

Supporting Information

Room temperature colloidal synthesis of CsPbBr₃ nanowires with tunable length, width and composition

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Experimental section:

Materials:

Lead (II) bromide (PbBr₂, 99.999 % trace metals basis), cesium bromide (CsBr, 99.999 %), oleylamine (OM, 70 %), oleic acid (OA, 90 %) were purchased from Sigma-Aldrich. Lead (II) iodide (PbI₂, CP), Lead (II) chloride (PbCl₂, AR) were purchased from Sinopharm Chemical Reagent. Toluene was purchased from Tianjin Fuyuhuangong. All chemicals were used as received without any further purification.

Synthesis of CsPbBr₃ NWs with increasing aging time:

CsPbBr₃ NWs were synthesized by a one-step room temperature strategy without inert gas protection. 10 mL acetone was loaded into a 25 mL 3-neckflask at 20 °C. Subsequently, 1 mL OA and 0.5 mL OM were added into the 3-neckflask with vigorous stirring. Then, solid powders of 0.4 mmol PbBr₂ (0.1468 g) and 0.4 mmol CsBr (0.0852 g) were added to the flask and aging for a certain time with vigorous stirring (2000 rpm). The products were collected by centrifugation at 6500 rpm for 5 min, then the powders were redispersed in toluene for further characterization.

Halide-exchange to tune the composition of the CsPbBr₃ NWs:

First, the Cl⁻ and I⁻ precursors were prepared by dissolving 0.188 mmol of PbCl₂ or PbI₂ powder in a mixture of 10 mL of toluene, 0.5 mL of OA and 0.5 mL of OM under continuous stirring. Then, the dissolved PbCl₂ or PbBr₂ precursors were diluted for 50 times, then, the toluene dispersion of the pre-dissolved Cl⁻ and I⁻ precursors were added into the flask containing NWs with diameters of 3.2 nm and 6.5 nm for the ion exchange reactions. 5 mL NWs dispersion in toluene was added into a glass bottle, Cl⁻ and I⁻ precursors were added at a rate of 50 μl a time at room temperature with continuous stirring. The contents of iodide and the chloride in the perovskite NWs are controlled by changing the amount of the Cl⁻ and I⁻ precursors added.

Characterization and measurements:

The crystallographic phase of CsPbBr₃ was measured by an X-ray Diffractometer (Rigaku D/Max 2200PC) with graphite monochromator and Cu K_α radiation (λ = 0.1548 nm) at 40 kV. SAXS data was obtained using an Anton Paar equipped with a Cu target radiation (λ = 0.1542 nm) at 40 kV and 50 mA, samples were under vacuum

at room temperature. The morphologies and microstructures of the samples were characterized by using transmission electron microscope (TEM, JEM 100-CXII) with an accelerating voltage of 100kV, high resolution TEM (HR-TEM, JEOL-2100F) with an accelerating voltage of 200kV and a field emission scanning electron microscope (FE-SEM, Hitachi SU8010) with an accelerating voltage of 5kV. Atomic force microscopy (AFM) study in this work was performed by using a Veeco Nanoscope IIIA Multi-Mode system. The absorption and photoluminescence spectra of CsPbX₃ perovskite NW dispersions were measured by a Cary Series UV-Vis Spectrophotometer (Agilent Technologies) and a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies), respectively. The fluorescence decay processes were recorded with time-correlated single-photon counting (TCSPC) technique on an Edinburgh FLS920 phosphorescence lifetime system equipped with a 377.8 nm width laser and a time-correlated single-photon counting system at room temperature. The photoluminescence quantum yields (PLQYs) were measured using an integrating sphere embedded in the Edinburgh FLS920 phosphorescence with a 400 nm excitation wavelength.

Table S1. A list of the publications reporting the synthesis of CsPbBr₃ NWs.

