

Electronic Supplementary Information

Fabrication of p-Cu₂O/n-Bi-WO₃ heterojunction thin films: optical and photoelectrochemical properties

Jin You Zheng, Chang Woo Kim, Amol Uttam Pawar and Young Soo Kang*

Korea Center for Artificial Photosynthesis (KCAP), Department of Chemistry, Sogang University, Seoul 121-742, South Korea.

E-mail: yskang@sogang.ac.kr; Fax: (+82)-2-701-0967

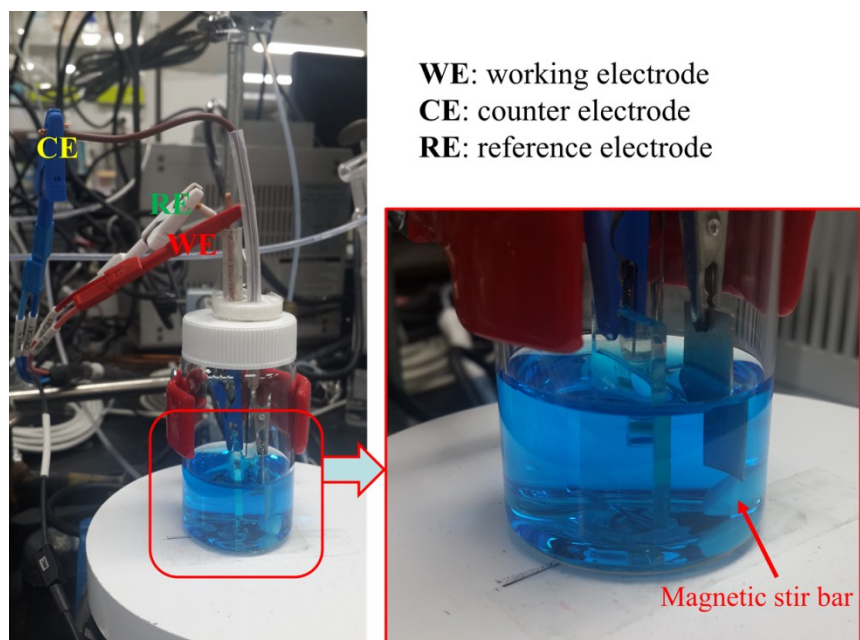


Fig. S1 Photographs of a home-made cell for electrodeposition of Cu_2O films.

