Electronic Supplementary Information (ESI)

Tree Branch-Shaped Cupric Oxide for Highly Effective Photoelectrochemical Water Reduction

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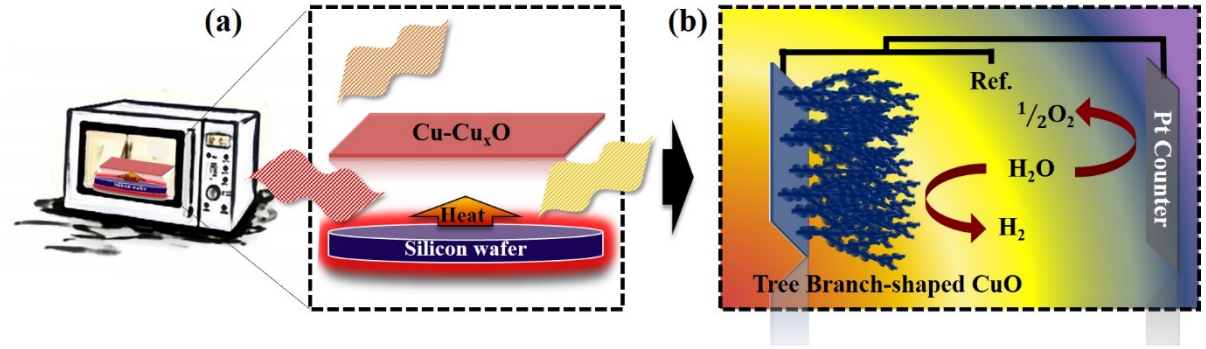

Figure S1. Schematics for hybrid microwave annealing process with a silicon susceptor (a) and photoelectrochemical (PEC) water splitting process using the tree branch-shaped CuO photocathode (b).

