Electronic Supplementary Information

Understanding the mechanism of metal-induced degradation in perovskite nanocrystals

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Table S1: Sizes of the as-synthesized NCs measured using ImageJ software with a sample of 100 particles.

NCs	Size (nm)
CsPbBr3	10.6 ± 1.6
CsPb(BrI)3	10.0 ± 1.7
CsPbI ₃	9.6 ± 1.5
Cu	10.2 ± 1.1
Ag	10.2 ± 1.5
Au	10.3 ± 0.9



Fig. S1: Control experiments where CsPbBr₃ and CsPbI₃ NCs are mixed with metals Cu, Ag, Au. It is observed that CsPbBr₃ is more stable CsPbI₃, which demonstrates PL-quenching in less than 10 minutes with each metal. The mixture CsPbBr₃ + Au NCs exhibits an interesting behavior: shift of the PL peak position and no quenching. Composition and structural analysis below does not point at very evident and drastic changes in the perovskite NCs, thus it must be related to some specific electronic interaction with the gold. This behavior is similar to what observed by Kamat et al.¹ and deserves future investigation.



Fig. S2: PL measurements over time for the pristine (A) CsPbBr₃, (B) CsPb(BrI)₃, and (C) CsPbI₃ under inert atmosphere. The excitation wavelength was 350 nm for CsPbBr₃ and CsPb(BrI)₃ and 450 nm for CsPbI₃. Perovskite emission maintains its intensity and energy, indicating that the shifts observed in the mixtures with metals in an inert environment are not due to perovskite instability alone.



Fig. S3: PL of CsPb(BrI)₃ one hour after mixing with (A) Cu, (B) Ag, and (C) Au in a 5:1 metal:perovskite ratio, after continuous irradiation (light) in the fluorometer and in dark conditions. The excitation wavelengths were 350 nm for CsPbBr₃ and CsPb(BrI)₃ and 450 nm for CsPbI₃. In the case of Cu and Au, there is negligible difference in energy shift. In the case of Ag, there is a 0.1 eV increase in emission energy during constant illumination. The slight acceleration of the reaction under constant irradiation can be explained by heating effects and some plasmon effects. However, it is clear that light is not a requirement for the chemistry to occur.



Fig. S4: XRD of the 5:1 ratio metal-to-perovskite NC samples after 1 hour from mixing. (A-C) show stability of the CsPbBr₃ with each metal. (D) shows CsPb(BrI)₃ peaks (originally 14.8° and 29.9°) shifted 0.5 degrees higher after mixing with Cu, approaching the position of the CsPbBr₃ peaks. (E) demonstrates perovskite peak shifts to where the position of the CsPb(BrI)₃ peaks match the CsPbBr₃ peaks (15.3° and 30.9°). (F) displays CsPb(BrI)₃ peaks shifted to the position of CsPbBr₃ peaks and gold sintering with sharpened gold peaks. (G-H) show complete degradation of the CsPbI₃ structure. (I) shows some CsPbI₃ stability with gold, meanwhile the gold sinters. It must be noted that larger nanocrystals were used for reference Cu patterns, as no diffraction peaks could be observed with 10-nm Cu nanocrystals used in this study. This is most likely due to low scattering factor of Cu.



Fig. S5: TEM images of the $CsPb(BrI)_3$ mixed with the denoted metals in a 5:1 metal-toperovskite ratio one hour after the mixing. Note that the little black dots on the perovskites NCs is Pb created under the electron beam, as they are present also in the pristine samples, and be ascribed to metallic lead.²



Fig. S6: Representative TEM images of the CsPbBr₃ and CsPbI₃ mixed with the metal NCs in a 5:1 metal-to-perovskite ratio one hour after the mixing. Some CsPbBr₃ cubes can still be observed but many are degraded, explaining the PL quenching observed in Fig. S1. On the contrary, the CsPbI₃ cubes are completely degraded, consistently with their faster reaction kinetics.



Fig. S7: XRD of CsPb(BrI)₃ mixed with the metals in a 10:1 ratio. The peak at 14.8° completely disappears in each case. The peak at 29.9° decreases in intensity and becomes broader from Cu to Ag and then disappears after mixing with Au. It should be noted that in the mixture with Au shows sharpened peaks to indicate sintering.



Fig. S8: HAADF-STEM images and corresponding EDX maps for $CsPb(BrI)_3$ mixed with (A) Cu, (B) Ag, and (C) Au. (A) visualizes the iodide leaching from the $CsPb(BrI)_3$ structure after mixing with Cu. This is also observed in (B) and (C), in the presence of Ag and Au, respectively. In the case of (C), we also observe larger gold particles due to sintering.



Fig. S9: Size distributions over 100 particles for (A) Cu and (B) Ag NCs after one hour from the mixing with the perovskite NCs. Au is not included as sintering is clearly evident in the case of $CsPbI_3$ and $CsPb(BrI)_3$ and very little change is observed with $CsPbBr_3$.



Fig. S10: XPS spectra of the Pb 4f region for (A) the pristine CsPb(BrI)₃ NCs and the mixed systems as denoted. (B) Comparison of pristine CsPbBr₃ and CsPb(BrI)₃ NC samples.

It must be noted that the leaching of Γ out of the NCs might disturb the charge balance in the structure, leaving behind positively charged defects. Hence, electron density from Pb can move towards these positive defect sites, which would result in the shifts we observe in the XPS spectra. Ag shows greater shifts compared to Cu as expected from the reactivity order given in the main text. However, the system mixed with Au shows smaller shifts compared to Cu and Ag. It is possible that this result correlates an increase of the electron density around Pb of the perovskite upon sintering of Au on top of cubes.



Fig. S11: TEM images of (A) Cu, (B) Ag, (C) Au mixed with CsPb(BrI)₃ in a 10:1 metal-toperovskite. Sintering is apparent only for gold even at such a high metal concentration.



Fig. S12: PL measurements over time for a thin film including CsPb(BrI)₃ NCs, referred to as PeNCs, and Au NCs, separated by a ~100 nm spiro-OMeTAD polymer spacer. (A) Shifts in the PL peak energy over 12 hours for the PeNC/ spiro-OMeTAD films with and without the Au NCs. A shift of around 60 meV occurs in the structure including the Au NCs. The initial shift between pristine PeNC films and PeNC/spiro-OMeTAD is due to the TMA treatment during the processing of the film, as outlined in the experimental section. (B,C) PL spectra before and after 12 hours for the samples with and without Au ,as denoted. The increased PL background at the high energy end of on both (B) and (C) is due to PL onset of the spiro-OMeTAD polymer with the emission peak at 2.95 eV.

The data above show that, albeit much slower than in solution, a PL shift is similarly observed despite the presence of 100 nm hole conducting layer interposing between the perovskite and Au NCs. The slower kinetics are expected as the polymer provides a diffusion barrier between the reacting entities. Differently from the solution-state experiments, a second additional PL

peak appears over time at 2.42 eV (~512 nm). This peak corresponds to the emission of PeNCs with a pure CsPbBr₃ composition. This result indicates an inhomogeneous reaction rate when the experiment is conducted in thin films. Such an effect might be due to spatial inhomogeneity across the films compared to the homogeneous mixing achieved in solution. The fact that the CsPb(BrI)₃/spiro-OMETAD structures without Au behave differently excludes the possibility of photo-induced phase segregation.

References

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