Multicomponent perovskite superlattices

Atanu Jana,1 Yongcheol Jo,1 and Hyunsik Im1,*

Developing multicomponent superlattices (SLs) using lead halide perovskite nanocrystals (NCs) is challenging due to weak ionic bonding and the high ionic mobility of halide ions. Recently, Kovalenko et al. developed multicomponent SLs, including binary cubic SLs, binary perovskite-like SLs, ternary perovskite-like SLs, and columnar binary SLs.

The cubic CsPbBr3 nanocrystals (NCs) are promising building blocks for SLs that produce short, intense bursts of light known as superfluorescence (SF) previously observed in HF gas, CuCl-doped NaCl, peroxide ion-doped KCl, and InGaAs/GaAs semiconductors.1 The monocomponent CsPbBr3 NC-based superlattices (SLs) showed SF due to their self-organized, highly ordered three-dimensional SL structures. Generally, the formation of SLs from monocomponent colloidal NCs is more favorable than multicomponent colloidal NCs.2 Interestingly, colloidal NCs mimic the symmetry of the molecular structures NaZn13, Cu3Au, NaCl, AlB2, and CaCu5 in the formation of binary and ternary SLs.3 The formation of SLs is governed by several factors such as entropy; van der Waals, ionic, or dipolar interparticle interactions; and the size and shape of NCs.4 In 1995, the first multicomponent SLs were reported using Au and CdSe NCs,5 whereas the first monocomponent CsPbBr3 SLs were developed by Kovalenko et al. in 2015 (Figure 1A).6 After that, different metal ions have been incorporated into CsPbBr3 SLs, including Au.7 However, the metal-doped NCs only showed the CsPbBr3 SLs without the formation of binary SLs. Different types of CsPbBr3 heterostructures have also been developed using metal oxides, chalcogenides, noble metals, and 2D materials without the formation of binary or ternary SLs.8 Although monocomponent CsPbBr3 NC-based SLs have excellent emissive qualities, multicomponent-based CsPbBr3 SLs have not been investigated.

Recently, Kovalenko et al. used different types of multiananocrystals, including spherical Fe2O3, spherical NaGdF4, and truncated-cuboid PbS along with cubic all-inorganic perovskite, CsPbBr3 NCs for growing AB2O3, NaCl, and AlB2-type SLs.9

The creation of multicomponent SLs...
utilizing cubic NCs is problematic because, unlike spherical NCs, these NCs adopt multiple orientations within the unit cell.

The A sites in binary ABO₃ SLs are occupied by larger spherical Fe₃O₄ or NaGdF₄ NCs, whereas the B and O sites are occupied by smaller cubic CsPbBr₃ NCs (Figure 1C). The B sites in ternary ABO₃-type SLs are inhabited by truncated-cuboid PbS nanocrystals and the other sites are similar to binary ABO₃ SLs (Figure 1D). In AlB₂ SLs, larger spherical Fe₃O₄ is found in the cube’s corners, while smaller cubic CsPbBr₃ NCs are found solely on the cube’s two opposite faces (Figure 1E). Partially ternary ABO₃ was also obtained using 19.8 nm Fe₃O₄, 10.7 nm PbS, and 8.6 nm CsPbBr₃ (Figure 1F). Columnar binary SLs: 5.3 nm CsPbBr₃ cubes and (16.6–21 nm) LaF₃ nanodisks (gray disk).

