Supporting Information

Vanadium-based oxyhalide photocatalysts for visible-light-driven Z-scheme water splitting: advancing conduction band engineering

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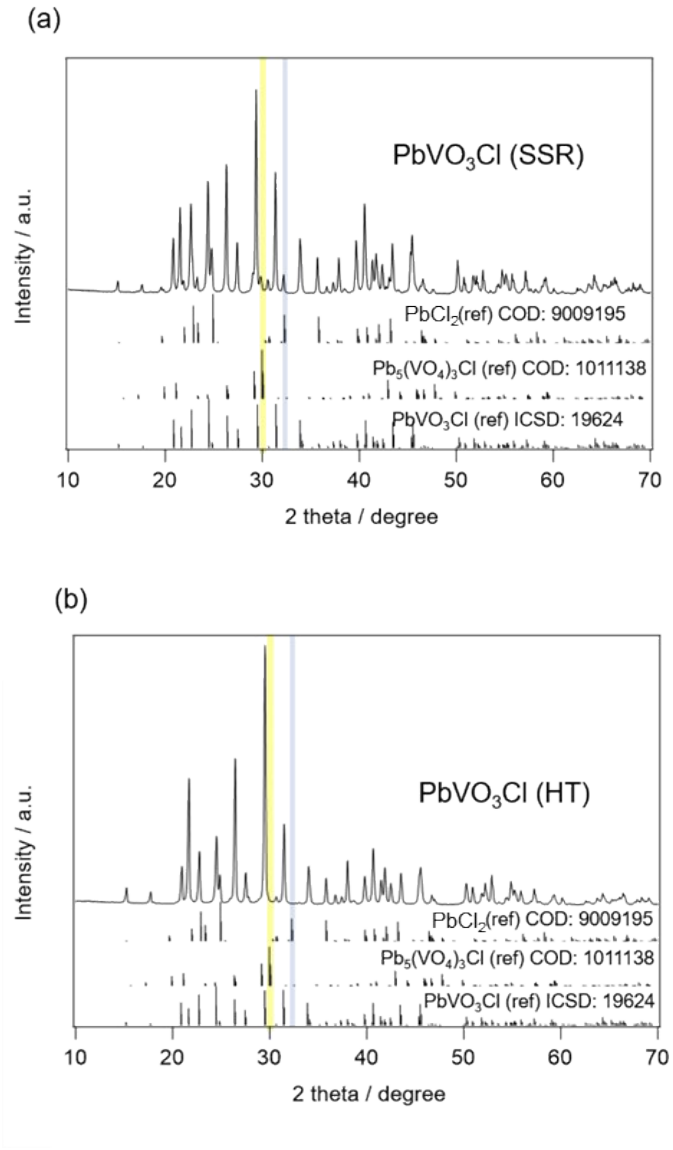

Figure S1. XRD patterns of $PbVO_3Cl$ synthesized by (a) solid-state reaction and (b) hydrothermal reaction.

