

PCCP

Supporting Information

Screening of Transition and Post-Transition Metals to Incorporate Into Copper Oxide and Copper Bismuth Oxide for Photoelectrochemical Hydrogen Evolution

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Chemicals

The following metal salts and chlorides were used to make arrays and films:

AgNO₃ (ACROS, p.a.)
Cu(NO₃)₂·xH₂O (Alfa Aesar, 99.999%)
Cd(NO₃)₂·4H₂O (Alfa Aesar, 99.999%)
Zn(NO₃)₂·xH₂O (Sigma-Aldrich, 99.999%)
Al(NO₃)₃·xH₂O (Alfa Aesar, 99.999%)
Ga(NO₃)₃·xH₂O (Alfa Aesar, 99.999%)
In(NO₃)₃·xH₂O (Alfa Aesar, 99.999%)
La(NO₃)₂·6H₂O (Alfa Aesar, 99.999%)
Ga(NO₃)₃·xH₂O (Alfa Aesar, 99.99%)
Y(NO₃)₃·xH₂O (Alfa Aesar, 99.99%)
Bi(NO₃)₃·xH₂O (Alfa Aesar, 99.999%)
SnCl₄·xH₂O (Alfa Aesar, 98%)
TiCl₄ (Alfa Aesar, 99.99%)
ZrCl₄ (Alfa Aesar, 99.5+%)
NbCl₅ (Sigma-Adrich, 99.995%)
TaCl₅ (Alfa Aesar 99.99%)
VCl₃ (Sigma Aldrich, 97%)
Cr(NO₃)₃·xH₂O (Alfa Aesar, 99.999%)
(NH₄)₆Mo₇O₂₄·4H₂O (Sigma-Aldrich, 99.98%)
(NH₄)₁₀W₁₂O₄₁·5H₂O (Sigma-Aldrich, 99.99%)
Mn(NO₃)₂·xH₂O (Alfa Aesar, 99.999%)
Co(NO₃)₂·6H₂O (Alfa Aesar, 99.999%)
Fe(NO₃)₃·9H₂O (Sigma Aldrich, 99.999%)
N₂NiO₆·6H₂O (Alfa Aesar, 99.9985%)

Additional Figures

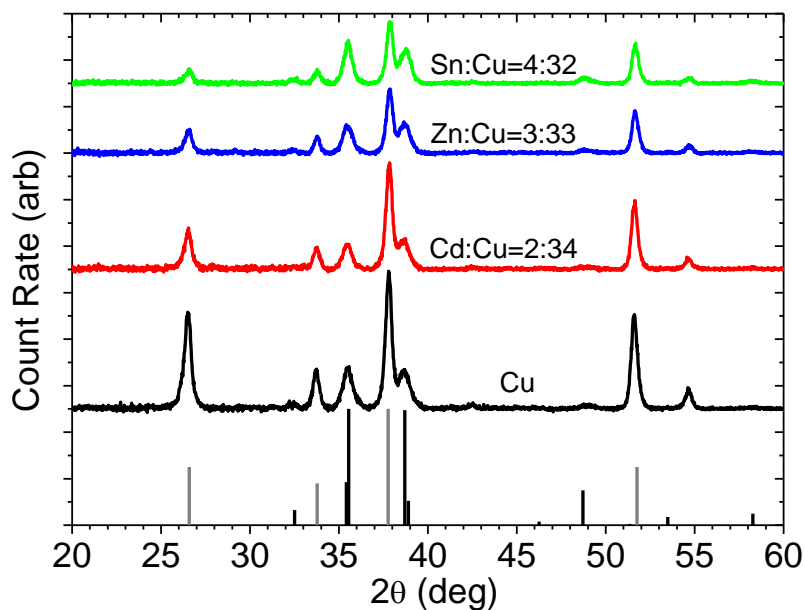


Figure S1. XRD spectra for Cu oxide and M-Cu oxide films synthesized by drop-cast with atomic ratios of Cd:Cu=2:34, Zn:Cu=3:33, and Sn:Cu=4:32. Grey vertical lines (|) represent the cassiterite, SnO₂ reference pattern (PDF# 00-042-0334). Black vertical lines (|) represent the CuO reference pattern (PDF#00-048-1548).

