ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Post-Synthetic Silver Ion and Sulfurization Treatment for Enhanced Performance in Sb_2Se_3 Water Splitting Photocathodes

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Metal Solutions	Photovoltage (V vs. RHE)	Photocurrent (mA/cm^2)	Fill Factor (%)
$CaCl_2$	0.261 ±0.0303	-15.1 ±0.832	31.4
$CoCl_2$	0.191 ±0.0474	-14.2 ±1.85	25.4
$NiCl_2$	0.0733 ±0.0367	-5.47 ±2.01	14.5
$CuCl_2$	0.286 ±0.0129	-15.1 ±1.10	23.5
ZnCl2	0.296 ±0.0133	-14.5 ±1.23	25.7
$Ga(NO_3)_3$	0.261 ±0.00380	-14.8 ±1.22	30.9
$AuCl_3$	-0.0400 ±0.00470	-0.526 ±0.0655	-
$AgNO_3$	**0.322 ±0.0105**	**-18.9 ±1.57**	**42.2**
Untreated	0.177 ±0.0346	-14.4 ±0.751	21.0
$AgNO_3$ + S	**0.390 ±0.00724**	**-18.0 ±1.42**	**28.6**

Table S1 – Screening of various simple metallic solution treatments at the interface of Sb_2Se_3 and TiO_2. Photovoltage, photocurrent at 0 vs. RHE, fill factor, and their respective standard deviations were measured and calculated.

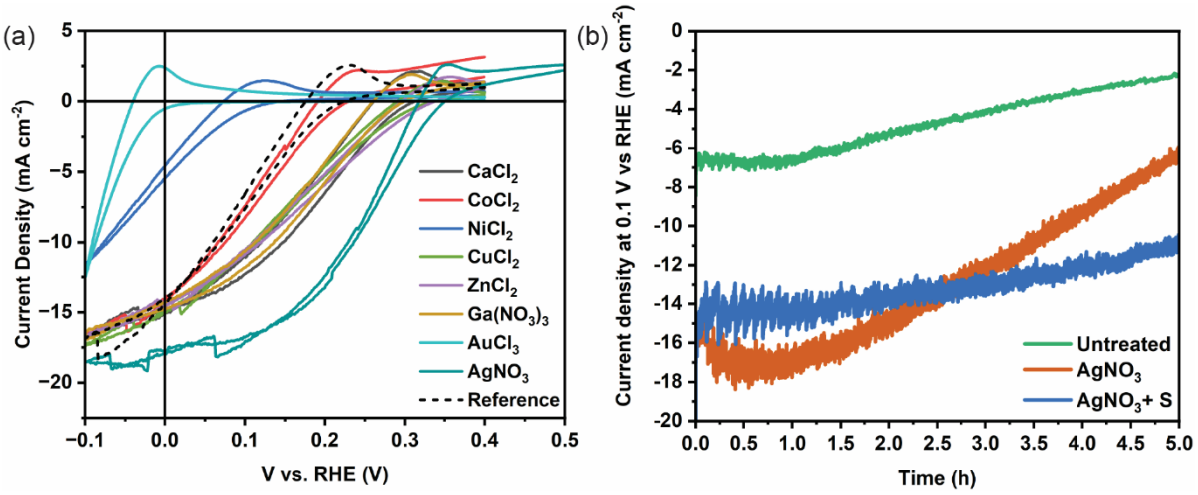

Figure S1 – (a) Cyclic voltammetry measurements of the metal screening experiment (b) Current density vs. time plots in 1 M H_2SO_4 at 0 V vs. RHE at 1 sun illumination (100 mW cm^{-2}) for 5 hours.

