

Electronic Supplementary Information (ESI)

Activation of a Pt-loaded $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ photocatalyst by alkaline chloride treatment for improved H_2 evolution under visible light

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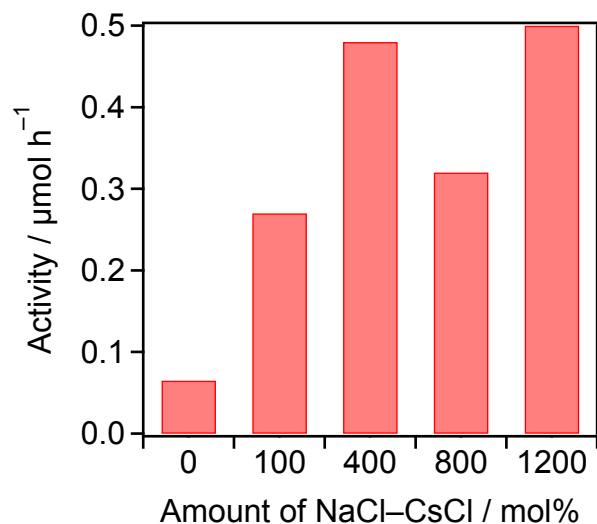


Fig. S1. Photocatalytic activities of $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ treated with different amounts of a NaCl–CsCl mixture at 723 K. Reaction conditions: catalyst, 100 mg (0.5 wt% Pt photodeposited); MeCN/TEOA mixture (13:1 v/v) 140 mL containing 1 mL water; light source, xenon lamp (300 W) with a cutoff filter (L42). Activities have an associated experimental error of ~15%.

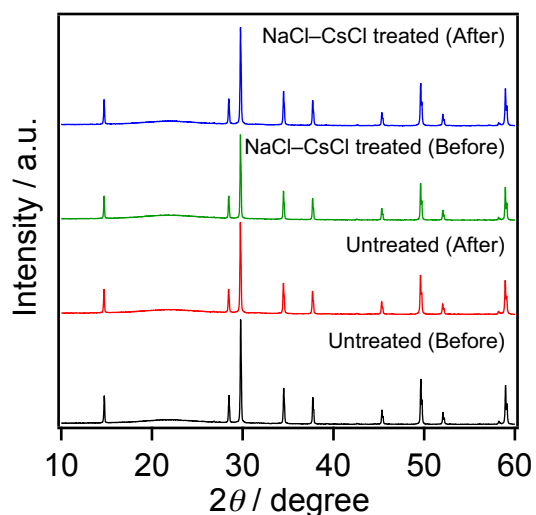


Fig. S2. XRD patterns for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ with and without NaCl–CsCl treatment at 723 K before and after the H_2 evolution reaction.

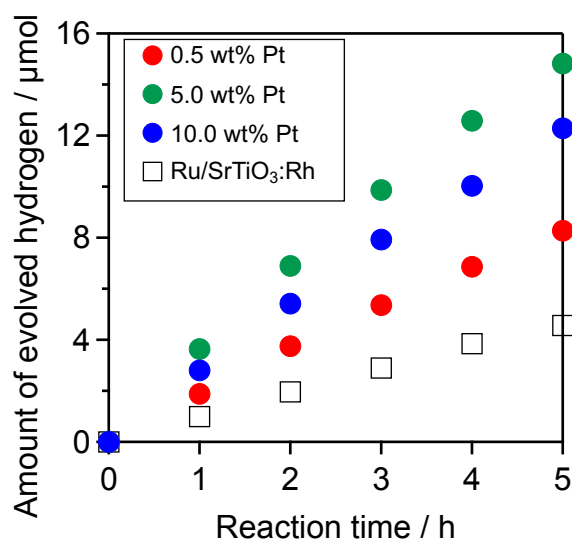


Fig. S3. Dependence of the rate of H₂ evolution using Pt/Pb₂Ti₂O_{5.4}F_{1.2} (treated with 400 mol% NaCl–CsCl at 723 K) on the loading amount of Pt. Reaction conditions: catalyst, 50 mg (reused after 20 h of UV and visible light irradiation); MeCN/TEOA mixed solution (13:1 v/v) 140 mL containing 1 mL water; light source, xenon lamp (300 W) with a cutoff filter (L42). Data for Ru/SrTiO₃:Rh is also shown. Activities contained experimental errors of ~15%. The optimized Pt(5.0 wt%)/Pb₂Ti₂O_{5.4}F_{1.2} showed AQYs of 0.83 and 0.26% at 365 and 420 nm, respectively.

Synthesis of Ru-loaded, Rh-doped SrTiO₃

Ru-loaded, Rh-doped SrTiO₃ (Ru/SrTiO₃:Rh), one of the most active H₂ evolution photocatalysts workable under visible light,^{S1} was synthesized by a hydrothermal synthesis according to our previous reports.^{S2,3} Briefly, Sr(OH)₂·8H₂O (22 mmol, >96.0%, Kanto Chemical Co.), TiO₂ (19.6 mmol, JRC-TIO-10) and Rh(NO₃)₃ (0.5 mmol, >80%, Kanto Chemical Co.) were mixed in 50 mL of water, which was subject to hydrothermal treatment in a Teflon-lined stainless-steel autoclave at 433 K for 42 h. The hydrothermal product was dried at 343 K in an oven, subsequently mixed with an additional Sr(OH)₂·8H₂O (1.4 mmol) and heated at 1273 K for 10 h in air. The Ru cocatalyst was deposited using RuCl₃ solution (Ru: 0.7 wt%) according to a photodeposition method reported by Kudo et al.^{S1}

