

Supporting Information

Modification of CO₂ Reduction Activity of Nanostructured Silver Electrocatalysts by Surface Halide Anions

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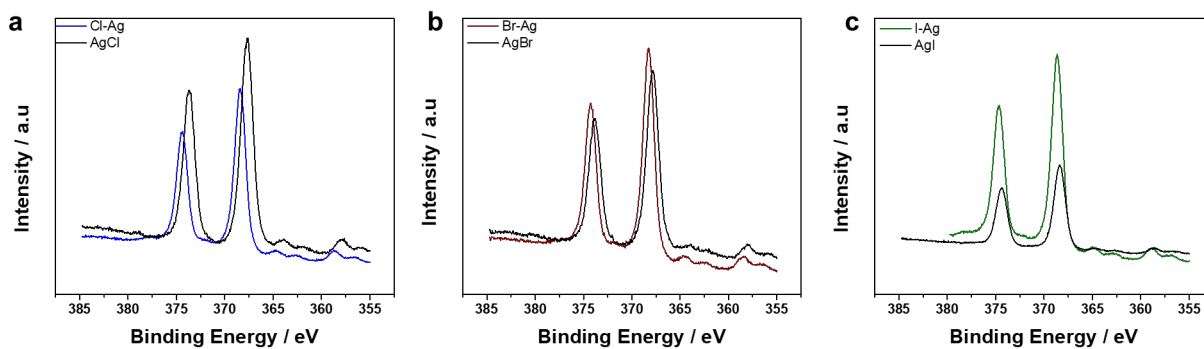


Figure S1. XPS spectra featuring Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks and comparing AgX and X-Ag samples. (a) X = Cl (b) X = Br and (c) X = I.

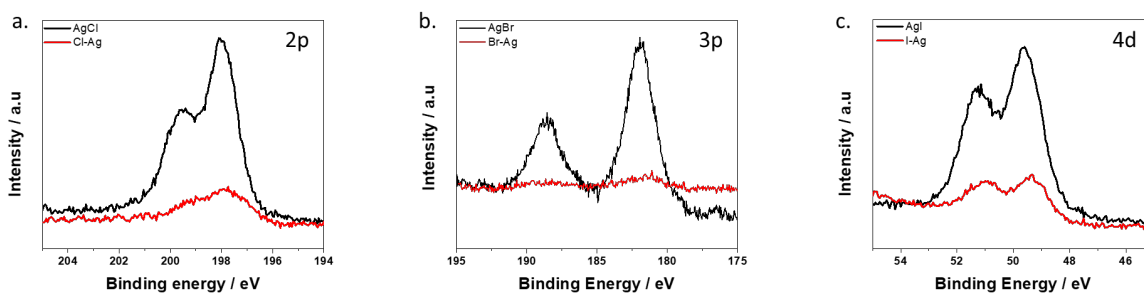


Figure S2. XPS spectra comparing AgX and X-Ag samples. (a) X = Cl, Cl 2p (b) X = Br, Br 3p and (c) X = I, I 4d.

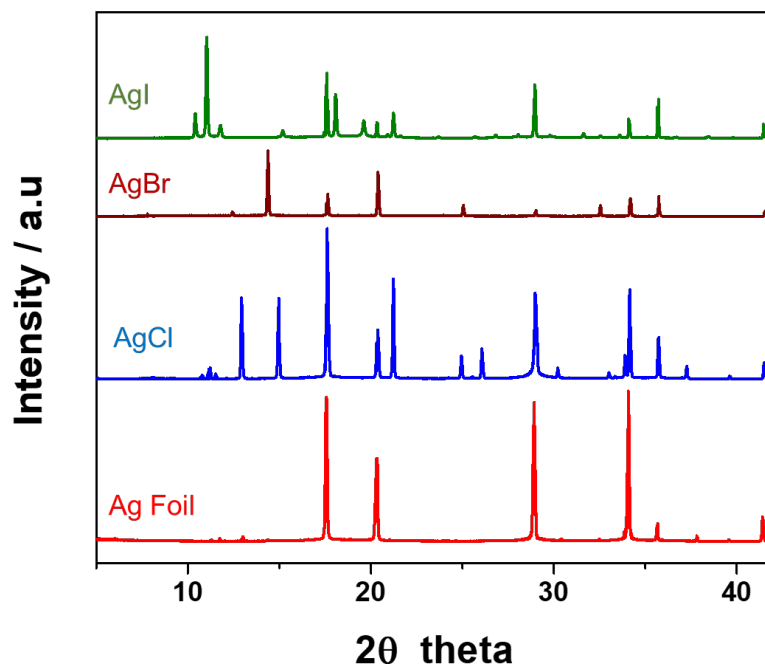


Figure S3. X-ray diffractograms of Ag foil (red), and AgX obtained after the oxidation treatment of Ag foil. AgCl (blue), AgBr (brown) and AgI (green) respectively. $\lambda = 0.72768 \text{ \AA}$.

