## Supporting Information

## For

## Visualization of Cation Diffusion at the TiO<sub>2</sub> Interface in Dye Sensitizd Photoelectrosynthesis Cells (DSPEC)

1. Molar absorptivity increase of  $TiO_2$ -**RuP** observed at (483 ± 3) nm with added proton or  $Li^+$  in solution. The curve was fitted to Langmuir isotherm model (eq s1) to obtain the equilibrium constant and maximum absorptivity change

$$\Box \ \varepsilon = \varepsilon_{\max} K_{eq}[C] / (1 + K_{eq}[C])$$
(s1)



Figure S1. Change in molar absorptivity of  $TiO_2$ -**RuP** at (482 ± 2) nm immersed in solutions with different concentrations of proton or Li<sup>+</sup>: (a) proton in aqueous solution; (b) Li<sup>+</sup> in aqueous solution; (c) Li<sup>+</sup> in propylene carbonate (PC) with 5% water; (d) Li<sup>+</sup> in PC. The solid curves are fit from eq S1.

Cation	Medium	$\Delta\lambda_{\text{Max}}$ (nm)	$\Delta \varepsilon_{\rm max} ({\rm M}^{-1} {\rm cm}^{-1})$	$K_{eq}(M^{-1})$
$\mathrm{H}^+$	TiO <sub>2</sub> /aqueous	484	2150	176
$Li^+$	TiO <sub>2</sub> /aqueous	484	1000	11.6
Li <sup>+</sup>	TiO <sub>2</sub> /PC/5% water	482	821	40
Li <sup>+</sup>	TiO <sub>2</sub> /PC	480	2230	144
$TBA^+$	TiO <sub>2</sub> /PC	-	-	-

Table S1 .Summary of cation titration parameters by fitting curves in Figure S1 to eq S1

2. Figure S2 (curve a) shows the spectral change of TiO<sub>2</sub>-**RuP** in PC upon addition of Li<sup>+</sup>. Applying forward bias to TiO<sub>2</sub>-**RuP** electrode in PC with 0.2 M TBA<sup>+</sup>, gave spectral change consistent with Stark effect (curve b), which was mirrored with curve a.



Figure S2 Differential spectrum of  $TiO_2$ -**RuP** (a) between with and without 0.1 M Li<sup>+</sup> in that PC; (b) between after and before electrolysis at -0.8 V vs. NHE. Electrolyte: 0.2 M TBA<sup>+</sup> in PC.

3. Figure S3 shows the relation between electron density on TiO<sub>2</sub> (calculated from the absorbance at 800 nm) and the observed Stark effect (calculated from the absorbance decrease at 483 ± 3 nm). The observed Stark effect with same amount of TiO<sub>2</sub>(e<sup>-</sup>) is most significant when using TBA<sup>+</sup> as electrolyte(□), because TBA<sup>+</sup> cannot adsorb onto TiO<sub>2</sub> surface nor intercalates into lattice to screen the electric field from TiO<sub>2</sub>(e<sup>-</sup>). A smaller stark effect was found with 0.2 M Li<sup>+</sup> (◊). This is consistent with screening of electric field by Li<sup>+</sup>. In aqueous solution with Li<sup>+</sup> (○), the absorbance change of TiO<sub>2</sub>-**RuP** was less than observed in PC, as expected from the permittivity of water and PC (80 vs. 64).



Figure S3. For TiO<sub>2</sub>-**RuP** immersed in different solution, the absorbance change at (483  $\pm$  3) nm corresponding to Stark effect is plotted against the absorbance change observed at 800 nm from TiO<sub>2</sub> (e<sup>-</sup>).

4. Absorption spectrum changes of TiO<sub>2</sub>-**RuP** observed for a DSPEC under open circuit condition, following one photolysis and subsequent relaxation cycles (a), showing features from Li<sup>+</sup> intercalation. Curve b is the spectrum change for the same photoanode after DSPECs operating under the same condition for seven times, with more significant Li<sup>+</sup> intercalation been observed.



Figure S4. (a) Spectrum change of  $TiO_2$ -**RuP** (7.2 × 10<sup>-8</sup> mol cm<sup>-2</sup>) in 300 s photolysis (445 nm , 7.2 mW) under open circuit condition, followed by a hour DSPEC relax under open circuit condition under dark; (b) Overall spectrum change of  $TiO_2$ -**RuP** by conducting same experiments in (a) for seven times.

5. Table S2. Maximum absorbance change of TiO<sub>2</sub>-**RuP** in DSPEC operating with 0.2 V bias vs. NHE. Rate of Li<sup>+</sup> release was obtained from absorption decrease after switching light off while kept applying bias.

