DNA-guided Assembly of Organized Nano-Architectures

Oleg Gang[1], Mathew M. Maye[1], Dmytro Nykypanchuk[1], Huiming Xiong[1], Daniel van der Lelie[2]

[1]Center for Functional Nanomaterials, [2]Biology Department,
Brookhaven National Laboratory, Upton, NY 11973, USA

ogang@bnl.gov

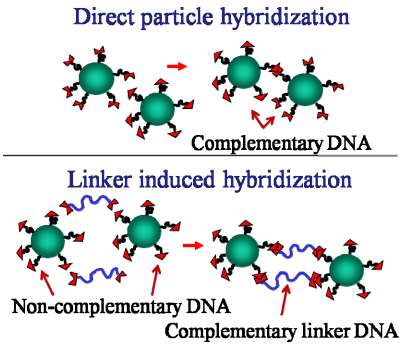
ABSTRACT

Incorporation of DNA into nano-object design provides a unique opportunity to establish highly selective and reversible interactions between the components of nanosystems. Assembly approaches based on the nano-object's addressability promise powerful routes for creation of rationally designed nano-systems for the development of novel magnetic, photonic and plasmonic metamaterials. DNA provides a powerful platform due its unique recognition capabilities, mechanical and physicochemical stability, and synthetic accessibility of practically any desired nucleotide sequences. Recently, strategies based on DNA programmability for a pre-designed placement of nanoparticles in one- and two-dimensions using scaffolds have been demonstrated [1, 2]. However, in three dimensions, where theory predicted a rich phase behavior[3, 4], experimental realization has remained elusive[5], with nanoscale systems forming amorphous aggregates.

Keywords: DNA, self-assembly, hybrid systems, nanoparticles, superlattices

1 DNA-GUIDED ASSEMBLIES

Two approaches are widely used for the DNA-guided assembly of 3D nanoparticle systems [6, 7] (Scheme 1): (i) direct hybridization of two types of complementary single-stranded (ss) DNAs attached to the particle's surface and (ii) particle hybridization with linker DNAs, whose two ends are complementary to the mutually non-complementary DNA attached to particles. Each approach has its own advantages: a direct hybridization allows for tailoring interparticle interaction via DNA shell design, while a linker strategy is attractive due to its potential of building various architectures from a given set of nanoparticle by changing a linker design. Herein we report a structural study of DNA-guided nanoparticle systems in which we have observed formation of crystalline ordered assemblies using both approaches described above.



Scheme 1. Approaches for DNA-guided assembly 3D structures from nanoparticles.

1.1 Direct hybridization

We have systematically studied [8] the structure of self-assembled aggregates in a binary system of nanoparticle coated with complementary single stranded (ss) DNA for various DNA lengths. In each assembly system, a set of DNA-capped gold nanoparticles, ~11 nm with different DNA shells were allowed to assemble via DNA hybridization into meso-scale aggregates. The complementary outer recognition sequences of the DNA-capping provided the driving force for A and B particle assembly. The length of the recognition sequence, N_a=15

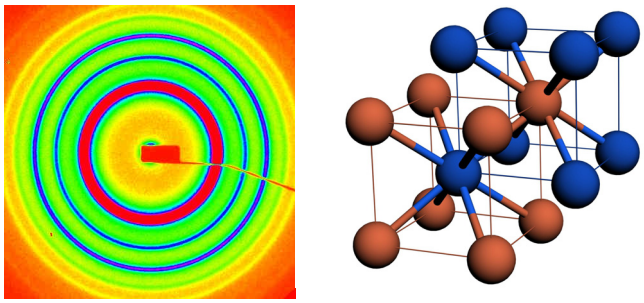


Figure 1. (Left) SAXS scattering pattern from crystalline DNA-guided nanoparticles assembly (50 bp DNA). (Right) Corresponding structure factor indicates bcc lattice.[8]

