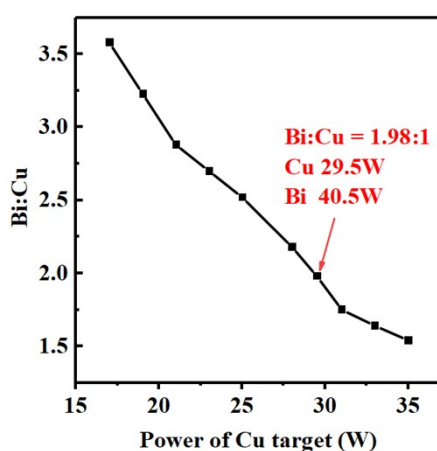
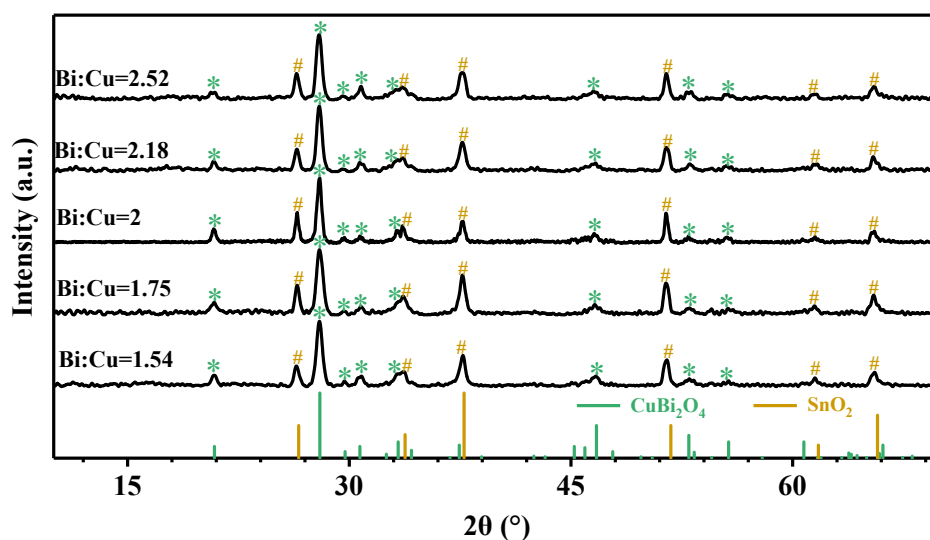


## Supplementary Information

### Ultrathin $\text{CuBi}_2\text{O}_4$ on bipolar $\text{Bi}_2\text{O}_3$ nano-scaffold: self-powered broadband photoelectrochemical photodetector with improved responsivity and response speed

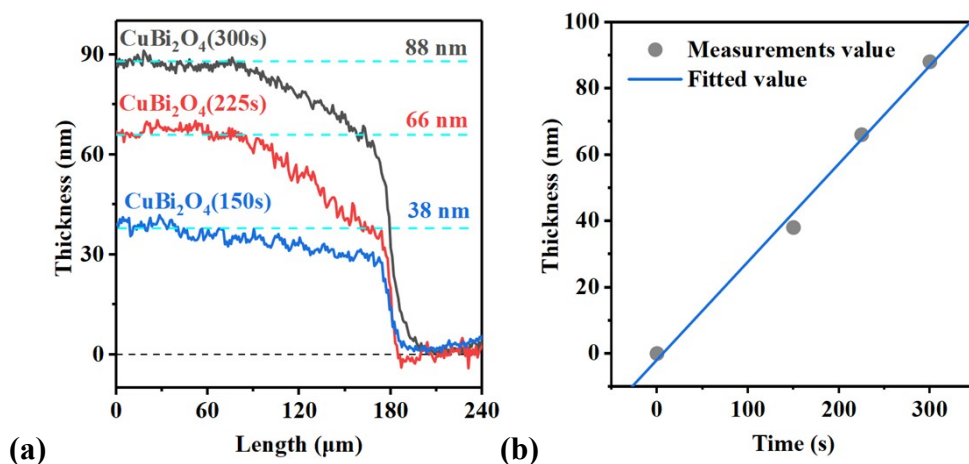


**Figure S1.** The Bi to Cu ratios of  $\text{CuBi}_2\text{O}_4$  films as a function of the power of Cu target; The power of Bi target remained 40.5W; The ratio of Bi to Cu was detected by the ICP-MS.