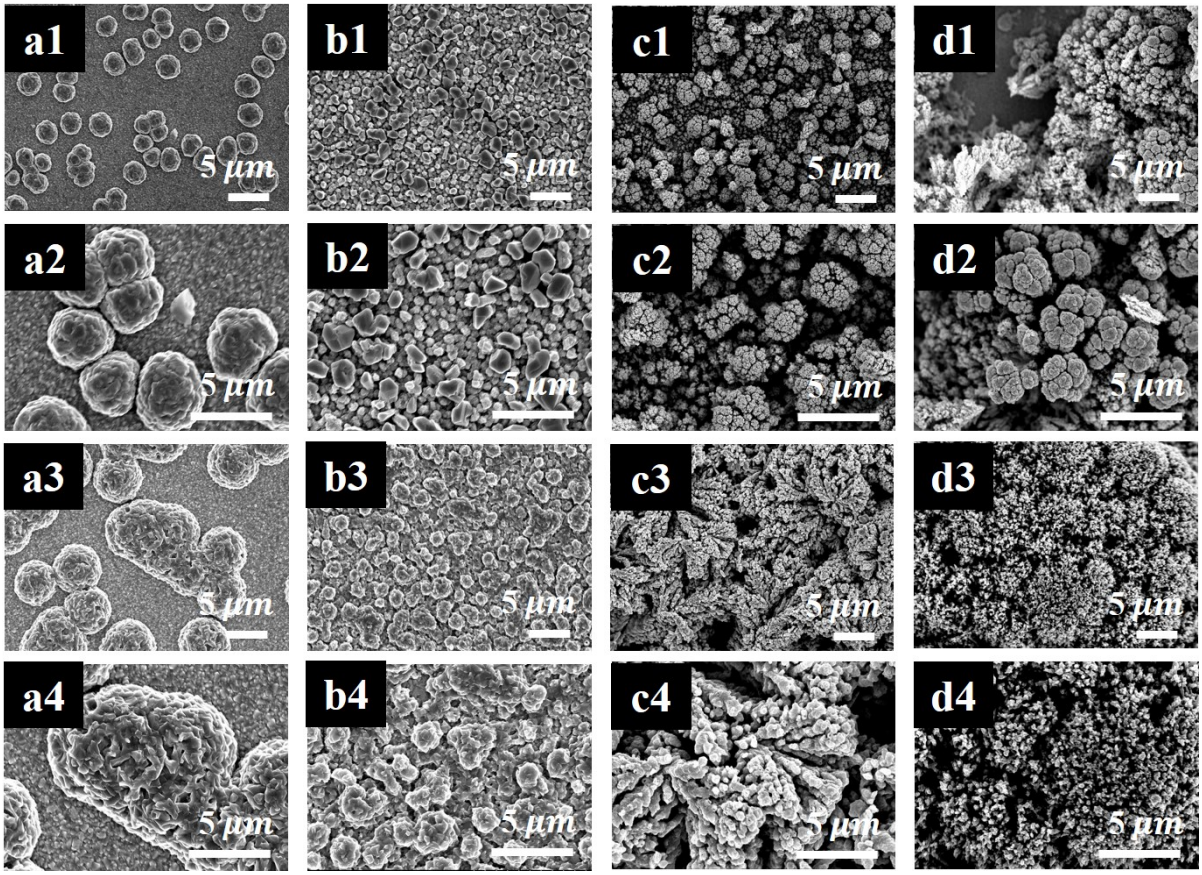

Figure S2. The SEM images of the as electrodeposited Cu-Cu oxide at various applied voltage ; (a1-a2) 1 Vdc, (b1-b2) 3 Vdc, (c1-c2) 5 Vdc, and (d1-d2) 10 Vdc, and the HMA treated CuO after electrodeposited at various applied voltage; (a3-a4) 1 Vdc, (b3-b4) 3 Vdc, (c3-c4) 5 Vdc, and (d3-d4) 10 Vdc,

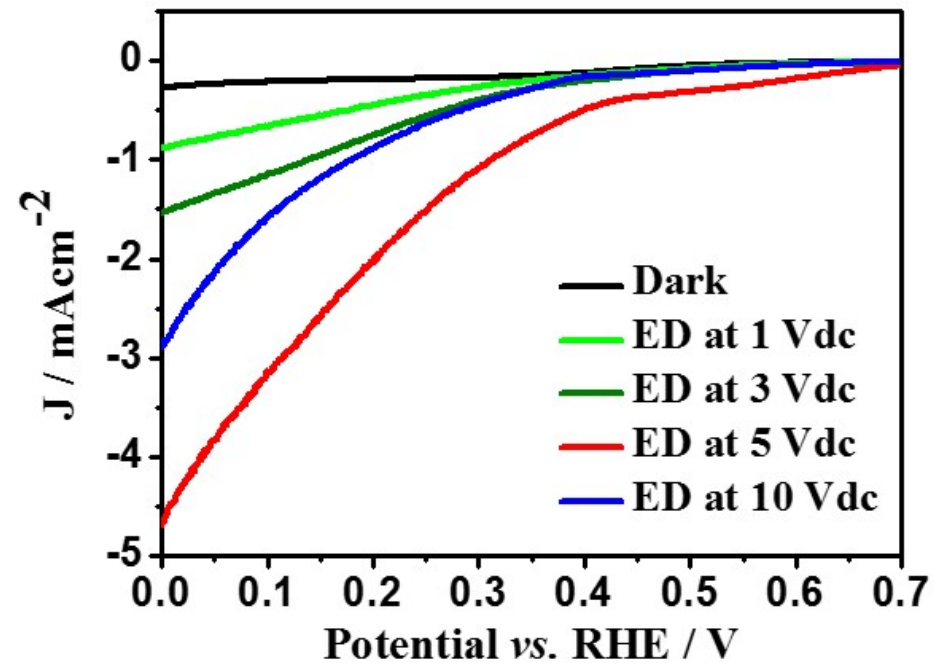

Figure S3. Photocurrent density (J) and applied potential (V) for HMA CuO electrodeposited at various voltage; 1, 3, 5 and 10 Vdc, under simulated 1 Sun illumination in the 0.5 M Na_2SO_4