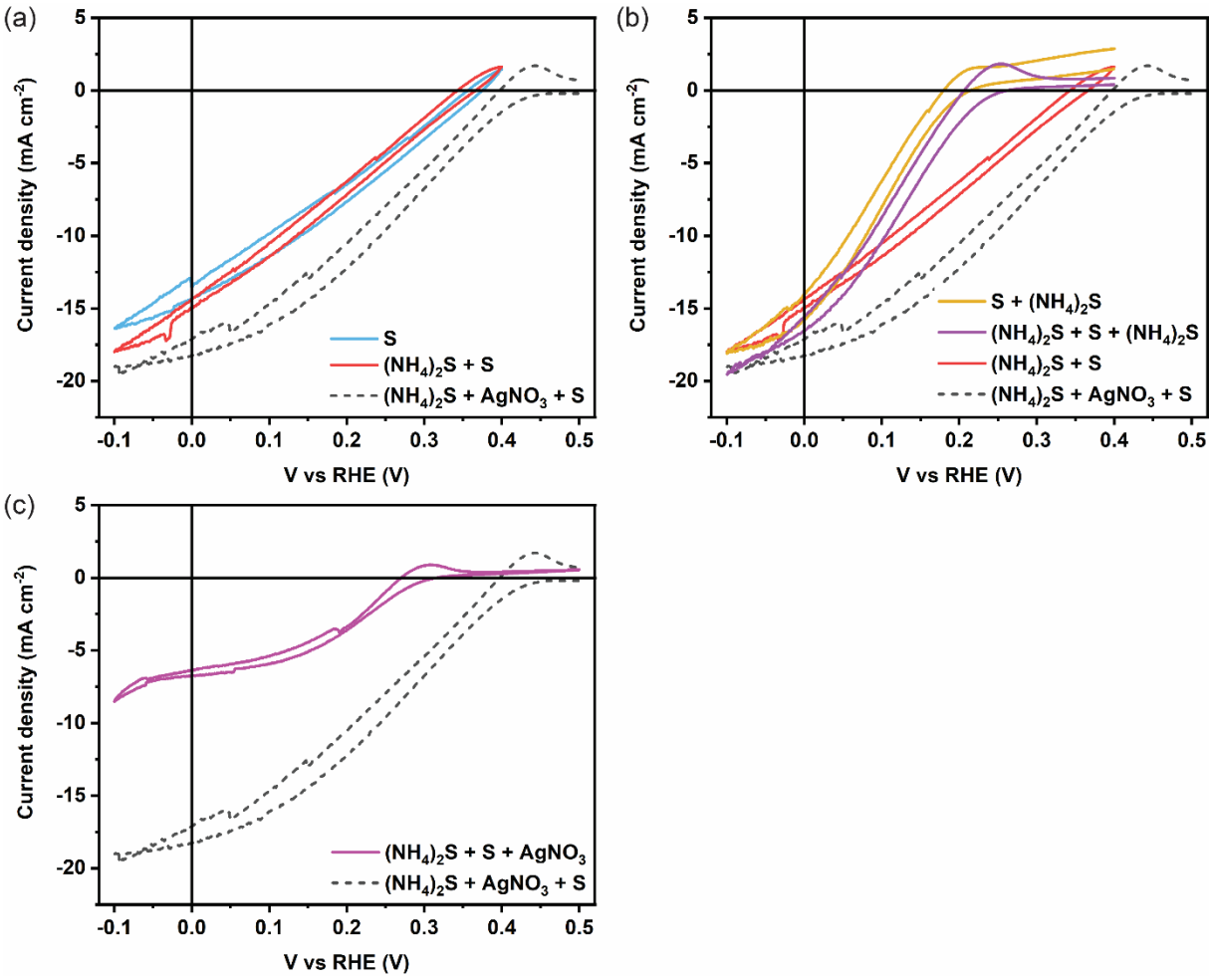

Figure S2 – All devices have a FTO/Ti/Au/Sb_2Se_3/TiO_2/Pt configuration (a) only sulfurization treatment (blue) and $(NH_4)_2S$ + sulfurization treatment (red) compared to the combined $(NH_4)_2S$ + $AgNO_3$ + sulfurization treatment (b) $(NH_4)_2S$ before (red), after (yellow) and both before and after (purple) sulfurization treatments compared to the combined $(NH_4)_2S$ + $AgNO_3$ + sulfurization (c) $AgNO_3$ treatment before and after sulfurizations.

