Supporting information for

Synthesis of Lead-free Cs₃Sb₂Br₉ Perovskite Alternative Nanocrystals with Enhanced Photocatalytic CO₂ Reduction Activity

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Chemicals:

Chemicals used include antimony bromide (SbBr₃, Alfa Aesar, 99.9%), cesium acetate (CsOAc, Alfa Aesar, 99.9%), cesium carbonate (Cs₂CO₃, Alfa Aesar, 99.8%), lead bromide (PbBr₂, Alfa Aesar, 99.9985%)

Ligands and solvents include octanoic acid (OnA, fisher scientific, 99%), oleic acid (OA, TCI America, 85%), oleylamine (OLA, Sigma-Aldrich, 98%), octadecene (ODE, Sigma-Aldrich, 90%), hexane (fisher scientific, 99%), methyl acetate (MeOAc, Alfa Aesar, 99%), acetone (Sigma-Aldrich, 99%), water (high purity, 99.9%, distilled)

CsOnA precursor preparation

Similar to cesium oleate which is not soluble under room temperature without a super stoichiometric oleic acid concentration¹, the cesium octanoate (CsOnA) reagent is insoluble under room temperature at stoichiometric amounts of OnA. However, unlike Cs oleate, the soluble CsOnA requires a 1:9.5 Cs:OnA ratio. We used 1:10 as the ratio to prepare room temperature soluble CsOnA. In a typical preparation, 0.8145 g (2.5 mmol) Cs₂CO₃ was loaded up in a 50 mL three-neck flask, along with 8 mL (~50 mmol) OnA and 17 mL of ODE. The mixture was under vacuum at 110 °C for 2 h to remove H₂O. When the solution ceased under vacuum, nitrogen was refilled and cool to room temperature. Then the ~0.2 M CsOnA solution was transferred to a vial and stored in a glove box.

Sb-OnA-OLA precursor preparation

Sb-OnA-OLA precursor was prepared in a glove box as the Sb precursor. In a typical preparation, 0.432 g (1.2 mmol) of SbBr₃ was mixed with dried 6 mL OnA, and 3 mL dried OLA, then this mixture was heated to 60 °C under vigorous stirring. It becomes a yellowish crystal-clear solution and the Sb-OnA-OLA was removed from the heating mantle and stored as a Sb precursor stock solution. It is worth noting that this precursor is a slurry under room temperature, so it needs to be heated up to 60 °C prior to use.

Synthesis of Antimony Perovskite Alternative Cs₃Sb₂Br₉ NCs

In a typical synthesis, 5.5 mL of ODE was placed under vacuum to remove water and air, then placed under nitrogen. Subsequently 1.5 mL preheated Sb-OnA-OLA was injected into the batch. The mixture was put under vacuum at 80 °C in order to remove any trace amount of moisture. Then nitrogen was filled, and temperature was raised to 210 °C. A solution of 0.2 M CsOnA was quickly injected into the batch at 210 °C. The heating mantle was kept in place to maintain high temperature for 30s, during which the color of solution shifted from brown yellow to bright yellow. Then the heating mantle was removed and the mixture was quenched with an ice bath to room temperature.

Cs₃Sb₂Br₉ NCs Separation and Purification

The crude solution was separated through centrifugation. Since the excess reagent CsOnA is fully soluble, the pellet could collect as it is primary $Cs_3Sb_2Br_9NCs$. We further re-dispersed the pellet in hexane/acetone mixture (v/v = 5/3), and centrifuge again. After 5 times, the sample is barely dispersed in non-polar solvent like hexane or ODE, then dried under air for further characterization and experiments.

For CsPbBr₃ NCs, MeOAc was used as the purification reagent following the method introduced in by Swarnkar et al².

