

Supplementary Information

General Strategy for Rapid Production of Low-Dimensional All-Inorganic CsPbBr₃ Perovskite Nanocrystals with Controlled Dimensionalities and Sizes

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Experimental Procedures:

1 Synthesis Methods

1.1 Reagents.

Cesium carbonate (Cs_2CO_3 , 99.99%), lead (II) bromide (PbBr_2 , 99%), oleic acid (OA, 90%), oleylamine (OAm, 80%), octadecene (ODE, 90%) and diethylene glycol butyl ether (DGBE, 98%) were purchased from Aldrich. Hexane (97%, anhydrous grade) was obtained from Beijing Chemical Reagent, China. All chemicals were used directly without further purification.

1.2 The application of DGBE.

In the previous studies, most of the organic-inorganic and all-inorganic perovskite NCs were synthesized through MW irradiation assisted by the reactants and surfactants,¹⁻³ in which the MW energy can't be absorbed effectively. In the present work, the DGBE with relatively higher polarity to partly replace ODE was introduced into the raw materials to enhance the absorption capacity. Figure S1 in Supporting Information (SI) shows the as-synthesized products under different MW powers with various amount of DGBE to replace ODE with the volume ratios from 10 to 50% (vs. ODE). It seems that, at a fixed amount of DGBE, the MW powers have little effect on the shapes of the resultant perovskite NCs. However, at a given MW power, with the increase of the DGBE introduced, their shapes are changed from nanocubes to nanosheets, suggesting that the dimensionalities of the perovskite NCs could be tailored by control on the concentrations of DGBE. With respect to the absorptive capacity of the solvent to the MW irradiation, 50 % DGBE is chosen for the following studies.

1.3 Preparation of Cs-oleate precursor.

The Cs-oleate precursor solution was prepared similar to the reported work.⁴ 0.8 g Cs_2CO_3 , 2.4 mL OA and 30 mL ODE were loaded together into a 3-neck flask, followed by being dried for 1 h at 120 °C, and then heated up to 150 °C for 30 min under N_2 , until the Cs_2CO_3 was dissolved completely. Before

the use, the as-prepared solution was preheated over 100 °C to limit the Cs-oleate precipitated out of ODE at room temperature.

1.4 Preparation of PbBr₂ precursor.

For the preparation of PbBr₂ precursor, the raw materials of 690 mg PbBr₂, 25 mL ODE and 25 mL DGBE were loaded into a 100 mL 3-neck flask, and dried at 120 °C for 1 h. Afterward, the dried OA and OAm with different amounts were injected into the flask at 120 °C under N₂. Subsequently, the resultant mixture was then heated up to 150 °C for 30 min under N₂, until the PbBr₂ was completely dissolved, followed by being cooled naturally. Here, the DGBE was applied to improve the MW absorbing ability of the solution.

1.5 Preparation of CsPbBr₃ NCs.

In a typical process, 0.4 mL of above-mentioned Cs-oleate solution and 5 mL of PbBr₂ precursor were mixed in a sample vial (20 mL), which was then transferred into the MW oven (NN-CS1000, Panasonic, Japan). After reacting at a given irradiation power for a fixed time, the mixture was cooled by the ice-water bath. The as-prepared crude CsPbBr₃ dispersions were purified by centrifugation at 10000 rpm for 3 min to get rid of unreacted precursors. Then the resultant NC precipitates were dispersed in the mixture of 30 mL hexane and 5 mL acetone, and subjected to be centrifuged at 5000 rpm for 3min. After that, the supernatant was discarded and the particles were dispersed in hexane for the formation of long-term stable solutions.

2 Characterization :

The obtained CsPbBr₃ NCs were characterized using field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan), transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDX, Quantax-STEM, Bruker, Germany) and X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The UV-Vis measurements were performed on a UV-Vis scanning spectrophotometer (U-3900, Hitachi, Japan). The PL spectra were recorded using a spectrometer (Fluoromax-4P, Horiba Jobin Yvon, France).

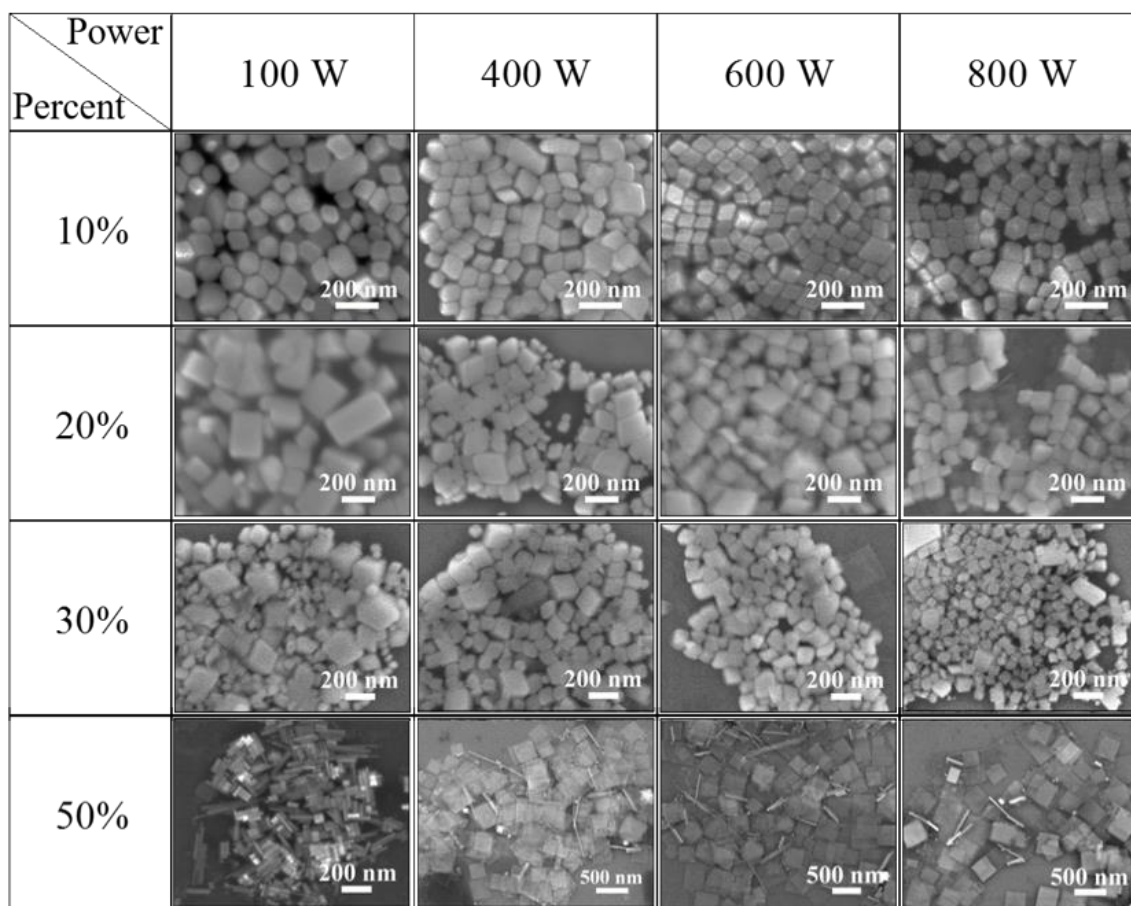


Figure S1 Typical SEM images of the CsPbBr₃ perovskite NCs with different percents of DGBE under different irradiation powers for 1 min.

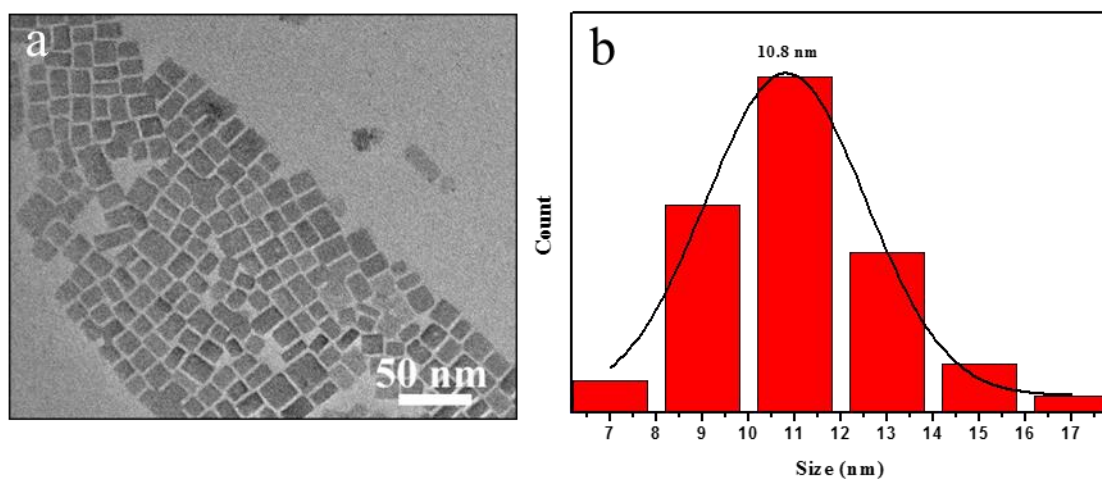


Figure S2 The typical TEM image (a) and size distribution (b) of sample S0D, respectively.

