

## Supporting Information

### Improved Photoelectrochemical Water Oxidation by $\text{WO}_3/\text{CuWO}_4$ Composite with Manganese Phosphate Electrocatalyst

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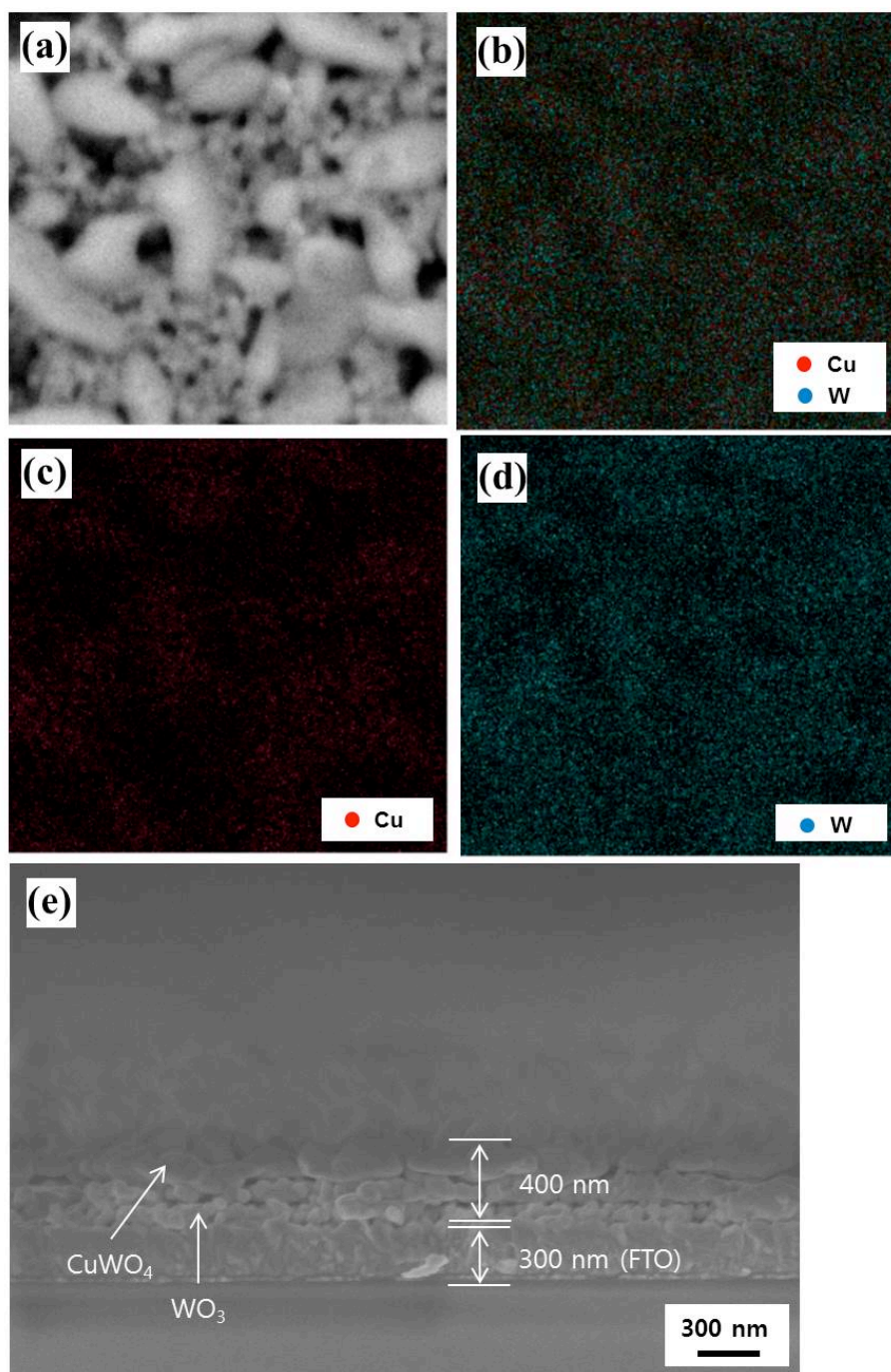
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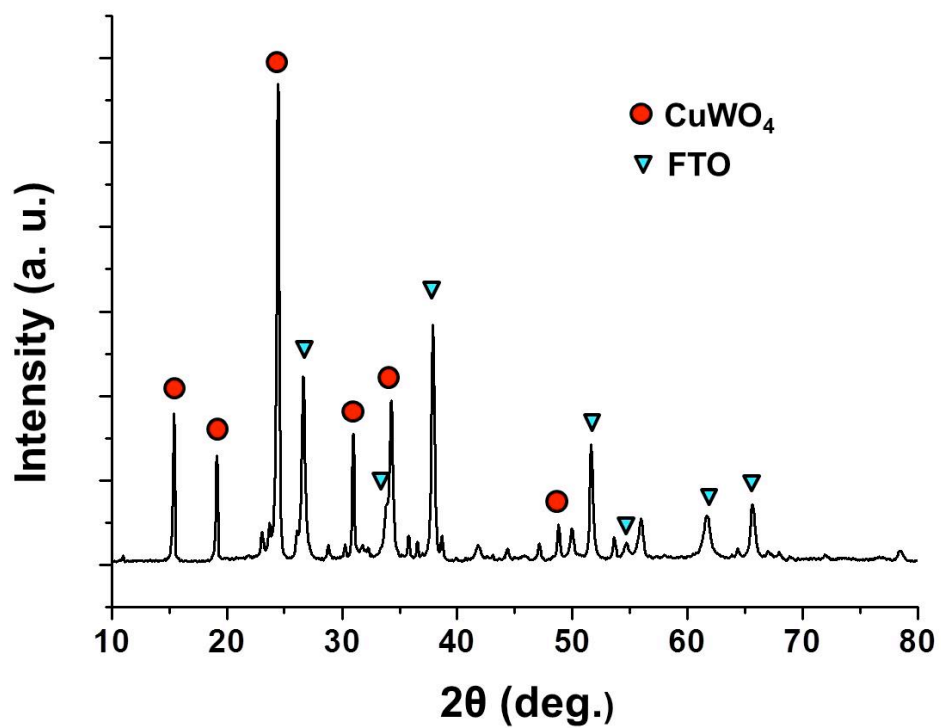