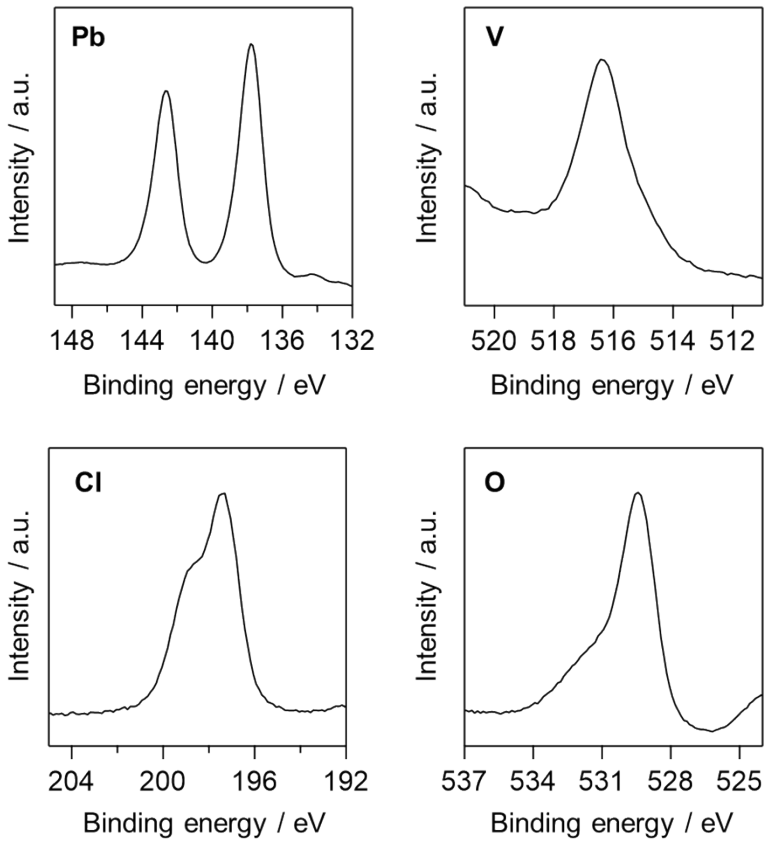

Figure S2. XPS spectra of Pb 4f, V $2p_{3/2}$, Cl 2p and O 1s for the hydrothermally synthesized $PbVO_3Cl$. The oxidation states were evaluated with reference to the NIST XPS Database.

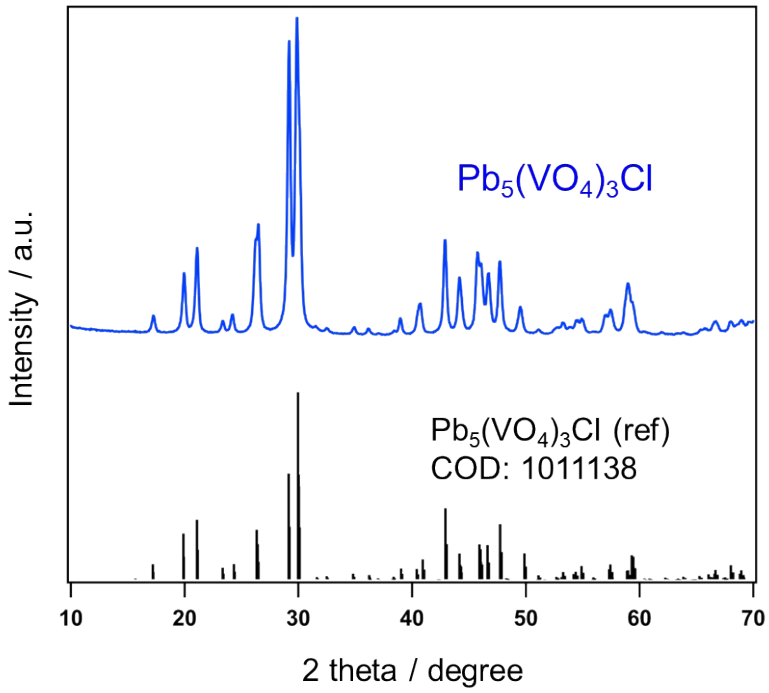

Figure S3. XRD pattern of $Pb_5(VO_4)_3Cl$ synthesized by precipitation method.