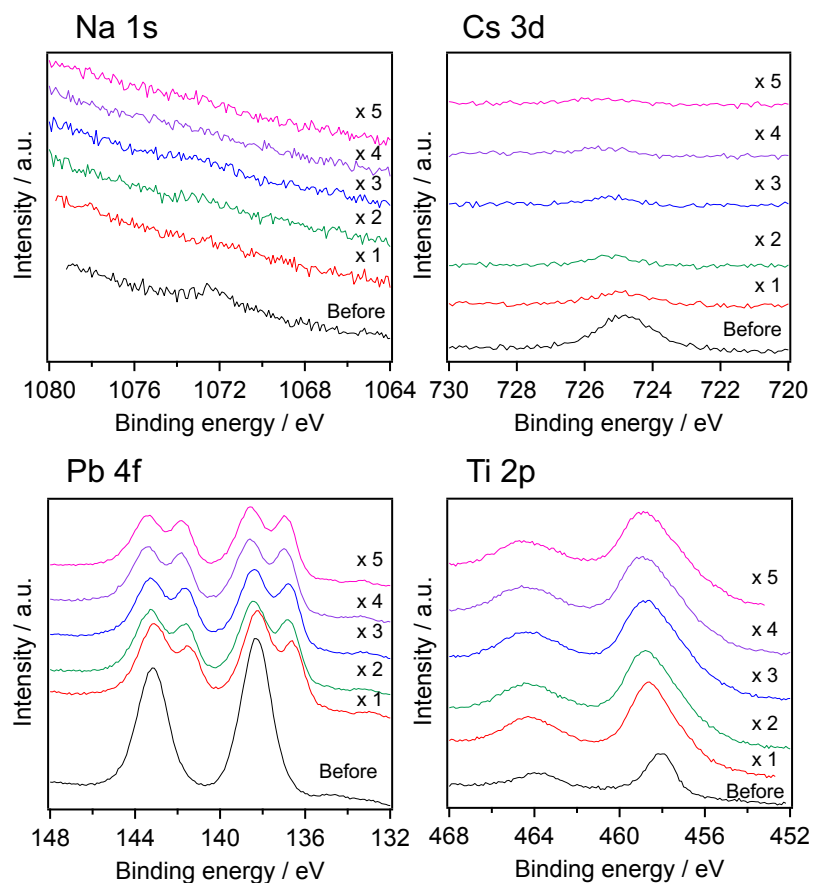


Fig. S4. Na 1s, Cs 3d, Pb 4f and Ti 2p XPS data for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ treated with NaCl–CsCl (400 mol%) at 723 K. Spectra are presented for varying Ar^+ etching applications, with each application lasting 5 s with an emission current of 40 mA and accelerating voltage of 0.6 V.

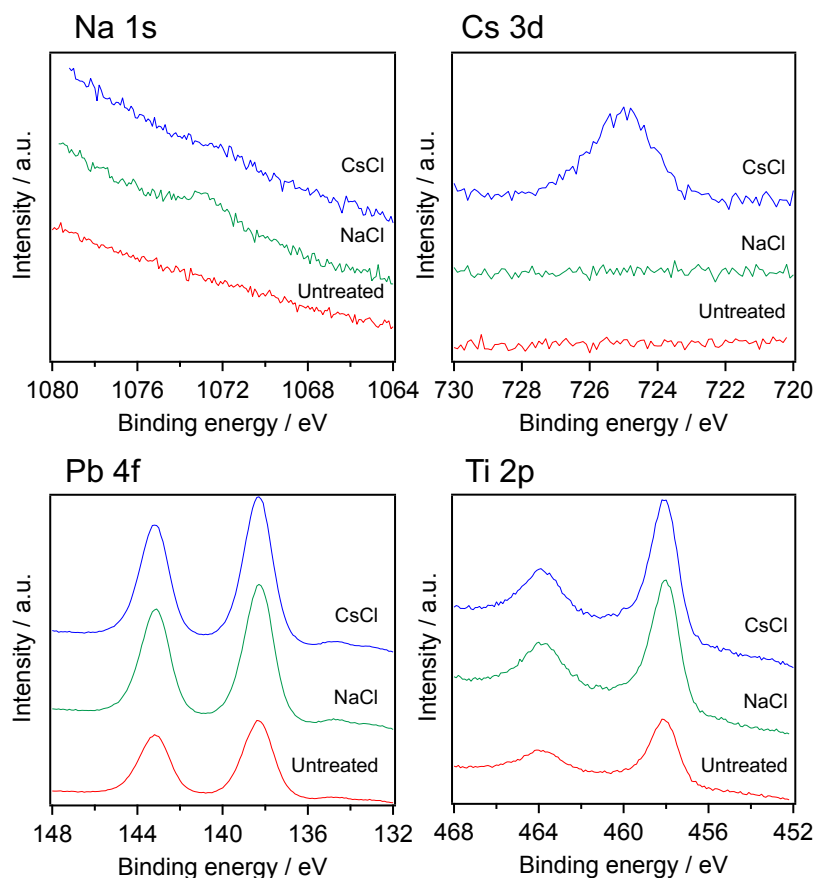


Fig. S5. Na 1s, Cs 3d, Pb 4f and Ti 2p XPS data for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ treated with either NaCl or CsCl (140 mol%) at 723 K.