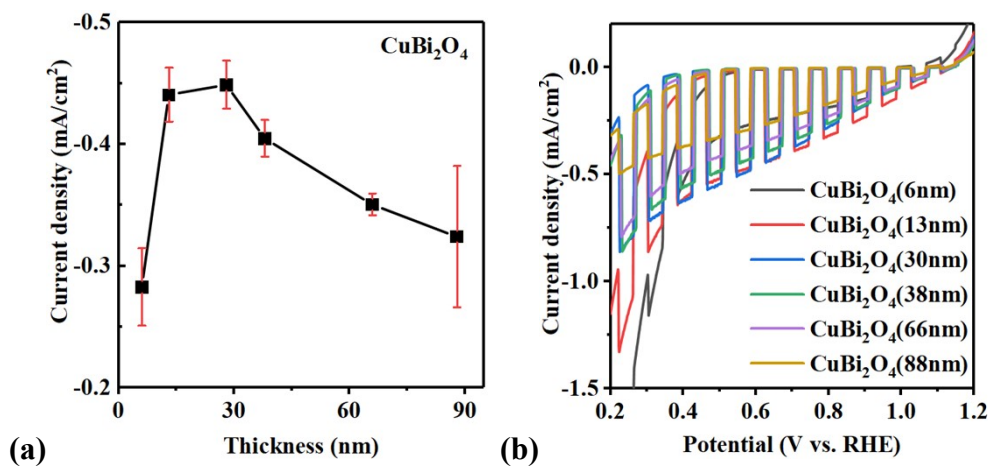


**Figure S2.** XRD spectra for  $\text{CuBi}_2\text{O}_4$  films on FTO substrates with different Bi to Cu

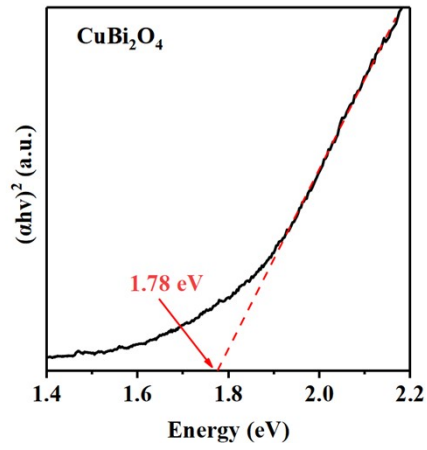
ratios.



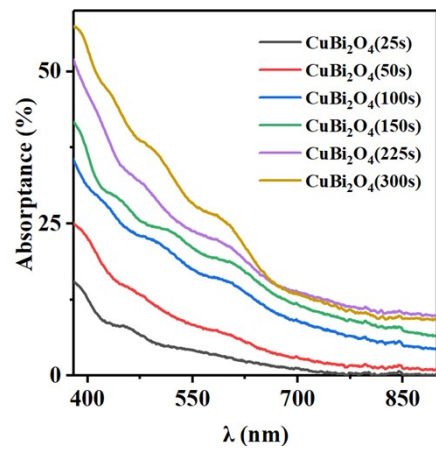
**Figure S3.** (a) Scanning results of optical profiler for CuBi<sub>2</sub>O<sub>4</sub> films with different deposition time; (b) Thickness of CuBi<sub>2</sub>O<sub>4</sub> films with different deposition time, where points and line represented measurement results and fitting results, respectively.



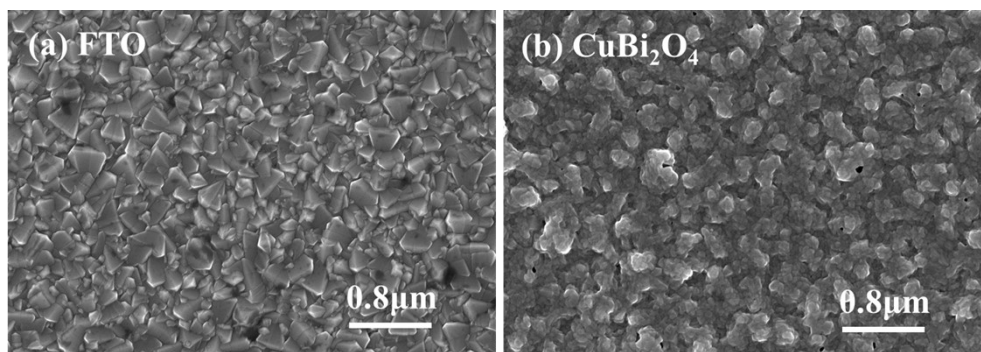
**Figure S4.** (a) Current density for CuBi<sub>2</sub>O<sub>4</sub> photoelectrodes with different film thickness; (b) Chopped LSV scans for CuBi<sub>2</sub>O<sub>4</sub> photoelectrodes with different film thickness. The measurements were performed under AM 1.5 illumination.