base pairs (bp), sets the scale of adhesion (per hybridized linker), thus attraction energy $E_a \sim N_a$, from ~30 kT at room temperature, to ~0 kT at DNA melting temperature. The length, N(15, 30, 50, 75), of DNA and the flexibility of the non-complementary internal spacer allowed for tuning the range, $d_r \sim N^{3/5}$, of repulsive interaction and its strength $E_r \sim (N^{3/5}/(N^{3/5}-cN_a)$,[9, 10] where c is defined by persistence length and molecule surface density and is constant for all studied systems and N is a length of ssDNA. Thus the use of multiple systems with constant E_a (i.e., recognition sequence), and varied d_r (i.e., spacer lengths), allowed for effective interparticle potential tuning. We have modulated

the interparticle potential via length of ssDNA and for sufficiently soft interaction potentials (long ssDNA) discovered the formation of 3D nanoparticle assemblies with crystalline long range order (~ micron) using synchrotron small angle x-ray scattering (SAXS) measurements (beamline x21 at NSLS, BNL). The SAXS patterns in Fig. 1 reveals multiple orders of resolution limited Bragg's peaks for a system containing DNA shells of 50 base pairs, demonstrating its crystalline 3D structure, remarkable degree of long-range ordering, and crystallite sizes of ~ micron, as estimated from scattering correlation length. The system with shorter or rigid DNA form only disordered structures. The measured lattice parameters for the observed bcc structure are ~35 nm at 30 ^{o}C and ~42.4 nm at 28°C for system with 50 bp and 75 bp. Once formed, near DNA melting temperature, these crystalline structures were reversible, as confirmed by multiple assembly-disassembly cycles, without a noticeable loss of ordering quality or changes in system behavior.

1.2 Hybridization via DNA linkers

To explore an assembly strategy using DNA linkers we generated a binary set of gold nanoparticles [11], which were covered with ssDNA containing a 15 bp outer recognition part and a 15 bp poly-dT, which serves as a spacer separating the recognition sequence from the particle surface [12]. The ends of the linker ssDNAs are complementary to the respective ends of ssDNAs on nanoparticles, and are separated by a central flexible poly-dT fragment which contains *n* nucleotides, having a length of 0, 15, 30 or 70 bp (denoted accordingly as Sys-L0, Sys-L15, Sys-L30 and Sys-L70). Each system was formed by mixing an equal mole of the two types of ssDNAs capped nanoparticles and a linker ssDNA (DNA/particle mole ratio 36:1) in 0.3 M PBS buffer.

Temperature dependent synchrotron SAXS is utilized to characterize the structure of assembled aggregates. Figure 2 illustrates SAXS patterns obtained after annealing samples at few degrees below assembly melting temperature for various studied linkers. At this temperature, a well-defined crystalline order is manifested by an increased number of diffraction rings and their decreased widths. Analysis of the detected seven orders of Bragg's peaks positions reveals a ratio $q/q_1 = 1:2^{1/2}:3^{1/2}:4^{1/2}:5^{1/2}:6^{1/2}:7^{1/2}$, which corresponds to bcc lattice. The relative intensities of the diffraction peaks are also in accordance with the predictions for bcc lattice. The first peak thus arises from diffraction of {110} planes. For Sys L15, the lattice constant of the unit cell (*a*) is ~39 nm and the nearest-neighbor distance d_{nn} is ~34 nm at 56 ^{o}C. As shown in Figure 2b, Sys-L70 with the longest linker is the most prone to order improvement during annealing. For Sys-L15, although there was little perfection during initial heating, the order increased tremendously after annealing. However, for Sys-L0 with no flexible part in the linker, the structure of nanoparticles assembly remains disordered after the annealing process.