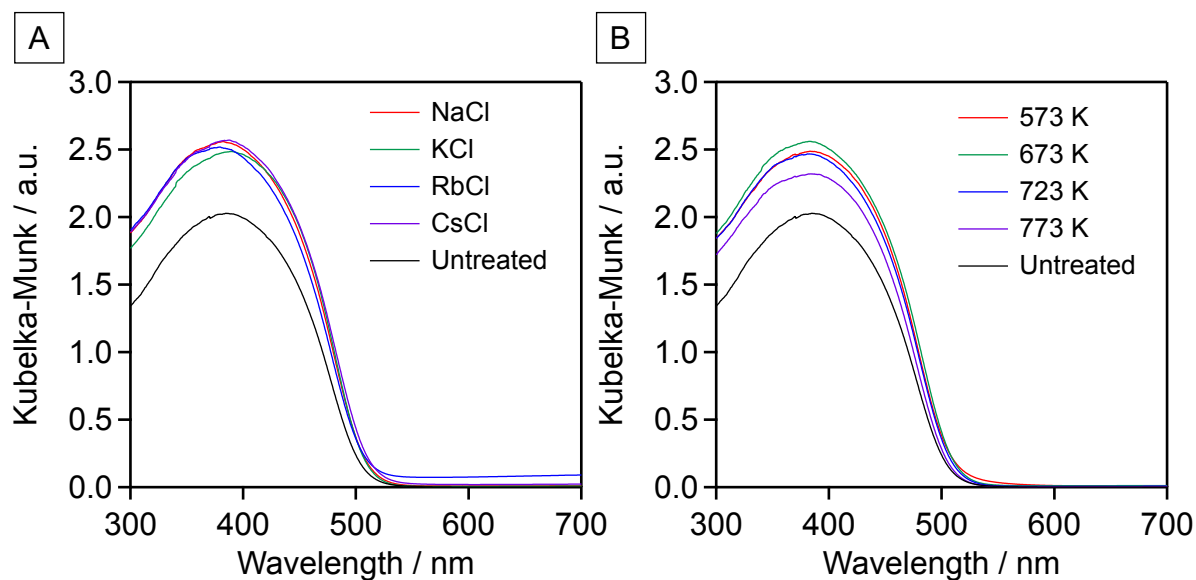


Fig. S6. UV-visible diffuse reflectance spectra of $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ treated with (A) various alkaline metal salts at 723 K and (B) a NaCl–CsCl mixture at different temperatures.

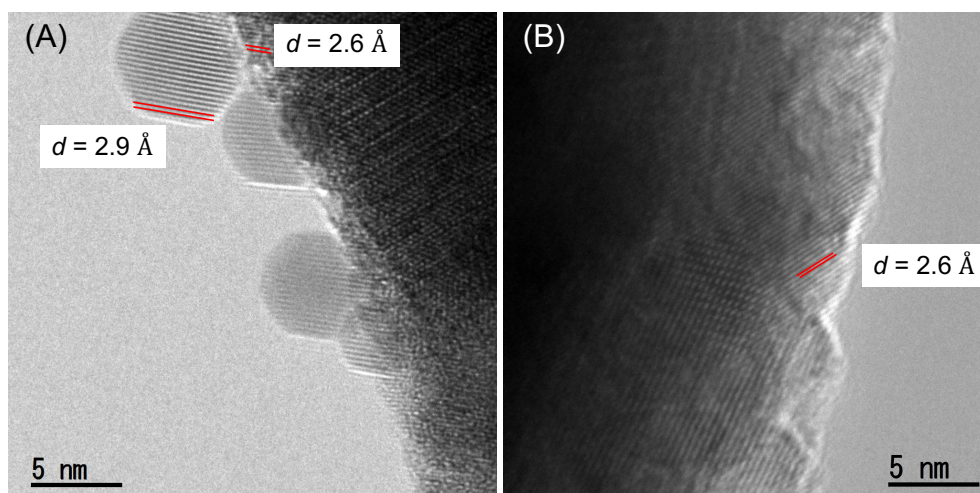


Fig. S7. TEM images of $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ (A) before and (B) after treatment with NaCl–CsCl (400 mol%) at 723 K. The lattice fringes in the darker area of panel A as well as in panel B have a period of approximately 2.6 Å, consistent with the d spacing of $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ (400) planes (2.6 Å).

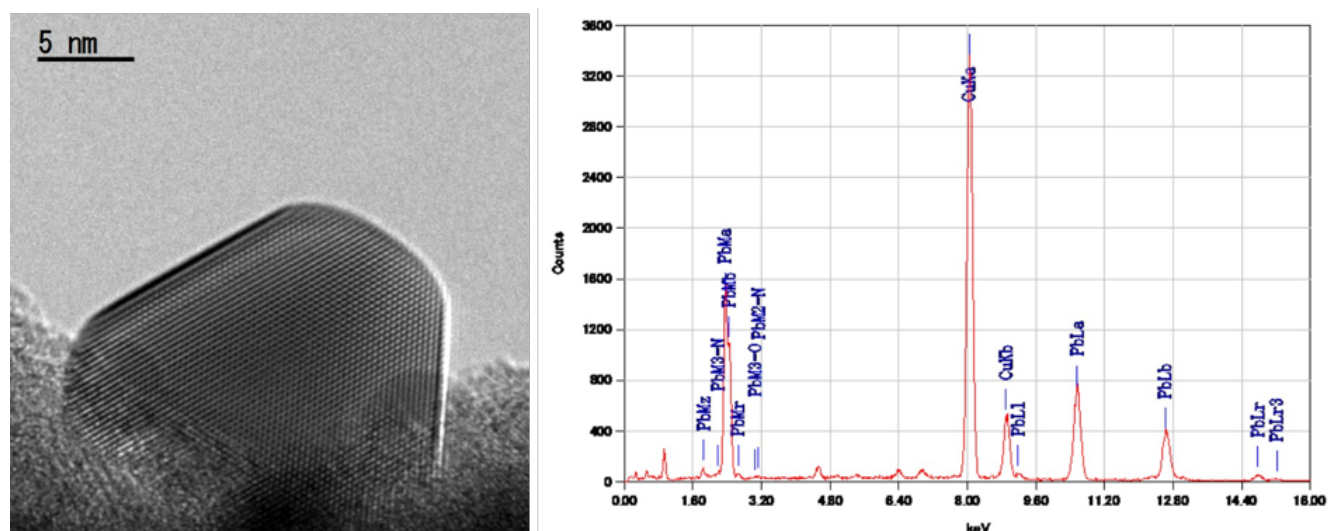


Fig. S8. A TEM image and EDS data for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ without any treatment.

