

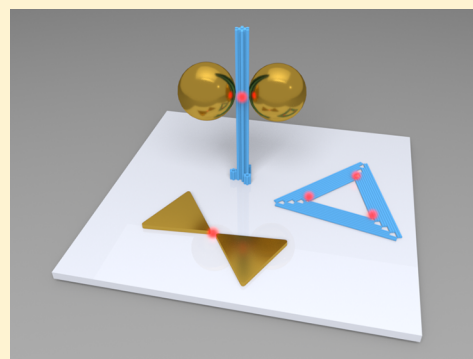
DNA Origami Nanophotonics and Plasmonics at Interfaces

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ABSTRACT: DNA nanotechnology provides a versatile toolbox for creating custom and accurate shapes that can serve as versatile templates for nanopatterning. These DNA templates can be used as molecular-scale precision tools in, for example, biosensing, nanometrology, and super-resolution imaging, and biocompatible scaffolds for arranging other nano-objects, for example, for drug delivery applications and molecular electronics. Recently, increasing attention has been paid to their potent use in nanophotonics since these modular templates allow a wide range of plasmonic and photonic ensembles ranging from DNA-directed nanoparticle and fluorophore arrays to entirely metallic nanostructures. This Feature Article focuses on the DNA-origami-based nanophotonics and plasmonics—especially on the methods that take advantage of various substrates and interfaces for the foreseen applications.



INTRODUCTION

The rapid evolution of structural DNA nanotechnology^{1–5} along with advanced and automated techniques, computer-aided design software, powerful simulation tools, and reduced cost of synthesis^{6–10} have enabled the effortless fabrication of custom DNA nanoarchitectures for many applications in materials science and bio-oriented research.^{3,11,12}

Examples of using versatile DNA shapes—especially DNA origami^{11,13–16}—have been reported, for example, in molecular electronics,^{17–22} super-resolution imaging,^{23–26} and drug delivery.^{27–31} These customized DNA objects can also find use as molecular-scale diagnostic tools,³² dynamic devices,^{33–37} and templates for controlling chemical reactions,^{38–40} and importantly, these structures are inherently biocompatible and readily modifiable for application-specific purposes.^{28,30,41–45} These examples are enabled by virtue of the sub-nanometer structural accuracy of DNA origami and nanometer-scale patterning resolution of multiple molecular components.^{11,13–16} In general, the DNA origami technique provides a straightforward route from the target shape to a functional product via a self-assembly process. In a one-pot assembly, one can create a very large number of customized and well-defined DNA origami nanostructures ranging from nano- to micrometer size¹⁵ and from mega- to gigadalton scale¹⁶ for various user-defined tasks and implementations.

In addition to these examples, DNA nanostructures can be used as precise templates for arranging metal nanoparticles and creating plasmonic assemblies and nanophotonic devices.^{46–49} Like in all of the other above-mentioned examples, building nanophotonic structures using DNA is also based on taking advantage of the programmability, modularity, and high addressability of the DNA nano-objects. Arguably, there are several benefits of integrating the plasmonic DNA nanostructures with interfaces; for example, substrate-based methods are

readily compatible with conventional top-down lithography methods, and they also enable characterization of individual nanodevices.^{50–53} Moreover, DNA lattice-based approaches can be improved by taking advantage of DNA structure diffusion on substrates.^{54,55} Importantly, anchoring of the nanostructures to interfaces facilitates coupling of nanodevices with outer circuitry,¹⁸ diagnostic and sensing tools,³² and fabrication of bioinspired substrates and metasurfaces.⁵⁶

In this Feature Article, we summarize the key aspects of DNA origami plasmonics and provide an overview of placement and arrangement methods for self-assembled DNA nanostructures. Finally, we combine the methodology of these two sections and discuss the recent progress of DNA-origami-based nanophotonics at interfaces.

