Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Efficient Hypochlorous Acid (HClO) Production *via* Photoelectrochemical Solar Energy Conversion Using a $BiVO_4$-based photoanode

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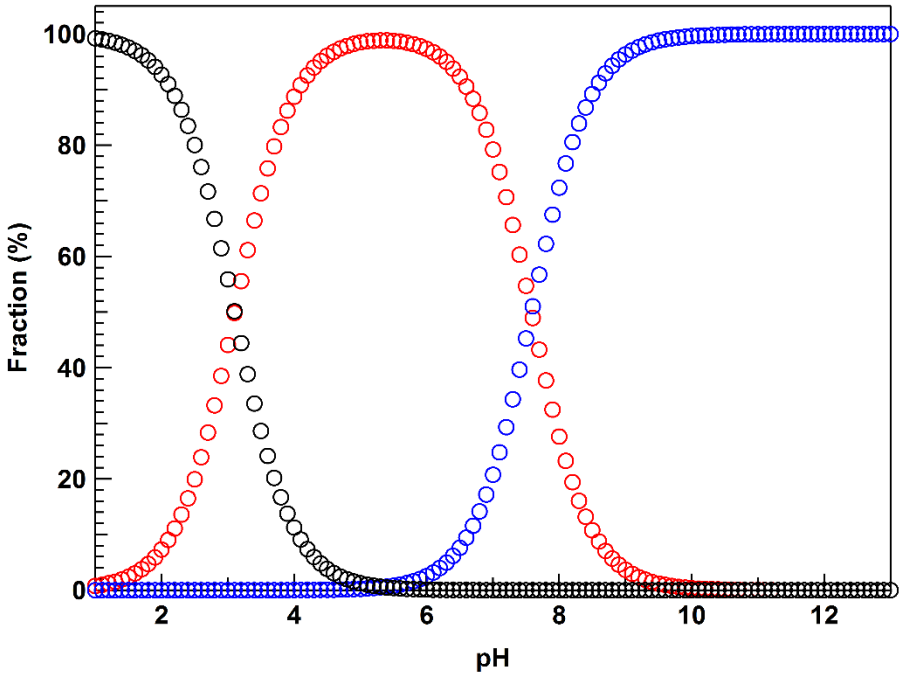

Figure S1 Molar fraction of Cl_2 (black), HClO (red), and ClO^- (blue) plotted versus pH of an aqueous solution based on ***Eq.1*** and ***2*** (equations are presented in the main text). $[Cl_2] + [HClO] + [ClO^-] = 0.01$ M. $[Cl^-] = 0.5$ M.

