

# From Nano to Macro: Thinking Bigger in Nanoparticle Assembly

Robert J. Macfarlane\*



Cite This: *Nano Lett.* 2021, 21, 7432–7434



Read Online

ACCESS |

Metrics & More

Article Recommendations

Nanoparticle assembly enables the synthesis of multiple complex nanoscale structures, but future investigation and application of these materials requires new processing methods to control micro- and macroscale structure as well.

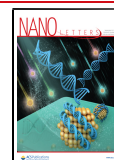
In the past few decades, nanoparticle (NP) self-assembly has advanced to the point that NP superlattice crystallization can be envisioned as a viable method for the fabrication of functional devices and technologies.<sup>1–3</sup> As with any new material whose synthetic methods are sufficiently developed, multiple questions now arise that must be addressed to progress the field. The two questions for the next phase in NP assembly research most commonly found in the current literature (either implicitly or explicitly) could arguably be stated as “What new properties do these materials have?” and “What are these superlattices good for?”.<sup>4–6</sup> Certainly, these are critical questions to transition NP superlattices from benchtop curiosities to useful materials. However, we run the risk of falling victim to a key blind spot in the standard materials development paradigm if we assume that the identification of properties and applications for these superlattices is the only hurdle remaining in their development. Specifically, advancing a material from its initial synthesis or discovery to its use in a functional application requires us to also answer the question of “How do we process these materials into a useful form?”.<sup>7,8</sup> Future research efforts with NP-based materials are going to rely on the ability to produce them in the right geometric configuration, as structure control beyond just nanoscale ordering is important in enabling both fundamental investigations of structure–property relationships and application in useful devices. Ultimately, the amount of impact NP superlattices will have in advancing both science and engineering depends on how well we can control their hierarchical structures beyond just their initial assembly.

Macroscopic structure control (e.g., mm-scale or larger) has obvious implications for the utility of NP superlattices, as the final form factor of the device or technological component dictates both how much material is needed and what its overall

shape needs to be. Processing the superlattices in a manner that does not disrupt all of the hard work spent making beautiful crystalline geometries is not necessarily a simple task, though, as most common material processing techniques designed for atomic, molecular, and macromolecular systems are not always compatible with the typically mild conditions used to form well-ordered NP arrays. Nominally 2D films and coatings from particle assembly can already be developed on the centimeter-scale or potentially larger,<sup>5,9–13</sup> but truly 3D macroscopic objects made via NP self-assembly that preserve nanoscale ordering are more rare.<sup>14–17</sup> Moreover, even in assembly methods capable of generating objects with at least some macroscopic dimension, manipulation of material microstructure is still underdeveloped. Microstructural features are key design factors used to control the characteristics and behavior of bulk atomic or molecular materials including mechanical (hardness, toughness, ductility), chemical (corrosion and etching, transport), and optical (light reflection and scattering) properties.<sup>7,18</sup> Understanding how factors like defects, grain sizes, or crystal texture in NP superlattices affect their performance is thus another critical area of investigation that is enabled by innovations in processing science.

So how do we establish processing methods for these NP superlattices to manipulate both micro- and macroscopic structure (without sacrificing nanoscale organization), and what are the key aspects of our various NP assembly techniques that we need to improve upon to enable such research? One of the obvious criteria for any processable NP superlattice is the ability to produce materials at an appropriate scale that the given processing technique being examined is physically feasible. This does not necessarily mean that we need to produce superlattice-based materials at the same tonnage as conventional bulk metals, ceramics, and polymers, but the amount of material has to match the form factor and scale of the proposed processing methods and applications. NP superlattice thin film architectures or micron-sized crystallites are valuable for 2D coatings or