Impurities associated with oleic acid synthesis



Fig S1. XRD pattern of a typical poor quality $Cs_3Sb_2Br_9$ NC synthesis when utilizing oleic acid. Reaction flask sampled at various steps prior to synthesis. XRD patterns of CsBr (bottom black) and $Sb_4O_5Br_2$ (bottom red, ICSD 416216) are shown for reference. Of note in the pattern is the clear formation of $Sb_4O_5Br_2$ starting at 200 °C prior to injection, and the lack of the desired $Cs_3Sb_2Br_9$ crystal phase present in the final product along this reaction pathway.



Fig S2. Elemental mapping for (a) Sb; (b) Cs; (c) O; (d) Br in product from attempted $Cs_3Sb_2Br_9$ NC synthesis utilizing oleic acid. Annotation highlights one of the regions of high Sb and O content that also does not exhibit high Cs content, indicative of SbO_x impurity. These results further suggest the formation of a mixed product as can be seen in the XRD pattern in Figure S1.



Fig S3. XRD pattern for reaction products at different injection temperatures utilizing octanoic acid, CsBr (bottom black) and Cs₃Sb₂Br₉ (bottom blue, ICSD 39824).



Fig S4. (a) SEM image of $Cs_3Sb_2Br_9$ NC; (b) Narrow size distribution based with an average diameter of 37 nm. (c)-(d) High resolution TEM image of $Cs_3Sb_2Br_9$ NC lattice showing regular spacing between lattice planes.



Fig S5. (a) SEM image of $Cs_3Sb_2Br_9$ NC.; (b) EDX spectrum for the elemental composition of samples in (a). Clear peaks for Br, Sb, and Cs, C and O are present, and the detailed elemental ratio is illustrated in the inserted table. Critically the ratio shows the expected amount of Sb, which is absent when CsBr salts are made.; Elemental mapping for (c) Cs; (d) Sb; (e) Br showing uniform distribution of those elements in $Cs_3Sb_2Br_9$ NC.

X-ray photoelectron spectroscopy results



Fig S6. Full spectrum of the as-synthesized Cs₃Sb₂Br₉NCs following 5 purification steps.



Fig S7. Full spectrum of the Cs₃Sb₂Br₉NCs after CO₂ RR.



Fig S8. XPS spectrum for (a) Cs 3d and (b) Br 3p in Cs₃Sb₂Br₉ NC, before (black) and after (red) catalysis. No change is observed.

| | Chemical S | State | Binding Energy | _ | |
|----------|-------------------|-------------|----------------|--------|--|
| | Sb meta | ıl | 528.3 | _ | |
| | Sb_2O_3 | | 529.9 | | |
| | Sb_2O_5 | | 530.9 | | |
| | SbF ₃ | | ~531.7 | | |
| | Organic C | C-O | 531.5-532 | | |
| | Metal oxi | des | 529-530 | | |
| | O-Br _x | | ~535 | _ | |
| | | | | | |
| c a b | | a 1 b | c C | b c | |

Fig S9. The unit cell of Cs₃Sb₂Br₉, [SbBr₆]³⁻ in the crystal structure shows similarity as the [PbBr₆]⁴⁻ in Pbbased perovskite.

DFT Calculations for band structure and reaction pathway

Density of states (DOS) and partial density of states (PDOS) of Cs₃Sb₂Br₉ NCs

The Cs₃Sb₂Br₉ single crystal file was downloaded from the inorganic crystal structure database (ICSD). DOS and PDOS were calculated by Quantum Espersso with a PWscf package, PWscf implements an iterative approach to reach self-consistency, using at each step iterative diagonalization techniques within the framework of the plane-wave pseudopotential method⁴. As shown in Fig S10, the bandgap is calculated

to be 2.04 eV at the Γ plane. Due to the method used, the bandgap is underestimated as expected. The corresponding PDOS was shown on the right side of Fig S10 and is similar to Pb-based perovskite where the valence band (VB) is comprised of Pb(s) and halide(p) orbitals, and the conduction band (CB) is constructed by Pb(p). Here, the VB of Cs₃Sb₂Br₉ is composed of Sb(s) and Br(p) and CB is of Sb(p). The DOS and PDOS show Sb-based perovskite has similarity with Pb-based perovskite in the band structure composition, and the calculated bandgap is consistent with visible light absorption.