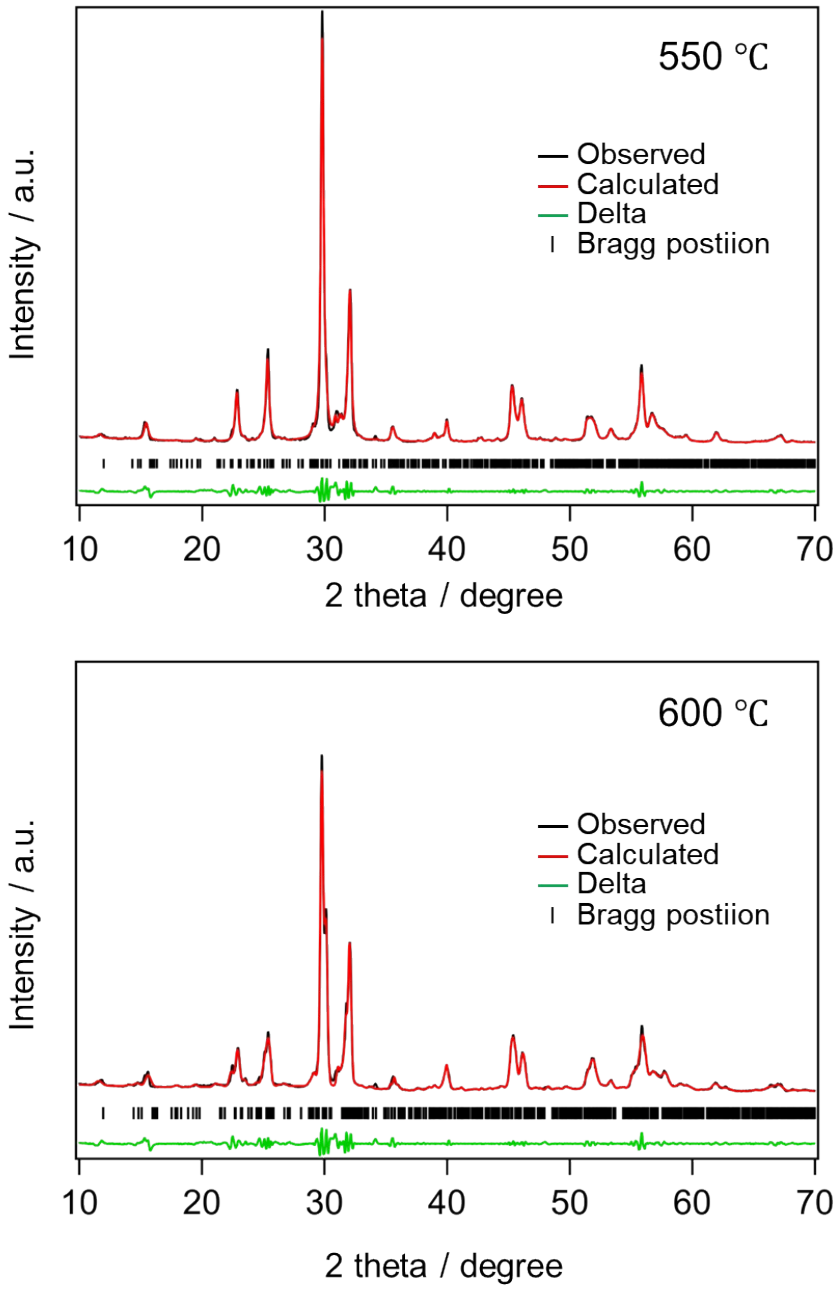

Figure S4. Le Bail refinements using XRD patterns of $Pb_{14}(VO_4)_2O_9Cl_4$ prepared at 550 ℃ and 600 ℃.

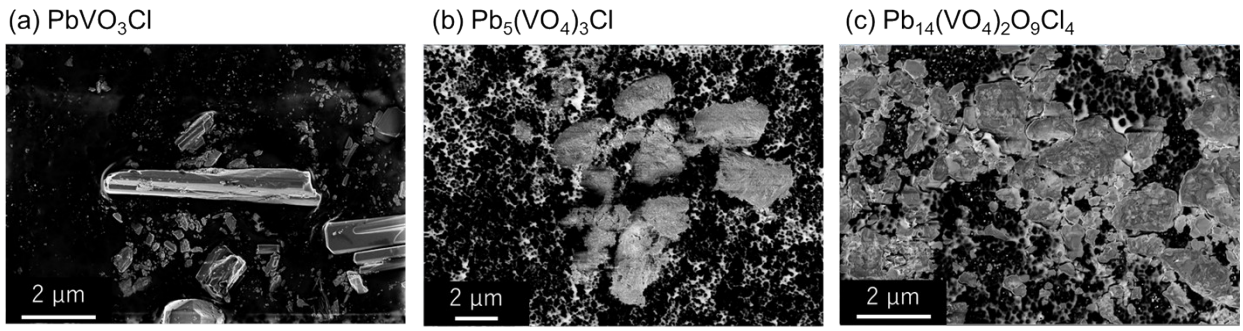

Figure S5. SEM images of (a) $PbVO_3Cl$, (b) $Pb_5(VO_4)_3Cl$, and (c) $Pb_{14}(VO_4)_2O_9Cl_4$. The $PbVO_3Cl$ sample was prepared by hydrothermal reaction, and the $Pb_{14}(VO_4)_2O_9Cl_4$ sample was prepared by solid-state reaction at 600 °C.

