Mini-Review Article

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Recent Advances in Novel DNA Guiding Nanofabrication and Nanotechnology

https://doi.org/10.1515/nanofab-2018-0003
Received July 3, 2018; accepted September 10, 2018

Abstract: DNA as life's genetic material has been widely investigated around the world. In recent years, with the fiery researches on nanomaterials, it also plays an important role in the development of material science due to its extraordinary molecular recognition capability and prominent structural features. In this mini review, we mainly overview the recent progresses of DNA guiding self-assembled nanostructures and nanofabrication. Typical DNA tile-based assembly and DNA origami nanotechnologies are presented, utilizing the recent 3D topology methods to fabricate multidimensional structures with unique properties. Then the site-specific nanomaterials synthesis and nano-DNA recognition on different DNA scaffolds/templates are demonstrated with excellent addressability, biocompatibility and structural programmability. Various nanomaterials, such as metals, carbon family materials, quantum dots, metal-organic frameworks, and DNA-based liquid crystals are briefly summarized. Finally, the present limitation and future promising development directions are discussed in conclusion and perspective. We wish this review would provide useful information toward the broader scientific interests in DNA nanotechnology.

Keywords: DNA; nanofabrication; nanotechnology; nanomaterials; biomedicine

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1 Introduction

Nucleic acid, as the carrier of genetic information, is one of the most basic substances of life, and has a profound impact on the production, heredity, variation and other important life processes. Besides that, nucleic acids, particularly deoxyribonucleic acids (DNAs), have been used as functional biomolecules for remarkable applications in materials science and nanotechnology. Since the early model of B-DNA structure, proposed in 1953 by Watson and Crick, DNA has sparked tremendous interests on the horizons of biological and materials science. Except the diverse conformations involving a series of important life events, it is also a powerful and versatile building block for the fabrication of nanostructures, with varied roles in nanodecives. The classic B-form DNA owns a right-handed double helix, with two antiparallel sugar phosphate backbones and the base pairs locating at the center of helix axis.[1] DNA also could adopt some other abundant secondary conformations, such as A-/Z- form, which was found by X-ray diffraction spectrum.[2] DNA B-Z transition has attracted much attention because of not only Z-DNA is biological important but also their relation to disease and DNA nanotechnology. Triple-helical DNA structure is formed by a duplex DNA and a third strand via Hoogsteen or reverse Hoogsteen hydrogen base pairing. It has become one of the most useful recognition motif in the design of new molecular biology tools, diagnostic agents and sophisticated DNA-based nanomaterials.[3] G-quadruplex and i-motif are also two types of four-stranded DNA structure. Classic human G-quadruplexs have been reported to inhibit telomere elongation, much effort has gone into the study of G-quadruplexs' potential capability in cancer diagnosis and therapy.[4] On the other side, DNA itself is a typical kind of nanomaterial with nano-sized conformation, and in the past decades DNA nanotechnology offers a variety of possibilities to the biodevice design and research.

Nanomaterials as the most promising materials of 21st century have inspired the researchers' interests due to their unique physical and chemical properties. R. Uyeda

and Gleiter et al., firstly acquired nanoparticles through evaporation and condensation in different inert gases or vacuum conditions.[5,6] Nowadays, more and more multifunction nanoparticles, multivariate composites and multidimensional structures are obtained, as well as nano-devices constructed on the basis of progress in nanofabrications.[7] DNA as a typical nanomaterial can be operated and assembled, and the rich obtained structures have been used as templates or anchors to synthesize nanomaterials in DNA nanotechnology, offering various possibilities to research nanomaterials. Novel DNA conformation polymorphism plays an important role as scaffold for metal nanofabrication and assembly. For instance, we have utilized high-stability triplex DNA as template to fabricate homogeneous, bright and site-specific silver nanoclusters, which simultaneously answered the questions of excellent site-specific nucleation and growth, homogeneity and stability against salt of DNA-templated nanoclusters.[8] Also rigid branched DNA motifs can be designed through the complementary Watson-Crick base pairing, then further assembled into discrete finite object or infinite periodic lattices through sticky-end cohesion.

In this review, we mainly focus on the recent innovations in DNA nanotechnology and nanofabrication. DNA tiles as the basic element for DNA self-assembled nanostructures are shortly summarized with various and multidimensional synthesis. DNA origami self-assembly is demonstrated, especially the most recent development of complex and multidimensional artificial objects design with DNA scaffolds, as well as the new methods to produce series 2D, 3D morphable structures with improved stability. In addition, various DNA-based nanomaterials fabrication, such as metal/carbon nanomaterials, quantum dots, and metal-organic frameworks, are briefly summarized with DNA as novel template to guide their construction.

2 DNA tile based self-assembled nanostructures

In the 1980s, Seeman's research team[9] invented a simple DNA structure with four-arm junction (DNA tile) and two double helix parallel DX modules (double-crossover).[10] This event was considered as the beginning of the era of DNA nanotechnology. On the basic of DNA tile and DX modules, Yan *et al.*[11] constructed a DNA structure containing four four-arm junctions (nine strands), which easily self-assembled into two infinite lattice forms: nanoribbons or two-dimensional (2D) nanogrids. Afterwards, Mao and colleagues successively fabricated infinite two-dimensional(2D) lattices with equilateral triangle motifs composed of three four-arm junctions[12] and n-point-star tile, including 3-,[13] 4-,[14] 5-,[15] and 6-point-star tiles.[16] DNA sequence symmetry was then introduced into the design of DNA nanostructures, which dramatically reduced the width of sequences and the number of DNA strands.[14] Moreover, based on a hypothesis that even-numbered, branched DNA junction (e.g. 4-, 6-, or 8-arm motif) will adopt stacked conformation in the presence of divalent cations, the authors developed a class of DNA double multi-arm junctions (DMaJs) (Figure 1a). This study hints on the limitation of exploiting the sequence symmetry approach to reduce the number of unique DNA strands.[17] On the contrary, by using self-assembly, Yan *et al.*[18] constructed a 2D pattern of square unit cell or triangular unit cell termed the Kagome lattice, whose advantages are less symmetry and proper matching rules (Figure 1b). In addition, Seeman and Mao added a triplex forming oligonucleotide for the self-assembly of 3D DNA crystals to enhance the inter-unit interactions (Figure 1c).[19] A six-arm DNA junction and a six-helix DNA nanotube has been constructed by incorporating unnatural base pairs into the double helices to enhance the thermal stability of integral DNA nanostructure (Figure 1d).[20] The initial designs of DNA tile and assemble lattices nanostructures lay a firm foundation for the development and applications of nanostructures.

Recently, a systematic study has performed on the effect of structural parameters of PX (a four-stranded structure that consists of two parallel right-handed DNA duplexes) motifs and confirmed the optimal assembly parameters of periodic two-dimensional arrays.[21] The result provided a mean to reduce the usage of traditional single-stranded sticky ends, thus increase possibility of building complex DNA structures from PX motifs and reduce the assembly error in DNA self-assembly. High-yielded 2D honeycomb-like and grid-like framework nanostructures have been designed by using 3-arm and 4-arm tiles with the smallest circular DNA as the pivotal of tile, instead the previous 3-point and 4-point star motifs.[22] Gothelf et al.[23] further reported an "inverse" hierarchical assembly strategy using 12-arm junction to construct a stable DNA lattices structure (0D, 1D, 2D, 3D) in one-step. In this strategy, the formation of the wires (double-stranded tiles DSTs and half double-stranded tiles HDSTs) are different from traditional assembly of DNA tiles (hybridization of sticky ends). The wireframe structures exhibit good stability in physiological conditions and are cost-effective due to the minimal amount of DNA.

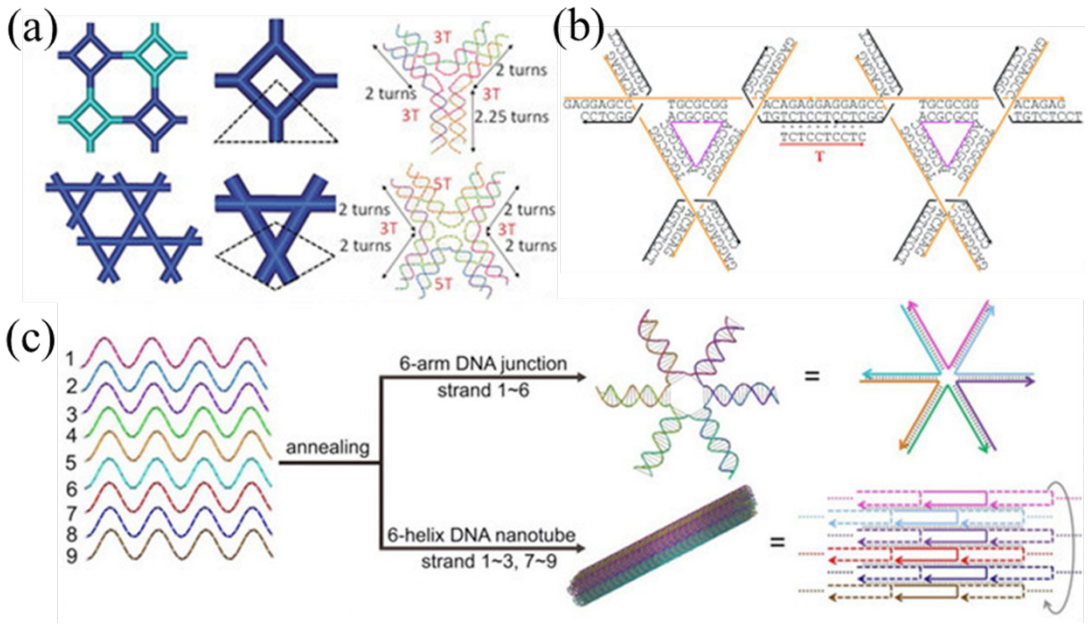

Figure 1. Various 2D DNA tile assemble lattices nanostructures. (a) Multi-arm DNA junction motifs with reduced symmetry. (b) The interaction between two triangle motifs stabilized by triplex formation. (c) A six-arm DNA junction and a six-helix DNA nanotube.[18-20] Reprinted with permission from Ref.[18-20]