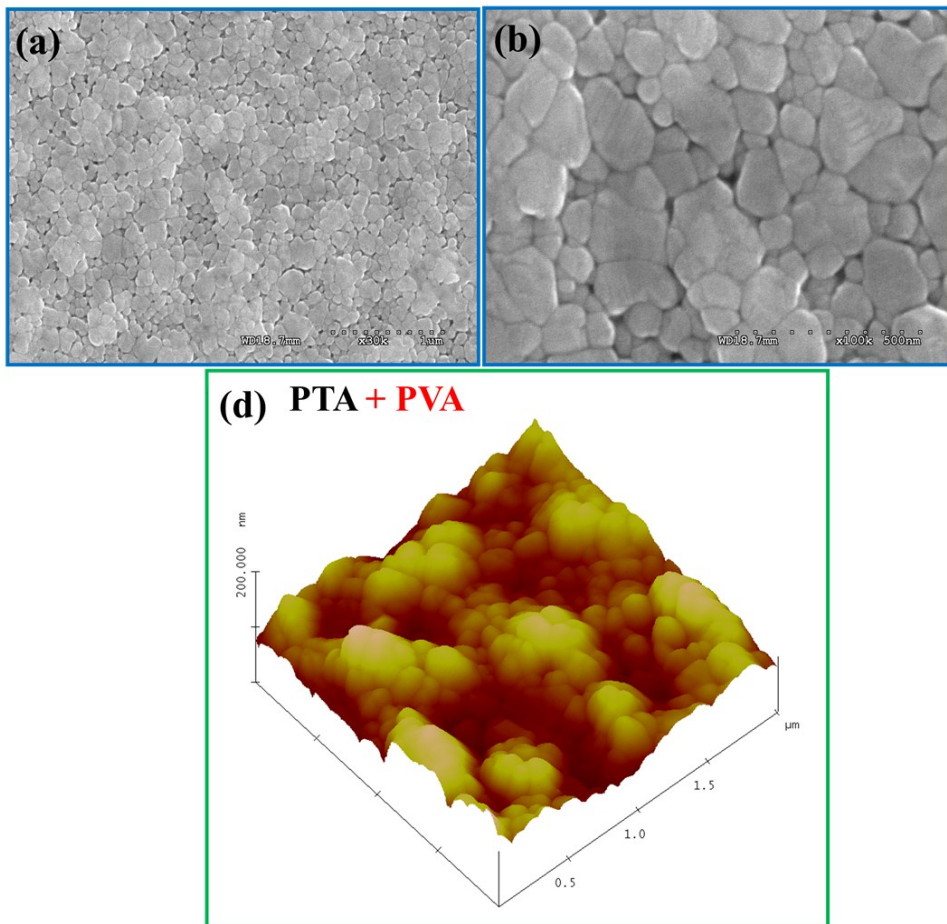


Fig. S2 (a and b) SEM images and (c) AFM image of the WO_3 thin film prepared by spin-coating of a PTA+PVA solution.

PTA+PVA solution^[1]: a solution was prepared by dissolving 1.5 g of H_2WO_4 and 0.5 g of poly(vinyl alcohol) (PVA) (Aldrich, 99+%) in 10 mL of 35 wt % H_2O_2 (Junsei, 35%).

The WO_3 was made by spin coating the PTA-PVA solution on FTO glass(1500 rpm for 20 s, Spin Coater ACE-200), followed by annealing at 500 °C for 2 h in air.

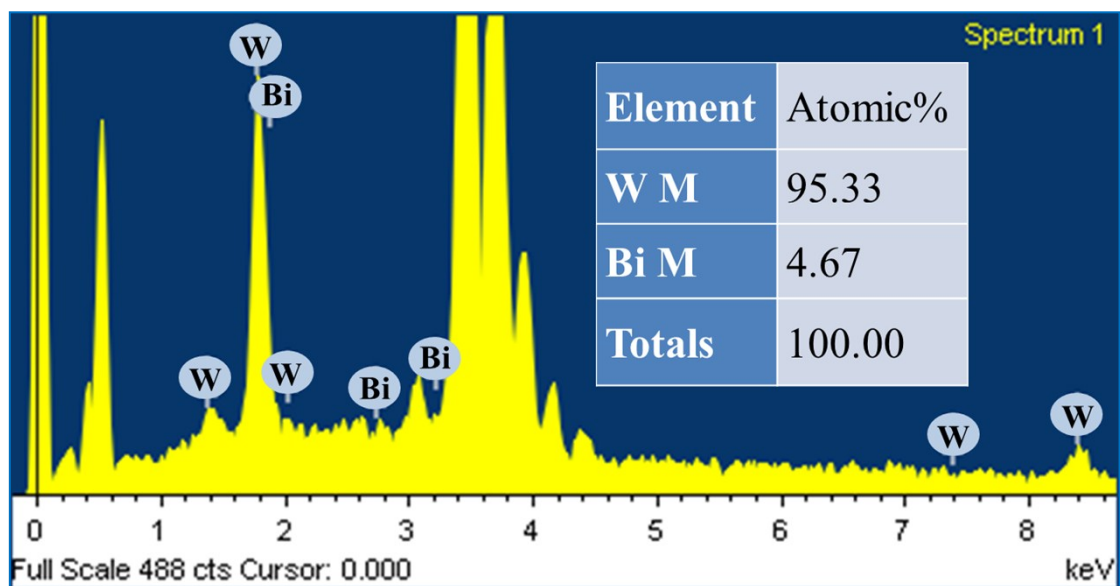


Fig. S3 The typical EDS spectrum and its corresponding W and Bi elements atomic% data of the Bi-WO₃ film on FTO glass.

