

A facile post-assembly approach for the fabrication of non-close-packed gold nanocrystal arrays from binary nanocrystal superlattices

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Experimental details

Chemicals

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium borohydride (NaBH_4), didodecyldimethylammonium bromide (DDAB), dodecanethiol (DDT), cesium carbonate (Cs_2CO_3), lead bromide (PbBr_2), octadecene (ODE), oleic acid (OA), and oleylamine (OLAM) were purchased from Sigma-Aldrich and used as received unless stated otherwise. Toluene, hexane, and ethanol were of analytical grade. Milli-Q[®] water was obtained using Advantage A10 Water Purification System (Merck Millipore, U.S.A.).

Synthesis of the colloidal Au NCs

Gold nanocrystals were synthesized following the methodology of reducing gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) with sodium borohydride (NaBH_4) and subsequent digestive ripening.¹ Specifically, 202 mg of didodecyldimethylammonium bromide (DDAB) was dissolved in 20 mL of anhydrous toluene by sonication in a round-bottom flask. Next, 65 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was added to the DDAB micellar solution. After forming clear orange solution mixture, 130 μL of a NaBH_4 solution (freshly prepared by dissolving of 0.7 g NaBH_4 in 2 mL of ice-cold water), was injected into the HAuCl_4 solution under vigorous stirring. Upon injection, the color changed from orange through brownish to intense red, indicating the formation of gold NCs. Afterward, 1.6 mL of dodecanethiol (DDT) was added dropwise, and the mixture was stirred for 2 h to finish the ligand exchange (here, the dispersion color turned from intense red to dark purple). The DDT-passivated nanocrystals were then washed with 20 mL of ethanol, precipitated by centrifugation at 7000 rpm for 10 min, dried under vacuum, and redispersed in 20 mL of anhydrous toluene and 1.6 mL of DDT by sonication. The solution was then refluxed in a flask with a cooling water condenser for 90 min for digestive ripening. This step is crucial to achieving a narrow size distribution of nanocrystals (here, the dispersion color returned from dark purple to intense red). After that, gold NCs were cooled down to room temperature. Here the colloid remains a very intense red. However, its tendency to form superlattices directly from the colloidal solution and precipitate has been reported in the literature and depends, among others, on the nanocrystal concentration and alkyl chain length of the thiol.^{2,3} Next, Au NCs were washed with ethanol, precipitated by centrifugation at 7000 rpm for 10 min, dried under vacuum, and redispersed by sonication in toluene. Finally, the

solution was centrifuged for 5 min at 7000 rpm to precipitate large clusters. The top solution was dried under vacuum, redispersed in hexane, and then stored in a glass vial at 4 °C until further characterization and the Cs₄PbBr₆-Au binary superlattice fabrication.

Synthesis of the colloidal Cs₄PbBr₆ NCs

Cs₄PbBr₆ nanocrystals were synthesized following the methodology of mixing Cs-oleate and PbBr₂ solutions in hexane at room temperature. Cs-oleate was prepared by loading Cs₂CO₃ (0.814 g), ODE (40 mL), and OA (2.5 mL) into 100 mL 3-neck flask, dried for 1 hour at 120 °C and then heated under argon to 150 °C until all Cs₂CO₃ reacted with OA. PbBr₂ was prepared by loading PbBr₂ (0.069 g) and ODE (5 mL) into a 25 mL 3-neck flask and dried under vacuum for 1h at 120 °C. Dried OLAM (0.5 mL) and dried OA (0.5 mL) were injected at 120 °C under argon flow. As prepared PbBr₂ and Cs-oleate solutions were stored in a glass vial at 4 °C until further use. For the NCs preparation PbBr₂ and Cs-oleate solutions were dissolved in 2mL hexane in 1:4 molar ratio (0.1 mL PbBr₂ + 0.1 mL Cs-oleate) in a 5mL vial and shaken at 900 rpm at 25°C for 10 minutes. As prepared Cs₄PbBr₆ nanocrystals were immediately used for characterization and the Cs₄PbBr₆-Au binary superlattice fabrication.

