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Shape evolution process of two-dimensional CdSe nanocrystals altered by seed concentration

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1. Experimental section

Materials. Stearic acid (99%), selenium powder (Se, 325 mesh, 99.5%) were purchased from Alfa-Aesar. 1-Octadecene (ODE, >90%), tetramethylammonium hydroxide pentahydrate (97%), oleic acid (99.0%), butylamine (98%) and cadmium acetate dihydrate ($Cd(Ac)_2 \cdot 2H_2O$, 99.99%) were purchased from Aladdin (Shanghai, China). Acetonitrile (analytical reagent), toluene (analytical reagent), methanol (analytical reagent) and chloroform (analytical reagent) were purchased from Sinopharm Chemical Reagents Co. Ltd., China. All chemicals were used without further purification.

Synthesis and purification of CdSe quantum dots as the seeds. The CdSe quantum dots were synthesized according to the Peng's method.[S1] Specifically, cadmium stearate was firstly synthesized. Stearic acid (2 mmol) and tetramethylammonium hydroxide pentahydrate (2 mmol) were added into methanol (20 ml). This mixed solution was stirred for 3 h. Then the solution of cadmium acetate dihydrate (1 mmol) dissolved into methanol (5 ml) was added dropwise into this mixed solution under stirring. The obtained white precipitate was filtrated and washed by methanol. The filtration and washing processes were repeated 3 times. At last, the separated white precipitate was dried in vacuum oven at 70 ºC for usage.

To synthesize the CdSe quantum dots. the cadmium stearate (0.4 mmol) and ODE (13 ml) were loaded into a 50 ml three-neck flask. After Ar flowing for 30 min, the reaction system was heated to 260 ºC under Ar protection. At this temperature, the 2 ml Se-ODE (0.1 M) was swiftly injected the reaction system. The reaction was taken for 60 s.

The purification of CdSe quantum dots was carried out by the following procedure. The samples were firstly centrifuged at 10000 rpm for 10 min. Then the precipitate was retained and dissolved into the mixture of chloroform (4 mL) and butylamine (60 μL). After oscillation, the mixture turned into a clear solution. The acetonitrile (4 mL) added into this clear solution was heated at 60 ºC. The obtained solution was centrifuged at 4000 rpm for 1 min. The precipitate was again dissolved into chloroform (1 mL). Acetonitrile (1.2 mL) was used again to start another precipitation of the CdSe quantum dots. The final centrifuged product (75.6 mg) was dispersed into ODE with different volume (2, 3 or 4 mL) to obtain the different concentration of CdSe seeds, which was respectively named lower (18.9 mg/mL), intermediate (25.2 mg/mL) and higher concentration (37.8 mg/mL) of the seeds. The low boiling point residuals was removed from the ODE solution by reduced pressure distillation.

Synthesis of CdSe 2D nanocrystals. Cadmium stearate (0.025 mmol) and ODE (7.4 mL) were loaded

into a 50 mL three-neck flask. After Ar flowing for 30 min, the mixture was heated to 250 ºC. cadmium acetate dihydrate (0.3 mmol) suspended in ODE (1 mL) was injected into the mixture. The seed solution (1 mL) with different concentration was subsequently injected into the mixture to investigate the effect of seed concentration on the shape of CdSe 2D nanocrystals. At different stages, fixed small aliquot (40 μL) was taken out from the reaction solution and diluted in 3 ml toluene for the measurements of UV-vis, photoluminescence (PL) and photoluminescence excitation (PLE) at room temperature.

Measurements. Spectra of UV-vis, PL and PLE measurements were performed on a UV–vis spectrophotometer (Cary 300, USA) and a fluorescence spectrophotometer (PL, Cary Eclipse Varian), respectively. XRD pattern was recorded by an X-ray diffractometer (Ultima IV-185, Rigaku). TEM images were taken on a transmission electron microscope (TEM, JEM-2100, JEOL, Japan) operating at 200 kV.

2. Supplementary Figures

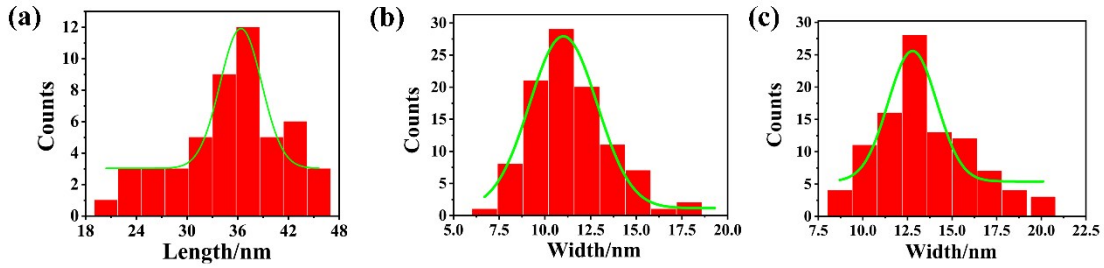

Fig. S1 Length- (a) and width-distribution histogram (b) for rectangular-shaped 2D CdSe nanocrystals and width-distribution histogram (c) for square-shaped 2D CdSe nanocrystals.