Published: September 3, 2021



components of microdevices (and many fantastic and promising examples of devices built from these assemblies are already beginning to emerge<sup>5,11,19</sup>), but other, larger geometries would expand the types of scientific investigations into properties or performance that we could conduct. Molding, pressing, extruding, or even additive manufacturing techniques to make macroscopic 3D objects become much more viable when the NPs can both be synthesized and assembled in large quantities.<sup>14,20</sup> Moreover, an important lesson we can learn from bulk materials processing is that a wider variety of available processing methods significantly improves our ability to control microstructural features like grain sizes or crystal texture in polycrystalline NP superlattices.<sup>14,21,22</sup> It will therefore be advantageous to develop NP assembly methods that are amenable to as many different processing techniques as possible. Progression in this research area requires us to think carefully about the composition of the NPs we choose to synthesize and assemble and to coordinate our efforts with those of chemists, materials scientists, and engineers in related areas that enable large batch fabrication of the NP building blocks we will need. It also requires that we think about methods to integrate our assemblies with other material types, as the use of NP superlattices as additives to traditional bulk materials is a key opportunity to extend their utility. Embedding, mixing, coating, or otherwise incorporating ordered NP arrays as small but active fractions of a much larger and more inherently scalable material would significantly increase our ability to take advantage of the optical, chemical, magnetic, and other properties exhibited by precisely organized particle lattices.<sup>10,11,17,23,24</sup>

It is also important to realize that scaling up is more than just “making more” of a material. As noted above, materials that can be shaped or molded into larger objects provide significant opportunities to ask questions about how structural features at those larger length scales influence the properties of a material, such as how grain size affects mechanical deformation or transport behavior (two areas well-known to have major impact on the properties of polycrystalline atomic solids).<sup>18</sup> The ability to hierarchically organize materials across the nano-, micro-, and macroscale also allows for the concept of “systems” development of materials, where factors like macroscopic interfaces, boundary conditions, and the collective behavior of multiple organized units can feed back to influence the behavior of individual building blocks.<sup>4,25,26</sup> This mode of using integrated design features across  $\sim 10^9$  differences in size is a crucial aspect of biological materials and living organisms that enables their hierarchical structures, and assembling NP superlattices at the same macroscopic scale would offer the exciting opportunity to mimic such complexity.

The field of NP assembly has expanded significantly in the past few decades to the point that we can make hundreds of different superlattices with control over their composition, crystal symmetry, and lattice parameters.<sup>27–33</sup> Research is now beginning on the next stages of the materials development life cycle, examining the types of properties that we can generate and inventing new functions for these materials in next-generation technologies. However, it is critical that we do not assume that our mastery of NP crystallization means that we are done exploring the area of materials formation and structure control or that the only challenge remaining is figuring out what the materials that we have made are good for. Structure–property relationship development is certainly a key aspect of advancing the field, but there is still much left to investigate in processing and integration of these materials into different micro- and

macroscale forms. It is essential to research those aspects of material synthesis with the same fervor that drove the development of new superlattice crystal structures over the past few decades. Indeed, now that we have this level of sophistication in synthesizing different NP-based crystals, the next important steps for this area of nanotechnology research paradoxically lie at size regimes well beyond the 1–100 nm length scale, by establishing methods to hierarchically organize solids with precisely designed and intentionally fabricated microstructural features and macroscopic forms. More simply, the future of NP assembly as a materials development tool is in “thinking bigger”.

## AUTHOR INFORMATION

### Corresponding Author

Robert J. Macfarlane – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;  
orcid.org/0000-0001-9449-2680; Email: rmacfarl@mit.edu

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.nanolett.1c02724>

### Funding

R.J.M. acknowledges support from the NSF via a CAREER award (CHE-1653289) and the Air Force Office of Scientific Research via a young investigator award (FA9550-17-1-0288).

### Notes

The author declares no competing financial interest.

## ACKNOWLEDGMENTS

R.J.M. acknowledges Matthew R. Jones for valuable discussions.