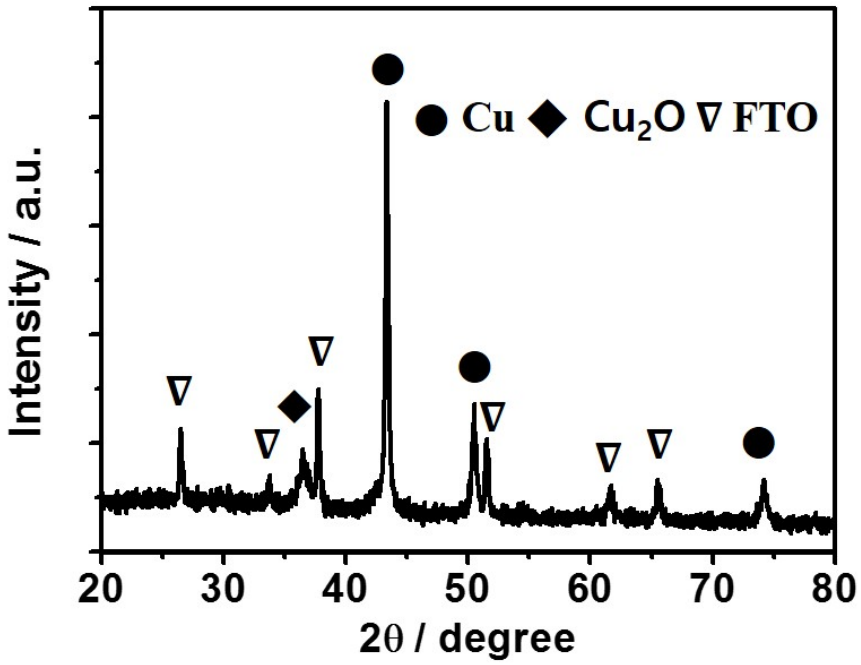

Figure S4. X-ray diffraction (XRD) pattern of conventional microwave-annealed Cu-Cu_xO oxide film on FTO (MA Cu_xO).

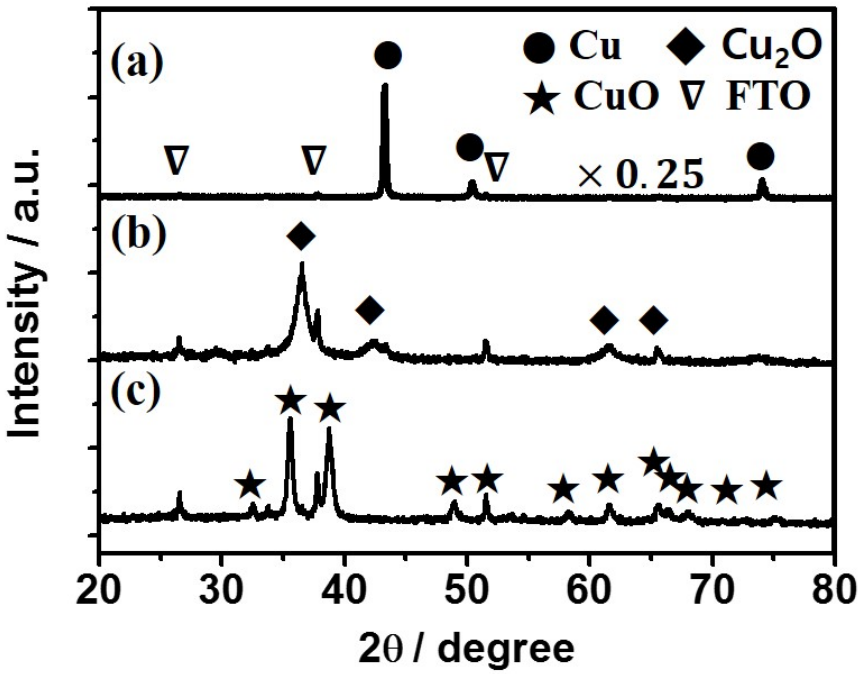

Figure S5. XRD patterns of (a) Cu FTO, (b) HMA-treated film with a graphite susceptor for 20s showing Cu_2O as the major phase, and (c) HMA-treated film with a graphite susceptor for 30s showing CuO as the major phase.