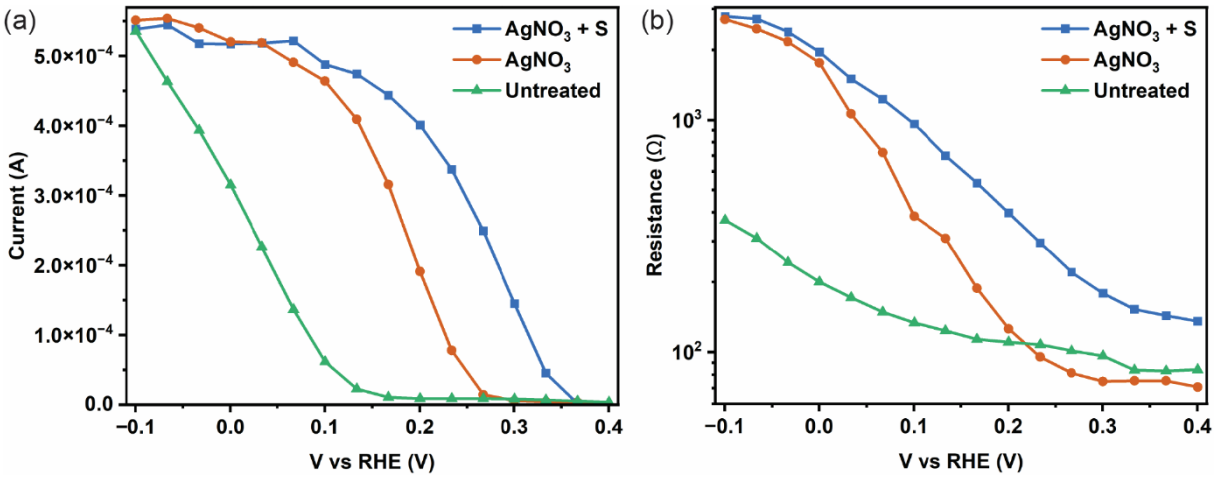

Figure S3 – All devices have a FTO/Ti/Au/Sb_2Se_3/TiO_2/Pt configuration and were measured in 1M H_2SO_4 at 10% white light from an LED light source (a) current vs voltage curves (b) resistance vs voltage determined from the EIS.

