# *Supplementary Figures*

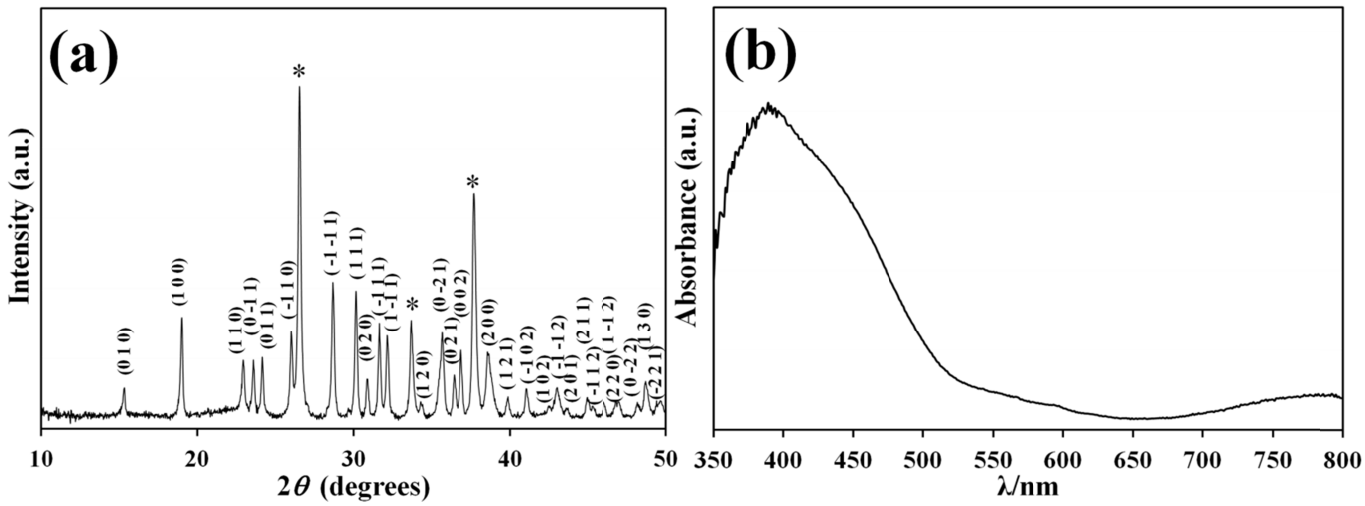


**Fig**. S1. Indexed XRD pattern of $CuWO_4$/FTO (a) and UV-Vis absorption profile of $CuWO_4$/FTO.

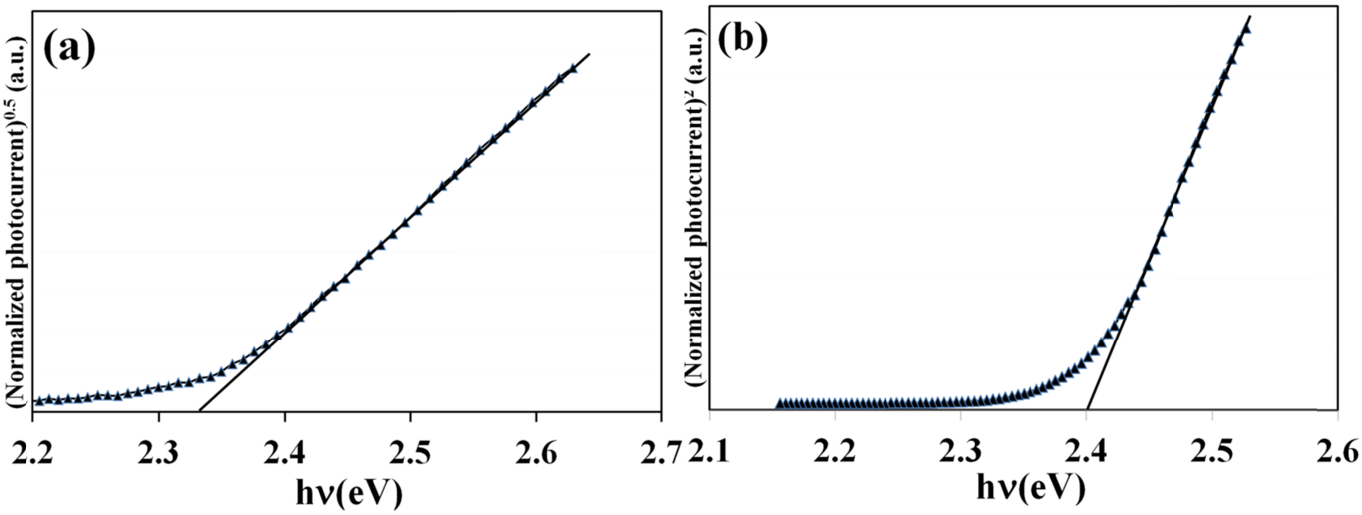


**Fig. S2** Photocurrent action spectra of (a) $CuWO_4$/FTO and (b) $BiVO_4$/FTO