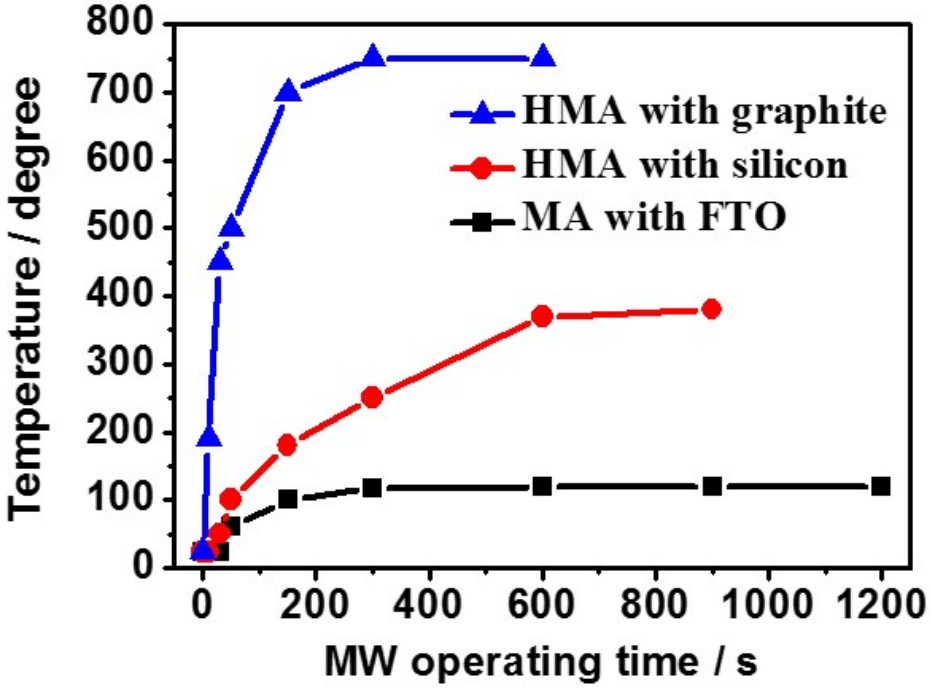

Figure S6. Temperature profiles of microwave (MW) operating time with FTO alone, HMA with a silicon susceptor and HMA with a graphite susceptor.

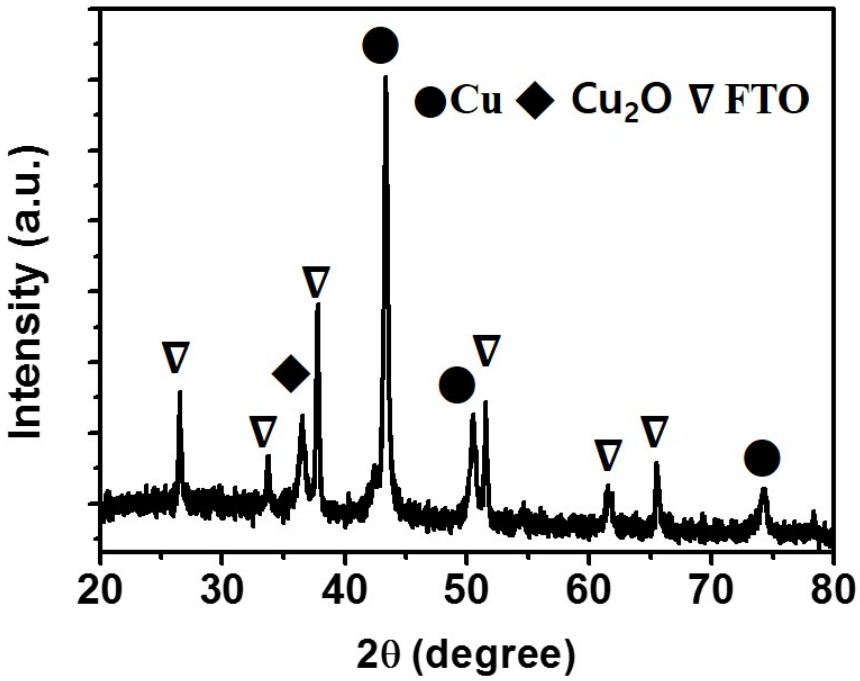

Figure S7. XRD pattern of Cu FTO film treated with HMA with a silicon susceptor for 10 min with a reduced power by 80%.