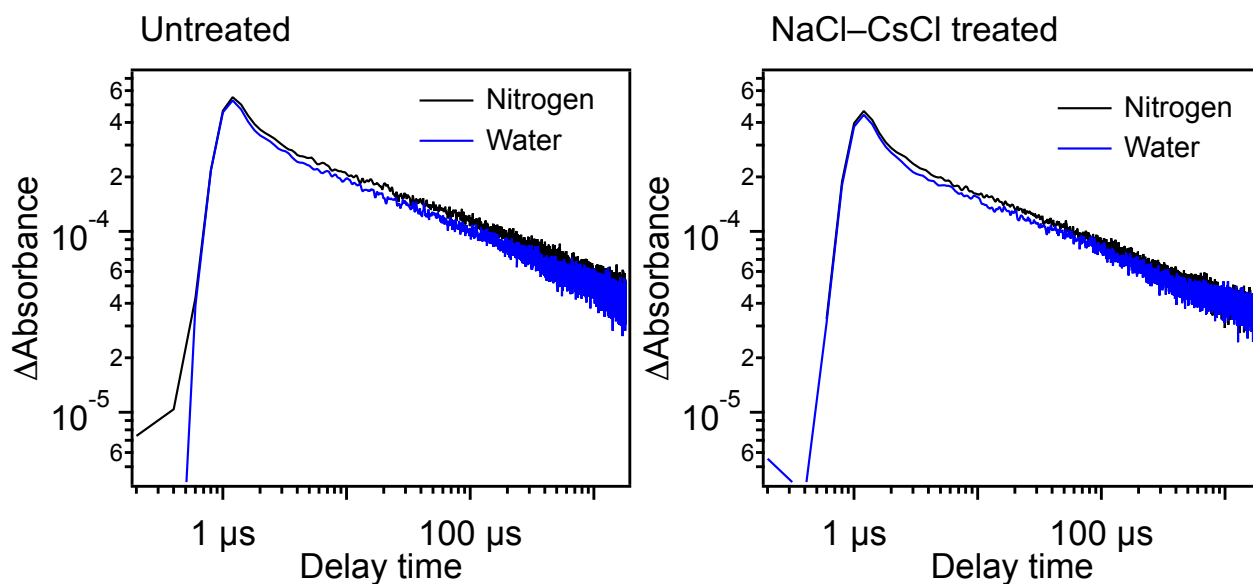


Fig. S9. Transient absorption intensity decay curves acquired at 2000 cm^{-1} for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ with and without NaCl–CsCl treatment in N_2 or H_2O vapor (20 Torr).

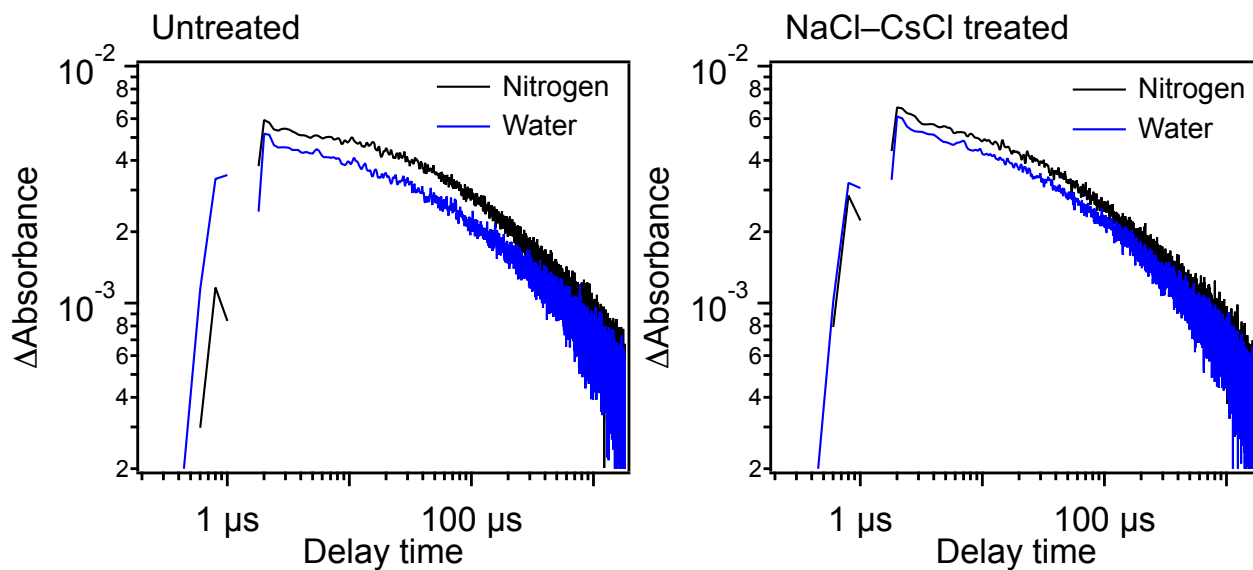


Fig. S10. Transient absorption intensity decay curves acquired at $21,000\text{ cm}^{-1}$ for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ with and without NaCl–CsCl treatment in N_2 or H_2O vapor (20 Torr). The phenomenon in the range of 1–2 μs is ascribed to leaked laser light and/or emission from the $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$.