With the rapid development of various 2D DNA lattices structures, a majority of 3D polyhedral assembly structures connected by DNA emerged. There are many potential applications for 3D polyhedral assembly structures, such as capsules for drug delivery, biosensors, nanoguest encapsulation and 3D protein/nanoparticle organization. Seeman and colleagues have established cube-like[24] and truncated octahedron[25] molecular complexes assembled from covalently closed DNA since 1990s that contain many equal-length double-helical edges and vertices. Afterwards, these researchers obtained more polyhedral structures in a similar method. A series of 3D typical polyhedra structures have been assembled from the above n-point-star blocks with symmetric DNA sequence, such as tetrahedron, dodecahedron and even truncated icosahedron (Buckyball) structure[26].

Recently, Mao et al.[27] proposed a directed and flexible strategy to assemble a range of complex DNA nanocages using directing tiles (D-tiles) and assembly tiles (A-tiles). All tiles used in this work are star-shaped motifs, which construct dodecahedron or buckyball structures with triangular faces. The shapes with larger molecular weight make these polyhedra non-deformable, while non-triangular face have deformable structures (Figure 2a). However, there are also some DNA nanocages that cannot be assembled directly, therefore they applied structural transformations to solve this problem[28]. In this strategy, the first step is assembling a precursor DNA nanocage(cage I), the second is transforming cageIinto a desired, complicated nanocage (cage II), the third is using isothermal strand displacement to convert cage II into cage III (Figure 2b). After that, they found there were dramatic and reversible changes between three DNA nanocages in the 3D structures and topologies. Also, they developed a layer-by-layer strategy to assemble multilayered "Russian doll"-like DNA tetrahedral nanocages (Figure 2c). In these DNA nanostructures, every layer has the same sequences strands, similar structure and different size. These structures can be used to control drug release.[29] Zhang and Mao introduced a new binary self-assemble symmetric DNA nanocages by deliberately engineering the sticky-end interaction between the component building blocks.[30] In this new approach, component motifs were no longer divided into directing motif or assembling motif but two types of DNA motifs which were equipped with different sticky-ends are employed. By changing the sequences of previously star-shape motifs (2-, 3-, 4-, 5-), the author modulated motifs' interactions, thus successfully synthesizing new types of more complicated DNA polyhedral structures, including rhombic dodecahedron and rhombic triacontahedron (fig. 2d). In the end, they claimed that, with unique sticky-end design, ternary or quaternary nanocages may be feasible in the future. DNA tiles as the basic element of tile self-assembled nanostructures can be designed in various forms to fabricate multidimensional nanostructures with unique advantages.

3 DNA origami nanostructures

In contrast to DNA tile based self-assembly, the scaffold DNA origami has an important impact on structural DNA nanotechnology over the past decade, especially on the fabrication of arbitrarily complex structures with finite-size, high molecular weight, and for highly addressable pixel in the nanoscale. DNA origami is usually obtained from a straightforward self-assembly process in which a long single-stranded scaffold folds into special desired shapes, with a multitude of short helper strands needed. The experiment processes are simple compared with the exact stoichiometric control and the lengthy synthetic processes of DNA tile based self-assembly. So far, nanostructures created by DNA origami have been widely used in biosensor, drug delivery, enzyme cascade and biomolecular analysis platforms.

Since 2006, Rothemund et al.[31] firstly described a simple method to fold 7-kilobase single-stranded DNA scaffolds into arbitrary two-dimensional desired shapes. By mixing this long single-stranded DNA strand with about 200 short oligonucleotides, called 'staple strands', shapes of squares, disks and five-pointed stars were obtained. Various rigid branched DNA motifs were further developed, such as an analogic China map in the nanoscale[32], 2D origami of a dolphin[33] and a nanoalphabet 'BYU'.[34] An addressable 3D origami structure with DNA box shape (42nm×36nm×36nm) that can be opened by DNA 'keys' was constructed by Andersen and coworkers.[35] Also a closed origami box by gradually adding joint strands was designed and constructed.[36] 3D structure can also be prepared through connection strands on 2D DNA scaffold structures, such as a honeycomb-pleated pattern was reported to construct different kinds of 3D objects.[37-38] Furthermore, a ribbon-like Möbius strip via reconfiguring the programmable DNA Möbius strip topological structure was assembled.[39] They proposed using the DNA origami folding technique to assemble high curvature nanostructures in three-dimensional (3D) space, which included 2D arrangements of concentric rings and 3D ellipsoidal shells, spherical shells, and nanoflask nanostructures.[40] Furthermore, Yin et al. reported the simplest 'single-stranded tile' that consists of an 42-base strand of DNA composed entirely of concatenated sticky ends to bind with four local neighbors during self-assembly, and constructed complex two-dimensional shapes.[41] In these previous examples, researchers found that the original DNA origami always needs a large number of staple strands. To solve this problem, Fan et al. proposed a simple and novel strategy to fold well-defined DNA nanostructures with only several staple strands by rolling circle amplification.[42]

Very recently, some novel DNA origami methods and structures have been reported. A new type of nanotube

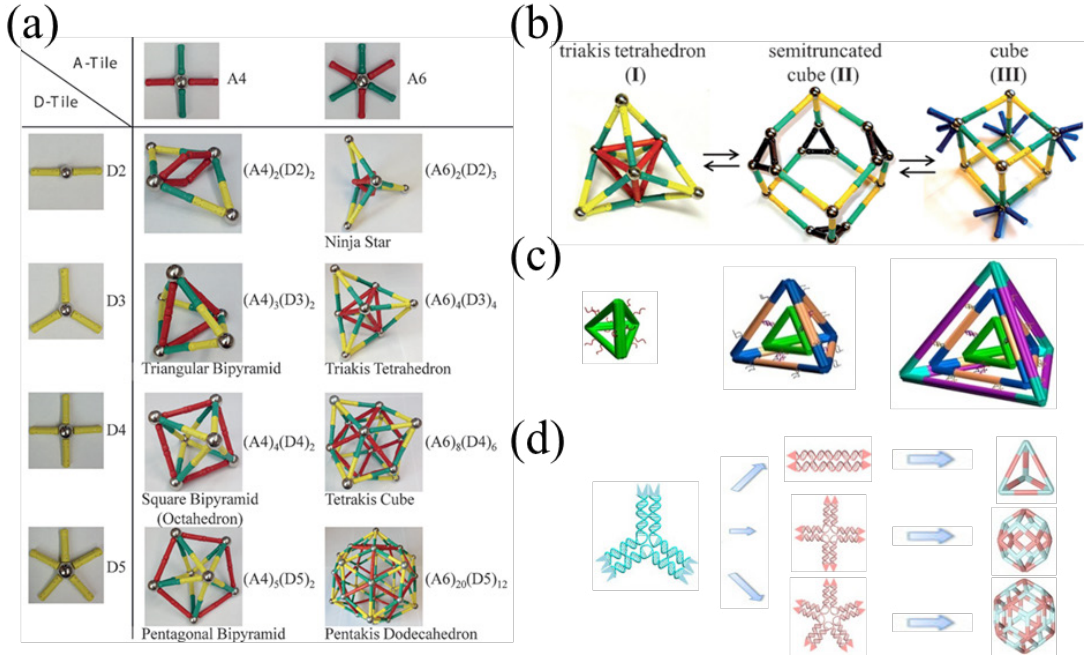

Figure 2. Series of 3D DNA tile assemble polyhedral nanostructures. (a) The component tiles and the resulting DNA cages. (b) Structural transformation of DNA nanocages. (c) Layer-by-layer self-assembly of a multilayered DNA tetrahedron. (d) Binary self-assembly of highly symmetric DNA nanocages. [27-30] Reprinted with permission from Ref.[27-30]

has been assembled from small circular DNAs (Figure 3a).[43] Compared to native DNA nanotubes, these novel nanotubes are composed of lateral double helices rather than longitudinal double helices. A fibrillar superstructure was built via pairing 3D DNA origami cuboids and first established the design principle of 3D DNA origami objects on switchable nanoparticle self-assemblies by Andreas and coworkers (Figure 3b).[44] This strategy will rear the merger of two relative independent fields, which is useful for fundamental studies and applications in self-assembled colloidal systems. To reduce the volume to base pair ratio, a triangulated DNA origami wireframe trusses structures was also designed and synthesized with only one double helix per edge.[45] In order to increasing the molecular weight, Yin *et al.* developed a series of massive polyhedras by using controllable inter-arm angles and arm lengths of DNA origami tripod motifs.[46] Also a highly ordered and orientation-controllable DNA origami array has been constructed by taking advantage of anti-parallel and parallel double crossovers DNA junctions (Figure 3c).[47] Björn's research group presented a general approach for replacing the close packed helices to a single DNA double helice at the edges of the folded arbitrary polygonal mesh.[48] In a similar pattern, Yan demonstrated an utility method to fabricate high complex and programmable wireframe DNA nanostructures, which integrated multi-arm junction vertices and antiparallel DNA crossover lines in scaffolded DNA origami.[49] This method is also adapted to generate various intricate wireframe 2D patterns and 3D polyhedra wireframe structures. Similar to previous 3D frameworks assembled by DX molecules and multi-arm junction motifs, they further developed the 3D multilayered framework[50] DNA origami structures with the aid of novel layered-crossover (LX) motifs. These motifs contain crossover pairs and connect neighboring layers of DNA double helices. Different to the traditional in-plane crossovers or multi-arm junction, the LX motifs have controllable angles, depths, geometries, and could be applied for the self-assembly for the growth of 2D or 3D crystals. Moreover, the framework based on the LX motifs

