 K overnight. The amount of adsorbed Ru(II) complex on a given substrate was estimated by using the following equation

adsorbed amount
$$(\mu \text{mol g}^{-1})$$

= $\frac{A_{\text{before}} - A_{\text{after}}}{A_{\text{before}}} \cdot \frac{C \ (\mu \text{mol } \text{L}^{-1}) \times V \ (\text{L})}{M \ (\text{g})}$ (1)

where A_{before} and A_{after} indicate the absorbance of the Ru(II) complex in a test solution at the ¹MLCT maximum wavelength before and after the adsorption procedure, *C* is the concentration of the complex in the solution before adsorption, *V* is the volume of the Ru(II) complex-containing solution, and *M* is the weight of the substrate powder, respectively. These Ru(II) complexes could be adsorbed onto the HCa₂Nb₃O₁₀ nanosheet surface by electrostatic attraction because the surface of the material is negatively charged.^{5,24}

Because it was difficult to adsorb Ru(II) complexes on the SrTiO_{3- δ} surfaces by electrostatic attraction, methylphosphonic acid-functionalized Ru(II) complexes were used. These Ru(II) complexes (**Ru-CF₃-P** and **Ru-CH₃-P**) were adsorbed by a stirring method. The substrate powder was suspended in acetonitrile containing a Ru(II) complex. After it was stirred magnetically overnight, the suspension was filtered, and the resulting powder was collected. Finally, the collected powder was dried in an oven at 343 K overnight. The amount of adsorbed Ru(II) complex on a given substrate was estimated by using eq 1. All these Ru(II) complexes adsorbed on oxide substrates were persistently bound and very little could be desorbed by rinsing with acetonitrile solution.

Characterization. The prepared substrate powders were studied by powder X-ray diffraction (XRD; MiniFlex 600 Rigaku; Cu K α) and UV-visible diffuse reflectance spectros-copy (DRS; V-670, Jasco). The Brunauer-Emmett-Teller





Figure 1. UV-vis DRS of Ru(II) complex adsorbed $HCa_2Nb_3O_{10}$ and $SrTiO_{3-\delta}$ powders.

(BET) surface area was measured by using a gas adsorption apparatus (MicrotracBEL, BELSORP-mini) at liquid nitrogen temperature (77 K). The absorption and emission of the Ru(II) complexes were measured by using UV-visible absorption spectroscopy (V-565, Jasco and Cary 6000i UV-Vis-NIR, Agilent Technologies) and spectrofluorometry (Fluorolog-3-21, Horiba and FP-8600, Jasco).

Time-Resolved Emission Spectroscopy. Time-resolved emission spectroscopy measurements were conducted with a time-correlated single-photon counting system (Horiba Jobin Yvon, FluoroCube, the excitation source: NanoLED-440L or nanoLED-455) at room temperature. A sample was dispersed in an acetonitrile solution (4 mL) in a Pyrex cell and purged with Ar for 20 min before the emission measurements. A nanoLED-440 or nanoLED-455 light source was used for excitation of the sample at 444 or 456 nm, and the emission at 710 or 750 nm was detected.

RESULTS

Characterizations of Oxide Substrates. $KCa_2Nb_3O_{10}$ powders were prepared by the polymerized complex method. The XRD patterns of layered $KCa_2Nb_3O_{10}$ after annealing at two different temperatures show clear differences in the peak intensities and full width at half-maximum (FWHM) between the two materials (Figure S2a). The diffraction peaks of the 1673 K-annealed specimen are sharper and more intense compared to the 1273 K-annealed one, indicating that the 1673 K specimen has higher crystallinity, and hence has lower defect density than the 1273 K specimen. These $KCa_2Nb_3O_{10}$ materials were subjected to proton exchange, followed by exfoliation with TBA⁺OH⁻ to colloidal nanosheets. Finally, the nanosheets were restacked by HCl. The exfoliating and restacking procedure resulted in very broad XRD patterns, as compared to the parent layered materials, reflected the

turbostratic structure of the restacked sheets. This is an indication that exfoliation and restacking were successfully achieved.²³ The HCa₂Nb₃O₁₀ nanosheets had similar specific surface areas (1273 K; 46 m² g⁻¹, 1673 K; 52 m² g⁻¹) and optical properties (Figure S2b). The absorption edges of both oxides are around 350 nm, which correspond to 3.5 eV. The defect density of the materials was qualitatively controlled by the final annealing temperature (1273 and 1673 K) in the polymerized complex procedure.²³ It is known that high-temperature annealing can decrease the density of oxygen defects in oxides due to crystal growth.³⁴ This has been confirmed to be the case for HCa₂Nb₃O₁₀, even after exfoliation and restacking.²⁶