electrodes measured in 1 mM $Na_2SO_3$ aqueous solution (pH7 phosphate buffered), applied bias 0.7 V *vs*. Ag/AgCl.

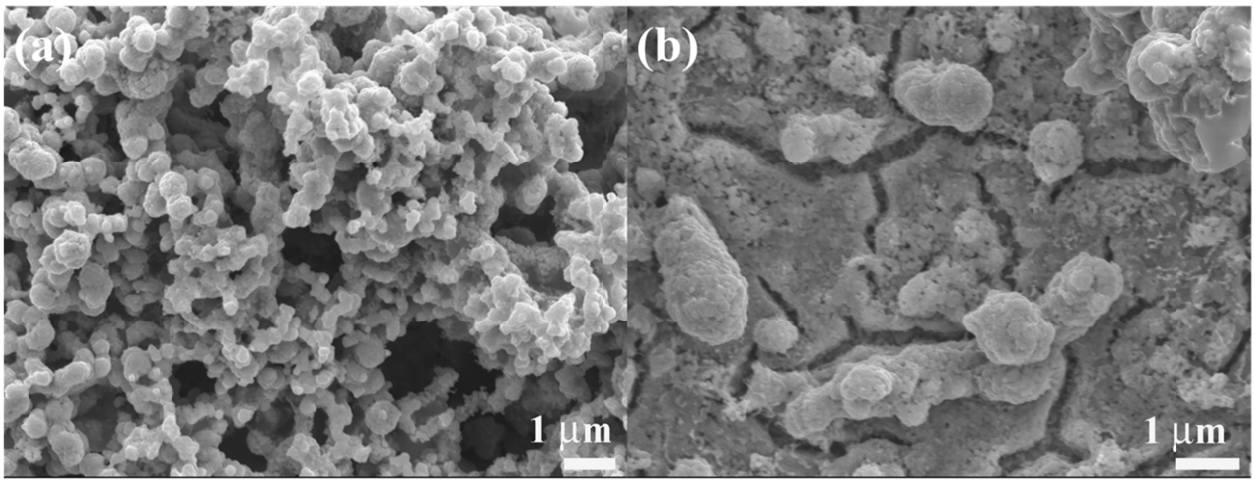


**Fig. S3** SEM image of $CuWO_4$/FTO electrodes prepared in the presence (a) and absence (b) of structure directing agent SDS.