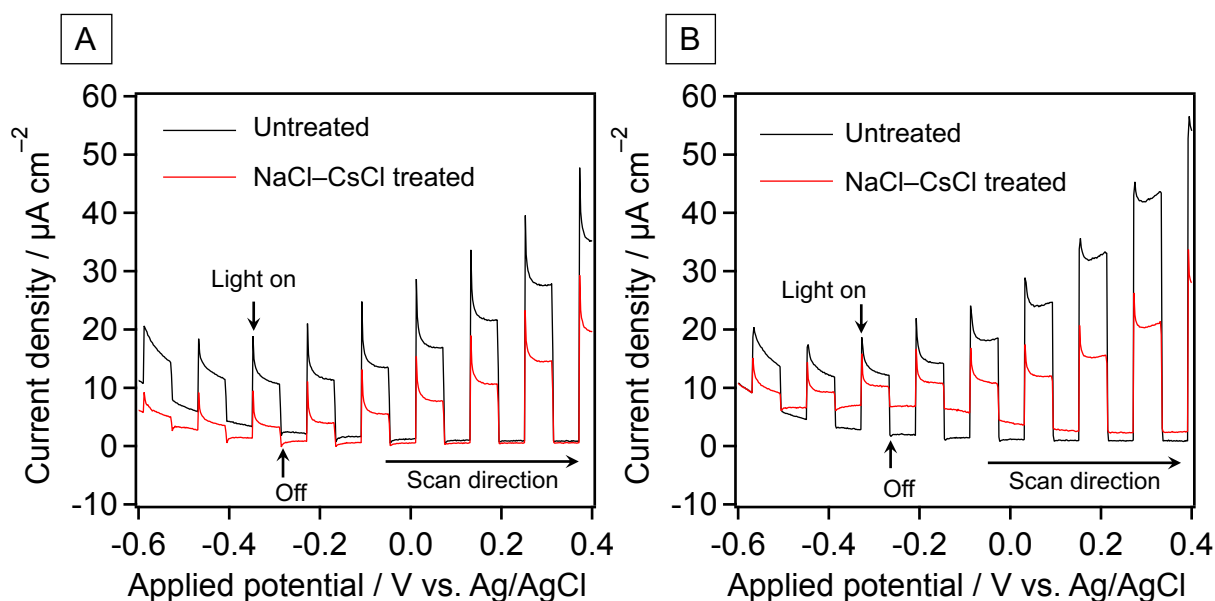


Fig. S11. Current-voltage curves obtained from $\text{TiO}_2/\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}/\text{FTO}$ electrodes under intermittent visible light in an aqueous phosphate buffer ($[\text{PO}_4^{3-}] = 0.1 \text{ M}$) in the (A) absence (pH 9.0) and (B) presence of 4.8 vol% TEOA (pH 9.1). Scan rate: 20 mV s^{-1} . Light source: 300 W xenon lamp ($\lambda > 440 \text{ nm}$). Irradiation area: 5.3 cm^2 .

Experimental detail of photoelectrochemical measurements

The electrodes were prepared by electrophoretic deposition in a 50 mL acetone solution containing 0.1 g $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ powder and 10 mg iodine. Two parallel fluorine-doped tin oxide (FTO) electrodes were immersed in this solution separated by approximately 15 mm and a 30 V bias was applied between the electrodes for 2 min using a potentiostat (PSW 80-13.5, GW Instek). The $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ -coated area was fixed at approximately $1.5 \times 3.5 \text{ cm}$ and included approximately 5 mg of $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$.

The TiCl_4 treatment was carried out by dipping each $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ electrode in a methanol solution containing 0.1 M TiCl_4 , followed by drying on a hot plate at approximately 423 K.^{S4} This procedure was repeated five times, after which the treated electrode was heated in air at 573 K for 1 h. The resulting TiO_2 layer on the $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}/\text{FTO}$ has previously been shown to reduce the resistance of the electrode, thereby contributing to enhanced photocurrent generation.^{S5}

Photoelectrochemical measurements using the as-prepared $\text{TiO}_2/\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}/\text{FTO}$ electrodes were carried out with a potentiostat (HSV-110, Hokuto Denko) and an electrochemical cell at room temperature. The cell was made of Pyrex glass and comprised a three-electrode-type system using Pt wire and an Ag/AgCl electrode as the counter and reference electrodes, respectively. An aqueous sodium phosphate solution ($[\text{PO}_4^{3-}] = 0.1 \text{ M}$) was used as the electrolyte and was saturated with argon gas prior to the electrochemical measurements. The pH of the phosphate solution was adjusted to pH 9.0 by mixing $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ while maintaining a total phosphate concentration of 0.1 M. In addition, 5 mL of TEOA (4.8 vol% in total) was also added to the electrolyte solution in some trials. The pH of the TEOA-containing solution was 9.1. The light source was a 300 W xenon lamp (Cermex, PE300BF) fitted with a cutoff filter (HOYA, Y44) such that it provided visible light. It should be noted that the TiO_2 component of the electrode did not undergo photoexcitation under these conditions because of its large band gap.^{S6} The irradiation area was approximately 5.3 cm^2 .

Additional discussion on photoelectrochemical properties

It should be noted that, under the present conditions, the TiO_2 component did not undergo photoexcitation because of its large band gap,^{S6} and so the observed photocurrent was primarily due to the $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$. The lower density of photocurrent from the NaCl–CsCl treated specimen (Fig. S11A) indicates that the treatment had a negative impact on photooxidation of water, consistent with the result of transient absorption spectroscopy (Fig. S10). Similar results were obtained in the presence of TEOA (Fig. S11B). Thus, the NaCl–CsCl treatment of the $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ was shown to lower the photooxidation ability of the material. This result, in turn, suggests that the alkaline chloride treatment improved the reduction characteristics of the material.

