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Review

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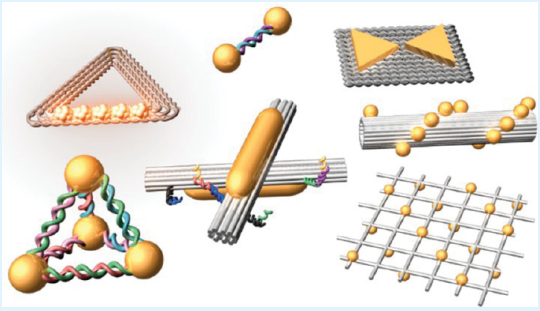
Fabrication of Metal Nanostructures on DNA Templates

Na Li,[†] Yingxu Shang,[†] Zihong Han,[†] Ting Wang,[†] Zhen-Gang Wang,*[,†] and Baoquan Ding*[,†,‡]

[†]CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for NanoScience and Technology, 11 Bei Yi Tiao, Zhong Guan Cun, Beijing 100190, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

ABSTRACT: Metal nanoarchitectures fabrication based on DNA assembly has attracted a good deal of attention. DNA nanotechnology enables precise organization of nanoscale objects with extraordinary structural programmability. The spatial addressability of DNA nanostructures and sequence-dependent recognition allow functional elements to be precisely positioned; thus, novel functional materials that are difficult to produce using conventional methods could be fabricated. This review focuses on the recent development of the fabrication strategies toward manipulating the shape and morphology of metal nanoparticles and nanoassemblies based on the rational design of DNA structures. DNA-mediated metallization, including DNA-templated conductive nanowire fabrication and sequence-selective metal deposition, etc., is briefly introduced. The modifications of metal nanoparticles (NPs) with DNA and subsequent construction of heterogeneous metal nanoarchitectures are highlighted. Importantly, DNA-assembled dynamic metal nanostructures that are responsive to different stimuli are also discussed as they allow the design of smart and dynamic materials. Meanwhile, the prospects and challenges of these shape-and morphology-controlled strategies are summarized.



KEYWORDS: *DNA nanotechnology, metal nanostructures, self-assembly, nanofabrication, surface plasmonics*

INTRODUCTION

Metal nanoparticles (NPs) are a class of novel materials, and the physicochemical properties are size- and shape-dependent. Control over the geometry of metal NPs leads to novel and tunable properties differing from those of bulk materials. These interesting properties are employed for the development of widespread applications, such as plasmonics, catalysis, biosensing, and nanoelectronics.[1−9] It is a challenge to control the dimension and shape of NPs to obtain populations with the desired characteristics. Up until now, research focused on the synthetic protocols for the production of NPs whereby the size and shape can be intimately controlled has been intensely studied and has led to substantial advances.[10−16] Moreover, the expansions of available nanostructures via rational design will generate functional materials with more sophisticated structures and a range of desired properties.[17−26] These properties are dependent on their sizes, shapes, chemical composition, and their spatial arrangement. Therefore, effective arrangement of NPs into desired nanostructures is the key to achieving the desired properties of nanomaterials and is critical to realize the innovative applications.

DNA nanotechnology offers great potential in bottom-up nanofabrication. DNA molecules or nanostructures can be used as the templates to control the growth and morphology of NPs.[26−40] The preparation of the various NPs structures based on DNA technology offers opportunities for the development of materials with novel properties. With the increasing ability to design DNA nanostructure, more sophisticated shapes of metal nanostructures can be envisioned. The last two decades have witnessed the fast development in the synthetic strategies of NPs on the DNA templates, which can be considered a process of biomineralization. Naturally occurring biomineralization is a process where a living organism excretes an inorganic material formed through a biologically guided process.[27] The role of the DNA molecule in biomineralization is to provide a microenvironment to control the inorganic phase morphology by manipulating a range of interactions. These processes exploit DNA templates to interact with the inorganic material to result in efficient syntheses. The rapid development of DNA nanotechnology has enabled a precise organization of nanoscale matter with ultimate structural programmability. In particular, the covalent bonding of DNA to discrete NP assemblies allows sophisticated functional realizations of inorganic nanomaterials via molecule-like structural controls.[41−43] It is noteworthy that the DNA origami nanostructures reported by Rothemund in 2006 provided a highly complex and tunable nanotemplate.[44] The sequence specificity and the spatial addressability of DNA origami nanostructure make it a promising candidate for the construction of nanomaterials with novel structures and functions. Scientists have used DNA origami to fabricate

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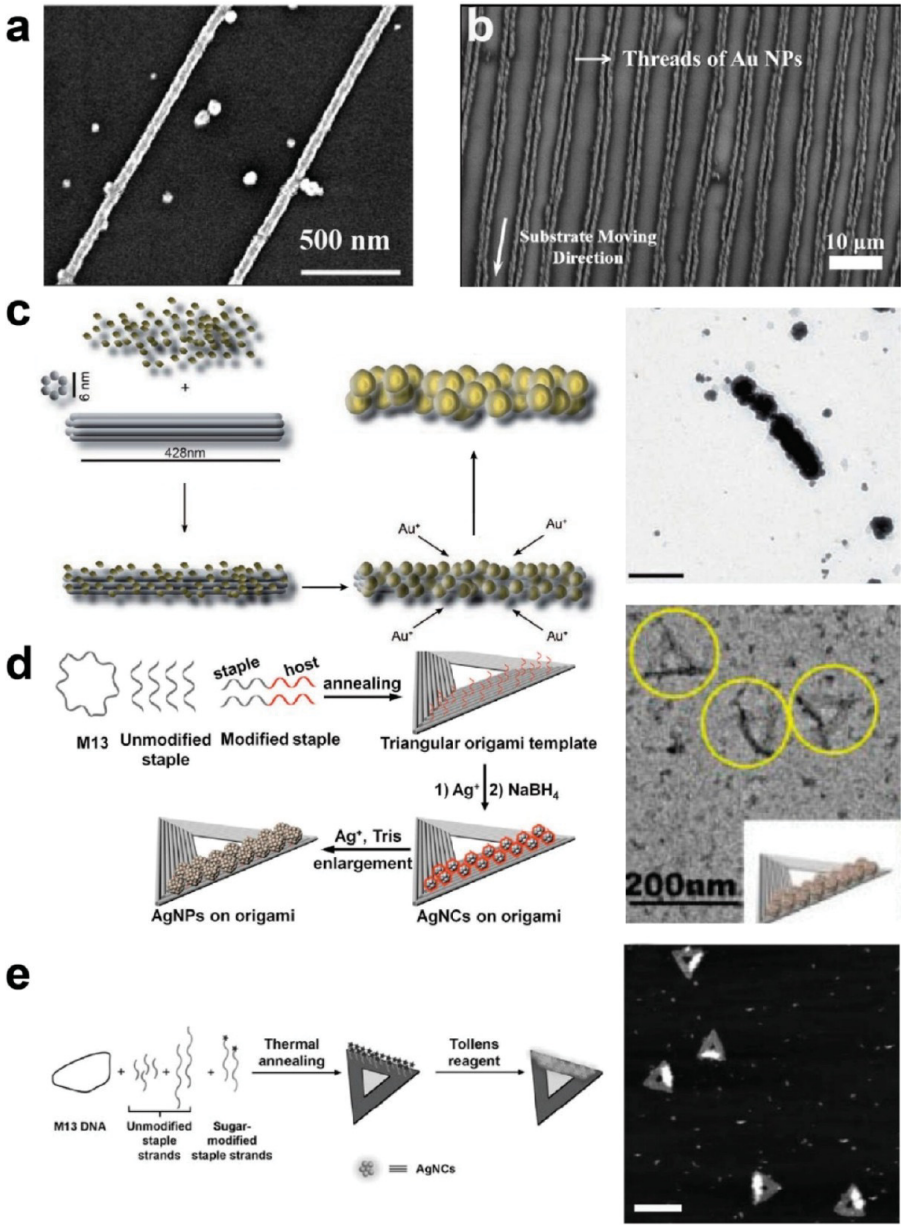

Figure 1. Directed and selective metallization on DNA template. (a) SEM image of Pd nanowires metalized on DNA scaffolds. Reproduced with permission from ref 36. Copyright 2008 John Wiley and Sons. (b) SEM image of large-scale aligned Au nanowires produced by flow-enabled self-assembly (FESA) strategy by highly oriented DNA nanowires. Reproduced with permission from ref 63. Copyright 2017 John Wiley and Sons. (c) Schematic illustration of shape-controlled metallization on DNA origami structures, and the corresponding TEM images of continuously metallized nano-objects of predetermined shapes on a set of DNA origami structures, e.g., gold nanowires, nanocuboids, nanodonuts, and polymerized nanorods of micrometer length; insets are schematic illustration of the corresponding DNA origami structures. Reproduced with permission from ref 38. Copyright 2011 John Wiley and Sons. (d) Schematic illustration of sequence-dependent site-specific synthesis of fluorescent AgNCs on DNA triangular origami template, and the corresponding TEM image. Reproduced with permission from ref 68. Copyright 2016 American Chemical Society. (e) Schematic representation of the site-specific immobilization of AgNCs on a triangular DNA origami scaffold by Tollens reaction, and the corresponding AFM image. Reproduced with permission from ref 75. Copyright 2011 John Wiley and Sons.

nanomaterials with controlled shapes. DNA origami has been considered as an appealing nanoscale building block.

