ChemPubSoc Europe

DOI: 10.1002/cbic.201600183

CHEMBIOCHEM Highlights

SPECIAL ISSUE

DNA-Nanoparticle Tinkertoys

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Nanoparticle superlattices can be self-assembled by using DNA linkers, which gives control over their size, shape, and composition. Recently, such programmable atom equivalents have been tailored to respond to chemical stimuli and result in specific crystalline lattices. Moreover, the molecular recognition properties and the robustness of designed DNA nanostructures have been used in combination with metallic nanoparticles for the production of the elusive diamond superlattice.

With its nanoscale features and highly specific molecular recognition,[1] DNA has been used as a building block for the construction of nanoscale objects and lattices,[2] including applications in materials science and biology.[3] DNA is also able to assemble into composite materials involving nanoparticles with control over their size, shape and composition.[4] Such DNA-conjugated nanoparticles, known as programmable atom equivalents (PAEs), can assemble into desired three-dimensional crystalline lattices through programmable DNA bonds (Figure 1 A). These assemblies can be optimized through parameters such as the linking DNA sequences, salt concentration, DNA shell structure, density of the DNA linkers, and the interparticle distances.[5]

Assembly of such nanoparticle lattices have been tuned by regulating the conformational changes of nanoparticle-bound DNA linkers.[6] Recently, this strategy was expanded to create "transmutable" nanoparticles in which chemical cues were used to trigger the interparticle bonds to form specific crystalline lattices.[7] In this case, the PAEs contained DNA-hairpin linkers tailed with sticky ends through which they can associate with other PAEs. When the hairpin is folded, the sticky ends on the linkers are buried in the DNA layer and do not initiate binding of PAEs (Figure 1 B, top). Upon the addition of an effector oligonucleotide that is complementary to the hairpin sequence, the hairpin is opened by the formation of a duplex (Figure 1 B, bottom). This pushes the sticky ends outward, thus activating the association of PAEs. The PAEs can further be inactivated by removing the effector strand by using toe-hold-based strand displacement. Such reconfigurable bonding elements allow the creation of transmutable nanoparticles with binding characteristics that can be selectively activated or deactivated. Assembly of different types of superlattices was controlled by changing four parameters: (i) bonding elements (sticky ends) at the end of the DNA linkers; (ii) effective stoichiometry of PAEs; (iii) density of bonding elements on each particle; (iv) hydrodynamic size (coordination number) of the particles.

To analyze the effect of sticky ends, PAEs were designed to contain both self-complementary and non-self-complementary sticky ends on linkers with different hairpin sequences. One of these was selectively activated by the addition of specific hairpin-binding strands. Activation of self-complementary sticky ends led to an FCC (face-centered cubic) lattice and that of non-self-complementary sticky ends led to the formation of a BCC (body-centered cubic) lattice. To study the stoichiometry of the particles, two sets of PAEs with different protecting-group sequences (20% containing the first sequence and 80% containing the second) but containing the same sticky ends were combined. These were then mixed in 5:1 ratio with non-transmutable particles containing complementary sticky ends. When the first hairpin was opened, the resulting particle to particle ratio was 1:1 and resulted in a BCC lattice. Activation of the second type resulted in 5:1 ratio (all sticky ends activated) and the formation of an AlB_2-type lattice. The density of the bonding elements was tested using PAEs that contained two sets of protecting sequences with the same sticky ends. By deprotecting one or both of the groups, the particles could be activated to be in their low-density or high-density states, resulting in BCC or AlB_2 lattices, respectively. The effect of the hydrodynamic size of the particles on lattice formation was studied by using two hairpins on the linkers with a duplex inserted between the sticky end and the hairpin. The hairpins can be specifically targeted by effector strands so that the radius of the particle can be increased from its folded state (35 nm) to the unfolded state (41 nm). This change affected the coordination number of the particle, and when combined with a complementary 14 nm particle, the folded state resulted in an AlB_2 lattice while the unfolded state caused the formation of a Cs_6C_{60} lattice. Such transmutable particles have promise for the creation of adaptive matter with precise control over their nanoscale arrangements.

Another recent development was the assembly of DNA-functionalized nanoparticles into diamond superlattices,[8] the construction of which, using self-assembly strategies, has so far been challenging. Anisotropic tetravalent DNA cages and isotropic spherical gold nanoparticles (AuNPs) were combined to self-assemble into a cubic diamond superlattice. The DNA origami cage was comprised of 10-helix bundles on each edge (~36 nm) of the tetrahedron and the vertices contained single stranded extensions to associate with a AuNP ("basis" particle, 14.5 nm). In addition, the inside of the tetrahedron contained single-stranded extensions that could bind to a guest particle.

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This manuscript is part of a Special Issue on DNA Nanotechnology.