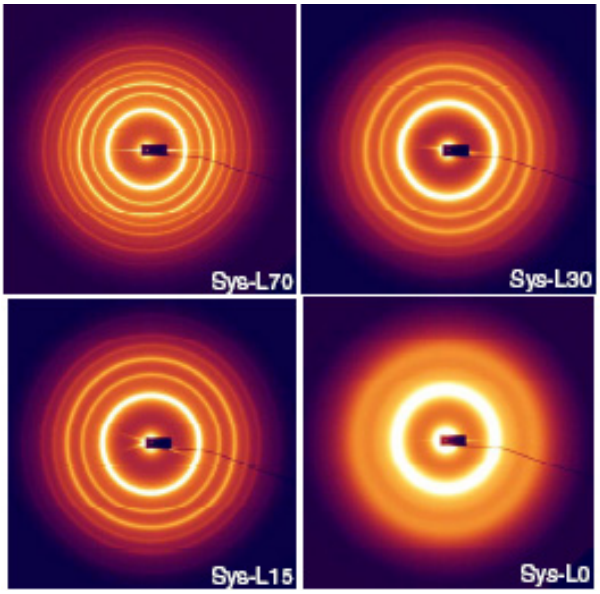


Figure 2. SAXS patterns for systems with different linkers length 0 bp (Sys-L0), 15 bp (Sys-L15), 30 bp bp (Sys-L30) and 70 bp (Sys-L70) at 25^{o}C after annealing at 55^{o}C for 2 hours [12].

SUMMARY

In summary, we have demonstrated that DNA mediated interaction between nanoparticles can result in formation of assemblies with 3D crystalline order (bcc lattice). For tailored DNA designs, ordered nano-architectures are obtained using both discussed assembly strategies, i.e. using a direct hybridization of particle DNA shells or DNA linkers. The flexibility of the DNA is determined to play an important role in the formation of ordered phase. The described approach offers a unique way for building 3D ordered materials from a broad range of nanoscale objects compatible with DNA functionalization. Phase behavior of these systems and formation more complex multi-component architectures are still to be explored.

Research was supported by the U.S. DOE Office of Science and Office of Basic Energy Sciences, under Contract No. DE-AC-02-98CH10886.

REFERENCES

[1] J. W. Zheng, P. E. Constantinou, C. Micheel, A. P. Alivisatos, R. A. Kiehl, and N. C. Seeman, "Two-dimensional nanoparticle arrays show the organizational power of robust DNA motifs" Nano Letters **6**, 1502 (2006).

[2] J. D. Le, Y. Pinto, N. C. Seeman, K. Musier-Forsyth, T. A. Taton, and R. A. Kiehl, "DNA-templated self-assembly of metallic nanocomponent arrays on a surface" Nano Letters **4**, 2343 (2004).

[3] A. V. Tkachenko, "Morphological diversity of DNA-colloidal self-assembly" Physical Review Letters **89**, 148303 (2002).
[4] D. B. Lukatsky, and D. Frenkel, "Phase behavior and selectivity of DNA-linked nanoparticle assemblies" Physical Review Letters **92**, Art. No. 068302 (2004).
[5] S. Y. Park, J. S. Lee, D. Georganopoulou, C. A. Mirkin, and G. C. Schatz, "Structures of DNA-linked nanoparticle aggregates" Journal of Physical Chemistry B **110**, 12673 (2006).
[6] S. J. Park, A. A. Lazarides, C. A. Mirkin, and R. L. Letsinger, "Directed assembly of periodic materials from protein and oligonucleotide-modified nanoparticle building blocks" Angew. Chem.-Int. Edit. **40**, 2909 (2001).
[7] M. M. Maye, D. Nykypanchuk, D. van der Lelie, and O. Gang, "DNA-Regulated micro- and nanoparticle assembly" Small **3**, 1678 (2007).
[8] D. Nykypanchuk, M. M. Maye, D. van der Lelie, and O. Gang, "DNA-guided crystallization of colloidal nanoparticles" Nature **451**, 549 (2008).
[9] S. T. Milner, and T. A. Witten, "Bending moduli of polymeric surfactant interfaces" J. Phys. **49**, 1951 (1988).
[10] D. Nykypanchuk, M. M. Maye, D. van der Lelie, and O. Gang, "DNA-Based Approach for Interparticle Interaction Control" Langmuir **23**, 6305 (2007).
[11] M. M. Maye, D. Nykypanchuk, D. van der Lelie, and O. Gang, "A Simple method for kinetic control of DNA-induced nanoparticle assembly" J. Am. Chem. Soc. **128**, 14020 (2006).
[12] H. Xiong, D. Van der Lelie, and O. Gang, "DNA Linker-Mediated Crystallization of Nanocolloids" J. Am. Chem. Soc. **130**, 2442 (2008).