

Electronic Supplementary Information for

**Highly efficient oxygen evolution and solar energy accumulation over a BiVO₄
photocatalyst employing Fe(III) as an electron acceptor**

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Evaluation procedure of photocatalytic performance of BiVO₄

• The quantitative analysis of photocatalytic Fe(II) production.

At first, we prepared the distill water controlled each solution temperatures (20 °C – 50 °C). And then, BiVO₄ powder (400 mg), 250 mM of Fe(ClO₄)₃ solution (1.2 mL), and conc. HClO₄ were added in the distil water (total volume of reaction solution: 150 mL). Finally, solar simulated light (San-Ei Electric Co., Ltd., XES-151S) through the mask (9 cm²) or monochromatic light (Asahi Spectra Co., Ltd., MAX-302) through the band pass filter was irradiated to the reaction solution. After each reaction time passed, the reaction solution (0.5 mL) was sampled and filtered using a disposable syringe (TERUMO Co, SS-02LZ) attached with filter (Shimadzu GLC Ltd., GLCTD-MCE1322).

Quantitative analysis of Fe(II) is conducted by the phenanthroline method. The reaction solution (0.2 mL) was mixed with 500 mM of acetic acid solution (0.25 mL), 0.017 g of CH₃COONa · 3H₂O, 5 mM of 1,10-phenanthroline solutions (0.25 mL), and distill water (3.3 mL), and then absorption spectrum from 450 to 550 nm was measured. Quantitative analysis was conducted by the absorbance at 510 nm using the calibration data as shown below (Table S1 and Figure S2).

Table S1 Standard solutions for the preparation of calibration curve.

| Sample solution | Actual concentration of Fe(II)/ μM ^a | Absorbance at 510 nm |
|---------------------------------|--|-------------------------|
| 2 mM Fe(III) and 0 mM Fe(II) | 0 | 0.01093 |
| 1.6 mM Fe(III) and 0.4mM Fe(II) | 20 | 0.23773 |
| 1.2 mM Fe(III) and 0.8mM Fe(II) | 40 | 0.46073 |
| 0.8 mM Fe(III) and 1.2mM Fe(II) | 60 | 0.68545 |
| 0.4 mM Fe(III) and 1.6mM Fe(II) | 80 | 0.91932 |
| 0 mM Fe(III) and 2mM Fe(II) | 100 | 1.13263 |

^aSample solution (0.2 mL) was measured as 20 fold dilution by mixing with 500 mM of acetic acid solution (0.25 mL), 0.017 g of CH₃COONa · 3H₂O, 5 mM of 1,10-phenanthroline solutions (0.25 mL), and distill water (3.3 mL).

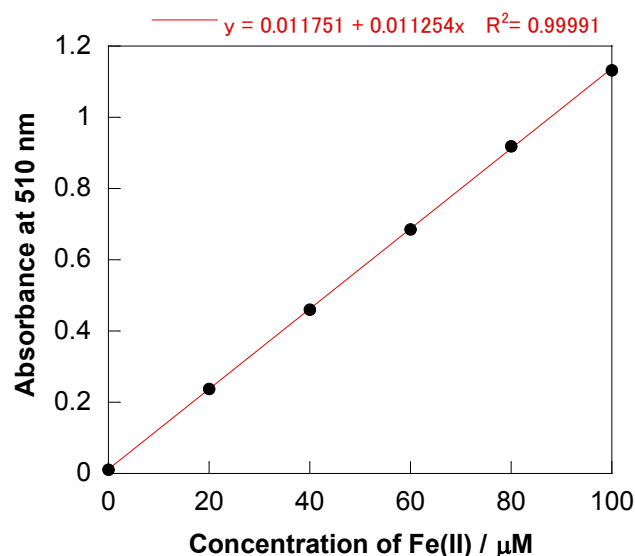


Figure S1 Calibration curve for quantitative analysis of Fe(II) ions.

• **The quantitative analysis of photocatalytic O_2 production (Figure 5).**

Photocatalytic reactions were performed in a Pyrex side-window cell connected to a gas-closed circulation system using a 300 W Xe illuminator (ILC Technology, Inc., CERMAX LX-300) as shown in Figure S6. Incident light was controlled using an L42 cut-off filter. Using a magnetic stirrer, the photocatalyst powder (400 mg) was dispersed in an aqueous solution (150 mL, pH 2.5) of 2 mM $\text{Fe}(\text{ClO}_4)_3$ solution. The quantity of evolved O_2 was determined via on-line gas chromatography (Shimadzu Corporation), equipped with an MS-5A column and a thermal conductivity detector (TCD), with an Ar carrier.

