Chirality and Complexity of Biomimetic Nanostructures

Nicholas A. Kotov, University of Michigan, Ann Arbor, USA

Chiral nanostructures are a large and rapidly evolving class of biomimetic materials. Besides fascinating optical, catalytic, and biological properties, the studies of chiral nanostructures represent a missing link in the emergence of complexity in Nature. *Complexity*, i.e. purposeful combination of order and disorder, leads to nontrivial combination of properties needed for many technologies. In the context of self-assembled particles, complexity manifests as spontaneous increase of structural hierarchy and correlated disorder seemingly prohibited by thermodynamics. These observations mirror the structural evolution of biological materials that combine nano-, meso- and microscale chirality. Taking an example of complex particles with twisted spikes and layer-by-layer-assembled nacre-like composites, we found that:

(a) formation of complex structures does not require monodispersity;

(b) competing thermodynamic restrictions in self-limited systems increase their complexity;

(c) synthetic particles can have higher complexity than their biological prototypes.

These findings were possible by applying graph theoretical (GT) measures of complexity to nanoparticle assemblies. Their applicability to 'imperfect' (nano)particles and ability to capture essential structural motifs made possible to include other nanoscale structures, such as complex porous particles and superlattices,[2] creating analogs of chemical formulas for complex particle systems (chiral, racemic and achiral). Understanding of intermolecular forces and expansion of self-limited assembly to bulk dispersions of diverse nano(particles) enabled the design of hierarchically organized bowtie-shaped particles with variable twist, size, and thickness and length.[3]

Structural complexity and technological significance are related. The simple pathways to complex particle systems with technological significance will be demonstrated for self-assembled chiral catalysts.[4] The complex particle nanosystems combining order and disorder with technological significance will be demonstrated for self-assembled analogs of cartilage that can be designed using GT for biomedical devices, batteries [5,6] and circularly polarized black-body emitters.[7]

References

[1] W. Jiang, et al., Emergence of Complexity in Hierarchically Organized Chiral Particles, *Science*, **2020**, 368, 6491, 642-648.
[2] S. Zhou, et al, Chiral assemblies of pinwheel superlattices on substrates, *Nature*, **2022,** 612, 259.
[3] P. Kumar, et al. Photonically Active Bowtie Nanoassemblies with Chirality Continuum, *Nature*, **2023**, 615, 418–424.
[4]. S. Li et al Single- and Multi-Component Chiral Supraparticles As Modular Enantioselective Catalysts, *Nature Comm*, **2019**, 10, 4826.
[5] Wang M. et al., Biomimetic Solid-State Zn^{2+} Electrolyte for Corrugated Structural Batteries, *ACS Nano*, **2019**; 13(2), 1107. PMID: 3060811
[6] Wang M. *et al.*, Biomorphic Structural Batteries for Robotics. *Sci. Robot.* **2020**, 5; https://doi.org/10.1126/scirobotics.aba1912.
[7] Jun Lu *et al*, Bright, circularly-polarized black-body radiation from twisted nanocarbon filaments, *Science*, **2024,** 386 (6728) 1400.