

(Invited) Marrying Top-Down Fabrication and Bottom-Up Assembly of Colloidal Nanocrystals to Construct Devices

C. R. Kagan

*Departments of Electrical & Systems Engineering, Materials Science & Engineering, Chemistry, University of Pennsylvania, Philadelphia, PA 19104
kagan@seas.upenn.edu*

Wet-chemical synthetic methods enable the preparation of a library of colloidal nanocrystals (NCs) tailored in their size, shape, and composition. These NCs typically consist of an inorganic core and an organic ligand shell. These NCs may be metallic, semiconducting, or magnetic and are prized for their size- and shape-dependent localized surface plasmon resonances, quantum confinement of carriers and excitons, and superparamagnetism, respectively. These NCs can be assembled to form functional solids with properties that depend on the individual NCs and their distance and arrangement in assemblies.

Here, we select plasmonic metal NCs as building blocks and by combining top-down fabrication and bottom-up assembly processes, we construct materials and devices with unconventional physical properties. To tailor interparticle distance, we chemically exchange the long ligands used in NC synthesis with more compact ligand chemistries.¹ This ligand-control of distance allows us to tailor a dielectric-to-metal phase transition seen by a 10^{10} range in DC conductivity and a dielectric permittivity ranging from everywhere positive to everywhere negative across the whole range of optical frequencies. We realize a "diluted metal" with optical properties not found in the bulk metal analog, presenting a new axis in plasmonic materials design and the realization of optical properties akin to next-generation metamaterials.

We harness the solution-processability and physical properties of colloidal plasmonic NCs to imprint NC superstructures for large-area, active metamaterials. We demonstrate quarter-wave plates with extreme bandwidths and high polarization conversion efficiencies in the near- to-mid infrared [Fig. 1a].² By combining superparamagnetic $\text{Zn}_{0.2}\text{Fe}_{2.8}\text{O}_4$ NCs and plasmonic Au NCs, we fabricate multifunctional, smart superparticles, which in suspensions, switch their polarization-dependent transmission in the infrared in response to an external magnetic field.³ We exploit the distinct chemical and mechanical properties of NC assemblies, in comparison to bulk materials, to create 2D, lithographically-defined NC/bulk bimorphs [Fig. 1b], which upon ligand exchange, transform to create functional 3D architectures [Fig. 1c].⁴

Time permitting, we will describe our use of lithography to define size- and shape-engineered topographical templates for the directed assembly of NC oligomer "metamolecules." Here, we explore the role of NC arrangement on the plasmon

resonances of NC assemblies. For example, we map the evolution in electric and magnetic dipole modes as we increase the number of nearest neighbor shells in close-packed spherical NC assemblies [Fig. 1d] and as we construct trimers of nanorods that assemble along the edges of equilateral triangles to form open structures [Fig. 1e].^{5,6} These NC assemblies may be used to sculpt the optical response of metamaterial assemblies.

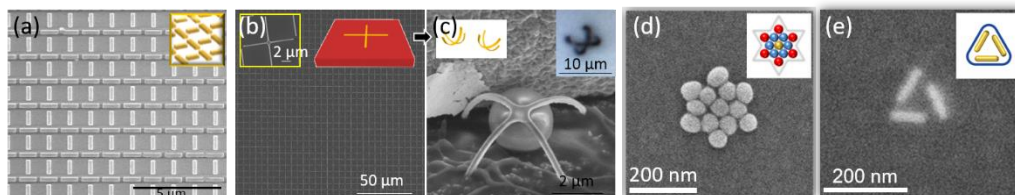


Figure 1: Nanoimprint lithography and solution-based deposition and ligand exchange of colloidal Au NCs are used to fabricate (a) Au NC-based quarter-wave plates and (b) 2D Au NC/Ti bimorphs that fold upon ligand exchange to form (c) 3D architectures, shown wrapping a silica bead. Lithography is used to define templates that direct the assembly of (d) spherical Au and (e) rod-shaped Au NCs to form "metamolecules."

¹ A.T. Fafarman, S.-H. Hong, H. Caglayan, X. Ye, B.T. Diroll, T. Paik, N. Engheta, C.B. Murray, and C.R. Kagan, *Nano Lett.* **13**, 350 (2013).

² W. Chen, M. Tymchenko, P. Gopalan, X. Ye, Y. Wu, M. Zhang, C.B. Murray, A. Alu, and C.R. Kagan, *Nano Lett.* **15**, 5254 (2015).

³ M. Zhang, D.J. Magagnosc, I. Liberal, Y. Yu, H. Yun, H. Yang, Y. Wu, J. Guo, W. Chen, Y.J. Shin, A. Stein, J.M. Kikkawa, N. Engheta, D.S. Gianola, C.B. Murray, and C.R. Kagan, *Nat. Nanotechnol.* **12**, 228 (2017).

⁴ M. Zhang, J. Guo, Y. Yu, Y. Wu, H. Yun, D. Jishkariani, W. Chen, N.J. Greybush, C. Kübel, A. Stein, C.B. Murray, and C.R. Kagan, *Adv. Mater.* 1800233 (2018).

⁵ N.J. Greybush, I. Liberal, L. Malassis, J.M. Kikkawa, N. Engheta, C.B. Murray, and C.R. Kagan, *ACS Nano* **11**, (2017).

⁶ N.J. Greybush, V. Pacheco-Peña, N. Engheta, C.B. Murray, and C.R. Kagan, *ACS Nano* acsnano.8b07619 (2019).