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Programming Macro-materials from DNA-directed Self-assembly

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Abstract: DNA is a powerful tool that can be attached to nano- and micro-objects and direct the self-assembly through base pairing. Since the strategy of DNA programmable nanoparticle self-assembly was first introduced in1996, it remains challenging to use DNA to make powerful diagnostic tools and to make designed materials with novel properties and highly-ordered crystal structures. In this review, we summarize recent experimental and theoretical developments of DNA-programmable self-assembly into three-dimensional (3D) materials. Various types of aggregates and 3D crystal structures obtained from experimental DNA-driven assembly are introduced. Furthermore, theoretical calculations and simulations for DNA –mediated assembly systems are described and we highlight some typical theoretical models for Monte Carlo and Molecular Dynamics simulations.

1. Introduction

In recent years, nanoparticle (NP) assemblies with special plasmonic, photonic and magnetic properties have attracted significant interest because of their potential applications in a variety of fields, such as sensing, drug delivery and material synthesis. [1, 2] Although several strategies have been used to prepare NP superstructures, the method that

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utilizing mutual recognition of bio-molecules, such as DNA and proteins, is probably the most widespread one.[3, 4] DNA is a powerful tool for nano- and micro-materials self-assembly [5-7] because (1) it can easily interact with a variety of materials through different chemical functionalities, (2) the complementary base pairs have almost perfect selectivity, (3) the process is reversible with increasing temperature, (4) the polymer length and sequence can be designed.

The concept that DNA-functionalized gold NPs can assemble into large assemblies was first introduced by both Mirkin *et al.* and Alivisatos *et al.* in1996.[8, 9] In the work of Alivisatos and coworkers [9], discrete numbers of gold NPs are attached with single DNA strands and they can assemble into small "nanocrystal molecules" by DNA base-pairing interactions. While Mirkin and coworker [8, 10] showed that gold NPs attached with many DNA strands (polyvalent DNA-NP bioconjugates) can be used as building blocks to form large aggregates or even crystal lattice. These two different strategies have resulted in two complementary research areas. In addition, various DNA origamis can be used to achieve extended templates to arrange NPs through different placement of single strand-binding sites.

In this review, we largely focus on the use of DNA to grow three-dimensional (3D) materials based on Mirkin's strategy. These 3D materials can be described as aggregates and crystals in both nano- and micro-sizes. In the early time, mainly amorphous aggregates were obtained experimentally as making lattice with DNA-capped NPs was extremely difficult. However, theoretical work by Tkachenko[11] was well ahead of experiments that several kinds of lattices were predicted by designing appropriate interactions between two particles. This work has simulated subsequent experimental studies. In 2008, body-centered cubic (bcc) and face-centered cubic (fcc) crystalline lattices were first realized experimentally by Mirkin group [12] and Gang group [13]. From then on, both experiment and theory have developed rapidly and a variety of superlattices have been realized and predicted.

Below, we provide a brief overview on the recent experimental and theoretical studies to show an overall understanding of DNA-programmaable self-assembly. As reviews of theoretical developments are limited, theoretical descriptions for DNA -mediated NP systems are shown in detail.

2. Experimental developments

2.1 Self-assembly strategies

Generally, two primary strategies are widely used in DNA-NP assembly systems. (Fig. 1) In one strategy [8], two kinds of gold NPs coated with single-stranded DNA (ssDNA) can self-assemble into macro-structures by adding a DNA linker with "sticky ends" that are complementary to the two grafted sequence. This approach is scientifically attractive because of its potential application of building various assemblies via different linker designs. For example, both ssDNA and double-stranded DNA (dsDNA) have been used as linkers to direct the self-assembly. Furthermore, the linker length L_n has been commonly used in real experiments to change interparticle distance when other conditions are kept constant. In the other strategy, direct assembly can be realized with fully or partially complementary ssDNA that are attached to surface of gold NPs, therefore, the linker DNA is not essential. The process of assembly is reversible when increasing temperature, which is considered as an important quality in material synthesis.