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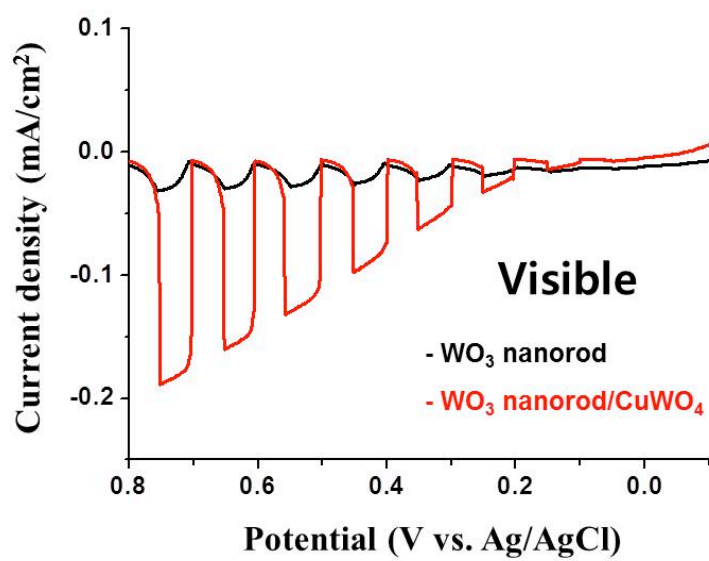
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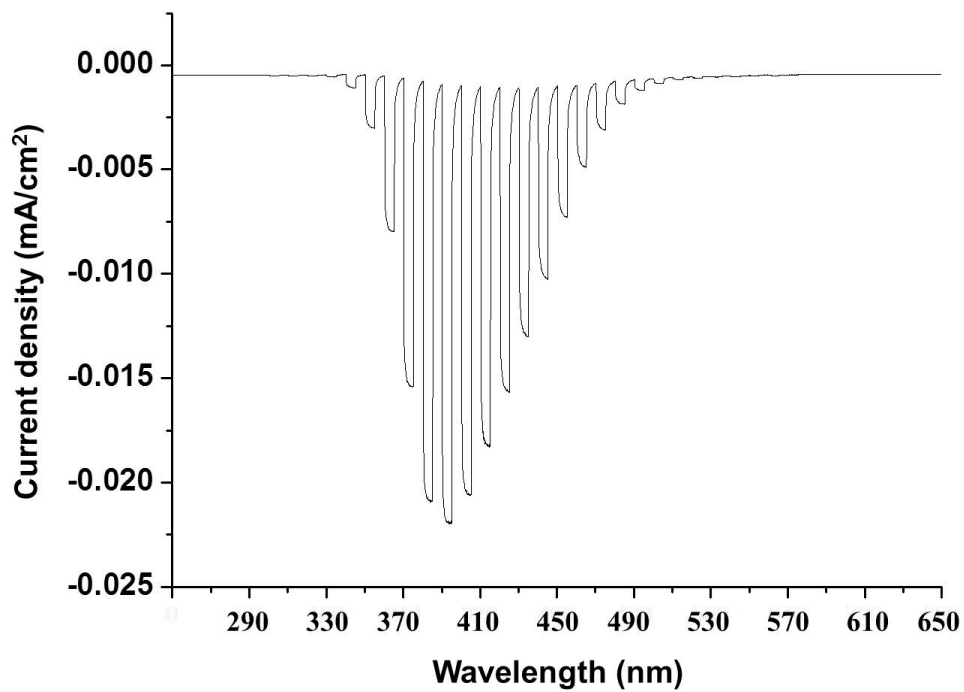
**Figure S1.** (a) SEM image, (b)-(d) energy-dispersive X-ray spectroscopy (EDS) mapping images, and (e) cross section SEM image of the  $\text{WO}_3/\text{CuWO}_4$  composite structure.