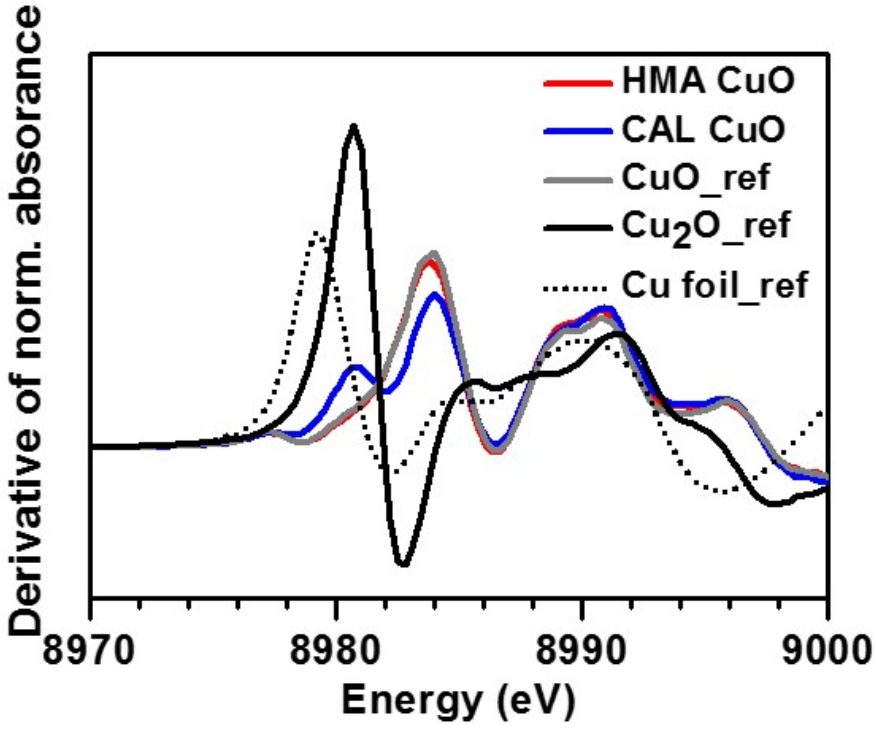

Figure S8. The derivatives of the normalized absorbance spectra of the photodeposited CuO films and reference materials.