When the first DNA-NP aggregates were synthesized, a striking color change from red to blue was observed with the naked eye and a red-shift of plasmon band was found in UV-vis spectroscopy, which was considered as the result of plasmon resonance of NPs in the assembled aggregates. It was also quickly discovered that the thermal melting transitions in these materials were quite sharper and the melting temperature (T_m) is even higher than that for the same DNA structures in solution.[15] Based on these additional properties, DNA-coated NPs have been widely used in making powerful diagnostic tools for DNA sequence, DNA-binding molecules, proteins and metal ions. [16] DNA-coated NPs also have a significant impact in intracellular gene regulation[17] because they can enter cells naturally without the need of a co-carrier.

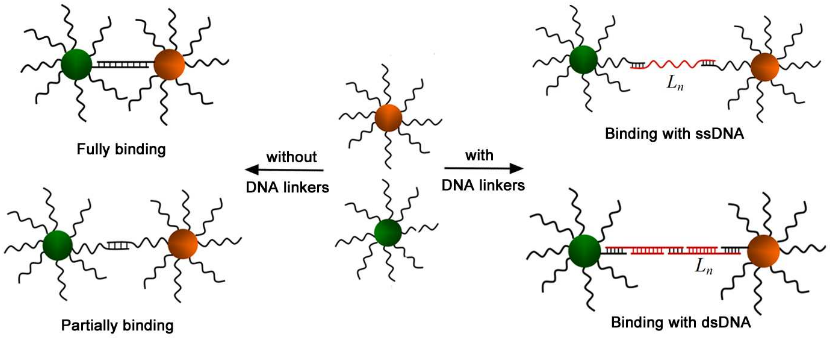

Fig. 1. Typical strategies of DNA-linked nanoparticle assemblies.

2.2 Aggregates

Based on the strategies above, more studies have focused on other kinds of aggregates via different parameters design. These parameters are primarily classified into four aspects as shown in Fig. 2.

Particle design. The core of the building blocks can be designed in different types, sizes and shapes. For example, in addition to gold NPs, core-shell NPs[18], liposome NPs[19], Janus NPs[20], gold NP clusters[21] and even proteins[22] have been used in DNA-linked assemblies. Binary network materials have also be prepared using two different sized DNA-capped particles.[18] Furthermore, shapes of particles have extended to nanorods[23] and triangular nanoprisms[24].

DNA strands design. Experimental studies have shown that changing polymer length [25] and rigidity of the DNA [26] can result in different aggregation states. Besides base pairing interactions, G-quartet binding domains have also been used to synthesize complex aggregates.[27] Further, switch self-protected attractions in DNA strands have been used to control inter-particle binding strength.[28] In addition, 'core-satellite' structures where a number of smaller NPs surround a large NP have been created and interpaticle expansions can be realized with the reconfigurable duplex DNA.[29]

Functionalization conditions. Several studies have proposed that interactions between particles can be controlled by fractions of non complementary linkers coated to NPs. Therefore, NPs have been functionalized with a composition of complementary linkers and non complementary linkers. [30] The non complementary linkers can also be replaced by polymer brushes [31]. Furthermore, asymmetric aggregates, such as cat paw, satellite and dendrimer-like structures have been realized by using asymmetric functionlization of NPs.[32]

Environment conditions. DNA has been utilized to template aggregates in conditions of different pH, where two different binding states have been obtained and one binding state can change to another through changes in pH.[33] The process of DNA-NP self-assembly system can also reversed through addition of short DNA sequence.[34] Moreover, a solid support has been introduced into DNA-NP assembly system to fabricate asymmetric Janus particles and clusters.[35]

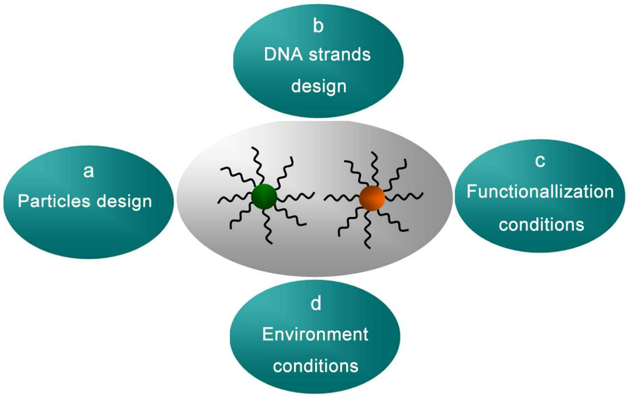

Fig.2. Extended aggregates can be realized by designing different parameters which are primarily classified into four aspects.

