

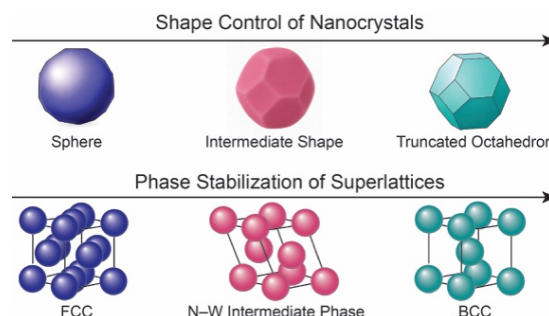


Capturing the Transient Phases of Nanocrystal Superlattice via Shape-Controlled Synthesis

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Abstract: Nanocrystal superlattices are ordered arrays of colloidal nanocrystals, often viewed as artificial solids in which nanocrystals replace atoms as the structural units. This article highlights a recent study in which the shape of silver nanocrystals was finely tuned to direct their assembly into superlattices from face-centered cubic to body-centered cubic structures, while accessing the transient intermediate structures along the Nishiyama-Wassermann martensitic pathway. By tuning nanocrystal sphericity and revealing the role of soft ligand-mediated interactions through computational simulation, this work shows how the shape of nanocrystal can be tailored to stabilize an intermediate superlattice phase and modulate its optical response.



Keywords: nanocrystal superlattice; Nishiyama-Wassermann pathway; phase-intermediate structure

Colloidal nanocrystals (NCs) can serve as “artificial atoms” to crystallize into periodic superlattices (SLs), in which the arrangement of NC centers defines lattice symmetry, unit cells, and diffraction features analogous to those of atomic crystals [1,2]. This analogy has made NC SLs a useful platform for translating crystallographic structures, such as face-centered cubic (FCC) and body-centered cubic (BCC) lattices, into mesoscale materials assembled from colloidal particles [3]. At the same time, NCs differ from atoms because they possess controllable size, shape, crystallographic facets, surface ligands, and degrees of rotational freedom, all of which provide additional handles for controlling SL structures [4–6].

The programmability makes NC SLs attractive for probing structural intermediates that are difficult to access in atomic crystals. During solid-state phase transitions, especially diffusionless martensitic transformations between high-symmetry lattices, intermediate configurations determine the transformation pathway and energy landscape [7]. Yet the intermediates are usually transient and unstable, making them difficult to isolate under ambient conditions. In NC assemblies, the larger size of the building blocks, together with tunable particle geometry and surface chemistry, make it possible to stabilize and structurally resolve such transition-related states. The technical challenge is to convert a normally transient crystallographic intermediate into a persistent and well-defined SL phase.

Writing in *Science*, Nagaoka and co-workers addressed this challenge using shape-controlled Ag-NCs as SL building blocks [8]. These SLs were obtained through slow evaporation of dispersions Ag-NCs in hexane over several weeks, a condition identified as critical for producing structurally rigid SLs with sharp and well-defined small-angle X-ray scattering (SAXS) peaks [9]. As shown in Figure 1A,B, spherical Ag-NCs crystallized into FCC SLs, whereas truncated octahedra (mecon)-shaped Ag-NCs assembled into BCC SLs. Most interestingly, when the shape of the NCs was tuned to an intermediate sphericity, synchrotron-based SAXS analysis identified a Nishiyama-Wassermann (N-W) phase-intermediate SL described by a base-centered monoclinic unit cell (Figure 1C). Taken together, by varying the shape of the Ag-NCs from sphere-like to mecon-like, the authors were able to trace a structural evolution from FCC to BCC and, most excitingly, stabilize an otherwise transient intermediate SL phase under ambient conditions.

As expected, the stabilization of the intermediate phase could not be explained by particle shape alone. In simulations using only the stiff interaction model, the SL showed an abrupt transition between FCC and BCC lattices as the sphericity parameter was changed (Figure 1D). In contrast, the total potential model, which combines



stiff and soft interactions, reproduced the experimentally observed continuous structural evolution. This result highlights the importance of soft ligand-mediated interactions in addition to NC geometry. Computational modeling further elucidated the evolution of orientational order and soft ligand-induced facet-to-facet interactions among neighboring Ag-NCs as the SL evolved from FCC to BCC through the intermediate phase (Figure 1E). These combined effects allow Ag-NCs with intermediate sphericity to access and stabilize the N-W intermediate phase.