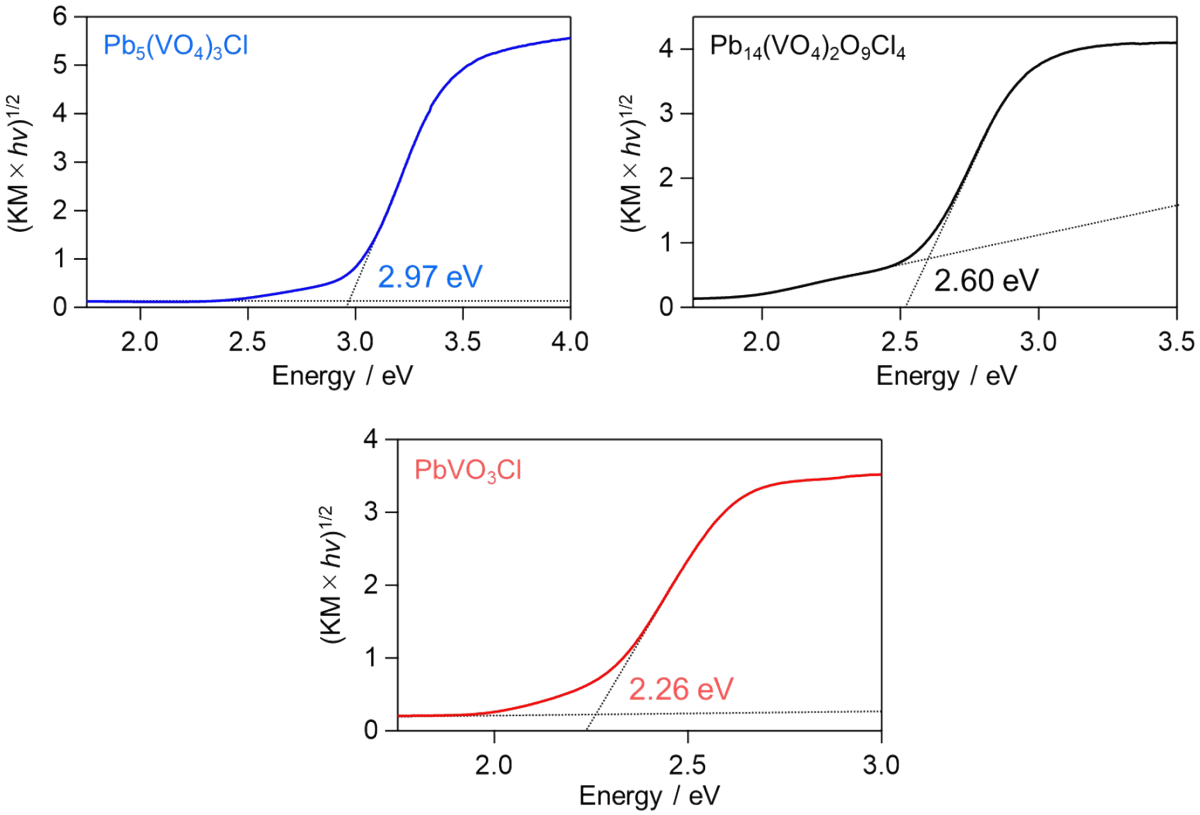

Figure S6. Tauc plots of $Pb_5(VO_4)_3Cl$, $Pb_{14}(VO_4)_2O_9Cl_4$, and $PbVO_3Cl$. Based on the band structure calculations (Figure S7), these materials were suggested to be indirect bandgap semiconductors; accordingly, the coefficient for indirect transition was applied in the calculations.