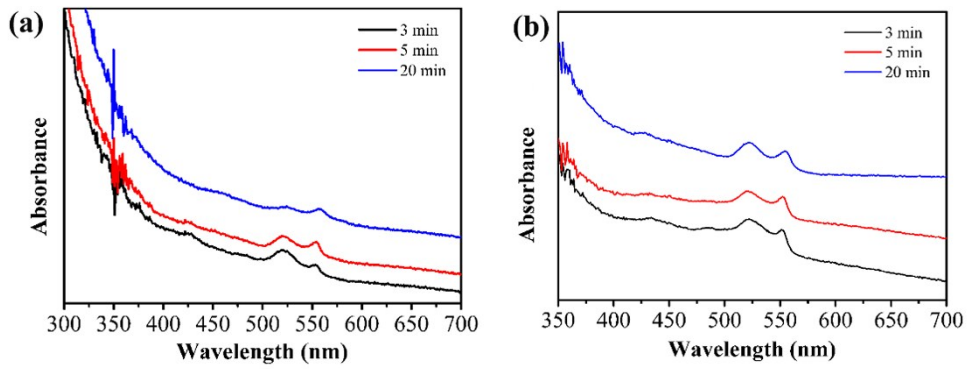

Fig.S2 The spectra of UV-vis of CdSe 2D nanocrystals at a lower concentration of the seeds (a) and at a higher concentration of the seeds (b).

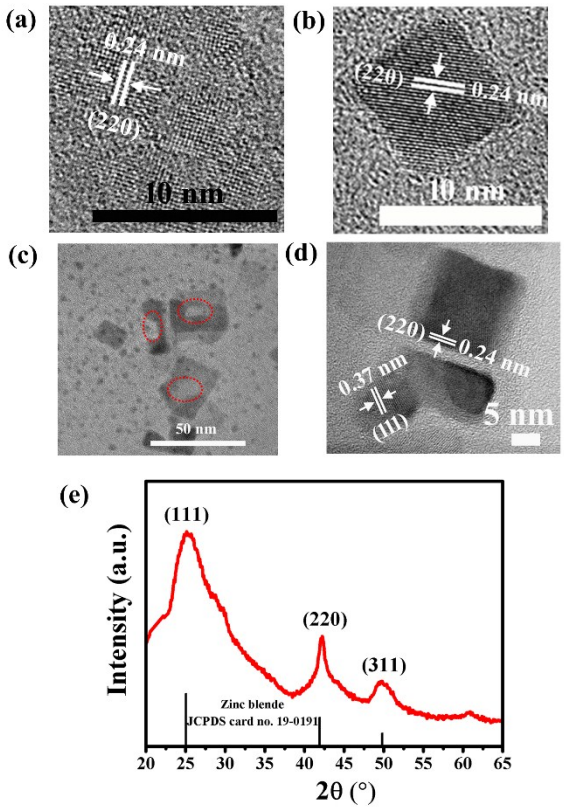

Fig. S3 (a, b, c and d) HRTEM images of CdSe 2D nanocrystals grown at the lower concentration of the seeds, (e) XRD pattern of the CdSe 2D nanocrystals, the standard zinc blende structure of CdSe (black line, JCPDS card no. 19-0191) inserted as references.

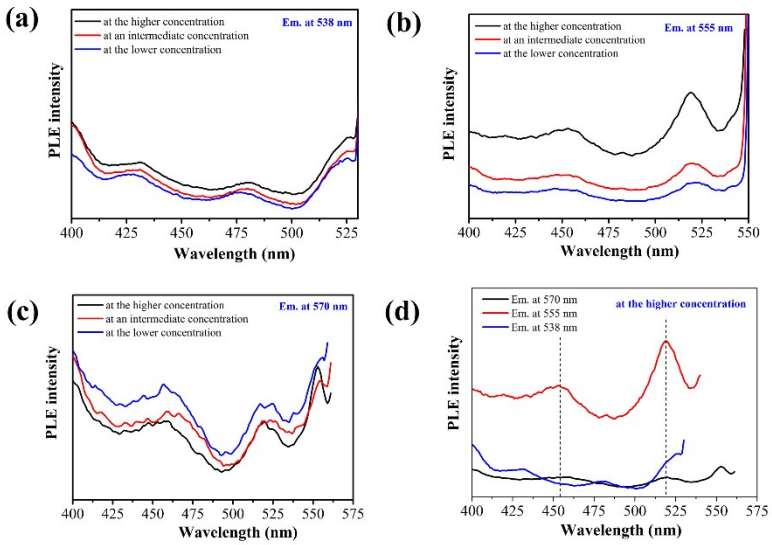

Fig. S4 The PLE spectra of the CdSe 2D nanocrystals obtained at different concentrations of CdSe seeds measured at PL peak position of 538 nm (a), 555 nm (b) and 570 nm (c) and normalized to its absorbance peak around at 554 nm, respectively. (d) the PLE spectra of the CdSe 2D nanocrystals grown at the higher concentration of CdSe seeds at different emission wavelength.

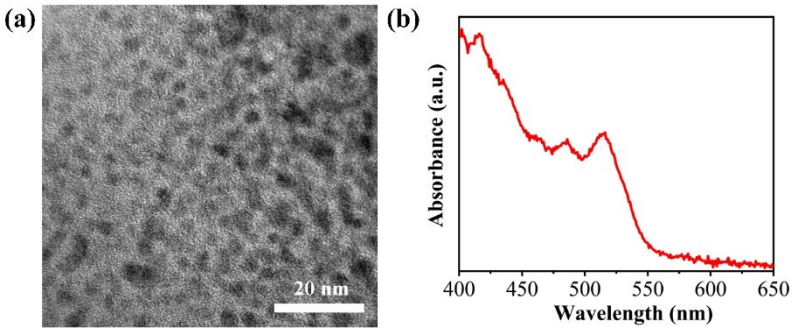

Fig. S5. TEM image (a) of CdSe 2D nanocrystals grown for 20 min at 230 ºC at an intermediate concentration of the seeds, and their corresponding absorption spectra (b).

References

1. Y. Chen, D. Chen, Z. Li and X. Peng, *J. Am. Chem. Soc.,* 2017, **139**, 10009-10019.