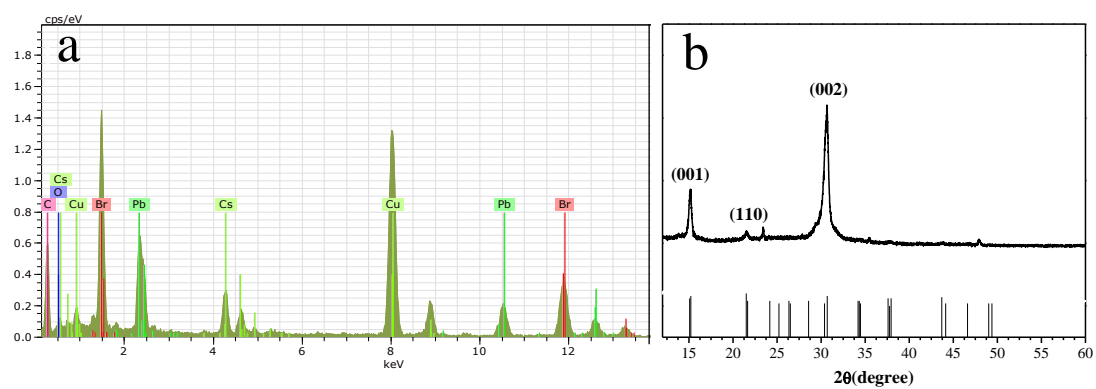


Figure S3 Typical EDX spectrum (a) and XRD pattern (b) of sample S0D, respectively.

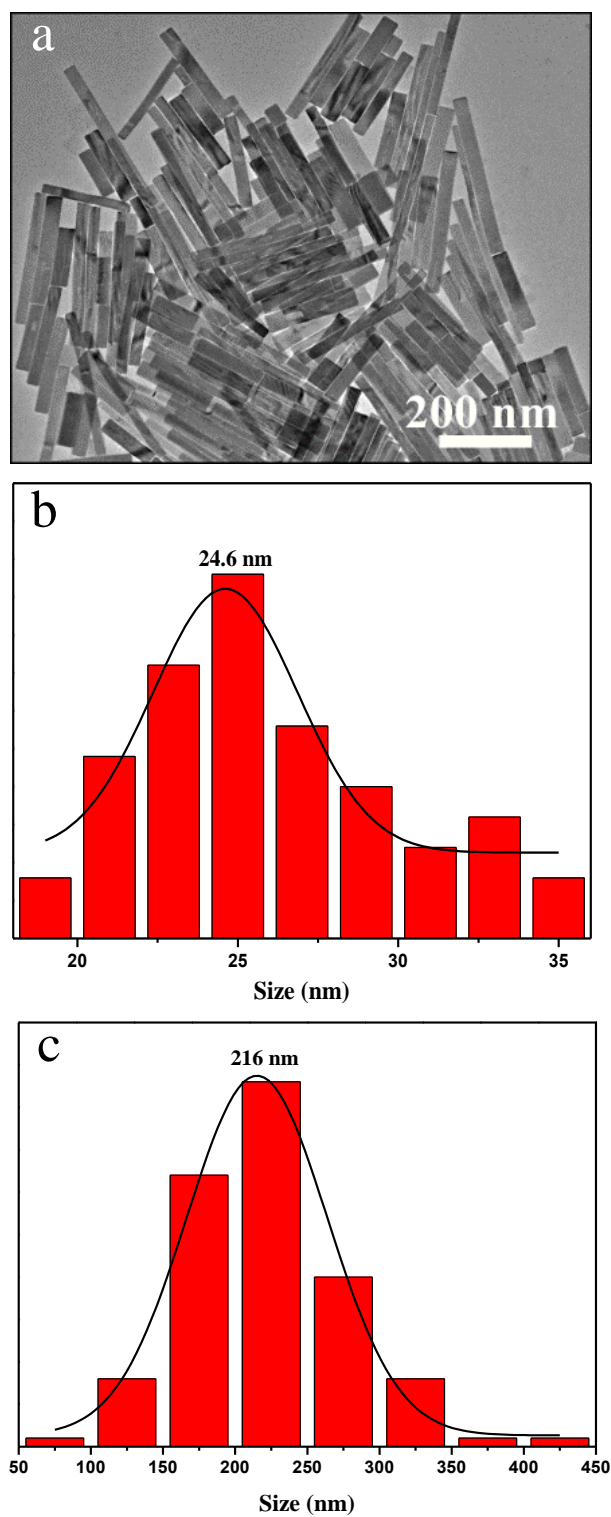


Figure S4 (a) Typical TEM image of sample S1D. (b-c) The size distributions in diameter and length of sample S1D, respectively.

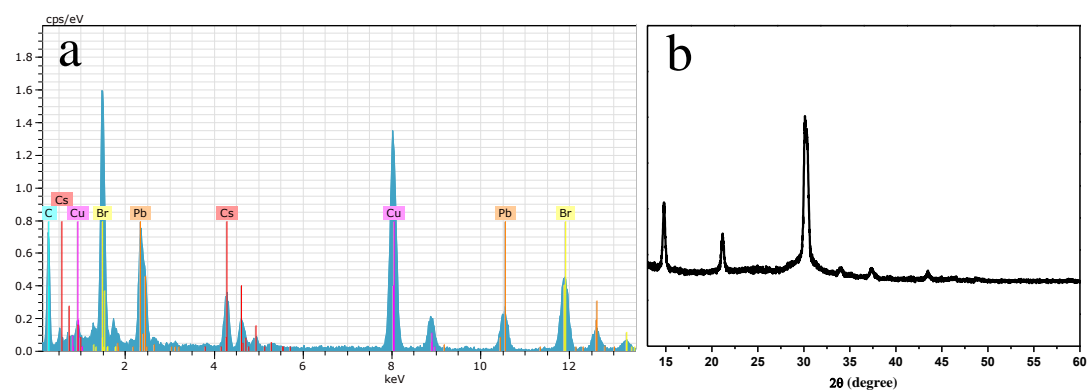


Figure S5 The representative EDX spectrum (a) and XRD pattern (b) of sample S1D, respectively.

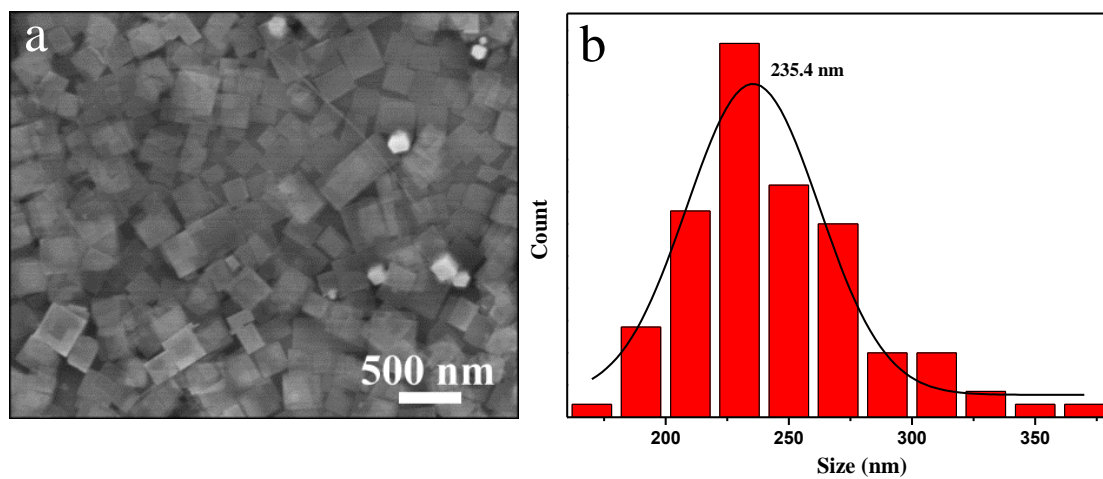


Figure S6 (a) The typical SEM image of sample S2D. (b) The lateral size distribution of sample S2D, respectively.