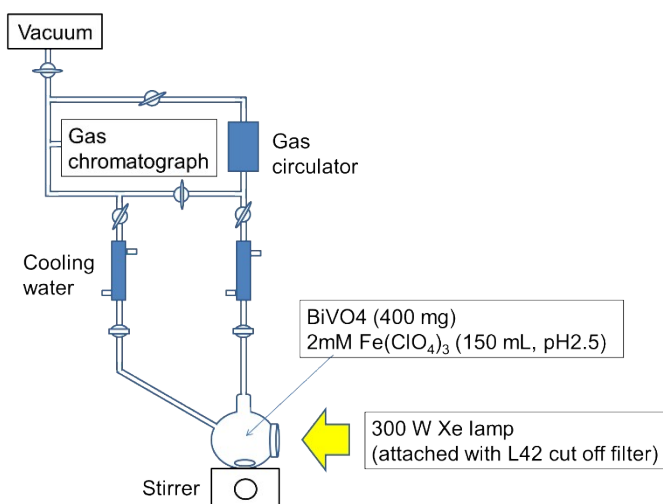


Figure S2 Reaction setup for evaluation of photocatalytic O_2 production

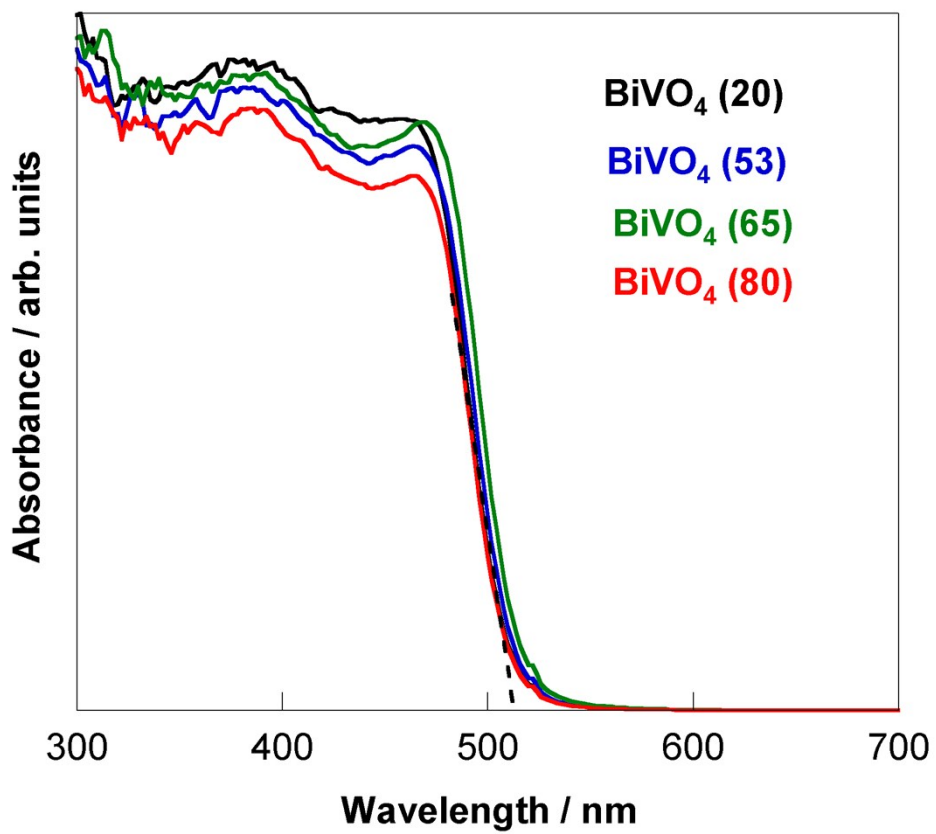


Figure S3 Diffuse reflection spectra of BiVO₄ powder prepared by the LSR method at various solution temperatures.