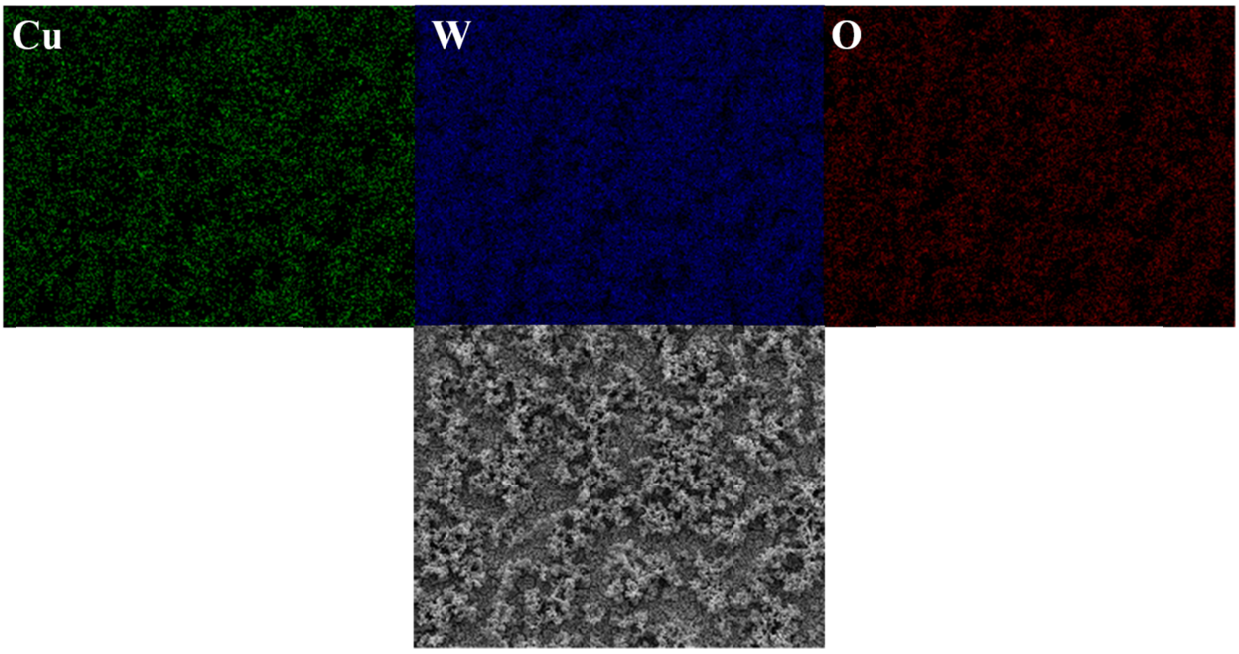


**Fig. S4** Energy dispersive X-ray analysis (EDX) maps of $CuWO_4$/FTO electrode investigated in the Cu (L), W (M) and O (K) transition at 10 keV.