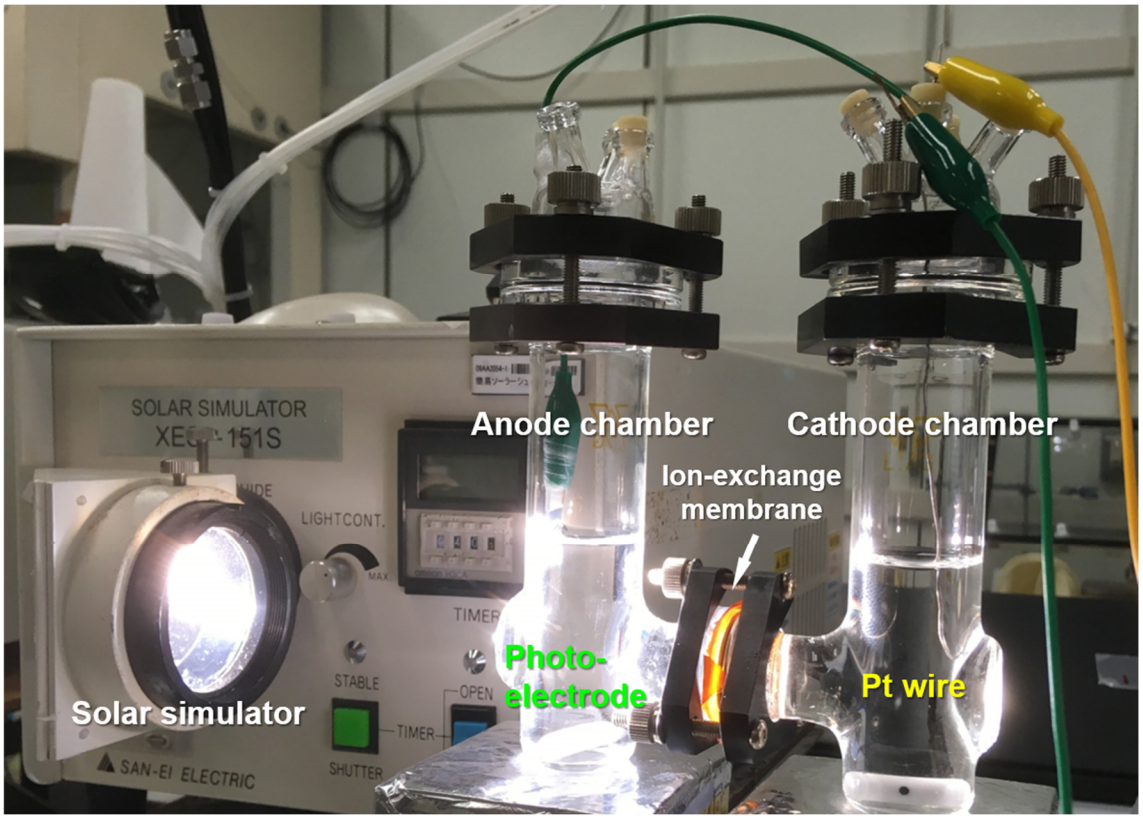

Figure S2 Photograph of experimental setup for the photoelectrochemical HClO production under simulated solar light irradiation.

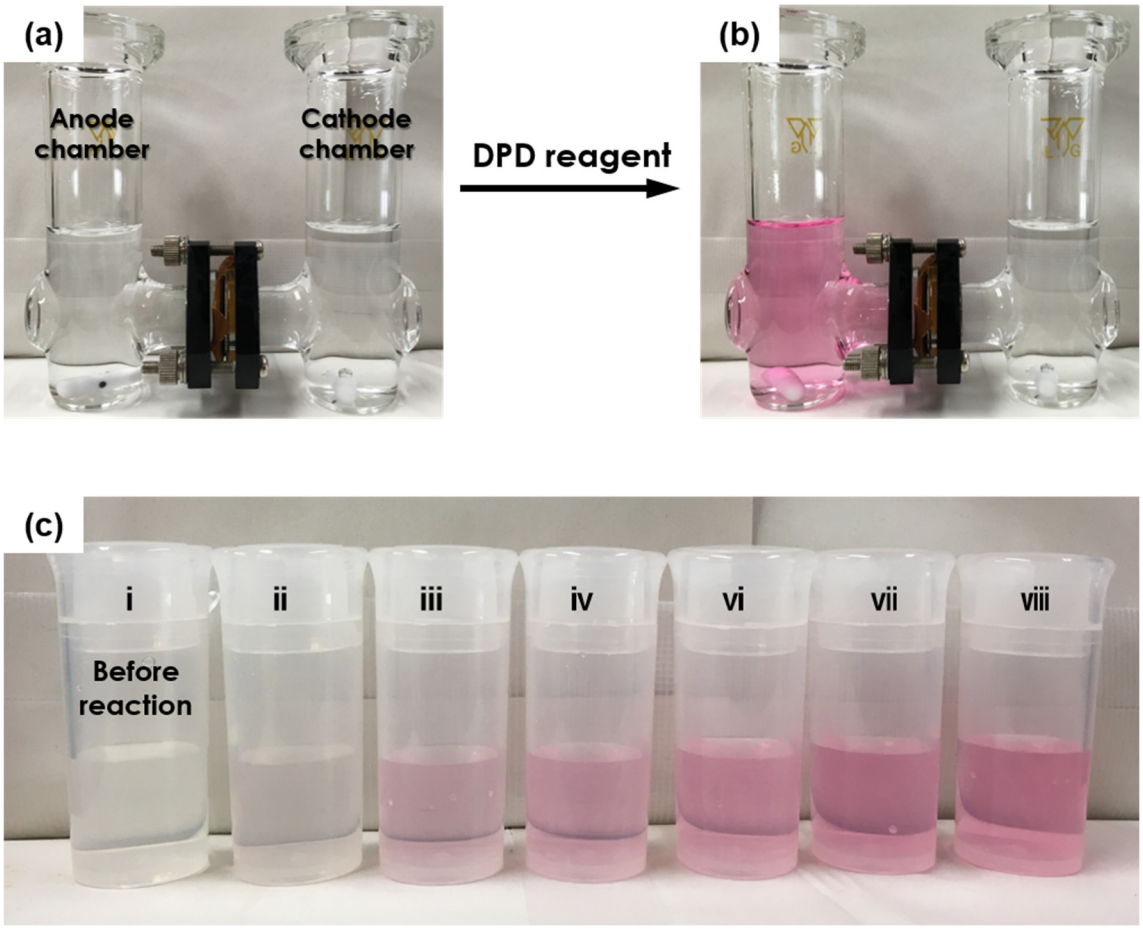

Figure S3 Change in colour of the anolyte solution containing the produced HClO by adding the DPD reagent. (a) before adding the DPD reagent (after the photoelectrochemical reaction). (b) anolyte solution was changed into pale red by adding the DPD reagent. (c) colour of the anolyte solution after adding the DPD reagent gradually became deeper with the photoirradiation (before the reaction (i), and during the reaction (ii) ~ (viii)).