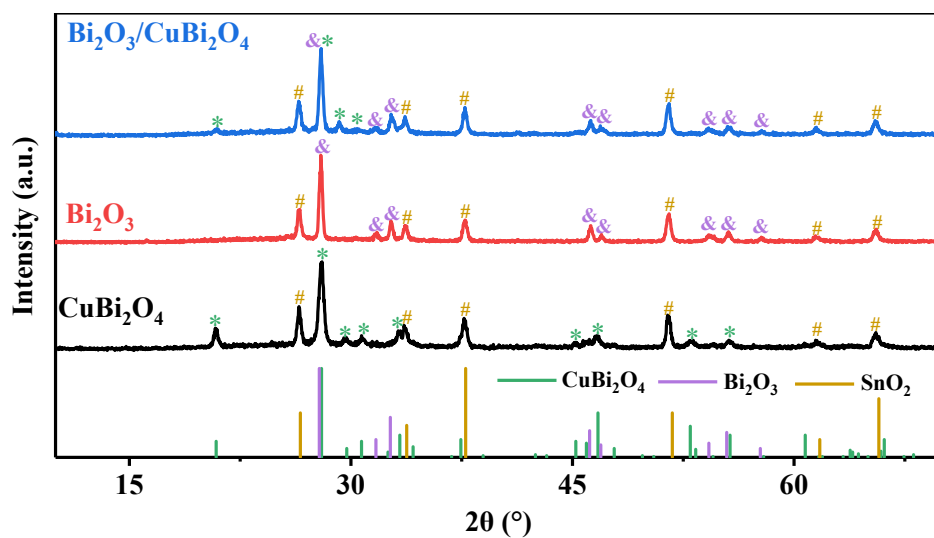
**Figure S5.** Tauc plots for  $\text{CuBi}_2\text{O}_4(100\text{s})$  film.



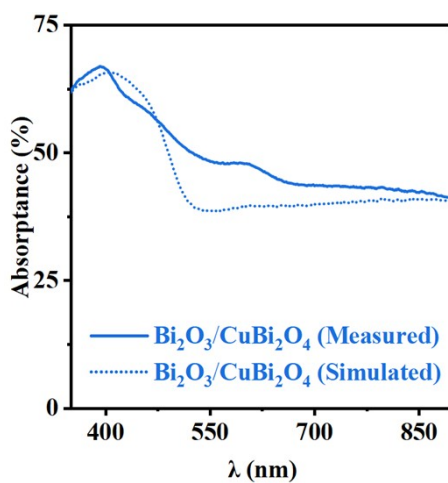
**Figure S6.** Absorption spectra for  $\text{CuBi}_2\text{O}_4$  films with different thickness.



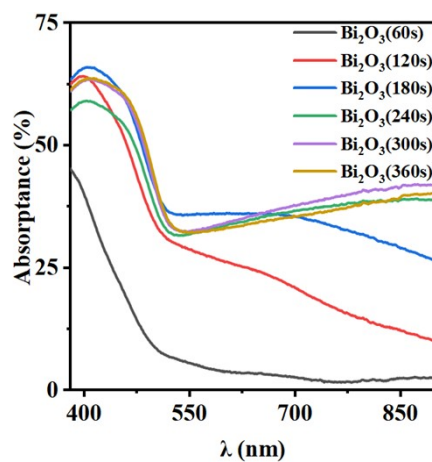
**Figure S7.** SEM images of (a) pure FTO and (b)  $\sim 30$  nm  $\text{CuBi}_2\text{O}_4$ .



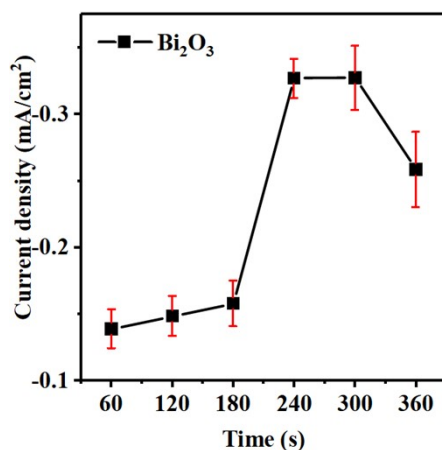
**Figure S8.** XRD spectra for  $\text{CuBi}_2\text{O}_4$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_3/\text{CuBi}_2\text{O}_4$  films.