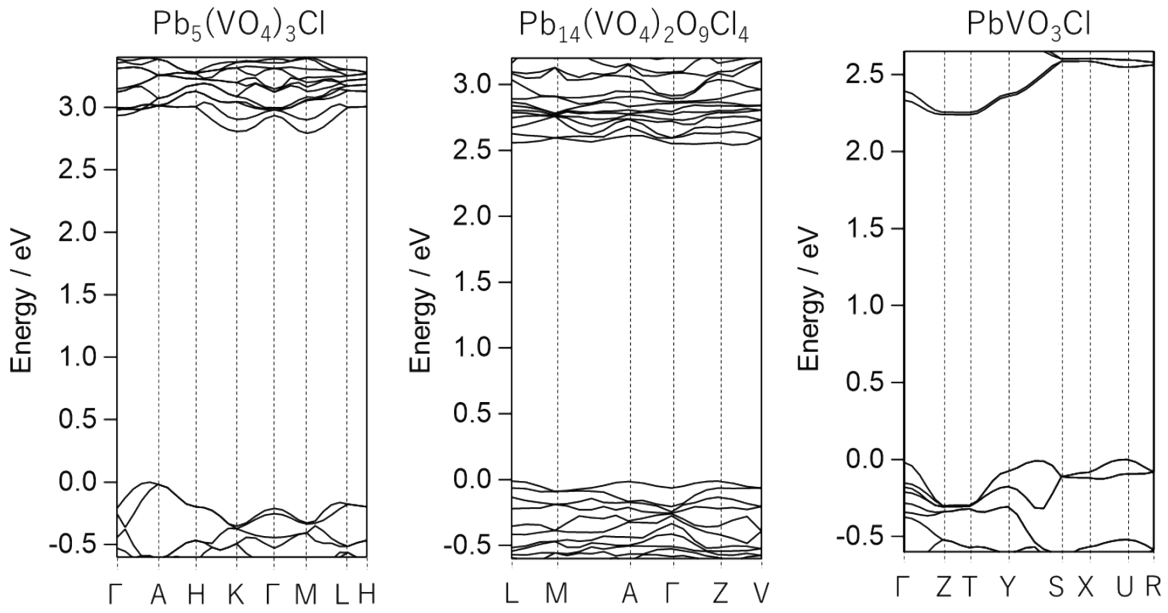

Figure S7. Band structures of $Pb_5(VO_4)_3Cl$, $Pb_{14}(VO_4)_2O_9Cl_4$, and $PbVO_3Cl$.

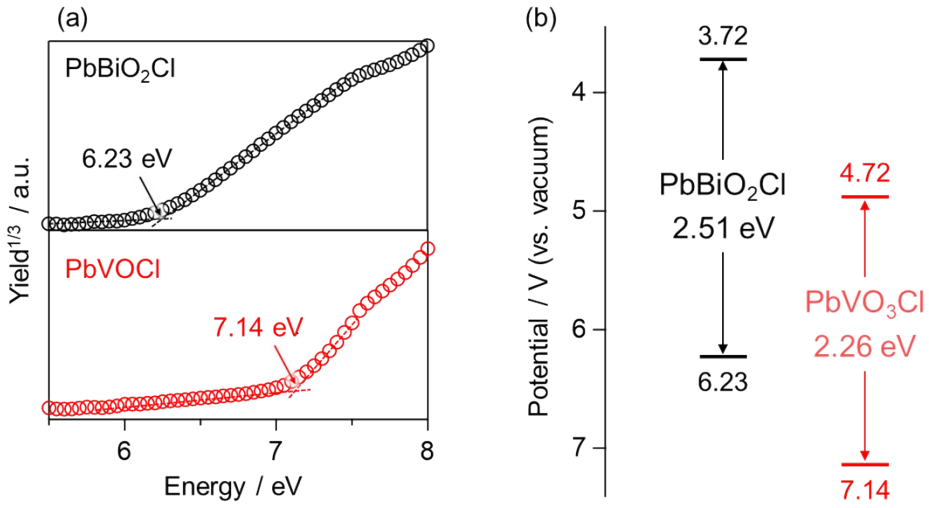

Figure S8 (a) Photoelectron yield spectra of $PbBiO_2Cl$ and $PbVO_3Cl$. The spectrum of $PbBiO_2Cl$ was cited from our previous work.[S1] (b) Band diagram estimated from the obtained ionization energies.