Nanocrystal number concentration calculation

Nanocrystals number concentration (N) was estimated according to the reported protocol.⁴ Specifically, the weight of single nanocrystal ($W_{NC} = \rho V_{NC}$) was estimated by taking into account its volume ($V_{NC} = 4\pi r^3/3$), and the density ρ of the material. The weight of the ligands was estimated by considering the number of the ligands. For this, the surface area of each nanocrystal ($S_{ANC} = 4\pi r^2$) was calculated, and the footprint of the capping agent (F) was taken 0.16 nm² (oleic acid capping Cs₄PbBr₆ NCs was taken to be equal to dodecanethiol capping Au NCs). The number of capping ligands per nanocrystal (N_{LIG}) was estimated by dividing the surface area of each nanocrystal by the areal footprint of the ligand. The weight contribution of the ligands per nanocrystal ($W_{LIG} = MW_{LIG} N_{LIG}/N_{AV}$), Avogadro's number N_{AV} , ligand molecular weight MW_{LIG} , and the nanocrystal concentration c , were used to the calculation of number concentration ($N = c/(W_{NC} + W_{LIG})$).

Cs₄PbBr₆-Au binary superlattice fabrication

1:1 Cs₄PbBr₆ and Au NC ratio mixture was prepared by mixing adequate portions of perovskite and gold NCs dispersions taking into account the calculated nanocrystals number concentration (N). After TEM characterization, the slight optimization on the number of Au NCs by increasing/decreasing the number of Au when preparing the mixture was performed. A 15 μL aliquot of the NC dispersion in hexane was carefully deposited onto the TEM grid. The grid was immediately covered with a Petri dish and left at room temperature to slowly evaporate hexane.

Non-close-packed gold nanocrystal arrays fabrication

As prepared Cs₄PbBr₆-Au nanocrystal superlattice was subsequently exposed to e⁻ beam irradiation (80 kV) for 90 s using the transmission electron microscope.

Characterization

Ultraviolet-visible (UV-Vis) absorption spectra were detected with the UV-1900 Spectrophotometer (Shimadzu Corp., Japan). Powder X-ray diffraction (XRD) data were collected on an ARL EQUINOX 1000 X-ray Diffractometer (Thermo Fisher Scientific, U.S.A.). The XRD patterns were matched to the International Centre for Diffraction Data (ICDD) PDF-4 database using a JADE software package. Transmission electron microscopy (TEM) measurements and e⁻ beam etching experiments were performed on the JEM-1400 Flash electron microscope (JEOL Ltd., Japan) at an acceleration voltage of 80 kV. High-resolution TEM (HRTEM) measurements were performed on FEI Tecnai G² F20 (Thermo Fisher Scientific, U.S.A.) at an acceleration voltage of 200 kV.

Results

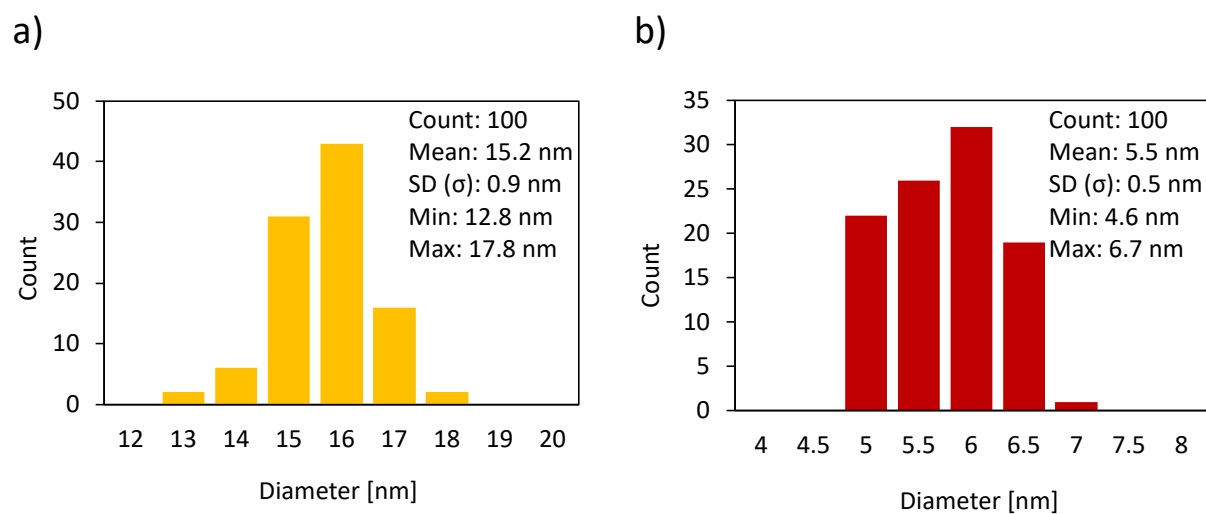


Figure S1. Size distribution histograms of Cs₄PbBr₆ (a) and Au (b) NCs. The average diameters are 15.2 nm and 5.5 nm, respectively.