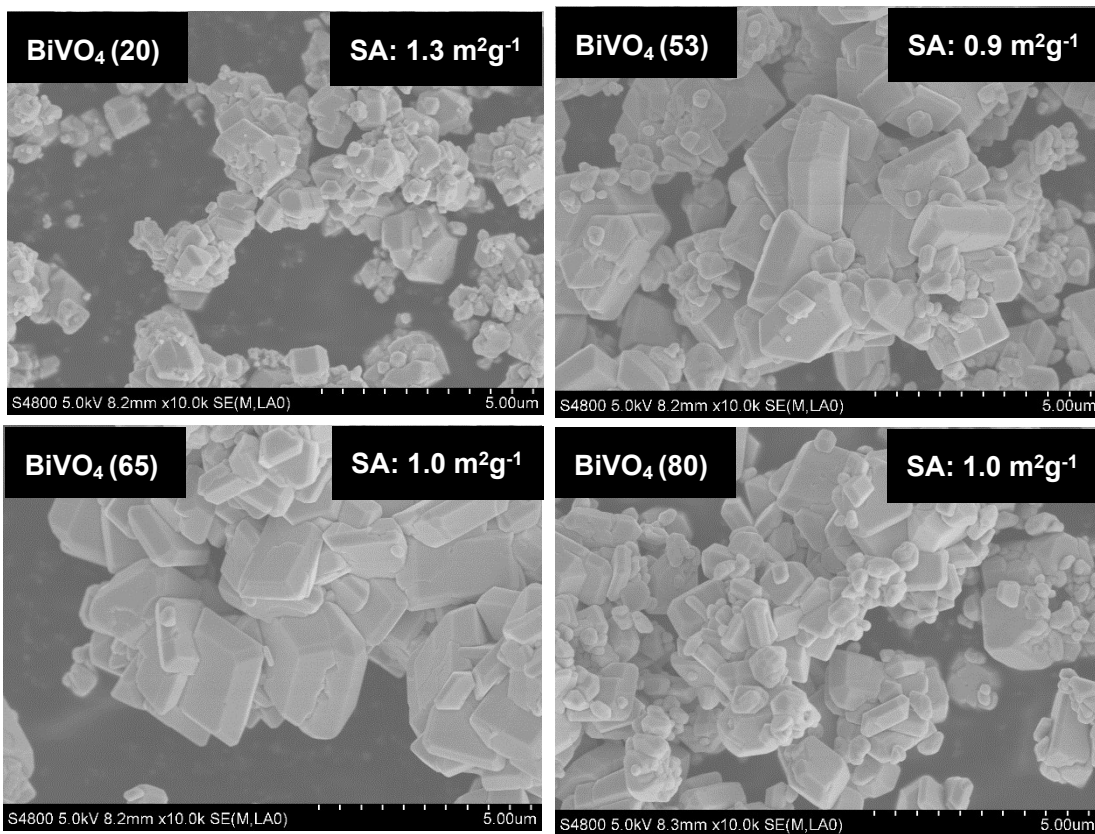


Figure S4 SEM images and surface area of BiVO₄ powder prepared by the LSR method at various solution temperatures.

