Mutual Transformation between Random Nanoparticles and Their Superlattices: The Configuration of Capping Ligand Chains

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Supporting Information



Figure S1. Monodisperse and random patterns of PbSe NPs. These NPs were quickly quenched at different temperature. (a) 150 °C; (b) 180 °C; (c) 240 °C; (d) 240 °C.



Figure S2. Different TEM patterns obtained at different quenching temperatures. (a) 100 °C; (b) 50 °C; (c) room temperature.



Figure S3. TEM images of PbSe NPs with stearic acids as ligands, which were quenched at different temperature. (a) 100 °C; (b) 50 °C; (c) room temperature.



Figure S4. TEM images of cubic PbSe NPs (a) and their superlattice structures (b and c). The wide-angle electron diffraction pattern inserted in Panel c indicates the cubic PbSe NPs were organized regularly. We utilized the approach performed in a three-neck flask to prepare these NPs and superlattices. The difference between this preparation and the one shown in the Experimental Section is that the reaction temperature should increase to 240 °C and was kept for 20min.

The influence of several conditions.

For the fabrication of NPs superlattices, there are several experimental conditions that have been investigated carefully, including:

1. Solution Effect. In our experiments, some different carrier solutions were used, such as TCE, hexane, dodecane, ethanol, toluene, etc. Taking the case of our PbSe NPs as an example, the purified PbSe NPs were dispersed into TCE, ethanol and toluene, respectively. In all these solutions, NPs could spontaneously assemble into their superlattice structures when dropped on the TEM grids (Figure S5).



Figure S5. TEM images of PbSe NP superlattices which were dispersed into different solutions. (a) toluene. (b) TCE. (c) ethanol.

2. Concentration Effect. When the crude NPs solution was naturally cooled down to RT, different packing morphologies were related to the NP concentration in solution. The diluted NP solution was easily arranged into an ordered monolayer shown in Figure S6a. With the increase of concentration, the periodic multilayer structure tended to be obtained (Figure S6b). On the contrary, when the NPs were quenched at high temperature, the periodic superlattices were difficultly observed (no matter what NP concentration in solution). Instead, the NPs appeared disperse and disordered.



Figure S6. (a) Ordered monolayer structures arranged by diluting the colloidal NPs solution. (b) Periodic multilayer structures arranged with the high-concentration NP solution (about two times higher than the concentration shown in Figure S6a)

3. Particle Size Distribution Effect. For the preparation of NP superlattices, the building block NPs should be quite uniform in size and shape, which is one of the important prerequisites. In our synthesis of PbSe NPs, the standard deviation (δ) of crystalline sizes was calculated to be 4.0-8.0% (Figure S7).



Figure S7. The standard deviation (δ) of crystalline size of PbSe NPs.

4. Solvent Evaporation Effect. Our experiments showed that the as-obtained monodisperse NPs could spontaneously self-assemble, not reliable on the evaporation time of solvents. We made all our superlattice samples by directly dropping the NPs solution on TEM grids in air (Figure S8).



Figure S8. A schematic illustration of dropping PbSe NP solutions on the TEM grids.

5. Ligand Effect. Monodisperse PbSe NPs with different acids as ligands (such as stearic acid and myristic acid) could also be synthesized by the one-pot approach. After the natural cooling and purification, they could spontaneously assemble into superlattice structures on TEM grids (Figure S9).



Figure S9. TEM images of PbSe NP superlattices which were synthesized by using different acids. (a) myristic acid (14C); (b) stearic acid (18C).



Figure S10. (a and b) The theoretic model in our calculations. (c) The cross section area and *D* value of stearic acid chains.



Figure S11. The transformation of ligand chains at elevated temperatures at D = 0.52 nm. (a) 300K, (b) 373K, and (c) 473K. (d) Time evolution of δ at 373K and 300K.



Figure S12. The transformation of capping ligand chains at elevated temperatures at D = 0.60 nm.