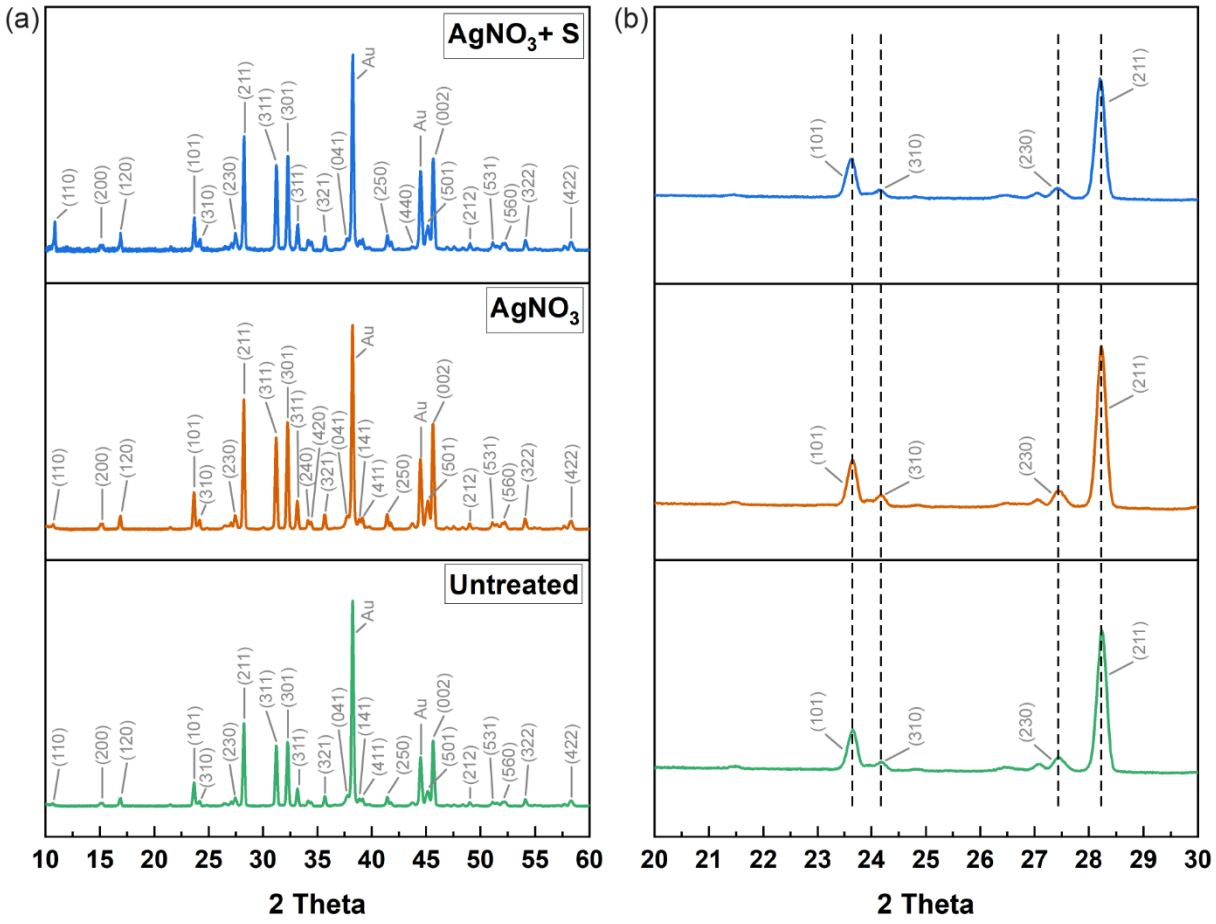

Figure S4 – (a) XRD patterns of untreated, $AgNO_3$ treated, and $AgNO_3$ + sulfurized treated Sb_2Se_3 samples (b) Zoomed in view of the spectra to highlight lack of peak shifting.

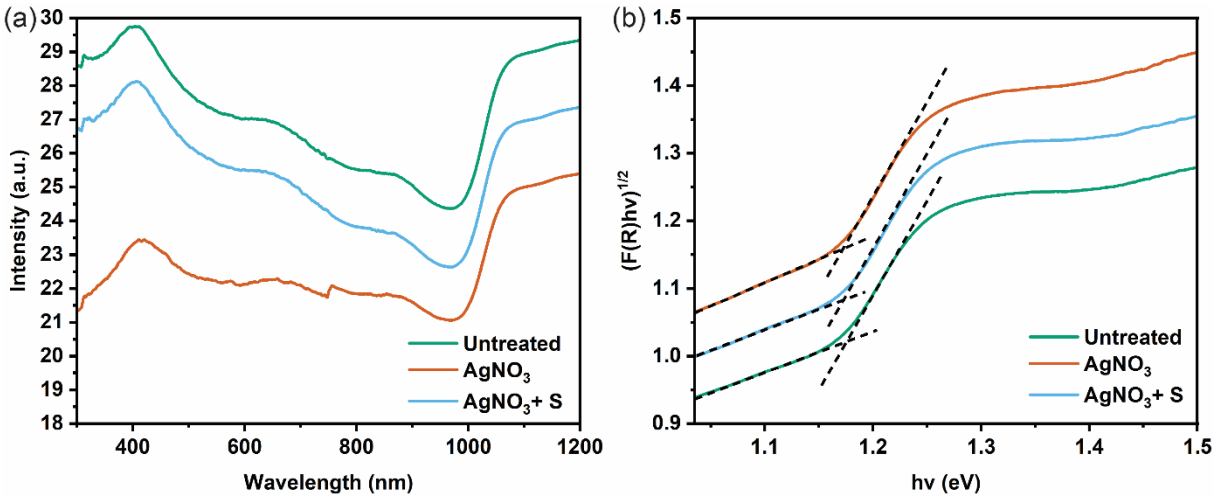

Figure S5 – (a) Diffuse reflectance spectra of the untreated, $AgNO_3$ and $AgNO_3$ + sulfurized Sb_2Se_3 devices (b) A band gap of ~1.18 eV for all three samples was determined via the Kubelka-Munk (K-M) function.