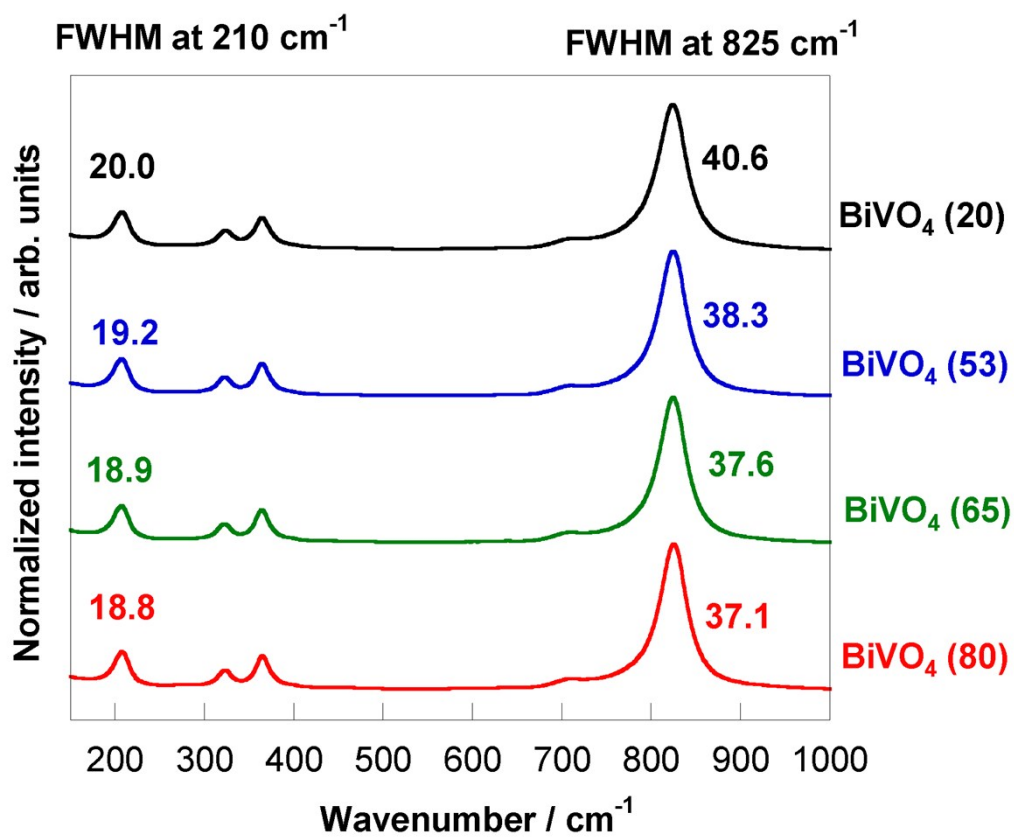


Figure S5 Raman spectra of BiVO_4 powder prepared by the LSR method at various solution temperatures.

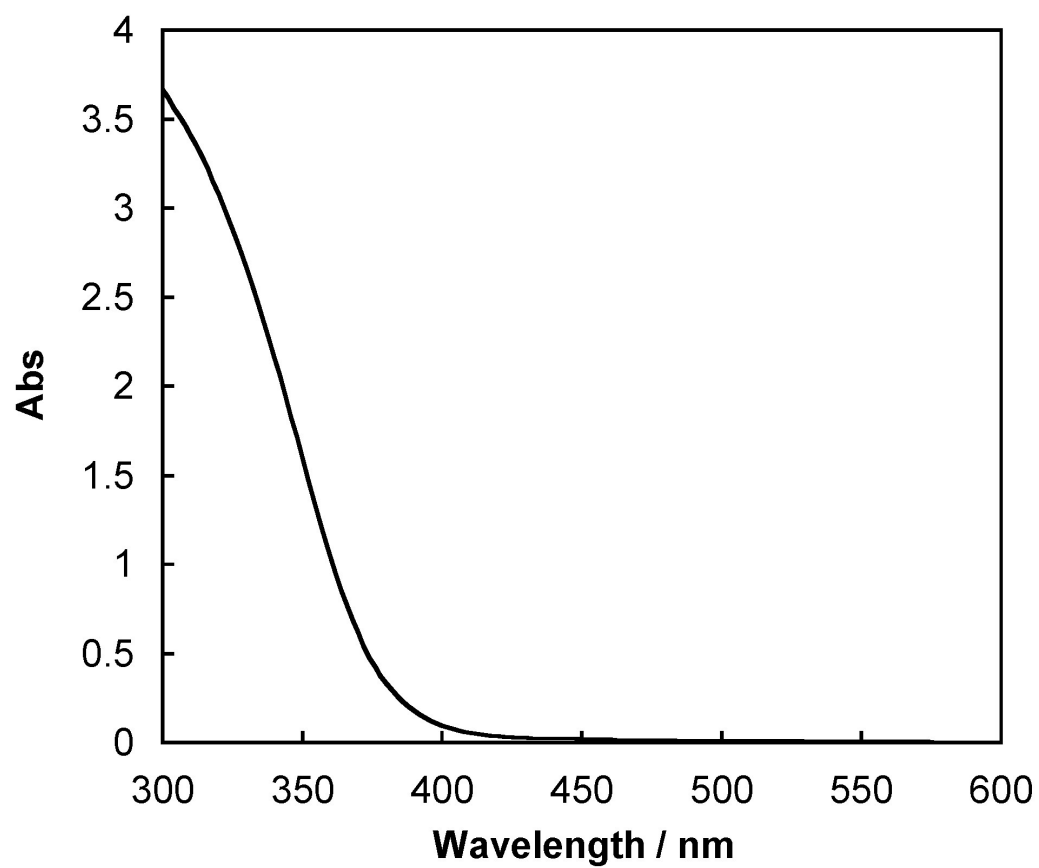


Figure S6 Absorption spectrum of 2 mM Fe(ClO₄)₃ solution.