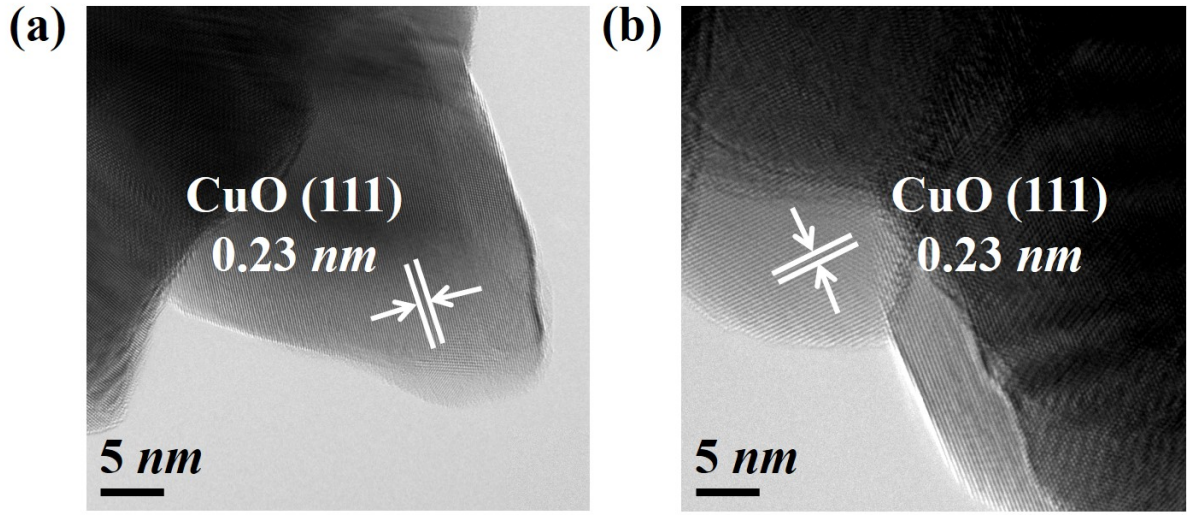

Figure S9. Transmission electron microscopy (TEM) images of (a) HMA CuO and (b) CAL CuO

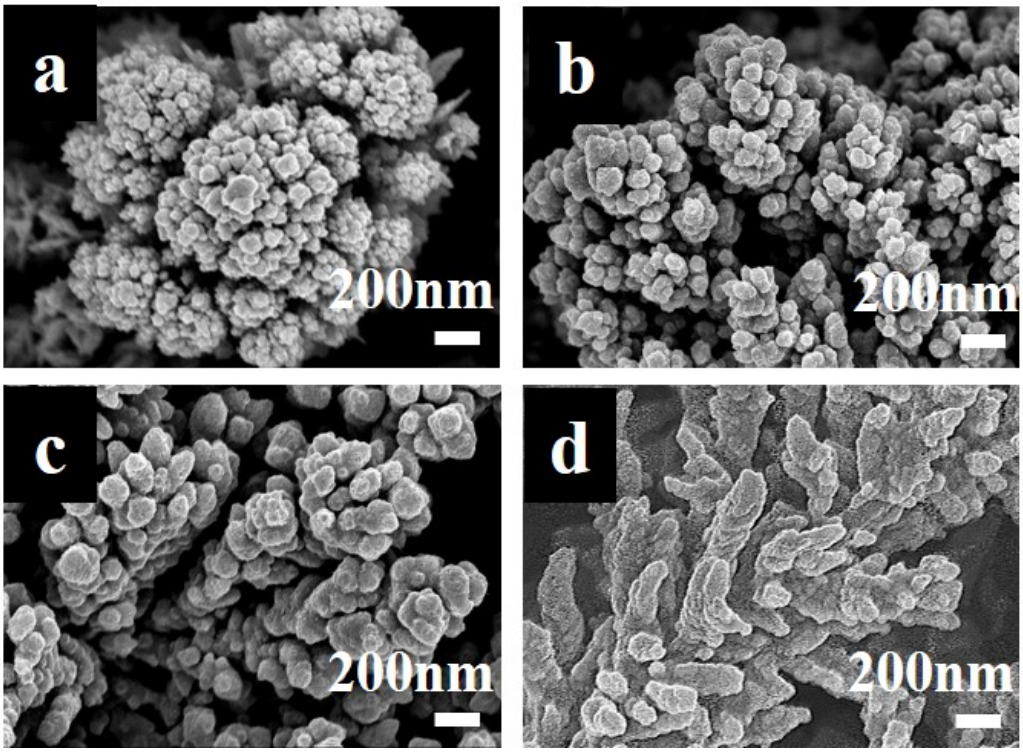

Figure S10. The SEM images of the as electrodeposited Cu-Cu oxide (a) and HMA treated CuO after 30s (b), 3min (c) and 10 min (d).