The oxygen defect density, $[V_0]$, of $SrTiO_{3-\delta}$ powders was calculated from the annealing oxygen partial pressure, $p(O_2)$, according to the previous report.²⁷ Table S1 lists the annealing conditions and defect densities of the synthesized $SrTiO_{3-\delta}$. Reduced $SrTiO_{3-\delta}$ powders have quite similar physicochemical properties (e.g., crystallinity, specific surface area, particle size distribution, and so on),²⁷ but their optical properties are different (Figure S3). While the intrinsic band gap absorption at around 380 nm remains unchanged, absorption in the visible region is enhanced with an increase in defect density. This is because electron density in $SrTiO_{3-\delta}$ is increased accompanied by the oxygen defect formation (as represented in Kröger–Vink notation,³⁵ eq 2).

$$O_0^{\times} = V_0^{\cdot} + e^{\prime} + \frac{1}{2}O_2$$
 (2)

Characterization of Ru(II) Complex-Adsorbed Oxide Substrates. The adsorption of the Ru(II) complexes onto oxide substrates was performed by impregnation and/or stirring method. UV-vis DRS of a Ru(II) complex/substrate is shown in Figure 1, along with the adsorption amounts of the Ru(II) complexes, which were measured by UV-visible



Figure 2. Emission decay profiles of (a) Ru-CH₃, (b) Ru-H, and (c) Ru-CF₃ on HCa₂Nb₃O₁₀ powders with 444 nm excitation, monitored at 750 nm.



Figure 3. Emission decay profiles of (a) Ru-CH₃-P and (b) Ru-CF₃-P on SrTiO_{3- δ} powders with 444 nm excitation, monitored at 750 nm.

absorption spectroscopy using the filtrate after adsorption, in the case of HCa₂Nb₃O₁₀ substrates. When SrTiO_{3- δ} was used as the substrate, Ru(II) complexes underwent adsorption almost quantitatively (3 µmol g⁻¹). All of the synthesized Ru(II) complex/substrate composites show visible light absorption at around 400–500 nm, attributed to ¹MLCT transition of the corresponding Ru(II) complexes. These absorption shapes were hardly changed with respect to the annealing temperatures of HCa₂Nb₃O₁₀ and [V_O] of SrTiO_{3- δ}, indicating that the light absorption properties were independent of the surface defect density.

Time-Resolved Emission Measurement. Time-resolved emission measurements were conducted using Ru(II) complex/oxide powders. Figures 2 and 3 show decay curves of emission intensity recorded at 750 nm. The average emission lifetimes are listed in Tables 2 and 3. The observed emission arises solely from the photoexcitation of Ru(II) complexes because the pump laser cannot induce band gap excitation of the oxide substrates. More concretely, the emission originates largely from the lowest ³MLCT excited state of Ru(II)

Table 2. Emission Lifetimes of Ru-CH₃, Ru-H, and Ru-CF₃ Adsorbed on HCa₂Nb₃O₁₀ Powders

	$ au_{ m average}$ and ns		
annealing temperature/K	Ru-CH ₃	Ru-H	Ru-CF ₃
1273	370	480	820
1673	350	610	850
	720 ^b	750 ^b	1340 ⁶

 ${}^{a}\tau_{\text{average}} = \sum_{i=1}^{n} A_{i} \tau_{i}^{2} / \sum_{i=1}^{n} A_{i} \tau_{i}^{, b}$ Data recorded in acetonitrile solution without adsorption on any oxide substrates.

