Supplementary Information

Ultrathin Colloidal Cesium Lead Halide Perovskite Nanowires

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Experimental details:

Chemicals: Cs_2CO_3 (99.9%, Aldrich), octadecene (ODE, 90%, Aldrich), oleic acid (90%, Aldrich), $PbBr_2$ (99.999%, Alfa Aesar), PbI_2 (99%, Aldrich), oleylamine (70%, Aldrich), 1-dodecylamine (Alfa Aesar, 98+%), ethyl acetate (99.9%, Fisher Scientific), toluene (99.9%, Fisher Scienfic), molecular sieves, 4Å (Aldrich). Oleic acid, oleylamine, ethyl acetate, and toluene were dehydrated using activated molecular sieves before use, and other chemicals were used as received without further purification.

Preparation of Cs-oleate solution: Cs-oleate solutions were prepared via a reported approach developed by Protesescu *et al.*[1] Briefly, 0.2 g Cs_2CO_3, 0.6 mL dried oleic acid, and 7.5 mL ODE were loaded into a 3-neck flass, degassed under vacuum at 120 °C (all of the temperature mentioned in the paper is referring to the temperature of the oil bath) for 20min, and then heated under Ar to 150 °C until all Cs_2CO_3 dissolved.

Synthesis of ultrathin $CsPbBr_3$ nanowires (NWs): 5 mL ODE, 0.2 mmol $PbBr_2$, and 4.3 g 1-dodecylamine were loaded into a 3-neck flask and degassed under vacuum for 20 min at 100 °C. 0.8 mL dried oleylamine and 0.2 mL dried oleic acid were injected at 160 °C under Ar successively. The solution was kept at 160 °C for 20 min for fully dissolution of the precursor. Afterwards, 0.7 mL of as-prepared Cs-oleate solution was quickly injected. After 20 min, the reaction mixture was cooled by an ice-water bath. A step-wise purification strategy then was applied in order to purify the ultrathin NWs.

Step-wise purification of ultrathin $CsPbBr_3$ NWs: The product gained from the reaction were centrifuged at 6000 rpm for 5 min, the supernatant was kept for further purification. 20mL ethyl acetate was added to the supernatant as an anti-solvent (the volume ratio of the original supernatant to anti-solvent is about 1:4), and the clear supernatant solution will immediately become cloudy. Afterwards, the solution was centrifuged at 6000 rpm for 5 min, and the supernatant was still kept for further purification. The similar washing steps were repeated for three more times by adding extra ethyl acetate to the purified supernatant with an overall volume ratio of the original supernatant to anti-solvent to be about 1:7, 1:10, and 1:35, respectively (described as Step 1-3 thereafter). For each time, the products in the precipitated pellet were kept and dissolved in toluene for further characterization. The TEM images of the products after each purification step are shown in Figure 1.

The purpose of the final purification step (described as Step 4 thereafter) is to further eliminate the remaining $CsPbBr_3$ nanoparticals, in order to study the unique optical features of the ultrathin NWs. In order to do that, the precipitation from Step 3 is dissolved in 2 mL of toluene, and the solution was centrifuged at 6000 rpm for 5min, and it was obtained by separating the precipitated pellet from the supernatant, and by dissolving it in toluene for further study.

Surface treatment: Anhydrous toluene (5 mL), $PbBr_2$ (0.188 mmol, X = Br), OA (0.5 mL), and OAm (0.5mL) were added to a scintillation vial all within an argon inert atmosphere glovebox. The solution was stirred at 100 °C within the glovebox until the complete dissolution of the $PbBr_2$ salt occurs, which may take several hours. The resulting concentrated stock solution is stable at room temperature, but it is stored in a glovebox to maintain the dryness of the solution over time. The precursor solution is diluted by 10 times, and 0.2 – 0.6 mL is added to purified nanowire solution. The solution is shook or stirred at room temperature for 1 min.