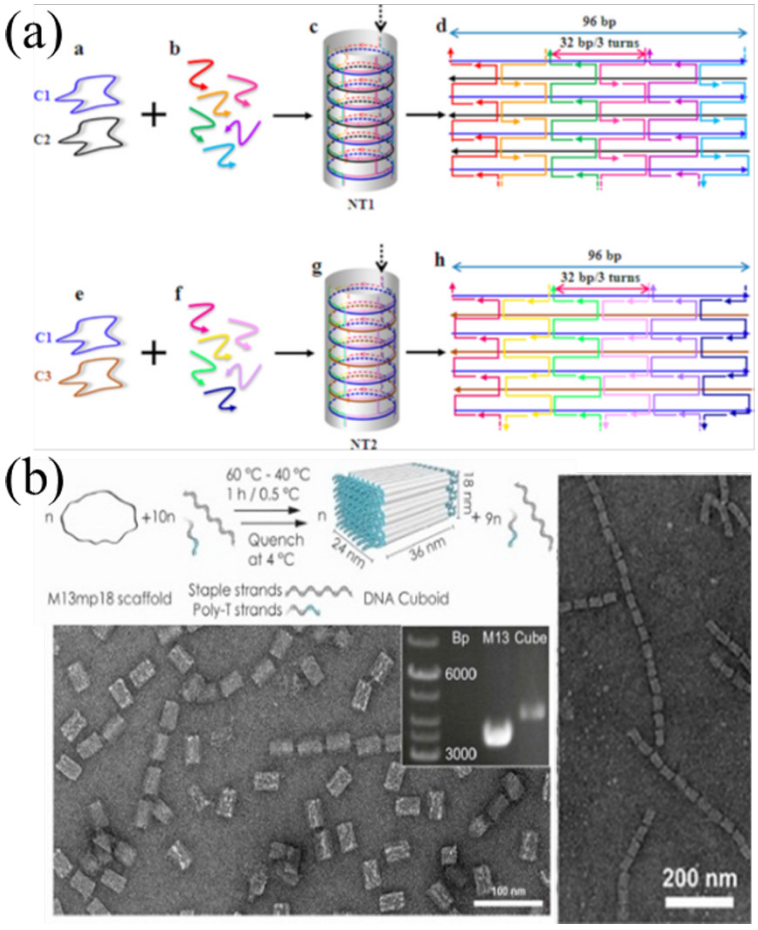

Figure 3. Various DNA origami multi-dimension nanostructures. (a) Folding strategies for the formation of nanotubes NT1 and NT2.[43] (b) 3D DNA origami cuboids and DNA cuboid fibrils.[44] Reprinted with permission from Ref.[43][44]

offers a wide range of potential applications in enzymatic reactions, the synthesis of heteronanomaterials and porous nanomaterials.

Various DNA nanotechnologies and products are springing up due to scientists long aspiring to construct complex and multidimensional artificial objects using self-assembly.[51] More recently, Tikhomirov *et al.* constructed the smallest Mona Lisa by using DNA origami fractal assembly.[52] Combining fractal assembly with fractile compiler software, these authors have the ability to make arbitrary DNA motifs, including the Mona Lisa, a bacterium, a rooster, a photoreceptor circuit, or a chess-game pattern (Figure 4a). Wagenbauer and coworkers developed wedge-shaped building blocks with alterable

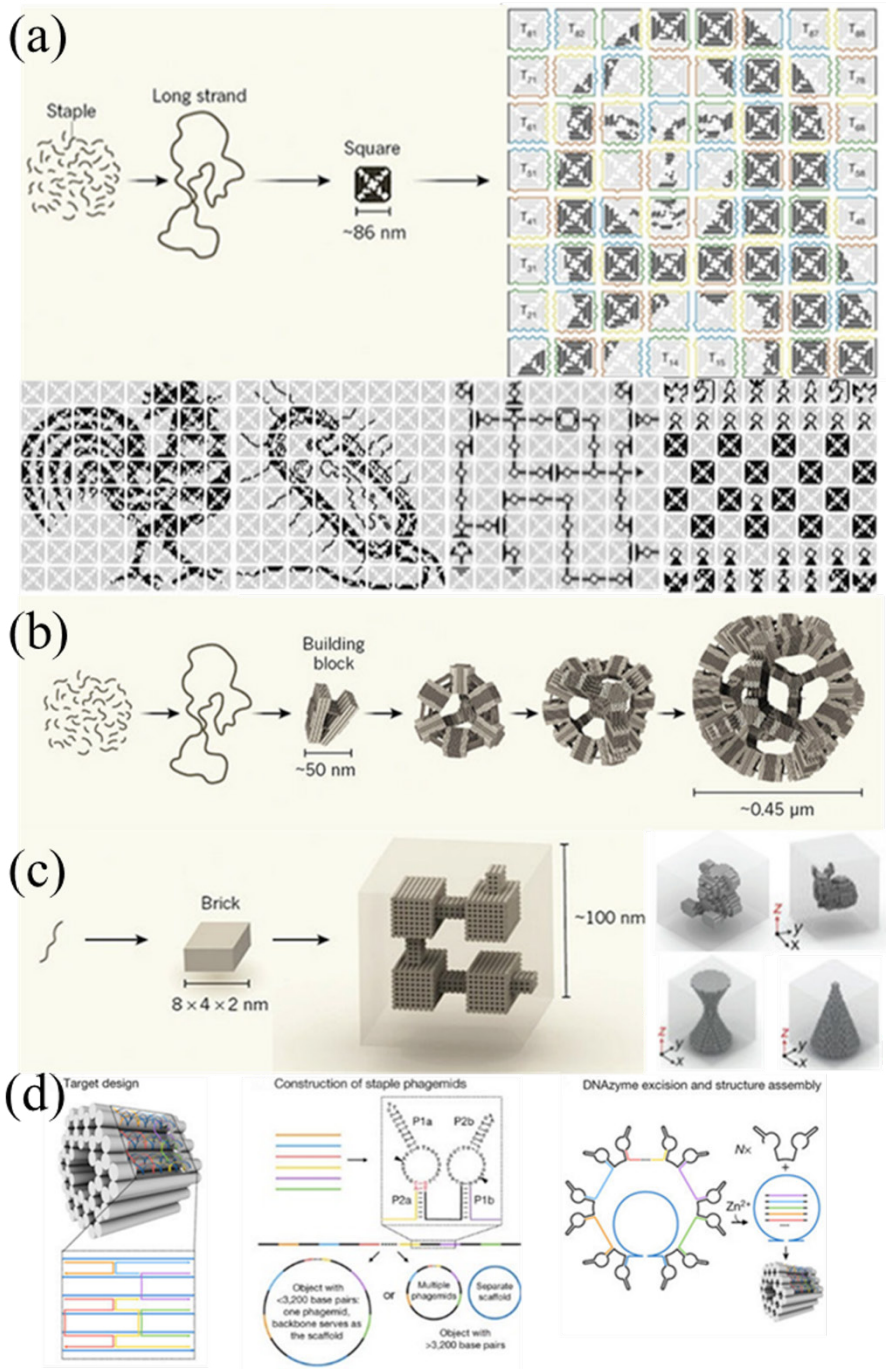

Figure 4. Novel DNA origami methods and structures. (a) Fractal assembly of micrometre-scale DNA origami arrays with arbitrary patterns. (b) Gigadalton-scale shape-programmable DNA assemblies. (c) 3 D nanostructures self-assembled from DNA bricks. (d) Biotechnological mass production of DNA origami.[52-55] Reprinted with permission from Ref.[52-55]

angle, large size and high yield, which used to assemble into controllable DNA origami structures in application (Figure 4b).[53] A novel nucleotides which have the ability to self-assemble into 0.1~1 gigadalton 3D structures was also presented (Figure 4c).[54]

At the same time, Praetorius *et al.* developed a new method to produce litre-scale single-stranded precursor DNA products by using bacteriophages.[55] Hundreds of target strand sequences were cleaved by self-excising 'cassettes' DNAzyme for DNA origami self-assemble, which greatly reduced the cost of the DNA origami structures to around 20 cents per milligram and showed competitive to conventional solid-phase chemical synthesis (Figure 4d). On the other hand, the DNA origami structures can be degraded quickly by nucleases in the necessarily higher ionic strength. To avoid this issue, Schmidt *et al.* used a cationic PEG-PLys block copolymer to develop DNA origami polyplex micelles with cost-effective and robust shell protection.[56] At the same time, a simplified modular architecture of complex DNA origami was also introduced to reduce the complexity[57]. By linking modular blocks with standardized connecting staples, authors easily constructed a series of 2D, 3D morphable structures.