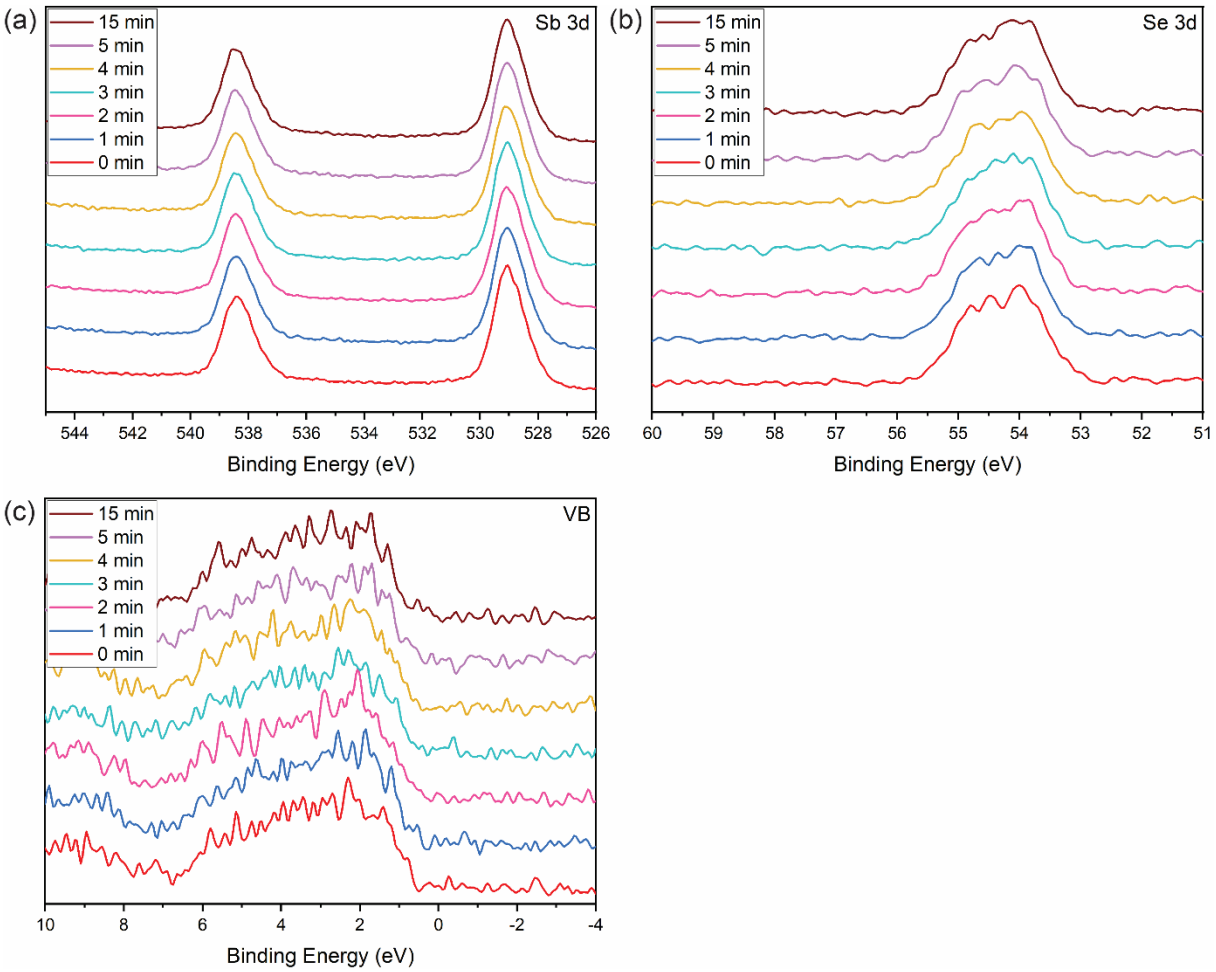

Figure S6 – XPS depth profiling of an untreated Sb_2Se_3 sample sputtered at a ~35 nm/min rate (a) Sb 3d core level (b) Se 3d core level, and (c) valence band maximum.