Anion-exchange reactions: Anhydrous toluene (5 mL), PbX_2 (0.188mmol, X=Cl or I), OA (0.5 mL), and OAm (0.5 mL) were added to a scintillation vial all within an argon inert atmosphere glovebox. The solution was stirred at 100 °C within the glovebox until the complete dissolution of the PbX_2 salt occurs, which may take several hours. The resulting concentrated stock solution is stable at room temperature, but it is stored in a glovebox to maintain the dryness of the solution over time. 0.05 – 0.6 mL 10% diluted precursor solution is added to the purified ultrathin $CsPbBr_3$ nanowire solution at room temperature, and color change will be observed immediately.

Characterization:

Powder X-ray diffraction (XRD) patterns of the obtained products were measured on a Bruker AXS D8 Advance diffractometer with a Co Kα source.

SAXS data was obtained using a Bruker NanoStar equipped with a Cu target, samples were under vacuum at room temperature.

The transmission electron microscopy (TEM) images were taken with a FEI Tecnai TEM at an accelerating voltage of 200 kV.

Absorption spectra were collected using a Shimudzu UV-3010 PC UV-VIS-IR Scanning spectrophotometer equipped with a Shimadzu ISR-3100 integrating sphere.

The energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were recorded using an FEI Titan microscope operated at 80 kV. This instrument was equipped with an FEI Super-X Quad windowless detector that is based on silicon drift technology. Elemental quantification data was analyzed using the Bruker Esprit EDS analysis package, which has been calibrated against mineral standards for quantitative accuracy.

Luminescense quantum yield of the ultrathin NWs was measured in a home-built integrating sphere spectrofluorometer.[2]

The aberration-corrected HRTEM (AC-HRTEM) images of $CsPbBr_3$ nanostructures were collected using TEAM 0.5, which is an aberration-corrected microscope equipped with a high-brightness Schottky-type field emission gun and a Wien-filter monochromator.[3] The accelerating voltage was 80 kV. The lens aberrations were measured and compensated prior to the image acquisition by evaluating the Zemlin tableau of an amorphous carbon area close to the area of interest in the specimen. According to the measurements, the residual lens aberrations were listed below: CS ~ -13 μm, two-fold astigmatism A1 < 2 nm, three-fold astigmatism A2 < 30 nm, axis

coma B2 < 20 nm. Image simulation was performed to compare with the AC-HRTEM experiments using the multislice method[4] as implemented in the MacTempas software.[5] The structure models of orthorhombic and cubic ultrathin $CsPbBr_3$ NWs were built up with the same diameter as that in the experimental image. Random noise was added into the simulated images.

Fluoresence spectra were measured on a Horiba Jobin-Yvon FluoroLog 2 spectrofluorometer.

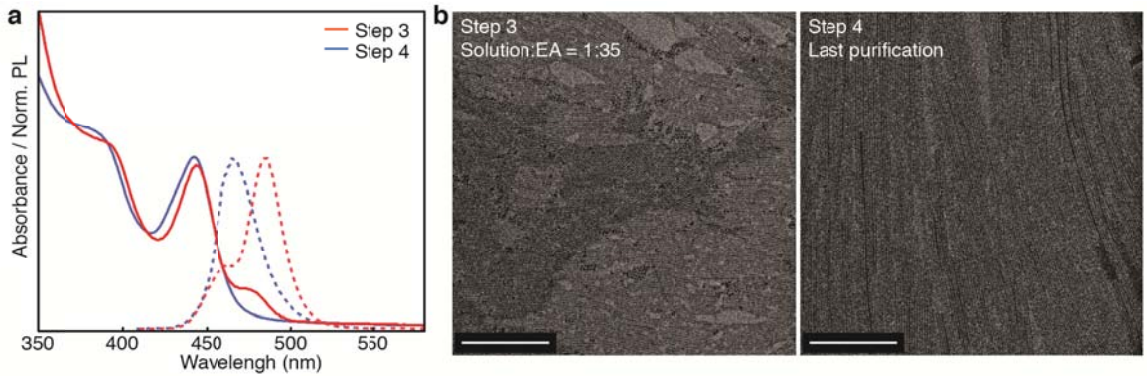

Figure S1: (a) Optical absorption (solid lines) and PL (dashed lines) spectra (b) Low-resolution TEM images of the products obtained during purification Step 3 and Step 4 (scale bar: 200 nm).