$\Gamma$ (mol cm <sup>-2</sup> )	Light intensity (mW)	Post photolysis cell condition	$\Delta$ [Li <sup>+</sup> ] (M)	Intercalation <sup>a</sup> (s)	Release <sup>b</sup> (s)	$\beta^{b}$
6.3 × 10 <sup>-8</sup>	1.2	0.2 V bias	0.054	7.6	78	0.7
	7.2		0.07	6	65.3	0.7
	15		0.08	4.9	77	0.67

<sup>a</sup> from single exponential fit

<sup>b</sup> from stretched exponential fit (eq 5)

6. Spectral change of TiO<sub>2</sub>-RuP in DSPEC with 0.2 V vs. NHE applied bias. Electrolyte was 0.4 M LiClO<sub>4</sub> in PC/5water with 28 mM 4-methoxy thioanisole as electron donor. The differential spectrum of photolyzed electrode and before photolysis (Figure S5 insert, red) suggested Li<sup>+</sup> intercalation. The accumulated Li<sup>+</sup> diffused back to electrolyte after switching light off, which lead to a spectral change that is opposite to Li<sup>+</sup> intercalation(Figure S5 insert, green)



Figure S5. (A) Absorption spectrum of  $TiO_2$ -**RuP** (  $3.8 \times 10^{-8} \text{ mol cm}^{-2}$ ) in the above DSPEC: (a, black) before photolysis, (b, red) with 20min 445nm 26.8 mW irradiation at

0.2 V applied bias vs. NHE under Ar, (c, green) 2 hours after switching light off. The difference of (b)-(a) and (c)-(b) are given in the insert.

Figure S6 shows the absorbance increase at 484 nm due to Li<sup>+</sup> intercalation in DSPEC with (a) PC or (b) PC/5% water as solvent. The cell was operating with 0.2 V applied bias vs. NHE. Electron donor was 4-methoxy thioanisole.



Figure S6. Change in absorbance at 484 nm, divided by maximum change for  $TiO_2$ -**RuP** in DSPEC with 4-methoxy thioanisole as electron donor in (a) 0.2 M LiClO<sub>4</sub> in PC (b) 0.4 M LiClO4 in PC/5% water. Irradiation was at 445 nm (26.8 mW), with 0.2 V bias vs. NHE applied to photoanode. Experiments were carried out under Ar.

8. Spectroscopic Response of TiO<sub>2</sub>-**RuP** in DSPEC induced by electrochemical injected electrons.

Applying forward bias to the TiO<sub>2</sub>-**RuP** photoanode (-0.6 V vs. NHE for 600 s) results in electron injection to give TiO<sub>2</sub>(e<sup>-</sup>)-**RuP**. The spectral changes during the charging process (Figure S7) demonstrated the Stark effect (Figure S7 insert). Discharging TiO<sub>2</sub>(e<sup>-</sup>)-Ru<sup>II</sup>P triggered an immediate disappearance of Stark effect, followed by a relatively slow spectral change indicative of Li<sup>+</sup> re-release (Figure S7 B). These results suggested that Li<sup>+</sup> intercalation occurs during electrochemical reduction of TiO<sub>2</sub>. The absorbancetime change at 484 nm as the electrode was discharged followed stretched exponential kinetics with  $\tau = 20$  s and  $\beta = 0.92$ .



Figure S7 (A) Absorption spectrum of TiO<sub>2</sub>-**RuP** ( $5.3 \times 10^{-8}$  mol cm<sup>-2</sup>) in pH 4.5 20 mM EDTA with 0.2 M LiClO<sub>4</sub>: (a) before applying bias, (b) after applying forward bias (-0.6 V vs. NHE) for ~30 s under Ar, (c) ~30 s after switching the bias potential to 0.2 V vs. NHE to discharge the electrode. The insert shows difference spectra with the original spectrum in (a) subtracted from (b). (B) Ratio of the absorption change to the maximum absorption change at 484 nm with time

after discharging  $TiO_2(e^{-})$ -Ru<sup>II</sup>P in the same measurement as in panel A, suggesting release of the intercalated Li<sup>+</sup> during electrolysis.

9.  $TiO_2(e^-)$  recombine with Ru<sup>III</sup>P under 445nm steady state irradiation

Under this irradiation condition, the back electron transfer rate, or more accurately, the pseudo electron flux to Ru<sup>III</sup>P, can be calculated by steady state assumption (eq S2) from the absorbed photoflux and amount of Ru<sup>III</sup>P at photo-equilibration.