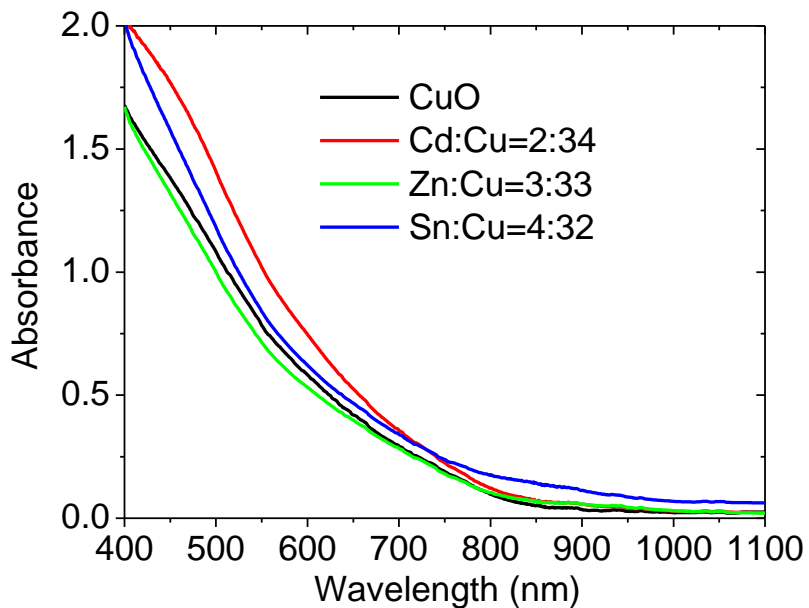


Figure S2. UV-Vis absorbance spectra for CuO and M-Cu oxide films with atomic ratios of Cd:Cu=2:34, Zn:Cu=3:33, and Sn:Cu=4:32.

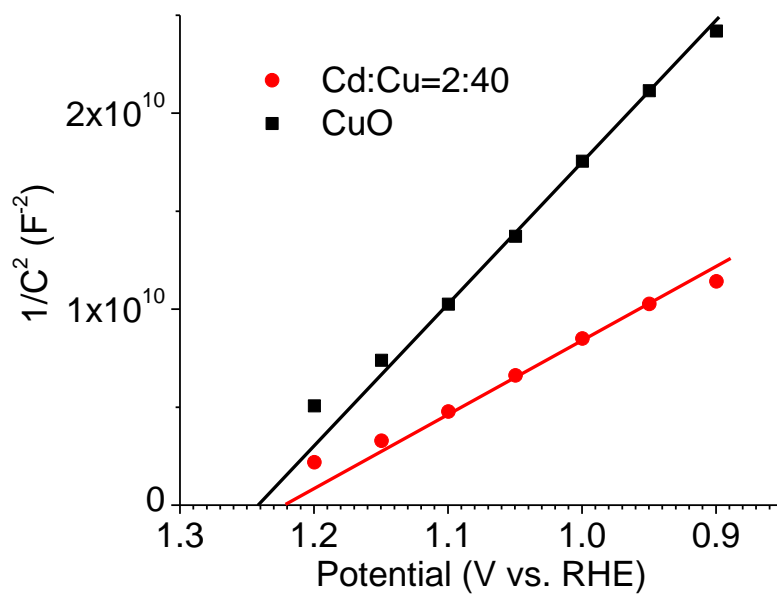


Figure S3. Mott-Schottky plot for CuO and Cd:Cu=2:34 oxide films. Measurements were conducted in 0.1 M Na_2SO_4 and 0.1 M phosphate buffer (pH 6.8) using a frequency of 1000 Hz.