Table 3. Emission Lifetimes of Ru-CH₃-P and Ru-CF₃-P Adsorbed on SrTiO_{$3-\delta$} Powders

	$ au_{ m average}^{a}/ m ns$	
oxygen defect density, $[V_O]/cm^{-3}$	Ru-CH ₃ -P	Ru-CF ₃ -P
1.5×10^{15}	430	240
9.4×10^{16}	400	180
4.5×10^{18}	380	170
6.2×10^{19}	390	190
	690 ^b	470^{b}

 ${}^{a}\tau_{\text{average}} = \sum_{i=1}^{n} A_{i}\tau_{i}^{2} / \sum_{i=1}^{n} A_{i}\tau_{i}$, ^bData recorded on Al₂O₃ by monitoring emission intensity at 710 nm with the use of a nanoLED-455 light source for excitation of the sample at 456 nm.

complexes because of the time resolution of our apparatus (>0.2 ns).³⁶ Figure 2 shows the emission decay curves of **Ru-CH₃**, **Ru-H**, and **Ru-CF₃** complexes on HCa₂Nb₃O₁₀ in acetonitrile suspensions. The emission decay curves from **Ru-CH₃** and **Ru-CF₃**-adsorbed on HCa₂Nb₃O₁₀ nanosheets were almost identical, regardless of the annealing temperature of the substrate powders (Figure 2a,c). **Ru-H**-adsorbed nanosheets, however, showed different emission decay behaviors. The HCa₂Nb₃O₁₀ nanosheet synthesized at lower temperatures exhibited more pronounced emission decay (in other words, shorter emission lifetime) than the higher temperature one, indicating that more efficient electron injection occurred in the former case.

Figure 3 shows emission decay curves from Ru-CH₃-P and Ru-CF₃-P complexes on SrTiO_{3- δ} in acetonitrile. As shown in Figure 3a, the emission decay from the Ru-CH₃-P/SrTiO_{3- δ} was accelerated with increasing [V₀] up to 4.5 × 10¹⁸ cm⁻³. The faster decay indicates more efficient electron injection

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Scheme 2. Energy Diagrams of Ru(II) Complex/HCa₂Nb₃O₁₀ and Ru(II) Complex/SrTiO_{3- δ} Samples Having (a) Low and (b) High Density of Defects in HCa₂Nb₃O₁₀ and (c) Low, (d) Intermediate, and (e) High Density of Defects in SrTiO_{3- δ}



from the excited state of **Ru-CH**₃-**P** into the semiconductor powder. On the other hand, the **Ru-CF**₃-**P**/SrTiO_{3- δ} samples showed different emission decay behaviors. Because E_{ox}^* of **Ru-CF**₃-**P** is more positive than E_C of SrTiO₃ (-1.16 V vs Ag/ AgNO₃),³⁷ one might expect the emission lifetime to remain unchanged. However, the emission lifetime was obviously shortened by increasing $[V_O]$ in SrTiO_{3- δ} (Table 3). The emission decay was accelerated with increasing $[V_O]$ up to 4.5 $\times 10^{18}$ cm⁻³, while in the $[V_O] = 6.2 \times 10^{19}$ cm⁻³ sample, the decay behavior became a little slower (Figure 3b). The longer emission lifetime indicates the deceleration of electron injection from **Ru-CF**₃-**P** into SrTiO_{3- δ}.

DISCUSSION

The data presented above show that the emission lifetime of Ru(II) complexes adsorbed on oxides clearly depends on the defect density of the oxide. The difference in the emission lifetime arises from different electron injection rates from the excited-state Ru(II) complex to the oxide surface.^{11,26} The behavior of the emission decay of Ru(II) complexes on $HCa_2Nb_3O_{10}$ can be rationalized from the model shown in Scheme 2, given that the $HCa_2Nb_3O_{10}$ samples annealed at lower temperature should have a higher density of defects (Scheme 2b) than the higher temperature ones (Scheme 2a).²⁶

The **Ru-CH**₃ adsorbed samples exhibited almost identical decay curves (Figure 2a). **Ru-CH**₃ has the most negative E_{ox}^* (-1.31 V vs Ag/AgNO₃; Table 1), which is more negative than the $E_{\rm C}$ of HCa₂Nb₃O₁₀ (-1.13 V).¹¹ Therefore, in the case of **Ru-CH**₃, we deduce that electron injection into HCa₂Nb₃O₁₀ (both into the conduction band and defect levels) should occur efficiently regardless of the defect concentration.