In this review, we summarized the recent efforts on the employment of DNA for the synthesis of NPs with various shapes and describe the innovative progress in the construction of metal nanostructures and nanoassemblies. We discussed the role of DNA in control over the shapes of NPs and the geometries of nanoassemblies. The functional groups on DNA backbones make DNA attractive template for the growth of nanosized NPs. Meanwhile, DNA self-assembly exploits the base-pairing specificity to arrange NPs in nanometer precision. Therefore, the synthetic strategies in this review are mainly categorized into two groups: (i) DNA is used as the ligand for modulating NPs growth; (ii) DNA nanostructures are used as the template to assemble metal NPs. This review is not meant to be comprehensive. We will not discuss research efforts on the applications of DNA-NPs hybrids, e.g., in photonics,[45−48] therapeutics,[49−52] and nanofabrication.[53−55] Instead, we will

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focus on the DNA-assisted NPs synthesis and particularly the use of DNA-linked NPs as building blocks for programmable and scalable self-assembly of multifunctional NP nanostructure, to realize control over the morphologies of the nanostructures. In addition, we will discuss prospects and challenges, as well as the future directions in this field.

1. METALLIZATION OF DNA

1.1. Directed DNA Metallization. DNA with rich chemical features can control the nucleation and growth of nanocolloids effectively by binding of metals or metal ions to the specific sites of its backbone. In general, two types of protocols have been used for the directed DNA metallization. In the first approach, metal cations initially bind to the phosphate backbone of the DNA scaffold through coordination or electrostatic interactions. The DNA-bound metal ions are reduced chemically or photochemically to form small clusters. These small clusters tend to grow into NPs and the aggregation is prevented by the surface-capping negatively charged DNA strands. The initial purpose of DNA metallization procedures was to construct the nanometer-scale circuits. Braun and co-workers[56] in 1998 first pioneered the idea of using DNA as a template for the growth of a 12 μm long and 100 nm wide silver nanowire. More work have since emerged to use DNA as template for guiding the growth of NPs into nanowires.[36,57−60] For example, Richter and co-workers[61] used λ DNA as template for Pd^{2+} adsorption, followed by the reduction of the ions to generate Pd^0 nanoclusters on the DNA template. The repeated association of Pd^{2+} ions and reduction led to the formation of continuous metallic nanowires that revealed ohmic conductivity. Filoramo and co-workers[36] developed a new approach involving the progressive growth of Pd nanowires by the slow and selective precipitation of PdO, followed by a reduction step (Figure 1a). This strategy can resolve the issue of fast kinetics and subsequent uncontrolled metal deposition, thus generating the homogeneous Pd nanowires on the entire surface of the substrate. The Pd nanowires have been observed to be 25 nm in diameter but still showed highly conductive ohmic behavior. Saraf and co-workers[62] reported a one-step in situ metallization of Au nanoclusters on DNA chains by exposing the DNA/Au salt solution to UV radiation. The nanostructures displayed ohmic behavior, with low resistance and no hysteresis, indicative of a continuous metallic structure. To meet the requirement of the mass production of integrated nanodevices, the ordered and continuous nanowires are highly demanded. Lin and co-workers[63] reported a flow-enabled self-assembly (FESA) strategy to achieve large-scale aligned Au nanowires templated by highly oriented DNA nanowires, as shown in Figure 1b. Large-scale one-dimensional nanostructures enabled their effective integration into nanodevices and the construction of hierarchical devices.

In another method, presynthesized DNA nanostructures with specific dimensions and structures have been used to create metallized objects with controlled shapes. DNA origami technique, where a long single-stranded DNA scaffold is folded into arbitrary shapes by the help of hundreds of short staple oligonucleotides, has opened a new area for fabricating complex nanostructures.[44] This offers the possibility to arbitrarily create metal nanostructures for the fabrication of materials with novel functions. Woolley and Harb groups[64] have first successfully metalized branched DNA origami with Ag as the seed and then plating with Au via an electroless deposition process. This work represents an important progress toward the realization of DNA-templated nanocircuits. They also metallized a circular circuit DNA origami using anionic seeding method with palladium followed by gold or copper electroless plating.[29] This process resulted in a high surface density of continuous metal nanostructures with small and well-defined features. The electrical resistance of both Au- and Cu-metallized DNA origami both showed typical ohmic behavior. The control over the shape of inorganic materials is of great importance because they can be used in diverse applications.[65,66] DNA is a highly programmable material that can be folded into arbitrary 2D or 3D shapes. Researchers have been trying to program custom-shaped inorganic materials with DNA, which is hard to realize with conventional methods. For example, in 2011, Liedl and co-workers[38] designed a set of DNA origami structures for shape-controlled metallization (Figure 1c). They used positively charged 1.4 nm gold clusters that were bound to the negatively charged DNA origami as seeds for the growth of the gold clusters, which would then continuously metallize into predetermined shapes, such as gold nanocuboids, nanodonuts, or polymerized nanorods of micrometer length, as shown in Figure 1c.

1.2. Selective Metallization on DNA Template. The direct growth of inorganic nanocrystals on DNA template based on the electrostatic interaction between metal cations and phosphate groups results in uniform metallization of DNA architectures.[4,12−15] However, this approach lacks addressability and is unable to fabricate arbitrary patterns of inorganic nanostructures. Therefore, the site-selective metallization on DNA template is expected. Sequence-selective metallization might provide the necessary microenvironment to confine and control the mineralization process and enables the fabrication of elaborate metal nanostructures. Kotlyar and co-workers reported a sequence-selective approach to silver deposition.[67] The higher affinity of silver to G and C rather than to A and T led to specific binding and the low ionization potential of guanine. The incubation of oligonucleotide-coated AgNPs of 15 nm in a diameter with poly(dG)/poly(dC) yielded a uniform DNA nanowire, while neither poly(dA)/poly(dT) nor the random sequence plasmid (pUC19) DNA underwent transition during incubation with the AgNPs. In addition, our group chose two specific sequences of the host strands for in situ synthesis of silver nanoclusters (AgNCs) within single-stranded DNA host strands that were preorganized on the self-assembled DNA nanostructure templates (Figure 1d). As a result, the site-specific formation of AgNCs with the specific fluorescence wavelength was observed.[68] The excitation/emission properties of AgNCs were tuned by adjusting the distance between nucleation site and the template, the sequence of the host strands, the template configuration, and the location of the nucleation site on the template. Woolley and Harb groups demonstrated the deposition of two different metals at designated locations on a single origami template to form a heterogeneous Au−Cu junction.[69]

The sequence-specific recognition properties and chemical reactivity of nucleic acids can be easily modulated by incorporating synthetic nucleotides endowed with custom functional groups. Ijiro's group[70] has prepared a triblock copolymer composed of poly(dG)/poly(dC) parts and a poly(7z-dG)/poly(dC) part with sequence-selective platinum metal deposition on the GC part of the DNA block copolymers. Braun and co-workers reported sequence-specific patterning of DNA metal coating using RecA protein that

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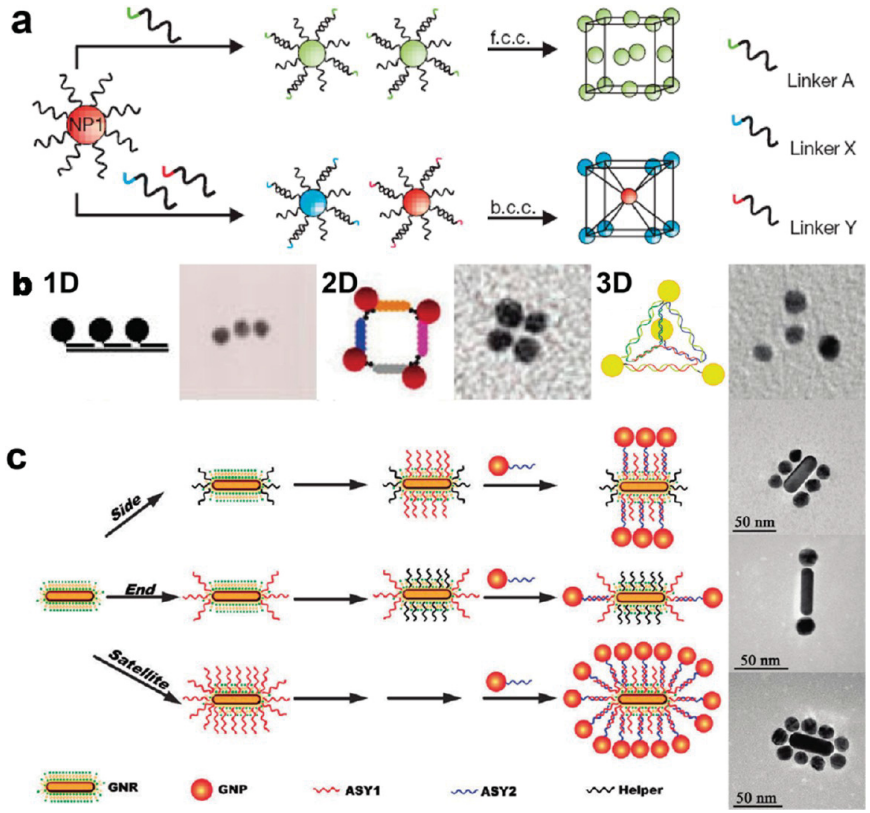