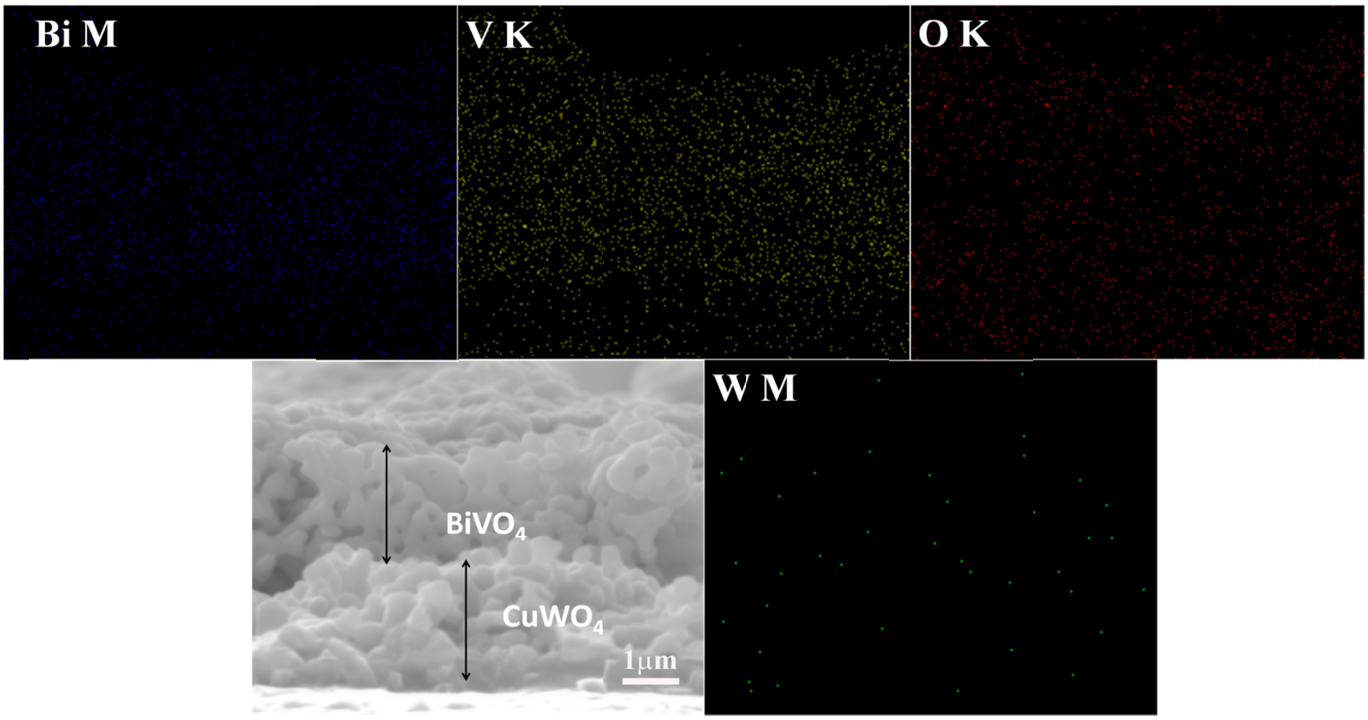


**Fig. S5** Energy dispersive X-ray analysis (EDX) maps of top layer of $BiVO_4/CuWO_4$/FTO electrode investigated in the Bi (M), V(K), O (K) and W (M) transition at 10 keV.

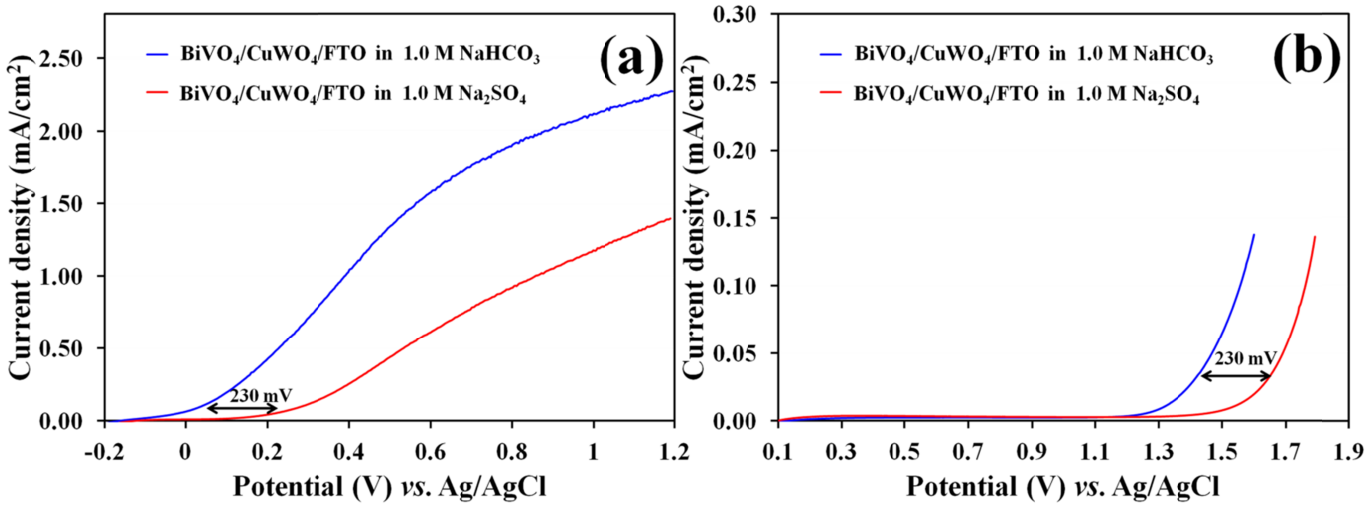


**Fig. S6** Linear sweep voltammograms of $BiVO_4/CuWO_4$/FTO electrodes in 1.0 M $NaHCO_3$ (blue), in 1.0 M $Na_2SO_4$ (red) electrolytes measured (scan rate, 25 mV/s) under (AM1.5 (100 mW/cm$^2$) light (a) and dark (b).

