Deterministic Nanocrystal Self-Assembly into Multifunctional Artificial Solids

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The nanoscale confinement of charge carriers results in the emergence of interesting physical phenomena that define the response of crystalline nanoparticles, nanocrystals (NCs), to external stimuli. In the last decade, the efforts of the scientific community have led to the optimization of synthetic protocols reproducibly yielding colloidal NCs with tunable sizes, shapes, and compositions, effectively establishing a “periodic table” based on NCs as the ultimate building blocks.

The controlled integration of NCs with distinct functionalities into dense superstructures represents a promising approach to establish a new class of metamaterials with physical properties directly defined from the bottom-up. However, our limited understanding of the nanoscale interactions controlling NC self-assembly has so far delayed the deterministic hetero-integration of NCs, hampering the investigation of their structure-property relationships, and ultimately limiting the discovery of new physics and the development of new applications.

In this talk, I will introduce a general and scalable approach to bias the assembly of NC into three-dimensional superstructures with a well-defined and reproducible morphology. We use an emulsion template to drive the formation of spherical colloidal superstructures composed of ordered NCs.[1] Following the assembly *in situ* via synchrotron-based X-ray scattering reveals a ligand-mediated hard-sphere-like crystallization process,[2] resulting in the growth of superstructures close to single-crystal quality.[3] The resulting superstructures display an intriguing combination of multiscale properties: While their refractive index is set by the choice of the constituent NCs, their interaction with light is that of a mesoscale dielectric sphere, resulting in enhanced absorption and scattering through Mie resonances.[4] Performing a ligand exchange on the supercrystals boosts the interaction between neighboring NCs, as observed by the transition of the biexciton from a bound to a free state, and by the emergence of whispering gallery modes that guide light across the sphere’s surface.[5-6] Finally, I will show the first direct observation of the formation of binary crystals under spherical confinement,[7] as revealed by a novel feedback process between *in situ* experiments and molecular dynamics simulations.

[1] E Marino, et al., Chem. Mater. 34, 6, 2779–2789 (2022).
[2] E. Marino, *et al.*, Advanced materials 30 (43), 1803433 (2018).
[3] E. Marino, *et al.*, The Journal of Physical Chemistry C 124 (20), 11256–11264 (2020).
[4] E. Marino, *et al.*, ACS nano 14 (10), 13806–13815 (2020).
[5] E. Marino, *et al.*, Nano Lett. 22, 12, 4765–4773 (2022).
[6] S.J. Neuhaus, E. Marino, et al., Nano Lett., In Press (2023).
[7] E. Marino,* A. LaCour,* *et al.*, Under review (2022).