Figure 2. Scheme of AuNP assembly methods. (a) AuNP-DNA conjugates can be programmed to assemble into different crystallographic arrangements by changing the sequence of the DNA linkers. Reproduced with permission from ref 86. Copyright 2008 Nature Publishing Group. (b) Representative examples of rational self-assembly of nanostructures by DNA-linked NP building blocks in 1D,[109] 2D,[110] and 3D.[41] Reproduced with permission from refs 109, 110, and 41. Copyright 1999 and 2007 John Wiley and Sons and 2009 American Chemical Society. (c) Schematics of synthetic method for regiospecific AuNPs assemblies and the corresponding representative TEM images of End, Side, and Satellite assemblies. Reproduced with permission from ref 111. Copyright 2012 American Chemical Society.

prevented Ag deposition by serving as a resist.[71] As a result, a gap was created between the Ag-loaded DNA segments. The subsequent electroless gold deposition was performed on the Ag aggregates, producing two continuous gold wires separated by the predetermined gap. This procedure was further developed by Braun's and other research groups.[72,73] The use of RecA is a clever method of utilizing protein-binding ability and DNA molecular recognition, and enables various types of nanoscale programmable metallization.[74] Yan's groups[75] described a novel DNA-based method for the site-specific synthesis of water-soluble fluorescent AgNCs with a narrow size distribution (Figure 1e). They covalently incorporated a small number of aldehyde sugar moieties into a DNA sequence at adjacent positions. The aldehyde sugar groups could reduce Ag^+ ions to Ag^0, and enabled the synthesis of AgNCs by Tollens reaction.[76] These Ag clusters could then act as nucleation sites for further Ag deposition under mild reductive conditions. The addressable DNA strands allowed site-specific synthesis of AgNCs on the predefined DNA scaffolds.

2. DNA-BASED ASSEMBLY OF NANOMATERIALS

2.1. Isotropic Functionalized NPs with DNA. The capability of precisely controlling the arrangement of NPs is a prerequisite to constructing complicated, anisotropic architectures. DNA holds great promise in positioning molecular and nanoscale objects with high spatial precision because of its unique molecular recognition properties. The development of effective strategies of nanoparticles functionalization is a key step to this goal. The isotropic functionalization of NPs was first introduced by Mirkin's group,[77] and they used two sets of noncomplementary alkanethiol group terminated DNA to modify 13 nm AuNPs. Linker DNA was added to the mixture of both sets of DNA-AuNPs to link these particles via complementary DNA hybridization to form a macroscopic network and the assembly process was found to be reversible as a function of temperature. This breakthrough was later employed for biodetection methods by the same group.[78−81] Using isotropic functionalized NPs as a building block, different assemblies were obtained. For examples, DNA has been used to construct both extended assemblies of binary networks of different particle sizes[82] and discrete "satellite" structures, where a few smaller NPs surrounded a large DNA-functionalized particle.[83−85] It is noteworthy that the parameters, such as particle size, shape, DNA length, and sequences, can be tuned independently. This allows the synthesis of colloidal crystals and the lattice parameters to be controlled in nanometer precision. Mirkin's group[86] and Gang's group[87] respectively demonstrated that DNA-AuNPs could be crystallized into highly ordered structure. Mirkin's group used a single DNA linker to form a close-packed fcc structure because of the equivalent binding affinities between NPs (see Figure 2a). Alternatively, binary DNA linkers favor assembly of the NPs into a nonclose-packed bcc structure.[86]

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Gang's group directly mixed two different ssDNA-capped NPs, each was modified with spacer regions of varying length and complementary base-pairing sequences, to bridge the NPs together into a 3D bcc structured superlattice.[87] The slow-cooling process was demonstrated to enable a DNA driven assembly and crystallization that favored the most thermodynamically stable crystal structure, such as a thermodynamic Wulff polyhedral structure with specific and uniform crystal habit.[88] It was further shown single crystals with different equilibrium Wulff shapes can be created using low symmetry, anisotropic NPs.[89] In addition, by controlling the crystallographic parameters, including particle size, periodicity and interparticle distance, it is possible to obtain different highly ordered crystal-lattices.[90−92] Mirkin's group has established six programming rules for the assembly of 50 DNA-AuNP crystal structures with nine different crystal symmetries.[86,90,93,94] The particle shape was demonstrated to have a strong influence on the crystallization parameters of DNA-functionalized NPs, affecting superlattice dimensionality, crystallographic symmetry and phase behavior.[89,95,96] A deal of great effort has been made on investigating the control over superlattice assembly[31,95,97−103] which was employed in nanophotonics, optoelectronics, and catalysis.[104−108] These studies highlighted the use of DNA as a robust and programmable assembly tool for the formation of highly ordered NP superlattices and further demonstrated the potential materials applications due to the unique properties of complexes.

Other types of NPs with desired optical, magnetic, or catalytic properties remain to be functionalized for the fabrication of multifunctional nanomaterials. This can be achieved by capping their surface with DNA possessing chemical head groups, such as thiol, amine, phosphine, carboxyl, etc. Gang's group[108] modified four typical functional nanoparticles with plasmonic (gold), catalytic (palladium), magnetic (Fe_2O_3), or luminescent (CdSe/Te@ZnS and CdSe@ZnS) properties, with carboxylic group grafting, which were then assembled into heterolattices. Novel optical and field-responsive properties of the assembled nanomaterials were exhibited. Our group reported DNA-assembled Au−Pd bimetallic plasmonic nanostructures.[26] DNA not only served as the construction material, but also a molecular spacer between two metal components, Au nanorods (AuNRs) and Pd satellite nanocrystals. The AuNRs were functionalized with DNA that subsequently hybridized with the complementary strand containing thiol group. The duplex strands containing thiol group served both as linkers and seeding sites for the growth of Pd NPs and the formation of Pd satellites around an AuNR at an ultrashort spacing in the nanometer range. Furthermore, we demonstrated that such Au−Pd bimetallic NPs can be used for the all-optical plasmonic detection of hydrogen in real time at room temperature.

2.2. Monofunctionalization of NPs with DNA. The accurate and fast assembly of heterogeneous nanoarchitecture with specifically designed geometries remains a challenge. This can be achieved using DNA as a ligand (through monofunctionalization and anisotropic functionalization) and/or as a template for spatial positioning of functionalized NPs. Monofunctionalization is nontrivial process as it typically involves careful design and substantial purification techniques.[109,112−114] Alivisatos and co-workers first demonstrated the feasibility of monofunctionalization of ultrasmall 1.4 nm NPs with DNA, and the limited surface area of NPs allowed only one ssDNA strand attach.[112] However, larger mono-functionalized NPs have to be isolated from stochiometric mixtures. Alivisatos' group controlled the number of DNA strands per gold nanoparticle (AuNP) by adjusting the DNA:NP ratio, and used gel electrophoresis to purify the discrete AuNP/DNA conjugates.[113] The discrete bands corresponded to a defined number of DNA strands per AuNP, which can be recovered from the gel. The isolation of even larger (20 nm) DNA-AuNPs with a discrete number of DNA strands were realized by the same research group via the anion exchange high performance liquid chromatography (AE-HPLC).[114] Xu's group fabricated AuNPs heterodimers with different-sized monofunctionalized AuNPs.[115] Later, Xu and co-workers demonstrated that deposition of silver shells around the AuNP heterodimers can enhance their chiroptical activity and the core−shell assemblies were used for zeptomolar DNA detection.[116] Monofunctionalization has the potential to enable the construction of the metal nanostructures containing any number of discrete metal NPs, with varied sizes and spatial arrangements. Modulation of the functionalization of a NP with DNA allows us to harness NP building blocks for customized construction of nanostructures with controlled dimensions and functionalities, as shown in Figure 2b.[41,42,82,109,110,114,117−124] More complex 3D chiral pyramidal plasmonic assemblies were constructed by Alivisatos's[141] and Kotov's[142] group, respectively, from four individual NPs monofunctionalized with distinct strands of ssDNA. Each of the ssDNA strands on four different-sized gold NPs were designed to be complementary to a third of the other strands, so that they hybridized to form a pyramidal configuration. Chan's group used a "core−satellite" architecture to build DNA-assembled superstructures, where one or multiple layers of satellite nanoparticles surround a central core nanoparticle.[28] Each layer of nanoparticles could be designed to possess different composition, size or surface chemistry. A linker DNA containing complementary regions to each layer connected the nanoparticles. In this way, the superstructures, from simple building blocks, can be constructed with controlled dimensions. The inherent dynamics of DNA allows NP nanostructures to exhibit stimulated reconfigurable topologies, such as responsive interparticle distances. Specifically, Willner reported the functionalization of DNA tweezers with AuNPs, and the NPs nanostructures were switched upon opening or closure of the tweezers.[125] The tweezers were further modified with a single AuNP and a single fluorophore that were positioned at different ends of the tweezers, and showed the reversible fluorescence quenching or enhancement following the opening or closing operation of the tweezers. They also constructed a AuNPs trimer using a DNA rotaxane nanostructure, where a DNA ring was threaded on a nucleic acid axle and locked in a nonseparable configuration by two Au NPs acting as stoppers at the 3′- and 5′-ends of the axle.[126] They tethered a AuNP to the rotaxane ring to assemble predesigned AuNP composites. Such ordered AuNPs structures allowed the programmed switchable transition of the ring on distinct sites of the axle, and the control of plasmonic properties via the mechanical operations of the DNA device.