Figure 1 was produced by H.I., Y.J., and A.J.

is detrimental to the formation of SLs. A short-chain surfactant was utilized to substitute the long-chain hydrocarbon to avoid this issue. These sharp cuboid CsPbBr₃ NCs become stuck in specific orientations in the SLs due to their cubic geometry and surface deformability. Mixing 8.6 nm CsPbBr₃ NCs with 14.5–20.7 nm Fe₃O₄ yielded ABO₃-type SLs. However, no ABO₃-type SLs were observed with CsPbBr₃ NCs (5.3 nm) of smaller size due to their increased softness. Interestingly, the ABO₃-, AlB₂-, and NaCl-type SLs compete for 8.6 nm CsPbBr₃ NCs paired with 15.6–19.8 nm Fe₃O₄ NCs. The NaCl-type SL is preferred when the size of A-site spheres is further raised to 25.1 nm. Kovalenko et al. carefully adjusted the relative diameters of the nanocrystals in the ternary ABO₃-type SLs of CsPbBr₃ nanocubes, Fe₃O₄ nanospheres, and truncated PbS nanocubes. Combining 8.6-nm CsPbBr₃ nanocubes with 15.2–19.5 nm NaGdF₄ NCs, ABO₃-type SLs were also achieved. These SLs showed SF at low temperatures with pulsed excitation due to long exciton coherence, high transition oscillator strength, and low disorder energy of each CsPbBr₃ NC. The SF pulses were as short as 22 picoseconds, making these SLs promising candidates for use as ultrafast light emitters with exceptional energy efficiency. ABO₃-type SLs showed better SF than NaCl-type SLs due to a higher perovskite NC to dielectric NC ratio, NaGdF₄, and a shorter distance between perovskite NCs. The characteristic SF of the ABO₃-type SLs may be further tuned by increasing the size of the NaGdF₄ NCs. These SLs on a dielectric Si₃N₄ membrane showed better SF than SLs on a carbon-coated Cu grid due to an enhanced SL-substrate interaction with the conductive carbon film. All these findings will pave the way for the development of next-generation solid-state light emitters.

A large amount of SLs is required for their practical applications. However,
Kovalenko et al. demonstrated the syntheses of SLs only on different kinds of substrates such as carbon-coated TEM (transmission electron microscope) grids, silicon nitride membranes, and hydrofluoric acid (HF)-treated silicon. A challenging question is: would it be possible to synthesize these SLs in large quantities without a substrate? Furthermore, if the transition-metal-based NCs are employed, the fluorescence characteristics of CsPbBr$_3$ NCs in multination crystal-based SLs may be dramatically reduced. In this regard, what optical properties would Fe$_3$O$_4$ and CsPbBr$_3$ NC-based, binary NaCl-type SLs have? In addition, only SLs based on CsPbBr$_3$ NCs showed superfluorescence. Would it be better to put non-fluorescent or near-infrared-emissive colloidal NCs within the green-light-emitting CsPbBr$_3$ SLs instead of the pure one? The superfluorescence of SLs largely depends on the choice of substrate. Therefore, the choice of a proper substrate will play an essential role in device performance. Furthermore, it is expected that SLs will demonstrate improved electron transport, catalytic activity, or light absorption and emission compared to scattered NCs. Further dedicated research is required to show the potential applications of these newly developed SL materials. Finally, we believe that various perovskites, metal oxides, chalcogenides, noble metals, and 2D materials could be used to create a library of SLs of perovskite NCs.

**ACKNOWLEDGMENTS**

This work was supported by the NRF (National Research Foundation), Korea (grant no. 2021R1A4A5031805).


**Molecular protectors: Superheroes for nanostructures**

Jon Babi, Azalea Uva, Abigail Mae Clapperton, Angela Lin, and Helen Tran

Protecting complex nanostructures from degradation in physiological fluids while preserving their function remains a major limitation toward their implementation in biosensing and drug delivery. Using peptoid oligomers, Gang and coworkers protect DNA origami structures from Mg$^{2+}$ depletion and enzymatic breakdown.

The advent of nanotechnology has led to the ability to program the self-assembly of nanomaterials into well-defined structures that can be tailored for use in biomedical applications such as biosensing, drug delivery, and imaging. The rational design of nanostructures for desired applications requires precise control over their size, shape, and morphology. As seen in nature, the precise folding of biological molecules (i.e., peptide chains and nucleic acids) into their secondary structures is fundamental to their activity as the loss of this well-defined structure translates into a direct loss of...