Fig S10. DOS and PDOS of Cs₃Sb₂Br₉ single crystal, bandgap is around 2.04 eV.

Theoretical Calculations Method

Periodic, self-consistent density functional theory calculations (DFT) were performed with the Perdew, Burke and Ernzerhof (PBE) implementation of the generalized gradient approximation (GGA)⁵, using Vienna Ab Initio Simulation Package, VASP.^{6,7} The ion-electron interaction was described with the projector augmented wave (PAW) method. A cutoff energy of 400 eV was used for the plane-wave basis set. Cs₃Sb₂Br₉ surfaces were modeled with a four-layers thick slab separated by 20 Å of vacuum along the z-direction of $(2 \times 3 \times 1)$ supercell for $(20\overline{2}1)$ surface and $(2 \times 2 \times 1)$ supercell for low index planes, (1000) and (0001). The bottom two layers were fixed at their bulk position and the top two layers with adsorbate were relaxed. The Brillouin zone was sampled by a $(6 \times 4 \times 1)$ Monkhorst-pack k-point mesh for $(20\overline{2}1)$ and $(6 \times 6 \times 1)$ for the low index planes. Similarly, CsPbBr₃ surfaces were modeled with four-layers thick slab separated by 20 Å of vacuum along the z-direction of $(2 \times 3 \times 1)$ supercell for (002) surface and $(2 \times 2 \times 1)$ supercell for low index planes (001). The Brillouin zone was sampled by a $(6 \times 4 \times 1)$ Monkhorst-pack k-point mesh for (002) surface and $(2 \times 2 \times 1)$ supercell for low index planes (001). The Brillouin zone was sampled by a $(4 \times 4 \times 1)$ Monkhorst-pack k-point mesh for (002) surface and $(2 \times 2 \times 1)$ supercell for low index planes (001). The Brillouin zone was sampled by a $(6 \times 6 \times 1)$ for the low index plane. All calculation parameters have been verified to ensure a force convergence threshold of 0.01eV/Å, except for COOH adsorption on Cs₃Sb₂Br₉ (0001) which was converged to 0.03eV/Å.

Adsorption free energy of each elemental step was calculated according to the computational hydrogen electrode (CHE) model, where each photo-electrochemical step is treated as a simultaneous transfer of a proton-electron pair⁸. The reaction mechanism for CO_2 reduction to CO is illustrated below,

$$\mathrm{CO}_2(g) + * + \mathrm{H}^+ + e^- \leftrightarrow \mathrm{COOH}^*$$

$$COOH^* + H^+ + e^- \leftrightarrow CO^* + H_2O(l)$$
$$CO^* \leftrightarrow CO(g) + *$$

where * stands for the adsorption site. Using the initial state in which gaseous CO₂ is unbound above an empty surface as a reference, the Gibbs free energy of interest are represented as,

$$\Delta G[\text{COOH} *] = G[\text{COOH} *] - (G[*] + G[\text{CO}_2] + G[\text{H}^+ + e^-])$$

$$\Delta G[\text{CO} *] = G[CO *] + G[\text{H}_2\text{O}] - (G[*] + G[\text{CO}_2] + 2G[\text{H}^+ + e^-])$$

$$\Delta G[\text{CO}] = G[\text{CO}] + G[\text{H}_2\text{O}] - (G[\text{CO}_2] + 2G[\text{H}^+ + e^-])$$