2.3 Crystals

To date, manufacturing long-range, quasi-crystalline NP structures remains challenging. Since the wide morphological diversity of crystals was theoretically predicted by Tkachenko,[11] experimental studies have been stimulated and various crystal structures have been realized by using DNA as a programmable linker.

2.3.1 Simple crystal structures

In 2004, the presence of short-range NP crystals was indicated by Park *et al.*.[25] Subsequently, microscopic crystallites were investigated.[36] In 2008, the first experimental observations of crystalline supperlattices (Fig. 3a) were reported by Gang group and Mirkin group.[12, 13] Gang *et al.* have used direct assembly of ssDNA-NP (with 15 complementary bases) to prepare bcc superlattice by varying the length of the ssDNA and controlling the temperature around T_m. While in Mirkin's work, a key development was that dsDNA and a short "sticky ends" (with 4 complementary bases) were utilized. When a self-complementary ''sticky ends'' was used, fcc superlattice was obtained. The bcc superlattice was realized when the ''sticky ends'' only interacted with the opposite type.

More studies have provided a detailed description of DNA-NP self-assembly systems with several parameters, such as linker length, particle size and number of DNA linkers attached to NPs. It has been found that the lattice parameters can be controlled with nanometer-scale precision via changes in the DNA linker length L_n under conditions that other parameters are kept constant. [37, 38] By utilizing NPs of different sizes and DNA of different lengths, Mirkin *et al.* [39] have obtained an interesting phase diagram. They found that the ratio between the NP size and the DNA length has a significant impact on the formation of ordered colloidal crystals. Gang *et al.* [40] have shown that the linker/AuNP ratio r is another significant factor on the formation of ordered colloidal crystals. In addition, pathway and kinetics of ordered crystal formation has been established experimentally [41] that the crystals grow via 3-step process: initial DNA-AuNP aggregation, small, well-ordered crystalline domains, then large crystal systems.

2.3.2 Extended crystal structures

Subsequently, a variety of modified methods have been developed to get other kinds of superlattices. Mirkin and coworkers have used anisotropic particles as building blocks to synthesize one-, two- and three-dimensional structures.[42] They demonstrated that both the DNA and the particle shape template the crystallographic symmetry of the NP superlattice. In addition to fcc and bcc structures, Mirkin *et al.* [43] have prepared seven other kinds of lattices by controlling the size ratio and DNA linker ratio between two particles.(Fig. 3b). Furthermore, they have presented a set of basic design rules to predict superlattice structure, which has provided the opportunity to construct new crystallographic arrangements. Interestingly, NP lattice parameters could be tuned through the use of DNA-hairpin schemes.[44, 45] This approach has also been applicable to multiple different crystal structures, such as fcc, bcc, CsCl, and AlB_2. Many types of superlattice structures could even be programmed by using a hollow three-dimensional spacer that can occupy specific lattice positions based on their DNA sequence.[46] By using this method, superlattices with five distinct symmetries were obtained. (Fig. 3c) Moreover, the Wulff equilibrium crystal structure (Fig. 3d) with a specific and uniform crystal habit has been observed under special conditions of slow cooling and over several days.[47]

2.3.3 More sophisticated superlattices

Most recently, 3D materials with greater complexity have been realized with controllable assembly of DNA-linked nano-scale objects. For example, the strategy of DNA-programmable assembly has been applied for binary systems containing two different types of particles. Park and coworkers have created a NaTl-type crystalline structure by DNA-programmed assembly of surface-modified Qβ phage capsid particles and gold NPs.[48] Gang *et al.* have also shown the successful assembly of heterogeneous 3D structures from two different kinds of nano-scale objects, such as metal NPs (Au, Pd), quantum dots and iron metal NPs (Fe_2O_3).[49, 50] It was observed that the assembled materials with fcc or bcc arrangements have novel optical and field-responsive properties. Mirkin *et al.* have presented the assemblies of other heterogeneous 3D structures, such as CsCl, AlB_2 and Cs_6C_{60} superlattices.[51]

NP superlattices consisted with three kinds of particles have also been synthesized by using the process of topotactic intercalation by inserting a third NP component at predetermined sites within a preformed binary lattice. Based on this methodology, five distinct crystals (Fig. 3e) were synthesized, which have provided a new approach for assembling highly ordered ternary NP superlattices whose structures can be predicted before their synthesis.[52]