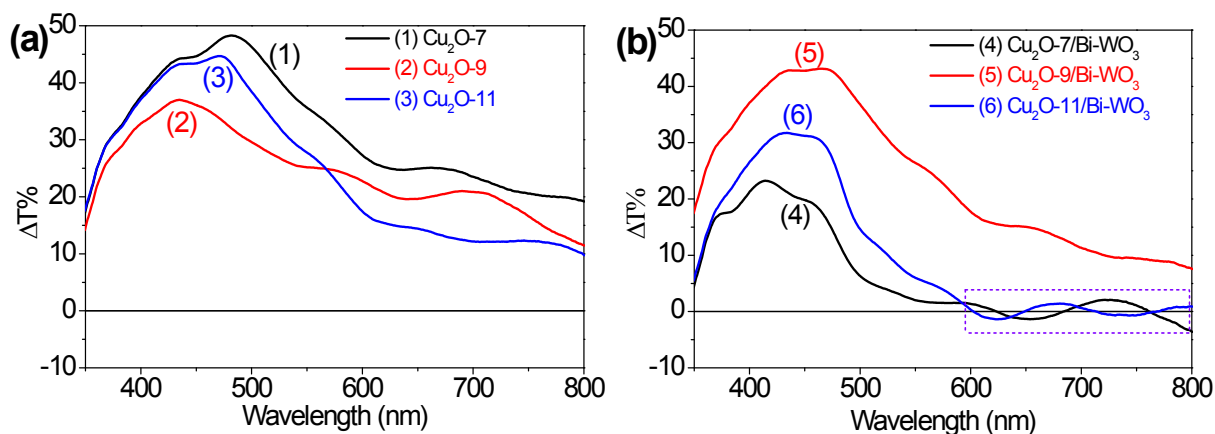


Fig. S4 The transmittance differences (ΔT , $\Delta T = T_{\text{FTO}} - T_{\text{sample}}$) between the bare FTO and the samples; (1) Cu₂O-7, (2) Cu₂O-9, (3) Cu₂O-11, (4) Cu₂O-7/Bi-WO₃, (5) Cu₂O-9/Bi-WO₃ and (6) Cu₂O-11/Bi-WO₃.