The CHE model assumes that the chemical potential of a proton-electron pair is equal to half of the chemical potential of gaseous hydrogen at a potential of 0V. This is because zero voltage is defined based on the reversible hydrogen electrode, in which the reaction

$$H^+ + e^- \leftrightarrow \frac{1}{2} \mathrm{H}_2$$

is defined to be in equilibrium at zero voltage, at all values of pH, at all temperatures, and with H_2 at 101325 Pa. Other adsorbed and non-adsorbed Gibbs free energies are calculated by the expression:

$$G = E_{DFT} + E_{ZPE} - TS$$

where E_{DFT} is the calculated electronic energy, E_{ZPE} is the zero-point vibrational energy and TS is the entropy contribution. The heat capacity temperature dependence was neglected in this work. Zero-point energies and entropic contributions were calculated by treating all 3N degrees of freedom of the adsorbate as vibrational and assuming that any changes in vibrations of the surface where minimal. All vibrations were treated in the harmonic oscillator approximation and the required quantities were calculated from this vibration using standard statistical mechanics method⁹.

The associated Gibbs free energy of hydrogen evolution reaction is defined as:

$$\Delta G_{\mathrm{H}*} = \Delta \mathrm{E}_{\mathrm{H}*} + \Delta E_{\mathrm{ZPE}} - T \Delta S_{\mathrm{H}}$$

where ΔE_{ZPE} and ΔS_{H} represent the differences in zero-point energy and entropy between the H* adsorbed state and H₂ in its gas phase respectively. The fact that the vibrational entropy of the adsorbed state is small means that the difference in entropy, ΔS_{H} , is approximately: $\Delta S_{\text{H}} \approx -\frac{1}{2}S_{H_2}^0$, where $S_{H_2}^0$ is the entropy of H₂ in the gas phase at standard conditions¹⁰. Zero-point energy was calculated from vibration analysis as explained above. The hydrogen binding energies $\Delta E_{\text{H*}}$ were calculated by

$$\Delta E_{\mathrm{H}*} = E_{\mathrm{ads}} - E_{\mathrm{surf}} - \frac{1}{2}E(\mathrm{H}_2)$$

where E_{ads} , E_{surf} and $E(H_2)$ are the total energies of the surfaces with a hydrogen atom adsorbed, the pristine surfaces and the gas phase hydrogen molecule respectively.



Fig S11. Minimum energy structures found for each surface modeled. Showing bare surface, surface with COOH* adsorbed, surface with CO* adsorbed. (Cs-green, Pb-gray, Br-red, Sb-blue, C-light gray, O-light red, H-white)



Fig S12. Space filling model showing the active sites for all structures calculated. Showing bare surface, surface with COOH* adsorbed, surface with CO* adsorbed. Top view and view angled by 40 degrees shown for clarity of structure.

Table S2 shows the energies at 0 V vs. RHE. Note that a stabilization of 0.11 eV for the first step and 0.22 eV for the second step is added to report ΔG at the equilibrium potential of CO₂ to CO. Table S3 summarizes the crystal information of both Pb and Sb-based perovskite.

Table S2. Surface energies $(eV/Å^2)$ and energies of adsorption for the reaction intermediates, reported at 0V versus RHE.

| Surfaces | Surface energy | COOH* | CO* | COOH* | CO* |
|-----------|----------------|----------------|----------------|----------------|----------------|
| | $(eV/Å^2)$ | $\Delta E(eV)$ | $\Delta E(eV)$ | $\Delta G(eV)$ | $\Delta G(eV)$ |
| Sb (2021) | 0.03181 | 0.169 | 0.120 | 1.025 | 0.783 |
| Sb (1000) | 0.00937 | 1.803 | 0.562 | 2.361 | 0.980 |
| Sb (0001) | 0.03592 | 0.721 | 0.431 | 1.809 | 0.810 |
| Pb (002) | 0.05973 | 0.356 | 0.241 | 1.463 | 0.5910 |
| Pb (001) | 0.01335 | N/A | N/A | N/A | N/A |

Table S3. Crystal structure comparison between CsPbBr3 and Cs3Sb2Br9.