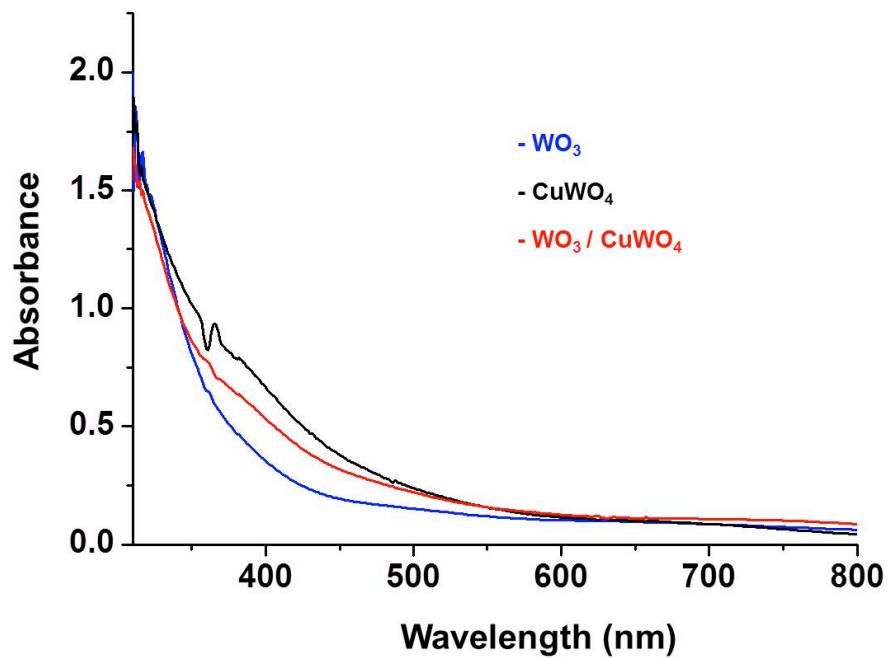
**Figure S2.** XRD pattern  $\text{WO}_3/\text{CuWO}_4$  composite electrodes on FTO substrate.