In contrast to **Ru-CH**₃, emission decay rates of **Ru-H**/ HCa₂Nb₃O₁₀ varied with respect to the calcination temperature (Figure 2b). Because the E_{ox}^* of **Ru-H** is almost the same as E_C of HCa₂Nb₃O₁₀, electron injection from the excited state of **Ru-H** into the conduction band of HCa₂Nb₃O₁₀ is not very efficient, and injection into defect levels is more likely to occur. As mentioned earlier, it is likely that $HCa_2Nb_3O_{10}$ synthesized at lower temperature contains more defects than the high-temperature samples.^{23,26} This idea is reasonably supported by the faster emission decay of the lower temperature calcination sample. In other words, the emission decay becomes faster when the density of defects in an oxide substrate is high.

When \mathbf{Ru} - \mathbf{CF}_3 was used as a photosensitizer, electron injection into the conduction band is not expected to be competitive with other excited state decay pathways because E_{ox}^* of \mathbf{Ru} - \mathbf{CF}_3 is more positive than E_C of $\mathbf{HCa}_2\mathbf{Nb}_3\mathbf{O}_{10}$. In this case, the identical decay curves of the \mathbf{Ru} - \mathbf{CF}_3 -adsorbed specimens shown in Figure 2c imply that relatively little electron injection into defect levels occurred as well. This consideration is supported by the longest emission lifetime of the \mathbf{Ru} - \mathbf{CF}_3 -adsorbed samples (Table 2).

On the basis of the discussion above, the electron-accepting defect levels of $HCa_2Nb_3O_{10}$ can be estimated to exist between E_{ox}^* of **Ru-H** and **Ru-CF**₃ (-1.13 to -0.70 V vs Ag/AgNO₃); in other words, ~0.4 V below the conduction band. The estimated defect levels are in good agreement with those reported in earlier reports, which claimed that the electron-accepting levels exist at 0.2–0.4 V below the conduction band.^{20,38}

A more quantitative analysis of the relationship between defect density and the electron injection from excited-state Ru(II) complexes is possible by using nonstoichiometric SrTiO_{3- δ}. The defect density of SrTiO_{3- δ} increases with increasing [V_O], and it is accompanied by an increase in electron density (eq 2). In a previous report, a trap-filling effect due to electron doping was observed by transient absorption spectroscopy.^{27,39} Schematic band diagrams, including trap levels formed by defect states and trap-filling with doped electrons, are depicted in Scheme 3. Previous transient absorption spectroscopy experiments revealed that an increase in [V_O] creates a new trap level just below the conduction

Scheme 3. Schematic Band Energy Diagram Showing Defect Levels in $SrTiO_{3-\delta}$, As Evidenced by Transient Absorption Spectroscopy²⁷



band edge (shallow traps) and that the doped electrons are trapped at the deepest available defect levels.²⁷

Keeping this in mind, the electron injection process from excited-state Ru(II) complexes to SrTiO_{3- δ} substrates can be understood, as shown schematically in Scheme 2c-e, to depend on the relative electron density of SrTiO_{3- δ} and E_{ox}^* of the Ru(II) complex. When Ru-CH₃-P was adsorbed onto SrTiO_{3- δ} substrates, the emission decay was more pronounced with increasing $[V_0]$ up to 4.5×10^{18} cm⁻³, and then remained unchanged upon further increase of $[V_0]$ (Figure 3a). The conduction band and defect levels of $SrTiO_{3-\delta}$ can accept electrons from photoexcited Ru-CH₃-P in all cases, because E_{ox}^* of Ru-CH₃-P (-1.18 V vs Ag/AgNO₃) is more negative than $E_{\rm C}$ of SrTiO₃ (-1.16 V), as depicted in Scheme 2c-e. The emission decay curve of the $[V_0] = 6.2 \times 10^{19} \text{ cm}^{-3}$ sample was almost identical to that of the $[V_{\rm O}]$ = 4.5 \times 10^{18} cm⁻³ one, probably because the electron-accepting trap levels were filled with electrons in the highest defect density sample $([V_0] = 6.2 \times 10^{19} \text{ cm}^{-3})$. In the $[V_0] = 6.2 \times 10^{19} \text{ cm}^{-3}$ sample, deep trap levels could not accept electrons from excited state Ru-CH₂-P due to electron filling, but the increased density of shallow trap levels could do so (Scheme 2e). The balance of decreasing and increasing electronaccepting levels can thus result in nonmonotonic emission decay behavior with respect to $[V_{\Omega}]$.