| Chemical Formula | CsPbBr ₃ | $Cs_3Sb_2Br_9$ |
|------------------|---------------------|----------------|
| Identifier | 243735-ICSD | 39824-ICSD |
| Space Group | P n m a | P -3 m 1 |
| Cell Lengths/Å | | |
| a | 8.25020 (21) | 7.930(1) |
| b | 11.75323 (22) | 7.930(1) |
| с | 8.20350 (18) | 9.716 (9) |
| Cell Angles/° | | |
| α | 90 | 90 |
| β | 90 | 90 |
| γ | 90 | 120 |

CO₂RR Photocatalytic Tests

The reaction batch was prepared with \sim 50-100 mg dried Cs₃Sb₂Br₉ or CsPbBr₃ (the exact amount is recorded) and pre-dried ODE. This mixture was put under vigorous sonication for a half hour to form a uniform yellowish (Cs₃Sb₂Br₉) or green-yellowish (CsPbBr₃) colored dispersion. The reaction vessel was sealed and purged with CO₂ under magnetic stirring for 2 h to create a CO₂ environment.

The photocatalytic CO₂ reduction performance of Cs₃Sb₂Br₉ NCs was determined under AM 1.5 irradiation (100 mW cm⁻²) in a water-jacketed Pyrex photoreactor with a quartz window. A 300 W Xenon lamp (Newport Corporation) was used as the light source with an AM 1.5 G filter to provide simulated solar light irradiation. All experiments were performed at 25 °C and cooling water was used during irradiation. Before illumination, 50 μ L high purity water was injected into the cell. The amount of CO produced was quantified by gas chromatography (HP 6890 with TCD detector, argon carrier).

Table S4. Photocatalytical performance of CO generation.

| | 1 h | 2 h | 3 h | 4 h | 5 h |
|---------------------|--------|--------|--------|--------|--------|
| CsPbBr ₃ | 15.82 | 36.16 | 44.01 | 46.34 | 53.80 |
| $Cs_3Sb_2Br_9$ | 312.35 | 419.94 | 487.73 | 512.23 | 516.44 |

*unit umol CO/g cat.



Fig S13. GC-TCD analysis of gaseous products from catalytical process of (a) $CsPbBr_3$; (b) $Cs_3Sb_2Br_9$ NC. After 3 h of reaction time, $Cs_3Sb_2Br_9$ produces significantly more CO compared with $CsPbBr_3$. The production of CH_4 by $Cs_3Sb_2Br_9$ is too low to determine.

| Table S5. | Catalyst | performance | stability | test by | v cyc | le reaction |
|-----------|----------|-------------|-----------|---------|-------|-------------|
| | -1 | | -1 | -1 | -1 | |

| | 1 st cycle | | | 2 nd cycle | | | 3 rd cycle | | |
|---|------------|--------|--------|------------|--------|--------|------------|--------|--------|
| | 1 h | 2 h | 3 h | 1 h | 2 h | 3 h | 1 h | 2 h | 3 h |
| CsPbBr ₃ | 15.82 | 36.16 | 44.01 | 12.25 | 21.35 | 33.04 | N/A | N/A | 14.29 |
| Cs ₃ Sb ₂ Br ₉ | 312.35 | 419.94 | 487.73 | 152.53 | 209.73 | 230.12 | 73.33 | 127.43 | 161.23 |

*unit umol CO/g cat.



Fig S14. CO generation over Cs₃Sb₂Br₉ (red) and CsPbBr₃ (blue) NCs during CO₂RR.