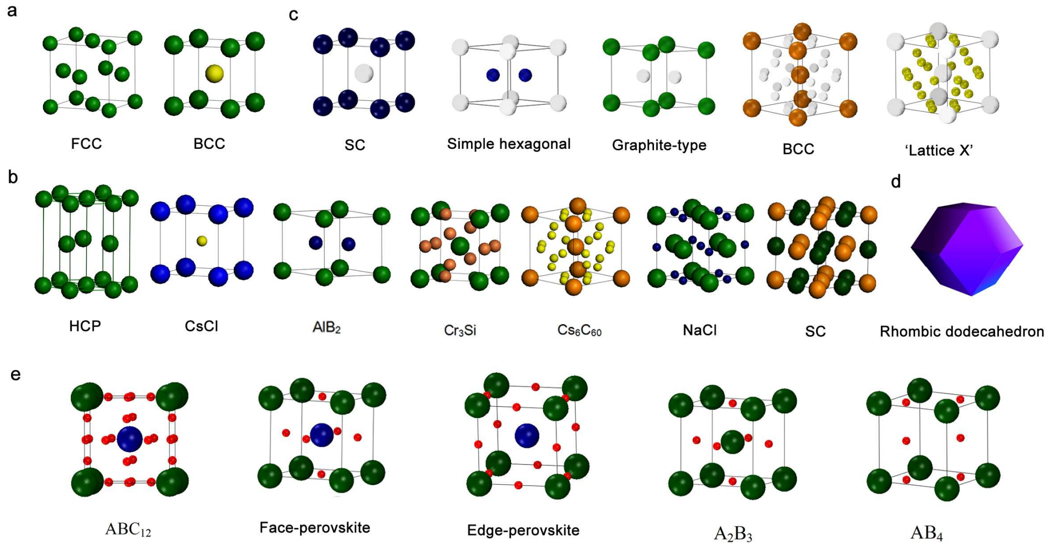

Fig. 3. Different kinds of NP superlattices that have been created experimentally. **a,** fcc and bcc superlattice. **b,** Seven different kinds of superlattices obtained by controlling the size ratio and DNA

linker ratio between two particles. [43] **c,** Superlattices with five distinct symmetries obtained by using a hollow three-dimensional spacer approach. [46] **d,** The Wulff equilibrium crystal structure. [47] **e,** Five distinct crystals synthesized by using the process of topotactic intercalation.[52]

3. Theoretical descriptions

Theoretical analysis and simulations have played a major role in understanding the process of self-assembly. The results have not only confirmed the experiments results but also stimulated the experiments by providing new predictions.

3.1 Theoretical analysis

The first analytical model was proposed by Tkachenko [11] in 2002 who obtained a phase diagram as a function of two dimensionless parameters. It was suggested that diamond, bcc and other lattices can be obtained by controlling interactions between two particles. In 2011, a theoretical discussion of the inverse problem of self-assembly was also presented by Tkachenko who identified the conditions for robust self-assembly into target structure.[53] The results showed that a floppy network with thermal fluctuations possesses entropic rigidity when the coordination number Z (the number of bonds per particle) is within certain range.

Starr and coworkers have provided theoretical descriptions for equilibrium properties and the dynamics of DNA-linked NPs with concepts from polymer physics, which was considered as a successful way to describe novel self-assembly systems.[54] Crocker and coworkers have developed a quantitative model partially based on experimental studies to directly predict DNA-mediated colloidal interactions, such as the spatial dependence strength and temperature-dependent strength.[55] This model can also successfully describe the more complex and practically relevant case of mixed DNA brushes, which motivates the approach of designing materials computationally. Similarly, Frenkel and coworkers have presented an accuracy theory that correctly incorporates the configurational and combinatorial entropic factors to predict valence-limited interactions of DNA-coated particles.[56]

Mirkin and coworkers have proposed a rule-based complementary contact model (CCM) to predict the crystal structures of DNA-grafted colloidal NPs.[43] In their work, the four crystal structures (BCC/CsCl, AlB_2, Cr_3Si and Cs_6C_{60}) experimentally observed were explained by using this model. Basing on the same CCM model, Srinivasan and coworkers[57] have used genetic algorithm to design DNA-grafted particles that can self-assemble into desired crystal structures. Their theoretical analysis was not only able to successfully reproduce the experimentally validated phase diagram proposed by Mirkin, but also predict the formation of four previously unobserved crystal structures (AgI, Cu_5Zn_8, Pd_5Th_3, and Pt_3O_4).

