

## Expansion of Semiconductor Ionic Nanocrystal Superlattice Library through Cation Exchange Reactions

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Semiconductor ionic nanocrystal (NC) superlattices (SLs) formed by assembling uniform NCs have gained widespread attention in novel applications due to the unique collective properties that cannot be realized by isolated NCs or corresponding bulk counterparts. To meet various target applications, NC SLs with designed morphology, composition, and NC size will be highly desirable. Nevertheless, the exploration of NC SLs is still hampered by the complexity and limited scalability of conventional preparation methods. Therefore, the expansion of the NC SLs library is meaningful for novel materials exploration and innovative application.

In this study, we first synthesized three-dimensional (3D)  $\text{Cu}_{2-x}\text{S}$  NC SLs with anisotropic and isotropic structures via a rapid one-step chemical liquid-phase reaction with controlled concentration of alkylamine ligands (Fig. 1a). Then, various new ionic NC SLs were easily obtained via rapid and scalable cation exchange (CE) reactions. All original  $\text{Cu}^+$  cations were successfully replaced with foreign metal cations, resulting in different metal sulfide NC SLs with the same morphology and arrangement system as the parent NC SLs. Notably, because the stacking mode of  $\text{S}^{2-}$  anion framework remains unchanged, the assembled NCs will also have a selective crystallographic arrangement in the new NC SL (Fig. 1b) and exhibit unique optical properties in anisotropic metal sulfide NC SLs. Furthermore, we found that the species of exchanged metal cations could affect the CE behavior in individual NCs and CE pathways of NC SLs. Based on the above one-step liquid phase synthesis mechanism and CE scheme, we also successfully synthesized 3D  $\text{Cu}_{2-x}\text{Se}$  NC SLs by adjusting the alkyl ligands and chalcogenide donors and expanded them into distinct metal selenide NC SLs through CE reactions. This work is expected to facilitate the expansion of NC SLs library<sup>1</sup> and the exploration of novel collective functions.<sup>2</sup>



**Fig.1** (a) Scheme of one-pot synthesis method of NC SLs and expansion of SLs species via CE, (b) preservation of crystallographic arrangement in the  $\text{Cd}^{2+}$  cation exchange.

- 1) Saruyama et al. *Chem. Sci.* **2024**, *15*, 2425.
- 2) Tahara et al. *Nat. Nanotechnol.* **2024**, *19*, 744-750.