4 DNA nanostructures as template for nanomaterials

Owing to the excellent addressability, biocompatibility, structural programmability, and site-specific binding, various DNA structures hold potentials to arrange and organize multi-dimension nanomaterials, such as metal/carbon nanomaterials, quantum dots, and metal-organic frameworks, and so on. DNA-mediated assembly of nanomaterials has received much attention due to the potential application in nanoelectronics, biosensing, clinical diagnostics and dynamic materials.

4.1 Metal nanomaterials

Typical gold nanoparticle work has been done by Lu's group. They studied in detail different factors that influence the DNA-linked gold nanoparticle (AuNPs) system. After that, to precisely control the position and distance of AuNPs, these researchers used DNA as template to decorate the phosphorothioate anchors coupled with a short bifunctional molecular fastener.[58,59] The mechanism effecting the morphology and spatial position of DNA-mediated metal nanoparticles has been systematically studied. DNA plays a significant role in changing the shape and the original biorecognition ability of gold nanoparticles.[60] Also, the morphological evolution of gold nanoprism in the presence of T30, G20, C30 and A30 was investigated (Figure 5a).[61] Then, the author reported that different DNA sequence combinations have the ability to synergistically control different morphologies of AuNPs in the growth process (Figure 5b).[62] These works demonstrate that DNA molecules serving as programmable ligands will fine-tune the morphologies of AuNPs and we can utility these mechanisms to code or predict the morphology of other NPs.

Besides, a systematic investigation of the effects of different DNA sequences on the morphologies of silver nanoparticles grown from Ag nanocube seeds was reported [63]. The presence of 10-mer oligo-A, -T, and -C directs AgNPs growth from cubic seeds into edge-truncated octahedra of different truncation extents and truncated tetrahedral AgNPs, while AgNPs in the presence of oligo-G remained cubic (Figure 5c). A facile approach has been demonstrated to prepare anisotropic DNA-functionalized gold nanoparticles (a-DNA-AuNP) with high yield. In comparison to previous work that DNA directs assembly of Janus nanoparticles, DNA density tunes the competition between thiolated hydrophilic DNA and thiolated hydrophobic phospholipid on the gold surface.[64, 65] The anisotropic feature allows regioselective assembly with high monodispersity by replacing different DNA strands on the a-DNA-AuNP. In biological engineering, this feature can meet the requirement of precise and specific target response. Simultaneously, Song *et al.* reported the use of programmable DNA sequences to control gold nanorod (AuNR) overgrowth, resulting in gold nanoparticles varying from nanodumbbell to nanooctahedron shape, as well as the composite shapes in middle (Figure 5d).[66] In addition to serving as the ligand to control the morphologies of single monometallic nanoparticles, DNA also directs the morphologies of bimetallic nanoparticles. For example, DNA-templated synthesis of Pd-Au bimetallic nanoparticles has been realized from palladium nanocube seeds. In the presence of T10, G10, C10 and A10 homo-oligomer DNA sequences, four distinct morphologies can be constructed, and it can be further considered as the foundation of preparation for composite materials (Figure 5e).[67] Furthermore, Ding *et al.* has reported an Au-DNA-Pd bimetallic nanorods sensor that DNA- functionalized AuNR served as linkers and seeding sites of Pd nanoparticles.[68]

Recently, much attention has been attracted to the distinct properties of nanoparticles in plasmonics, particularly of gold nanoparticles. Using the DNA origami template, two 40 nm Au-Ag nanoparticle heterodimers

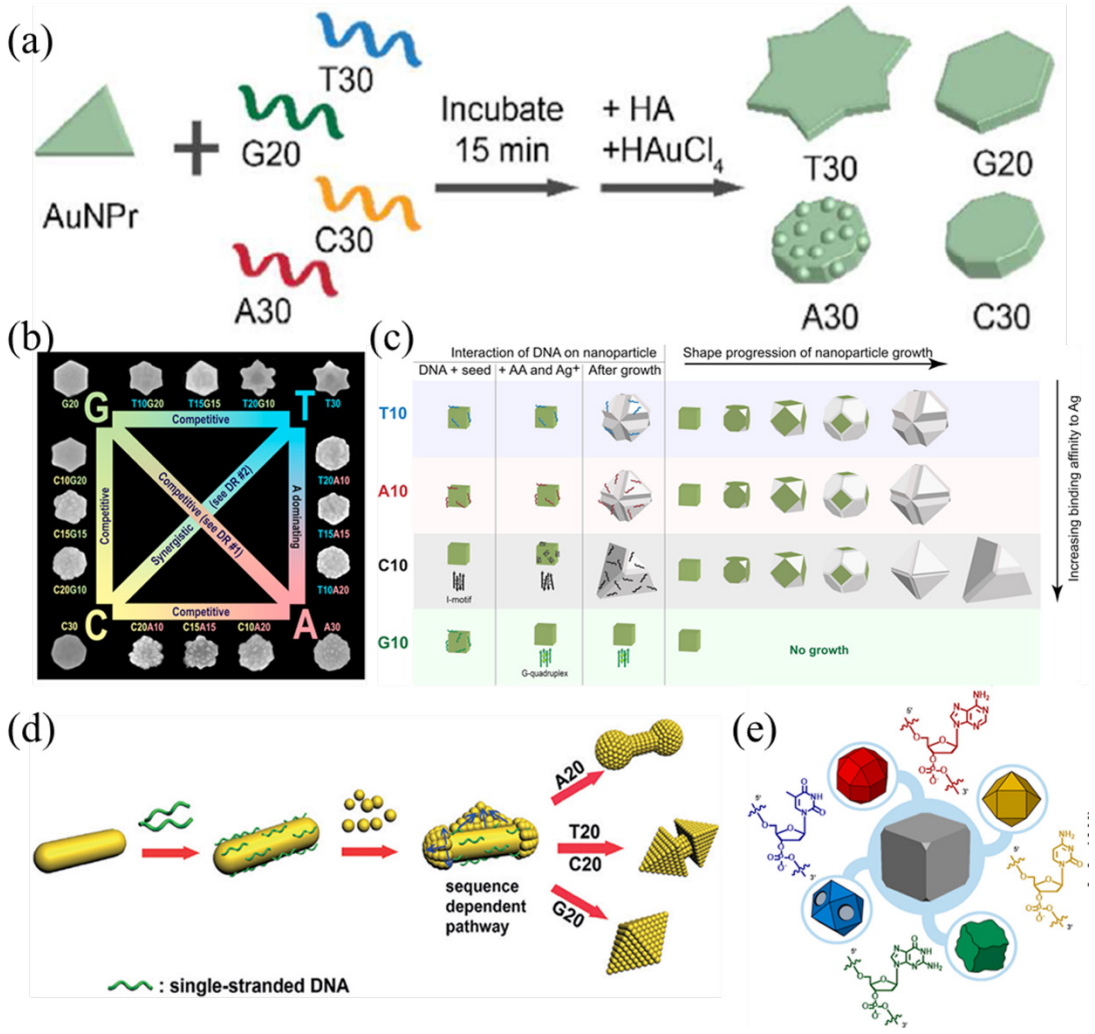

Figure 5. The morphological evolution of metal nanomaterials dependent on diffierent DNA sequence. (a) DNA encoded growth of Au nanoprism seeds.[61] (b) AuNP morphologies grown from Au prism seeds in the presence of different DNA sequences combinations.[62] (c) DNA-mediated shape control of silver nanoparticles.[63] (d) gold nanoparticles with shapes from nanodumbbell to nanooctahedron with programmable DNA linker to control gold nanorods overgrowth processes and shapes.[66] (e) The overgrowth of AuNRs by homooligomeric DNA with different sequences.[67] Reprinted with permission from Ref.[61-63, 66, 67]

were fabricated, separated by sub-5 nm gaps similar to the previous report of Au-Au dimers (Figure 6a).[69, 70] This heterodimer was employed in exploring the interaction between Ag-Au nanoparticles of the same size for direct dipolar coupling of the Au and Ag electrons. Gates and Woolley further systematically studied the effects of several experimental parameters (hybridization time, magnesium ion concentration, ratio of Au NPs to DNA origami, and the age of the AuNPs solution) on AuNPs attachment density and spacing along single-file DNA origami structures.[71] Their results provided a helpful guiding for creating high-density, continuous nanoparticles in thin DNA origami structures. It is helpful to further use those materials as conductive wires in nanoelectronics. The attachment yield of AuNPs to DNA origamis was also investigated and prepared self-assembled plasmonic devices.[72] Besides, novel right- and left-handed AuNPs nanostructures on DNA origami have been fabricated by carefully arranging the nanomaterials attachment behavior.[73] Various applications are reported on novel plasmonic properties with DNA as scaffold. Au-Ag-core-shell NPs on DNA origami substrates were arranged in order to increasing the SERS sensitivity as a biosensor (Figure 6b).[74] A series of triangular DNA origami structures as templates for the organization of AuNRs have been investigated.[75, 76] Similarly, a stimulus-responsive plasmonic nanosystem based on DNA origami-organized gold nanorods has been demonstrated as seen in Figure 6c.[77] The constructed chiral system can be operated by adjusting to medium pH and optical conditions. All of these are expected