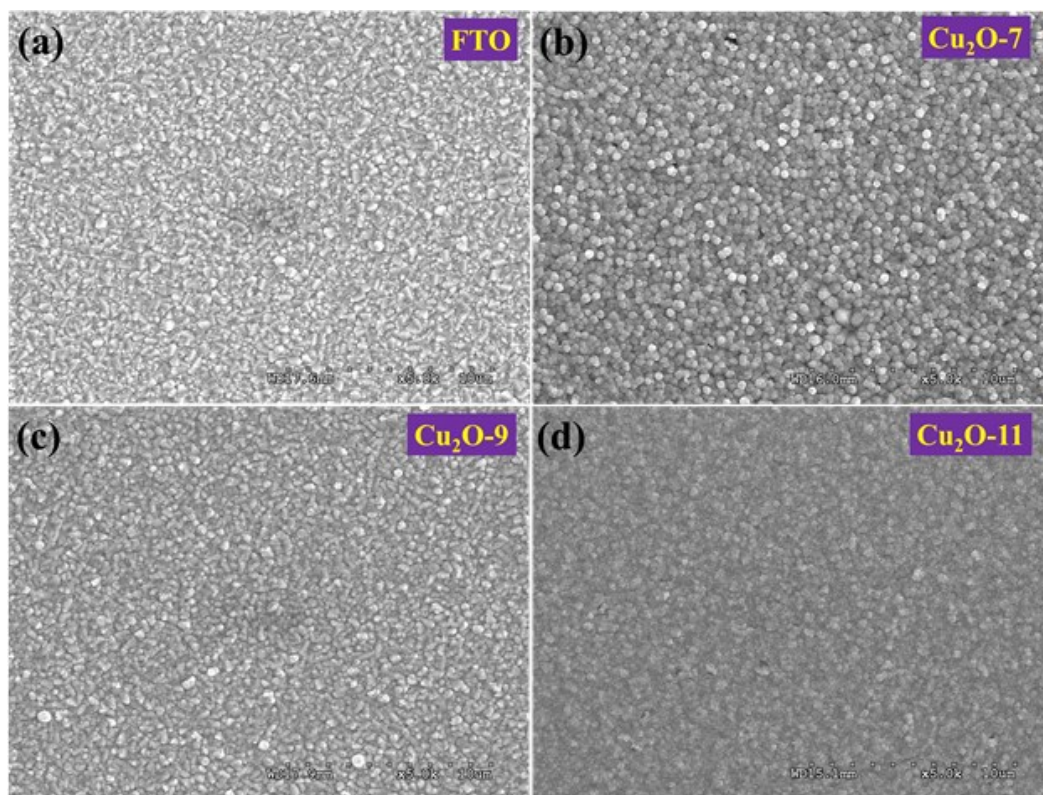


Fig. S5 Low magnified SEM images of the bare FTO substrate and the electrodeposited Cu₂O films at different pHs. (a) FTO substrate, (b) Cu₂O-7, (c) Cu₂O-9, (d) Cu₂O-11.

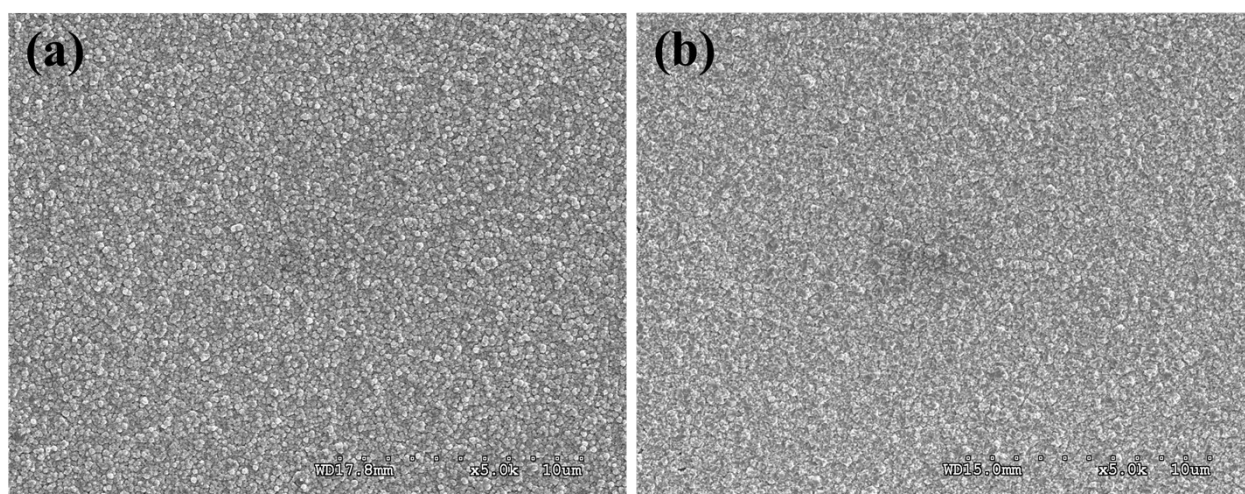


Fig. S6 Low magnified SEM images of the electrodeposited Cu_2O films with stirring at different pHs. (a) Cu_2O -7s, (b) Cu_2O -11s.