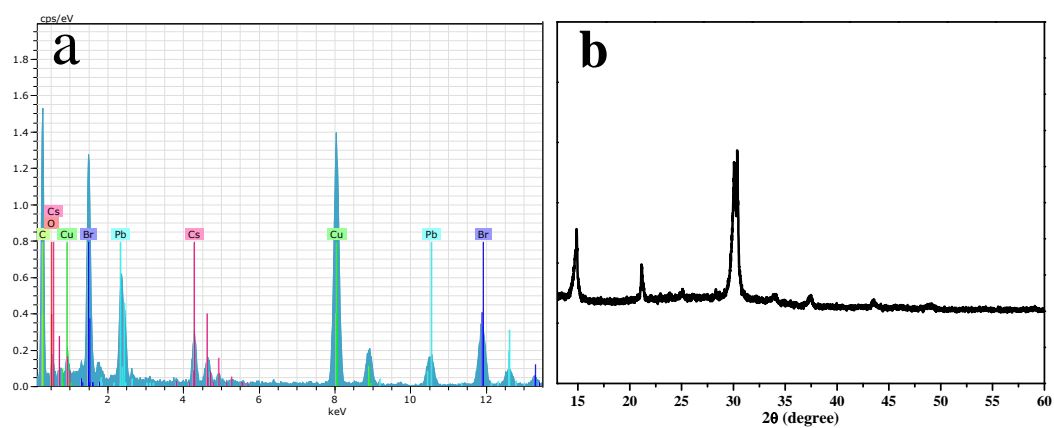


Figure S7 The typical EDX spectrum (a) and XRD pattern (b) of sample S2D, respectively.

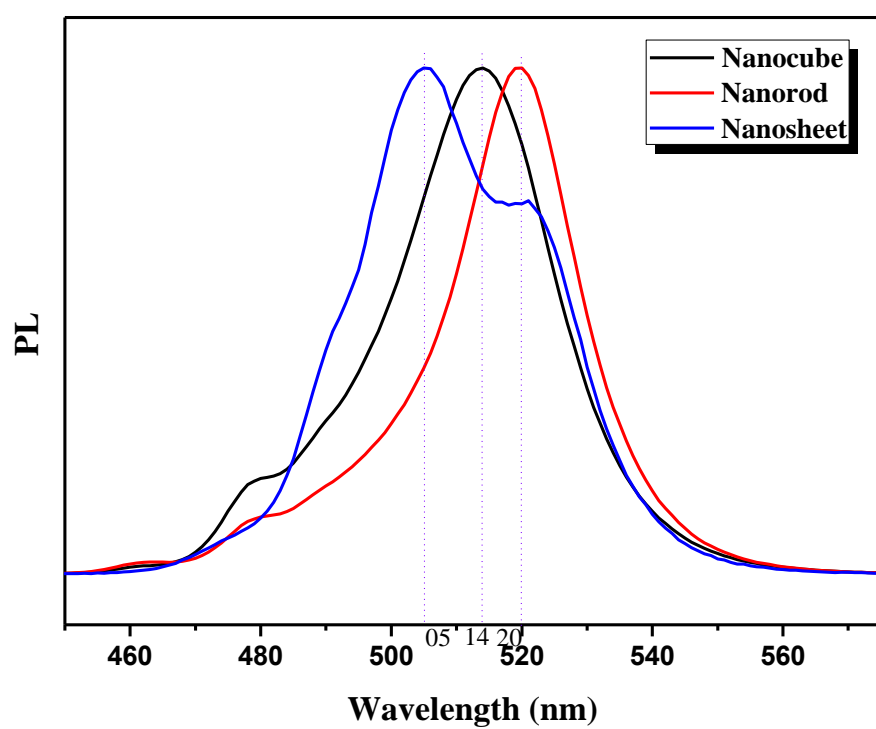


Figure S8 The typical PL spectra of samples S0D, S1D and S2D.

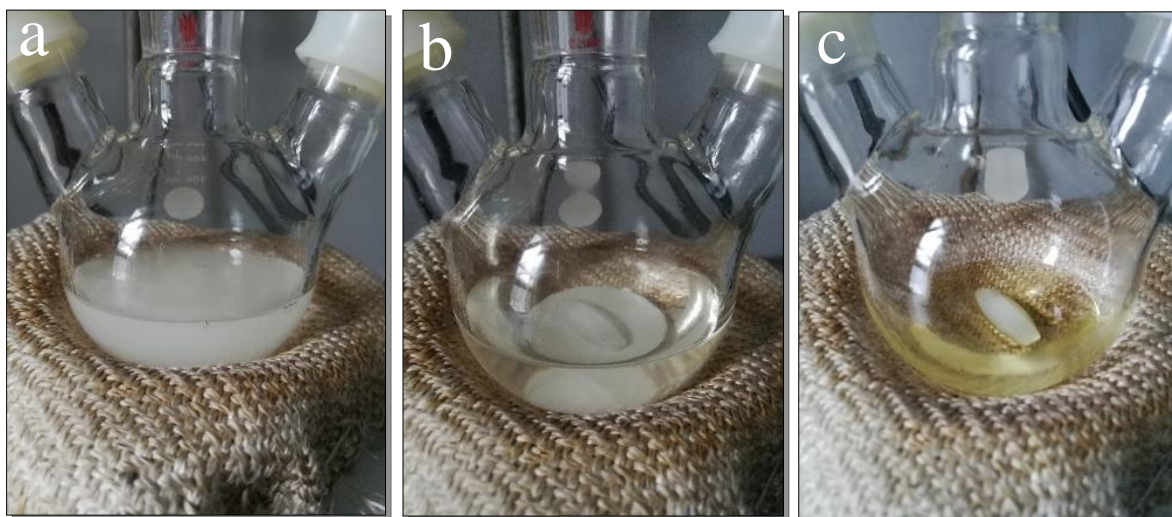


Figure S9 (a-b) The digital photographs of the as-prepared PbBr₂ precursors with 10 mL OA without OAm introduced as the surfactant before and after cool down to RT, respectively. (c) The digital photograph of the as-prepared PbBr₂ precursor with 9 mL OA and 1mL OAm introduced.

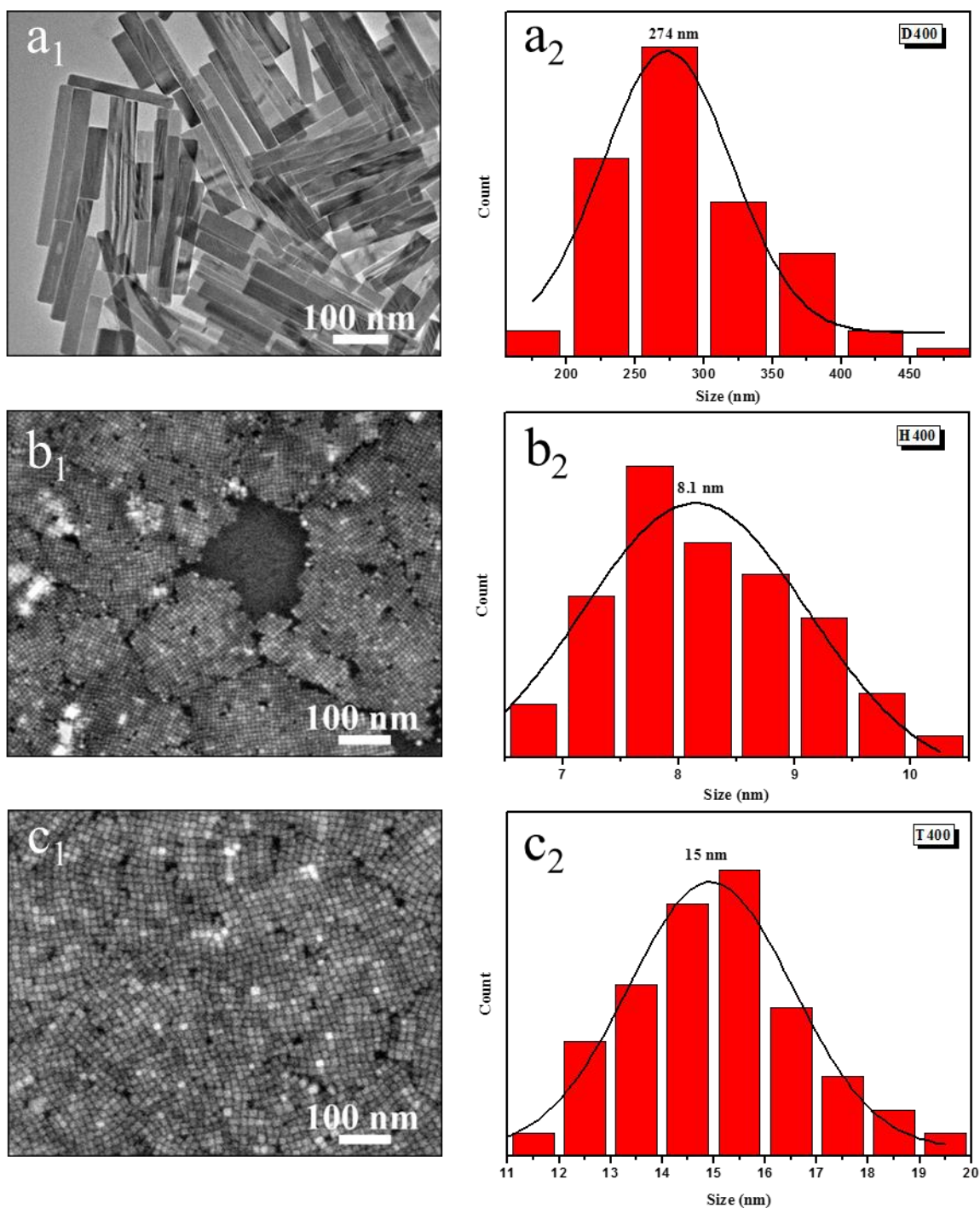


Figure S10 (a₁-a₂) The typical TEM image and size distribution of sample D400. (b₁-b₂) The typical SEM image and size distribution of sample H400. (c₁-c₂) the typical SEM image and size distribution of sample T400.

