

# Superfluorescence from halide perovskite nanocrystal superlattices

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Progress has been made in accurately manipulating the size and shape of monodisperse nanocrystals over past 30 years. In 1993, Bawendi *et al.* synthesized monodisperse CdS, CdSe and CdTe nanocrystals with similar size by a hot-injection method<sup>[1]</sup>. After two years, they prepared CdSe nanocrystal superlattices by self-assembling method with two distinct morphologies: faceted colloidal crystals and ordered thin films. The size and spacing of nanocrystals were controlled with a nearly atomic precision<sup>[2]</sup>. Then, engineering morphology, interaction and surrounding environment are encouraged to construct superlattices at atomic scale. Meanwhile, the advanced technologies like electron microscopy and X-ray related tools help scientists to deeply understand the structures and properties of nanocrystal superlattices<sup>[3]</sup>. Compared to individual nanocrystal, their superlattices indicate collective properties due to coupling between nanocrystals<sup>[4]</sup>. For instance, their original properties are enhanced because the ordered nanocrystals interact with each other under the light, electric or magnetic field; new properties can be generated by the periodically ordered structures of the assembly; and comprehensive properties can be obtained *via* assembling nanocrystals with different functions.

Halide perovskite nanocrystals rapidly advances in recent years due to the tunable bandgaps, narrow emission, high photoluminescence quantum yields, and short radiation lifetime. They can be synthesized by a hot-injection method with narrow-distributed sizes, yielding nanoscale building blocks of superlattices. Especially, CsPbBr<sub>3</sub> nanocrystal superlattices attract wide attention because of the minibands caused by electronic coupling between neighboring nanocrystals<sup>[5]</sup>, low-threshold two-photon-induced gain<sup>[6]</sup>, long-range exciton diffusion<sup>[7]</sup>, tunable anisotropic light emission, and superfluorescence<sup>[8]</sup>. Superfluorescence is a collective emission from lots of light-excited individual dipoles unlike fluorescence. By exchanging virtual photons, the quantum states of dipoles spontaneously synchronize and are excited together, yielding a strong emission, called superfluorescence. Its intensity is much stronger than the sum of individual emitters.

CsPbBr<sub>3</sub> nanocrystals self-assembled into structurally well-defined, long-range ordered, and densely-packed cuboidal superlattices on silicon substrates by a solvent-drying-induced process, indicating quantum coherence for emitting superfluorescence<sup>[8]</sup>. Till now, superfluorescence was only observed in a very few systems because of the stringent produ-

cing conditions, e.g. high oscillator strength, low inhomogeneity, small exciton dephasing. Cubic CsPbBr<sub>3</sub> nanocrystals with a mean size of 9.5 nm can moderate quantum-confinement effect, offering narrow-band emission. The superlattices exhibited dynamically red-shifted emission peak with more than 20-fold accelerated radiative decay, extension of the first-order coherence time by more than a factor of four and photon bunching. Moreover, the superfluorescence decay demonstrates Burnham-Chiao ringing behavior at high excitation density, reflecting the coherent Rabi interaction. This iconic work provides potential candidates for high-brightness and multi-photon quantum light sources, enabling the utilization of coupling effects for long-range quantum transport and ultra-narrow tunable lasers.

In 2020, Zhou *et al.* generated a quantum coherence of dipoles in CsPbBr<sub>3</sub> nanocrystal superlattice and tuned the ultrafast radiation of the quantum systems by introducing optical microcavities<sup>[9]</sup>. The stimulated radiation in the superlattice microcavity was not limited by classical population-inversion condition, resulting in the dissipation of all in-phase dipoles in picoseconds. The highly symmetric and long-range ordered superlattice microcavity could have characteristics of both superfluorescence and stimulated radiation to realize cavity-enhanced superfluorescence (CESF). Compared to monodisperse CsPbBr<sub>3</sub> nanocrystals (~12 ns), the irradiation time of superfluorescence (~30 ps) was shortened by ~400 times, while that for CESF (~4 ps) was shortened by ~3000 times. Then, the essential difference between CESF and classical lasers was analyzed through a number of experiments. In classical lasers, excitons radiate rapidly above the threshold density, and radiate slowly below the threshold density. While in CESF, excitons have collaborative quantum states, and all dipoles in the same phase dissipate rapidly by a single pulse. Based on the quantum properties of cooperative excitons, a perovskite nanocrystal superlattice microcavity was proposed as a THz quantum container. The excited light can quickly induce carriers with high concentration, and the cooperative state is quickly established spontaneously *via* exchanging virtual photons, called the "Filled" state. When the relaxation channel of CESF opens, the quantum container is quickly emptied, called the "Void" status.

In 2021, ABX<sub>3</sub> superlattices were created *via* shape-directed co-assembly of binary or ternary elements, analogous to the lattice structure of ionic perovskites<sup>[10]</sup>. A, B and X positions are required to form nanocrystals for the single-component superlattices. In binary ABX<sub>3</sub> superlattice, larger spherical Fe<sub>3</sub>O<sub>4</sub> or NaGdF<sub>4</sub> nanocrystals occupy A sites, while smaller cubic CsPbBr<sub>3</sub> nanocrystals locate at B and X sites. Tiny change

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in sizes and fractions of spherical  $\text{Fe}_3\text{O}_4$  and cubic  $\text{CsPbBr}_3$  nanocrystals can transform NaCl-type to  $\text{ABX}_3$ -type binary superlattices. In ternary  $\text{ABX}_3$  superlattice, B position is replaced by truncated cubic PbS nanocrystals. The respective nanocrystal sizes are carefully adjusted in ternary superlattices consisting of cubic  $\text{CsPbBr}_3$  nanocrystals, spherical  $\text{Fe}_3\text{O}_4$  nanocrystals and truncated cubic PbS nanocrystals, which can assemble to fill  $\sim 92\%$  of the space. The spherical nanocrystals exhibit random orientation. While cubic  $\text{CsPbBr}_3$  nanocrystals exhibit highly ordered orientation in all superlattices, giving the superfluorescence.  $\text{ABX}_3$ -type superlattices offer strong collective emission than NaCl-type superlattices, due to stronger coherent coupling. The superfluorescence features ultrafast radiative decay (22 ps) and Burnham-Chiao ringing behavior.

Superfluorescence was observed at extremely low temperature, because the synchronized dipoles can be disturbed by thermal noise. In 2022, room-temperature superfluorescence was discovered in quasi-2D PEA: $\text{CsPbBr}_3$  films<sup>[11]</sup>. The long PEA cations separate  $\text{PbI}_6$  octahedra layers to form quantum-well structures, which can be considered as 2D hybrid perovskite superlattices. The electronic coherence time for PEA: $\text{CsPbBr}_3$  films is at least two orders of magnitude longer than that of inorganic semiconductors. Large electronic dipoles have strong coupling to protect quantum coherence at temperature as high as 300 K.

In short, quantum coherence yields superfluorescence. However, the superfluorescent superlattice is only found in highly-oriented  $\text{CsPbBr}_3$ -containing assembly so far, more perovskite superlattices need to be developed. Future research will involve perovskite materials<sup>[12]</sup>, perovskite crystallization<sup>[13]</sup>, perovskite nanocrystals<sup>[14]</sup>, stimulated emission<sup>[15]</sup>, and probably applications in light-emitting diodes<sup>[16]</sup>.

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