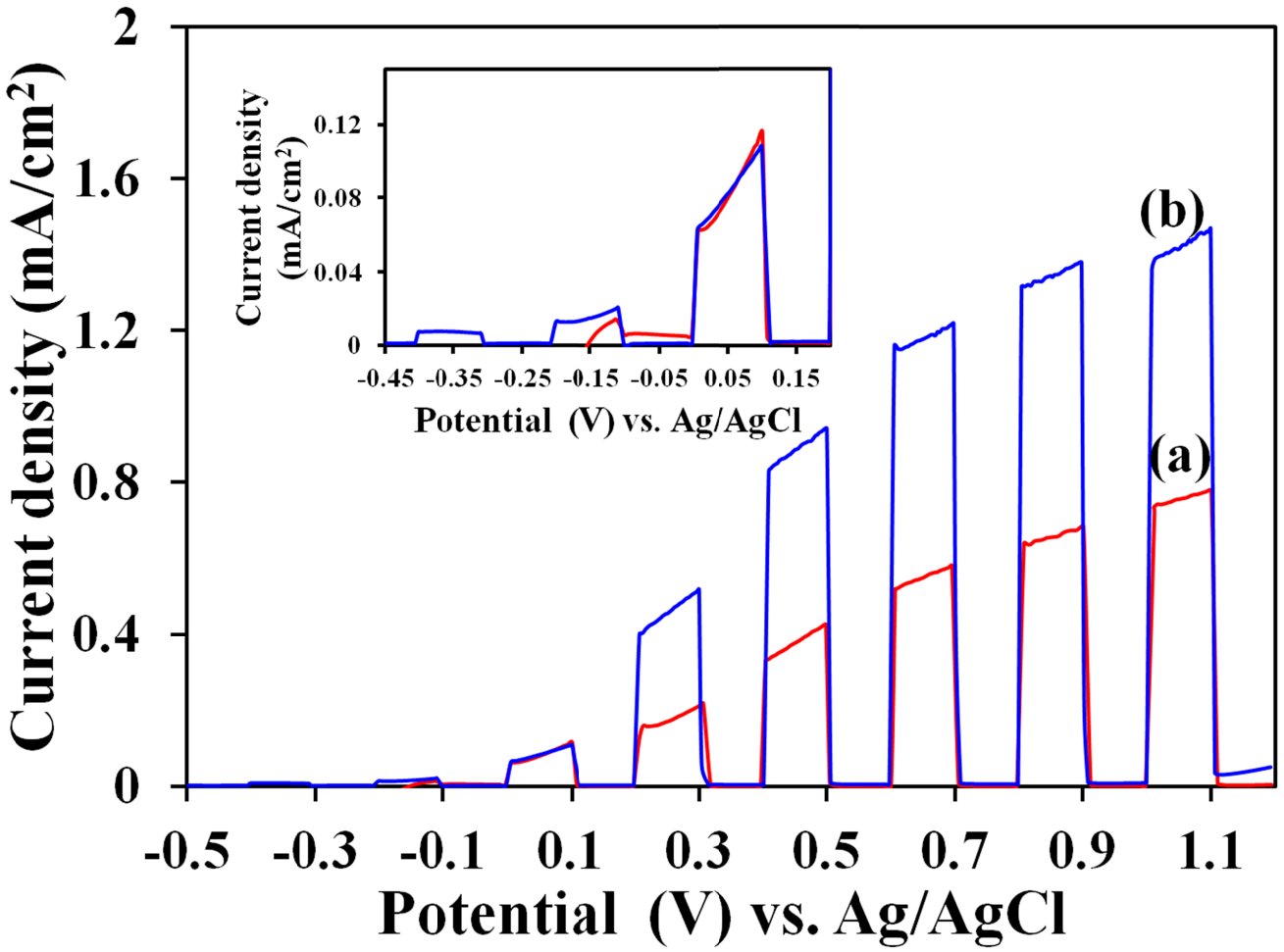


**Fig. S7** Photocurrent-potential characteristics of (a) $CuWO_4$/FTO and (b) $BiVO_4$/FTO electrodes measured at scan rate, 25 mV/s with chopped light (100 mW/cm$^2$) in 1.0M $NaHCO_3$ aqueous electrolyte solution. The inset shows the I-V characteristics in -0.45 to 0.20 V regions.

