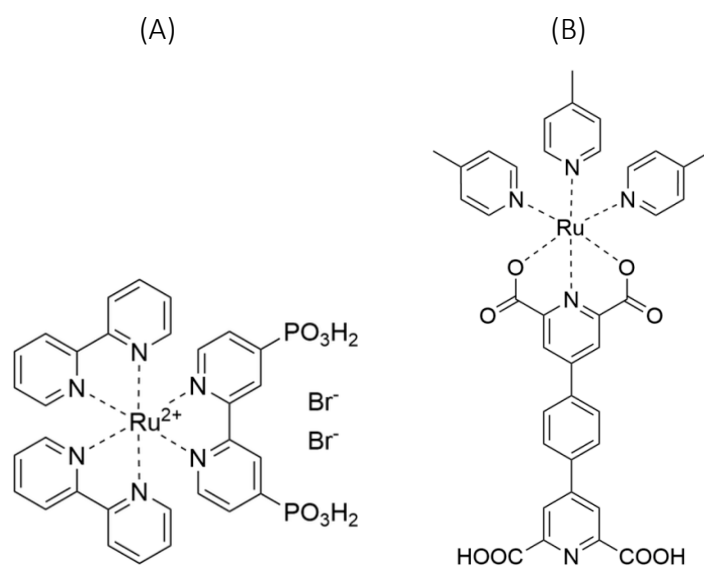


# **Supplementary Materials: The Effect of Chloride Anions on Charge Transfer in Dye-Sensitized Photoanodes for Water Splitting**

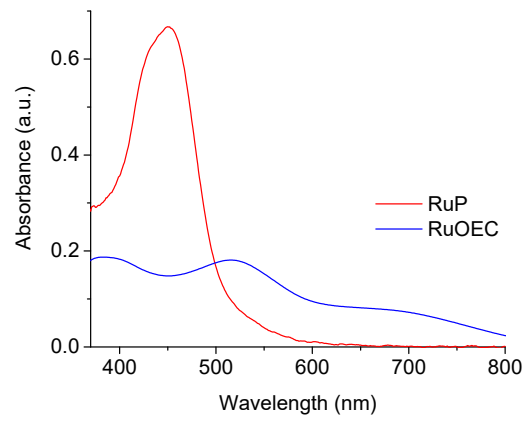
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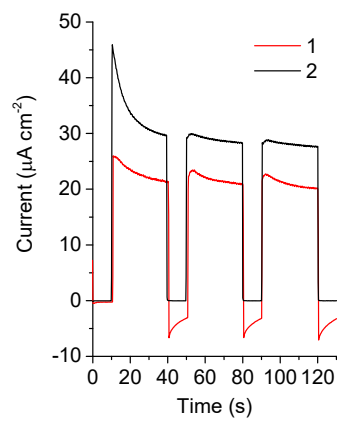
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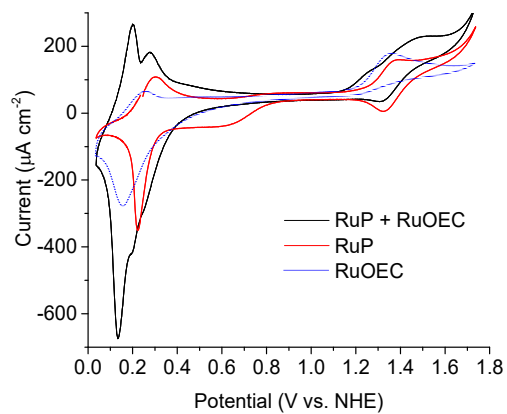
**Figure S1.** The chemical structures of (A) RuP and (B) RuOEC.



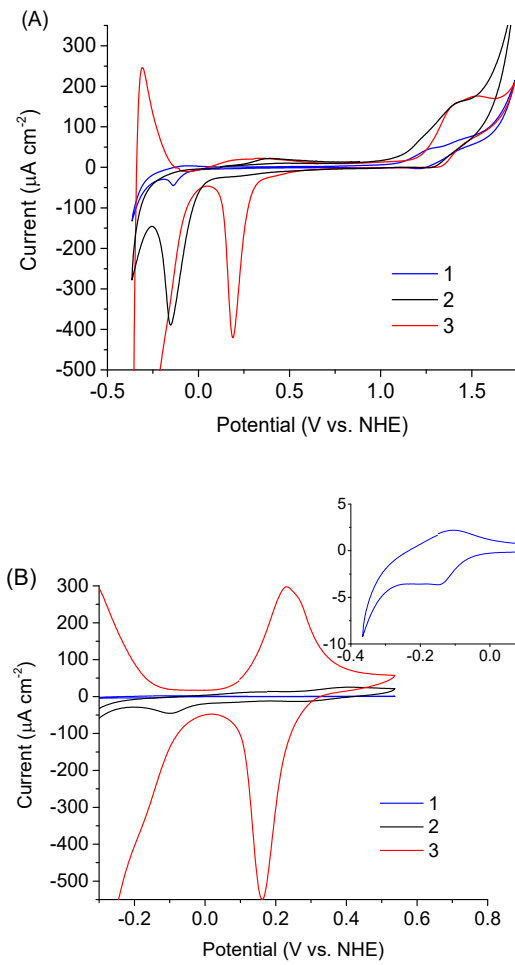
**Figure S2.** Absorption spectra of photoanodes sensitized in RuP (for 16h) and RuOEC (for 16h).