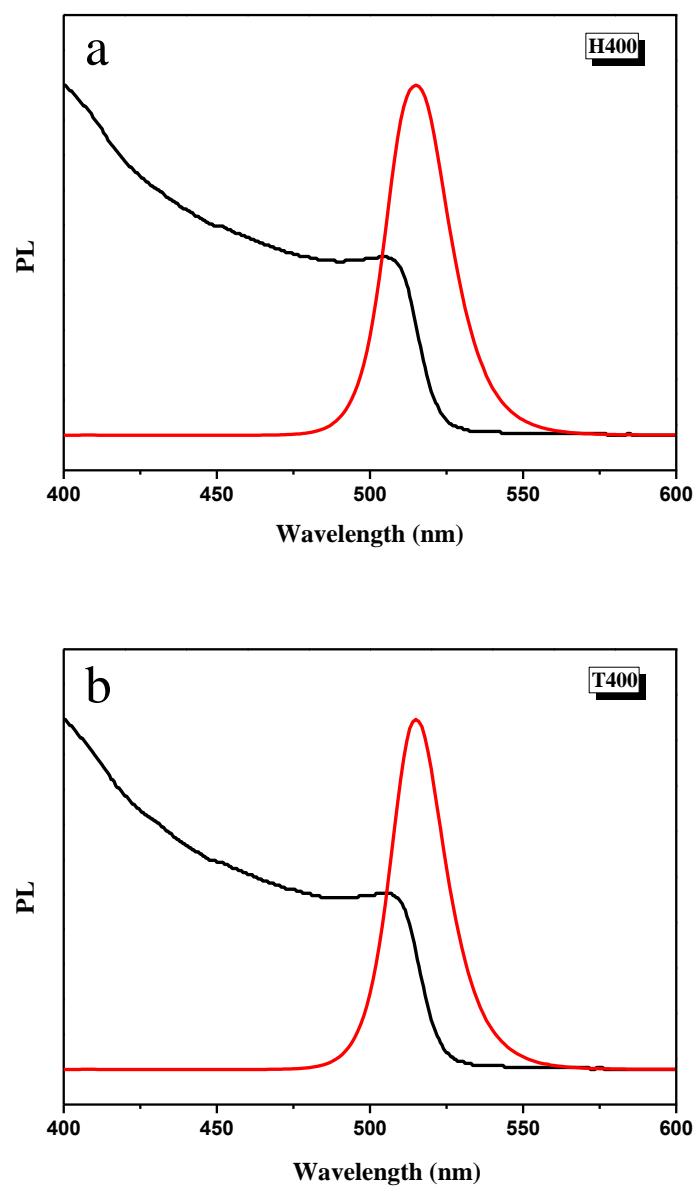


Figure S11 The representative UV-vis absorptions and PL spectra (excited at 365 nm wavelength) of sample H400 (a) and T400 (b), respectively.

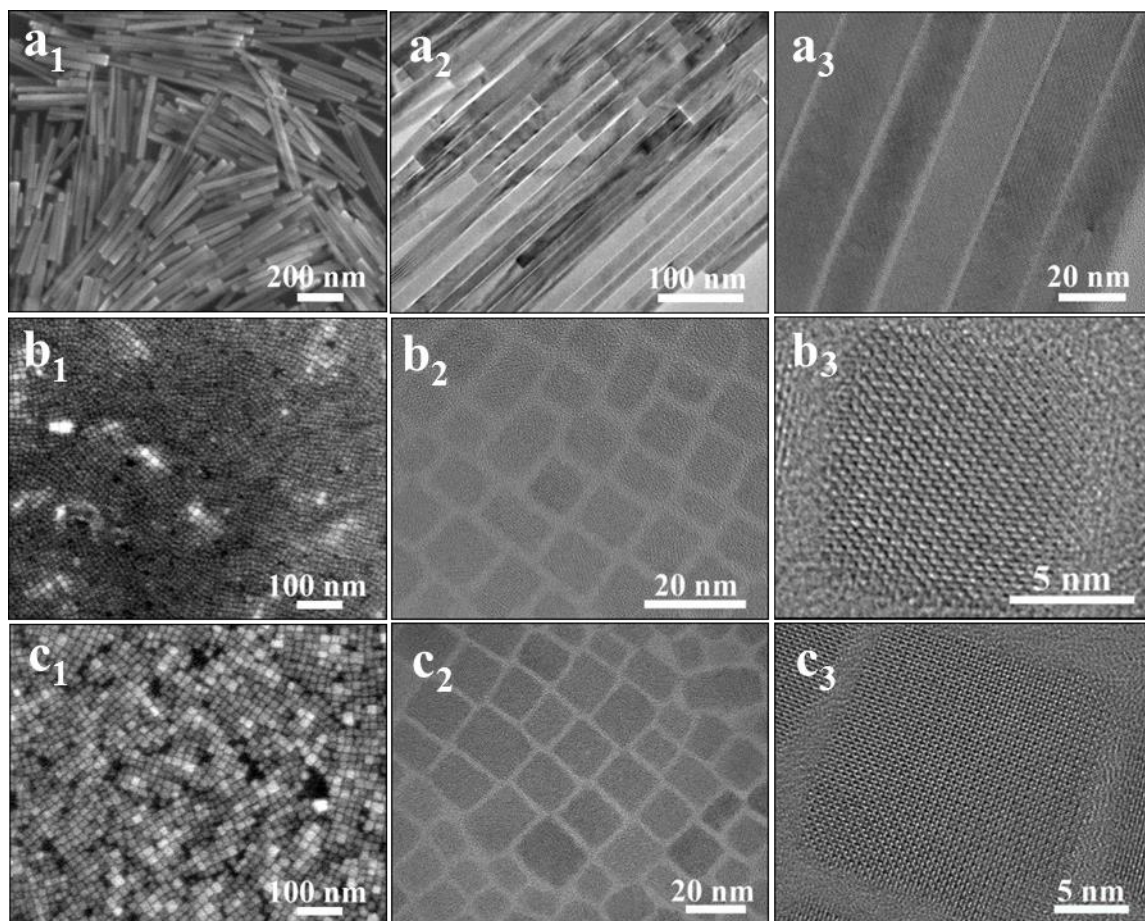


Figure S12 The typical SEM, TEM and HRTEM images of the samples D600 (a₁-a₃), H600 (b₁-b₃) and T600 (c₁-c₃) obtained from different precursor concentrations under different irradiation powers for 1 min.