2.3. Anisotropic Functionalized NPs with DNA. Anisotropic functionalization, especially the site-specific functionalization, is another route that can program the spatial arrangement of NPs into the desired self-assembled nanostructures. The site-specific functionalization allows multiple DNA molecules to attach to the NP's surface in a well-defined

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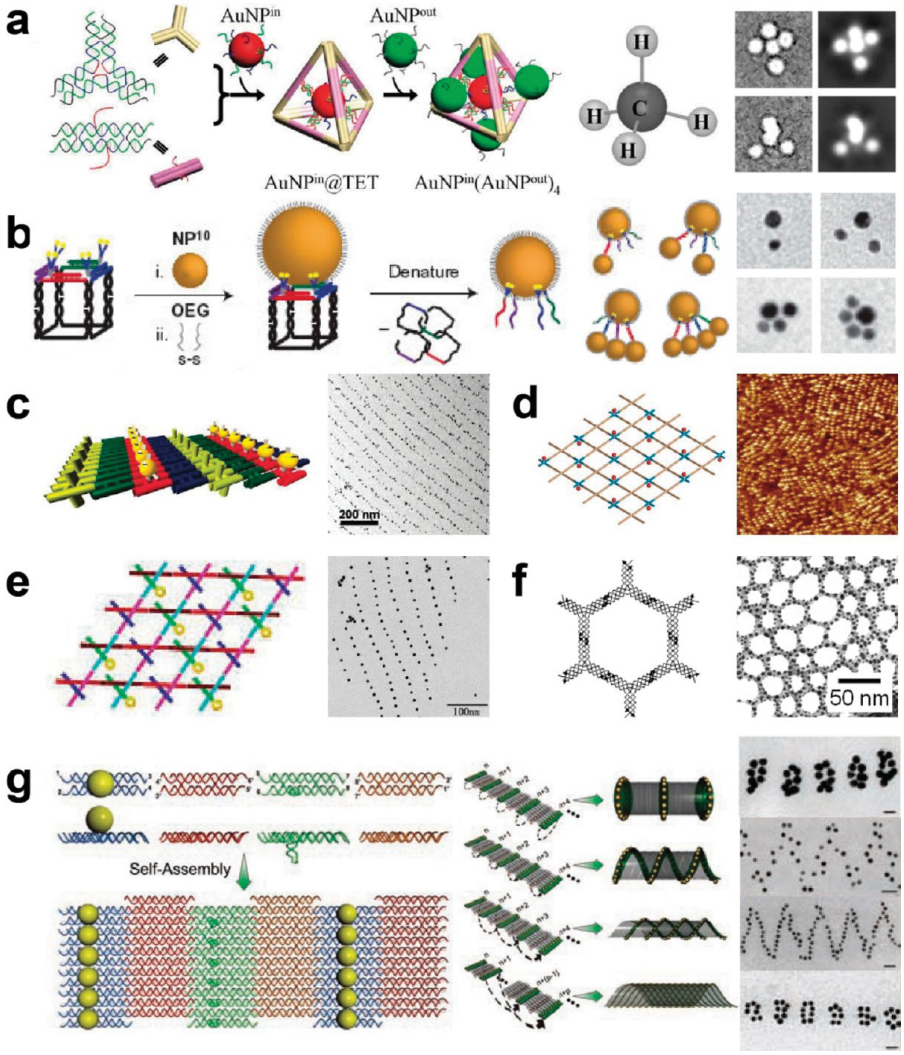

Figure 3. (a) Moleculelike DNA valences of DNA-coated AuNPs encased in wireframe DNA polyhedra. (Left) Assembly processes of (CH_4)-like NP molecules. (Middle) Configurations of CH_4. (Right) Pairwise comparison between the raw cryoEM images of individual NP-molecules (left) and the 2D projections (right) back calculated from the reconstructed 3D models. Reproduced with permission from ref 43, Copyright 2015 American Chemical Society. (b) (Left) General strategy to produce sequence-specifically patterned AuNPs using the asymmetric DNA scaffold. (Middle) Range of anisotropic satellite structures and (right) the corresponding TEM images. Reproduced with permission from ref 146. Copyright 2016 Nature Publishing Group. (c−e) Schematic representation of assembly of DNA-AuNPs on different 2D DNA templates and the corresponding TEM or AFM images. Reproduced with permission from refs 147, 148, and 150, respectively. Copyright 2004 and 2006 American Chemical Society and 2006 John Wiley and Sons. (f) Schematic representation of hexagonal DNA arrays and the corresponding TEM images. Reproduced with permission from ref 30. Copyright 2011 American Chemical Society. (g) (Left)Variety of tubular structures from the assembly of AuNPs and DNA tiles: top and side views of four DX tiles, and the parallel lines of AuNPs on self-assembled DNA tiles. (Middle) Possible ways for the origin of different tubular patterns and (right) the corresponding TEM images. Reproduced with permission from ref 151. Copyright 2009 AAAS.

and stoichiometric manner. Different DNA linkers can be placed at different locations on NP, and the location of individual NP can be precisely controlled, thus increasing the complexity of the structures. For example, Kotov and coworkers prepared three types of assemblies denoted as end, side, and satellite isomers from AuNPs and AuNRs based on site-selective modification of AuNRs with DNA oligomers, as shown in Figure 2c.[111] They can control regioselectivity of the assembly process via tuning the ratio of DNA to AuNRs. When thiolated DNA was in low concentrations, the covalent attachment of the oligonucleotides occurred exclusively in the "end" positions because of the coating of Cetyltrimethylammonium bromide (CTAB).[127] Increasing the concentration of modifying ssDNA led to the surface modification of NRs both in the ends and sides and therefore to the satellite route in these assemblies. In addition, the angles between DNA on a NP could also be controlled by modulating the physicochemical interactions between DNA and NP. Kim's group[128] utilized a sequential strand-by-strand attachment approach to control the number, position, and relative orientation of DNA strands on the surface of AuNPs to maximize its programmability and to realize enhanced control over the shape and function of the self-assembled structures. In detail, AuNP was functionalized by DNA strand-by-strand, i.e., a NP modified with one DNA strand acted the starting material for the second DNA attachment, and the NP with two DNA strands for the