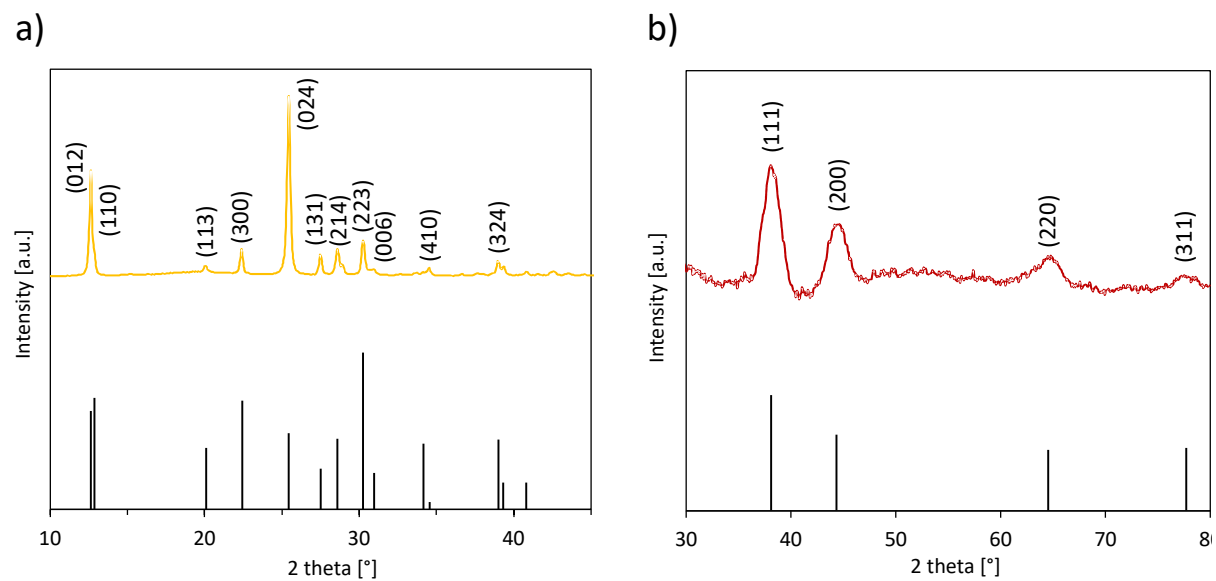


Figure S2. XRD patterns of drop casted and dried Cs₄PbBr₆ (a) and Au (b) NCs dispersions. Tick marks below the patterns correspond to the positions of the respective Bragg reflections expected for Cs₄PbBr₆ and Au.