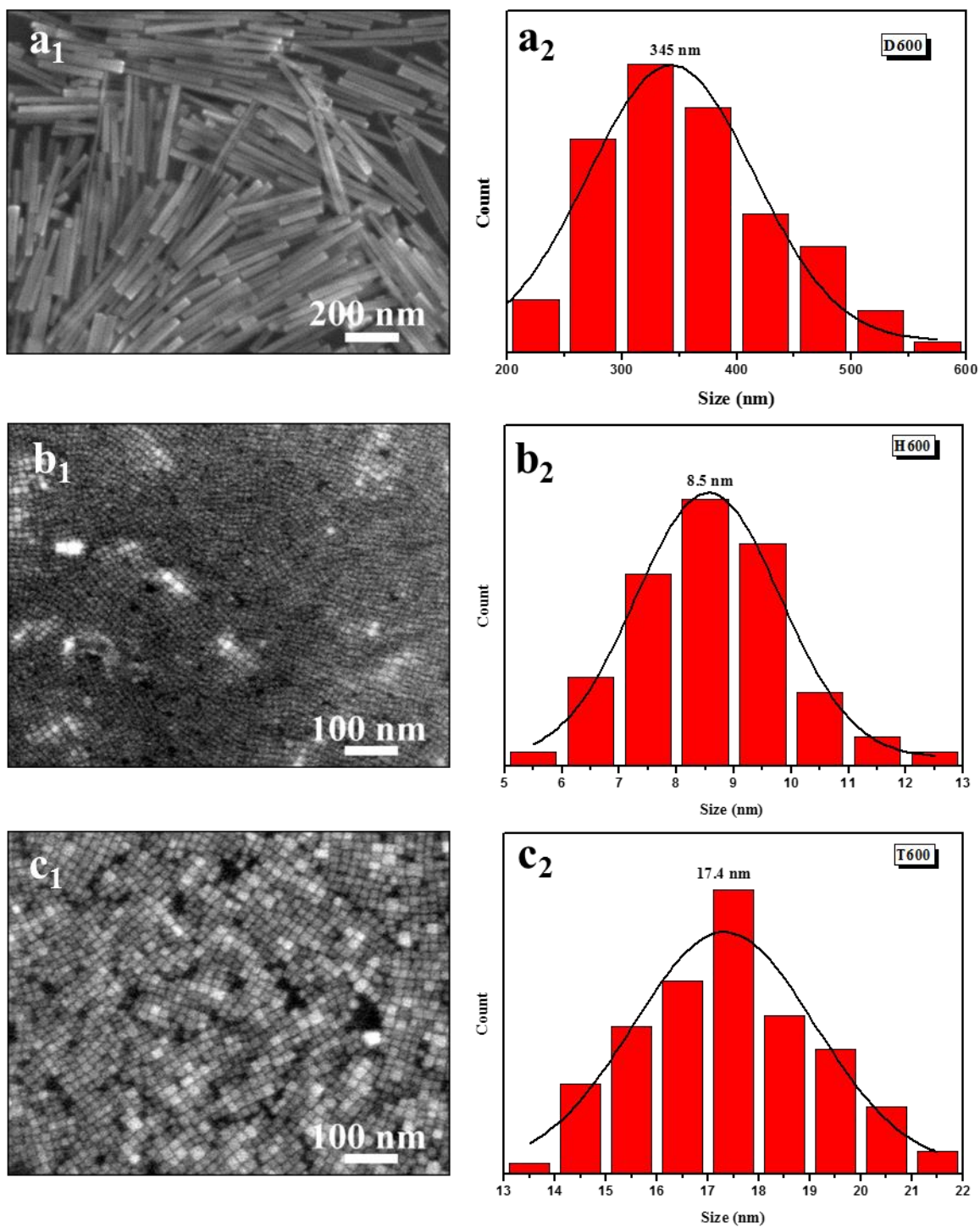


Figure S13 The typical microstructures and size distributions of the samples D600 (a₁-a₂), H600 (b₁-b₂) and T600 (c₁-c₂), respectively.

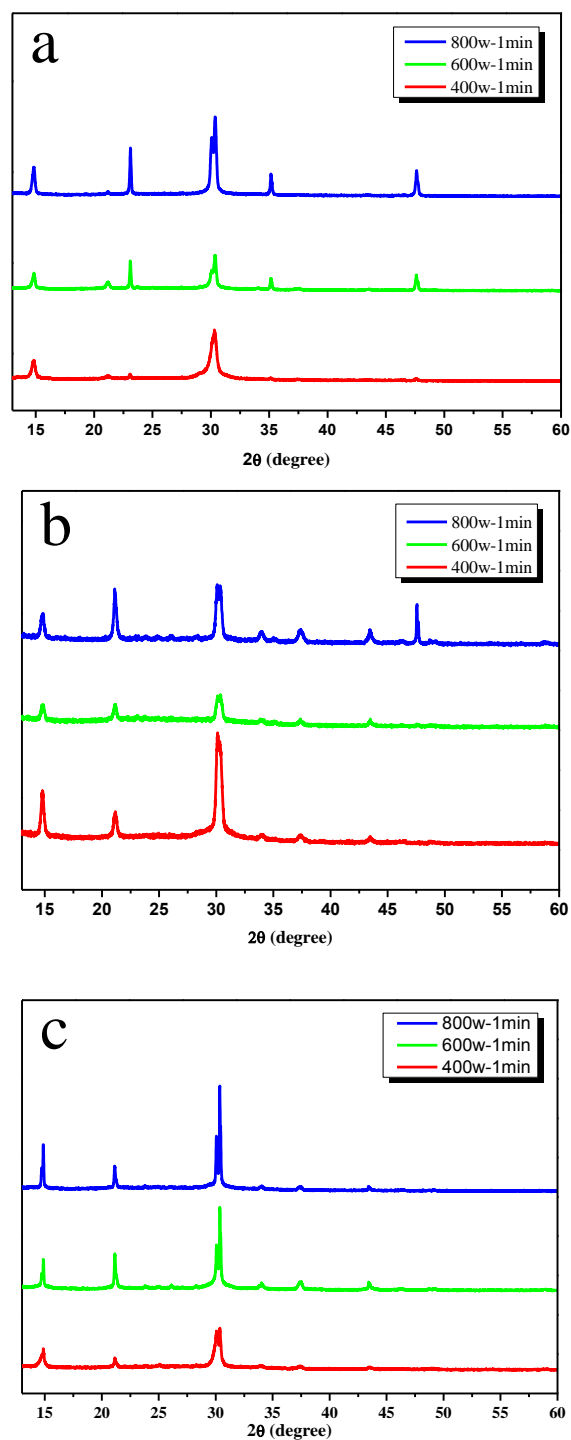


Figure S14 (a-c) The typical XRD patterns of samples S0D, S1D and S2D subjected to irradiation powers of 400, 600 and 800 W, respectively.

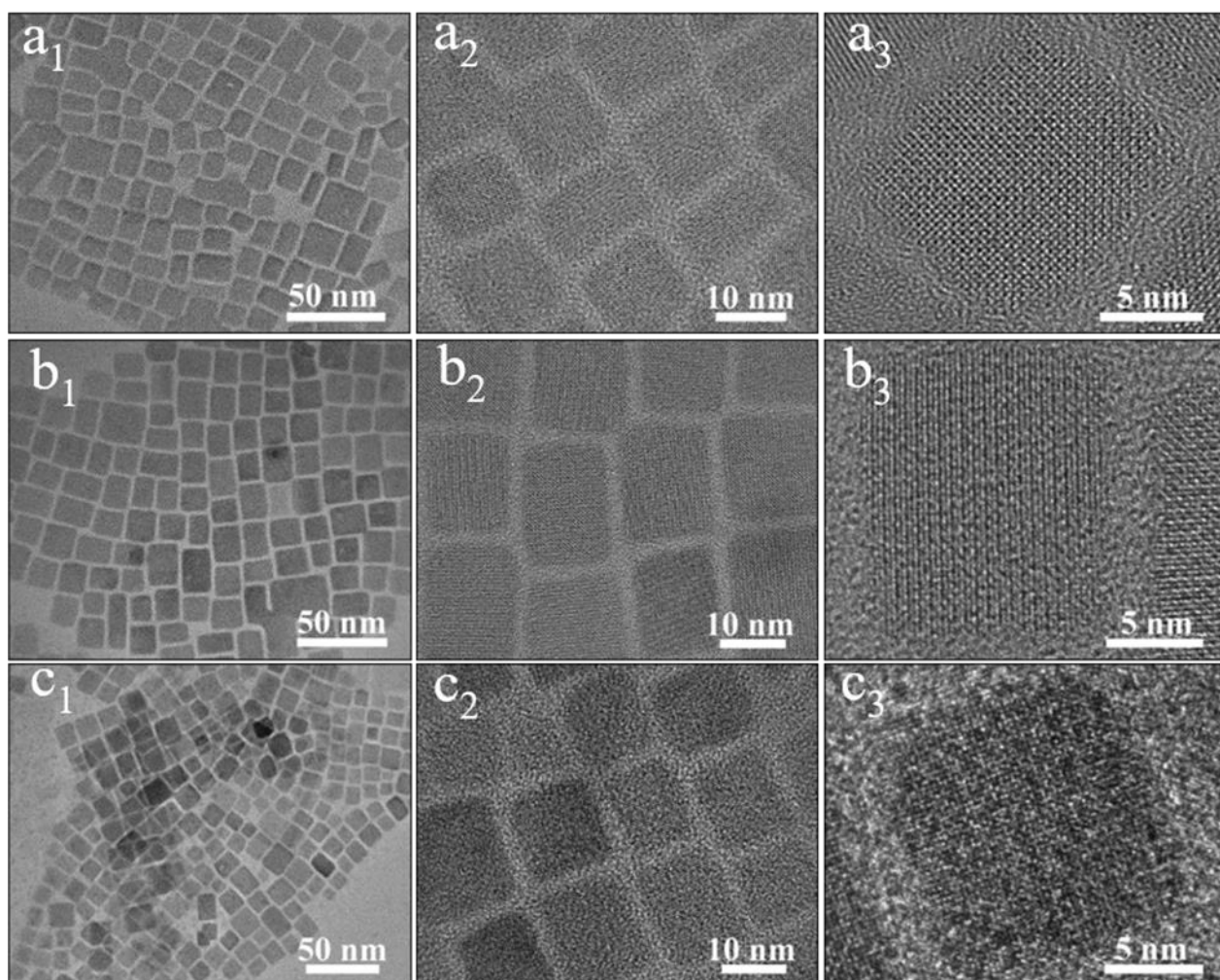


Figure S15 The typical TEM and HRTEM images of sample S0D subjected to the irradiation powers of 400 W (a₁-a₃), 600 W (b₁-b₃) and 800 W (c₁-c₃), respectively.