**Figure S9.** Measured and simulated ( $\text{Bi}_2\text{O}_3 + \text{CuBi}_2\text{O}_4$ ) absorption for  $\text{Bi}_2\text{O}_3/\text{CuBi}_2\text{O}_4$  film.

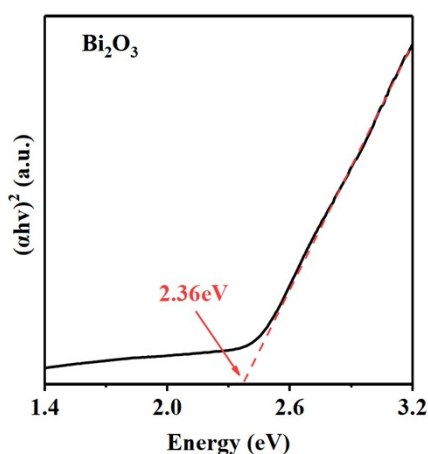


**Figure S10.** Absorption spectra for  $\text{Bi}_2\text{O}_3$  films with different deposition time.

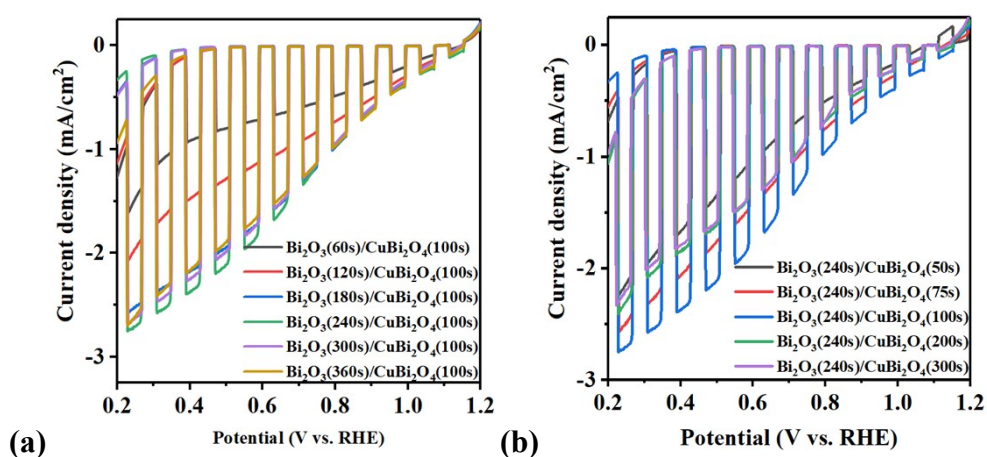


**Figure S11.** Current density for  $\text{Bi}_2\text{O}_3$  photoelectrodes with different deposition time.

The measurements were performed under AM 1.5 illumination.