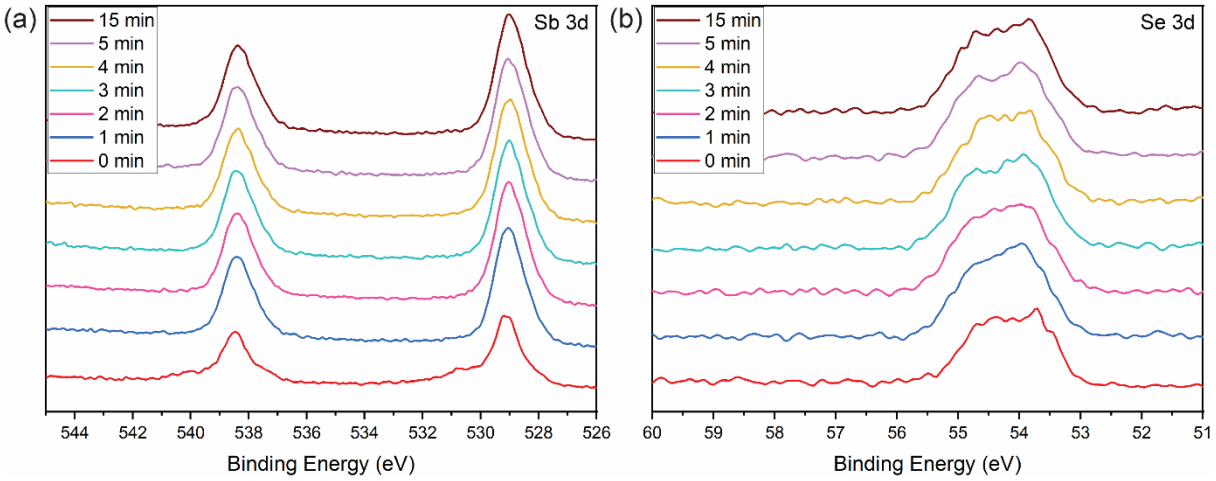

Figure S7 – XPS depth profiling of an $AgNO_3$ treated Sb_2Se_3 sample sputtered at a ~35 nm/min rate (a) Sb 3d core level (b) Se 3d core level.