	CsBr/ Cs ₂ CO ₃	Ligands and solvents	Temp. (°C)	Diameter (nm)	QY(%)
1	Cs ₂ CO ₃	OA, OM, ODE	25	1.5±0.5	1
2	Cs ₂ CO ₃	OA, OM, ODE, etc.	65-120	3-23	12-77
3	Cs ₂ CO ₃	OA, OM, ODE, DMF	80	3	/
4	CsBr	OA, OM, DMF	0	2.6	/
5	Cs ₂ CO ₃	OA, OM, ODE	sonication	12	10.8
6	Cs ₂ CO ₃	OA, OM, ODE	150	12	/
7	Cs ₂ CO ₃	OA, OM, ODE	160	2.2±0.2	30

- (1) H. W. Huang, M. Liu, J. Li, L. H. Luo, J. T. Zhao, Z. L. Luo, X. P. Wang, Z. Z. Ye, H. P. He, J. Zeng, *Nanoscale*, 2017, **9**, 104-108.
- (2) M. Imran, F. Di Stasio, Z. Y. Dang, C. Canale, A. H. Khan, J. Shamsi, R. Brescia, M. Prato, L. Manna, *Chem. Mater.*, 2016, **28**, 6450-6454.
- (3) D. Amgar, A. Stern, D. Rotem, D. Porath, L. Etgar, *Nano Lett.*, 2017, **17**, 1007-1013.
- (4) A. Kostopoulou, M. Sygletou, K. Brintakis, A. Lappas, E. Stratakis, *Nanoscale*, 2017, **9**, 18202-18207.
- (5) Y. Tong, B. J. Bohn, E. Bladt, K. Wang, P. Müller-Buschbaum, S. Bals, A. S. Urban, L. Polavarapu, J. Feldmann, *Angew. Chem. Int. Ed.*, 2017, **56**, 13887-13892.
- (6) D. D. Zhang, S. W. Eaton, Y. Yu, L. T. Dou, P. D. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 9230-9233.
- (7) D. D. Zhang, Y. Yu, Y. Bekenstein, A. B. Wong, A. P. Alivisatos, P. D. Yang, *J. Am. Chem. Soc.*, 2016, **138**, 13155-13158.

Table S2. Fitting parameters and average lifetimes for the produced CsPbBr₃ with morphology evolution from NPs to s-NWs, l-NWs and ul-NWs ($E_{ex}=433$ nm) .

Reaction time (h)	τ_1 (ns)	τ_2 (ns)	A ₁	A ₂	τ_{av} (ns)
1	1.5905	5.0365	0.658	0.155	3.062772
2	1.9683	5.1738	0.425	0.143	3.474564
2.5	2.0519	5.0753	0.431	0.14	3.396708
4	2.1901	5.654	0.344	0.096	3.639049

Table S3. Fitting parameters and average lifetimes for the produced CsPbBr₃ with morphology evolution from NPs to s-NWs, l-NWs and ul-NWs ($E_{ex}=448$ nm) .

Reaction time (h)	τ_1 (ns)	τ_2 (ns)	A ₁	A ₂	τ_{av} (ns)
1	1.9259	5.1589	0.411	0.173	3.639297
2	2.4939	5.9405	0.368	0.119	3.993566
2.5	2.4034	5.6162	0.367	0.155	3.999225
4	2.5285	6.0621	0.345	0.116	4.10564

Table S4. NWs with different diameters by changing the stirring speed and reaction time at 20 °C.

Sample	Reaction temperature (°C)	Reaction time (h)	Stirring speed (rpm)	Diameter (nm)
1	20	4	2000	2.5
2	20	4.5	1700	3.2
3	20	5	1400	4.1
4	20	5.5	1200	5.2
5	20	6	1000	6.5
6	20	7	800	14
7	20	9	600	32

Table S5. NWs with different diameters by changing the reaction temperature from 20 °C to 50 °C.

Sample	Reaction temperature (°C)	Reaction time (h)	Stirring speed (rpm)	Diameter (nm)
1	20	4	2000	2.5
2	30	3	1500	6.5
3	40	2.5	1000	13
4	50	1.5	1000	32

Table S6. Fitting parameters and average lifetimes for the CsPbBr₃ nanowires with different width.