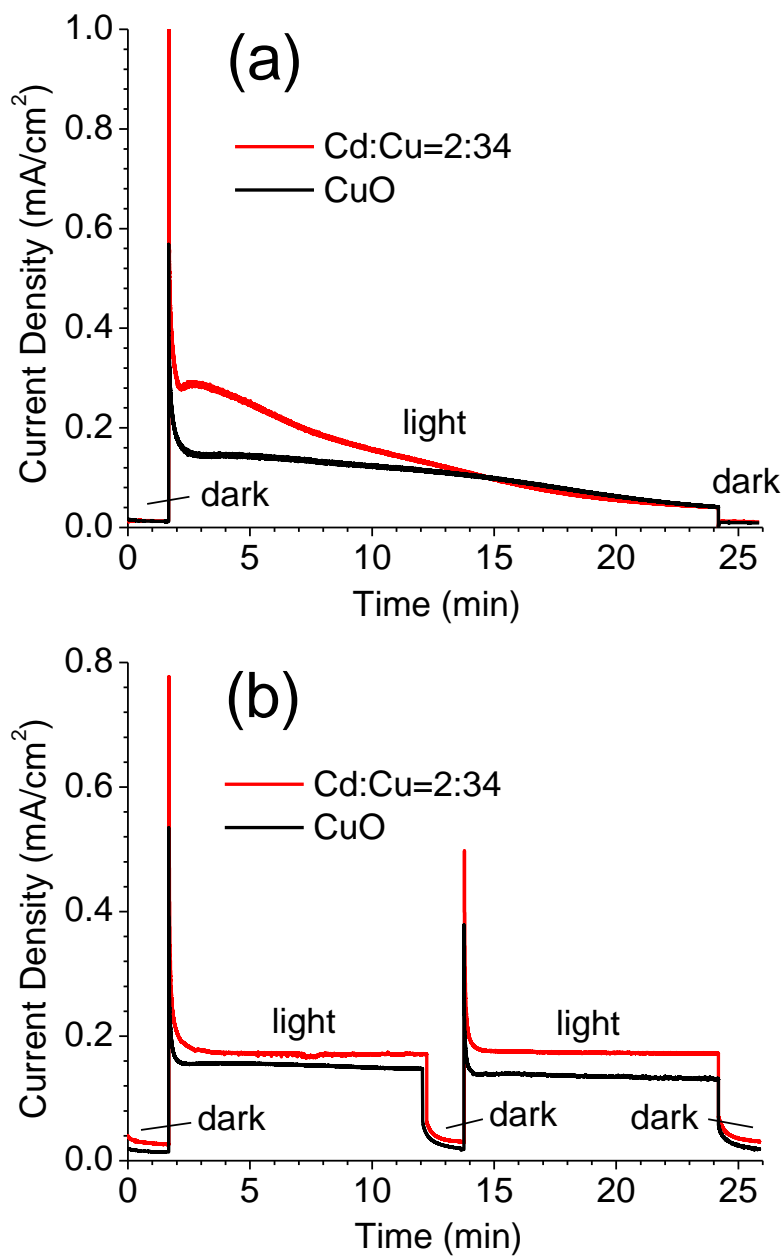


Figure S4. Amperometric *i-t* measurement for CuO and Cd:Cu=2:34 oxide films. Measurements were done in (a) 0.1 M Na₂SO₄ and 0.1 M phosphate buffer solution (pH 6.8) at 0.6 V vs. RHE and (b) 10 mM I₂, 50 mM NaI in acetonitrile at 0.2 V vs. NHE. The films were illuminated from the backside with 100 mW/cm².