Table S6. Survey of catalyst performance.

| Catalyst | Light Source | R _{CO prod} . | R _{CO prod.} | Reference |
|--|-----------------------------|---|-----------------------|-----------|
| | | $(\mu mol g^{-1} h^{-1})^*$ | $(\mu mol g^{-1})$ | |
| Cs ₃ Sb ₂ Br ₉ | AM 1.5G | - | 510 | This Work |
| CsPbBr ₃ | AM 1.5G | - | 20.9 | [11] |
| Co-CsPbBr ₃ | Xe with 400 nm filter | - | 247 | [12] |
| CsPbBr ₃ @Re(dcbpy) | AM 1.5G | - | 509.14 | [13] |
| CsPbBr ₃ @ZIF-67(1,4) | AM 1.5G | - | 2.301 | [14] |
| CsPbBr ₃ /Pd | 150 W Xe with 420 nm filter | - | 12.623 | [15] |
| CsPbBr ₃ /UiO-66(NH ₂) | 300 W Xe with 420 nm filter | - | 98.57 | [16] |
| CsPbBr ₃ @g-C ₃ N ₄ | 300 W Xe with 420 nm filter | 149 | - | [17] |
| Cs_2AgBiX_6 | AM 1.5G | - | 5.5 | [18] |
| NaTaO ₃ | UV-Vis | 50.7 | - | [19] |
| SrTiO ₃ | UV-Vis | 352 | - | [19] |
| ZnO | 300 W Xe | 44.68 ppm h ⁻¹ | - | [20] |
| N-TiO ₂ | 300 W Visible (UV < 5%) | 338 ppm g ⁻¹ h ⁻¹ | - | [21] |
| IO-B-TiO ₂ /Ni | 300 W Xe | 12.13 | - | [22] |
| *D · · | 1 -1 1 1 1 1 1 1 1 | | | |

*R_{CO prod}: unit is μ mol g⁻¹ h⁻¹ unless otherwise stated.



Fig S15. TEM images of (a) CsPbBr₃ NCs before catalysis; (b) CsPbBr₃ NCs after catalysis, NCs tend to become more spherical and aggregated; (c) Optical feature of CsPbBr₃ NCs from absorption and emission spectrum. Weak absorption remains for CsPbBr₃ NCs; (d) XRD pattern of CsPbBr₃ NCs before and after catalysis.



Fig S16. (a)-(b) Stability of $Cs_3Sb_2Br_9$ NCs in octadecene to the addition of 1% and 10% by volume water. (c)-(d) Stability of $Cs_3Sb_2Br_9$ NCs in octadecene to the same intensity of light used for CO_2 reduction under nitrogen environment in ODE.

Transient adsorption measurements

Fig S17 shows the time dynamics for spectral regions centered at 480 nm and 550 nm. The results for 550 nm show that the rate of initial decrease in optical density is similar for both systems. However, the data taken at 480 nm emphasizes the completely different dynamics in terms of fluorescence, in which no negative signal is observed for the $Cs_3Sb_2Br_9$ NCs indicating no fluorescence. This is consistent with the lack of fluorescence signal by steady-state fluorescence measurements.



Fig S17. Time dynamics from the transient adsorption spectrum of CsPbBr₃ and Cs₃Sb₂Br₉ NCs at 480 nm and 550 nm.

Thermal Stability Comparison of Cs₃Sb₂Br₉ NCs and CsPbBr₃ NCs

Thermogravimetry and differential scanning calorimetry (TGA-DSC) for both NCs was conducted under the flow of air, and ramp temperature from room temperature to 600 °C with a 5 °C/min rate. Both NCs have been purified multiple times to remove the majority of the ligands on their surface, thus the weight loss could be mainly attributed to the perovskite itself. Under the same conditions, the Pb-based perovskite decomposes beginning at 110 °C, while the Sb-based perovskite starts to decompose when the temperature is above 200 °C. This variation shows the enhanced thermal stability of Cs₃Sb₂Br₉ NCs compared with CsPbBr₃ NCs.



Fig S18. (a) TGA-DSC spectra for $Cs_3Sb_2Br_9NCs$ after 5 purification steps; (b) the TGA comparison between $CsPbBr_3$ and $Cs_3Sb_2Br_9NCs$, both of them have been washed 5 times and fully dried before the measurement.

FTIR results



Fig S19. FTIR for solvent references of ODE, OLA, OnA, and CsOnA.

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