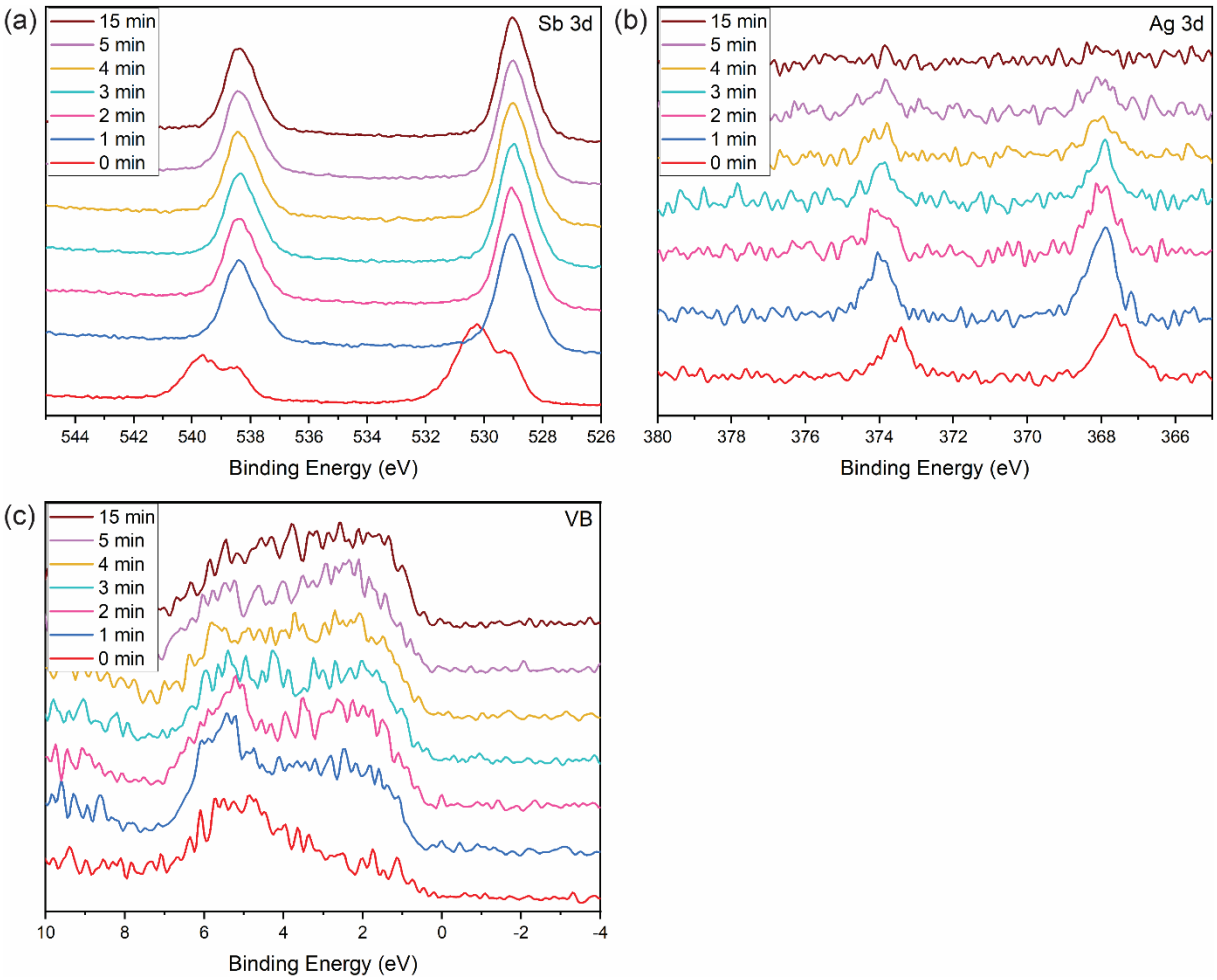

Figure S8 – XPS depth profiling of an $AgNO_3$ + sulfurized Sb_2Se_3 sample sputtered at a ~35 nm/min rate (a) Sb 3d core level (b) Ag 3d core level, and (c) valence band maximum.

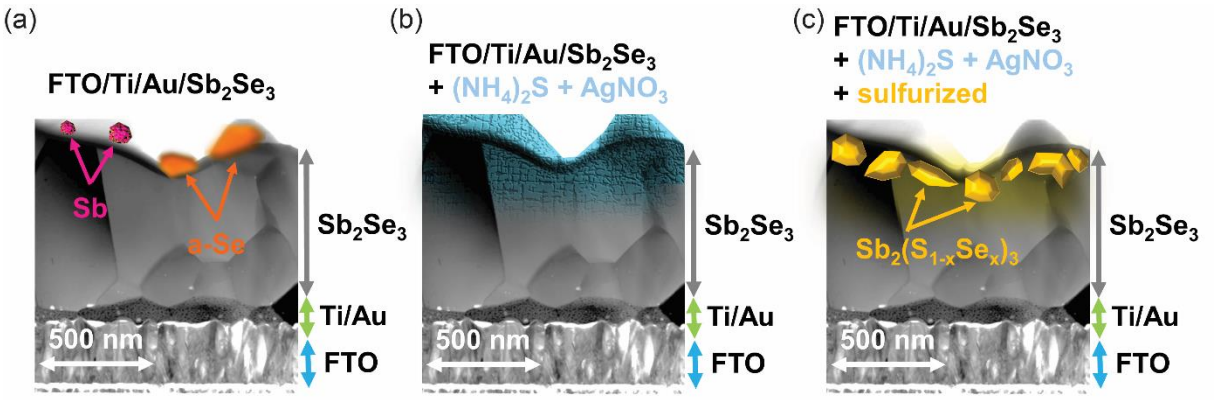

Figure S9 – Visual representation of each Sb_2Se_3 sample based on Raman measurements (a) Metallic Sb and amorphous Se in an untreated Sb_2Se_3 sample (b) Removal of metallic Sb and amorphous Se and integration of Ag into the Sb_2Se_3 film (c) Formation of $Sb_2(S_{1-x}Se_x)$ on the surface of the Sb_2Se_3 film.