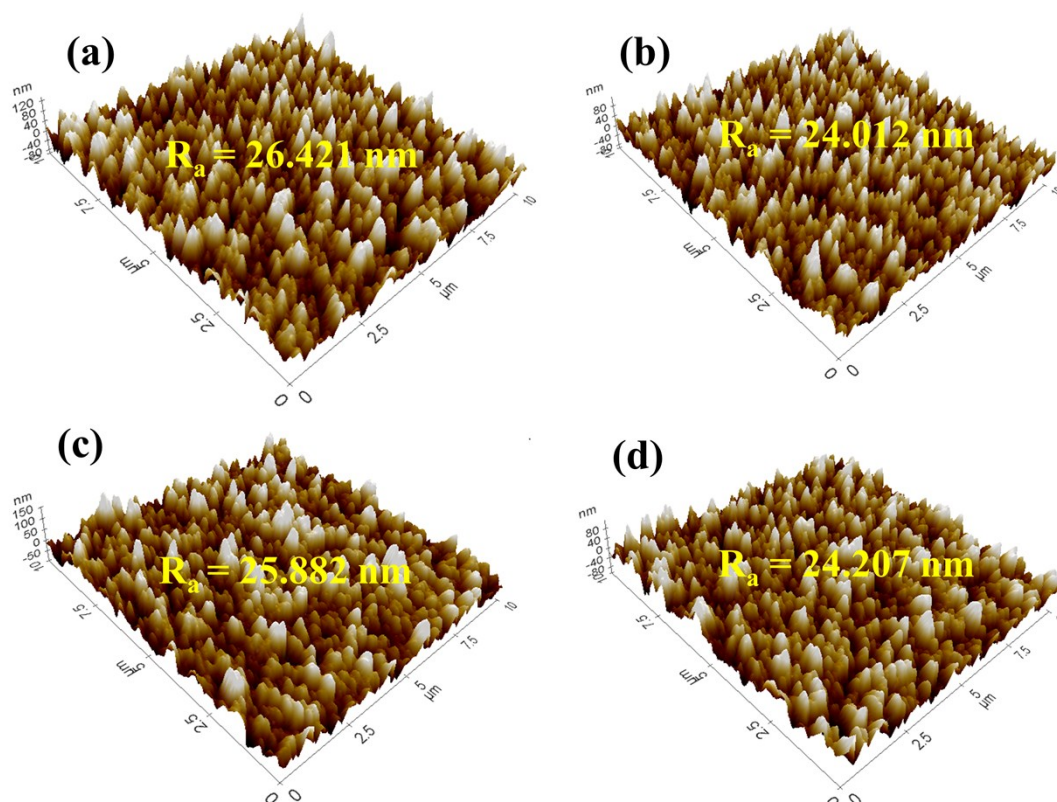
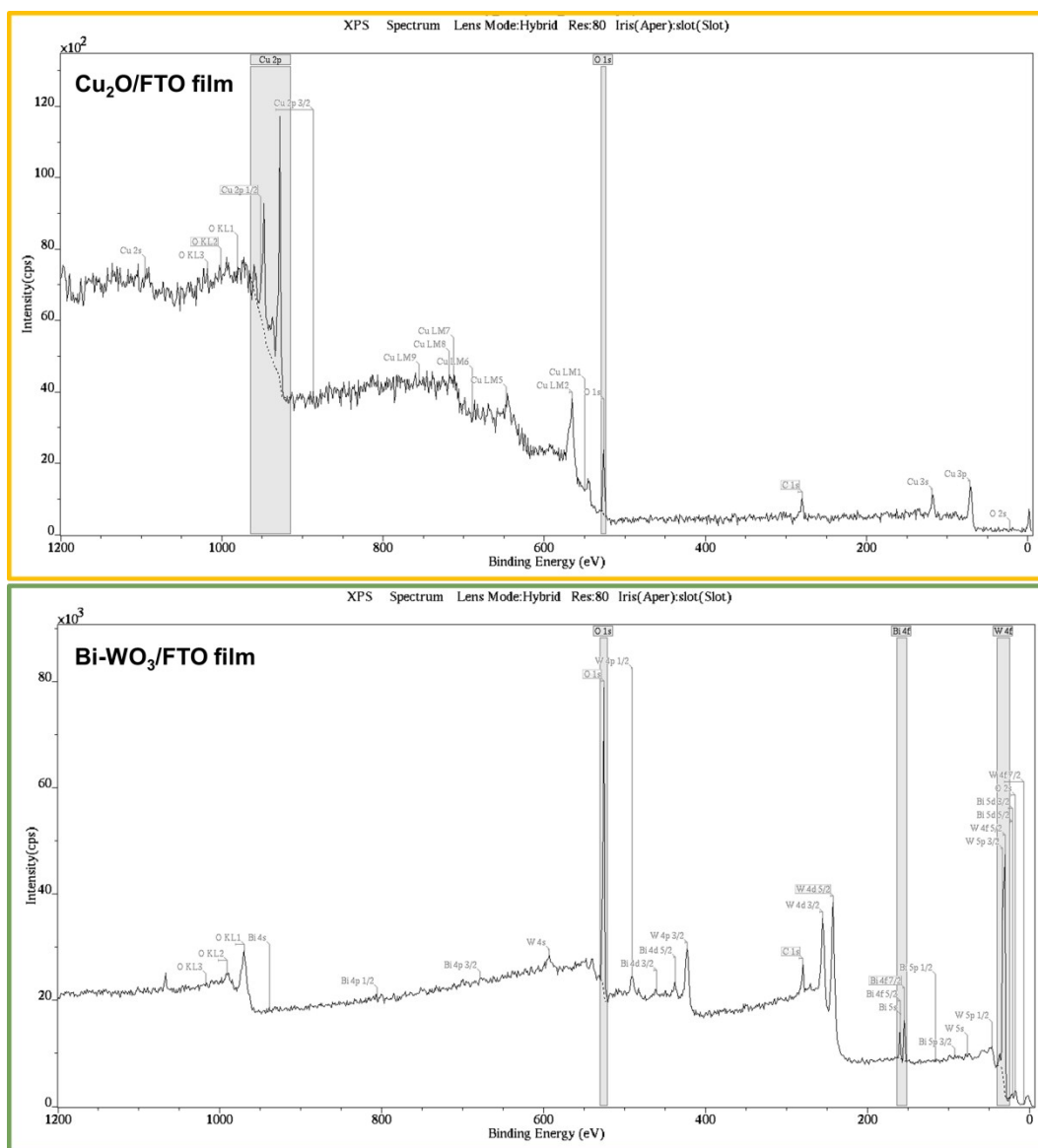