Sample	τ_1 (ns)	τ_2 (ns)	A_1	A_2	τ_{av} (ns)
2.5 nm	2.5292	8.5414	0.643	0.083	4.354416
3.2 nm	1.4968	4.6896	0.467	0.14	3.043194
4.1 nm	2.1485	7.7067	0.684	0.086	3.876097
5.3 nm	7.2688	72.0207	0.406	0.023	30.54768
6.5 nm	12.7065	72.1787	0.442	0.052	36.53008
14 nm	20.8201	137.6533	0.473	0.035	59.20107
32 nm	34.7668	139.2284	0.351	0.076	83.27984

Equation used for the biexponential curve fitting:

$$y = A_1 e^{-(x-x_0)/t_1} + A_2 e^{-(x-x_0)/t_2}$$

Equation used for the average lifetime calculation:

$$\tau_{av} = \frac{A_1 \times t_1^2 + A_2 \times t_2^2}{A_1 \times t_1 + A_2 \times t_2}$$

Supplementary Figures:



Figure S1. The OA, OM can be well-suspended in acetone and a Tyndall effect of the reaction suspension can be observed (a) with and (b) without daylight.

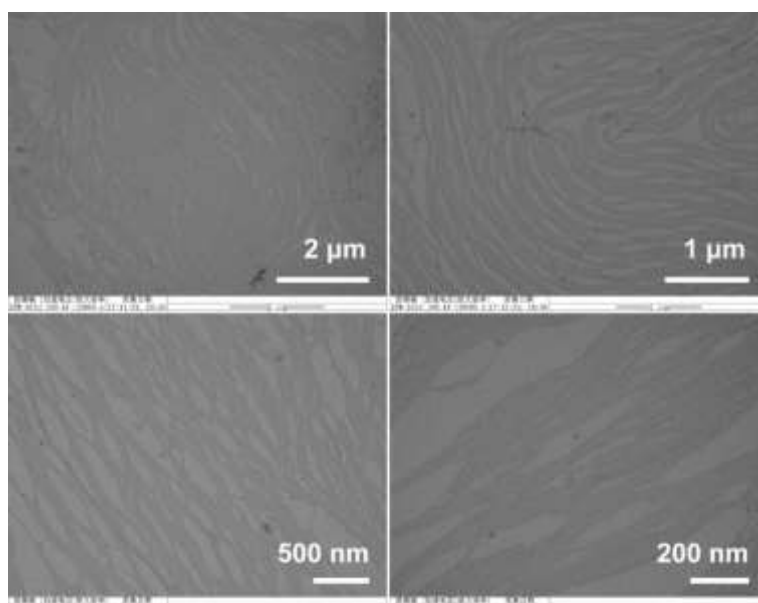


Figure S2. Typical TEM images of the CsPbBr₃ products after aging for 4 h show the majority of the products are homogeneous ultrathin, ultralong nanowires.

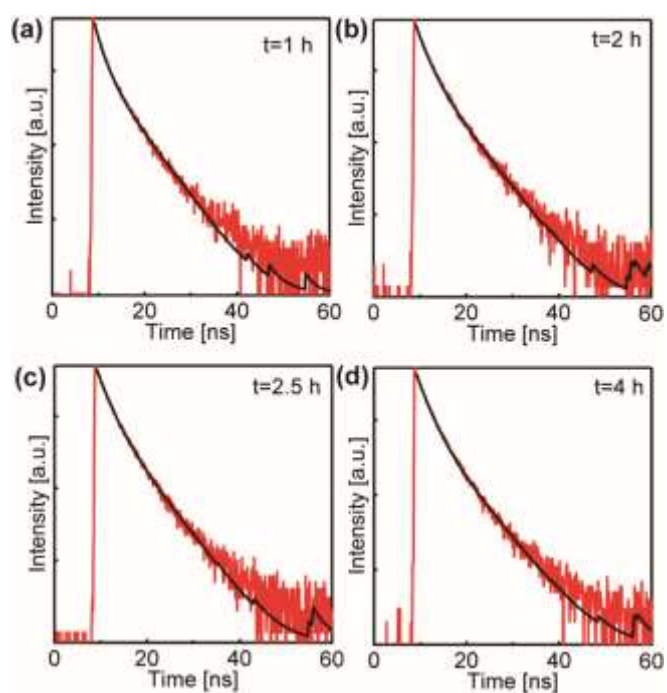


Figure S3. Fitting curves and parameters of the time decay data for the produced CsPbBr₃ with morphology evolution from NPs to s-NWs, l-NWs and ul-NWs ($E_{ex}=433$ nm) .