DNA-Nanostructure-Based Nanophotonics and Plasmonics: An Overview. The highly addressable DNA origami provides an excellent platform to organize nanophotonic components into systems with emerging optical properties because of its nanometer-scale precision control. The most common photonic objects arranged with DNA origami are metallic nanoparticles (NPs) and fluorophores. When NPs interact with light, their conduction-band electrons can enter a collective oscillation mode, that is, a so-called localized surface plasmon resonance (LSPR). The plasmon oscillation is highly sensitive to the polarizability of the particle; in other words, the composition, geometry, and surrounding media of the NP all have a significant influence on the resonance. In addition, when two NPs are in close proximity, their plasmon oscillations can

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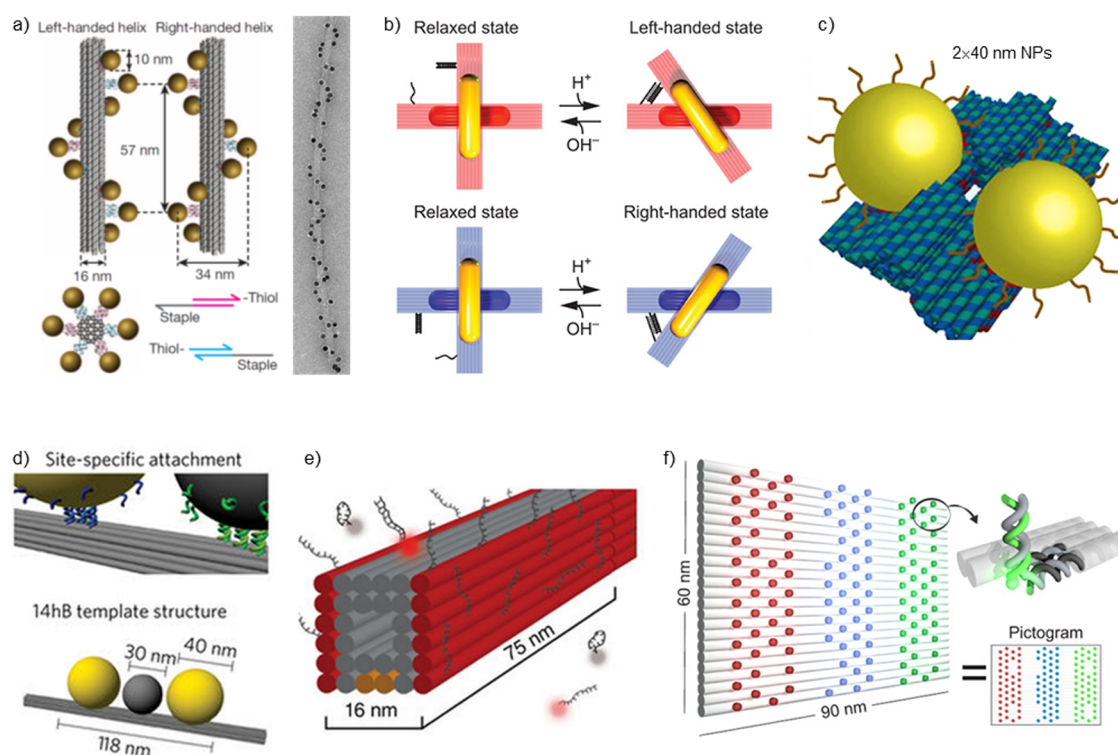


Figure 1. (a) Left: DNA-origami-based left- and right-handed chiral plasmonic nanoassemblies that show strong circular dichroism.⁶¹ Right: Transmission electron micrograph of stacked assembly. (b) Dynamic chiral metamolecule that is sensitive to the pH change of solution.³⁶ (c) AuNP dimer with defined distance assembled on a DNA origami platform.⁷⁸ (d) Heterotrimer assembly with a AgNP between two AuNPs on a DNA origami beam.⁸¹ (e) Bar-shaped DNA origami with docker strands on sides to capture transient imager strands for super-resolution imaging.²⁵ (f) DNA origami with multiple programmable fluorescent dye binding sites acts as a metafluorophore.⁸⁴ Part a is reprinted with permission from ref 61. Copyright 2012 Springer Nature. Part b is reprinted with permission from ref 36. Part c is reprinted with permission from ref 78. Part d is reprinted with permission from ref 81. Copyright 2017 Springer Nature. Part e is reprinted with permission from ref 25. Copyright 2014 Springer Nature. Part f is reprinted with permission from ref 84.