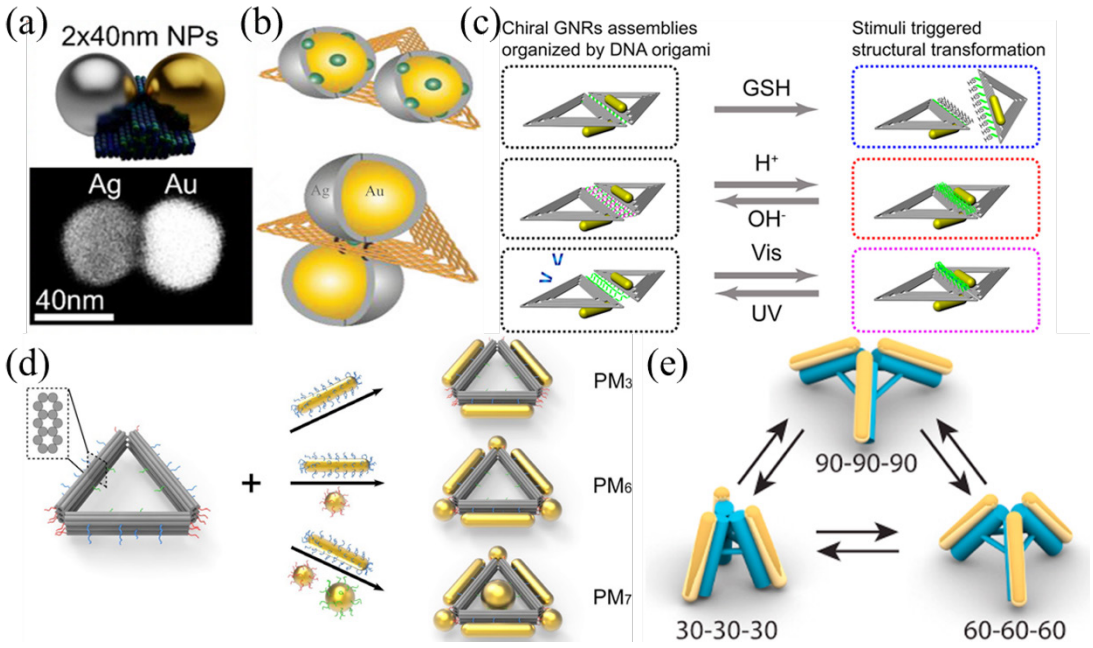

Figure 6. (a) Ag-Au nanoparticle heterodimers on DNA origami platform.[70] (b) Au-Ag-core-shell nanoparticle dimers on triangular DNA origami nanostructures.[74] (c) stimulus-responsive chiral gold nanorods on triangular DNA origami.[77] (d) Plasmonic metamolecules on DNA origami.[78] (e) The reconfigurable DNA origami tripod with gold nanorods.[79] Reprinted with permission from Ref.[70][74][77][78][79]

to apply in cancer diagnosis and therapy in vitro/vivo with highly sensitive plasmonic readout. Different gold structures can be arranged together easily with DNA as scaffold. For example, Au nanoparticles and nanorods are designed in prescribed positions on 3D DNA origami triangles to form various heterogeneously plasmonic metamolecules (Figure 6d).[78] Another 3D reconfigurable plasmonic nanostructure has been constructed with controllable, reversible conformational transformation using bottom-up DNA self-assembly. Three gold nanorods were positioned onto a reconfigurable DNA origami tripod (Figure 6e).[79] Similar to the previous work, the DNA tripod contains a tunable internanorod angle and distance by displacing strands [46].

Furthermore, DNA tubes are generally constructed from either multi-helix DNA bundle structures or 2D DNA tile lattices. By arranging gold nanoparticles on specific sites of DNA origami structures, rolling and stapling the former complex, various single or double helical arrangement, stacked rings, and nested spirals chiralities plasmonic architecture that exhibit unusual optical properties can be formed.[80-83] The self-assembly of micrometer-scale 2D honeycomb lattices and tubes, have been successfully demonstrated, in which a family of hexagonal DNA-origami tiles were used for the arrangement of gold nanoparticles into cluster and superlattice geometries (Figure 7a).[84] Very recently, Liu's research team firstly showed the hierarchical assembly of plasmonic toroidal metamolecules, which exhibited tailored optical activity in the visible spectral range. Each metamolecule consists of four identical origami-templated helical building blocks (Figure 7b).[85] Furthermore, a unique and effective strategy has been developed to pattern DNA recognition sites in a helical arrangement around AuNR. This fabricated a new set of heterogeneous AuNR@AuNP plasmonic helices by attaching complementary-DNA-modified AuNPs to the predesigned sites on the AuNR surface (Figure 7c).[86]

3D plasmonic chiral metamolecules have been synthesized through grouping of two AuNRs on DNA origami. These AuNRs form a 90 twisting angle and exhibit strong circular dichroism.[87] By adding designed DNA fuel strands, the 3D plasmonic metamolecules of AuNRs attached on DNA origami bundle structure were reconfigured.[88-90] Anisotropic AuNRs helical chiral superstructures can be arranged by two-dimensional DNA origami template. By designing the 'X' pattern of the arrangement of DNA capturing strands on both sides of a two-dimensional DNA origami template, AuNRs functionalized with the complementary DNA sequences were positioned on the origami and were assembled into AuNRs helices with the origami intercalated between neighboring AuNRs (Figure 8a).[91] Subsequently, Liu *et al.* demonstrated a light-driven plasmonic nanosystem by assembling reconfigurable DNA origami templates into

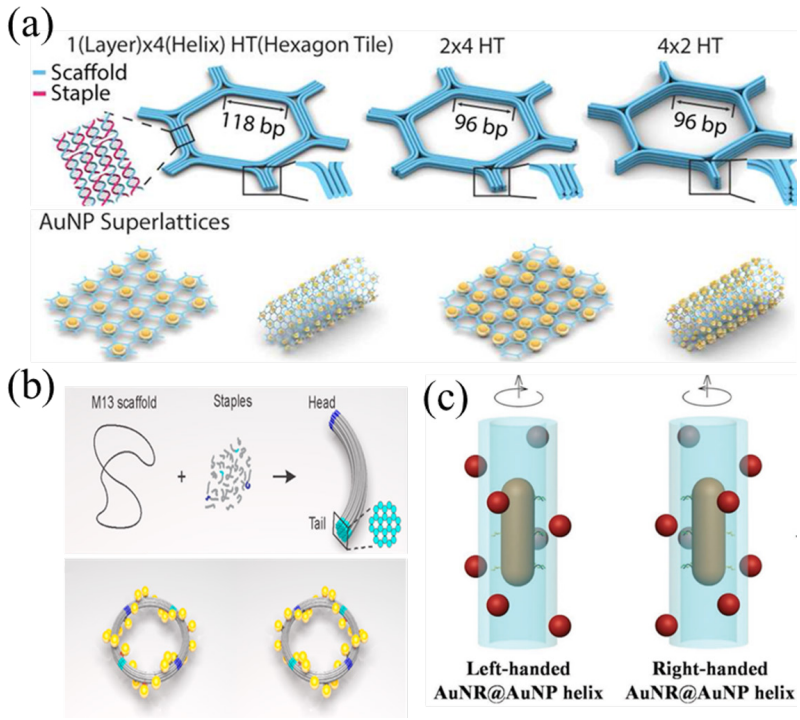

Figure 7. (a) Programming self-assembly of DNA origami honeycomb two dimensional lattices and plasmonic metamaterials. (b) The left- and right-handed 3D plasmonic toroidal metamolecules assembled by DNA origami. (c) the DNA origami-guided self-assembly of AuNR@AuNP helices. [84-86] Reprinted with permission from Ref.[84-86]