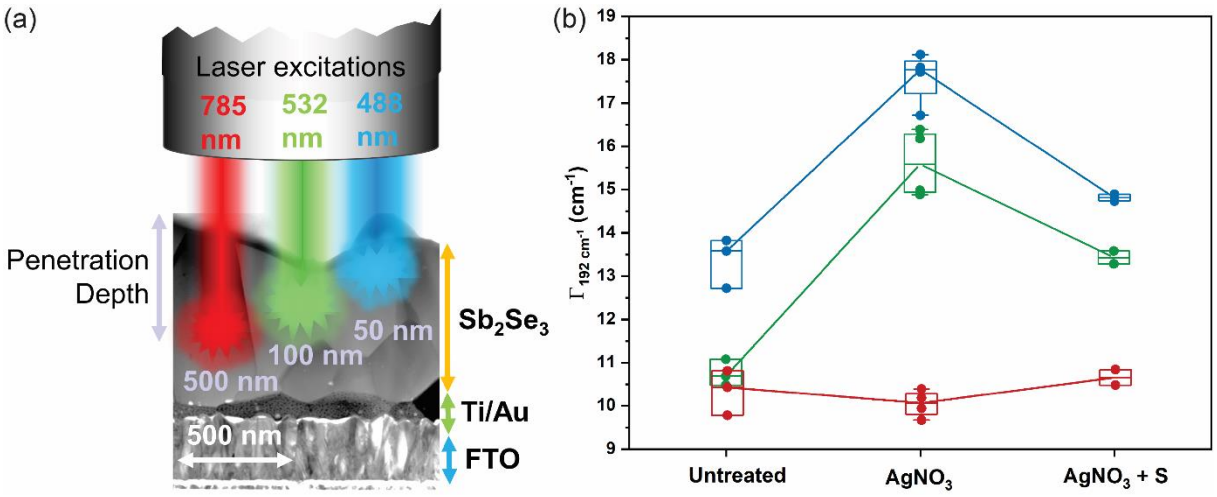

Figure S10 – (a) Visual representation of the penetration depth of the Raman lasers of each wavelength (b) Defect density and disorder levels of each sample when measured by the three different wavelengths of the Raman laser.

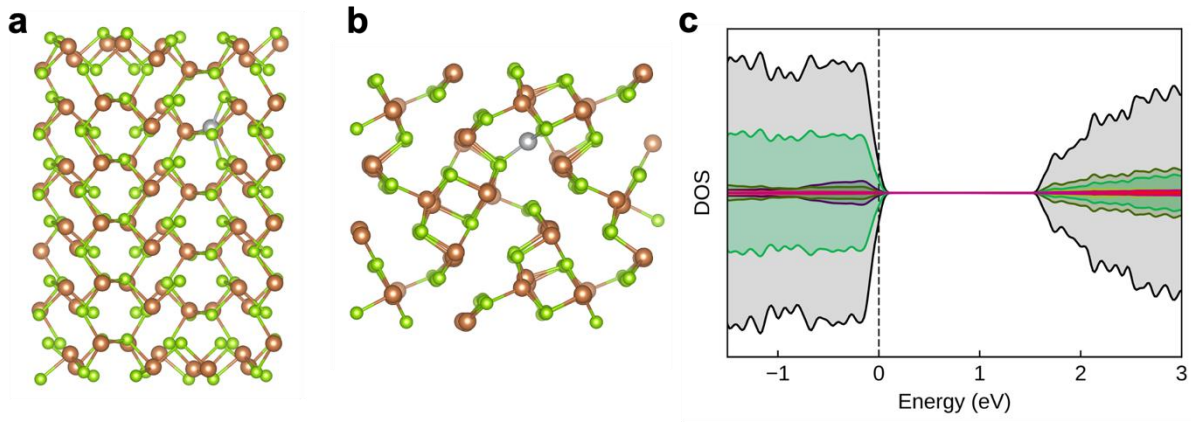

Figure S11 – (a) Side and (b) top views of the structure of the optimized structure of the Sb_2Se_3(001) surface with Ag^+ incorporated between Sb_2Se_3 ribbons below the surface. (c) The corresponding computed density of states showing no states are introduced within the band gap. Brown, green, silver, and yellow spheres represent Sb, Se, Ag, and S, respectively.