On the other hand, because E_{ox}^* of Ru-CF₃-P (-0.67 V vs Ag/AgNO₃) is more positive than $E_{\rm C}$ of SrTiO_{3- δ}, the electron that is generated by photoexcitation of Ru-CF3-P cannot be transferred into the conduction band of $SrTiO_{3-\delta}$. Therefore, the acceleration of emission decay with increasing [Vo] (Figure 3b) suggests electron injection into deep trap states. This is supported by the fact that the sample having $[V_0] = 1.5$ \times 10¹⁵ cm⁻³ showed a particularly long emission lifetime compared with the others (Table 3). In this case, the excited state of Ru-CF₃-P should undergo deactivation by radiative and nonradiative processes without electron injection into the oxide, because the sample has a lower density of defects that can accept electrons. With higher defect density samples, however, the acceleration of emission decay was clearly observed up to $[V_0] = 4.5 \times 10^{18} \text{ cm}^{-3}$. The deceleration of emission decay in the sample having $[V_0] = 6.2 \times 10^{19} \text{ cm}^{-3}$ probably arose from the filling of deep trap levels by doped electrons, as discussed above. It is reasonable that the filling of deep trap levels by doped electrons lowers the probability of electron injection into deep traps. In contrast to the Ru-CH₃-P case, the $[V_0] = 6.2 \times 10^{19} \text{ cm}^{-3}$ sample with Ru-CF₃-P had a

longer emission lifetime than those of the $[V_0] = 4.5 \times 10^{18}$ and 9.4 \times 10¹⁶ cm⁻³ samples. This is because electrons in photoexcited Ru-CF2-P could not be transferred to shallow traps, but only to traps that had more positive potential than E_{ox}^{*} of **Ru-CF₃-P** and were not completely filled with electrons (Scheme 2e). The results of emission decay measurements for the adsorbed Ru(II) complexes suggest a wide distribution of shallow trap levels, consistent with the transient absorption spectroscopy data.²⁷ We note that electron injection from Ru-CH₃-P and Ru-CF₃-P into traps can occur even in the defectpoor sample ($[V_0] = 1.5 \times 10^{15} \text{ cm}^{-3}$), as judged from shorter emission lifetimes than the same sensitizers adsorbed on insulating Al_2O_3 (Table 3). This is because the defect-poor sample also contains a certain amount of defects as revealed by earlier transient absorption spectroscopy measurements,² although the density should be much lower than that of the other more heavily doped samples. It is also noted that reductive quenching of the Ru complexes cannot occur in this system because $SrTiO_{3-\delta}$ has negligible reduction ability under visible light irradiation.

CONCLUSIONS

Electron injection from excited-state Ru(II) complexes into defects in an oxide semiconductor was clearly observed by means of time-resolved emission spectroscopy with two different metal oxide materials, $HCa_2Nb_3O_{10}$ and $SrTiO_{3-\delta}$. Using three different Ru(II) polypyridyl complexes and $HCa_2Nb_3O_{10}$ nanosheets that possessed different defect densities, the electron-accepting defect levels of $HCa_2Nb_3O_{10}$ could be estimated to exist ~0.4 V below the conduction band edge. Nonstoichiometric $SrTiO_{3-\delta}$ having a homogeneous distribution of defects and controlled defect density enabled us to establish the relationship between electron injection from excited-state Ru(II) complexes and defect density. Electron injection was accelerated with increasing defect density but was inhibited in a highly defective sample due to an increase in the doped electron density in $SrTiO_{3-\delta}$. (i.e., a trap-filling effect).