Most recently, Mirkin and coworkers have constructed a simplified model to study the kinetics of the crystallization process, in which a given particle will transition between free, singly bound and doubly bound states.[58] Based on numerically solving the thermodynamic equations, variation of melting temperature and annealing window were predicted, suggesting the model is useful in the design of future crystals.

3.2 Theoretical simulations

3.2.1 MD simulations

MD simulation is probably the most successful way to describe of the dynamics of self-assembly. Generally, four types of potentials have been used to describe the force field of a coarse-grained model to capture the basic characteristics of DNA-NP assembly system.[59-61]As seen in Table 1, typical potentials and parameters used by three major groups (Sciortino group, Travesset group and de la Cruz group) are listed. Neighboring monomers are connected via spring potential, such as harmonic spring potential or FENE anharmonic spring potential. The characteristic rigidity of DNA is described by two kinds of angel potentials. The repulsive interaction between all monomers can be modeled with the Weeks-Chandler-Andersen (WCA) soft-core repulsive potential with a cutoff distance of $r_c=2^{1/6}\sigma$ or a purely repulsive potential. The attractive base pair interactions are modeled with the shifted Lennard-Jones (LJ) potential.

Table 1. Typical potentials and parameters used in MD simulations of DNA-NP assembly system.

Potentials	**Function Form**		
	Sciortino group [59]	Travesset group [60]	de la Cruz [61]
Spring potential	$V_{FENE}=-k(\frac{R_0^2}{2})\ln(1-(\frac{r}{R_0})^2)$ $k=30, R_0=1.5$	$V_{(r)}=\frac{1}{2}k_s(r-r_0)^2$ $k_s=330, r_0=0.84$	$V_{(r)}=\frac{1}{2}k_s(r-r_0)^2$ $k_s=330, r_0=0.84$
Angle potential	$V=k_l(1-\cos\theta)$ $k_l=5.0$	$V=\frac{1}{2}k_\theta(\theta-\theta_0)^2$ $k_\theta=100, \theta_0=\pi$	$V=\frac{1}{2}k_\theta(\theta-\theta_0)^2$ $k_\theta=10, \theta_0=\pi$
Repulsive potential (excluded volume)	$U_{(r)}=4\varepsilon[(\frac{\sigma}{r})^{12}-(\frac{\sigma}{r})^6]$ $\varepsilon=1.0, r_c=2^{1/6}\sigma$	$U_{(r)}=4\varepsilon(\frac{\sigma}{r})^{12}$ $\varepsilon=1.0$	$U_{(r)}=4\varepsilon[(\frac{\sigma}{r})^{12}-(\frac{\sigma}{r})^6]$ $\varepsilon=1.0, r_c=2^{1/6}\sigma$
LJ potential (base pair interaction)	$U_{LJ}=4\varepsilon_{bp}[(\frac{\sigma}{r})^{12}-(\frac{\sigma}{r})^6]$ $\varepsilon_{bp}=1.0, r_c=2.5\sigma$	$U_{LJ}=4\varepsilon_{bp}[(\frac{\sigma}{r})^{12}-(\frac{\sigma}{r})^6]$ $\varepsilon_{bp}=10.0, r_c=3.0\sigma$	$U_{LJ}=4\varepsilon_{bp}[(\frac{\sigma}{r})^{12}-(\frac{\sigma}{r})^6]$ $\varepsilon_{bp}=7.0, r_c=3.0\sigma$

The first coarse-grained model for MD simulations was introduced by Sciortino *and* *coworkers.*[59] As seen in Fig. 4a, four arms of ssDNA are attached to a NP in tetrahedral orientation. Each nucleotide is represented by two parts, the large sphere represents the bonds of the backbone and each base on DNA strands is described as a small sphere force site that can only bind to the complementary one. The diameter of the large sphere and the small sphere are σ and 0.35σ, respectively. By choosing a palindromic base sequence, two ssDNA can bond in a head-to-tail order to form dsDNA. A phase diagram as functions of density and temperature has been presented by using this model, which has provided guidelines for designing stable, equilibrium self-assembled low-density networks. However, this model has some limitations for description of real experimental systems. For example, the number of grafted DNA strands is too small to form long-range ordered structures.