[S1] H. Suzuki, M. Higashi, O. Tomita, Y. Ishii, T. Yamamoto, D. Kato, T. Kotani, D. Ozaki, S. Nozawa, K. Nakashima, K. Fujita, A. Saeki, H. Kageyama, R. Abe, *Chem. Mater.* 2021, **33**, 9580-9587.

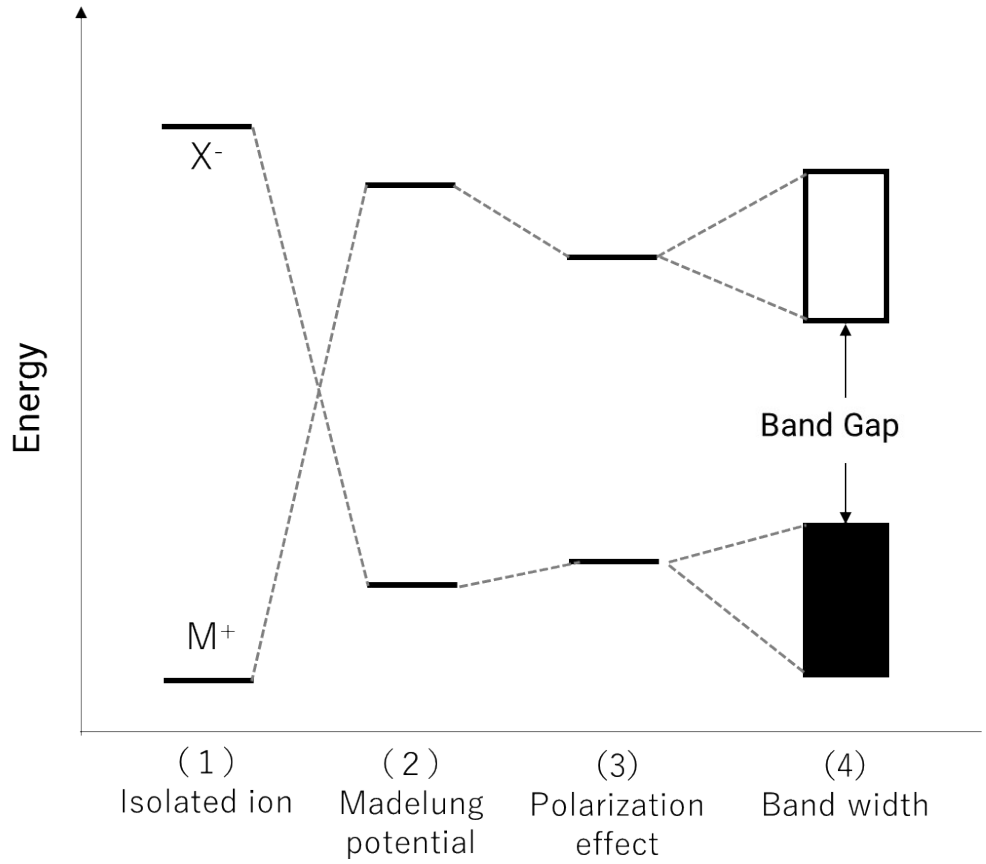

Figure S9. Band formation in solids from isolated atoms adopted and modified from Ref [S2].

[S2] P. A. Cox, *The Electronic Structure and Chemistry of Solids; Oxford Science Publications: Oxford*, 1986, 146.