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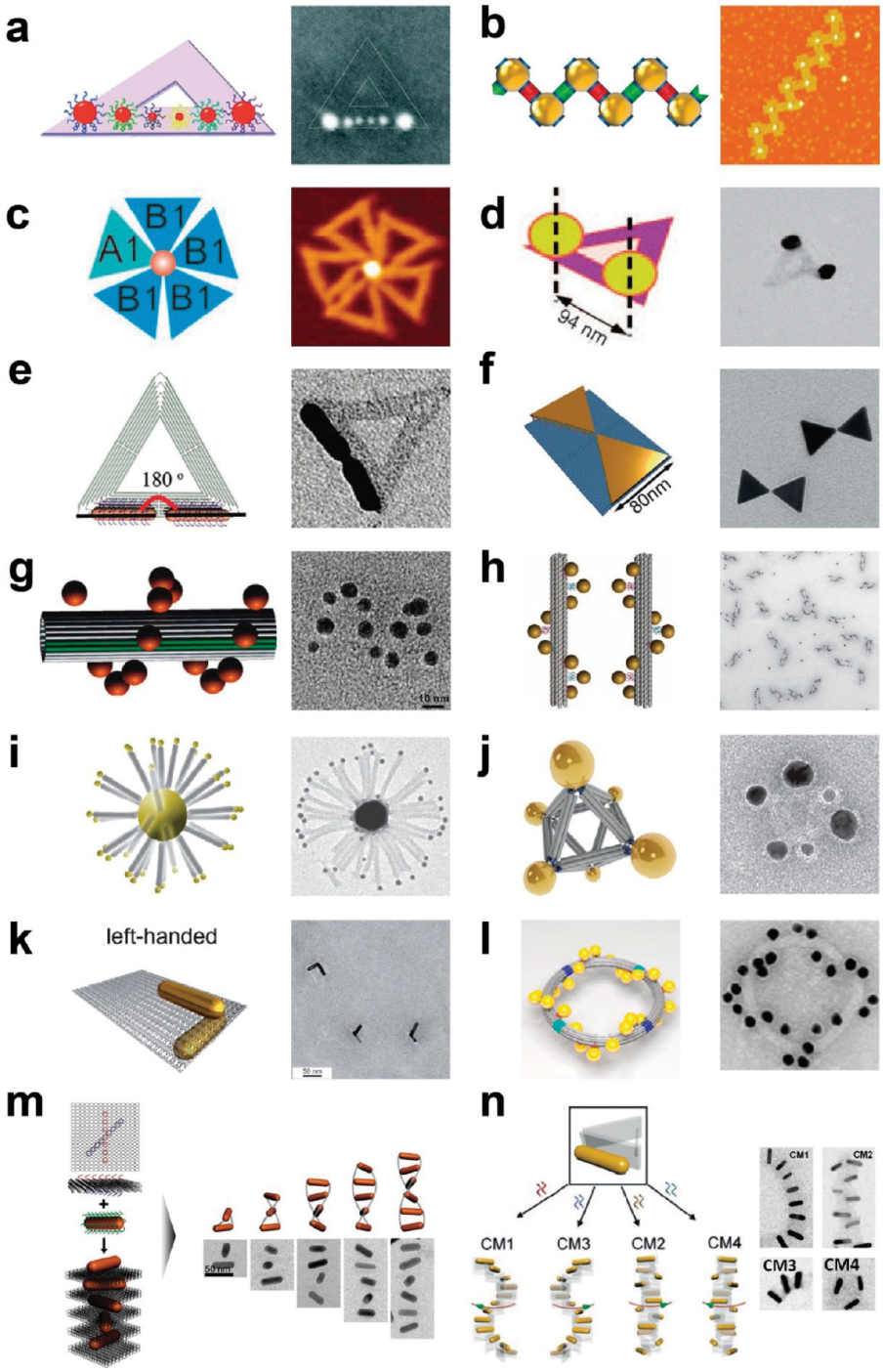

Figure 4. Representative examples of rational self-assembly of NPs into (a–f) 2D[37,40,154–157] or (g–n) 3D[34,160,162,164,168–171] nanostructures by DNA origami. Images show the schematic representation of assembly of DNA-AuNPs, AgNPs, AuNRs, or Au prisms on different DNA origami structures and the corresponding TEM images. a, e, g, l, and m reproduced with permission from refs 154, 157, 160, 171, 169, respectively. Copyright 2010, 2011, 2012, 2016, and 2015 American Chemical Society. c, d, f, and n reproduced with permission from refs 156, 37, 40, and 170, respectively. Copyright 2015, 2010, 2018, and 2017 John Wiley and Sons. b, h, i, and j reproduced with permission from refs 155, 34, 162, and 164, respectively. Copyright 2016, 2012, 2013, and 2015 Nature Publishing Group. k reproduced with permission from ref 168. Copyright 2014 Royal Society of Chemistry.

third DNA attachment, and so on. This approach yielded the optimal arrangement of DNA on a NP and led to the synthesis of AuNP assemblies possessing a discrete number of AuNPs.

2.4. Assembling Metal NPs to DNA Tile. DNA tile-based assembly is used for the fabrication of periodic DNA nanostructures containing many tile repeats. DNA tile building blocks are constructed by hybridizing several DNA strands, each of which has a unique sequence at specific locations, forming the nanostructures in one, two, and three dimensions.[129–144] Mao's group reported a class of core–

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shell complexes (AuNP@DNA cages).[43,145] In particular, nanostructures, in which NPs had defined valences and directional bonds, were constructed to mimic the atom-molecule relationship (see Figure 3a).[43] They built such nanostructures by encapsulating AuNPs into self-assembled DNA polyhedral nanocages, which guided further assembly of the AuNPs. A series of configurations, resembling CH_4-like, SF_6-like, $W(CH_3)_6$-like or C_2H_6-like, were obtained.[43] Sleiman's group employed DNA nanostructures as permanent transient and reusable templates to transfer essential information, as shown in Figure 3b.[146] In detail, DNA strands with different sequences were positioned into geometrically controlled patterns on one AuNP. A series of wireframe DNA prisms as pro-ligands were constructed to carry specific DNA ligands on their polygonal base frames, leading to trigonal, tetragonal, and pentagonal DNA valences. When the superstructured pro-ligands were attached to AuNPs through gold−thiol bonding, steric hindrance from the DNA prisms guaranteed a high yield production of 1:1 conjugates. After a denaturation to remove nonthiolated DNA from the prisms, the polygonal arrays of the DNA ligands were transferred to the gold surface. This method allowed a decoration of identical or different DNA sequences on a NP with a prescribed layout and produced NPs that had inherited molecular recognition information from the parent template. These information-rich NPs are unique building blocks that can be functionalized with different components site specifically, such as AuNPs with different spacer arms or different combinations of fluorescent probes. Dynamic assembly processes, such as strand displacement, can also be performed on the NPs.

AuNPs can be organized into regular 2D arrays with defined particle locations and interparticle spacing by hybridizing to the preassembled 2D DNA scaffolding. Kiehl and co-workers demonstrated the first use of self-assembled 2D DNA lattices to organize AuNPs into periodic striped patterns.[147] 6 nm AuNPs conjugated with T15 sequences were assembled into closely packed rows, through in situ DNA hybridization, to a preassembled 2D DNA scaffold surface with a precisely defined interrow spacing of ∼63 nm (Figure 3c). In a different method adopted by Yan and co-workers, they prepared AuNP-embedded 2D DNA arrays by the self-assembly of differently sized AuNP-conjugated DNA tiles (Figure 3d).[148] In this method, the periodicity and interparticle spacings of the AuNP nanoarrays were precisely controlled through varying the DNA-tile dimensions. Later, the same group prepared AuNP arrays of periodic squarelike configurations on self-assembled DNA nanogrids.[149] The center-to-center interparticle spacing between neighboring particles was controlled to be ∼38 nm. Each particle sat on only a single DNA tile. Seeman and co-workers utilized double crossover (DX) triangular DNA tiles to organize AuNPs into a 2D honeycomb lattices (see Figure 3e).[150] They demonstrated that cohesion by two sticky ends on each end of a DX molecule was more robust than that by a single sticky end. Mao and co-workers developed a thermal evaporation approach for the preparation of 2D AuNP arrays, as shown in Figure 3f.[30] Using this strategy, the tetragonal and hexagonal AuNP superlattices were prepared. The shapes of AuNP patterns were determined by the DNA templates, and the AuNP size was dependent on the amount of thermally evaporated gold. As a big step forward by Yan and co-workers, they created a group of complex 3D geometric architectures of AuNPs based on rational design of the DNA tiles, as shown in Figure 3g.[151] By controlling the locations of stem loops on DX-DNA tiles 1D spiral chains, double helices and even nested spiral tubes were constructed, based on the steric effects and electrostatic interactions between NPs. These work reflected the ability of DNA tiles to control the position and the distance between NPs. By further engineering the tile structures, it should be possible to create superstructures with enhanced complexities leading to a substantial advancement in small-scale device applications.