Later, Starr and coworkers [62, 63] modified the model above. As shown in Fig. 4b, a large number of partially complementary ssDNA strands (about 12-30) are tethered to NP core. By designing ssDNA sequence, two types of self-assemblies can be realized: using a single linking NP type generates NP1-NP1 self-assembly and NP1-NP2 self-assembly is realized with a binary linking system. It was found that binary systems are preferable to form bcc lattice, while a single linking NP type generates the fcc crystal structure. These conclusions are in agreement with Mirkin's experimental results. Furthermore, a number of factors that impact the stability of bcc and fcc crystals have been studied: the linker sequence and length; the number of attached DNA strands; the NP size and the rigidity of DNA strands. However, this model has a limitation for description of real experimental systems because a ssDNA strand can hybridize with more than one complementary ssDNA strand in the process of simulations.

In 2011, Travesset and coworkers [60] provide a new modified coarse-grained model to study the crystallization dynamics of DNA-coated NP systems. A key development of this model was that flanking beads (FL) were utilized to protect any base from binding to more than one complementary base. As seen in Fig. 4c, two particles with the same size of $R = 3\sigma$ are functionalized with ssDNA strands which are consisted with ssDNA spaces and "sticky ends" (size of each bead is σ). The "sticky ends" have additional structure with smaller CT beads and FL beads of size 0.6σ. The hybridization is achieved through the attractive interaction between a CT bead and its complementary one. By cooling from higher temperature (T=1.4), disordered bcc superlattice was found at the temperature of T=1.3. Upon further cooling, CsCl-bcc superlattice was obtained at intermediated temperatures (near T=1.2). Furthermore, a phase diagram as a function of r (the number of ssDNA grafted to each NP) and η (volume fraction) was provided, which was in agreement with experimental results. [13, 40] In addition, the pathway of crystallization was investigated on large systems [64] by using the same model and results showed that crystallization is consistent with classical nucleation theory and the internal energy of the system remains constant during crystallization.

This model has also been applied in other MD simulations. Travesset and coworkers [65] have used this model to study the ssDNA-linked nano-cube systems and a phase diagram was presented as a function of temperature and fractional DNA length. Simulation results predicted that for relatively short DNA strands DNA-linked nanocubes are oriented face to face to form sc lattices and a bcc phase was obtained as DNA length increasing. A more complex phase diagram was obtained by subjecting the system to an external osmotic pressure.

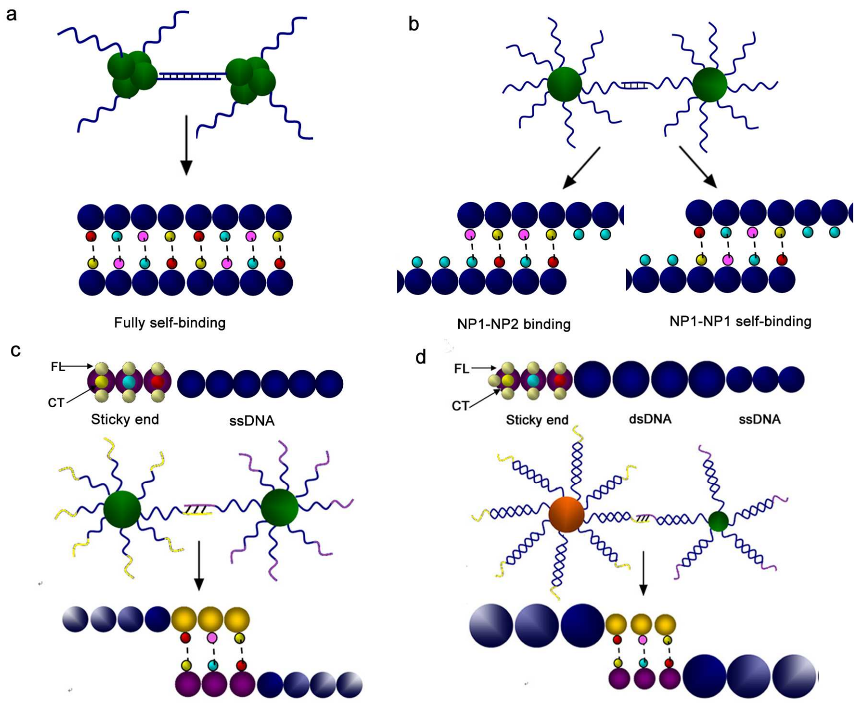

Fig. 4. Different kinds of coarse grained models of DNA-NP assembly systems for MD simulations.