Thus, the present study highlights that electron-accepting energy levels of defects in oxide substrates can be estimated by time-resolved emission spectroscopy of emissive Ru(II) polypyridyl complexes that have different E_{ox}^* values. Carefully synthesized oxide substrates that possess controlled defect densities enable us to monitor trends in the efficiency of electron injection to defect levels in a more quantitative manner. While further design of dyes as emissive probes that have controlled E_{ox}^* values is necessary for precise estimation of defect levels, the present methodology that relies on emission spectroscopy of emissive metal complexes may become a new measure of defects that are present at the semiconductor surface. A quantitative analysis of the effect of surface defect on the electron transfer kinetics has not been performed due to the wide distribution of trap states but will be investigated further as part of our future works.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b09781.

Additional characterization data (PDF)

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Author Contributions

K.M. designed the project. S.N. conducted most of the experiments and analysis with K.M, O.I., and T.E.M. M.O. performed part of time-resolved emission measurements, R.M. performed part of emission spectroscopy measurements. Ya.Y., K.S., G.S., R.K., and D.S. synthesized and characterized Ru(II) complexes, T.O. prepared $\text{KCa}_2\text{Nb}_3\text{O}_{10}$. J.H. and Yo.Y. designed and prepared nonstoichiometric $\text{SrTiO}_{3-\delta}$. S.N. and K.M. wrote a draft of the manuscript. All authors discussed and provided comments on the experiments and the manuscript during preparation.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Houlding, V. H.; Grätzel, M. Photochemical H_2 Generation by Visible Light. Sensitization of TiO₂ Particles by Surface Complexation with 8-Hydroxyquinoline. *J. Am. Chem. Soc.* **1983**, *105*, 5695–5696.

(2) Shimidzu, T.; Iyoda, T.; Koide, Y. An Advanced Visible-Light-Induced Water Reduction with Dye-Sensitized Semiconductor Powder Catalyst. J. Am. Chem. Soc. **1985**, 107, 35–41.

(3) Furlong, D. N.; Wells, D.; Sasse, W. H. F. Colloidal Semiconductors in Systems for the Sacrificial Photolysis of Water: Sensitization of Titanium Dioxide by Adsorption of Ruthenium Complexes. J. Phys. Chem. A. **1986**, 90, 1107–1115.

(4) Kim, Y. I.; Salim, S.; Huq, M. J.; Mallouk, T. E. Visible Light Photolysis of Hydrogen Iodide Using Sensitized Layered Semiconductor Particles. J. Am. Chem. Soc. **1991**, 113, 9561–9563.

(5) Maeda, K.; Eguchi, M.; Youngblood, W. J.; Mallouk, T. E. Niobium Oxide Nanoscrolls as Building Blocks for Dye-Sensitized Hydrogen Production from Water under Visible Light Irradiation. *Chem. Mater.* **2008**, *20*, 6770–6778.

(6) Grätzel, M. Dye-Sensitized Solar Cells. J. Photochem. Photobiol., C 2003, 4, 145–153.

(7) Grätzel, M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorg. Chem.* **2005**, *44*, 6841–6851.

(8) Jose, R.; Thavasi, V.; Ramakrishna, S. Metal Oxides for Dye-Sensitized Solar Cells. J. Am. Ceram. Soc. 2009, 92, 289-301.

(9) Roose, B.; Pathak, S.; Steiner, U. Doping of TiO_2 for Sensitized Solar Cells. *Chem. Soc. Rev.* **2015**, *44*, 8326–8349.

(10) Weidmann, J.; Dittrich, T.; Konstantinova, E.; Lauermann, I.; Uhlendorf, I.; Koch, F. Influence of Oxygen and Water Related Surface Defects on the Dye Sensitized TiO_2 Solar Cell. Sol. Energy Mater. Sol. Cells **1999**, 56, 153–165.

(11) Maeda, K.; Sahara, G.; Eguchi, M.; Ishitani, O. Hybrids of a Ruthenium(II) Polypyridyl Complex and a Metal Oxide Nanosheet for Dye-Sensitized Hydrogen Evolution with Visible Light: Effects of the Energy Structure on Photocatalytic Activity. *ACS Catal.* **2015**, *5*, 1700–1707.