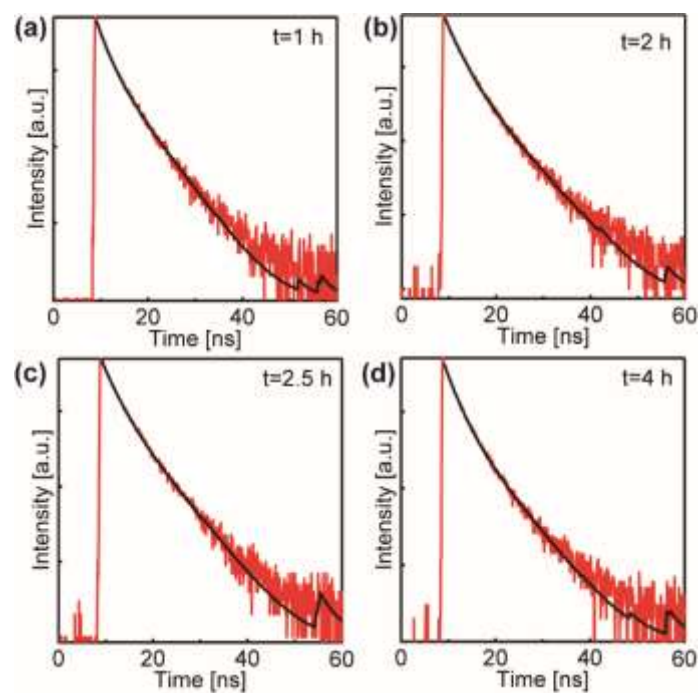


Figure S4. Fitting curves and parameters of the time decay data for the produced CsPbBr_3 with morphology evolution from NPs to s-NWs, l-NWs and ul-NWs ($E_{\text{ex}}=448\text{nm}$) .

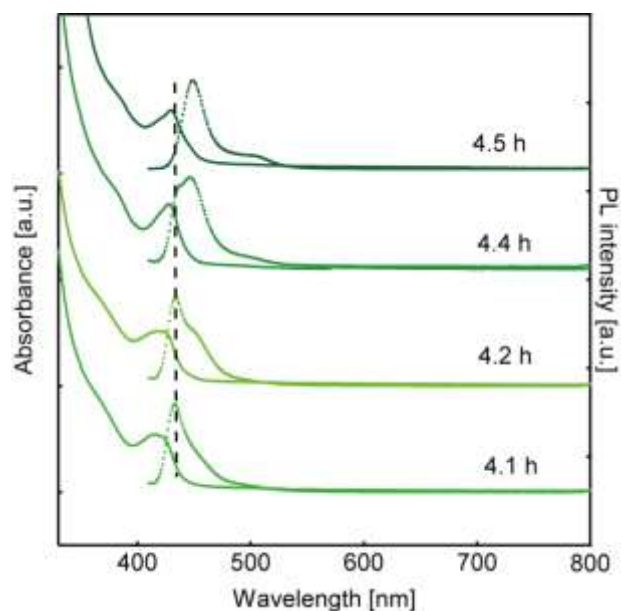


Figure S5. The normalized UV-vis and PL emission spectra of the NWs with aging time from 4.1 h to 4.5 h.

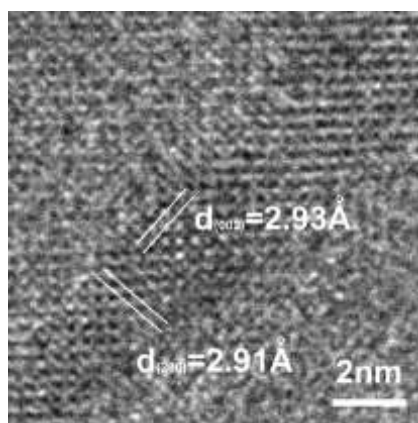


Figure S6. The HRTEM image of CsPbBr₃ NWs after aging for 4.5 h.