As Travesset's model is limited to simulate the formation of many kinds of lattices that have been realized with dsDNA experimentally,[12, 41, 43] de la Cruz and coworkers proposed a new modified model [61, 66] to better describe these systems. It is to date the most detailed model that is able to capture crystallization process of many NPs. As seen in Fig. 4d, there are two main modifications in the model. First, the linker DNA chain contains both ssDNA and dsDNA and the dsDNA is modeled with the bead size two times larger than that of ssDNA. Secondly, the sizes of two NPs, the number and the lengths of grafted DNA chains can be different. Their MD simulation results showed that binary superlattices of bcc, CsCl, AlB_2, Cr_3Si and Cs_6C_{60} can be assembled from binary mixtures of DNA-linked NPs. The phase diagrams as a function of the particle size ratio and the DNA coverage ratios for three stoichiometric ratios (1:1, 1:2 and 1:3) were in accord with experimental results. They also found that the crystallization process is accompanied with a slight decrease of enthalpy. Furthermore, suitable linker sequences for future nano-materials design were proposed.[45]

de la Cruz and coworkers have also used LAMMPS molecular package to study the growth dynamics for DNA-NP crystallization.[47, 67] They found that the growth law of isolated crystals is in agreement with experimental observations. In addition, MD simulations of binary DNA-NP systems have produced a rhombic dodecahedron microcrystal that was in keeping with experimental observations.

3.2.2 MC simulations

Recently, three major groups have studied DNA-programmable assembly using MC method. The recent work of Starr group has emphasized the complicated phase and assembly behavior of nano-systems,[68-70] while, most studies of Crocker group [71-73] and Frenkel group [74-79] have focused on the DNA-coated colloidal assembly systems.

The initial coarse-grained model used by Starr and coworkers was first put forward for MD simulations [59] and it has been described in a simple way for MC simulations[80] as listed in Fig. 5a. In the process of developing the coarse-grained model, ssDNA stands are represented by rigid arms and the effective potential between two particles are described with center-to-center distance r, the two angles θ_1 and θ_2 and temperature T. Based on this coarse-grained model, Starr and coworkers have studied the phase behaviors depending on DNA sequence length[69] and number (from 3 to 6) of grafted DNA strands[68, 70]. (Fig. 5b)

Theoretical results have suggested the possibility of long range-ordered structures with distinct properties. It was found that crystallization of DNA-NP system proceeds via a two-step process with a highly connected amorphous state as intermediate. Furthermore, the reason accounting for difficulty of forming crystals is due to the slow dynamics of unzipping strands for lower temperature quenches. Theodorakis and coworkers have revisited this model in 2013.[81] By calculating the effective potential between two DNA-functionalized particles of equal size, they found that the transition from bonded to unbonded configurations takes place at considerably lower temperatures and increasing colloid size hinders the hybridization of the DNA strands.

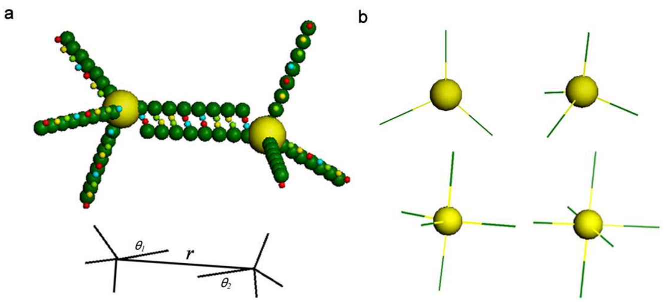

Fig. 5. Coarse-grained models for MC simulations. The concept on this figure originated from ref. 68 and ref. 80.