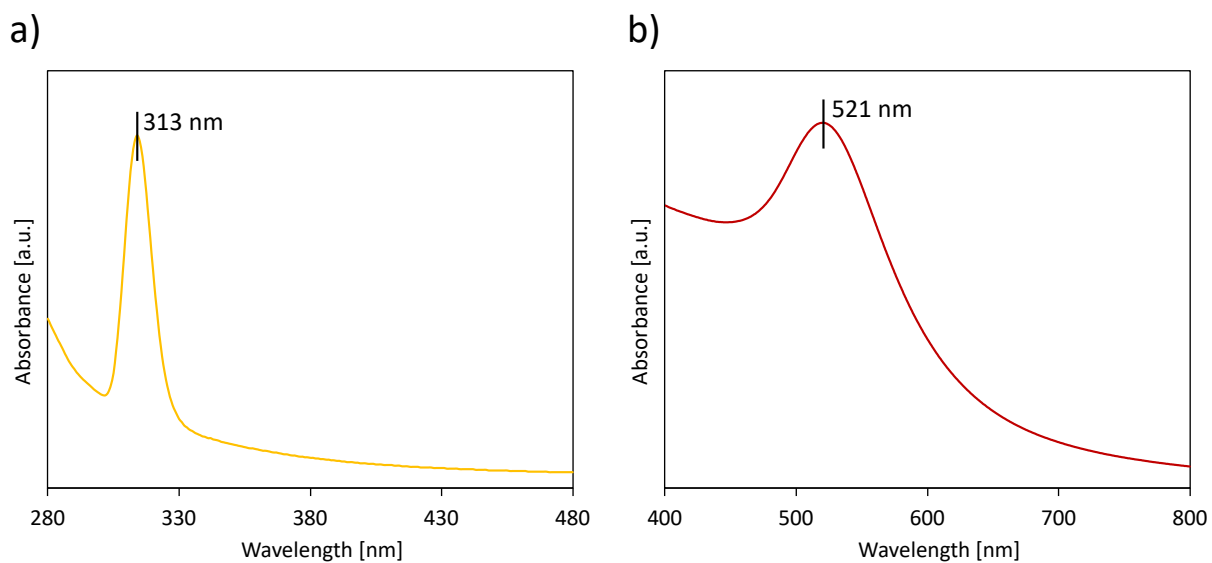


Figure S3. UV-Vis absorption spectra of Cs₄PbBr₆ (a) and Au (b) NCs dispersions. The Cs₄PbBr₆ NCs absorbance peak is present at 313 nm, and the surface plasmon resonance (SPR) peak of Au NCs is present at 521 nm. The intensities of the peaks correlate to the concentration of NCs.

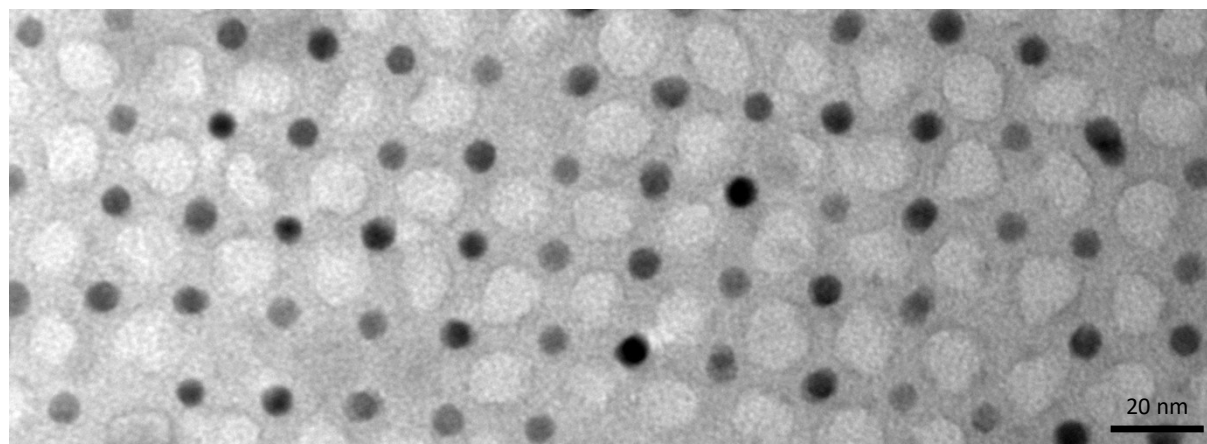


Figure S4. TEM image illustrating Au nanoarray along the radial direction from the center of the electron beam toward its edge (keeping reasonable contrast of the image on both sides) at the intermediate stage of the etching process, demonstrating consistent etching of the perovskite phase.