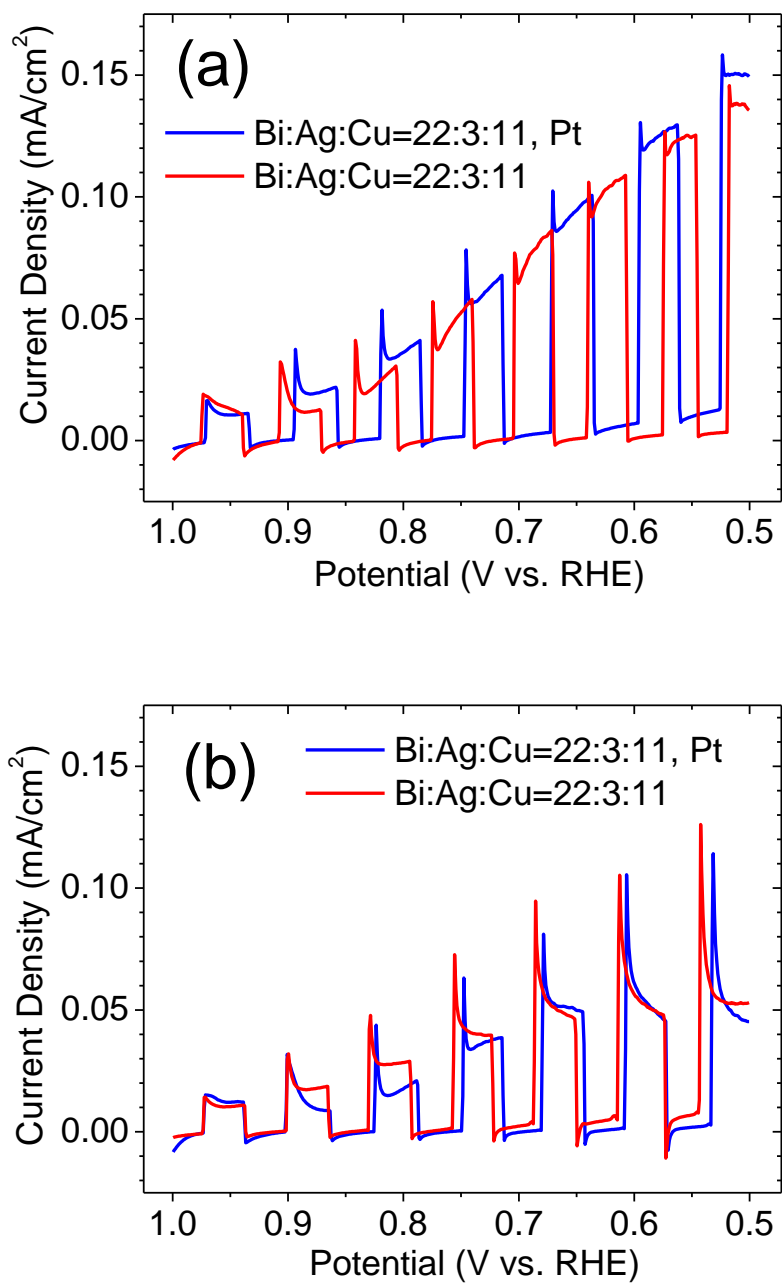


Figure S5. Chopped (dark/light) LSV scans for Bi:Ag:Cu=22:3:11 oxide films as synthesized by drop-cast and after depositing

Pt on the surface. Measurements were done in 0.1 M Na₂SO₄ and 0.1 M phosphate buffer (pH 6.8) using backside illumination (100 mW/cm²) and a scan rate of 0.025 V/s. The electrolyte was used (a) as prepared and (b) after purging with N₂ for 30 minute prior to the measurements.

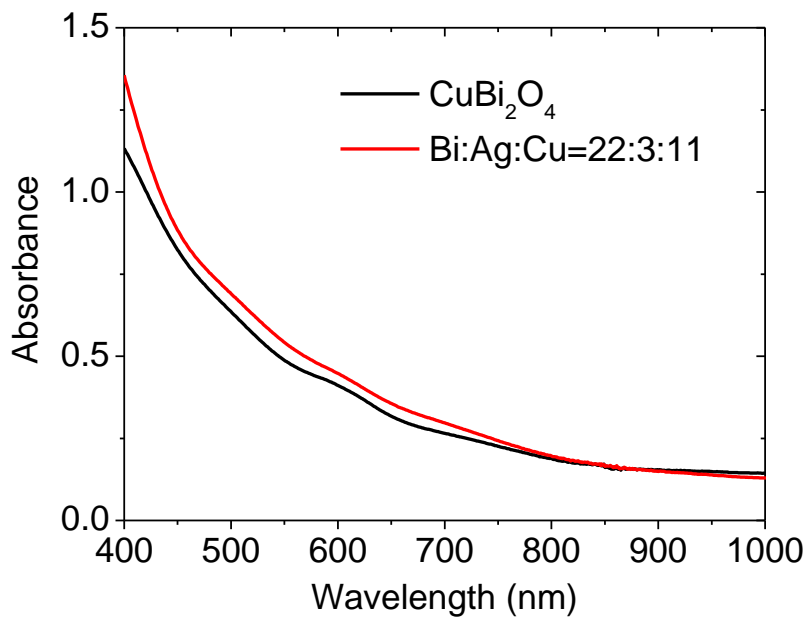


Figure S6. UV-Vis absorbance spectra for CuO and Bi:Ag:Cu=22:3:11 oxide films.