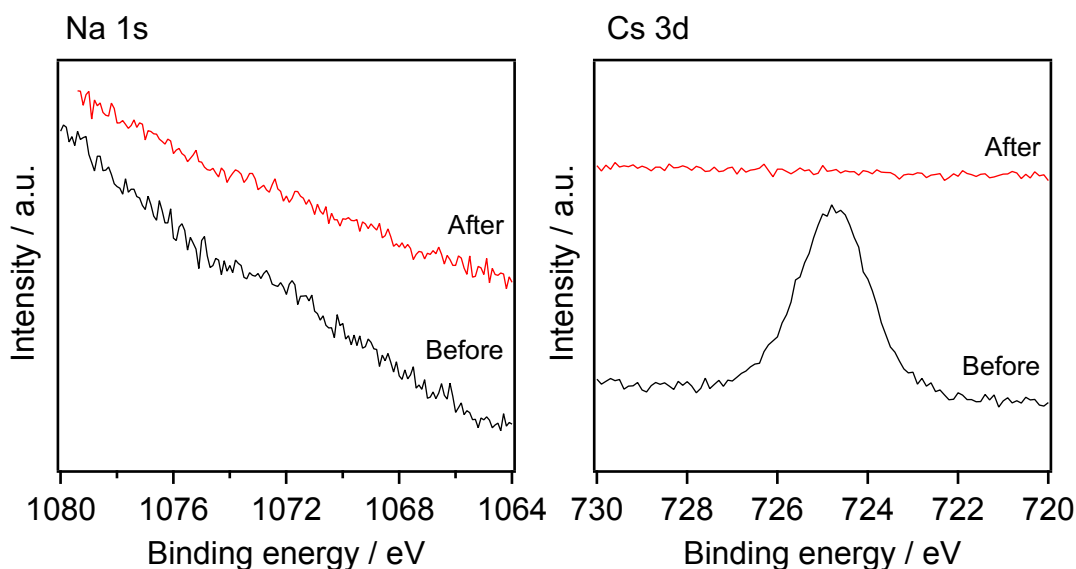


Fig. S12. Na 1s and Cs 3d XPS data for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ treated with NaCl–CsCl at 723 K before and after Pt photodeposition.

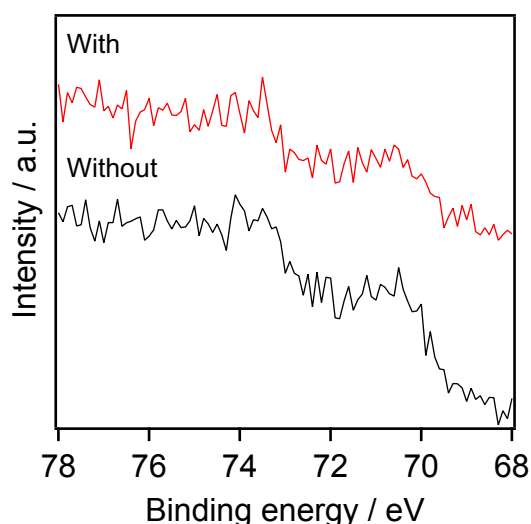


Fig. S13. Pt 4f XPS data for Pt-photodeposited $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ with and without NaCl–CsCl treatment at 723 K.

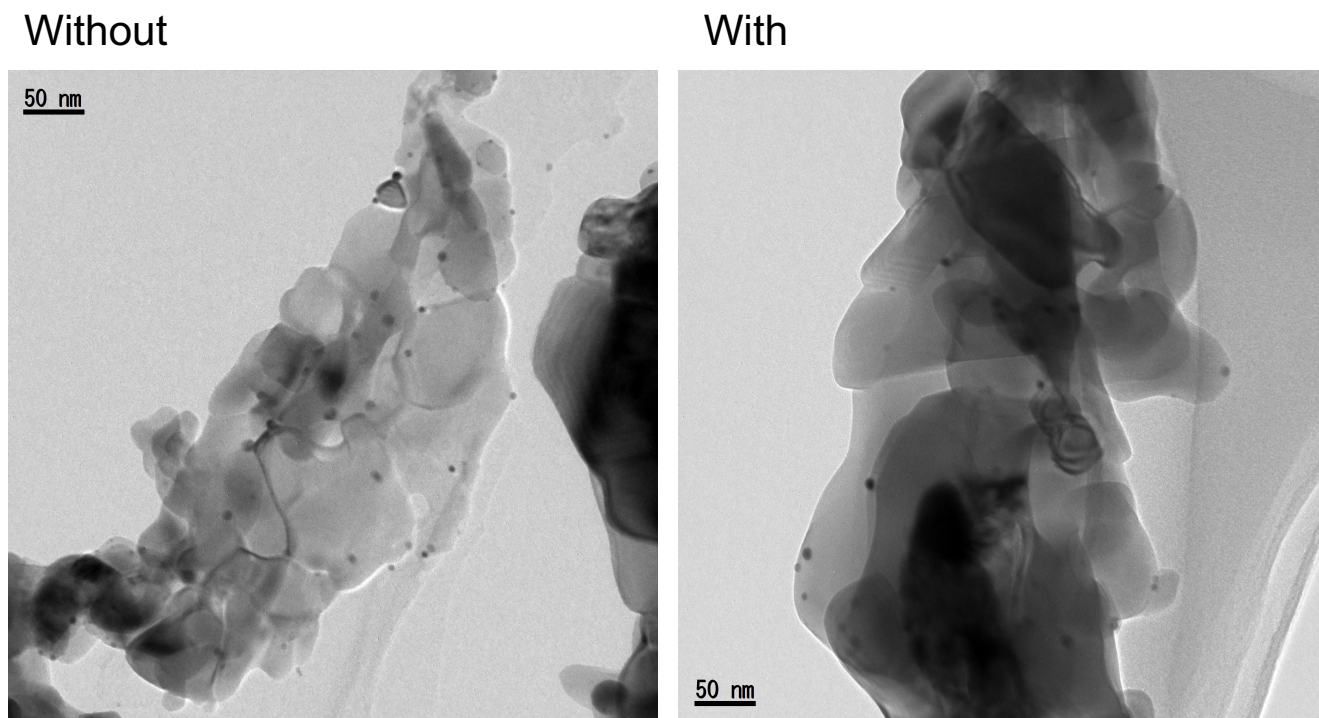


Fig. S14. TEM images of Pt-photodeposited $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ with and without NaCl–CsCl treatment at 723 K.