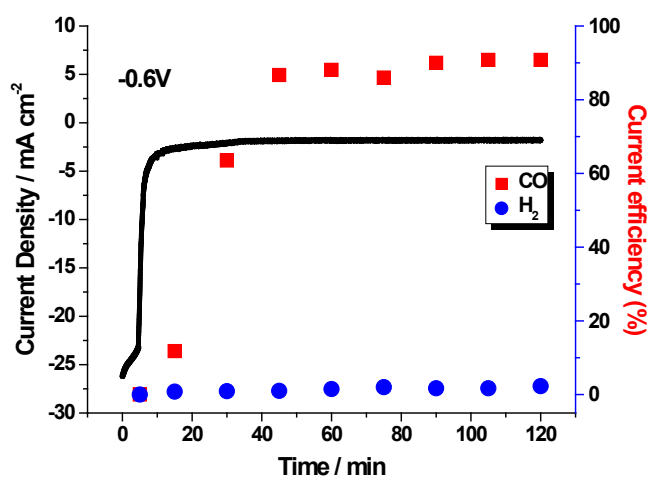


Figure S4. Total current density (left axis) and current efficiencies (right axis) for the formation of CO (red squares) and H₂ (blue circles) as a function of time using as-prepared AgCl, measured in CO₂-saturated 0.1 M KHCO₃ at -0.6 V (vs. RHE). The potential of -0.6 V reported for as-prepared AgCl samples is not *i*R-corrected, due to the strong influence of the released Cl⁻ on the solution resistance.

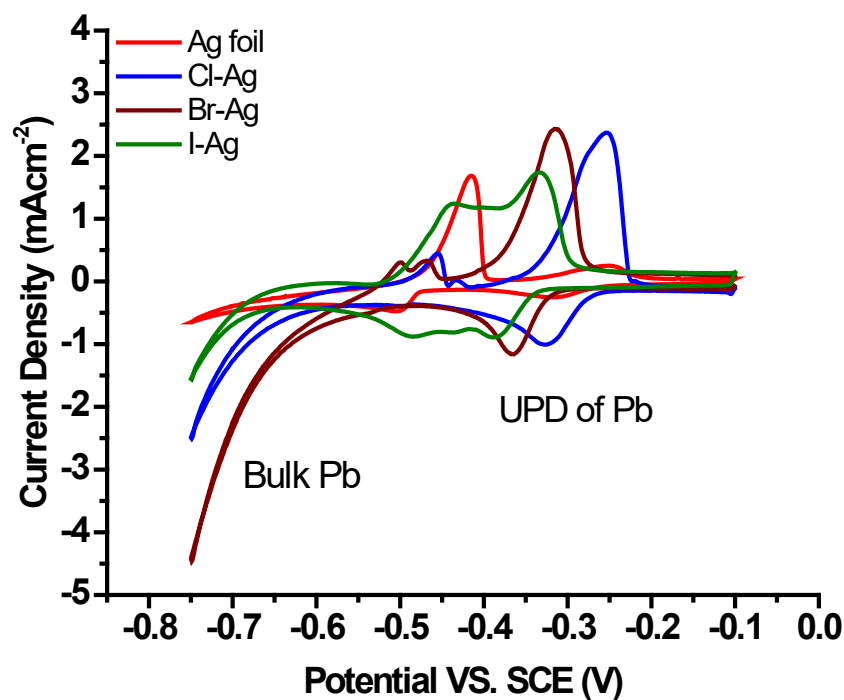


Figure S5. Lead (Pb) underpotential deposition (UPD) and bulk deposition, in 1 mM Pb(acetate)₂ + 1 mM HClO₄ + 0.5 M NaClO₄ solution, at the sweep rate of 10 mV s⁻¹, in the same potential range, for Ag foil (red), Cl-Ag (blue), Br-Ag (wine) and I-Ag (green) samples. The electrochemically active surface area determined by Pb UPD measurements is 2 cm² for Ag foil, 19.2 cm² for I-Ag, 41 cm² for Br-Ag and 40.8 cm² for Cl-Ag.