Figure S8 shows the change of  $TiO_2$ -**RuP** spectum under photolysis, due to photoinduced electron injection equilibrated with back electron transfer. The back electron transfer was estimated to be 5.6 s<sup>-1</sup>(open circuit) and 2.3 s<sup>-1</sup> (0.2 V vs. NHE bias) respectively, which were ~ 6 magnitudes slower than we observed on transient absorption in the same electrolyte (7.5µs characteristic lifetime).

Calculation by steady state assumption for Ru<sup>III</sup> in the absence of external electron donor (eq S2).

Here  $[Ru^{III}]$  is the photogenerated amount of  $Ru^{III}P$  on TiO<sub>2</sub> photoelectrode in mol, I<sub>0</sub> is the total light intensity at 445 nm in Einstein s<sup>-1</sup>, A<sub>445</sub> is the absorbance of TiO<sub>2</sub>-RuP at 445 nm,  $\Phi$ inj is the electron injection efficiency at pH 4.5 (~ 0.7), k<sub>bet</sub> is the pseudo back electron transfer rate constant in s<sup>-1</sup>;  $[Ru^{III}]$ ss is the steady state amount of  $Ru^{III}$  in mol under equilibrium state. The amount of  $Ru^{III}$  was calculated by eq (S3).  $\Gamma(Ru^{III})$  is the surface coverage of  $Ru^{III}$  calculated by absorbance changes during photolysis at 460 nm,  $\Delta\varepsilon$  is the difference in molar absorbativity between  $Ru^{III}$  and  $Ru^{II}$ , ~ 13000 M<sup>-1</sup> cm<sup>-1</sup>. The irradiation area of a 1 cm diameter beam is 0.785 cm<sup>2</sup>

$$\begin{array}{l} d[Ru^{III}]/dt = I_0 \times (1\text{-}10^{\text{-}A445}) \times \Phi_{inj} - k_{bet} \times [Ru^{III}] \text{ss} = 0 & (eq \ S2) \\ [Ru^{III}] = \Gamma(Ru^{III}) \times irradiation \ area = \Delta A / \Delta \epsilon / 1000 \times 0.785 \text{cm}^2 & (eq \ S3) \end{array}$$



Figure S8. UV-vis spectrum of  $TiO_2$ -**RuP:** (a) before photolysis, (b) after 5 min 445 nm 7.2 mW irradiation under open circuit condition, and (c) after 5 min 445 nm 7.2 mW irradiation with 0.2 V bias vs. NHE. Electrolyte was 20 mM pH 4.5 acetate buffer with 0.1 M LiClO<sub>4</sub>. Experiment was performed under Ar.

10. Photocurrent of DSPEC before and after 1800 s open circuit photolysis at 445 nm (7.2 mW). The light intensity in photocurrent measurement was 1.2 mW. **RuP** surface coverage:  $5.3 \times 10^{-8}$  mol cm<sup>-2</sup>. Electrolyte: 0.2 M LiClO<sub>4</sub> and 20 mM EDTA. The absorbed photon to current conversion efficiency (APCE) was calculated by eq s4, where

 $I_{\text{photo}}$  is photocurrent,  $I_0$  is the light intensity and  $A_{445}$  is the photoanode absorption at 445 nm.

$$APCE = I_{photo} / 96500 / I_0 (1 - 10^{-A445})$$
(s4)



Figure S9. Photocurrent under 1.2 mW 445 nm irradiation with applying 0.2 V bias. (a) before photolysis and (b) after 1800 s 445 nm 7.2 mW photolysis under open circuit condition.

11. Table S3. Change in DSPEC performance in forward(600s)/reverse(300s) bias treatment for TiO<sub>2</sub>-**RuP** 

Forward bias	$\tau TiO_2(e)^a$	$[\text{TiO}_2(e)]_{ss}^{b}$	$V_{oc}$	I <sub>photo</sub>
(V vs. Ag/AgCl)	(s)	$(nmol cm^{-2})$	(V)	(µA)
Without treatment	363	8.8	0.569	176
by forward bias				
-0.7	474	10.8	0.571	173
-0.8	849	14.4	0.58	175

<sup>a</sup> by fitting absorbance decay at 800 nm with single exponential decay

<sup>b</sup> concentration of  $TiO_2(e)$  accumulated with 60 s 445 nm 1.2 mW irradiation calculated by absorbance change at 800 nm

12. Figure S10. O 1s XPS spectra of  $TiO_2$ -**RuP** (a) before and (b) after photolysis (445 nm, 7.2 mW 30min) in a DSPEC configuration with 0.2 M LiClO<sub>4</sub> and 20 mM EDTA under open circuit condition. The relatively higher intensity of O 1s at higher binding energy most likely resulted from overlayers on  $TiO_2$  interface due to intercalated lithium/hydroxide during photolysis.