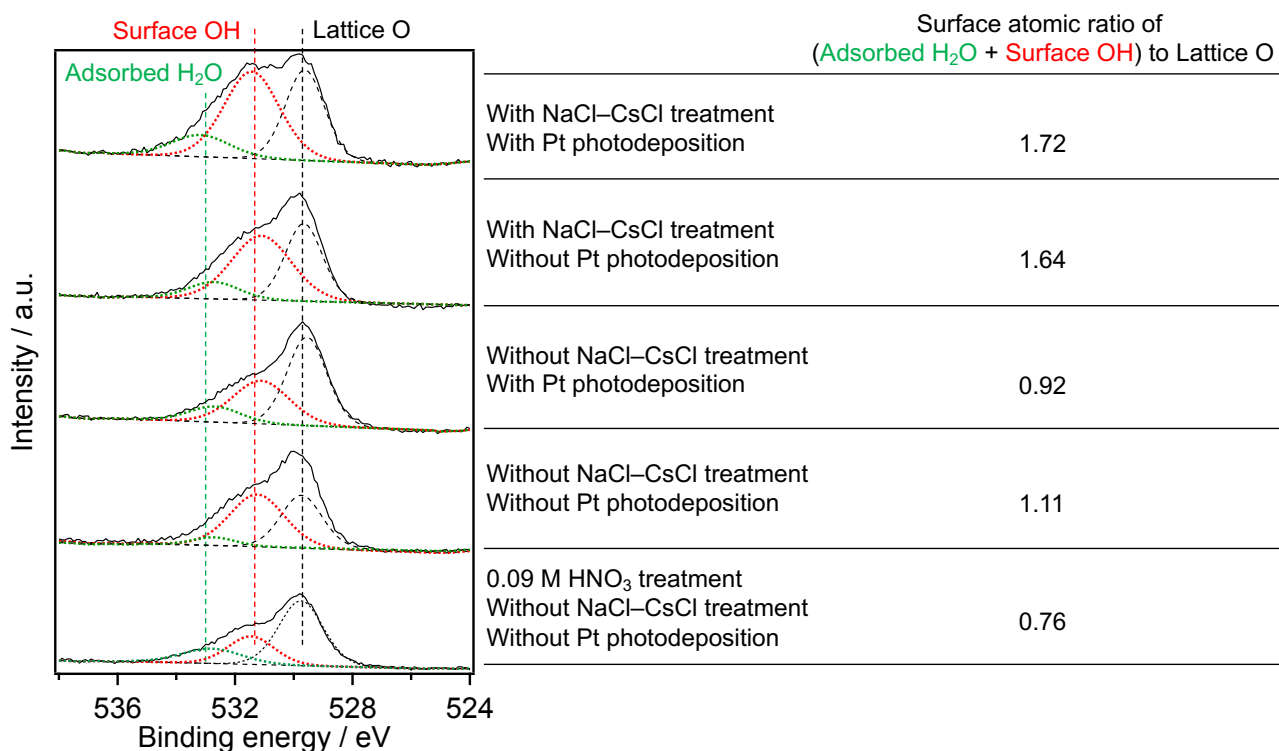


Fig. S15. O 1s XPS data for $\text{Pb}_2\text{Ti}_2\text{O}_{5.4}\text{F}_{1.2}$ after various modifications. Surface atomic ratios of hydrophilic species relative to the amount of lattice oxygen are also presented.

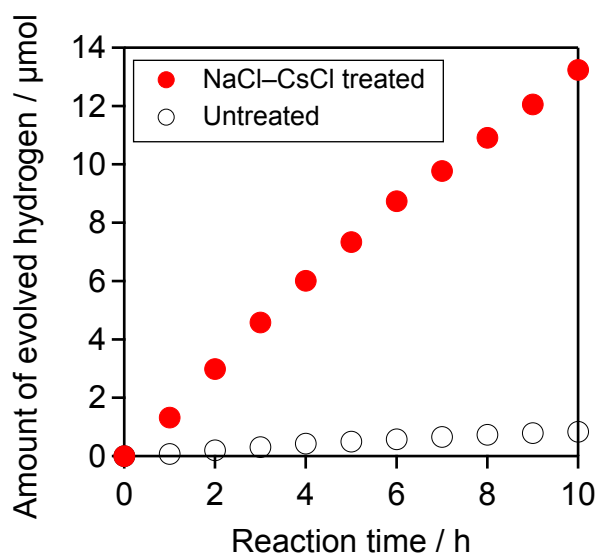


Fig. S16. Time courses of H₂ evolution using Pb₂Ti₄O₉F₂ with and without NaCl–CsCl treatment under UV irradiation ($\lambda > 350$ nm). Reaction conditions: catalyst, 100 mg (0.5 wt% Pt photodeposited); MeCN/TEOA mixture (13:1 v/v) 140 mL containing 1 mL water; light source, xenon lamp (300 W).