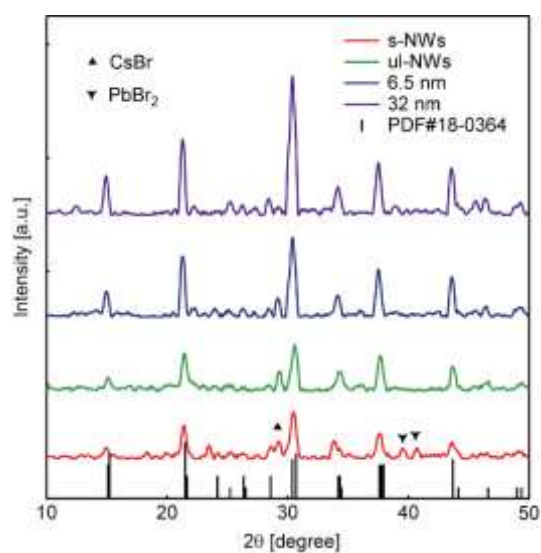


Figure S7. The XRD patterns for CsPbBr₃ NWs obtained with aging for 1.5 h (s-NWs), 4 h (ul-NWs), 6 h (NWs with diameter of ~6.5 nm) and 9 h (NWs with diameter of ~32 nm).

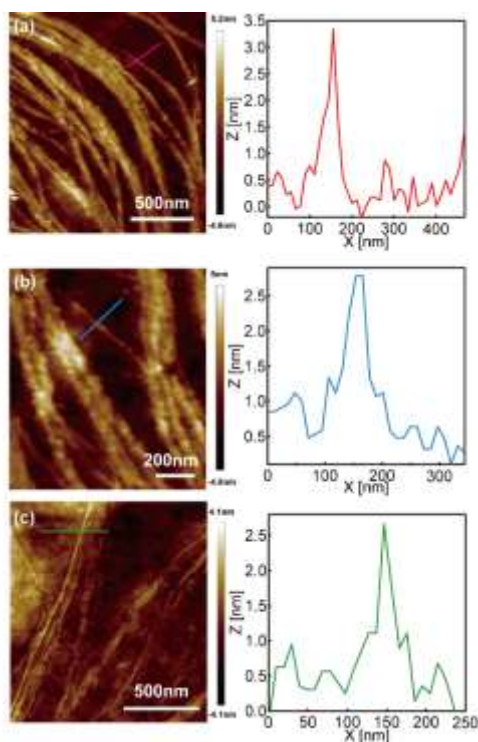


Figure S8. (a) AFM height image of CsPbBr₃ NWs after aging for 4.5 h. (b, c) AFM height images of CsPbBr₃ NWs after aging for 4 h. The right parts of the images are the cross sections along the profile defined by the colored line reported in the images on the left.