- The demonstration of photocatalysis-electrolysis hybrid system.

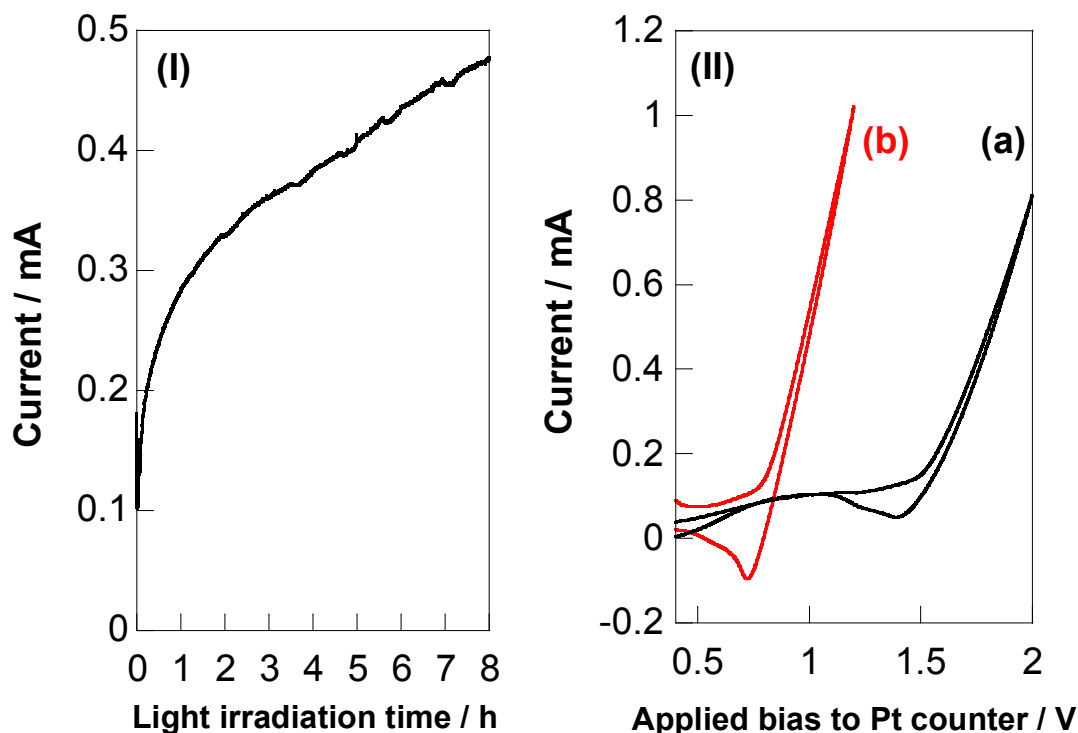


Figure S7 (I) The dependence of current on light irradiation time about hydrogen production via photocatalysis-electrolysis hybrid system using a two-compartment cell with ion-exchange membrane. The applied bias between working and counter electrode was 1.0 V. (II) The CV curves (a) before and (b) after irradiation of solar simulated light for 8 hours. Working electrode: carbon-felt (EC FRONTIER CO., Ltd., diameter: 10 mm, thickness: 5 mm), counter electrode: Pt wire, anode chamber: 2mM $\text{Fe}(\text{ClO}_4)_3$ (200 mL, pH2.3) dispersing BiVO_4 powder (600 mg), cathode chamber: HClO_4 solution (200 mL, pH2.3).

When the applied bias between working and counter electrode was 1.0 V, the current was hardly observed before irradiation, and then the current was increased as light irradiation time passed due to the accumulation of Fe^{2+} in the anode chamber (Figure S7(I)). Moreover, it was found that the CV curve after irradiation of solar simulated light was clearly shifted compared to that before irradiation (Figure S7(II)). It indicates that H_2 is produced with a low applied bias, owing to the low redox potential and low overpotential associated with $\text{Fe}(\text{II})$ oxidation.