Fig. S7 AFM 3D images of (a) Cu_2O -7, (b) Cu_2O -7s, (c) Cu_2O -11, (d) Cu_2O -11s. Average roughness (R_a) is the mean height as calculated over the entire measured length in the specific area ($10 \mu\text{m} \times 10 \mu\text{m}$).



Films	Peak	Type	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
Cu ₂ O/FTO	O 1s	Reg	526.000	2.803	5146.1	0.780	15.999	43.07	16.00
	Cu 2p	Reg	928.000	2.601	49782.0	5.321	63.549	56.93	84.00
Bi-WO ₃ /FTO	O 1s	Reg	526.000	2.144	142291.8	0.780	15.999	76.62	22.06
	W 4f	Reg	31.000	3.870	167479.8	3.523	183.847	22.09	73.07
	Bi 4f	Reg	155.000	1.929	25762.3	9.140	208.980	1.30	4.87

Fig. S8 XPS quantification reports of Cu₂O and Bi-WO₃ films by XPS survey spectra. The quantification is calculated according to the peak area.

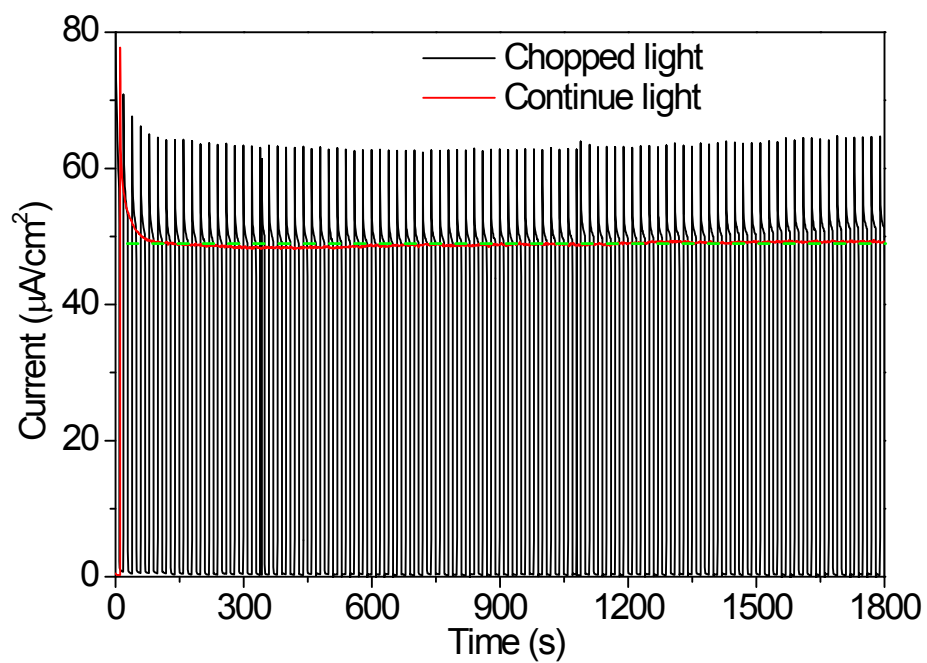


Fig. S9 Stability measurements at +0.65 V of Bi-WO₃ film measured in 0.5 M Na₂SO₄ electrolyte solution under a chopped 1 sun illumination (black color) and a continue 1 sun illumination (red color).