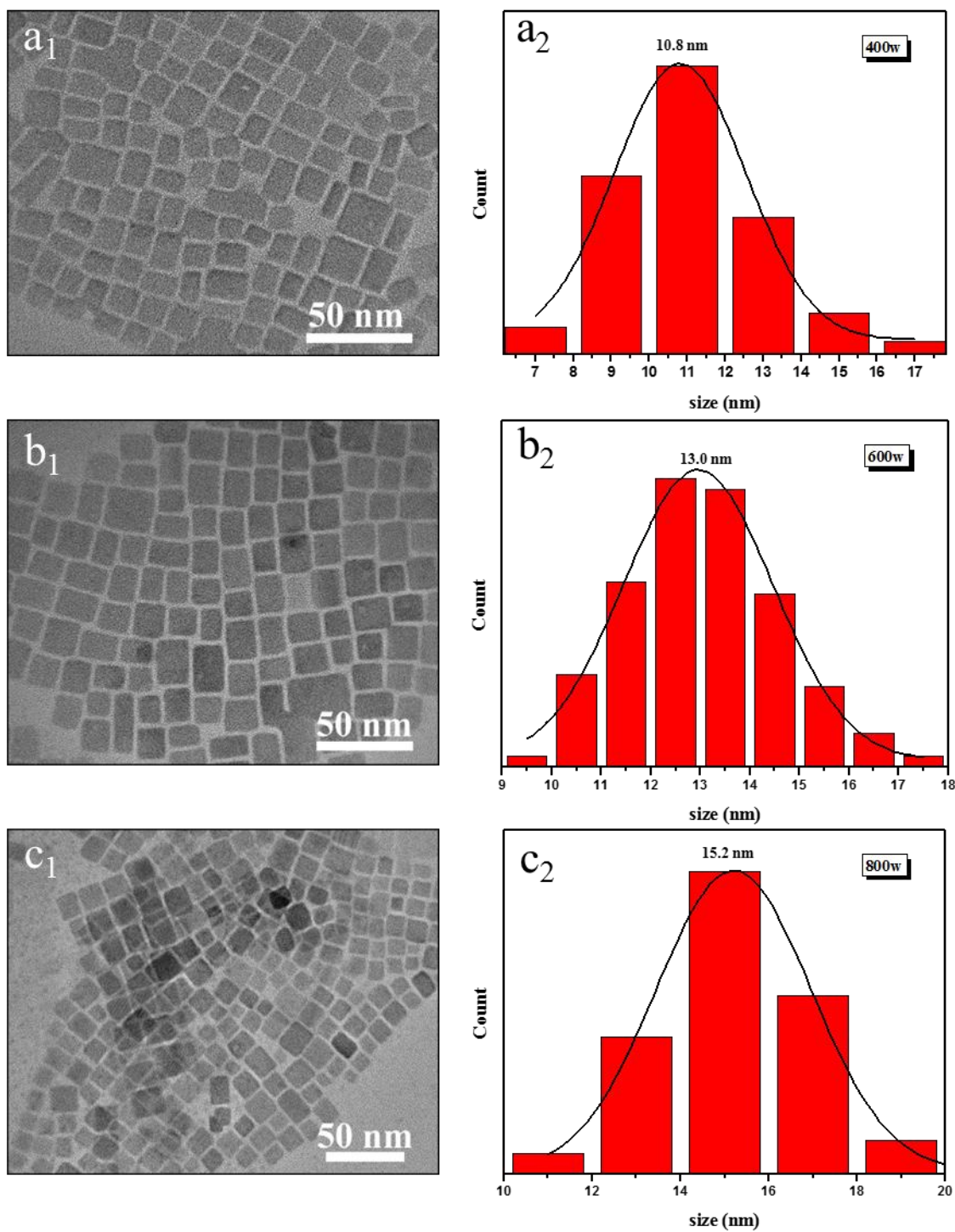


Figure S16 The typical microstructures and size distributions of sample S1D when subjected to irradiation powers of 400 W (a₁-a₂), 600 W (b₁-b₂) and 800 W (c₁-c₂), respectively.

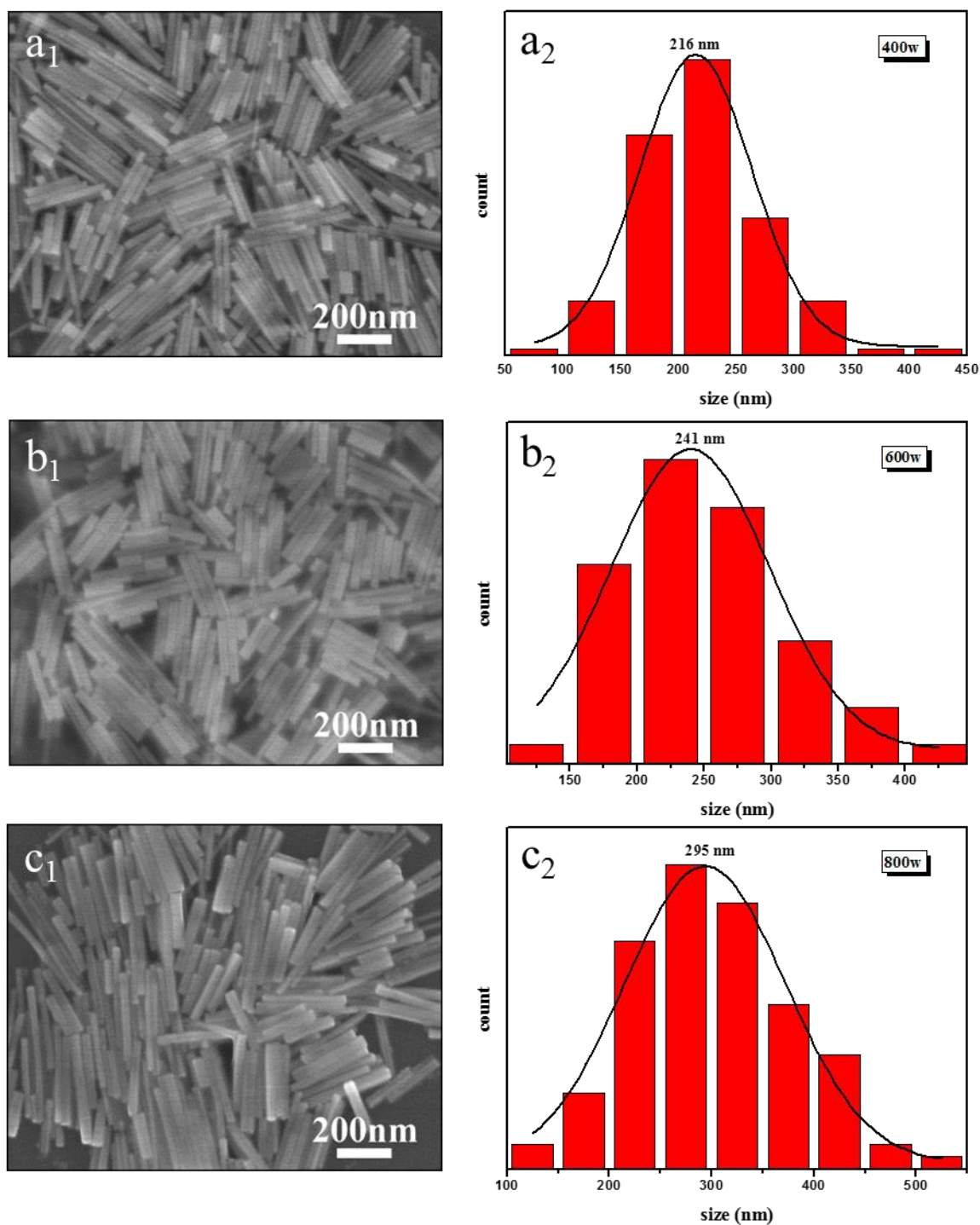


Figure S17 The typical microstructures and the size distributions of sample S1D in length when subjected to irradiation powers of 400 W (a₁-a₂), 600 W (b₁-b₂) and 800 W (c₁-c₂), respectively.