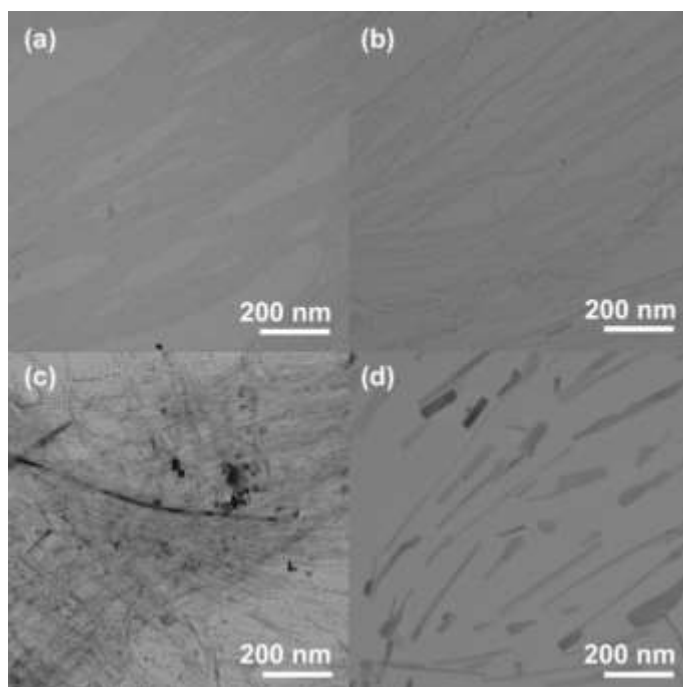


Figure S9. Stirring speed under $2000 \text{ r} \cdot \text{min}^{-1}$, TEM images of CsPbBr₃ NWs with different reaction time, (a) 4 h, (b) 5 h, (c) 6 h and (d) 8 h.

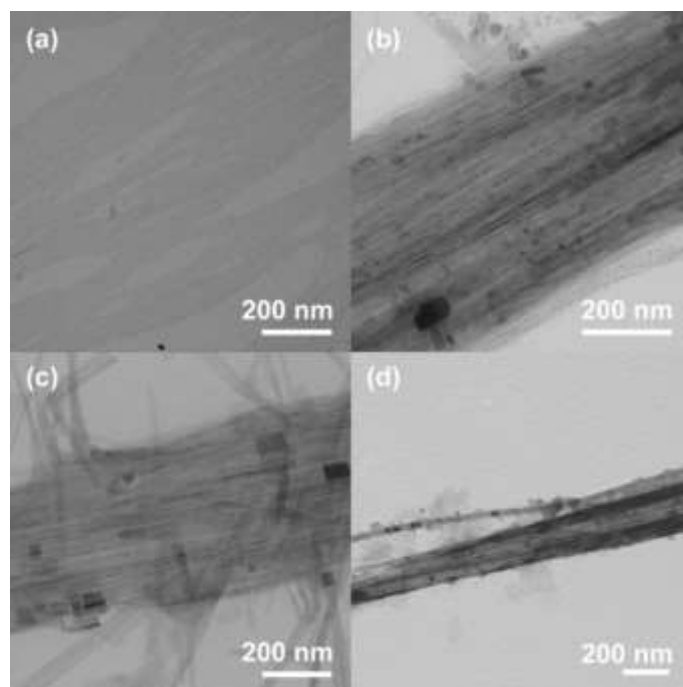


Figure S10. TEM images of CsPbBr₃ NWs with different reaction temperature, (a) 20 °C, (b) 30 °C, (c) 40 °C and (d) 50 °C.

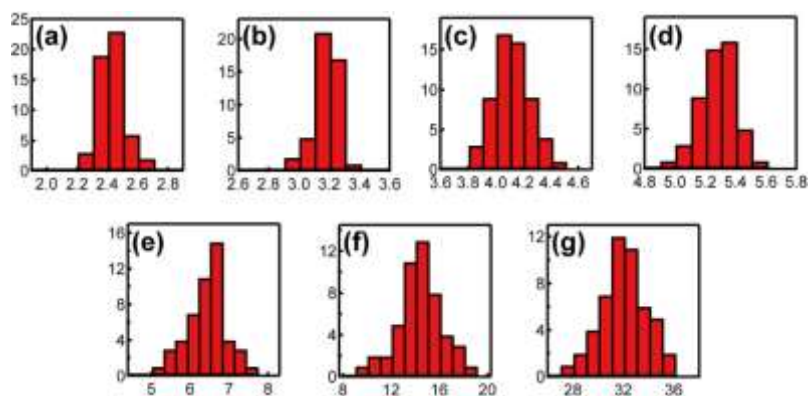


Figure S11. The corresponding size distributions of the TEM images in Figure 4(a-g) with count numbers as y axis and diameter as x axis.