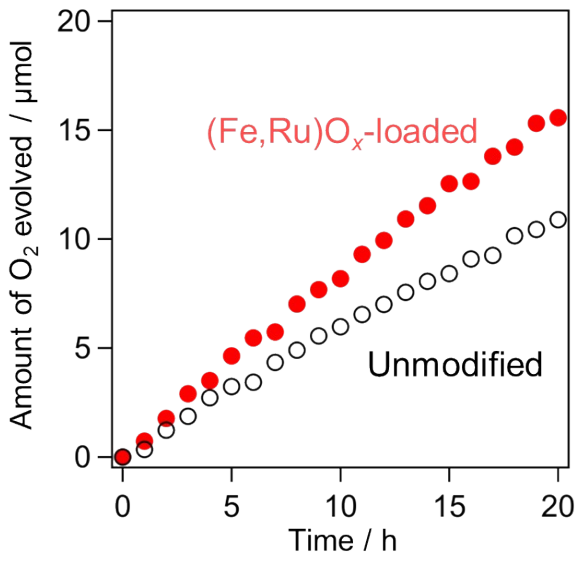

Figure S10. Photocatalytic O_2 evolution using unmodified or (Fe,Ru)O_x-loaded $PbVO_3Cl$ in aqueous $Fe(NO_3)_3$ solution (5 mM, 250 mL, pH 2.4) under visible light irradiation ($\lambda > 400$ nm).

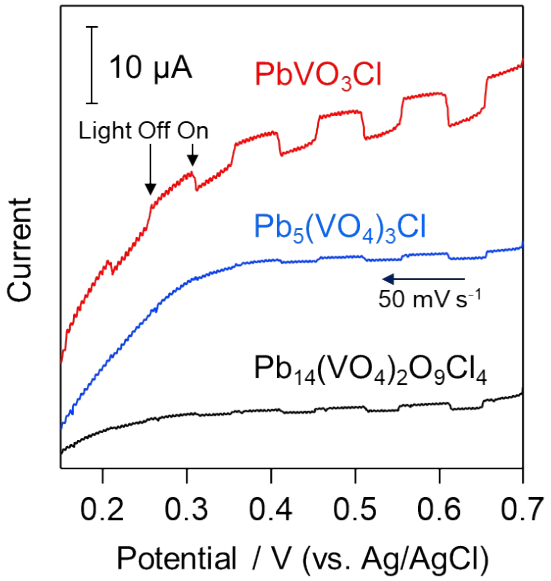

Figure S11. Current–potential curves for electrodes composed of $PbVO_3Cl$, $Pb_5(VO_4)_3Cl$, and $Pb_{14}(VO_4)_2O_9Cl_4$ in a phosphate-buffered solution (0.1 M, pH 6.0) under chopped visible light from a 300-W Xe lamp with a cutoff filter (L-42).

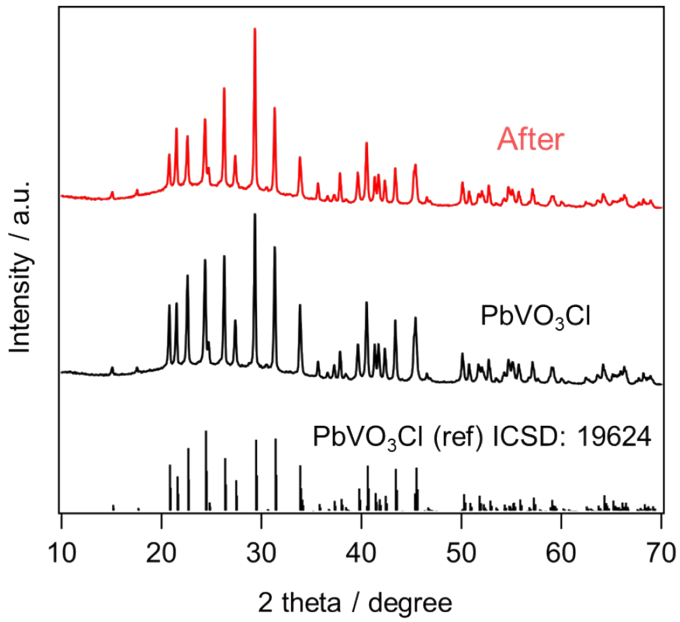

Figure S12. XRD pattern of (Fe,Ru)O_x-$PbVO_3Cl$ after photocatalytic O_2 evolution in aqueous $Fe(NO_3)_3$ solution (5 mM, 250 mL, pH 2.4) under visible light irradiation (λ > 400 nm), shown in Figure 6a.