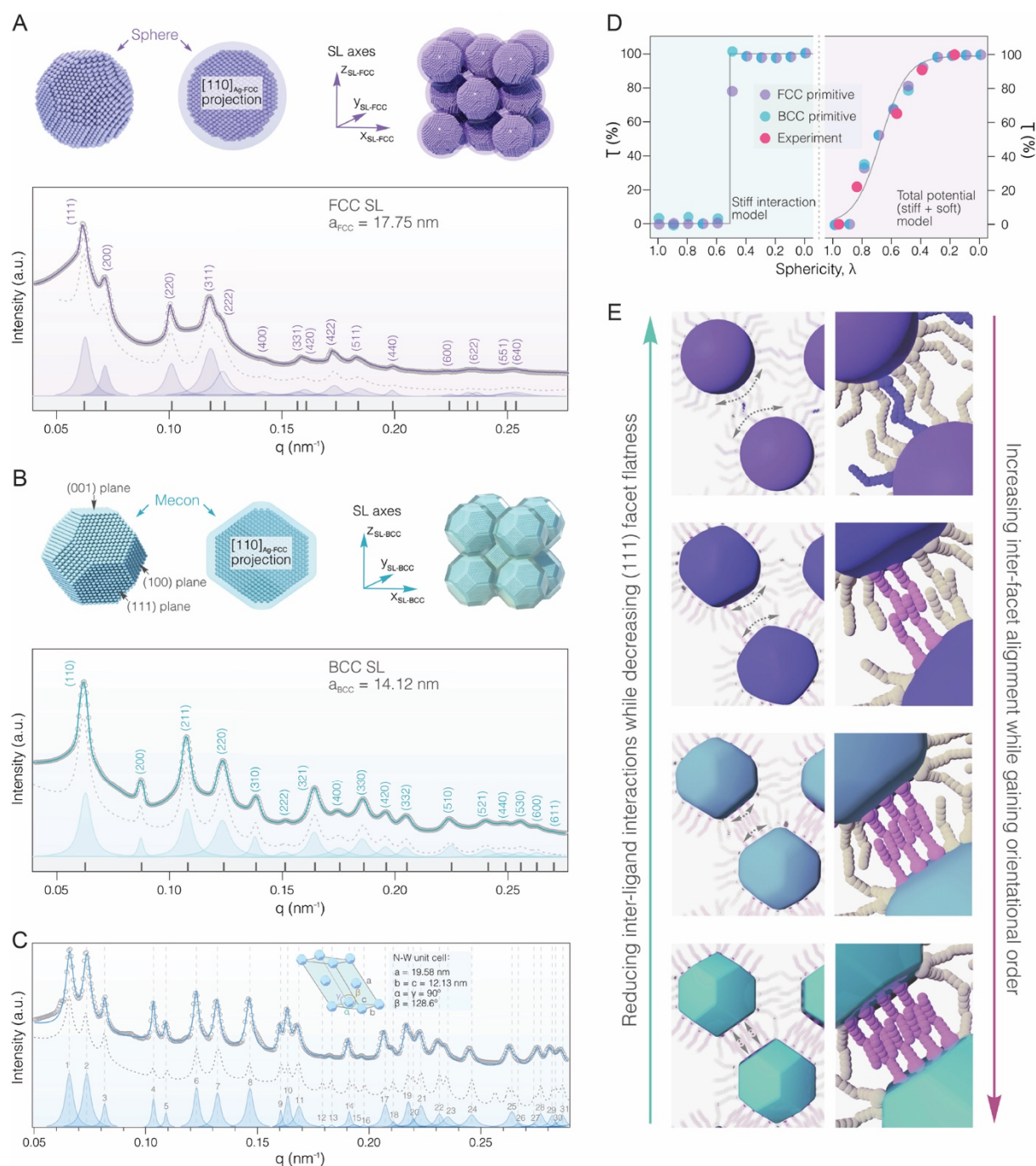


Figure 1. Stabilization of SLs comprised of shape-controlled Ag-NCs. **(A,B)** Spherical and mecon-shaped Ag-NCs crystallized into FCC and BCC SLs, respectively, as confirmed by SAXS analysis. **(C)** Ag-NCs with intermediate sphericity formed an N-W phase-intermediate SL described by a base-centered monoclinic unit cell. **(D)** Simulations showed that the stiff interaction model gave an abrupt FCC-to-BCC transition, whereas the total potential model, which combined stiff and soft interactions, reproduced the experimentally observed structural evolution. **(E)** Computational models of neighboring Ag-NCs in FCC, intermediate phase, and BCC SLs, highlighting the evolution of orientational order of the constituent Ag-NCs and soft ligand-induced facet-to-facet interactions. Modified from Ref. [7] with permission. Copyright 2026, The American Association for the Advancement of Science.

Beyond structural control, the ability to stabilize SLs in intermediate phases may create opportunities for tuning their collective properties [10]. In the reported Ag-NC SLs, FCC, N-W intermediate phase, and BCC structures all exhibited plasmon-photon hybridization and reached the deep-strong light-matter coupling regime [8,11]. The stable intermediate structure therefore provides an experimentally accessible bridge for examining how optical coupling evolves between the two endpoint lattices. To sum up, this work shows that shape control of NCs can stabilize otherwise transient intermediate structures while preserving tunable collective optical responses.

Looking forward, the broader impact of this work will depend on both conceptual generality and operational stability. It remains unclear whether shape control can stabilize intermediate phases beyond the Ag-NC FCC-to-BCC/N-W pathway, particularly for other NC compositions or transformation pathways. In addition, although the N-W phase-intermediate SLs remained stable for at least 6 months under ambient conditions, their use as optical metamaterials or in polaritonic devices will require stability under thermal cycling, mechanical vibration, light exposure, and large-area film-processing conditions. Addressing these issues would move transient SL phases from structural curiosities toward practical functional materials.

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