Crocker and coworkers have performed detailed studies on colloidal crystallization by utilizing Metropolis Monte Carlo (MMC) simulations. By using a quantitative interaction model, phase behavior and growth kinetics of DNA-directed particle self-assembly were obtained.[71] The results suggested that kinetic effects play a role in process of forming crystals. Later, influences of colloid size, interaction strength and interaction range on the process of crystallization were probed.[72] Furthermore, sub-micron binary systems have been studied by using a realistic model to construct a detailed mechanistic picture for binary superlattice formation. [73] In the model, A and B spheres of the same size are functionalized with different ssDNA and dynamic bridges between them are created by linker DNA strands. Upon MMC simulations and perturbation theory for free energy estimation, both the quality of the superlattice crystals and their crystalline structure have been presented. For example, bcc, fcc, face-centered tetragonal (fct) and hexagonal close-packed (hcp) superlattices have been predicted.

Frenkel and coworkers have simulated both micro- and nano-assembly systems with MC methods. They have used a coarse-grained model where colloids are represented as hard-spheres and each DNA chain is described by its center-of-mass position to study the phase behaviors of DNA-directed colloidal assemblies.[74-76] A vapor-liquid transition was observed under certain conditions due to the increase in entropy associated with re-arrangement of sticky end bonds or bond disorder. They have also confirmed that colloids with a small number of DNA strands can not generate crystals as the vapor-liquid-solid triple point on the phase-diagram disappears. Furthermore, the distance-dependent interaction between two surfaces functionalized with DNA sticky ends were simulated with MC method. It was found that NPs and micrometer-sized colloids will follow different routes to crystallization as stable gas–liquid separation only occurs for particles with radii smaller than a few tens of nanometers.[77] A new strategy was also proposed to improve the self-assembly properties and make systems crystallize in a wide temperature window.[78] In addition, the aggregation behaviors of four different DNA coated particles have been studied.[79] In that case a hexagonal crystal can be formed with two alternating bands containing two of the four possible particles.

4. Prospects

There has been great progress in the areas of sensing and making designed structures by controlling assembly of DNA-functionalized particles since the first experiment on DNA-directed NP self-assemblies were reported. In this review, recent developments of DNA-driven self-assembly of nano- and micro-objects into aggregates and 3D crystals are provided. Furthermore, theoretical descriptions for DNA -mediated assembly systems are presented and some typical coarse-grained models for MD and MC studies and the simulation results are introduced in detail.

At present, crystals contained two or three types of NPs have been obtained and a series of rules have been discovered to predict lattice structure. These developments have provided us with new insights and opened the way to create even more complicated structures. However, the resulting structures of DNA-mediated NP assemblies are often only stable in solution. To date, a few studies have focused on the transition of these systems to solid states.[82, 83] It is speculated that solid materials with numerous applications may be realized in future.

The realization of new DNA materials from experiments has provided important challenges for theory and resulted in many new methods and models. These theoretical results have not only confirmed and explained the experiments results but also stimulated the experiments by providing new predictions. To date, most of the coarse-grained models have focused on binary systems. Although a theoretical simulation of four types of NPs assembly has been provided, much more models have to be constructed to capture crystallization process of many kinds of NPs.

Biography

Xuena Zhang is currently a Ph.D candidate under the guidance of Prof. Rong Wang and Prof. Gi Xue. Her research interests focus on dynamics of DNA-nanopartilce self-assembly.

Rong Wang is currently a Professor at Nanjing University. She received her Ph.D at Sichuan University in 2001. She was a visiting scholar at Singapore –MIT Alliance of National University of Singapore in 2006−2008. She was a Humboldt research fellow at Institut für Physics of Johannes Gutenberg-Universität Mainz in 2009.06-08 and 2011.06-08**.** Her current research interests focus on theory and simulation of self-assembly of polymers, biomacromolecules and nanoparticles.

Gi Xue is currently a professor at Nanjing University. He received his Ph.D at Case Western Reserve University in 1983, under the supervision of Prof. J. L. Koenig and Prof. H. Ishida. He worked as a postdoctoral researcher at Case Western Reserve University in 1983-1988 and 1989-1990. He joined Nanjing University in 1988. His current research interests focus on structure and dynamics of geometrically confined polymers, interfacial structural characterization and control and theory of polymer physics.

Notes

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Programming Macro-materials from DNA-directed Self-assembly

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DNA-mediated self-assembly of nanoparticles into designed materials with novel properties and highly-ordered crystal structures.