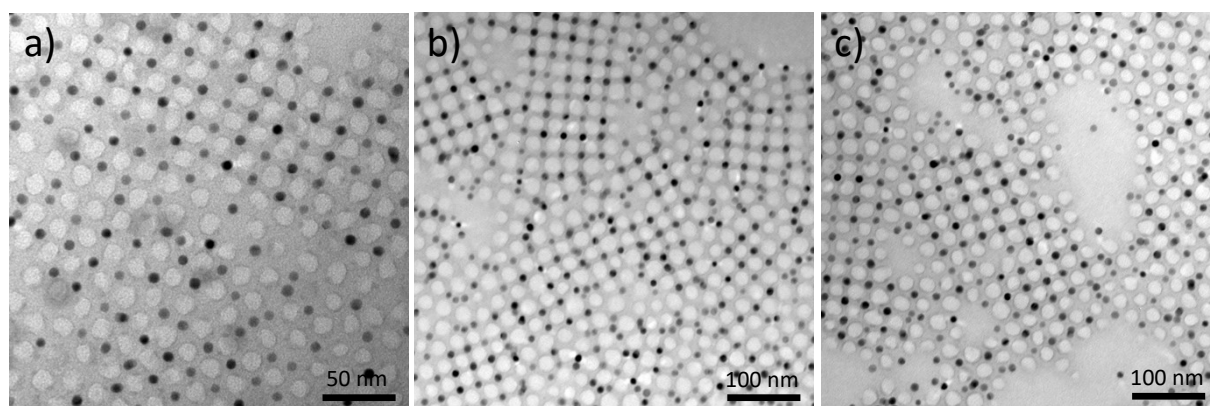


Figure S5. Low-magnification TEM images illustrating consistent etching of the perovskite phase from Cs_4PbBr_6 -Au binary nanocrystal superlattice domains collected at the random areas of the sample.

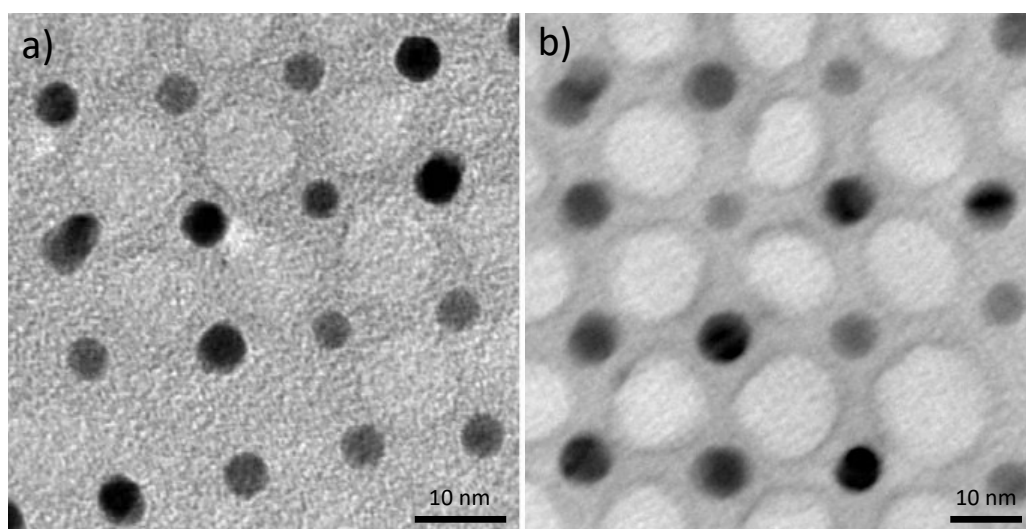


Figure S6. TEM images of a residual carbonaceous film (image in low contrast) observed after thermal and e^- beam treatment of Fe_3O_4 -Au binary nanocrystal superlattice followed by etching with aqueous HCl (Fig. S10 from Thumu et al., *Science* 2017) (a), and a residual carbonaceous film observed after e^- beam treatment of Cs_4PbBr_6 -Au binary nanocrystal superlattice (b).

References

- 1 X. M. Lin, G. M. Wang, C. M. Sorensen and K. J. Klabunde, *J. Phys. Chem. B*, 1999, **103**, 5488–5492.
- 2 B. L. V Prasad, S. I. Stoeva, C. M. Sorensen and K. J. Klabunde, *Langmuir*, 2002, **18**, 7515–7520.

- 3 S. I. Stoeva, B. L. V Prasad, S. Uma, P. K. Stoimenov, V. Zaikovski, C. M. Sorensen and K. J. Klabunde, *J. Phys. Chem. B*, 2003, **107**, 7441–7448.
- 4 D. K. Smith, B. Goodfellow, D.-M. Smilgies and B. A. Korgel, *J. Am. Chem. Soc.*, 2009, **131**, 3281–3290.
- 5 T. Udayabhaskararao, T. Altantzis, L. Houben, M. Coronado-Puchau, J. Langer, R. Popovitz-Biro, L. M. Liz-Marzán, L. Vuković, P. Král, S. Bals and R. Klajn, *Science*, 2017, **358**, 514–518.