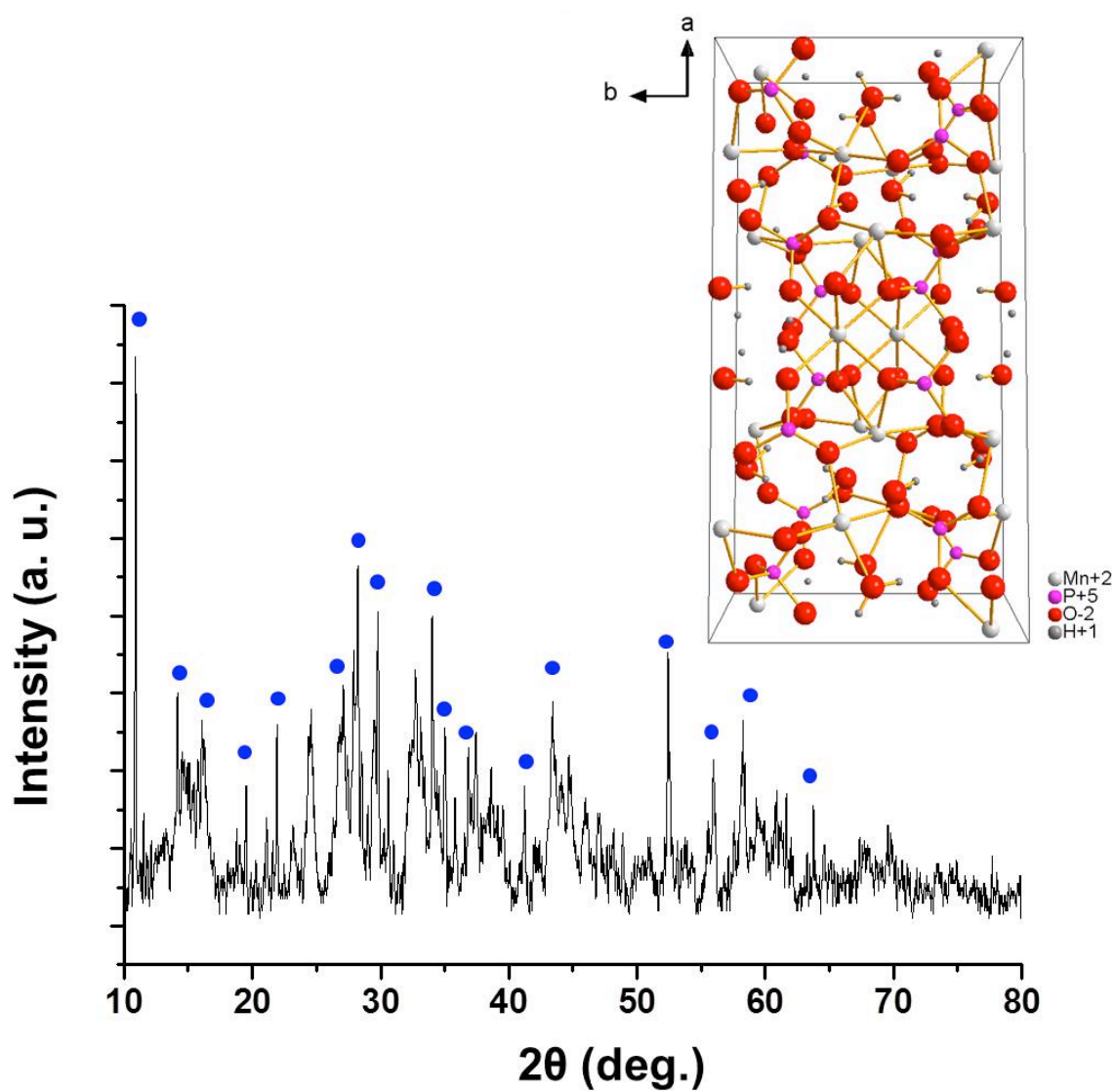
**Figure S3.** LSVs of FTO/WO<sub>3</sub>/CuWO<sub>4</sub> layered electrodes in phosphate buffer (pH 7) under visible illumination. Scan rate: 20 mV/s.