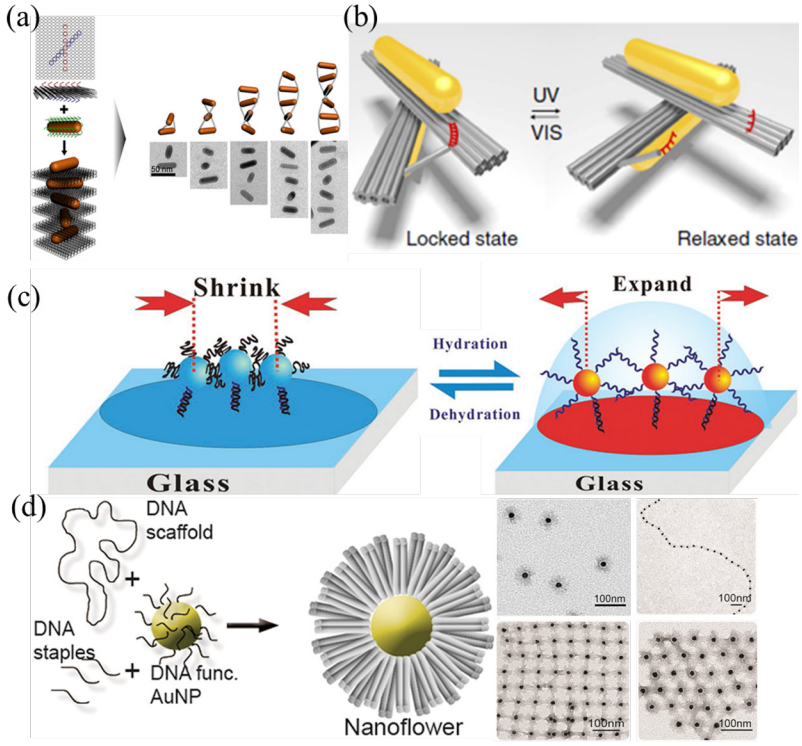

Figure 8. (a) Au nanorod helical superstructures with designed chirality. (b) Light-driven 3D plasmonic nanosystem. (c) Humidity-responsive SNL plasmonic films. (d) Ordering AuNPs with DNA origami nanoflowers.[91-94] Reprinted with permission from Ref.[91-94]

two AuNRs.[92] With optical addressability, reversibility and modulability, this nanosystem has the ability to transform molecular motion into reversible chiroptical function (Figure 8b). Also, a series of DNA-mediated humidity-responsive single-nanoparticle-layer plasmonic films have been fabricated with reversible chromogenic properties, which was smartly controlled by the nanoparticles distance (Figure 8c).[93] Turberfield *et al*. further presented a nanoflower structure where AuNPs were wrapped by flower-shaped DNA origami structures.[94] The nanoflower was assembled into two-dimensional gold nanoparticle lattices, which can be controlled by auxiliary DNA strand. The final materials own a significant effect on optical metamaterials and catalytic superlattices (Figure 8d).

Till now, Au,[95-97] Ag,[11, 98-101] Cu,[102] Ni,[103, 104] Pd,[105-110] Pt,[111-113] and Co[114] etc., have been successfully demonstrated as idol metals to metalize DNA templates for making nanowires. However, most of these studies have turned λ-DNA into a linear form that doesn't meet the needs of the device. Therefore, DNA origami was adopted as an ideal template for making nanowires.

Based on the optimization of AuNPs attachment density, spacing and yield in DNA origami, Harb *et al.* studied a series of metallized DNA origami that form electrically conductive nanowires through an electroless deposition process. For instance, the branched, open-structured DNA origami used to fabricate conductive elements has good selectivity. By modifying staple strands for fabrication of conductive wires onto branched DNA origami templates, the densities and continuity of AuNPs onto branched DNA origami structures were increased.[115] The work addressed the challenges and limitations of DNA origami as template of site-specific attachment and metallization of gold nanoparticles.[116] It was also the first demonstration of obtaining conductive gold and copper nanostructures by using circuit-like DNA origami as template. Furthermore, the multiple Pd seeding steps could play a key role in improving seed uniformity and density during the process.[117] Selective deposition of copper and gold on predesignated locations of a single DNA origami template represented an important step in the creation of metalized DNA origami.[118] Recently, the researchers used gold nanorod seeds to manufacture completely continuous and small diameter conductive nanowires, which have fewer connection points and lower resistivity values than the corresponding from spherical seeds. The key contribution of this work is the using of anisotropic electroless gold deposition to fill the gaps of neighboring nanorod seeds on DNA origami templates (Figure 9a).[119]

Apart from metallization of DNA templates, the metal-mediated base pairs show great attraction to develop metallo-DNA nanowires for electronic devices and the genetic-code therapeutics research fields. However, only short metal-DNA hybrid duplexes were synthesized by bottom-up methods, such as Au,[120] Ag,[121-123] Cu,[124] Hg,[125-128] Mn[129], K,[130] metallo-DNA nanowire.[131] Compared to other metals, Ag is more flexible in integrating with natural base pairs. Gan's research team reported a DNA structure composed of two C-Ag-C pairs and a G-Ag-G pair in a short DNA sequence (GCACGCGC) strand (Figure 9b).[132] Based on previously observed four different metallobase pairs, Jiro Kondo and co-workers constructed the uninterrupted silver metallo-DNA nanowires with a large aspect ratio of 50,000[133] It consists of numerous dodecamer duplexes with G overhangs and in these nanowires, every unit is linked by four different metallobase pairs (the frequently observed C-Ag-C, as well as G-Ag-C, G-Ag-G and T-Ag-T).[134] Moreover, the nanowires with residual adenine can be assembled into 3D lattices with application in electronic devices and high-performance transparent conductive films (Figure 9c). Additionally, by reducing gold ions on the surfaces of silver nanoparticles seeds with sunlight irradiation, Liu et.al[135] synthesized novel silver-core-gold-shell and silver-gold bimetallic nanostructures based on Ag-DNA network templates, which - used as the substrates - show an enhancement in Raman scattering and a lower the detection limit of biosensors for carcinoembryonic antigen and TNT.

4.2 Carbon nanomaterials

Carbon nanomaterials (CNMs), such as graphene or carbon quantum dots (GQDs or CQDs), carbon nanotubes (CNTs) and 2D graphene, are regarded as a rising star of biomedical nanomaterials. Also, the excellent physical and chemical properties allow a wide application of CNMs in biomedical and biosensing applications. The interaction of CNMs with DNA has been employed for the regulation of DNA conformational transitions with specific molecular recognition in biotechnology and biomedicine.[136]

The adsorption of DNA on single-walled carbon nanotubes (SWNTs) is beneficial to the separation and dispersion of SWNTs varying with different sequences and lengths of DNA,[137]and the SWNTs can prevent the DNA from enzymatic cleavage.[138, 139] Qu's group has studied a series of DNA conformational transitions regulated by SWNTs and constructed a lot of nanodevices.[140-142] For instance, they found that SWNTs induce the B-A conformation transition and melting temperature decreased to 40 °C in GC-DNA due to SWNT. Also, they found that the carboxylated

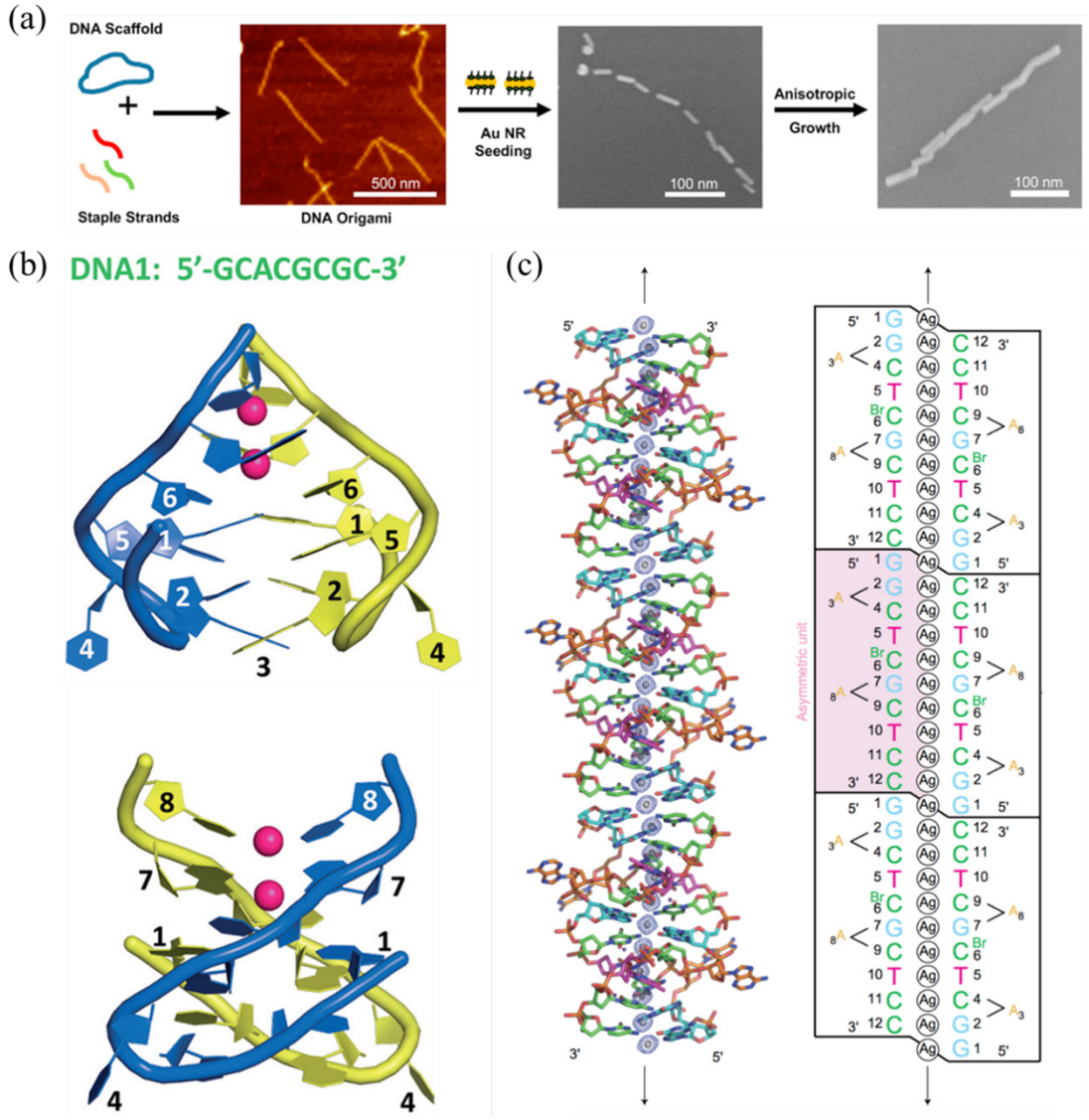

Figure 9. (a) Small diameter conductive nanowires based on anisotropic electroless deposition on DNA origami templates.[119] (b) Sequence of DNA (GCACGCGC) and the overall structure of the DNA-Ag^{I} complex.[132] (c) DNA duplex with silver-mediated base pairs.[134] Reprinted with permission from Ref.[119][132][134]