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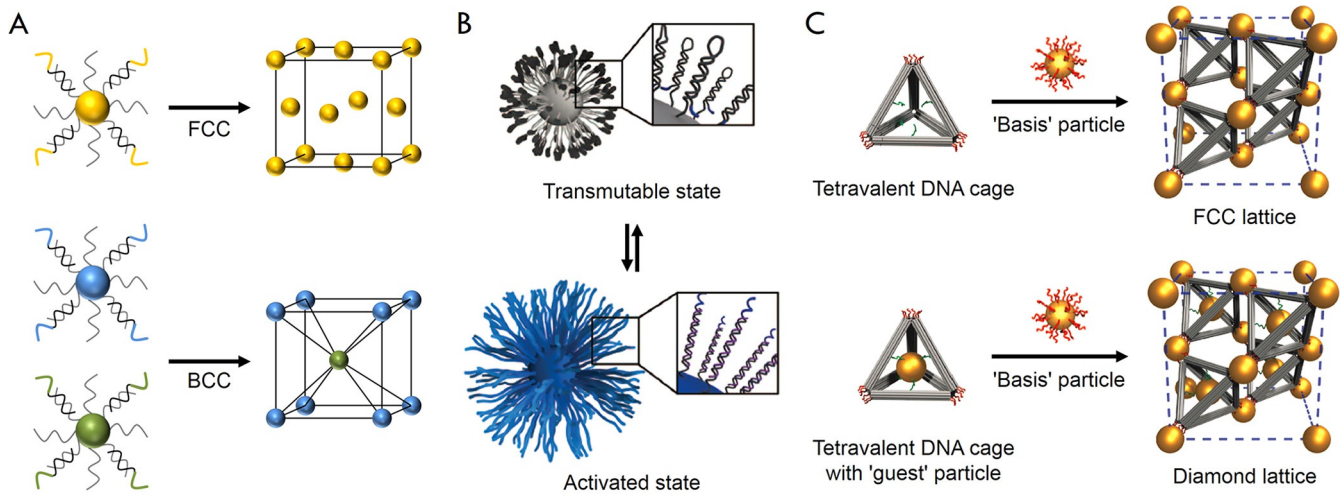

Figure 1. DNA-linked nanoparticle superlattices. A) DNA-nanoparticle conjugates can associate with specific types of complementary particles to form distinct superlattices.[4c] B) The DNA-linker portion of the PAEs can be triggered to activate assembly into lattices. C) A DNA-origami tetrahedron can be used to connect and host specific gold nanoparticles leading to the formation of an FCC lattice or a diamond superlattice. B) and C) were adapted with permission from the American Association for the Advancement of Science.[7,8]

Organization of the AuNPs at the vertices of the DNA cage lead to an open FCC lattice, and by introducing an additional particle to be caged within the DNA tetrahedron, the assembly could be directed to form a diamond lattice (Figure 1 C). A variant of the cubic diamond lattice, a zinc blende lattice, was also constructed by replacing the 14.5 nm basis particle with a smaller 8.7 nm particle. Further, by replacing the 14.5 nm guest particle with two smaller 8.7 nm particles, and using an 8.7 nm basis particle, a new "wandering" zinc blende variant was also created. Construction of the elusive diamond superlattice using DNA nanotechnology could lead to applications as a photonic bandgap material.

Polycrystalline DNA-linked nanoparticle superlattices[9] have been optimized to result in uniform crystal habit[10] and specific large-ordered crystalline superlattices. In such assemblies, the defined positioning of nanoparticles gives emergent properties based on the interparticle distance and crystal symmetry, which are different from those of the individual particles. Similar strategies have been used to assemble heterogeneous structures comprised of both nanoparticles and quantum dots.[11] Moreover, the ability to trigger specific linker molecules have led to the development of reconfigurable superlattices.[12] These studies have resulted in design rules for DNA-linked nanoparticle superlattices[13] that would enable the production of tailor-made assemblies with desired characteristics. Further research into using these design principles will aid in the construction of single crystals with unique photonic and catalytic properties. In addition, these strategies can be expanded to shape-directed crystallization of anisotropic particles into colloidal crystals that exhibit new properties.[14]

The main advantage of DNA-based self-assembly is that the intricacy and precision of the DNA linkers with which these structures are created is not feasible using other techniques such as lithography. Such tunable assemblies with controllable kinetics and reversibility allows for the production of composite metamaterials and hybrid systems that have applications in plasmonic-based circuitry or waveguides, photonic bandgap materials, and energy-harvesting or -storage materials owing to the collective properties of the self-assembled nanoparticles.[15] In addition, variable DNA linkers provide a route to creating specifically designed lattices that can host a variety of guest molecules. Furthermore, a library of DNA-tagged nanoparticles with different materials and characteristics would be useful to assemble architectures with custom designs for various purposes.

Keywords: designed lattices · DNA nanostructures · DNA nanoparticles · self-assembly · superlattices

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Manuscript received: March 29, 2016
Final article published: April 15, 2016

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