The Collective Behavior of Nanoscale Building Blocks

Not long ago, controlled synthesis of nanoparticles with a new composition was considered a substantial advance in nanotechnology. Over the last 15 years, our community has refined the synthesis and purification methods for nanoparticles, and an immense variety of nanocolloid materials and shapes have been reported. At some point, this becomes an exercise in linguistics and in the invention of a new nano vocabulary to accommodate all of these new nanomaterials.

This issue of *ACS Nano* is an excellent representation of the dramatic changes to the state-of-the-art in nanoscale science. Nanotechnology has reached the stage of development where the subject of most investigations is not individual nanoparticles or nanowires but rather systems of much greater complexity. Although the concepts of collective behavior of nanoparticles and hybrid nanoscale systems have surfaced before, these ideas are transitioning from pioneering studies to the mainstream of nanoscience. Several papers appearing in this issue also demonstrate the diversity of the ultimate functionalities of these complex nanomaterial systems. These applications include such far-reaching challenges as solar energy conversion, biological sensors, mechanical and optical devices, and potential methods for cancer diagnostics.

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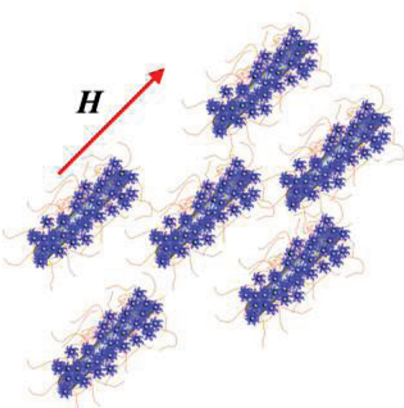
In many cases, the first challenge is in assembling the nanomaterials into a complex hierarchical or supramolecular system. The team of scientists led by Axel Müller from Universität Bayreuth devised a clever method for aligning Te nanorods using an external magnetic field.[1] To make the Te nanorods magnetic, magnetite nanoparticles were first assembled on them; after alignment of the nanorods, the nanoparticles were removed using an acid etch. This is an excellent example of combining different functionalities in superstructures made from different nanoscale materials.



Magnetite nanoparticles assembled on Te nanorods make up a complex system, described in this issue of *ACS Nano* by Yuan *et al*. Adapted from ref 1. Copyright 2009 American Chemical Society.

Preparation of nanorod arrays is a common method for fabrication of nanoscale superstructures. The group of Patrick Theato from the University of Mainz used anodic aluminum oxide templates to make parallel columns of cross-linkable triphenylamine derivatives, which have utility for organic photovoltaics.[2] In order to maintain the alignment of the nanorods after removal of the template, they had to optimize the aspect ratio. In another application of nanomaterials for photovoltaics, Prashant Kamat and co-workers from the University of Notre Dame report complex systems made from CdSe and CdTe nanocrystals linked to nanostructured TiO_2 films using 3-mercaptopropionic acid as a linker molecule.[3] External quantum efficiencies for the CdSe system reach ~70% for these systems, quite promising for engineering solar cells!

The assembly of nanomaterials into multilayered structures is also demonstrated in this issue. Aurora Rizzo and Giuseppe Gigli and colleagues at National Nanotechnology Laboratory of CNR-INFM used multilayer inorganic/organic superstructures based on highly ordered arrays of CdSe/CdS nanorods as the active species.[4] Alignment of the nanorods resulted in strongly polarized photoluminescence. The higher level of organization was attained by patterning using poly(dimethyl siloxane) stamps.

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Complex nanostructures are also finding application in biomedicine and biotechnology. Victor Puntes and Jorge Lloberas and colleagues from the Institut Català de Nanotecnologia and the University of Barcelona describe a unique phenomenon indicative of complex system behavior involving gold nanoparticles coated with peptides.[5] When these bioconjugates were exposed to macrophage cultures, the secretion of pro-inflammatory cytokines by macrophages was observed while the separate peptide and nanoparticle components of the conjugates did not induce the same immune response. The synergistic effect of these two types of building blocks in one superstructure can be used to tune the design of biomedical nanoparticle conjugates, either to activate the immune response or to act as "camouflage" from it.

Cancer diagnostics and treatment can be substantially improved by nanoparticles composed of magnetic cores with continuous gold shells created in the laboratory of Naomi Halas and co-workers from Rice University.[6] Tetracubic nanocrystals made of wüstite with magnetite-rich corners and edges retain magnetic properties when coated with gold, while the spectral characteristics of plasmons from the gold shells are strongly influenced by magnetic oxide. These hybrid nanoparticles combine the magnetic and optical properties of both component materials in a single nanostructure, enabling their use in a wider variety of applications.

Mehmet Sarikaya and colleagues from the University of Washington discuss the problems of biomineralization using a model system of proteins on gold.[7] It was observed that building blocks made from genetically engineered peptide form ordered supramolecular films of gold binding protein.

In these and other papers in this issue, it is clear that the organization of nanostructures into complex assemblies results in a substantial improvement in their functional properties because many processes from biological recognition to charge transfer are strongly dependent on the organization, complexity, and interconnectivity of nanoscale components of superstructures. Empirically, we know this to be true; now it is time for conceptual formalization of this idea and development of theoretical methods to describe the organization and complexity parameters of nanoscale structures.

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