## REFERENCES

- (1) Gabrys, P. A.; Zornberg, L. Z.; Macfarlane, R. J. Programmable Atom Equivalents: Atomic Crystallization as a Framework for Synthesizing Nanoparticle Superlattices. *Small* **2019**, *15* (26), 1805424.
- (2) Boles, M. A.; Engel, M.; Talapin, D. V. Self-Assembly of Colloidal Nanocrystals: From Intricate Structures to Functional Materials. *Chem. Rev.* **2016**, *116* (18), 11220–11289.
- (3) Grzelczak, M.; Liz-Marzán, L. M.; Klajn, R. Stimuli-Responsive Self-Assembly of Nanoparticles. *Chem. Soc. Rev.* **2019**, *48*, 1342.
- (4) Grzybowski, B. A.; Fitzner, K.; Paczesny, J.; Granick, S. From Dynamic Self-Assembly to Networked Chemical Systems. *Chem. Soc. Rev.* **2017**, *46* (18), 5647–5678.
- (5) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem. Rev.* **2010**, *110* (1), 389–458.
- (6) Jones, M. R.; Osberg, K. D.; Macfarlane, R. J.; Langille, M. R.; Mirkin, C. A. Templated Techniques for the Synthesis and Assembly of Plasmonic Nanostructures. *Chem. Rev.* **2011**, *111*, 3736–3827.
- (7) Callister, W. D.; Rethwisch, D. G. *Materials Science and Engineering: An Introduction*; Wiley-VCH, 2012.
- (8) Begley, M. R.; Gianola, D. S.; Ray, T. R. Bridging Functional Nanocomposites to Robust Macroscale Devices. *Science* **2019**, *364* (6447), eaav4299.
- (9) Dong, A.; Chen, J.; Vora, P. M.; Kikkawa, J. M.; Murray, C. B. Binary Nanocrystal Superlattice Membranes Self-Assembled at the Liquid–Air Interface. *Nature* **2010**, *466* (7305), 474–477.
- (10) Cho, H.; Pan, J.-A.; Wu, H.; Lan, X.; Coropceanu, I.; Wang, Y.; Cho, W.; Hill, E. A.; Anderson, J. S.; Talapin, D. V. Direct Optical Patterning of Quantum Dot Light-Emitting Diodes via In Situ Ligand Exchange. *Adv. Mater.* **2020**, *32* (46), 2003805.
- (11) Choi, J.-H.; Wang, H.; Oh, S. J.; Paik, T.; Sung, P.; Sung, J.; Ye, X.; Zhao, T.; Diroll, B. T.; Murray, C. B.; Kagan, C. R. Exploiting the

Colloidal Nanocrystal Library to Construct Electronic Devices. *Science* **2016**, 352 (6282), 205.

(12) Hattton, B.; Mishchenko, L.; Davis, S.; Sandhage, K. H.; Aizenberg, J. Assembly of Large-Area, Highly Ordered, Crack-Free Inverse Opal Films. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, 107, 10354–10359.

(13) Ye, X.; Zhu, C.; Ercius, P.; Raja, S. N.; He, B.; Jones, M. R.; Hauwiler, M. R.; Liu, Y.; Xu, T.; Alivisatos, A. P. Structural Diversity in Binary Superlattices Self-Assembled from Polymer-Grafted Nanocrystals. *Nat. Commun.* **2015**, 6, 10052.

(14) Santos, P. J.; Gabrys, P. A.; Zornberg, L. Z.; Lee, M. S.; Macfarlane, R. J. Macroscopic Materials Assembled from Nanoparticle Superlattices. *Nature* **2021**, 591 (7851), 586–591.

(15) Dreyer, A.; Feld, A.; Kornowski, A.; Yilmaz, E. D.; Noei, H.; Meyer, A.; Krekeler, T.; Jiao, C.; Stierle, A.; Abetz, V.; Weller, H.; Schneider, G. A. Organically Linked Iron Oxide Nanoparticle Supercrystals with Exceptional Isotropic Mechanical Properties. *Nat. Mater.* **2016**, 15 (5), 522–528.

(16) Nagaoka, Y.; Tan, R.; Li, R.; Zhu, H.; Eggert, D.; Wu, Y. A.; Liu, Y.; Wang, Z.; Chen, O. Superstructures Generated from Truncated Tetrahedral Quantum Dots. *Nature* **2018**, 561 (7723), 378–382.