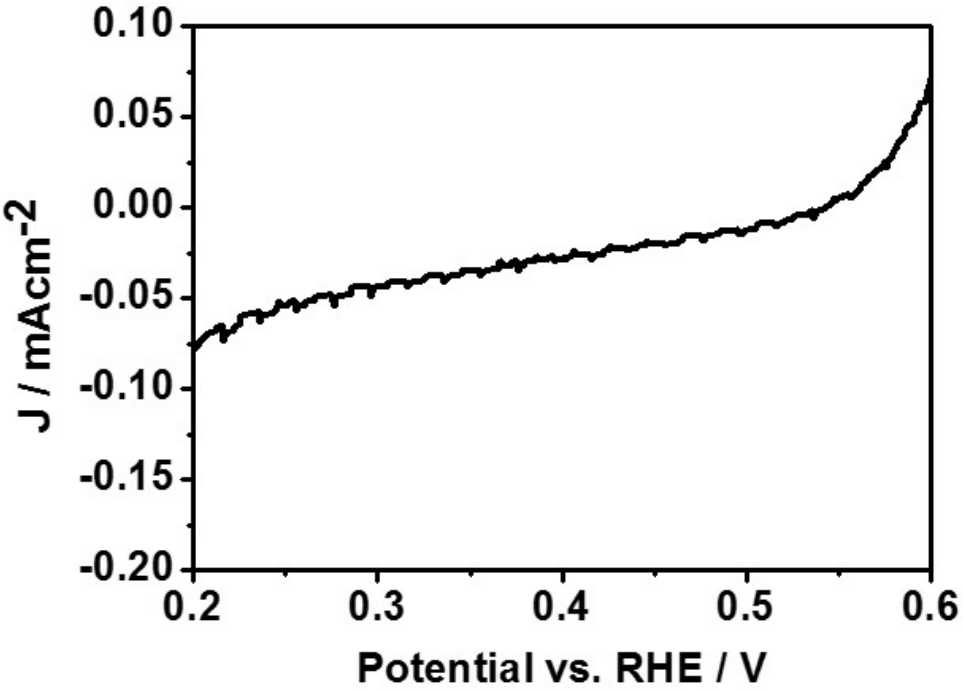

Figure S11. Photocurrent density (J) – applied potential (V) curve of as electrodeposited Cu FTO.

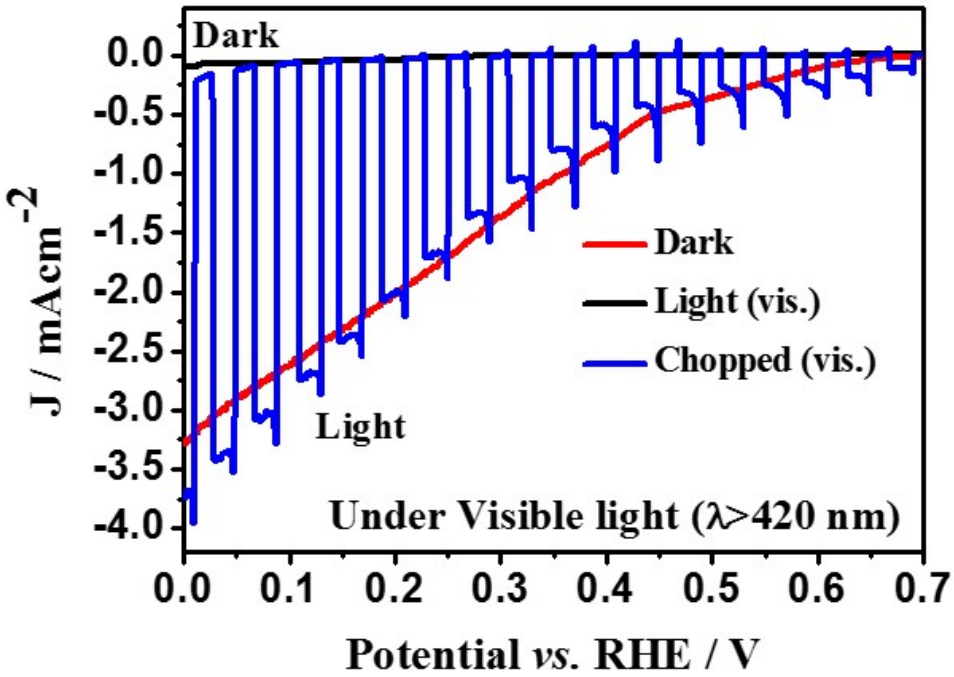

Figure S12. Photocurrent density (J) and applied potential (V) for HMA CuO under visibly light illumination (λ>420 nm) in the 0.5 M Na_2SO_4.