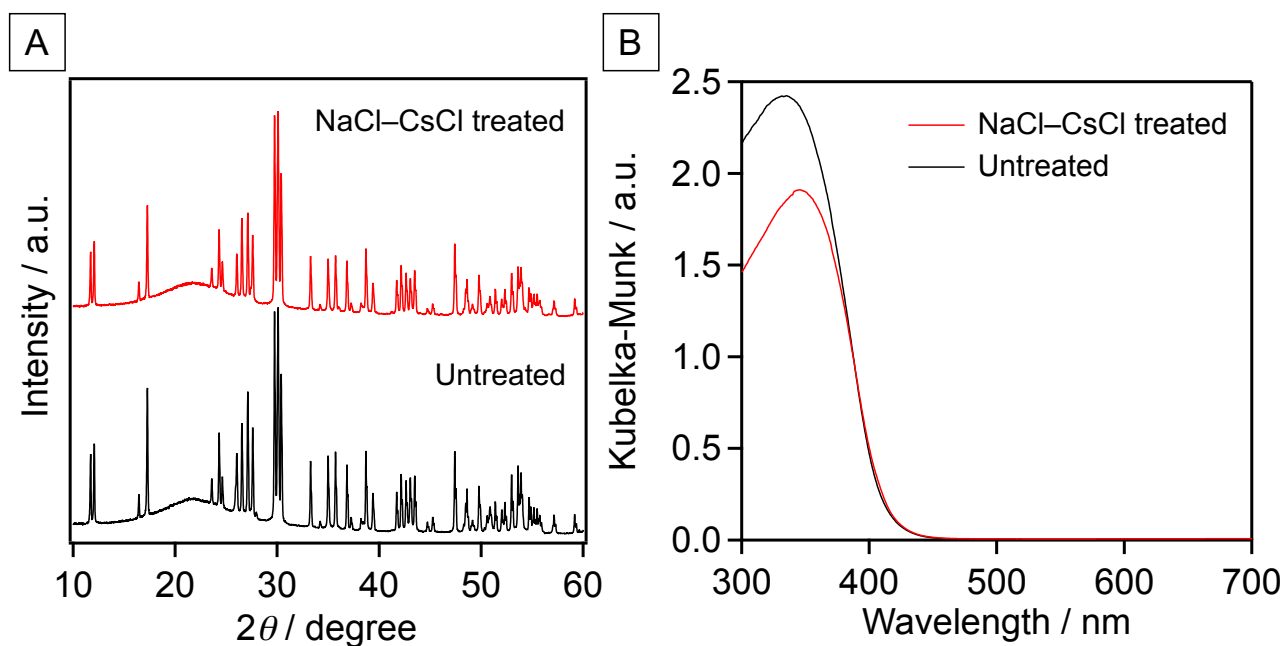


Fig. S17. (A) XRD patterns and (B) UV-visible diffuse reflectance spectra of Pb₂Ti₄O₉F₂ with and without the NaCl–CsCl treatment.

Preparation of Pb₂Ti₄O₉F₂ and post-treatment

Pb₂Ti₄O₉F₂ was synthesized using a solid state reaction from a mixture of PbO (99.9%, Rare Metallic Co., Ltd.), PbO₂ (99%, Rare Metallic Co., Ltd.), PbF₂ (99.9%, Mitsuwa Pure Chemical.) and TiO₂ (99.99%, Rare Metallic Co., Ltd.) powders according to a previously reported procedure with some modifications.^{S7} These powders were mixed in a PbO/PbO₂/PbF₂/TiO₂ molar ratio of 0.60:0.20:1.2:4.0. The mixture was subsequently heated at 823 K for 12 h in an evacuated Pyrex tube. Post-treatment of the as-prepared Pb₂Ti₄O₉F₂ with NaCl–CsCl (35:65 molar ratio) was the same as that applied to the Pb₂Ti₂O_{5.4}F_{1.2}. Specifically, 250 mg of Pb₂Ti₄O₉F₂ was mixed with 400 mol% NaCl–CsCl (relative to the amount of Pb₂Ti₄O₉F₂) using a mortar and pestle at room temperature under ambient pressure. The mixture was sealed in a Pyrex tube under vacuum then heated at 723 K for 5 h with a ramp rate of 1 K min⁻¹. After uncontrolled cooling to room temperature, the resulting solid was washed with water to remove residual alkaline chloride species and then dried in an oven at 343 K.

Table S1. Surface atomic ratios and photocatalytic activities of the post-treated Pb₂Ti₂O_{5.4}F_{1.2}

Entry	Sample	Surface atomic ratios ^a			Activity ^b / μmol h ⁻¹
		F/Ti	Na/Ti	Cs/Ti	
1	Before treatment	0.83	n.d.	n.d.	0.065
2	Treated with NaCl–CsCl	0.80	0.02	0.12	0.48
3	Treated with 0.09 M HNO ₃	0.55	-	-	0.23
4	Treated with first 0.09 M HNO ₃ , then NaCl–CsCl	0.55	n.d.	0.02	0.11
5	Treated with first NaCl–CsCl, then 0.09 M HNO ₃	0.55	n.d.	n.d.	0.44

^a Determined by the corresponding XPS peak area. ^b Reaction conditions: catalyst, 100 mg (0.5 wt% Pt photodeposited); MeCN/TEOA mixed solution (13:1 v/v) 140 mL containing 1 mL water; light source, xenon lamp (300 W). The NaCl–CsCl treatment was done at 723 K in all cases. Activities contained experimental errors of ~15%.

References

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 S2. A. Nakada, S. Nishioka, J. J. M. Vequizo, K. Muraoka, T. Kanazawa, A. Yamakata, S. Nozawa, H. Kumagai, S.-i. Adachi, O. Ishitani and K. Maeda, *J. Mater. Chem. A*, 2017, **5**, 11710-11719.
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