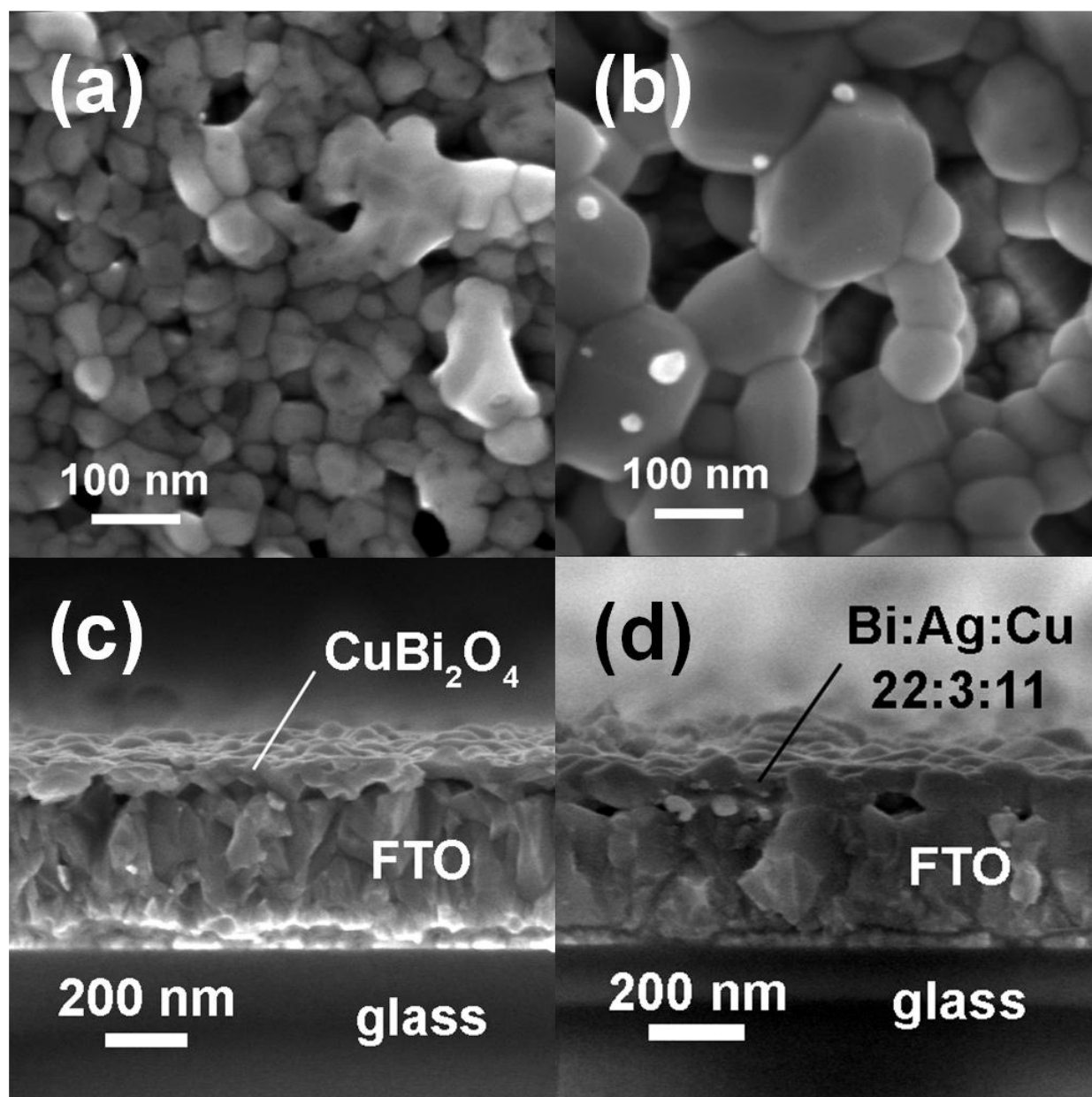


Figure S7. SEM images of films synthesized by drop-cast. On the left are (a) top-view and (c) cross section view images of a CuBi_2O_4 film. On the right are (b) top view and (d) cross-section images of a Bi:Ag:Cu=22:3:11 oxide film.