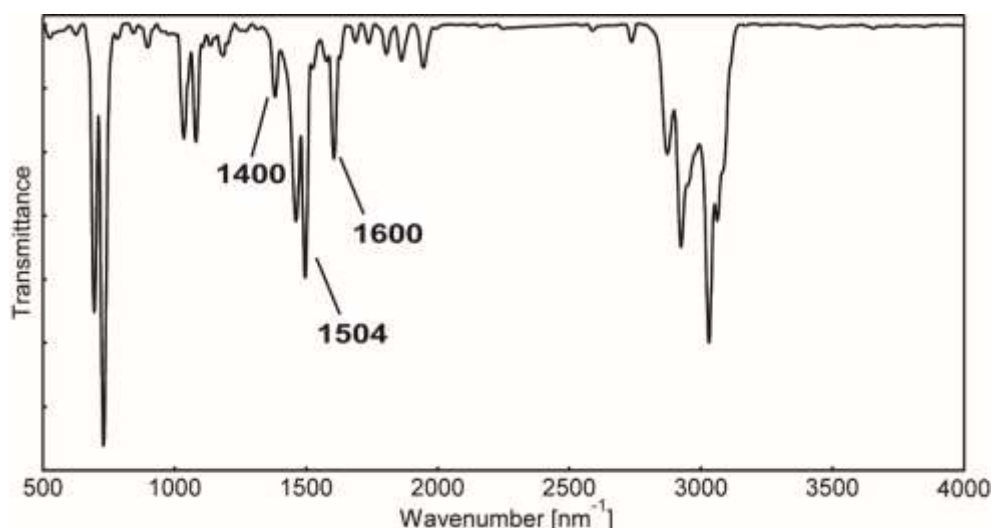


Figure S12. The IR spectrum of the OA, OM mixtures. As shown in the spectrum, using Fourier transform infrared spectra (FTIR) analysis, we can identify IR peaks at 1600 cm⁻¹ as antisymmetric stretching vibrations of C=O in COO⁻, owing to the existence of the deprotonated COO groups, meanwhile the peaks at 1504 cm⁻¹ is the symmetric bending vibrations of the protonated NH₃ groups, which can confirm the existence of the protonated oleylamine.

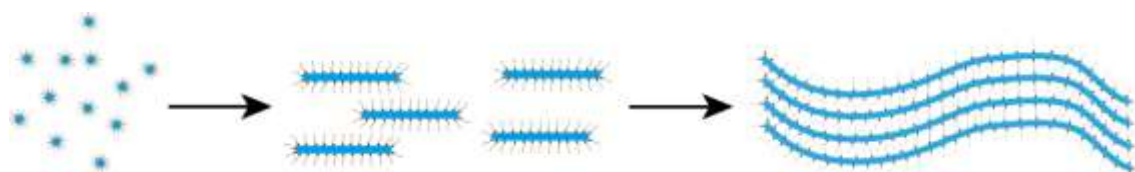


Figure S13. Illustration of the transformation of the initial CsPbBr₃ nanoparticles forming short NWs through oriented attachment, then these short NWs further transform into long NWs.