SWNTs can selectively induce the forming of human telomeric i-motif by interacting with $C{\cdot}C^{+}$ base pairs at the 5′-end major groove in physiological conditions, and this result suggests the possible regulation of SWNTs in human telomeric DNA (Figure 10a).[143] Moreover, SWNTs have the ability to induce triplex DNA formation through electrostatic interactions under physiological conditions (Figure 10b).[144]

Graphene, as a star carbon material, has been widely used in DNA related biosensors, biomedicine and bioimaging.[145, 146] Among various graphene derivatives, graphene oxide (GO) is easy to fabricate in chemical lab with remarkable dispersibility, operability and manufacturability. Like SWNTs, similar interactions between DNA and GO have been widely investigated.[147,148] For example, multivalued logic gates have been constructed by using GO-DNA and thiol-metallized DNA on the GO sheets, which were used to regulate the multiple emissions of rare earth upconversion NPs and synthesize natural calf thymus DNA modified graphene PdNP (DNA-graphene-Pd) for efficiently catalyzing the Suzuki reaction (Figure 10c).[149] Carbon nanotubes and graphene are typical 1D and 2D members of the carbon family. In recent years, photoluminescent carbon quantum dots (GQDs or CQDs) as types of 0D materials have attracted much attention for biocompatibility and low toxicity.[150,151] Typical B-Z transition

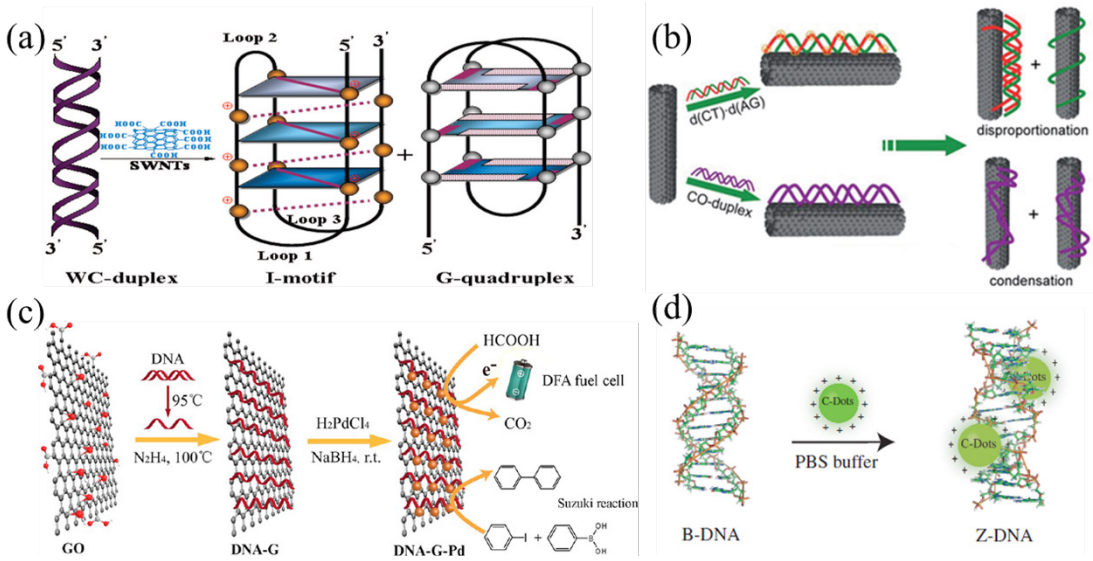

Figure 10. (a) Human telomeric i-motif formation by SWNTs.[143] (b) Stabilization of unstable CGC⁺ triplex DNA by SWNTs under physiological conditions.[144] (c) DNA-modified graphene/Pd hybrid and the catalysis application in direct formic acid fuel cell and Suzuki reaction.[149] (d) the B-Z DNA transition induced by SC-dots.[152] Reprinted with permission from Ref.[143][144][149][152].

have been induced by nitrogen-doped carbon dots, which demonstrates the first example that carbon materials force DNA chiral change from right-handed B-form structure to left-handed Z form (Figure 10d). Furthermore, inspired by the DNA nanotechnology, several types of DNA logic gate were constructed between CQDs and DNA intercalators.[152] Based on these phenomenon, photoluminescent carbon materials are expected to be introduced into the research fields of optoelectronic devices, bioimaging, sensors and drug delivery.

4.3 Quantum dots

Quantum dots (QDs) represent strong and stable luminescence and are widely used for detecting cell components in vitro and in vivo.[145, 153] Very recently, Kelley and colleagues synthesized multifunctional quantum dot DNA hydrogels via using DNA complementarity.[154] Their method can precisely control QDs' size and spectral emission, with high photostability, good biocompatibility and high quantum yield. These multifunctional quantum dot DNA hydrogels successfully incorporated QDs into network with a single controllable self-assemble step. It further promoted the aptamer as binding motif and improved the deliveries of doxorubicin and siRNA with a trackable and unique way (Figure 11a). Additionally, Fan *et al.* reported a single-step and purification-free DNA programmed strategy to precisely control the valency of QDs.[155] Four types of functionalized QDs with high modularity were developed and used to precisely construct complex fluorescent resonance energy transfer nanostructures. By carefully control the three-dimensional structure between QDs and AuNPs through DNA linker, four kinds of composites with monovalent, divalent, trivalent and tetravalent configuration were fabricated and applied for quantitative imaging and analysis in living cells (Figure 11b). These typical application of DNA functionalized QDs have shown the promising potential applications in nanoprobes, nanophotonic and biological diagnostics.

4.4 Metal-organic frameworks

In recent years, metal-organic frameworks (MOFs) have triggered substantial research efforts and have developed rapidly. Due to the high surface areas and structural tenability, MOFs hold promise for versatile applications by acting as a type of modular, crystalline and porous nanomaterials.[156] Different applications of MOFs have been demonstrated, especially in industrial catalysis, fuel cells, gas storage, and drug delivery.[157-163] Willner *et al.* used three different DNA switching motifs to construct pH and K⁺ responsive DNA-functionalized MOFs, which paved the way for DNA-MOF hybrids responding to other stimuli (Figure 11c).[164] They also developed two different stimuli-responsive capped metal organic framework nanoparticles referred to as pH-responsive NMOFs and ion-responsive NMOFs. The latter are mainly responsive

to metal-ion-dependent DNAzyme complexes and can be used in multiplexed sensing and logic-gate systems.[165] Mirkin's group described a coordination chemistry-based strategy to obtain high density and functionalized MOF nanoparticles.[166, 167] By using either terminal phosphate-modified oligonucleotides or covalent conjugation, they provided an approach to the synthesis of nucleic acid-nanoparticle conjugates, which is useful for programmable assembled material building blocks to design materials with biological functions, catalysis and optical use.[168-170] However, the cost of modified DNA and the lack of valid mechanisms for releasing MOF-bound DNA in response to environmental stimuli would limit its therapeutic applications. Fan group further exploited the intrinsic, multivalent coordination-based between DNA phosphate backbone and Zr centers to construct DNA-Zr-MOF nanoparticles.[171] By using unmodified oligonucleotides, the CpG-based immunostimulatory DNA-MOFs was developed, which represented excellent biocompatibility, low immunogenicity, high efficiency intracellular delivery and release. Their work paved a novel way for targeted and precision nanomedicine (Figure 11d). Peng *et al.* developed a DNA@ZIF-8 membrane based on solid-confined conversion strategy and applied for methanol fuel cells with high proton conductivity and low methanol permeability lately (Figure 11e).[172]

4.5 DNA-based liquid crystals (LCs)

Liquid crystals (LCs) are widely known as an excellent sensing materials used in display due to its intrinsic properties of short-range positional and long-range orientational order.[173-175] They can be divided into lyotropic liquid crystals (LLC) and thermotropic liquid crystals (TLC) depended on the transformation driving force. Various biomolecules, including nucleic acids, proteins and virus have been formed LCs, which play important roles in biology.[176-181] Since DNA exhibits persistent structures with dimensions and unique electrical characteristics, it has prompted the utilization in the fields of LCs materials applied to electronic devices, as well as distinguishable performances in electrical conductivity with different Watson-Crick base pairs. [182]