(12) Ghann, W.; Rahman, A.; Rahman, A.; Uddin, J. Interaction of Sensitizing Dyes with Nanostructured TiO_2 Film in Dye-Sensitized Solar Cells Using Terahertz Spectroscopy. *Sci. Rep.* **2016**, *6*, No. 30140.

(13) Benkö, G.; Skårman, B.; Wallenberg, R.; Hagfeldt, A.; Sundström, V.; Yartsev, A. P. Particle Size and Crystallinity Dependent Electron Injection in Fluorescein 27-Sensitized TiO_2 Films. J. Phys. Chem. B **2003**, 107, 1370–1375.

(14) Anderson, N. A.; Lian, T. Ultrafast Electron Transfer at the Molecule-Semiconductor Nanoparticle Interface. *Annu. Rev. Phys. Chem.* **2005**, *56*, 491–519.

(15) Dittrich, T. Porous TiO_2 : Electron Transport and Application to Dye Sensitized Injection Solar Cells. *Phys. Status Solidi Appl. Res.* **2000**, *182*, 447–455.

(16) Meng, S.; Kaxiras, E. Electron and Hole Dynamics in Dye-Sensitized Solar Cells: Influencing Factors and Systematic Trends. *Nano Lett.* **2010**, *10*, 1238–1247.

(17) Li, Z.; Zhang, X.; Lu, G. Electron Dynamics in Dye-Sensitized Solar Cells: Effects of Surface Terminations and Defects. *J. Phys. Chem. B* **2010**, *114*, 17077–17083.

(18) Huber, R.; Spörlein, S.; Moser, J. E.; Grätzel, M.; Wachtveitl, J. The Role of Surface States in the Ultrafast Photoinduced Electron Transfer from Sensitizing Dye Molecules to Semiconductor Colloids. *J. Phys. Chem. B* **2000**, *104*, 8995–9003.

(19) Hao, E.; Anderson, N. A.; Asbury, J. B.; Lian, T. Effect of Trap States on Interfacial Electron Transfer between Molecular Absorbates and Semiconductor Nanoparticles. *J. Phys. Chem. B* **2002**, *106*, 10191–10198.

(20) Olsen, C. M.; Waterland, M. R.; Kelley, D. F. Electron Injection Dynamics of $Ru^{II}(dcbpy)_2(SCN)_2$ on Zirconia. *J. Phys. Chem. B* **2002**, *106*, 6211–6219.

(21) She, C.; Anderson, N. A.; Guo, J.; Liu, F.; Goh, W.-H.; Chen, D.-T.; Mohler, D. L.; Tian, Z.-Q.; Hupp, J. T.; Lian, T. pH-Dependent Electron Transfer from Re-bipyridyl Complexes to Metal Oxide Nanocrystalline Thin Films. *J. Phys. Chem. B* 2005, *109*, 19345–19355.

(22) Ishizaki, R.; Fukino, R.; Matsuzaki, H.; Katoh, R. Effect of Adsorbed Water Molecules on Light Harvesting and Electron Injection Processes in Dye-Sensitized Nanocrystalline TiO₂ Films. *J. Phys. Chem. C* **2017**, *121*, 16266–16274.

(23) Maeda, K.; Eguchi, M.; Youngblood, W. J.; Mallouk, T. E. Calcium Niobate Nanosheets Prepared by the Polymerized Complex

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Method as Catalytic Materials for Photochemical Hydrogen Evolution. *Chem. Mater.* **2009**, *21*, 3611–3617.

(24) Maeda, K.; Eguchi, M.; Lee, S.-H. A.; Youngblood, W. J.; Hata, H.; Mallouk, T. E. Photocatalytic Hydrogen Evolution from Hexaniobate Nanoscrolls and Calcium Niobate Nanosheets Sensitized by Ruthenium(II) Bipyridyl Complexes. *J. Phys. Chem. C* **2009**, *113*, 7962–7969.

(25) Maeda, K.; Mallouk, T. E. Two-Dimensional Metal Oxide Nanosheets as Building Blocks for Artificial Photosynthetic Assemblies. *Bull. Chem. Soc. Jpn.* **2019**, *92*, 38–54.