**Figure S3.** Photocurrent–time behaviour of TiO<sub>2</sub> in HCl (pH  $\approx$ 3) (1) and 0.07 M phosphate buffer (pH  $\approx$ 7) solution (2). The photoanodes were biased at 0.236 V vs. NHE.



**Figure S4.** Cyclic voltammograms of  $\text{TiO}_2$  photoanode sensitized with RuP, RuOEC and RuP + RuOEC recorded under illumination in HCl electrolyte (pH  $\approx$ 3).



**Figure S5.** Cyclic voltammograms of TiO<sub>2</sub> photoanode sensitized with RuP + RuOEC in electrolytes: 0.07 M phosphate buffer (pH ≈7) (1), 0.1 M KCl (pH ≈5) (2), and 0.001 M HCl (pH ≈3) (3) recorded (A) in dark condition and (B) upon illumination when UV cut-off filter was used.

**Table S1.** Parameters of the time traces of the photocurrent recorded at 0.236 V vs. NHE.

Type of Photoanode	Electrolyte	pH	$J_0$ ( $\mu\text{A}/\text{cm}^2$ )	$J_{\text{stab}}$ ( $\mu\text{A}/\text{cm}^2$ )	$J_{\text{dark}}$ ( $\mu\text{A}/\text{cm}^2$ )	$J_{\text{stab}}/J_0$
RuOEC	0.001 M HCl	$\approx 3$	220	5	-120	0.02
RuP			10	0	-80	0
RuP + RuOEC			640	5	-140	0.01
TiO <sub>2</sub>			25	20	-5	0.80
RuOEC	0.07 M Phosphate buffer	$\approx 7$	65	30	0	0.46
RuP			55	15	-20	0.27
RuP + RuOEC			240	50	-20	0.20
TiO <sub>2</sub>			45	30	0	0.67

$J_0$ : Initial photocurrent;  $J_{\text{stab}}$ : Steady-state photocurrent;  $J_{\text{dark}}$ : Dark photocurrent;  $J_{\text{stab}}/J_0$ : Ratio for the photoanode sensitized with RuOEC, RuP and both.

**Table S2.** Parameters of the time traces of the photocurrent recorded at 0.736 V vs. NHE.

Type of Photoanode	Electrolyte	pH	$J_0$ ( $\mu\text{A}/\text{cm}^2$ )	$J_{\text{stab}}$ ( $\mu\text{A}/\text{cm}^2$ )	$J_{\text{dark}}$ ( $\mu\text{A}/\text{cm}^2$ )	$J_{\text{stab}}/J_0$
RuOEC			290	40	-45	0.14
RuP	0.001 M HCl	$\approx 3$	70	10	-10	0.14
RuP + RuOEC			420	25	-5	0.06
RuOEC			25	25	0	1
RuP	0.07 M Phosphate buffer	$\approx 7$	85	30	-5	0.35
RuP + RuOEC			60	35	0	0.58

$J_0$ : Initial photocurrent;  $J_{\text{stab}}$ : Steady-state photocurrent;  $J_{\text{dark}}$ : Dark photocurrent;  $J_{\text{stab}}/J_0$ : Ratio for the photoanode sensitized with RuOEC, RuP and both.



**Table S3.** Onset of cathodic current peak obtained from CV skans recorded in dark conditions (from -0.36 to 1.74 V vs. NHE) for RuP + RuOEC photoanodes in different electrolytes.

Electrolyte	Molar Ionic Strength (M)	pH	Onset of Cathodic Current (V vs. NHE) <sup>1</sup>
0.07 M Phosphate buffer	0.15	≈7	-0.06
0.1 M KCl	0.1	≈5	-0.02
0.001 M HCl	0.001	≈3	0.28
EPA	≈0.001		0.11
EPA + 0.001 M KCl	≈0.002		0.13
EPA + 0.01 M KCl	≈0.011	≈3	0.13
EPA + 0.1 M KCl	≈0.101		0.12

<sup>1</sup> Relative error ±0.01 V.