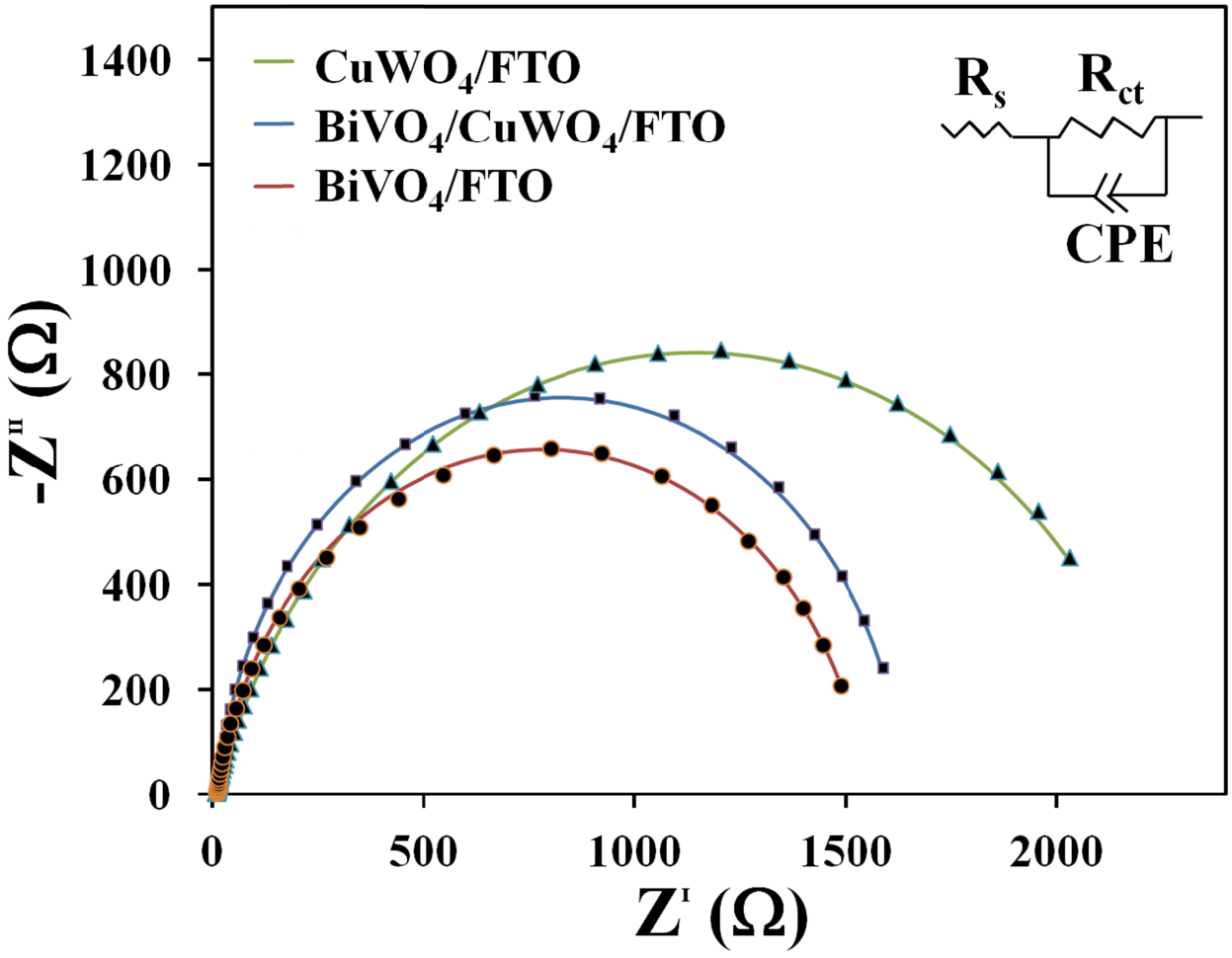


**Fig. S8** Nyquist plots for $CuWO_4$/FTO, $BiVO_4$/FTO and $BiVO_4$/$CuWO_4$/FTO electrodes measured in 1.0M $NaHCO_3$ aqueous solution at 0.3 V (vs. Ag/AgCl) under AM 1.5 (100 $mW/cm^2$) illuminations. The inset shows the equivalent circuit.