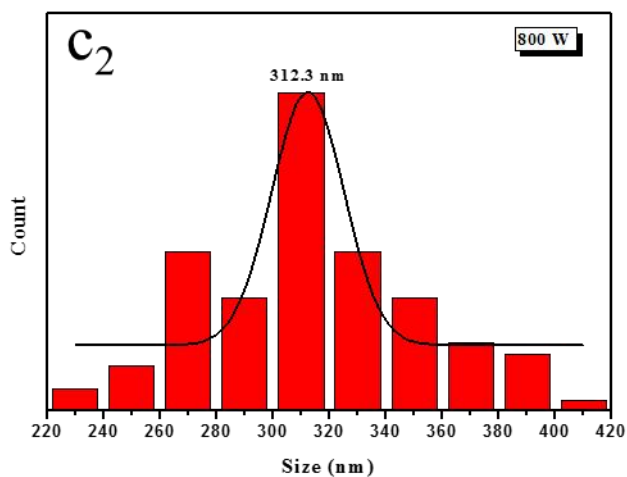
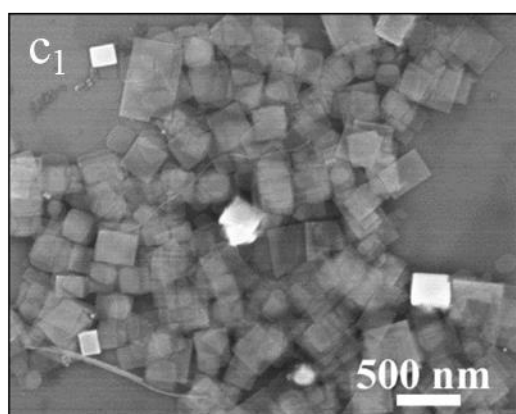
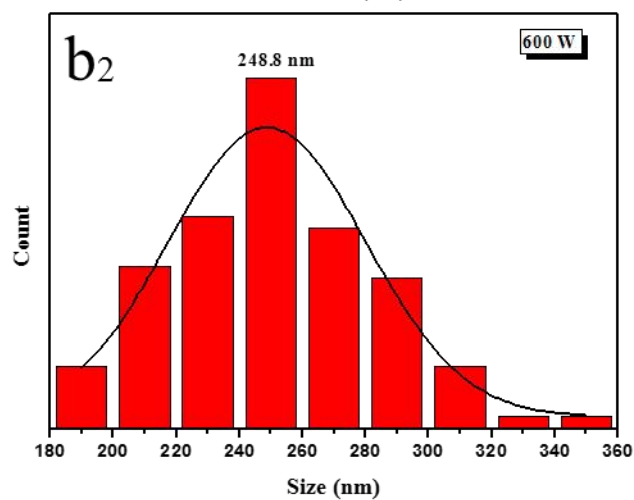
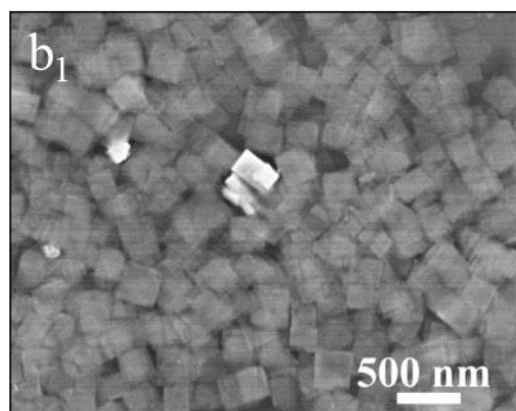
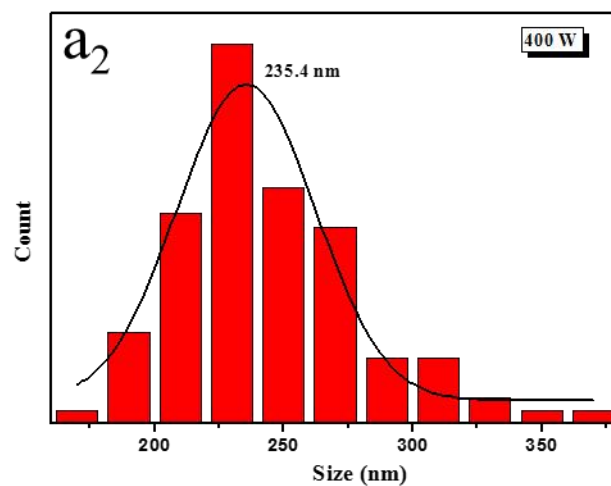
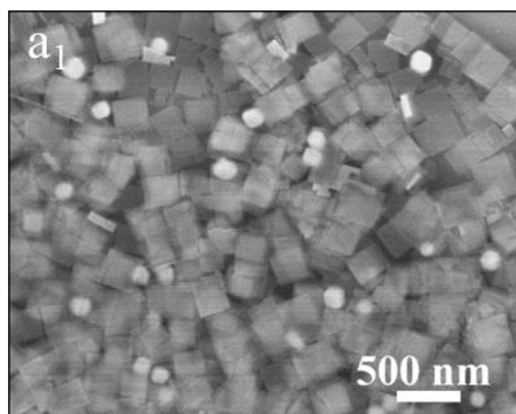


Figure S18 The typical microstructures and the size distributions of sample S2D in lateral sizes when subjected to irradiation powers of 400 W (a_1 - a_2), 600 W (b_1 - b_2) and 800 W (c_1 - c_2), respectively.

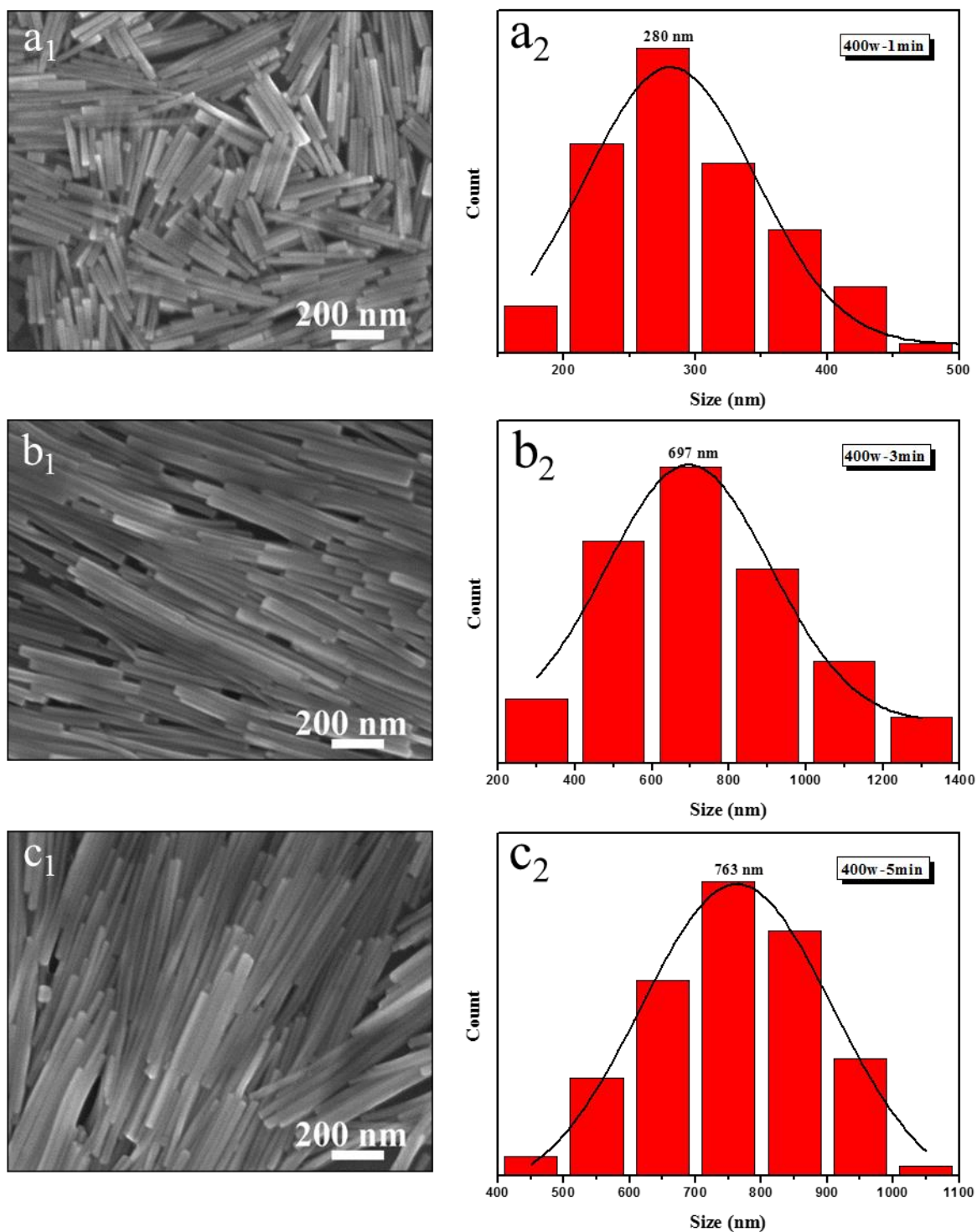


Figure S19 The typical microstructures and their corresponding size distribution of sample S1D in length under 400W with different irradiation times of 1min (a₁-a₂), 3min (b₁-b₂) and 5min (c₁-c₂) respectively.