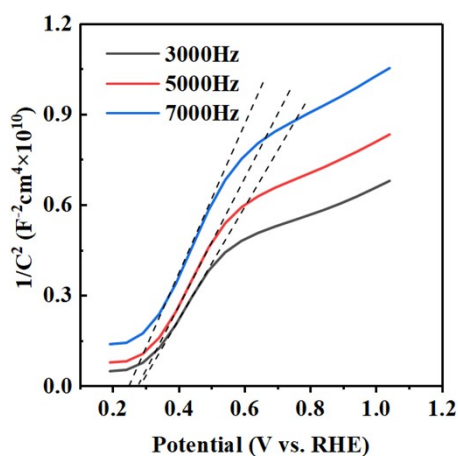


**Figure S12.** Tauc plots for  $\text{CuBi}_2\text{O}_4(240\text{s})$  film.

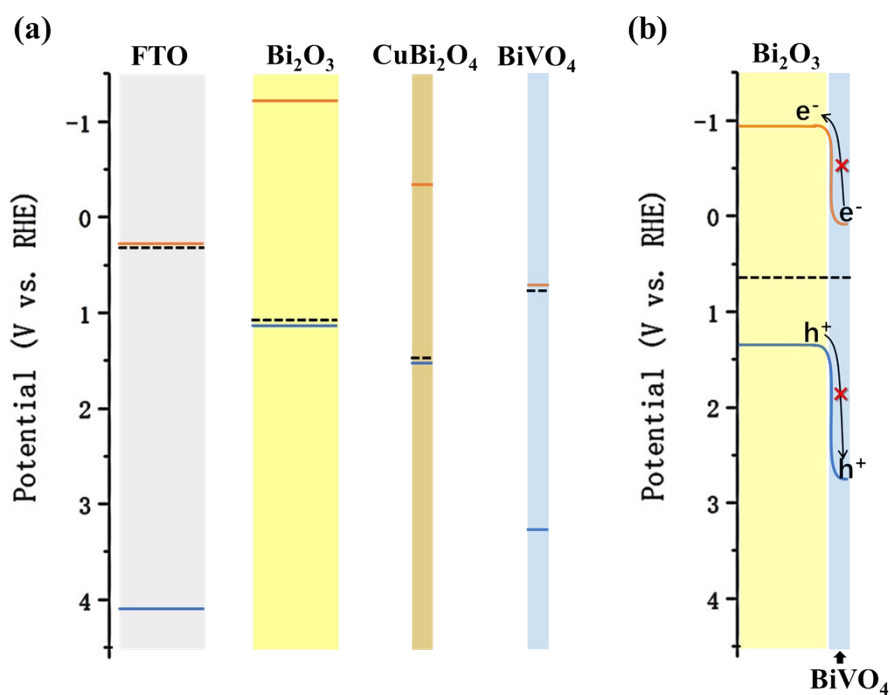


**Figure S13.** Chopped LSV scans for  $\text{Bi}_2\text{O}_3/\text{CuBi}_2\text{O}_4$  photoelectrodes; (a) The deposition time of  $\text{CuBi}_2\text{O}_4$  remains unchanged for 100s, and the deposition times of  $\text{Bi}_2\text{O}_3$  were changed between 60s-360s; (b) The deposition time of  $\text{Bi}_2\text{O}_3$  remained

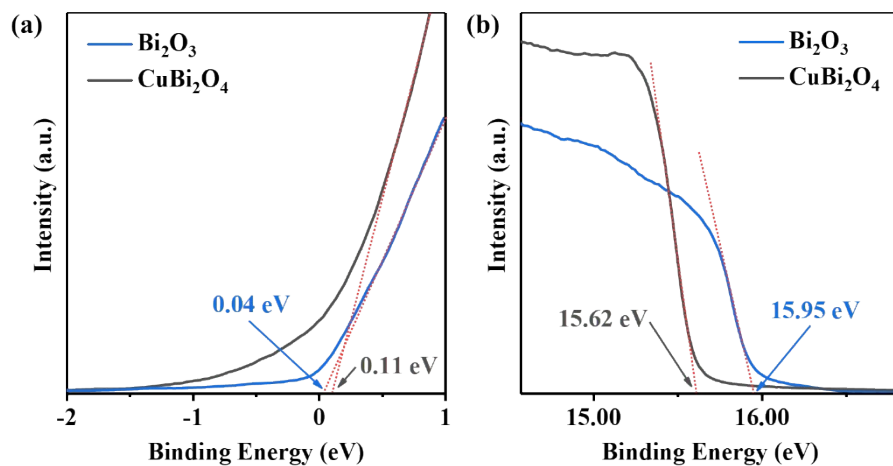
unchanged for 240s, and the deposition times of  $\text{CuBi}_2\text{O}_4$  were changed between 50s-300s. The measurements were performed under AM 1.5 illumination.