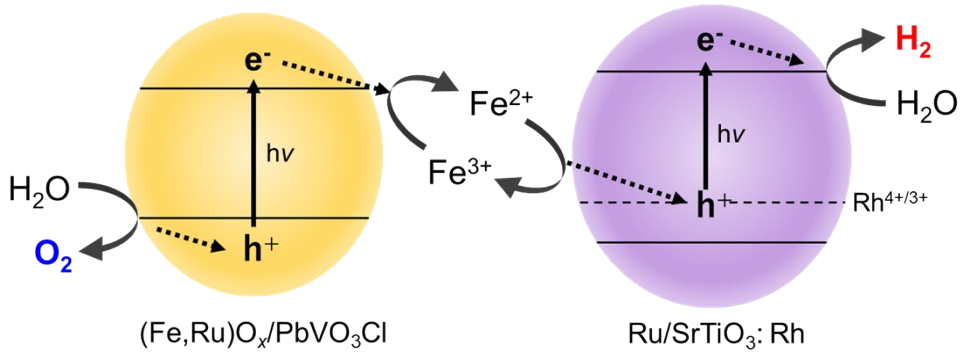

Figure S13. Schematic of Z-scheme water splitting using a mixture of $Ru/SrTiO_3$:Rh as a H_2-evolution photocatalyst and (Fe,Ru)O_x/$PbVO_3Cl$ as an O_2-evolution photocatalyst. The dotted arrows represent the electron flow.

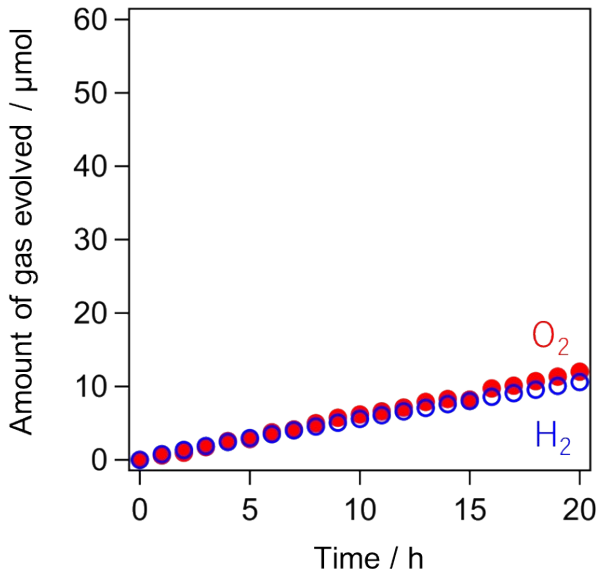

Figure S14. Time courses of photocatalytic evolution of H_2 and O_2 using a mixture of $Ru/SrTiO_3$:Rh and $(Fe,Ru)O_x/PbVO_3Cl$ under visible light ($\lambda >$ 400 nm) in an aqueous $Fe(NO_3)_3$ solution (5 mM, 250 mL, pH 2.4).

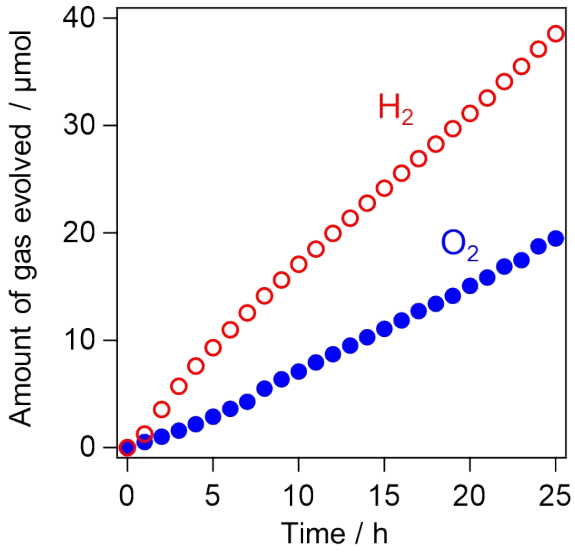

Figure S15. Z-scheme water splitting using unmodified $PbVO_3Cl$ as an OEP and $Ru/SrTiO_3$:Rh as a HEP under visible light ($\lambda >$ 400 nm) in an aqueous $Fe(ClO_4)_3$ solution (5 mM, 250 mL, pH 2.4).