2.5. Assembling Metal NPs on DNA Origami. DNA origami provides an efficient template for organizing metallic NPs into different geometries. Differing from DNA tile-based assembly, DNA origami utilizes hundreds of short oligonucleotide "staple" strands to bind distinct points within a long single strand DNA scaffold, which was then folded into an arbitrary 2D or 3D shape.[44] This allows for high-yield synthesis, high structural fidelity with few errors, high tolerance to stoichiometric imbalances and resistance to enzymatic digestion.[152] Meanwhile, DNA origami with custom designer structures and unique addressability enable complicated nanoarchitectures to be designed and constructed. Yan, Liu, and co-workers first realized discrete AuNP patterns using DNA origami.[153] Later, Ding, Bokor and co-workers[154] reported the use of DNA origami to arrange AuNPs of different sizes in a linear fashion on a triangular DNA origami (see Figure 4a). More recently, Gang's group used a predefined set of different DNA-framed NPs to create diverse planar architectures, which included periodic structures and arbitrarily shaped meso-objects, e.g., square-shaped, cross-shaped, linear chain, zigzag chain, and 1D or 2D arrays, as shown in Figure 4b. Objects of nontrivial shapes, such as a nanoscale model of Leonardo da Vinci's Vitruvian Man, were self-assembled.[155] Fan's group developed a AuNP-mediated Jigsaw-puzzle-like assembly strategy to control the formation of DNA origami-AuNP complexes to break the size limitation of DNA origami (Figure 4c).[156] They used AuNP-based universal joints for the one-pot assembly of DNA origami of triangular shape to form submicroscale superorigami nanostructures. AuNPs were anchored at predefined positions of the superorigami and a range of supersized DNA origami with higher-order nanostructures were formed. Other than AuNPs, silver nanoparticles (AgNPs) were positioned on DNA origami templates that had well-defined geometries and distances, as shown in Figure 4d.[37] The center-to-center distance between adjacent AgNPs was precisely controlled from 94 to 29 nm. Such control of the spatial distance of AgNPs may have significance in photonic applications. Liu and Yan's groups assembled gold nanorods (AuNRs) with defined inter-rod angles, producing >70% yield and exhibiting tunable plasmonic properties (Figure 4e).[157] Eskelinen et al. constructed AgNPs into a bow-tie antenna configuration with a rectangular DNA origami which could be used as a DNA sensor according to finite-difference time-domain simulations.[158] Our group recently described the use of a DNA origami template to assemble Au nanoprisms into Au bowtie nanostructures, as shown in Figure 4f. The geometrical configuration of the bowtie structure was precisely controlled and an approximate 5 nm gap was achieved, which was employed as plasmonic antennas in single-molecule surface-enhanced Raman scattering (SM-SERS) measurements. This design achieved repeatable local field enhancement of several orders of magnitude.[40]

DNA origami was employed to highly complex 3D nanostructures. A minimum of four identical spherical nanoparticles are needed to compose a 3D chiral geometry.

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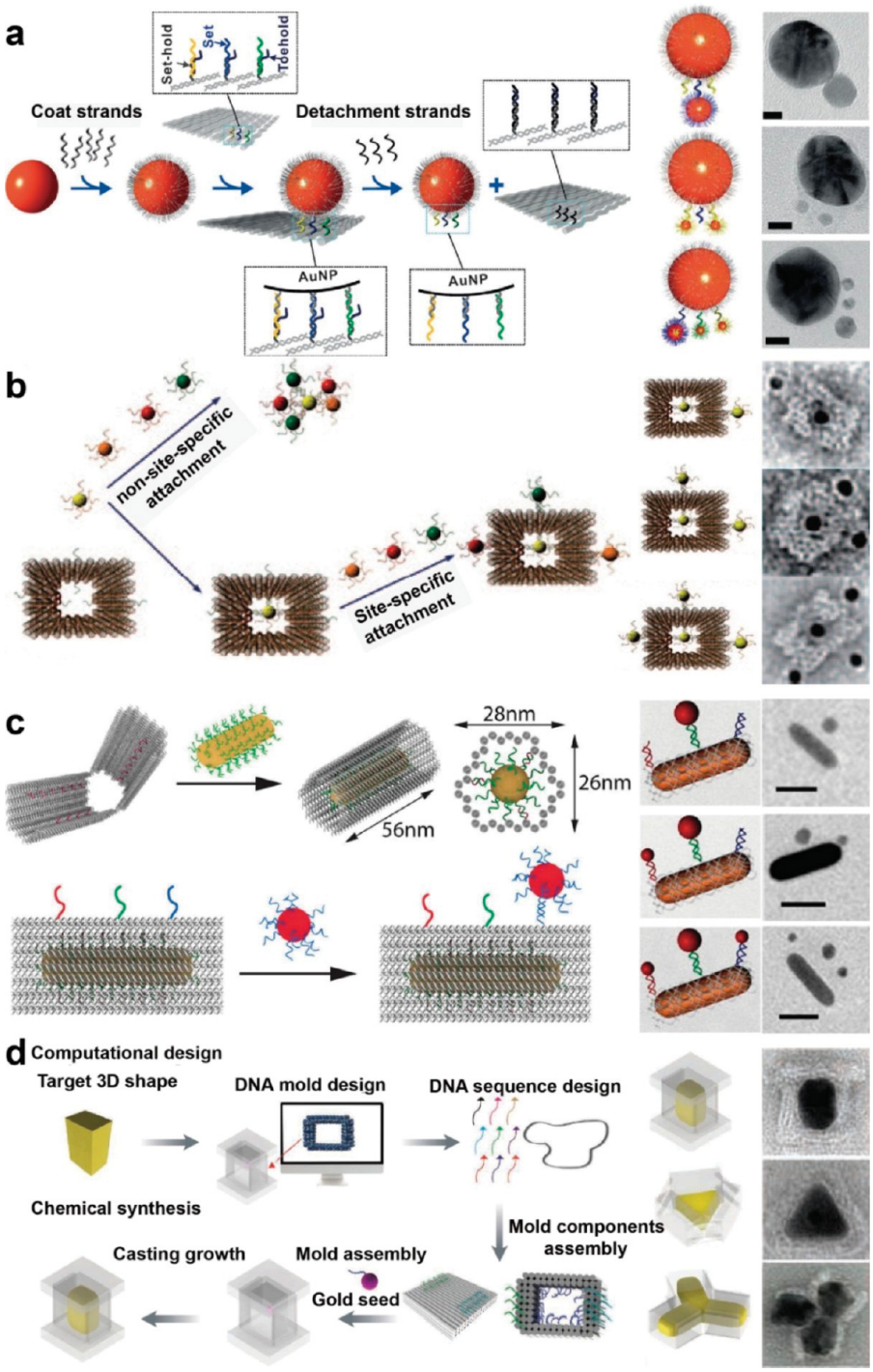

Figure 5. Site specific surface modification of NPs with DNA origami. (a) Schematic representation of programmable number and position control of DNA ligands on an AuNP by replicating the structural information on DNA pro-ligands on a planar DNA origami during DNA ligand transfers and the corresponding representative TEM images. Reproduced with permission from ref 172. Copyright 2016 John Wiley and Sons. (b) Illustration of a DNA nanocage encapsulated AuNP with programmable DNA valences on the inner and outer origami surface for the site-selective functionalization of the AuNP surface and the corresponding representative TEM images. Reproduced with permission from ref 173. Copyright 2011 John Wiley and Sons. (c) Scheme showing the process for surface functionalization of a AuNR with programmable DNA valences on the outer DNA origami clamp surface and the corresponding representative TEM images. Reproduced with permission from ref 174. Copyright 2016 American Chemical Society. (d) Schematic of assembly of the DNA origami mold and the corresponding representative TEM images of casting growth of user-specified 3D shape of AuNPs. Reproduced with permission from ref 175. Copyright 2014 AAAS.

The size difference and heterogeneity of the particles can break the symmetry of the frame, resulting in enantiomers that exhibit mirrored CD signals. Our group utilized DNA origami as a rigid template for accurately positioning four identical spherical AuNPs into an asymmetric tetrahedron and produced left- and right-handed 3D plasmonic structures. The

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constructed 3D plasmonic structures exhibited characteristic mirrored bisignate peak-dip and dip-peak CD profiles.[39] The CD shapes of the 3D plasmonic geometries agreed well with classical electrodynamics calculations. Increasing the number of the arranged AuNPs can lead to helices that theoretically generated a strong CD response.[159] Using the strategy of rolling up a 2D structure, Ding, Liu, and co-workers assembled AuNPs into the helices on DNA origami nanotubes (Figure 4g).[160] The interparticle spacing was controlled by the locations of the capture strand groups. Upon the addition of folding strands complementary to the protruding sequence of the long sides of the origami template, the sheet rolled up to minimize steric and electrostatic interparticle repulsion, leading to AuNP helices with defined helical parameters. The nanoparticle helices exhibited a bisignate peak-dip CD line shape in the vicinity of the plasmonic resonance of AuNPs. Furthermore, the increase in the nanoparticle size resulted in smaller interparticle distances and stronger plasmon coupling effects, producing an enhanced chiral response. As a step forward, Liedl and co-workers used rigid DNA cylindrical nanostructures with nine helically arranged binding sites on the outer surface to assemble DNA-coated AuNPs into a left- or right-handed helical geometry (Figure 4h).[34,161] Pronounced CD signals with characteristic bisignate mirrored shapes were achieved. The CD response could be enhanced by increasing the particle size or by plating silver onto gold, because of the enhanced interparticle near-field coupling. The origami-AuNP architectures have since then been expanded. For example, Liedl's group has created a great variety of planet−satellite AuNP nanoclusters with customized material properties and defined sizes by DNA-origami-guided self-assembly, as shown in Figure 4i. The planet-satellite distances were controlled from a few nanometers to 200 nm and precisely positioned along the radial spacers.[162] Turberfield's group reported a strategy to embed a AuNP with a number of DNA origami bundles to form a flower-shaped core−shell structure.[163]