**Figure S14.** Mott-Schottky plots for FTO.

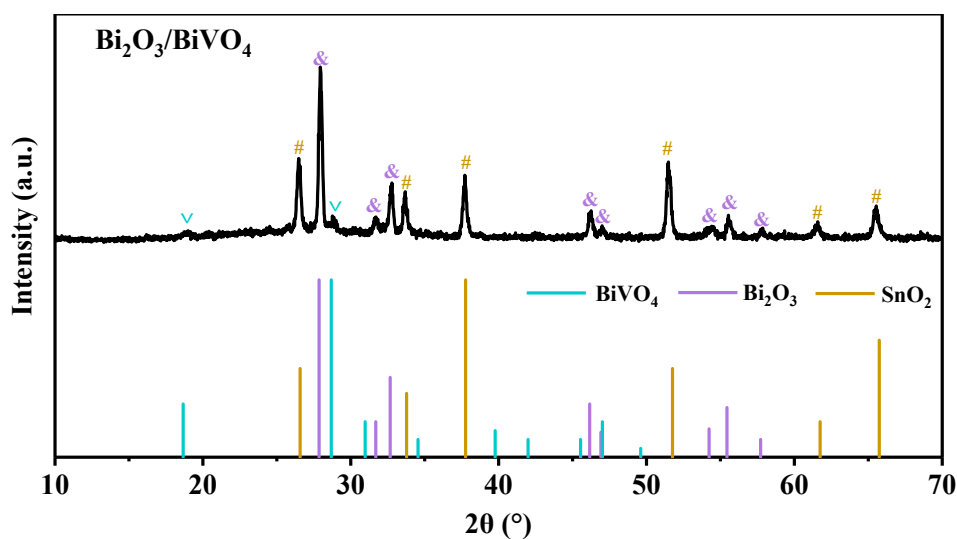


**Figure S15.** (a) Estimated band diagrams of FTO,  $\text{Bi}_2\text{O}_3$ ,  $\text{CuBi}_2\text{O}_4$  and  $\text{BiVO}_4$ ; (b) Estimated band diagrams of  $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ , where the orange solid line, the blue solid line and the black dashed line represented the CB, VB, and Fermi energy level, respectively.

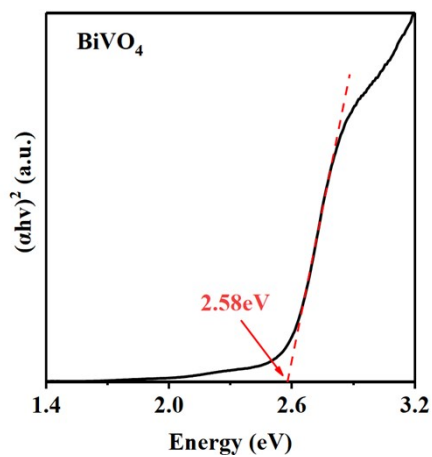


**Figure S16:** UPS of Bi<sub>2</sub>O<sub>3</sub> and CuBi<sub>2</sub>O<sub>4</sub> tested at (a) 0 V bias and (b) -5 V bias, respectively.

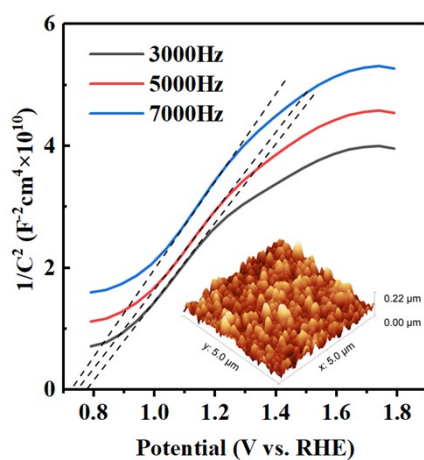
As shown in Figure S16a, the Fermi level of Bi<sub>2</sub>O<sub>3</sub> and CuBi<sub>2</sub>O<sub>4</sub> lied 0.04 eV and 0.11 eV above the VB edge, respectively. As shown in Figure S16b, the work function of Bi<sub>2</sub>O<sub>3</sub> and CuBi<sub>2</sub>O<sub>4</sub> were estimated to be 5.27 eV (21.22 eV – 15.95 eV = 5.27 eV) and 5.60 eV (21.22 eV – 15.62 eV = 5.60 eV), respectively.



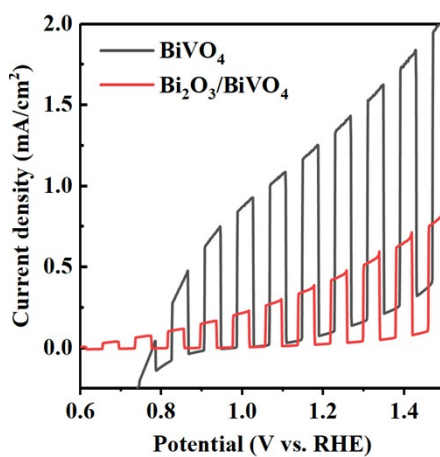
**Figure S17.** XRD spectra for Bi<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> film on FTO substrate, blue represents BiVO<sub>4</sub>.



**Figure S18.** Tauc plots for BiVO<sub>4</sub> film.



**Figure S19.** Mott-Schottky plots and AFM (insert) for BiVO<sub>4</sub>.



**Figure S20.** Chopped LSV scans for BiVO<sub>4</sub> and Bi<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> photoelectrodes. The measurements were performed under AM 1.5 illumination.