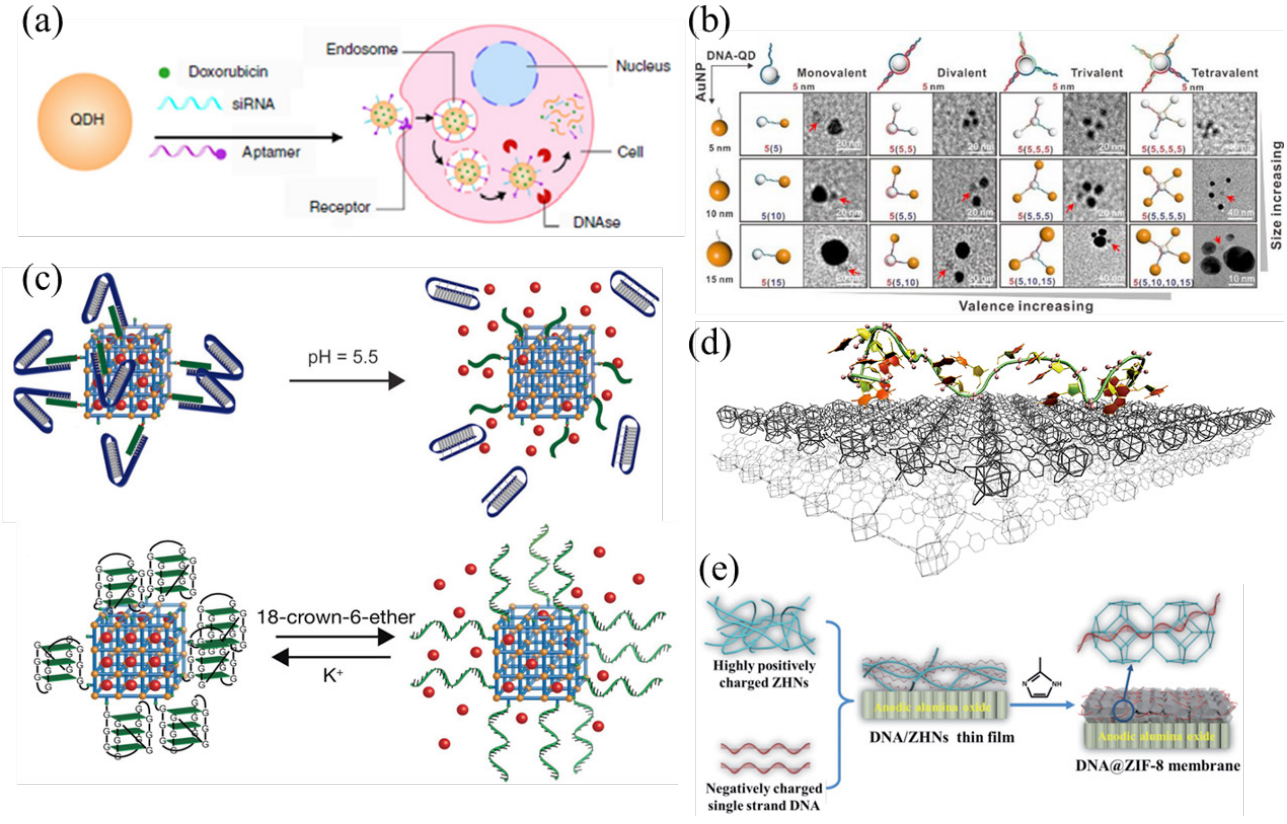

Figure 11. (a) Modifications of QDH for cell-specific targeting with an aptamer and siRNA/ DOX are released upon cellular uptake via endocytosis.[154] (b) QDs-QDs and QDs-Au clusters fabricated with multivalent QDs.[155] (c) Stimuli-responsive DNA-functionalized metal-organic frameworks.[164] (d) Organelle-specific triggered release of immunostimulatory oligonucleotides from DNA-metal-organic frameworks with soluble exoskeleton.[171] (e) The synthesis of DNA-Threaded ZIF-8 Membrane.[172] Reprinted with permission from Ref.[154][155][164][171][172]

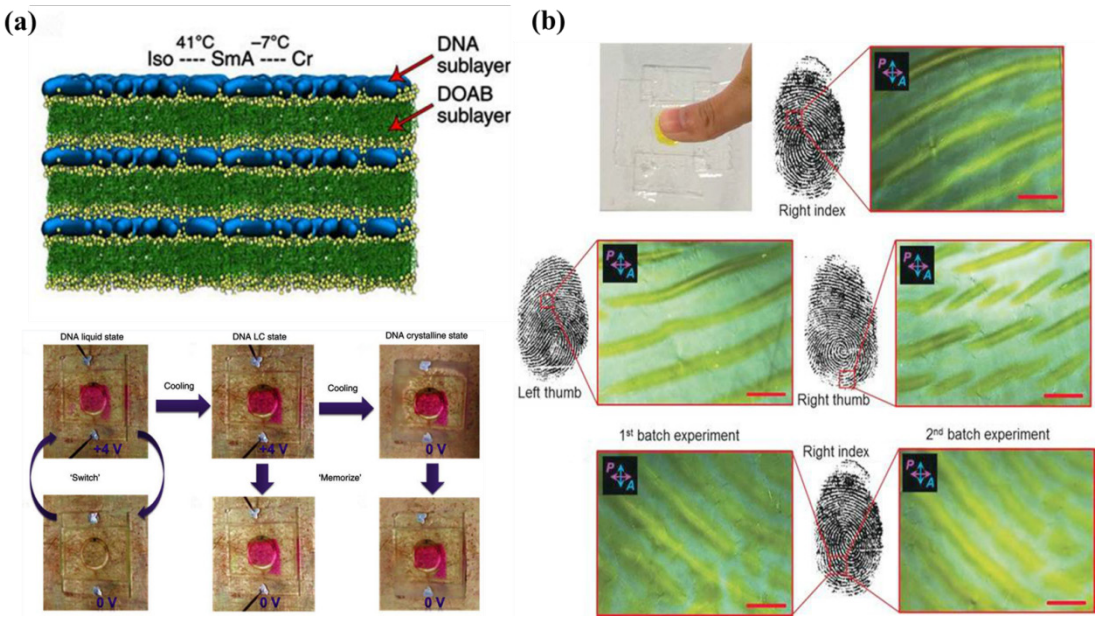

Figure 12. (a) The lamellar bilayer structure and phase-dependent electrochromism of DNA-surfactant complex is made of one sublayer of single-stranded DNA and one sublayer of interdigitated surfactants.[193] (b) The isotropic-LC phase transition of the SUP-AZO fluids triggered by finger pressing.[197] Reprinted with permission from Ref.[193][197]

Over the last decades, a series of DNA-based LLC nanostructures have been obtained ranging from nematic phases, over smectic and hexagonal states to cubic phases.[176, 183, 184] The Safinya group has investigated the mechanisms and parameters of the dendritic lipid-based cationic liposome-DNA complexes.[185, 186] Dendritic lipid-DNA self-assemblies were obtained from lamellar, hexagonal, and DNA bundles, and exhibited various LC phases.[187, 188] Lindman and colleagues studied the phase behavior and phase structures of DNA-surfactant complex mixed with lecithin and water.[189, 190] By varying the co-surfactant, different self-assembly structures and tailored phase behavior were obtained.[191] However, most investigations of DNA LCs were obtained in aqueous solutions limiting their practical application, thus, research examining anhydrous DNA TLCs is gaining momentum.[192] A novel solvent-free nanoDNA-based TLCs system based on DNA-surfactant complex material was developed by Liu.[193] It exhibits distinctive electrically controlled optical absorption induced by applied voltage, as well as optical memory depending on the phase transitions between isotropic liquid, liquid crystals and crystalline phases (Figure 12a). The system has paved the way for further developing the anhydrous DNA-based nanodevices.[192, 194-196] Very recently, they also prepared a new type of biological fluid from supercharged polypeptide materials. The isothermal phase transition from isotropic liquid phase to nematic ordered state was successfully realized by mechanotransduction, resulting in an easily recordable birefringence read-out for complex fingerprint patterns (Figure 12b).[197]

5 Conclusions and perspectives

DNA is a type of nature-optimized molecule in the river of life's evolution. It not only acts as a substance carrier of genetic information, but also as a unique material to construct various nanostructure, especially since the beginning of DNA self-assembly nanotechnology. The development of DNA origami technology further provides alternative option to fabricate numerous complex DNA nanostructures with multiple geometries, dimensions and functionalities for various applications, e.g. biosensors, DNA logic gates and DNA molecular machines, and so on. Up to now, although numerous research works have been reported, there are still some challenges need to be addressed in near future. For instance, the thermodynamic and kinetic principles of DNA assembly are still ambiguous, which determine the limitation of DNA base pair match and the yield of specific DNA nanostructures. Also, the numerous applications of DNA nanotechnology still are restricted in the laboratory stage due to the complicated construction, as well as the instable and high-cost synthesis of DNA nanodevice in complex condition. Therefore, much efforts are

urgently needed to transfer DNA-based nanofabrication and nanostructures into practical utilizations. Even so, DNA guiding nanotechnology is still considered as a promising methodology in the diverse nano world and easily integrated into other techniques, like DNA biochip, microfluidic devices and nanomedications.

Acknowledgements: The authors thank the National Natural Science Foundation of China (Grant No: 21705106 and 21401127). Dr. Feng also thanks the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (No. TP2016023), Shanghai Natural Science Foundation (No. 18ZR1415400) and Shanghai Sailing Program (17YF1406400).

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