(17) Hueckel, T.; Hocky, G. M.; Palacci, J.; Sacanna, S. Ionic Solids from Common Colloids. *Nature* **2020**, 580 (7804), 487–490.

(18) Gottstein, G. *Physical Foundations of Materials Science*; Springer: Berlin Heidelberg, 2013.

(19) Park, D. J.; Zhang, C.; Ku, J. C.; Zhou, Y.; Schatz, G. C.; Mirkin, C. A. Plasmonic Photonic Crystals Realized through DNA-Programmable Assembly. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, 112 (4), 977–981.

(20) Tan, A. T. L.; Beroz, J.; Kolle, M.; Hart, A. J. Direct-Write Freeform Colloidal Assembly. *Adv. Mater.* **2018**, 30 (44), 1803620.

(21) Zornberg, L. Z.; Gabrys, P. A.; Macfarlane, R. J. Optical Processing of DNA-Programmed Nanoparticle Superlattices. *Nano Lett.* **2019**, 19 (11), 8074–8081.

(22) Gabrys, P. A.; Macfarlane, R. J. Controlling Crystal Texture in Programmable Atom Equivalent Thin Films. *ACS Nano* **2019**, 13 (7), 8452–8460.

(23) Auyeung, E.; Macfarlane, R. J.; Choi, C. H. J.; Cutler, J. I.; Mirkin, C. A. Transitioning DNA-Engineered Nanoparticle Superlattices from Solution to the Solid State. *Adv. Mater.* **2012**, 24, 5181–5186.

(24) Kubiak, J. M.; Morje, A. P.; Lewis, D. J.; Wilson, S. L.; Macfarlane, R. J. Dynamic Manipulation of DNA-Programmed Crystals Embedded in a Polyelectrolyte Hydrogel. *ACS Appl. Mater. Interfaces* **2021**, 13 (9), 11215–11223.

(25) Santos, P. J.; Cao, Z.; Zhang, J.; Alexander-Katz, A.; Macfarlane, R. J. Dictating Nanoparticle Assembly via Systems-Level Control of Molecular Multivalency. *J. Am. Chem. Soc.* **2019**, 141 (37), 14624–14632.

(26) Yang, P.; Tarascon, J.-M. Towards Systems Materials Engineering. *Nat. Mater.* **2012**, 11 (7), 560–563.

(27) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. Structural Diversity in Binary Nanoparticle Superlattices. *Nature* **2006**, 439 (7072), 55–59.

(28) Macfarlane, R. J.; Lee, B.; Jones, M. R.; Harris, N.; Schatz, G. C.; Mirkin, C. A. Nanoparticle Superlattice Engineering with DNA. *Science* **2011**, 334, 204–208.

(29) Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. Electrostatic Self-Assembly of Binary Nanoparticle Crystals with a Diamond-like Lattice. *Science* **2006**, 312, 420–424.

(30) Liu, W.; Tagawa, M.; Xin, H. L.; Wang, T.; Emamy, H.; Li, H.; Yager, K. G.; Starr, F. W.; Tkachenko, A. V.; Gang, O. Diamond Family of Nanoparticle Superlattices. *Science* **2016**, 351, 582–587.

(31) Lewis, D. J.; Zornberg, L. Z.; Carter, D. J. D.; Macfarlane, R. J. Single-Crystal Winterbottom Constructions of Nanoparticle Superlattices. *Nat. Mater.* **2020**, 19, 719.

(32) Zhang, J.; Santos, P. J.; Gabrys, P. A.; Lee, S.; Liu, C.; Macfarlane, R. J. Self-Assembling Nanocomposite Tectons. *J. Am. Chem. Soc.* **2016**, 138 (50), 16228–16231.

(33) Girard, M.; Wang, S.; Du, J. S.; Das, A.; Huang, Z.; Dravid, V. P.; Lee, B.; Mirkin, C. A.; Olvera de la Cruz, M. Particle Analogs of Electrons in Colloidal Crystals. *Science* **2019**, 364 (6446), 1174–1178.