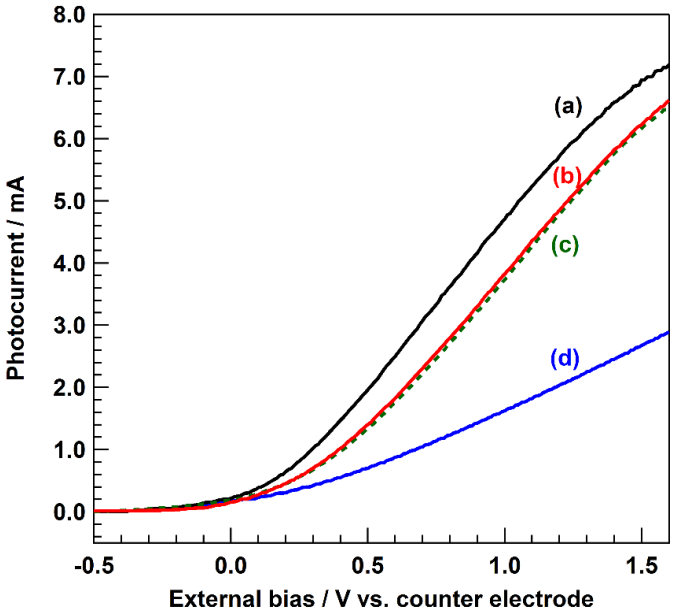

Figure S4 I-V curves of $BiVO_4/WO_3$/FTO photoelectrode measured in (a) 0.5 M NaCl, (b) 0.1 M NaCl + 0.4 M $NaClO_4$, (c) 0.5 M $NaClO_4$, and (d) 0.1 M NaCl aqueous solution. Light source: simulated solar light (AM 1.5) with L-42 cut off filter, anode chamber: Air atmosphere, cathode chamber: O_2 atmosphere, irradiation area: ca. 4.0 cm^2.

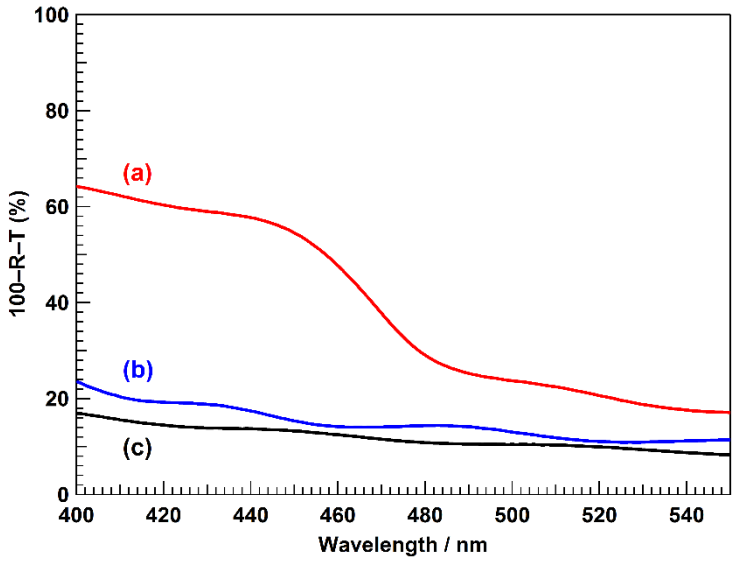

Figure S5 Absorption spectra of (a) $BiVO_4/WO_3$/FTO, (b) WO_3/FTO, and (c) bare FTO substrate. R: reflectance, T: transmittance.