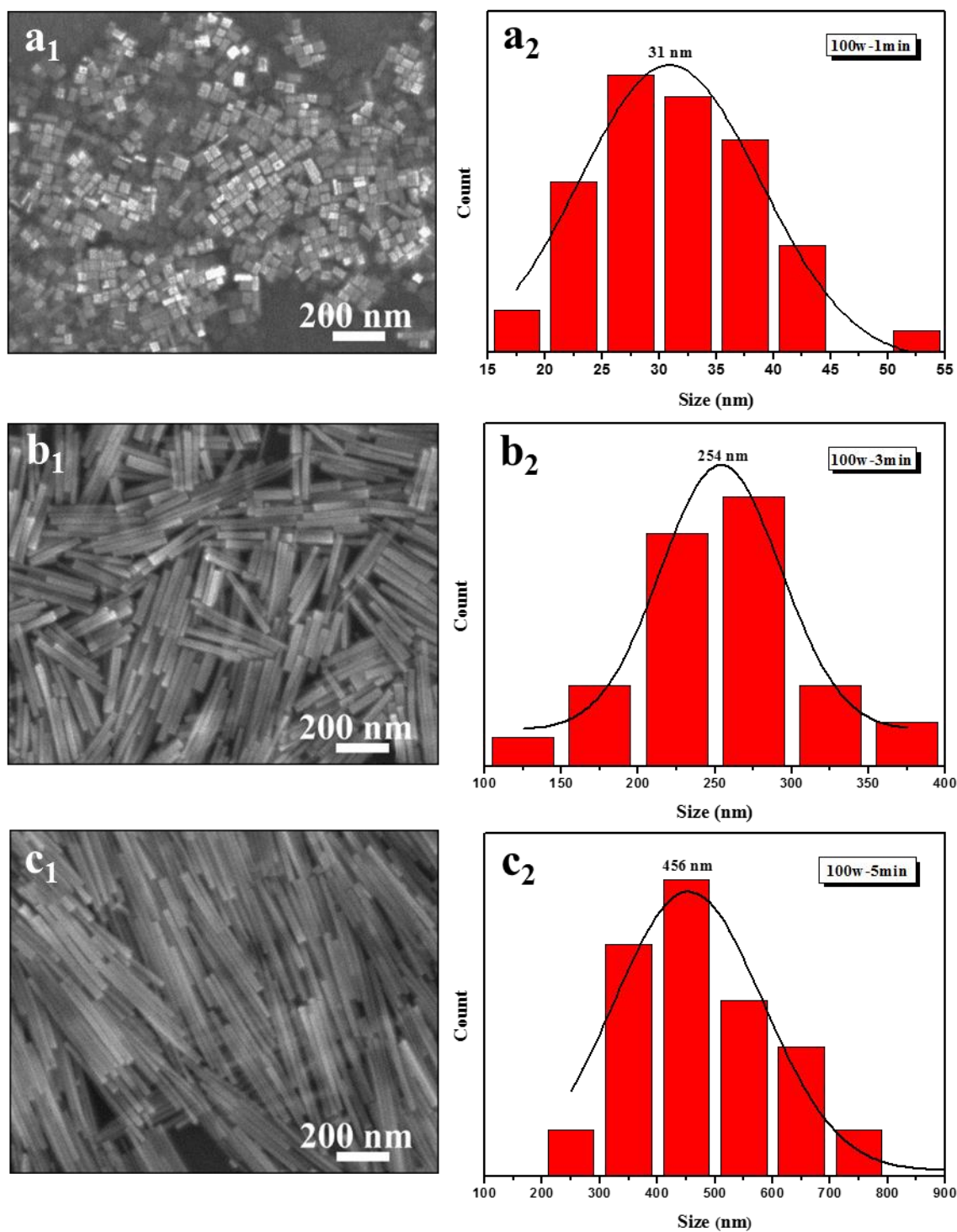


Figure S20 The typical SEM images and size distribution of sample S1D in length under 100 W with irradiation times of 1 min (a₁-a₂), 3 min (b₁-b₂) and 5min (c₁-c₂), respectively.

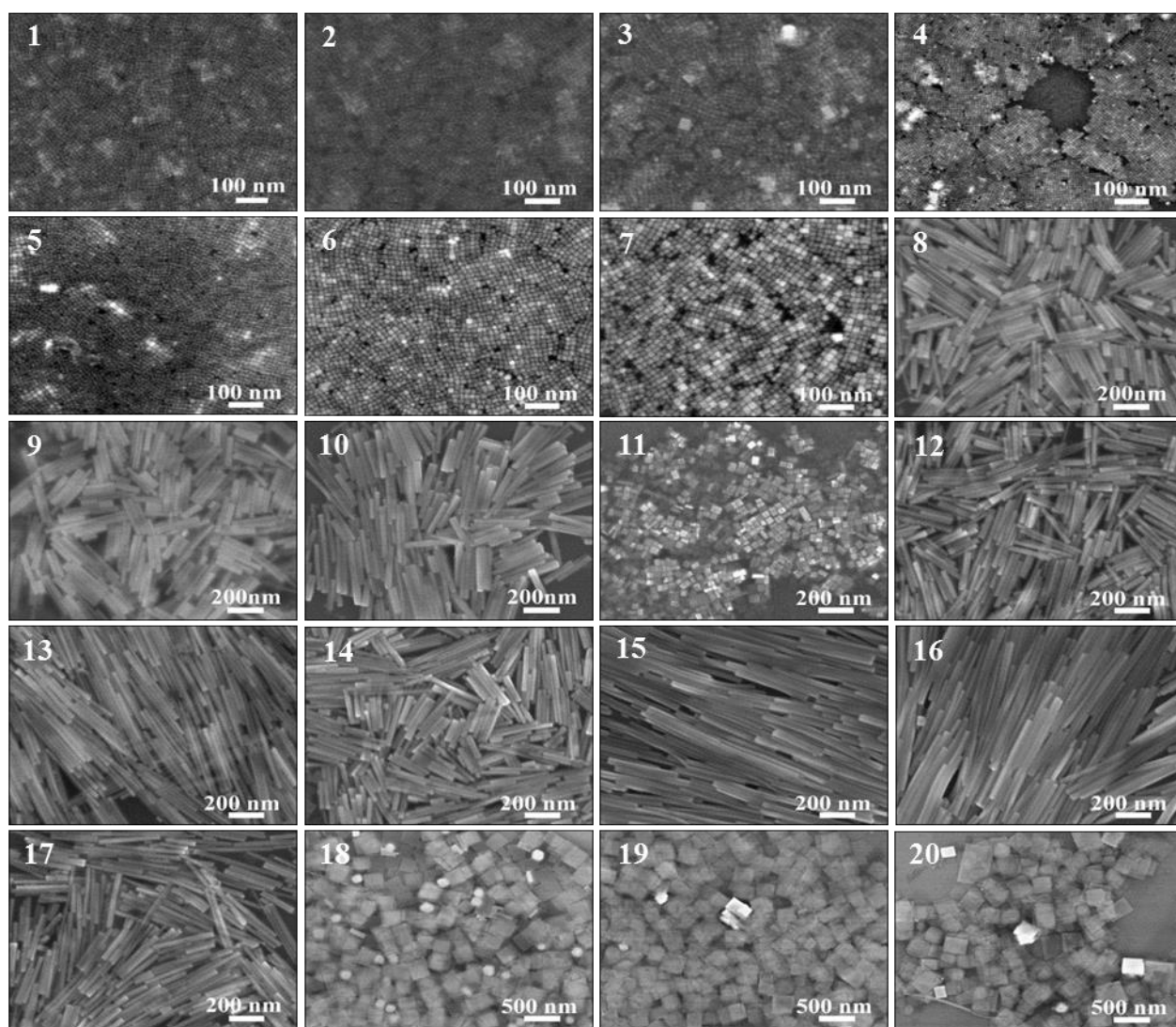


Figure S21 The representative SEM images of as-fabricated perovskite NCs corresponding to the used experimental parameters as listed in Table 1, respectively.

References

- (1) Long, Z.; Ren, H.; Sun, J.; Ouyang, J.; Na, N. High-Throughput and Tunable Synthesis of Colloidal CsPbX₃ Perovskite Nanocrystals in a Heterogeneous System by Microwave Irradiation. *Chem. Commun.* **2017**, 53, 9914-9917.
- (2) Cao, Q.; Yang, S.; Gao, Q.; Lei, L.; Yu, Y.; Shao, J.; Liu, Y. Fast and Controllable Crystallization of Perovskite Films by Microwave Irradiation Process. *ACS appl. Mater. Interf.* **2016**, 8, 7854-7861.
- (3) Kollek, T.; Fischer, C.; Göttker-Schnetmann, I.; Polarz, S. Microwave Induced Crystallization of the Hybrid Perovskite CH₃NH₃PbI₃ from a Supramolecular Single-Source Precursor. *Chem. Mater.* **2016**, 28, 4134-4138.
- (4) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X= Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, 15, 3692-3696.