couple with each other, resulting in intriguing optical properties and remarkable electromagnetic field enhancement. This coupling is strongly dependent on the spatial arrangement of NPs. For the tailoring of the optical response of the NP systems, techniques to position specific NPs with accurate spatial configuration are of vital importance. To date, DNA origami is one of the most promising candidates to tackle this issue with its sub-nanometer- to nanometer-scale positioning precision for molecules and nanoparticles.^{57,58} In addition to this extreme positioning resolution, the accessibility and absolute incorporation efficiency of the single strands in DNA origami can reach 95%.⁵⁹

In 2010, the first DNA-origami-guided arrangement of spherical gold NPs (AuNPs) was demonstrated.⁶⁰ The desired NP arrangement was achieved via coating AuNPs with oligonucleotides and further via their hybridization with complementary strands extended from the specific positions of origami. Later on, a plethora of NP assemblies with customized optical properties have been developed.^{46,48,49} A representative example of such a rationally designed plasmonic DNA device is a chiral plasmonic structure assembled from a rodlike DNA origami and nine AuNPs that go around the DNA rod in a helical fashion (Figure 1a).⁶¹ These chiral plasmonic nanostructures exhibited significant circular dichroism (CD) in the visible range, and their CD responses could be tuned by altering the NP size and the helical handedness. Spherical AuNPs can also be arranged into a ring conformation to obtain tunable electric and magnetic plasmon resonances at the visible frequencies.⁶² In

addition to AuNPs, spherical silver NPs (AgNPs) have also been organized by DNA origami.^{63–65}

Since the LSPR is sensitive to the geometry of NPs, metallic NPs with shapes other than a sphere could offer more diverse optical properties and therefore further facilitate the design of nanophotonic devices. DNA origami conjugates with gold nanorods (AuNRs),^{34–36,66,67} gold nanotriangles (AuNTs),⁶⁸ or hybrid assemblies of particles with different geometries^{69,70} have also been explored.

In addition to static nanophotonics, dynamic and reconfigurable plasmonic DNA devices have been developed. They are considered dynamic since the geometric configuration of such devices could be changed and switched after assembly. For example, by attaching two AuNRs to DNA origami beams connected via a single Holliday junction, a metamolecule with different rotational states—and therefore different CD signal states—can be formed. The reconfiguration of the states can be induced by the introduction of DNA displacement strands,³⁴ by light,³⁵ or by changing solution pH (see Figure 1b).³⁶ In addition to these, Turek et al. have demonstrated how thermoresponsive polymer-equipped DNA tweezers could be used as an actuator for surface-enhanced fluorescence.⁷¹ Instead of reconfiguring the whole metamolecule, the AuNR itself can also “walk” between different sites on a DNA origami by fueling the system with displacement strands⁶⁷ using a similar strategy as originally introduced by Yurke et al.⁷²

Significant effort has been put into developing techniques to position NPs in extremely close proximity to form hot-spots for