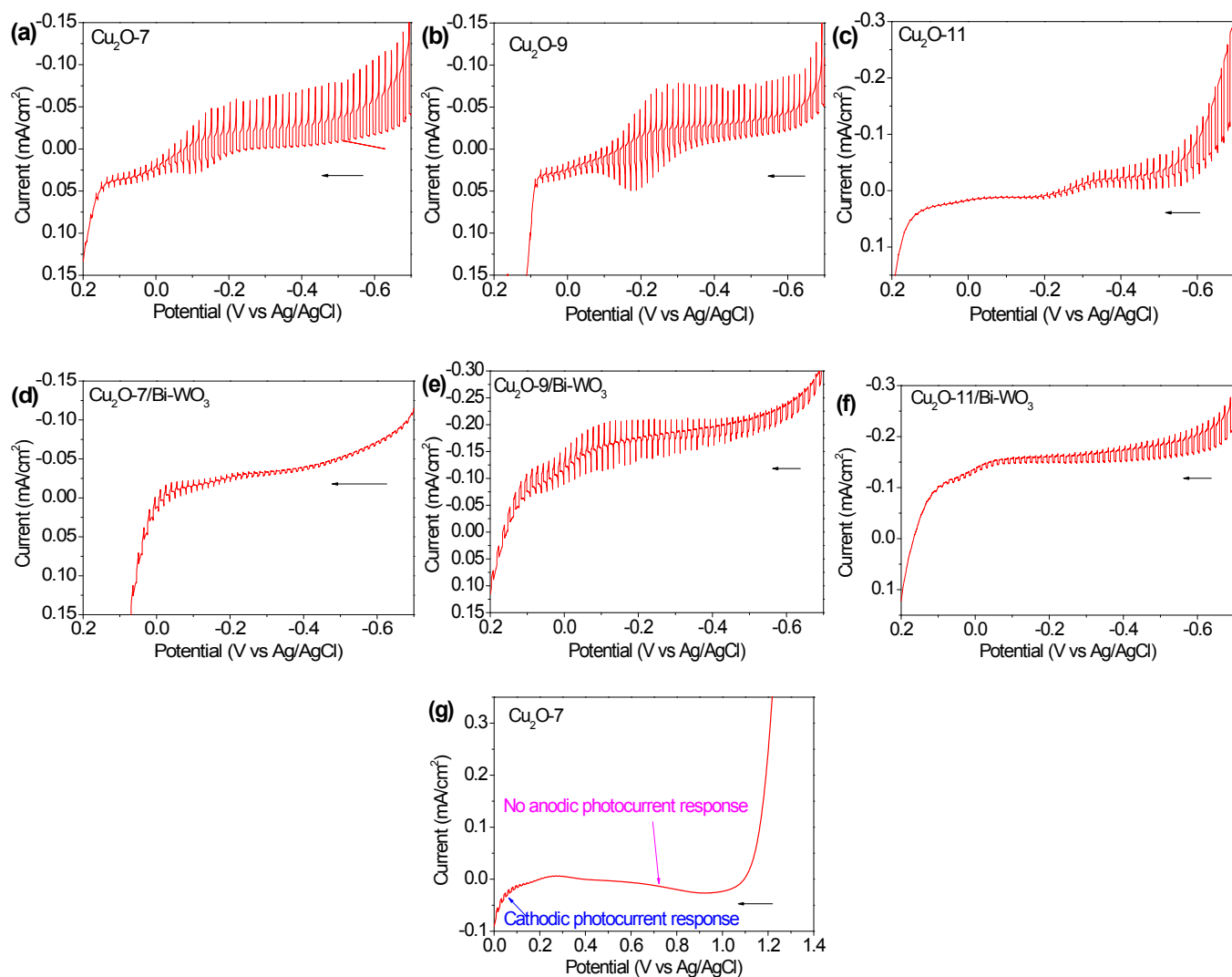


Fig. S10 Cathodic photocurrents of (a) Cu_2O -7, (b) Cu_2O -9, (c) Cu_2O -11, (d) Cu_2O -7/ Bi-WO_3 , (e) Cu_2O -9/ Bi-WO_3 and (f) Cu_2O -11/ Bi-WO_3 , and (g) anodic photocurrent checking of Cu_2O -7 under the chopped 1 sun light illumination. The black arrows indicate the scanning direction.

