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## **Supporting Information**

## The Role of Gold Oxidation State in the Synthesis of Au-CsPbX<sub>3</sub> Heterostructure or Lead-free Cs<sub>2</sub>Au<sup>I</sup>Au<sup>III</sup>X<sub>6</sub> Perovskite Nanoparticles

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Figure S1. Photograph of suspension  $CsPbCl_3$  nanocrystals after gold deposition or cation exchange reactions.  $CsPbCl_3$  (left), Au-CsPbCl\_3 (middle), and  $Cs_2Au_2Cl_6$  (right). The photogrpahs were taken after 1 minutes of reaction.



Figure S2. Photograph of suspension of CsPbBr<sub>3</sub> nanocrystals after gold deposition or cation exchange reactions. CsPbBr<sub>3</sub> (left), Au-CsPbBr<sub>3</sub> (middle), and Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> (right), . The photogrpahs were taken after 5 minutes of reaction.



Figure S3. Absorbance of  $CsPbCl_3$  nanocrystals before and after Au metal deposition compared to the cation exchange product,  $Cs_2Au_2Cl_6$ .



Figure S4. Absorbance of CsPbBr<sub>3</sub> nanocrystals before and after Au metal deposition compared to the cation exchange product, Cs<sub>2</sub>Au<sub>2</sub>B



Figure S5. Absorbance of CsPbI<sub>3</sub> nanocrystals before and after Au metal deposition.





Figure S6. TEM image of CsPbCl<sub>3</sub>. Average particle edge length is  $8.3 \pm 1.3$  nm



Figure S7. TEM image of CsPbBr<sub>3</sub>. Average particle edge length is  $8.2 \pm 1.1$  nm



Figure 8. TEM image of CsPbI<sub>3</sub>. Average particle edge length is  $9.6 \pm 1.6$  nm



Figure S9. Left) HRTEM image of an Au-CsPbCl<sub>3</sub> NCs showing the fringes of the Au nanoparticles (yellow square). (Right) Fast Fourier transform revealing the lattice spacing between (111) planes of cubic gold.



Figure S10. Left) HRTEM image of an Au-CsPbBr<sub>3</sub> NCs showing the fringes of the Au nanoparticles (yellow square). (Right) Fast Fourier transform revealing the lattice spacing between (111) planes of cubic gold.



Figure S11. Left) HRTEM image of an Au-CsPbl<sub>3</sub> NCs showing the fringes of the Au nanoparticles (yellow square). (Right) Fast Fourier transform revealing the lattice spacing between (111) planes of cubic gold.

Sample	Fluorescence Quantum Yield (FQY)
CsPbBr₃	63.28 %
Au-CsPbBr <sub>3</sub>	52.07 %
CsPbCl <sub>3</sub>	6.27 %
Au-CsPbCl <sub>3</sub>	2.97 %
CsPbl <sub>3</sub>	35.62 %
Au-CsPbl <sub>3</sub>	23.05 %

Table S1. PLQY of CsPbX<sub>3</sub> perovskite nanocrystal before and after Au deposition.



Figure S12. Normalized XRD diffractograms showing the presence and absence of CsPbBr<sub>3</sub> and Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> peaks as 300  $\mu$ L of 1.58 mM AuBr<sub>3</sub> or AuBr are added to identical amounts of CsPbBr<sub>3</sub>. The peak located at a 2 $\theta$  value of 32.56 degrees (yellow trace) correspond to the (220) reflection of tetragonal phase Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub>. The black ticks on the bottom horizontal axis denote reflections of tetragonal Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub>.



Figure S13. Normalized XRD diffractograms showing the presence and absence of CsPbBr<sub>3</sub> and Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub> peaks as 300 μL of 6.28 mM AuBr<sub>3</sub> or AuBr are added to identical amounts of CsPbBr<sub>3</sub>. The black ticks on the bottom horizontal axis denote reflections of tetragonal Cs<sub>2</sub>Au<sub>2</sub>Br<sub>6</sub>.



Figure S14. Normalized XRD diffractograms showing the presence and absence of CsPbBCl<sub>3</sub> and Cs<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub> peaks as 300  $\mu$ L of 1.58 mM AuCl<sub>3</sub> or AuCl are added to identical amounts of CsPbCl<sub>3</sub>. Shoulder peaks at a 2 $\theta$  values of 16.73 and 32.93 degrees (yellow trace) can be attributed to the (110) and (004) reflections of tetragonal phase Cs<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub>. The black ticks on the bottom horizontal axis denote reflections of tetragonal Cs<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub>.



Figure S15. Normalized XRD diffractograms showing the presence and absence of CsPbCl<sub>3</sub> and Cs<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub> peaks as 300  $\mu$ L of 6.28 mM AuCl<sub>3</sub> or 6.28 mM AuCl are added to dentical amounts of CsPbCl<sub>3</sub>. The black ticks on the bottom horizontal axis denote reflections of tetragonal Cs<sub>2</sub>Au<sub>2</sub>Cl<sub>6</sub>.



Figure S16. TEM images of Au-CsPbBr $_3$  after Au deposition with 0.3 mL of a 6.28 mM AuBr solution.



Figure S17. TEM images of Au-CsPbCl $_3$  after Au deposition with 0.3 mL of a 6.28 mM AuCl solution.