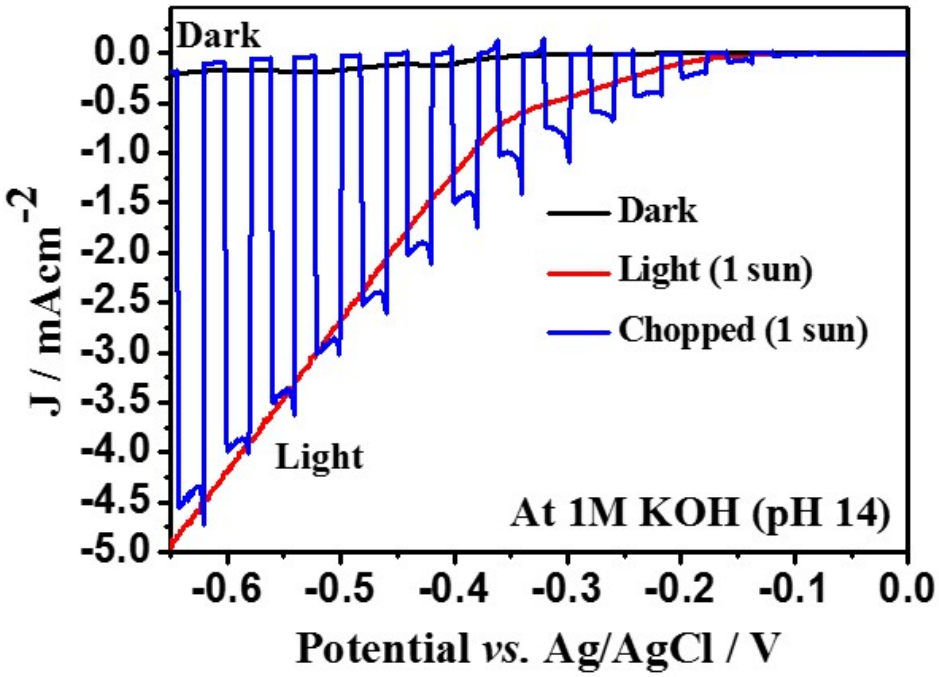

Figure S13. Photocurrent density (J) and applied potential (V) for HMA CuO under simulated 1 Sun illumination in the 1M KOH.

Table S1. Summary of PEC water splitting performances with copper oxide based photocathodes before post surface modification treatment under AM 1.5 light illumination

Electrode	**Fabrication Method**	**Electrolyte**	**Photocurrent density [$mAcm^{-2}$]**	**Ref.**
CuO	Spin coating and Sintering	KOH	-1.2 (0.55 V *vs*. Ag/AgCl)	*3*
Cu/Cu_2O/CuO	Thermal Oxidation	Na_2SO_4	-1.8 (0 V *vs*. RHE)	*7*
Cu/Cu_2O/CuO	Anodization and Thermal Oxidation	K_2SO_4	-0.36 (0.36 V *vs*. Ag/AgCl) 300W Xe lamp	*12*
Cu_2O/CuO	Electrodeposition , Anodization and Thermal Oxidation	Na_2SO_4	-1.54 (0 V *vs*. RHE)	*21*
Cu_2O	Electrodeposition	Na_2SO_4	-2.4 (0.25 V *vs*. RHE)	*22*
CuO	Sputter	KOH	-3.15 (0.55 V *vs*. Ag/AgCl)	*23*
CuO	Electrodeposition and Hybrid Microwave Annealing	Na_2SO_4	-4.4 (0 V *vs*. RHE)	*Present study*
CuO	Electrodeposition and Hybrid Microwave Annealing	KOH	-3.62 (0.55 V *vs*. Ag/AgCl)	*Present study*

Table S2. The results of EIS fitting into equivalent circuit model for HMA and CAL CuO

Element	**Rs**	**R1**	**CPE 1-T**	**R2**	**CPE 2-T**
HMA CuO	15.55	144.3	1.818×10^{-4}	592	7.625×10^{-4}
CAL CuO	20.72	535.1	1.314×10^{-4}	2181	3.163×10^{-4}