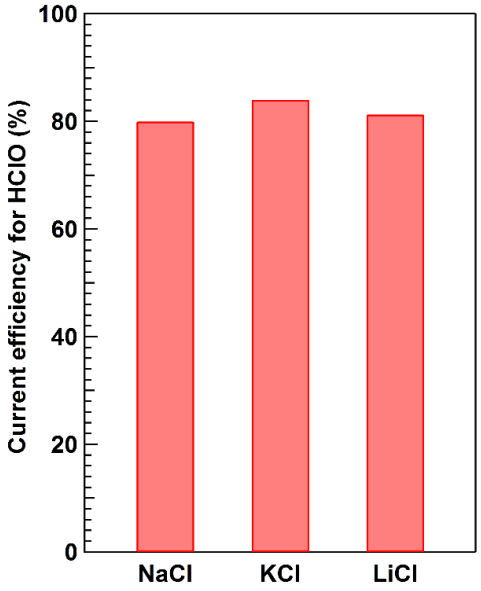

Figure S6 Current efficiency for HClO production (η_{HClO}) in the photoelectrochemical Cl^- oxidation using $BiVO_4/WO_3$/FTO photoanode. Concentration of electrolyte: 0.5, light source: simulated solar light (AM 1.5) with L-42 cut off filters, stable anodic current: 0.5 mA, photoirradiation time: 1000 s, anode chamber: air atmosphere, cathode chamber: O_2 atmosphere, irradiation area: ca. 4.0 cm^2.

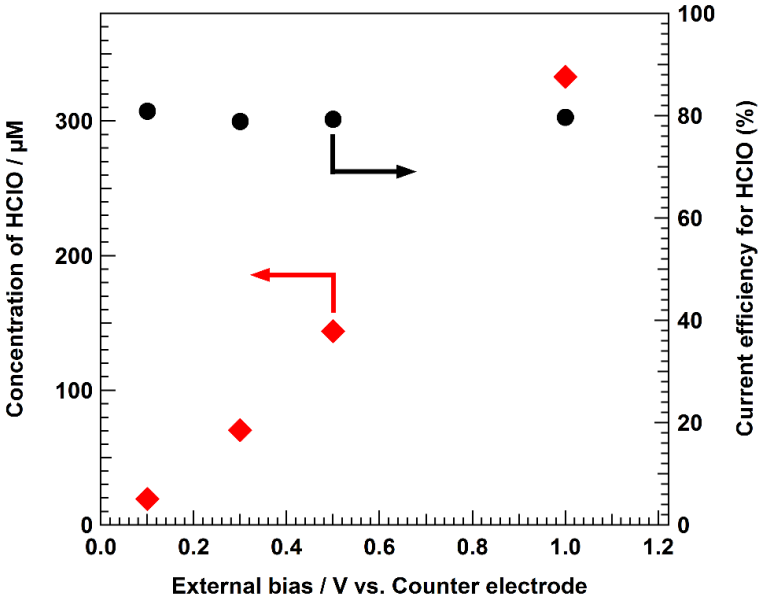

Figure S7 External bias dependence on the concentration of HClO produced in the electrolyte solution (C_{HClO}, left axis) and the current efficiency for HClO production (η_{HClO}, right axis) in the photoelectrochemical Cl^- oxidation using $BiVO_4/WO_3$/FTO photoanode. Electrolyte: 5.0 M NaCl, light 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.

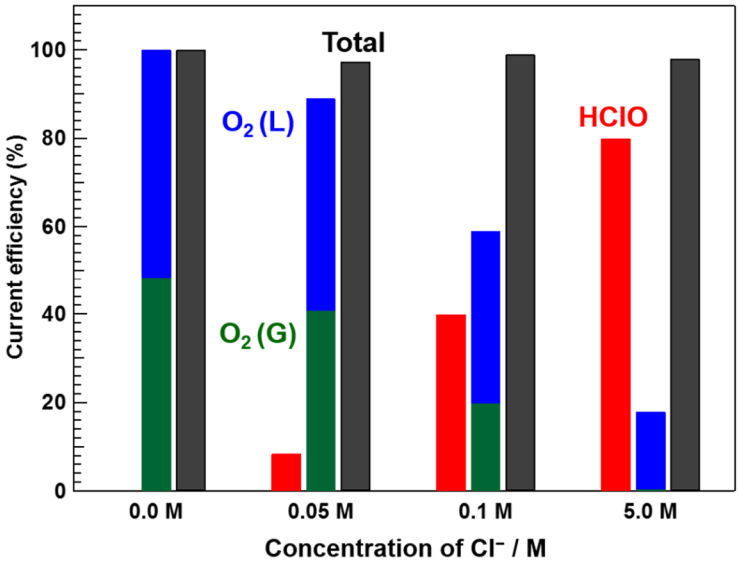

Figure S8 Current efficiency for HClO (red), O_2 in gas phase (green), and O_2 dissolved in the electrolyte solution (blue) in the photoelectrochemical Cl^- oxidation using $BiVO_4/WO_3$/FTO photoanode. Amount of O_2 evolved was determined by using O_2 sensor (Optical Oxygen Meter, FireStingO_2, pyro science). Total current efficiency is the sum of HClO, O_2 in gas phase, and O_2 dissolved in the electrolyte solution. In the case of 0.0 M NaCl concentration, NaH_2PO_4 aqueous solution was used as the electrolyte solution.