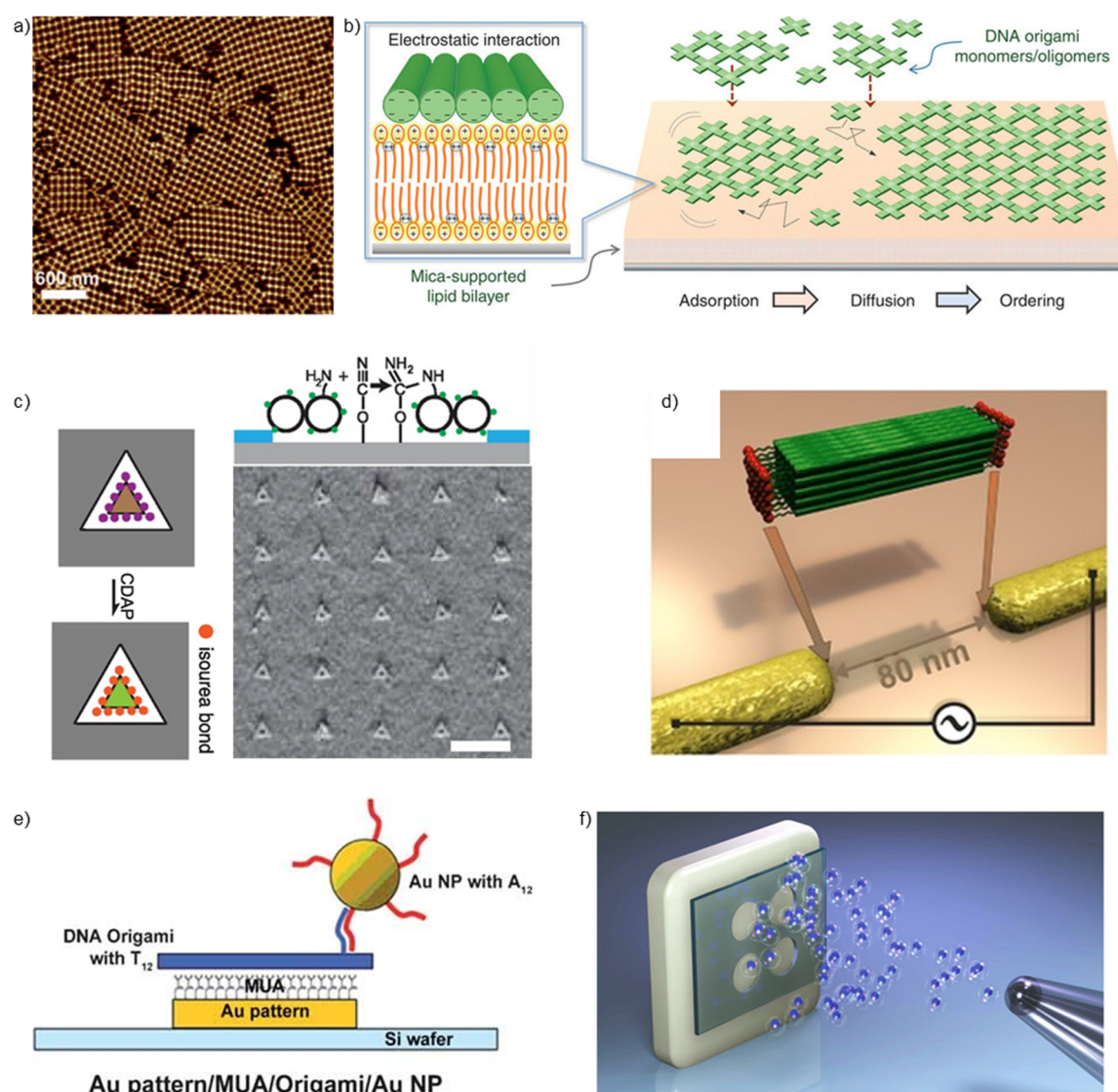


Figure 2. (a) AFM image of DNA origami cross-tiles assembled into a lattice configuration by cation-induced diffusion.⁵⁴ (b) Lipid-bilayer-facilitated 2D-lattice formation from DNA origami cross-tiles.⁹³ (c) Triangular DNA origami is covalently immobilized to binding sites patterned on a silicon substrate by lithography.⁵⁰ (d) Dielectrophoretic trapping of 3D DNA origami between lithographically fabricated gold nanoelectrodes.¹⁸ (e) DNA origami equipped with a AuNP is selectively attached to a gold pattern on a silicon substrate.¹⁰¹ (f) Large-scale spray-deposition of DNA origami nanostructures to the selected substrate through a mask.¹⁰³ Part a is reprinted with permission from ref 54. Copyright 2014 John Wiley and Sons. Part b is reprinted with permission from ref 93. Part c is reprinted with permission from ref 50. Copyright 2014 American Chemical Society. Part d is reprinted with permission from ref 18. Copyright 2015 John Wiley and Sons. Part e is reprinted with permission from ref 101. Copyright 2009 John Wiley and Sons. Part f is reprinted with permission from ref 103.