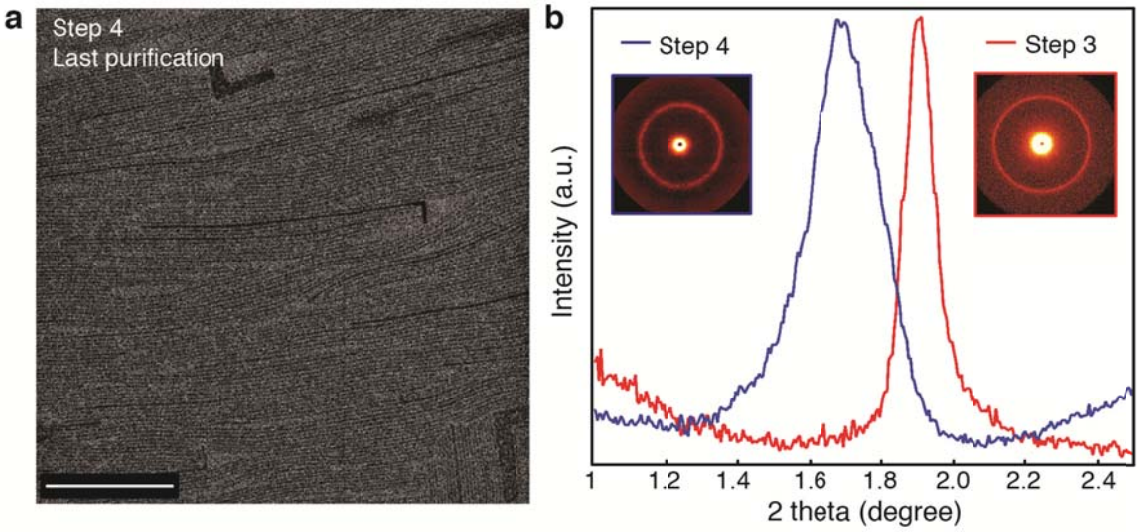

Figure S2: (a) TEM image of the sample after final purification, showing the formation of some thicker wires and right-angle-shaped species (scale bar: 200 nm). (b) SAXS spectra recorded on ultrathin NWs attained from purification Step 3 and Step 4, with the latter showing larger diameters and wider size distributions, demonstrate that extensive washing will do some damage to the ultrathin NWs. The inset shows the corresponding SAXS patterns.