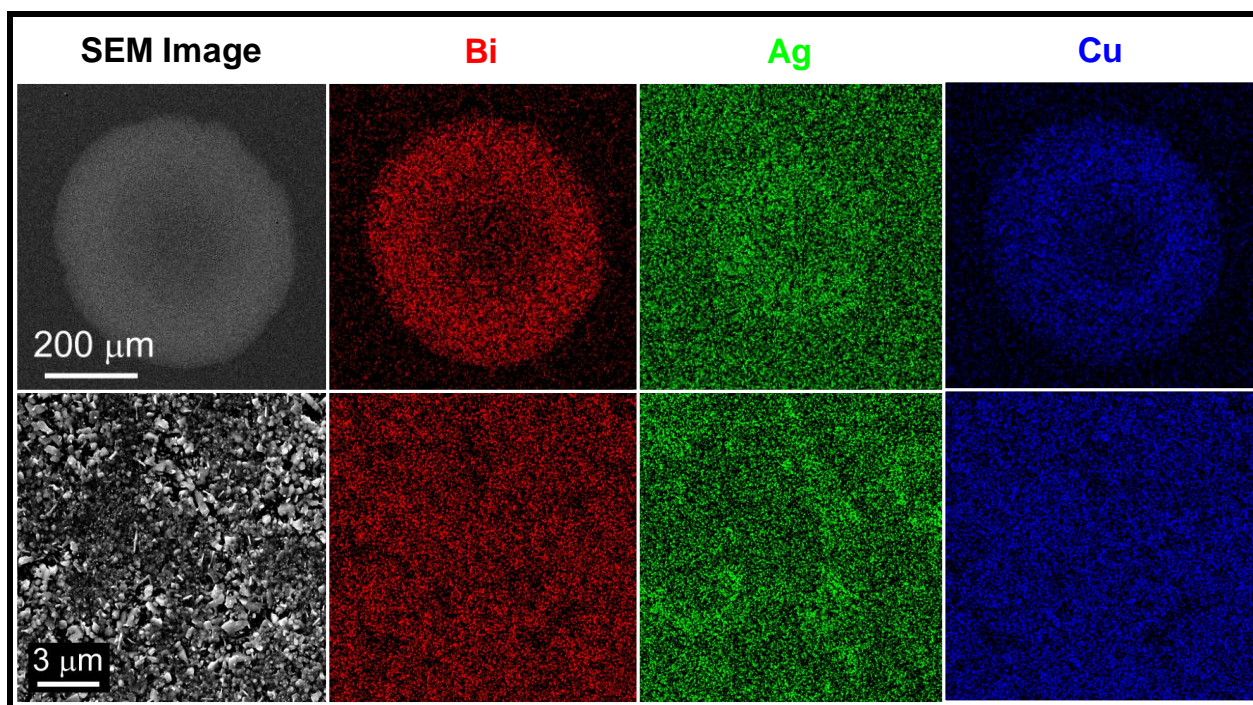


Figure S8. EDS mapping data for a Bi:Ag:Cu=22:3:11 spot on a fine detail Bi-Ag-Cu array. The top row shows mapping data for the entire spot and the bottom row shows data for a smaller area near the centre of the spot. Ag mapping data shows up on the FTO substrate around the spot due to overlap in signal from the Ag L series (2.983 keV) and the Sn L series (3.444 keV) peaks.

Array Pattern	Total Number of Drops	Expected Atomic Ratio	EDS Measured Atomic Ratio
Initial 19 x 19	18	Bi:Cu = 12:6	Bi:Cu = 12.8:5.2
Fine Detail	36	Bi:Cu = 24:12	Bi:Cu = 24.1:11.9
Fine Detail	36	Bi:Ag:Cu = 22:3:11	Bi:Ag:Cu = 22.6:1.8:11.5

Table S1. EDS quantification results for various array spots. The expected atomic ratios are based on the number of drops dispensed for the array pattern (Figures 3 and 11). The EDS measured atomic ratios were calculated by averaging three different locations per spot. The voltage setting was 20 keV and the following peaks were used for quantification: Bi K series (10.839 keV), Ag L series (2.983 keV), Cu K series (8.046 keV), Sn L series (3.444 keV), and O K series (0.525 keV). There was significant overlap in the signal from the Ag and Sn peaks near 3 keV resulting in error for Ag quantification.