**Figure S4.** Action spectrum of WO<sub>3</sub> electrode at an applied potential of 0.6 V versus Ag/AgCl in phosphate buffer (pH 7).



**Figure S5.** UV-vis absorption spectrum of  $\text{WO}_3$ ,  $\text{CuWO}_4$ , and  $\text{WO}_3/\text{CuWO}_4$  composite electrode.

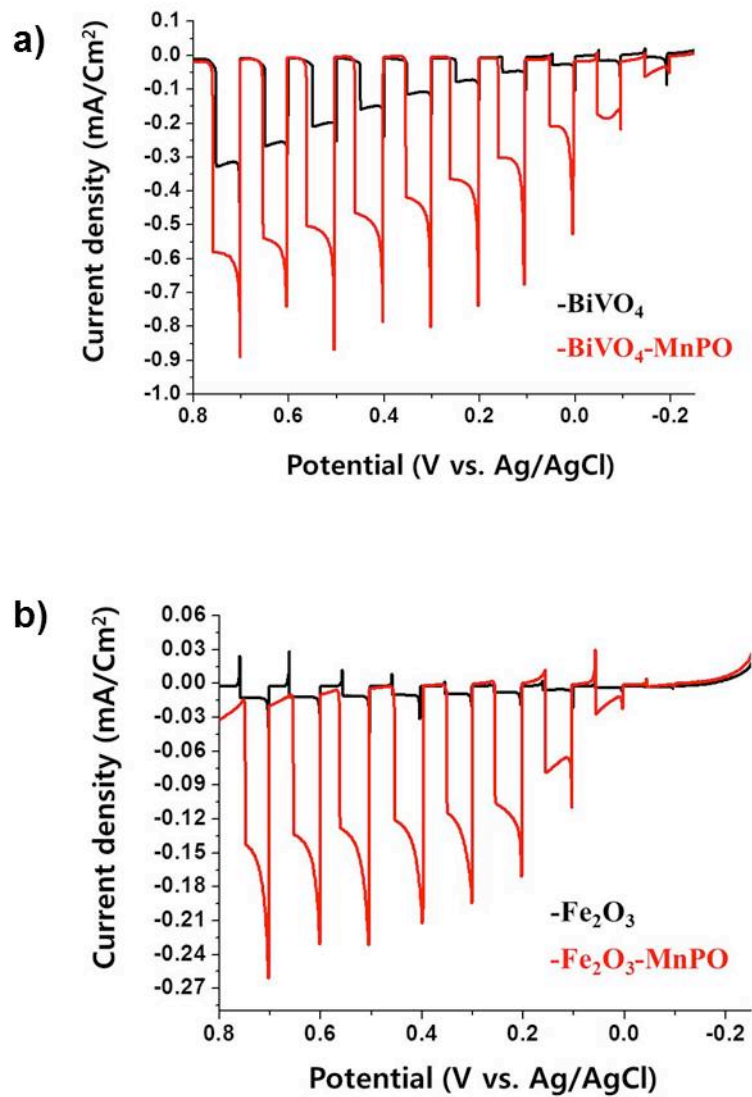


**Figure S6** . XRD patterns and crystal structure (inset) of manganese phosphate ( $\text{Mn}_5(\text{PO}_3(\text{OH}))_2(\text{PO}_4)_2(\text{H}_2\text{O})_4$ , MnPO) nanoplates.

