LEGO Materials

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In the 1930s, the name LEGO was coined from the Danish phrase *leg godt*, which means "play well". It was later realized that the word also meant "I put together" in Latin.[1]

I n spite of obvious progress in computational chemistry and modeling, the discovery of new functional materials remains a highly empirical and serendipitous process that is often more of an art than a science.[2] Modern technologies require a vast diversity of materials and "metamaterials" with highly specific functions, and at times multiple functions have to be combined in a single material. Design of such materials by traditional synthetic methods is difficult because the starting entities (atoms and molecules) do not maintain their properties after reaction, leading to poor correlation between reactants and products. As an example, both chemical and physical properties of NaCl are so different from those of sodium and chlorine atoms that it does not seem feasible to predict the behavior of NaCl from the properties of its constituents. This fundamental problem could be solved if materials were assembled not from atoms but from the "modules" or building blocks that already carry some useful function, like a magnet or a semiconductor. We can draw analogies here with the well-known LEGO bricks, where every piece is the functional unit (Figure 1); exchange coupling between the pieces generates a multifunctional response of the material. Such modular approaches could enable materials with programmable chemical and physical properties for catalysis, electronics, energy, and other applications. It sounds attractive, but is there a practical way of accomplishing this?

What could be the smallest functional "module" of a material? From general principles, the quantum mechanical coupling of hundreds of atoms is necessary to develop the band structure of metals, semiconductors, and magnetic materials.[3,4] The corresponding physical size of the smallest functional unit should fall in the nanometer range. Thanks to recent developments in colloidal chemistry, many metals, semiconductors, and magnetic materials can be synthesized as uniform sub-10-nm crystallites; multiple materials can be combined in the form of core−shell, dumbbell, or more sophisticated structures.[4–6] As-synthesized nanocrystals form stable colloidal solutions convenient for processing and deposition.

The second part of the puzzle is how to put different "modules" together. Any kind of top-down approach where individual nanoparticles are arranged one-by-one will be prohibitively expensive for practical use. Fortunately, under certain conditions, natural forces such as entropy, electrostatics, and van der Waals interactions can assemble nanocrystals into ordered structures.[7,8] This process is generally known as self-assembly.[9,10] Nanocrystal

ABSTRACT Two papers in this issue report important developments in the field of inorganic nanomaterials. Chen and O'Brien discuss self-assembly of semiconductor nanocrystals into binary nanoparticle superlattices (BNSLs). They show that simple geometrical principles based on maximizing the packing density can determine BNSL symmetry in the absence of cohesive electrostatic interactions. This finding highlights the role of entropy as the driving force for ordering nanoparticles. The other paper, by Weller and co-workers, addresses an important problem related to device integration of nanoparticle assemblies. They employ the Langmuir—Blodgett technique to prepare long-range ordered monolayers of close-packed nanocrystals and transfer them to different substrates.

See the accompanying Article by Chen and O'Brien on p 1219, and by Aleksandrovic *et al.* on p 1123.

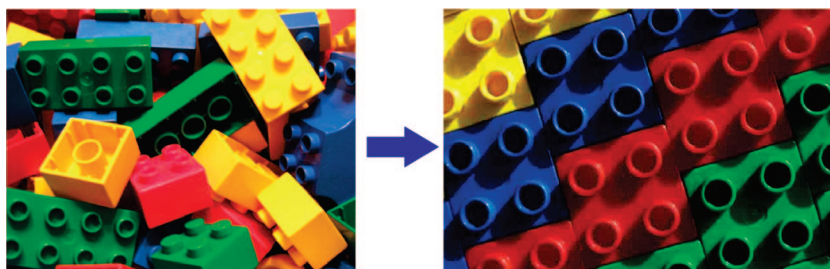*Address correspondence to dvtalapin@uchicago.edu.