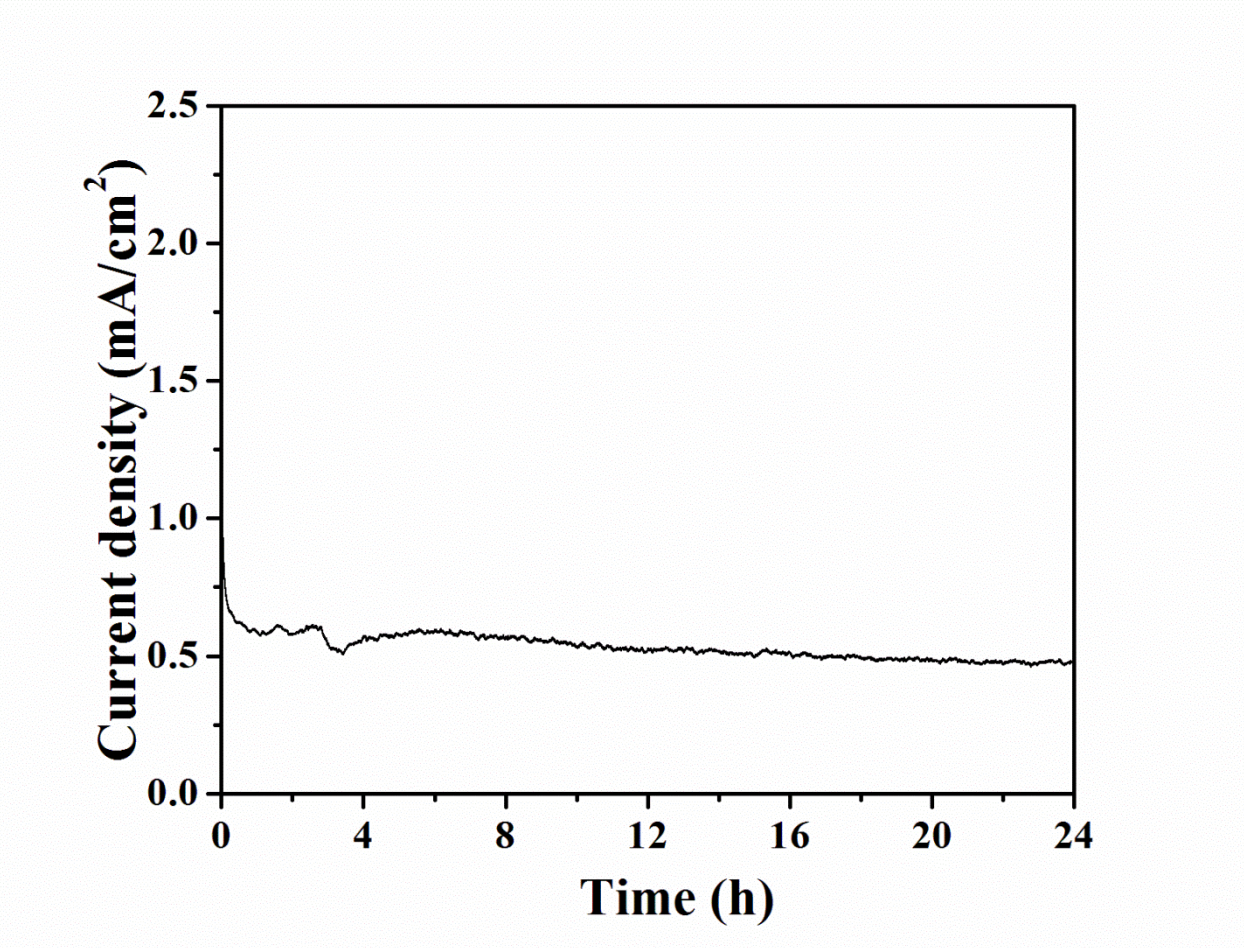


**Fig. S9** The photocurrent vs. time (chronoamperometry) plot of $CuWO_4/BiVO_4$/FTO photoanode measured at an applied bias of 0.4 V *vs*. Pt counter electrode in 1.0M $NaHCO_3$.. The measurements were performed under continuous 1 sun, AM 1.5 simulated solar irradiation for 24 h.