Supplementary Information

Efficient Hypochlorous Acid (HClO) Production via Photoelectrochemical Solar Energy Conversion Using a BiVO₄-based photoanode

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Figure S1 Molar fraction of Cl₂ (black), HClO (red), and ClO⁻ (blue) plotted versus pH of an aqueous solution based on *Eq. I* and 2 (equations are presented in the main text). \([\text{Cl}_2] + [\text{HClO}] + [\text{ClO}^-] = 0.01 \text{ M} \). \([\text{Cl}^-] = 0.5 \text{ M}\).
Figure S2 Photograph of experimental setup for the photoelectrochemical HClO production under simulated solar light irradiation.
Figure S3 Change in colour of the anolyte solution containing the produced HClO by adding the DPD reagent. (a) before adding the DPD reagent (after the photoelectrochemical reaction). (b) anolyte solution was changed into pale red by adding the DPD reagent. (c) colour of the anolyte solution after adding the DPD reagent gradually became deeper with the photoirradiation (before the reaction (i), and during the reaction (ii) ~ (viii)).
Figure S4  I-V curves of BiVO₄/WO₃/FTO photoelectrode measured in (a) 0.5 M NaCl, (b) 0.1 M NaCl + 0.4 M NaClO₄, (c) 0.5 M NaClO₄, and (d) 0.1 M NaCl aqueous solution. Light source: simulated solar light (AM 1.5) with L-42 cut off filter, anode chamber: Air atmosphere, cathode chamber: O₂ atmosphere, irradiation area: ca. 4.0 cm².
**Figure S5** Absorption spectra of (a) BiVO$_4$/WO$_3$/FTO, (b) WO$_3$/FTO, and (c) bare FTO substrate. R: reflectance, T: transmittance.
Figure S6 Current efficiency for HClO production ($\eta_{\text{HClO}}$) in the photoelectrochemical Cl$^-$ oxidation using BiVO$_4$/WO$_3$/FTO photoanode. Concentration of electrolyte: 0.5, light source: simulated solar light (AM 1.5) with L-42 cut off filters, stable anodic current: 0.5 mA, photoirradiation time: 1000 s, anode chamber: air atmosphere, cathode chamber: O$_2$ atmosphere, irradiation area: ca. 4.0 cm$^2$. 
Figure S7 External bias dependence on the concentration of HClO produced in the electrolyte solution (CHClO, left axis) and the current efficiency for HClO production (ηHClO, right axis) in the photoelectrochemical Cl\(^-\) oxidation using BiVO\(_4\)/WO\(_3\)/FTO photoanode. Electrolyte: 5.0 M NaCl, light source: simulated solar light (AM 1.5) with L-42 cut off filters, photoirradiation time: 600 s, anode chamber: air atmosphere, cathode chamber: O\(_2\) atmosphere, irradiation area: ca. 4.0 cm\(^2\).
**Figure S8** Current efficiency for HClO (red), O₂ in gas phase (green), and O₂ dissolved in the electrolyte solution (blue) in the photoelectrochemical Cl⁻ oxidation using BiVO₄/WO₃/FTO photoanode. Amount of O₂ evolved was determined by using O₂ sensor (Optical Oxygen Meter, FireStingO₂, pyro science). Total current efficiency is the sum of HClO, O₂ in gas phase, and O₂ dissolved in the electrolyte solution. In the case of 0.0 M NaCl concentration, NaH₂PO₄ aqueous solution was used as the electrolyte solution.