The geometries of the origami frames provide a well-defined template for the 3D lattice of NPs assembly. Gang's group designed a 3D octahedral DNA frame with attachment sites on the vertices, and the AuNPs can be arranged in prescribed locations determined by the frame vertices encoded by the specific DNA sequences (Figure 4j).[164] Later, they designed a tetrahedron-shaped DNA origami with AuNPs attached to the four vertices.[165] These NPs then acted as connectors to organize the tetrahedron origami-NP units into a well-ordered fcc lattice structure. The final lattice structure was the shape of a diamond when another AuNP was positioned inside the tetrahedron shaped origami structure. By varying the size and number of particles inside, a zinc blend and a "wandering" zinc blend lattice style was achieved. Then, they successfully designed a variety of DNA origami structures with polyhedron shapes, including an octahedron, a cube, an elongated square bipyramid, a prism, and a triangular bipyramid, to assist in the construction of a 3D NP lattice.[166] Controlling NPs anchoring points on a DNA frame, and the combination of different frame shapes will allow the creation of more complicated unit cells. It opens up opportunities for high-yield precise assembly of 3D building blocks, in which NPs of different structures and functions can be integrated. Besides spherical NPs, Wang's group[167] and our group (Figure 4k)[168] respectively reported the discrete 3D anisotropic Au nanorod dimer nanoarchitectures formed using bifacial DNA origami as a template, in which the 3D spatial configuration was precisely tuned by rationally shifting the location of AuNRs on the origami template. A distinct plasmonic chiral response was experimentally observed from the discrete 3D AuNR dimer nanoarchitectures and appeared in a spatial configuration-dependent manner. These work represented great progress in the fabrication of 3D plasmonic nanoarchitectures with tailored optical chirality. Later, Wang's group successfully realized anisotropic AuNR helical superstructures with designed configurations including precise inter-rod spacing and inter-rod angle, and deterministic handedness by assembling two AuNRs into an X-shape on the bottom and top surfaces of a rectangular DNA origami structure, as shown in Figure 4m.[169] Two types of optically reversed AuNR helices were self-assembled under the guidance of DNA origami with fixed inter-rod spacing of 14 nm and inter-rod angle of 45°, by solely designing the mirrored-symmetric patterns of capturing strands on the origami. Circular dichroism (CD) spectra showed that the assembled AuNR helices displayed strong and predicted chiroptical activities, which matched well with the calculation. As a significant step further forward by Yan and co-workers, they created a versatile DNA origami adapter for tunable self-assembly of various DNA chiral supramolecular architectures (Figure 4n).[170] The DNA adapter, which was rationally designed with distinct binding domains arranged in mirror-asymmetric manner, enabled creation of DNA chiral superstructures with facilely tuned handedness and hierarchy. Moreover, the distinct optical chirality relevant to the ensemble conformation, was strongly affected by the spatial arrangement of neighboring nanorod pair. This strategy opens new possibility for the programmable construction of a variety of superstructures with new topographical and functional properties. Other than the helical arrangement of nanoparticles along a cylinder, Urban et al. constructed a plasmonic toroidal structure through the hierarchical self-assembly of four identical origami units, which were bent at a 90° angle (Figure 4l).[171] The hierarchical assembly of plasmonic toroidal metamolecules exhibited tailored optical activity in the visible spectral range and showed a stronger chiroptical response than monomers and dimers of the building blocks. This work provided a new strategy to create chiral plasmonic devices with sophisticated nanoscale architectures, which may be applied in chiral sensing.

Precise control over surface functionalities of nanomaterials, such as labeling the NP surface with a single copy of a functional group or displaying multiple unique molecules on the NP surface, may offer opportunities for fabricating complex functional nanoarchitectures. DNA origami has proven to be a promising technique to realize site specific surface modification of NPs. Recently, a few elegant strategies have been developed to obtain NPs with stoichiometric control over the number of attached ligands. Fan's group developed a DNA origami-based nanoimprinting lithography (DONIL) strategy to transfer prepatterned DNA sequences on a planar DNA origami to AuNPs (Figure 5a).[172] The bulky size of the DNA origami facilitated a monofunctionalization of the AuNPs with a set of different DNA sequences. This work transferred essential DNA configurations to the surface of the AuNPs through a toehold-initiated displacement reaction. The same method was adopted for a site-specific decoration of AuNRs with DNA.[35] More recently, Yan's group[173] and Wang's group[174] utilized DNA nanocage or clamp encapsulation for regulated the anchoring of DNA on AuNPs to produce "atom-like" AuNPs with a fixed number of DNA strands. Yan's group designed a cubic DNA

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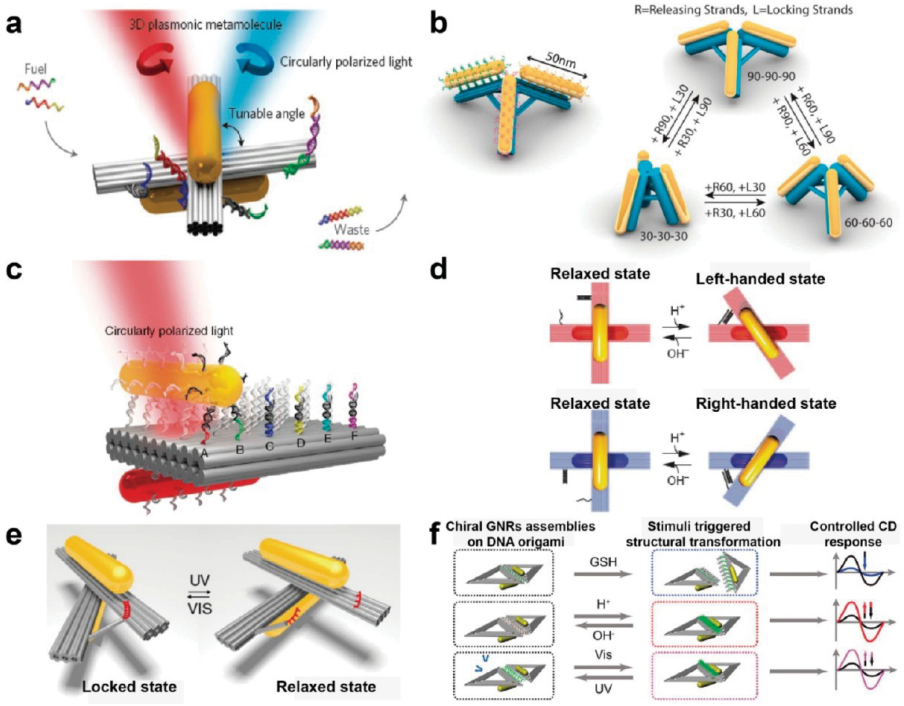

Figure 6. DNA-assembled dynamic nanostructures. (a) Reconfigurable 3D plasmonic nanostructures consist of AuNRs hosted on switchable DNA origami templates. Relative angle between the AuNRs within the structure can be controlled using DNA locks, therefore giving rise to dynamic plasmonic chiral responses. Reproduced with permission from ref 179. Copyright 2014 Nature Publishing Group. (b) Reconfigurable DNA origami tripod with AuNRs. Toehold-mediated strand displacement reaction is used to tune the angle between the arms. Sets of releasing strands (R) and locking strands (L) are employed stepwise to change the angle between the DNA arms. Reproduced with permission from ref 180. Copyright 2017 American Chemical Society. (c) Plasmonic walker that can perform stepwise walking on origami. Walking of the AuNR is enabled through toehold-mediated strand displacement. Reproduced with permission from ref 181. Copyright 2015 Nature Publishing Group. (d) pH regulation of DNA origami-based plasmonic chiral nanostructures. Plasmonic system can be switched between the relaxed and the LH/RH state by opening/closing the pH-triggered DNA locks. Reproduced from ref 188. Copyright 2017 AAAS. (e) Light-driven 3D plasmonic nanosystem reversibly regulated by UV and visible light for switching between a right-handed and a relaxed state. Dynamic function of the origami structure is enabled by introducing the azobenzene-modified DNA segment on the origami template. Reproduced with permission from ref 185. Copyright 2016 Nature Publishing Group. (f) L-shaped AuNR dimers assembled on rhombus-shaped DNA origami templates display chiroplasmonic signals that are responsive to different stimuli, such as glutathione reduction, pH changes or photo irradiation. The nucleic acid linkages between the origami blocks were designed to be responsive to different stimuli and a configuration transformation of the L-shaped nanorods can be in situ transduced into CD changes in the near-IR wavelength range. Reproduced with permission from ref 33. Copyright 2017 American Chemical Society.

origami cage with specific DNA functionalities on its inner and outer walls (Figure 5b).[173] The DNA strands protruding from the inner walls were used to encapsulate an AuNP, which was coated with a structured DNA. The DNA sequences displayed on the outer surface of the DNA origami were used to capture other particles at addressable locations. Wang's group modified a DNA origami clamp with a AuNR at specific surface recognition sites (Figure 5c).[174] AuNRs were encapsulated by the DNA origami through hybridization of single-stranded DNA on the AuNRs with complementary capture strands inside the clamp. Another set of capture strands on the outside of the clamp created the specific recognition sites on the AuNR surface. By means of this strategy, AuNPs were attached AuNRs at the top, middle, and bottom of the surface, respectively, to construct a series of well-defined hetero-structures.