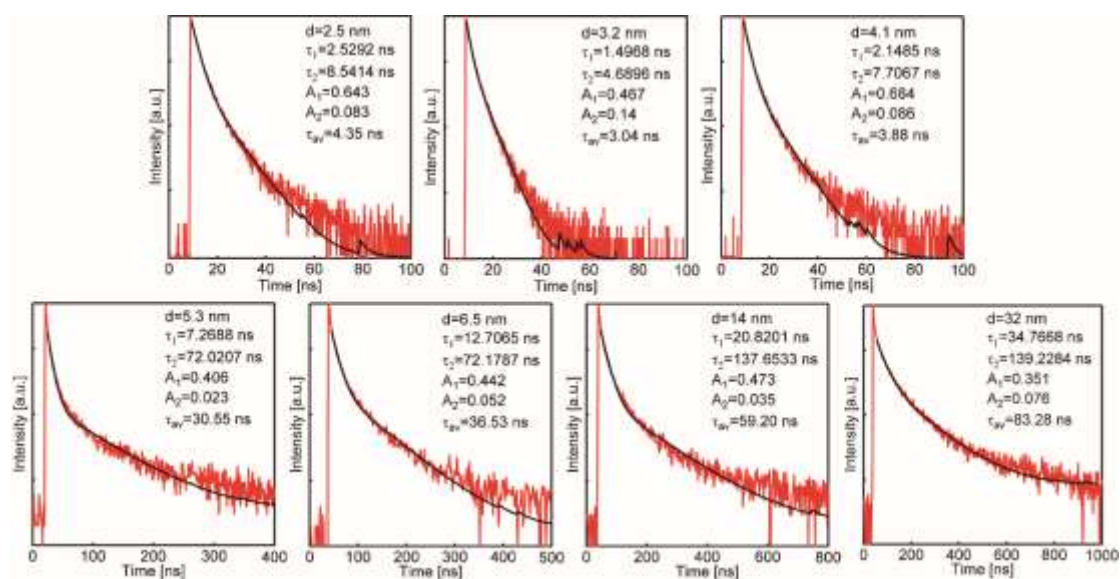


Figure S14. Fitting curves and parameters of the time decay data for CsPbBr₃ nanowires with different width.

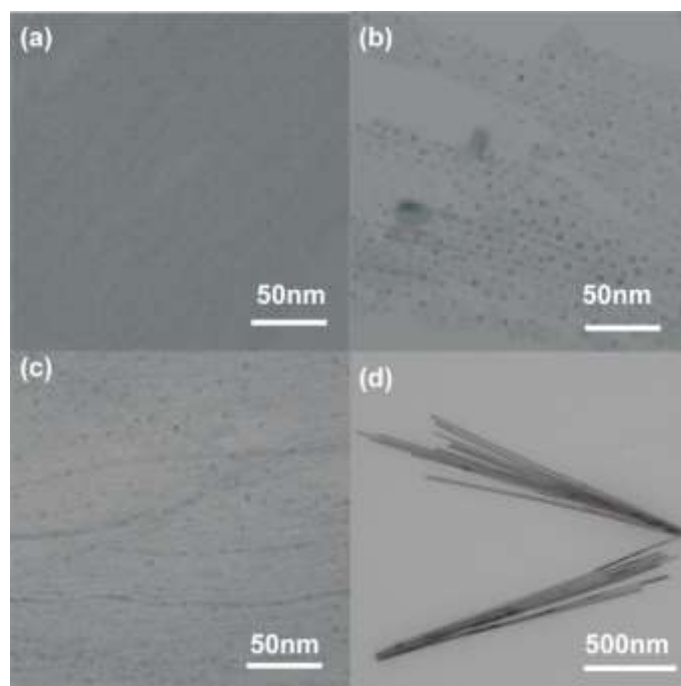


Figure S15. TEM images of the products after (a) Cl⁻ and (b) I⁻ exchange of the CsPbBr₃ NWs with initial diameter of ~3.2 nm. (c) Cl⁻ and (d) I⁻ exchange of the CsPbBr₃ NWs with initial diameter of ~6.5 nm.



Figure S16. Photographs showing the emission color of the CsPbBr₃ NWs (d=6.5 nm) with different compositions after halide-exchange under day light and UV illumination.

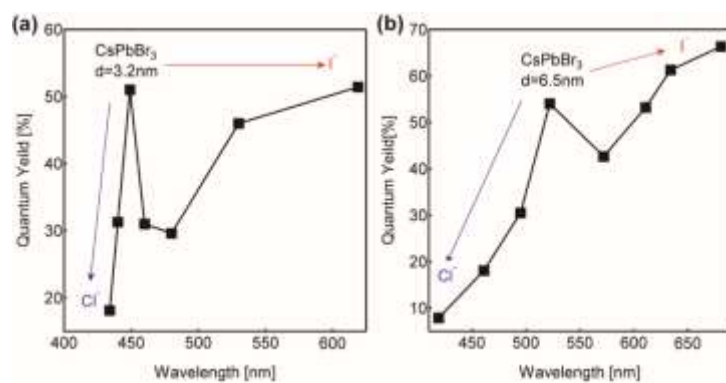


Figure S17. The changes of the PLQY in the Br/Cl and Br/I ion exchange processes for nanowires with different width. The x-axis is the emission peak position after ion exchange.