the field enhancement, which is essential for surface-enhanced Raman spectroscopy (SERS) and fluorescence enhancement (FE). To achieve the nanometer-scale distance, different strategies have been employed. For example, “seed-NPs” that are attached to DNA origami could be grown larger by chemical methods to shorten their distance.^{19,73,74} Upon conjugation of NP dimers on different sides of DNA origami, the DNA helices between NPs can act as binding sites and as a spacer of a few nanometer thickness.^{75–77} Rationally designed DNA origami structures could also be used to dock NP dimers with a gap of only a few nanometers, as shown in the work of Thacker et al. (see Figure 1c)⁷⁸ and Roller et al.⁷⁹ In these works, the local field was enhanced by several orders of magnitude and demonstrated by SERS or FE characterization.

To fully take advantage of the addressability and versatility of DNA origami, plasmonic systems with different metal

compositions have also been assembled. These heteroparticle assemblies^{80,81} have shown optical modes that are challenging to obtain with any other method. For example, a nondissipative and ultrafast plasmon passage has been observed in a heterotrimer system consisting of both a AuNP and AgNP arranged on top of DNA origami (see Figure 1d).⁸¹

Fluorophores form another group of nanophotonic components that are widely combined with DNA nanostructures. DNA origami can work as a nanoadapter to enable manipulation of individual or a few fluorescent molecules. In addition to the well-known Förster resonance energy transfer (FRET) studies,^{49,82} DNA origami structures equipped with dye-labeled oligonucleotides have been used in DNA-point accumulation for imaging in nanoscale topography (DNA-PAINT) in super-resolution microscopy (see Figure 1e),^{24,25,83} and as a nanoruler for spatial calibration.²³ Upon combination of various different fluores-

cence dyes on a single rectangular DNA origami, it is possible to assemble a so-called metafluorophore (see Figure 1f).⁸⁴

DNA Origami Placement at Interfaces. As already explained, there are a number of advantages in anchoring the DNA-based devices to the substrates or incorporating them into larger systems for nanophotonics. This section deals with the approaches suitable for assembling DNA structures at the interfaces.

DNA nanostructures can be immobilized onto substrates merely by electrostatic interactions, and one of the most common methods is adhesion to mica with the presence of magnesium ions.⁸⁵ Upon adjustment of the amount of cations of the deposition buffer, DNA nanostructures can be placed, for example, on silicon and silicon oxide.^{50,51,53} Interestingly, monovalent cations can be used for surface-assisted assembly of higher-order structures.^{54,55} Aghebat Rafat et al. used cross-tile structures (Figure 2a), and created 2D lattices by controlling the diffusion of the structures on a mica substrate with monovalent cations.⁵⁴ The cross-tiles were similar to ones designed by Liu et al.,⁸⁶ except that the tiles were “twist-corrected”, (i.e., the undesired twist caused by the square-lattice design⁸⁷ was removed), and they formed the close-packed crystalline structures via blunt-end stacking interactions^{88,89} instead of sticky-end cohesion. A similar approach of lattice organization on the substrate has also been demonstrated for a rectangular origami⁵⁵ and an origami triangle¹³ that has a void in the middle of the structure. The triangles form a close-packed lattice that could be further used as a removable mask for protein patterning of the substrate through the openings of the triangle layer.⁹⁰ Moreover, blunt-end stacking of DNA origami objects could be applied to arranging DNA origami in 3D lattices. Recently, Zhang et al.⁹¹ used three-dimensional and rigid origami tensegrity triangles—similar to simpler tensegrity triangles in the very first 3D DNA crystal by Zheng et al.⁹²—to form a 3D lattice with voids via blunt-end stacking. They also demonstrated the addressability of the origami lattice by attaching gold particles to the lattice voids, thus creating a hybrid DNA–gold nanoparticle superlattice.