Figure 1. LEGO bricks: Can we use a similar approach for designing multifunctional materials? Image courtesy of J. J. Urban, Lawrence Berkeley National Laboratory.
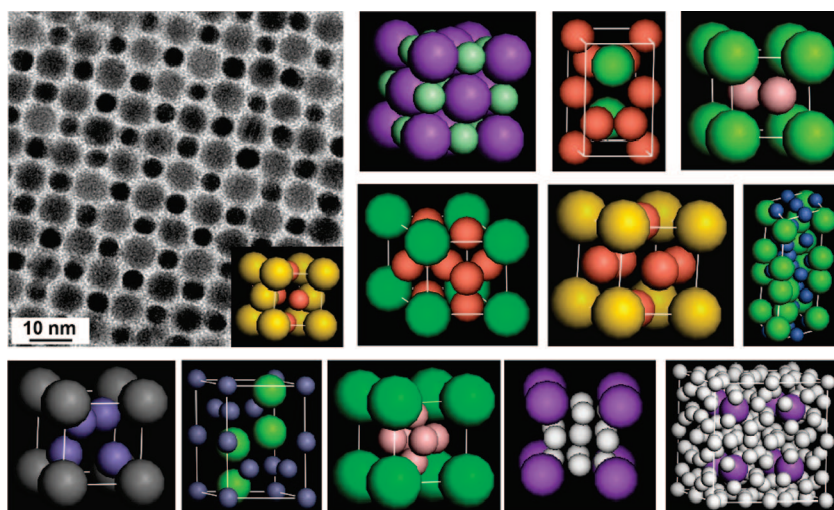
Figure 2. Mixtures of nanoparticles can self-assemble into binary nanoparticle superlattices with an amazing diversity of packing symmetries. Sketches show the unit cells observed in binary superlattices self-assembled from spherical nanocrystals. Many structures have complex low-symmetry unit cells. Adapted with permission from refs 14 and 15. Copyright 2006 Nature Publishing Group, and Copyright 2006 American Chemical Society.

samples with a narrow size distribution can self-assemble into long-range ordered superlattices upon slow evaporation of a colloidal solution. If the sample contains only one kind of particles, the packing rules are quite simple: nanocrystals with spherical shapes form face-centered cubic (fcc) and hexagonal close-packed (hcp) structures with maximum packing densities ($\sim$0.74).[4,7] Faceting or dipolar interactions can lead to other packing symmetries, such as simple hexagonal[11] or liquid crystalline phases assembled from nanorods.[12]

The assembly rules are much more complex when two types of nanocrystals are mixed together. Evaporation of the carrier solvent can lead to the formation of binary nanoparticle superlattices (BNSLs). For this situation, instead of several stable structures theoretically predicted for packing of two kinds of hard spheres, a complex zoology of low-symmetry lattices is possible (Figure 2). Superlattices with AB-AB_6 and AB_{13} particle stoichiometries with cubic, hexagonal, tetragonal, and orthorhombic symmetries have been identified.[13–16] Assemblies with the same stoichiometry can be produced in several polymorphous forms by tailoring the particle size and deposition condi-

tions. To date, BNSLs that are isostructural with NaCl, NiAs, CuAu, AlB_2, $MgZn_2$, $MgNi_2$, Cu_3Au, Fe_4C, $CaCu_5$, CaB_6, $NaZn_{13}$, and *cub*-AB_{13} compounds have been assembled using various nanoparticle combinations.[14–17] The observed structural diversity is rather challenging to understand. If nanocrystals were simple hard spheres, most of these structures would be unstable relative to phase separation.[18]

The formations of multiple low-symmetry BNSLs could be explained only if we accept the fact that nanocrystals interact with each other in a rather complex manner. From previous studies, we know that colloidal nanocrystals can have electric charges, dipole moments, and polarizabilities and exhibit strong van der Waals and ligand—ligand interactions.[14,19–22] The next logical steps would be to put all these known parameters into the expressions for the interparticle potentials, calculate ranges of stability for different lattices, simulate their growth using Monte Carlo algorithms, and declare victory. In fact, the reality is quite different. Even approximating the nanocrystals as point charges and dipoles and using textbook equations to estimate roughly the relative contri-

butions of different interactions does not provide a clear picture. The striking finding is that *all* electrostatic terms fall within the same order of magnitude, *i.e.*, the structural diversity of BNSLs comes from the interplay of multiple comparable energetic contributions (Figure 3). This is a theoretician's worst nightmare—no single parameter can be neglected; every term has to be calculated (or measured) with great accuracy or the model will make no sense. This situation is unique and typical only for 2−15 nm particles. On smaller (atomic) or larger (micrometer) scales, the same interactions span over several orders of magnitude in energy (Figure 3).