Yin et al.[175] and Seidel et al.[32] used DNA origami mold as a spatially programmable functionalization surface to anchor a single AuNP as Au seed inside of the DNA origami mold (like a barrel), and the seed grew within a cavity of a DNA origami. As shown in Figure 5d, the shape of the resulting AuNP mimicked that of the cavity of DNA origami mold. With this strategy, DNA origami was designed to have a cavity with the shape of the target inorganic material. One AuNP was anchored to the interior surface of the cavity, and the origami barrel was fully enclosed with two lids, resulting in a box like structure with a single Au seed trapped inside. Under suitable chemical conditions, the Au seed grew to fill the entire cavity, thereby replicating its prescribed 3D shape. Using this method, a variety of inorganic materials of different shapes were synthesized at a resolution of ~3 nm, such as a cube, triangle, and Y-shaped structure.

3. DYNAMIC METAL NANOSTRUCTURES BASED ON DNA SELF-ASSEMBLY

Importantly, DNA origami-NP nanostructures are not limited to static systems. The DNA origami technique offers an unprecedented pathway to manipulate both spatial and temporal arrangements of metal NPs that are assembled on DNA origami templates, enabling stimulated reconfigurable, via toehold-mediated strand displacement reactions,[173] pH,[176] ion concentration,[177] magnetic, light,[178] or thermal triggers.[177] A typical reconfigurable plasmonic nanosystem was reported by Liu's group by tuning intergold rod angles, as shown in Figure 6a.[179] Two AuNRs were assembled with a heteroplanar

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X-arrangement on a reconfigurable DNA origami, into which two DNA locks were incorporated with different strand sequences for independent control. The switchable chiroptical response among three different states could be realized in multiple cycles by successive additions of corresponding fuel strands. Ding, Ke, and Zhang et al. used DNA origami as the template to construct a 3D reconfigurable tripod-shaped plasmonic nanostructure that consisted of three AuNRs (see Figure 6b).[180] The internanorod angle and distance were precisely tuned through mechanical operation of the origami tripod via toehold-mediated strand displacement. The transduction of conformational change manifested into a controlled shift of the plasmonic resonance peak, which agreed well with electrodynamic calculations.

It is also possible to rearrange metal NPs on static DNA origami templates. Herein, NPs act as walkers that were driven via toehold-mediated strand displacement reactions.[181,182] Liu's group demonstrated a dynamic plasmonic system in which one AuNR performed stepwise walking directionally and progressively on DNA origami (see Figure 6c).[181] A walker AuNR and a stator AuNR (an immobilized AuNR) were placed on two opposite surfaces of a rectangular DNA origami platform, forming a chiral geometry. Along the track that was place on the origami surface, six parallel rows of footholds were utilized to establish five walking stations, evenly separated by 7 nm. The stepwise walking was powered by DNA hybridization and triggered by the addition of the respective blocking and removal strands. The dynamic walking process was monitored via time-dependent CD response changes. In the experiments, the plasmonic walker functioned not only as a walking element but also as an optical reporter, which could deliver its translocation information through optical spectroscopy in real time. Later, the same group demonstrated the implementation of two plasmonic walkers that walked both individually and collectively on the same origami track.[182] A sensitive plasmonic coupling scheme was introduced for in situ optically monitoring the dynamic walking of the two walkers with steps below the diffraction limit. The chiroptical response of the entire system was jointly determined by the positions of both walkers relative to the stator. This allowed optical discrimination of the walking directions and the individual steps of the two walkers. The number of the walkers and the optical response of the system were also correlated.

Strand displacement reactions usually generate DNA duplex waste in each cycle as well as dilution effects. In comparison, the use of light as an input is noninvasive and waste-free, offering high spatial and temporal resolution as it can be switched on and off rapidly. Photoresponsive molecules such as azobenzene can be employed through incorporation into DNA backbones to activate the mechanical activation of DNA upon light stimuli.[178,183,184] Liu's group designed an all-optically controlled dynamic plasmonic system by integration of a photoresponsive DNA lock, i.e., azobenzene, on DNA origami (Figure 6e).[185] This dynamic plasmonic system was comprised of two AuNRs which were assembled on a reconfigurable DNA origami, and a DNA segment was modified with azobenzene. Light can "write" and "erase" the conformation states of the nanostructure through photoisomerization of azobenzene at a localized region. The different conformation states could be triggered and read-out cyclically in real time. This system thus translated the light-triggered molecular motion of azobenzene into strong and reversible plasmonic CD responses.

pH can also trigger structural reconfiguration of DNA origami over a wide pH range using pH-sensitive DNA triplex as the "locks", which can be protonated upon acidification.[186,187] pH control shows advantages over strand displacement in simpler implementation, faster modulation, and no generation of waste products. By integrating DNA locks on reconfigurable DNA origami, Liu's group created a series of chiral plasmonic nanostructures that were programmed to respond to environmental pH changes. (Figure 6d).[188] These plasmonic nanostructures showed considerably narrow transition pH windows and rapid responses on the order of tens of seconds. This approach enables discrimination of chiral plasmonic quasi-enantiomers and arbitrary tuning of chiroptical effects.

The ability to modulate the plasmonic assemblies as optical probes can be used to enhance signal-to-noise ratios for imaging and sensing within complicated biological environments, such as intact cells.[189,190] Our group described the dynamic modulation of chiral plasmonic signals of AuNRs, which was attributed to the stimuli-responsive origami/AuNR complexes, as shown in Figure 6f.[33] L-shaped AuNR dimers were assembled on rhombus-shaped DNA origami templates to create plasmonic nanoarchitectures that displayed chiroplasmonic signals. The DNA linkages between the origami blocks were designed to be responsive to glutathione reduction, restriction enzyme activity, pH changes or photo irradiation, which were common indicators of the biochemical environment. A configuration transformation of the L-shaped nanorods was triggered by these biological indicators and can be in situ transduced into CD changes in the near-IR wavelength range.

4. FUTURE PROSPECTS AND CHALLENGES

DNA has demonstrated its capability of controlling the shapes of NPs. DNA-templated NP synthesis through directed DNA metallization is a rapidly evolving field. The major challenges in directed DNA metallization are the low resolution and the poor quality of the final metal nanostructure because of the uncontrolled growth. The ability to tune the size and physicochemical properties of NPs depends on DNA's structure, composition, and sequence, which hold enormous potential for the rational design of NPs. The use of modified nucleotides incorporating reactive chemical groups would facilitate further modulation of metal−DNA interactions and thus holds great promise for the synthesis of NPs with controlled shapes and novel properties.

Many efforts have been made to achieve desired shapes and functions of the self-assembled nanostructures by modifying the NP building blocks with DNA in defined numbers and geometric configurations. Great challenges remain. Some strategies of controlling the number and position of DNA ligands on NPs are either too complicated or unfavorable for large-scale production. In the future, efforts should be made on simpler and more general strategies for controllable DNA decoration on both isotropic and anisotropic nanomaterials with widened compositions and physical/chemical properties.

Great advances were achieved in the past ten years in the area of DNA nanotechnology. Versatile methods to assemble 1D, 2D, and 3D DNA-NP systems were developed. DNA nanostructures have shown capability of characteristic of programming their shapes and positioning NPs with nanometer scale precision. Despite success on the creation of custom molecular structural designs with DNA origami, there

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are many challenges and opportunities. For example, current experimental studies are generally quite specific for some particular designs and are limited by the cost of the materials or the assembly time. These challenges could be overcome by further development in DNA nanotechnology and software systems for structural design. The rational and systematic design, along with the control over the self-assembling conditions, will create novel complex metal nanostructures with well-defined shapes and functions. Additionally, further development in the scalability of metal nanostructures fabrication and processing methods is required to fabricate integrated system that can perform sophisticated tasks. Recent success on combining the bottom-up DNA-guided self-assembly of nanostructures with top-down lithography may provide a means to scale up the final systems for desired applications.[191−193] Meanwhile, synthesis of multicomponent nanohybrids consisting of the nanoscale components is still in its early stages and needs to be explored extensively for a synergistic effect on the enhancement of their physical and chemical properties.

Despite the challenges, DNA-based technology has provided an effective route for the organization of multifunctional nanoarchitectures with "programmable/customizable" functions, and stimulates a plethora of new areas and applications. The interdisciplinary research among different fields will continuously develop new methods and generate novel ideas. It is anticipated that DNA/NP hybrid system, with unprecedented control over shape, size, mechanical flexibility and anisotropic surface modification, could be further developed and integrated with progress in other areas (e.g., medicine, materials science, optics) to bring a bright future to multidisciplinary research.

AUTHOR INFORMATION

Corresponding Authors

*Email: wangzg@nanoctr.cn.

*Email: dingbq@nanoctr.cn.

ORCID

Baoquan Ding: 0000-0003-1095-8872

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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