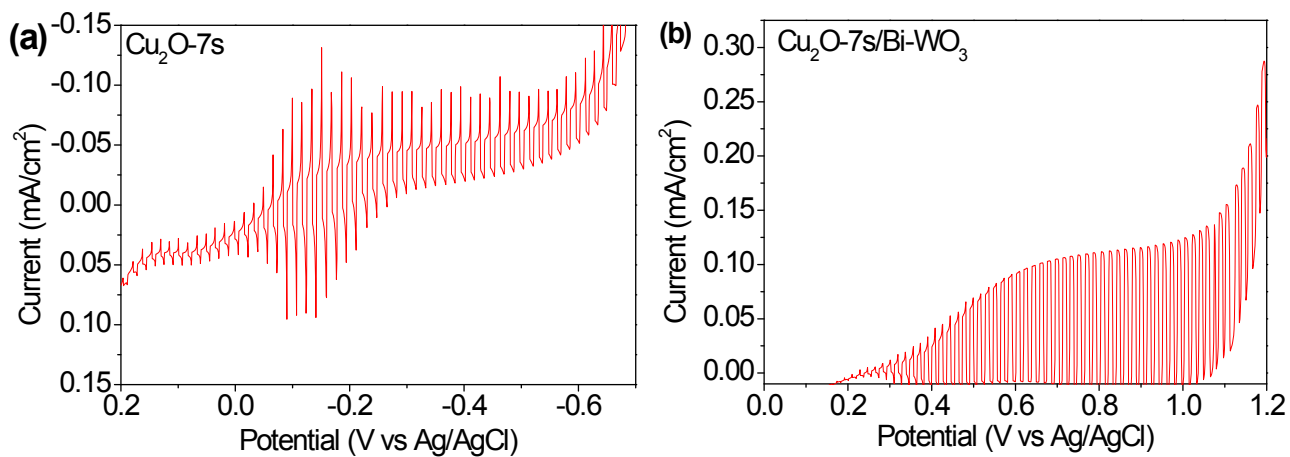


Fig. S11 Photocurrents of (a) $\text{Cu}_2\text{O-7s}$ and (b) $\text{Cu}_2\text{O-7s/Bi-WO}_3$ films obtained by electrodeposition with stirring condition.

References:

- [1] J. Y. Zheng, G. Song, J. Hong, T. K. Van, A. U. Pawar, D. Y. Kim, C. W. Kim, Z. Haider and Y. S. Kang, *Cryst. Growth Des.*, 2014, **14**, 6057–6066.