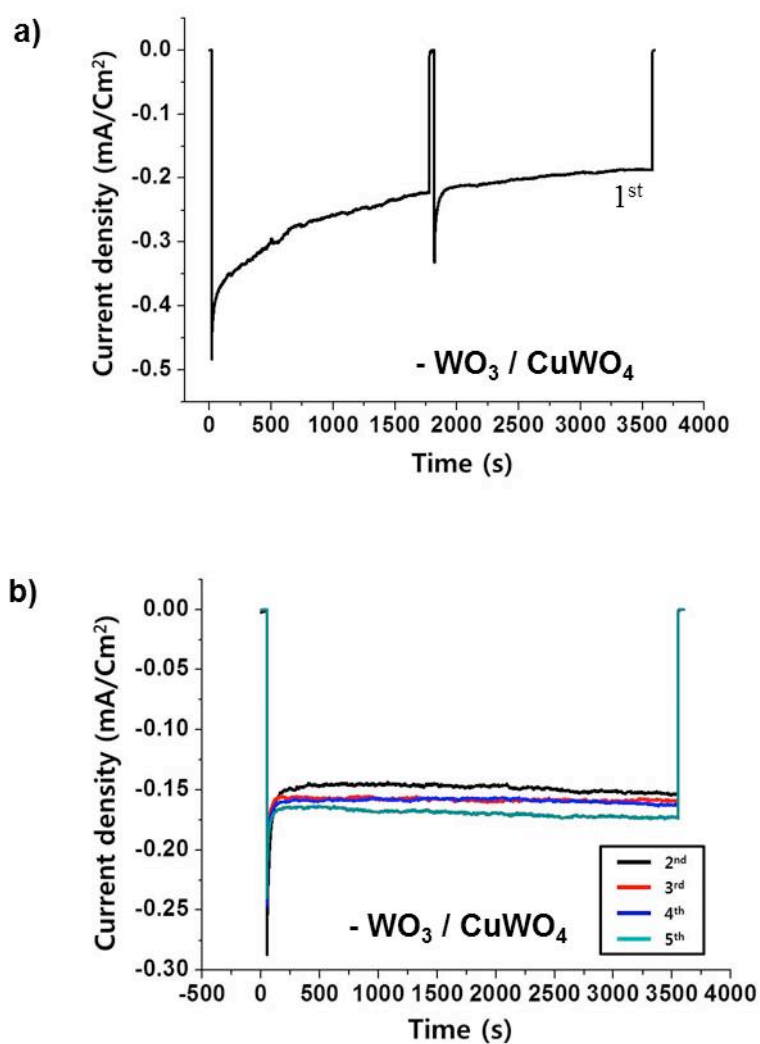


**Figure S7.** Oxygen bubbles on the surface of MnPO electrode. For the qualitative detection of O<sub>2</sub>, chronoamperometry was carried out at 1.4 V vs. Ag/AgCl for 30 min under phosphate buffer (pH 7).





**Figure S8.** LSVs of FTO/BiVO<sub>4</sub>/MnPO and FTO/Fe<sub>2</sub>O<sub>3</sub>/MnPO layered electrodes in phosphate buffer (pH 7) under UV-visible illumination. Scan rate: 20 mV/s.



**Figure S9.** (a) The first photocurrent-time profile of  $\text{WO}_3/\text{CuWO}_4$  ( $\text{Cu}/\text{W} = 0.8/1.2$ ) was obtained over 60 min at an applied potential of 0.5 V vs Ag/AgCl in phosphate buffer (pH 7), and (b) the current-time response curve of the same electrode to study the long-term stability of the prepared film.