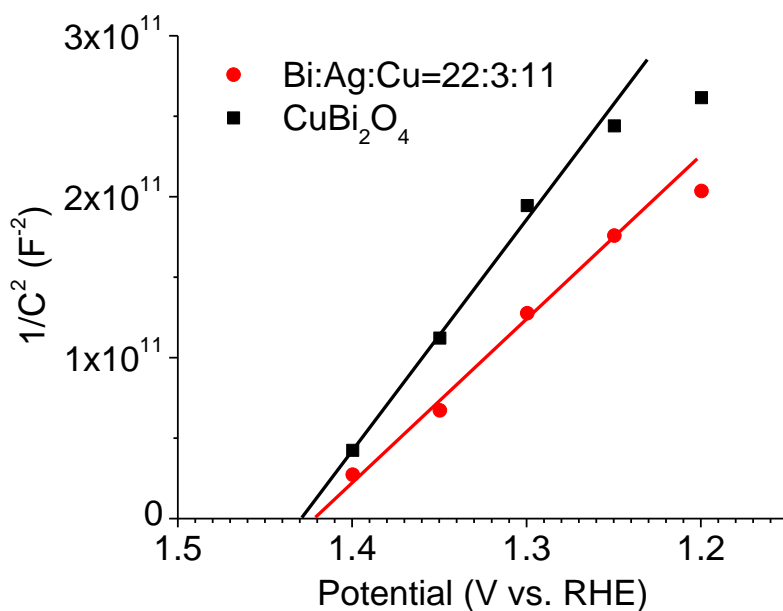


Figure S9. Mott-Schottky plot for $CuBi_2O_4$ and Bi:Ag:Cu=22:3:11 oxide films. Measurements were conducted in 0.1 M Na_2SO_4 and 0.1 M phosphate buffer (pH 6.8) using a frequency of 1000 Hz.

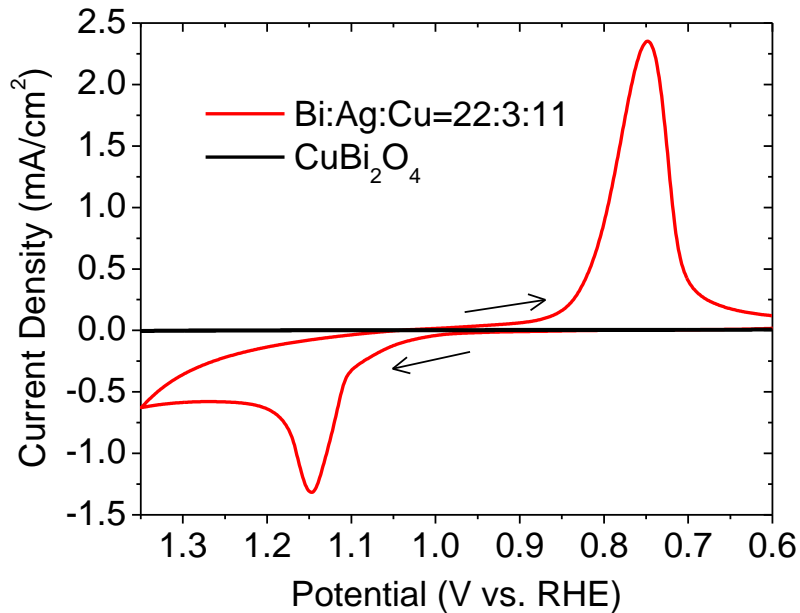


Figure S10. CV measurements of $CuBi_2O_4$ and Bi:Ag:Cu=22:3:11 oxide films. Measurements were done in 0.1 M Na_2SO_4 and 0.1 M phosphate buffer (pH 6.8) with a scan rate of 0.05 V/s.