If the problem is too hard to be solved by a frontal attack, we should attack it on the flank. In their article in this issue, Chen and O'Brien make important steps toward understanding and rationalizing BNSL formation.[23] They studied self-assembly of BNSLs in a mixture of CdSe and CdTe nanocrystals where electrostatic and van der Waals interactions are weak and can be neglected. Instead, other factors such as entropy and ligand—ligand interactions should play the dominant role in this system. Chen and O'Brien explored the effect of nanocrystal size ratio on the BNSL structure and demonstrated that BNSL packing symmetry corresponds to the highest possible packing density for a given size ratio. This observation points to the important role of entropy as the driving force for self-assembly. How can entropy, which is a measure of *disorder*, drive the *ordering* of nanocrystals into a long-range ordered superlattice? The answer is found in the introduction to the paper by Chen and O'Brien. The authors observed only four BNSL types, isostructural with AlB_2, $MgZn_2$, $CaCu_5$, and $NaZn_{13}$ intermetallic compounds. Does it imply that the formation of other BNSL structures shown in Figure 2 requires cohesive electrostatic components in the interparticle poten-
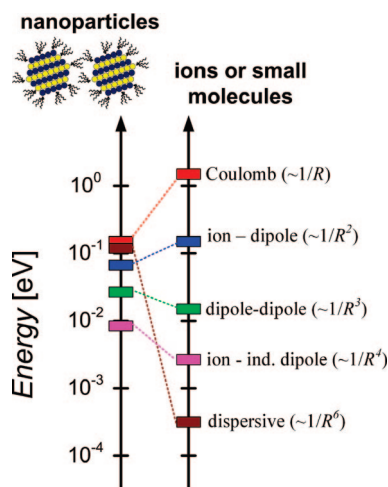
Figure 3. Contributions of different forces to the potential between two nanoparticles compared to the typical interactions between atoms or small molecules. The scaling law for each interaction is shown in parentheses.

tials? Further studies should help answer this and other questions about self-assembly of nanoscale building blocks into modular materials with programmable properties.

Self-assembly of nanocrystals allows creation of ordered assemblies and three-dimensional supercrystals.[4,7] To date, the largest superlattices grown this way have had sub-millimeter dimensions. Is it possible to form much larger ordered nanocrystal assemblies and to transfer them to different substrates? For example, is it possible to deposit a single layer of nanocrystals over an entire 12-in wafer? These are important questions, directly related to the fabrication of nanocrystal-based devices. Weller and colleagues address this problem in their article in this issue by employing the Langmuir–Blodgett technique.[24] Typically, wa-

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ter is used as a subphase for Langmuir–Blodgett manipulations with molecular species. However, this approach does not work well for nanocrystals because they aggregate at the aqueous surface. As a solution, Weller and colleagues replaced the aqueous subphase with diethylene glycol and obtained nicely ordered close-packed nanocrystal monolayers over areas of many square centimeters. These nanocrystal monolayers could be transferred to any surface by simply dipping the substrate in the subphase and pulling it out at a certain angle to the surface. This approach can be extended to different materials and used to deposit close-packed monolayers of nanocrystals on substrates with any reasonable size and shape. Another advantage of replacing the water subphase by diethylene glycol is its chemical inertness. The difference in chemical properties of water and diethylene glycol can play an important role in the case of transition metal and semiconductor nanocrystals that are often susceptible to hydrolysis.

The technique proposed by Weller and co-workers can find broad use in the fabrication of nanocrystal-based electronic and optoelectronic devices. When cost or large dimensions do not allow the use of single crystals, nanocrystal arrays may successfully compete with organic electronic materials.[25] Nanocrystal solar cells offer exciting opportunities for solar energy conversion.[26] Many scientists predict a bright future for nanocrystal-based photovoltaics because of inexpensive solution-based fabrication and precisely tunable bandgap energies and absorption spectra of colloidal quantum dots. Moreover, colloidal semiconductor nanocrystals can efficiently capture the infrared region of the solar spectrum, a task challenging for organic materials.[27,28]

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