(26) Maeda, K.; Oshima, T.; Ishitani, O. Emission Spectroscopy of a Ruthenium(II) Polypyridyl Complex Adsorbed on Calcium Niobate Lamellar Solids and Nanosheets. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17962–17966.

(27) Nishioka, S.; Hyodo, J.; Vequizo, J. J. M.; Yamashita, S.; Kumagai, H.; Kimoto, K.; Yamakata, A.; Yamazaki, Y.; Maeda, K. Homogeneous Electron Doping into Nonstoichiometric Strontium Titanate Improves Its Photocatalytic Activity for Hydrogen and Oxygen Evolution. *ACS Catal.* **2018**, *8*, 7190–7200.

(28) Dreeskamp, H.; Salthammer, T.; Läufer, A. G. E. Time-Correlated Single-Photon Counting with Alternate Recording of Excitation and Emission. *J. Lumin.* **1989**, *44*, 161–165.

(29) Koester, V. J.; Dowben, R. M. Subnanosecond Single Photon Counting Fluorescence Spectroscopy Using Synchronously Pumped Tunable Dye Laser Excitation. *Rev. Sci. Instrum.* **1978**, *49*, 1186– 1191.

(30) Kakihana, M. "Sol-Gel" Preparation of High Temperature Superconducting Oxides. J. Sol–Gel Sci. Technol. **1996**, *6*, 7–55.

(31) Takeda, H.; Koizumi, H.; Okamoto, K.; Ishitani, O. Photocatalytic CO_2 Reduction Using a Mn Complex as a Catalyst. *Chem. Commun.* **2014**, *50*, 1491–1493.

(32) Caspar, J. V.; Meyer, T. J. Photochemistry of $Ru(bpy)_3^{2+}$. Solvent Effects. J. Am. Chem. Soc. **1983**, 105, 5583–5590.

(33) Nagle, J. K.; Young, R. C.; Meyer, T. J. Chemically Catalyzed Disproportionation of $\text{Ru}(\text{bpy})_3^{2+*}$. *Inorg. Chem.* **1977**, *16*, 3366–3369.

(34) Maeda, K.; Murakami, N.; Ohno, T. Dependence of Activity of Rutile Titanium(IV) Oxide Powder for Photocatalytic Overall Water Splitting on Structural Properties. *J. Phys. Chem. C* **2014**, *118*, 9093–9100.

(35) Kröger, F. A.; Vink, H. J. Relations between the Concentrations of Imperfections in Crystalline Solids. *Solid State Phys.* **1956**, *3*, 307–435.

(36) Yui, T.; Takeda, H.; Ueda, Y.; Sekizawa, K.; Koike, K.; Inagaki, S.; Ishitani, O. Hybridization between Periodic Mesoporous Organosilica and a Ru(II) Polypyridyl Complex with Phosphonic Acid Anchor Groups. *ACS Appl. Mater. Interfaces* **2014**, *6*, 1992–1998.

(37) Sharma, D.; Upadhyay, S.; Satsangi, V. R.; Shrivastav, R.; Waghmare, U. V.; Dass, S. Improved Photoelectrochemical Water Splitting Performance of Cu₂O/SrTiO₃ Heterojunction Photoelectrode. *J. Phys. Chem. C* **2014**, *118*, 25320–25329.

(38) Ikeda, S.; Sugiyama, N.; Murakami, S.; Kominami, H.; Kera, Y.; Noguchi, H.; Uosaki, K.; Torimoto, T.; Ohtani, B. Quantitative Analysis of Defective Sites in Titanium(IV) Oxide Photocatalyst Powders. *Phys. Chem. Chem. Phys.* **2003**, *5*, 778–783.

(39) Vequizo, J. J. M.; Nishioka, S.; Hyodo, J.; Yamazaki, Y.; Maeda, K.; Yamakata, A. Crucial Impact of Reduction on the Photocarriers Dynamics on SrTiO₃ Powders Studied by Transient Absorption Spectroscopy. *J. Mater. Chem. A* 2019, in press. DOI: 10.1039/C9TA08216F.