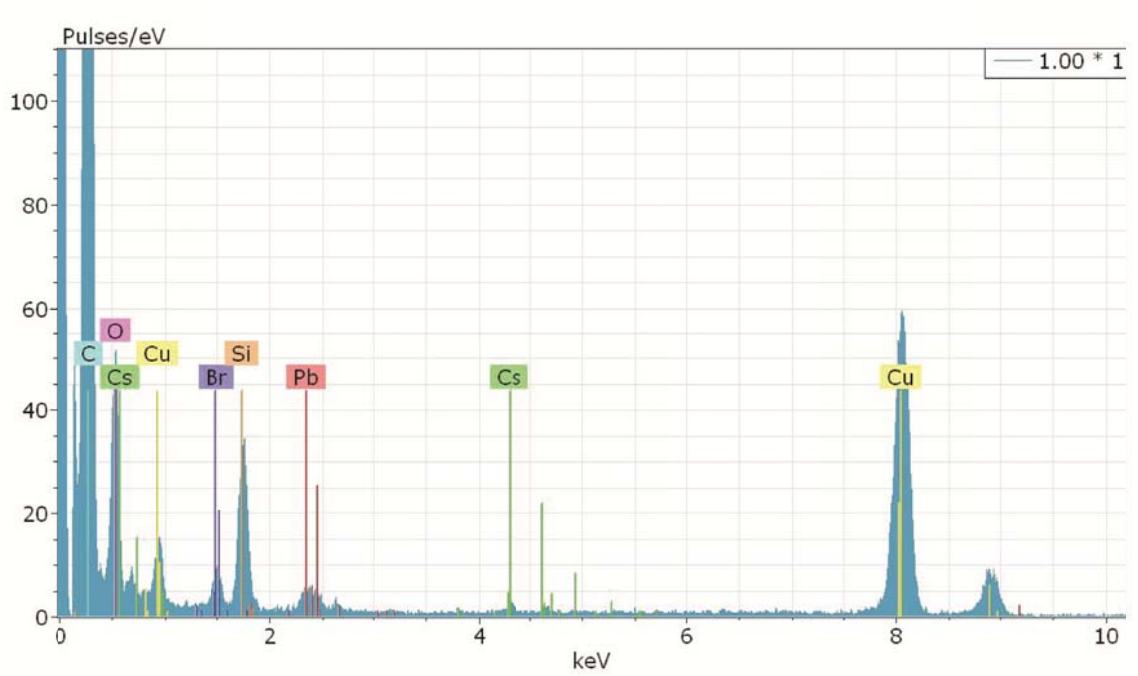

Figure S3: The EDS spectrum of the ultrathin $CsPbBr_3$ NWs, showing the existence of cesium, lead, and bromide elements in the ultrathin $CsPbBr_3$ NWs.

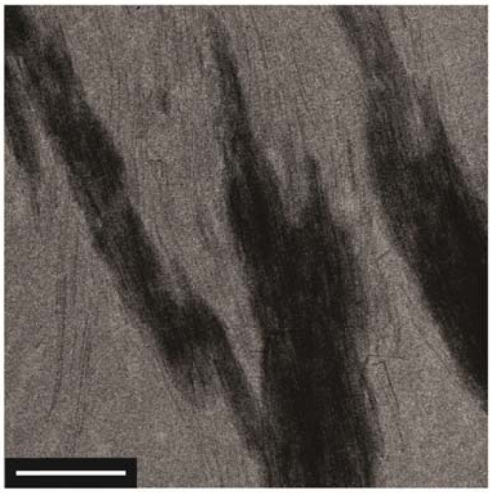

Figure S4: Low-resolution TEM image of the ultrathin $CsPbBr_3$ NW bundles (scale bar: 500nm).

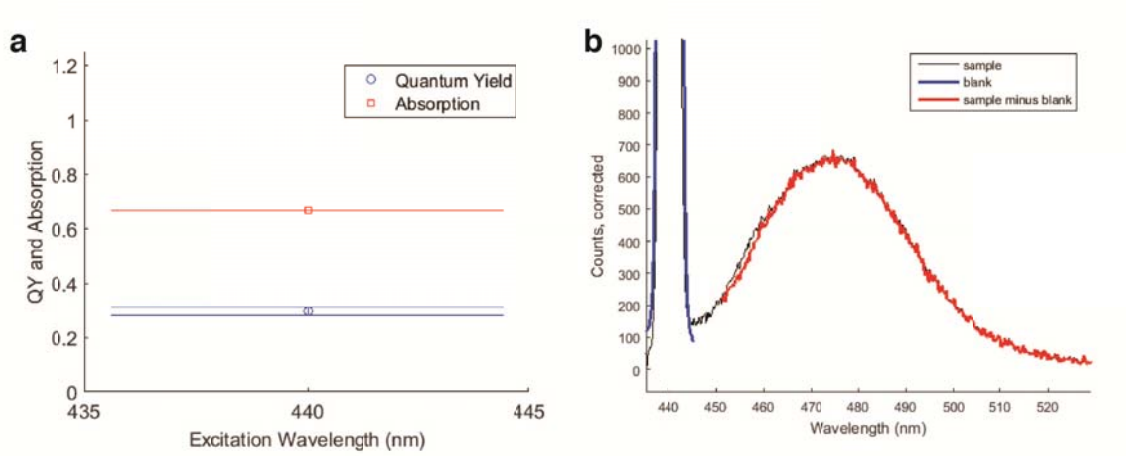

Figure S5: (a) Photoluminescence quantum yield and absorption plot of ultrathin NWs. (b) Emission spectrum of the same sample from which the PLQY is calculated; excitation at 440 nm is visible and highlighted in blue.

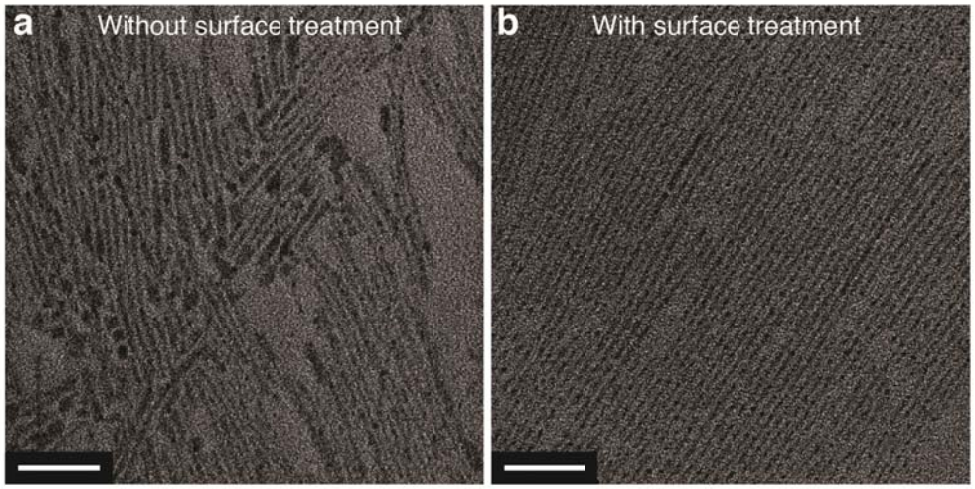

Figure S6: (a) Ultrathin $CsPbBr_3$ NWs without surface treatment, drop-casted and dried on TEM grid, and stored in desiccator for 3 days. The thin wires have broken and ripened to form thicker rods. (b) Ultrathin $CsPbBr_3$ NWs after surface treatment, and storage for 7 days in the same desiccator, the sample quality is still good (scale bar: 50 nm).

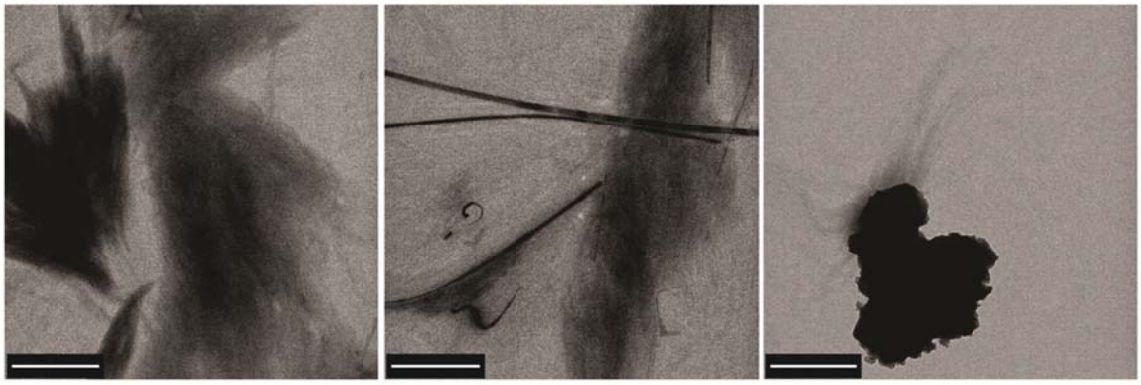

Figure S7: TEM images of the ultrathin NWs (dispersed in toluene and stored in N_2 box for two days). Even though the major products are still bundles of the ultrathin NWs, there are also some thicker wires and large crystals formed gradually (scale bar: 1 μm).

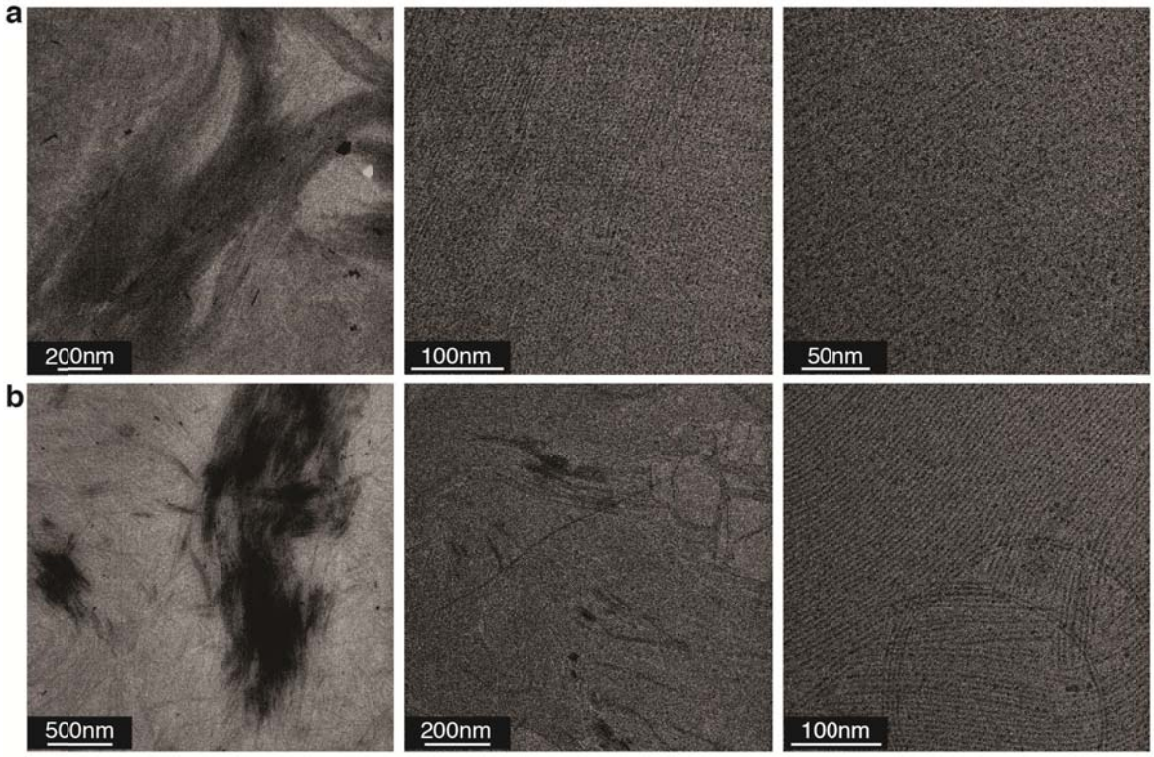

Figure S8: (a, b) TEM images of the ultrathin anion-exchanged $CsPb(Br/Cl)_3$ and $CsPb(Br/I)_3$ NWs with different magnifications. The ultrathin $CsPb(Br/Cl)_3$ NWs with even smaller diameters can hardly provide enough image contrast for low-resolution images.

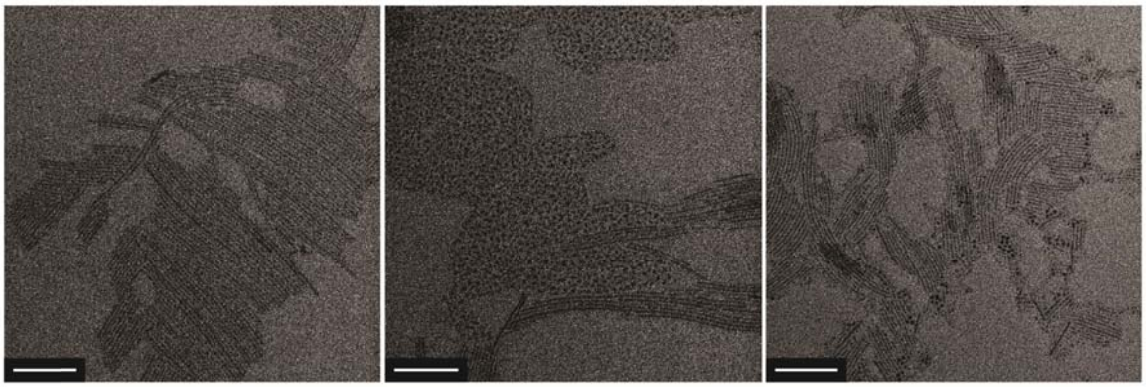

Figure S9: TEM images of Br-I exchanged product after adding excess amount of PbI_2 precursor, showing the breakdown of the ultrathin wires and the formation other products with undesirable morphologies (scale bar: 100nm).

References:

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