In addition to mica substrates, lipid bilayers can also be employed in the organization of DNA origami lattices and other higher-order assemblies^{93–95} as seen in Figure 2b. The lattice formation process can be controlled using cholesterol-modified DNA origami and connector staples⁹⁴ or different lipid membrane phases (liquid-disordered or solid-ordered).⁹⁵ Moreover, the growth of arrays can be triggered by adjusting monovalent cation concentration as well as the concentration of deposited origami structures.⁹⁵

One approach to pattern substrates with the resolution beyond conventional lithography techniques is to combine top-down approaches with the high addressability of DNA origami. Kershner et al.⁹⁶ fabricated arrays of DNA origami triangles by attaching origami to lithographically revealed precise triangular areas of silicon oxide in a hexamethyldisilazane (HDMS) film. To demonstrate the potential of the method in high-resolution nanoscale patterning, Hung et al.⁹⁷ attached AuNPs to the corners of the origami triangle and organized them to the lithographically confined wells.

Later on, Gopinath & Rothmund⁵⁰ optimized the assembly of DNA origami triangle nanoarrays (Figure 2c) on silicon and silicon oxide substrates. They reported how DNA origami triangles could be covalently coupled to the lithographically patterned wells with high yields using the isourea bond (as shown in Figure 2c) or amide bond for linking. Attaching DNA

origami to silicon or silicon oxide usually requires deposition buffers with high magnesium content, but by employing covalent linking instead of simple electrostatic bonds between DNA origami and the substrate, a much wider magnesium concentration range could be used. Recently, Brassat et al.⁹⁸ further studied DNA origami adsorption onto a silicon oxide surface in nanohole arrays by varying Mg and DNA origami concentration, buffer strength, adsorption time, and nanohole size. They observed that buffer strength plays a critical role in origami deposition.

In addition to fabricating origami-shaped wells in the films, one can also use other lithographic features for directing DNA origami to predefined locations with targeted geometries. One example is to take advantage of the (directional) polarizability of DNA origami and guide the structure by electromagnetic fields. Kuzyk et al.⁹⁹ and Shen et al.¹⁸ have demonstrated how dielectrophoresis (DEP) can be used to trap various 2D and 3D DNA origami shapes between gold nanoelectrodes. By applying ac voltage to the nanoelectrodes, one can create a highly localized electric field that traps DNA origami in the electrode gap (see Figure 2d). The proper immobilization (and coupling to outer electrical circuitry) can be ensured through the covalent gold–sulfur bond by incorporating thiolated strands into DNA origami. Nevertheless, DEP could also allow transfer of the achieved trapping geometries to the chosen electrodeless substrate by the imprint technique.¹⁰⁰

Moreover, Gerdon et al.¹⁰¹ used lithographically patterned gold patches functionalized with 11-mercaptopundecanoic acid (MUA) to selectively immobilize DNA origami (see Figure 2e). The carboxylic acid groups of the functionalized layer chelate magnesium ions in the deposition buffer, and thus, a salt bridge is formed between a negatively charged DNA origami and the positively charged Mg ions. However, compared to other lithographically achieved patterning methods, this technique lacks the control over spatial orientation of the delivered DNA origami. To achieve directionality and to align the structures in a controllable way, Ding et al.¹⁰² showed that small gold islands—patterned by e-beam lithography in different geometries—could be connected by thiol-modified DNA origami nanotubes. The nanotubes had exactly matching length with the distance of the neighboring gold islands.

To achieve large-scale deposition, Linko et al.¹⁰³ developed a spray-coating technique (Figure 2f), which allows straightforward and efficient delivery of DNA origami to the substrate without a need of chemical treatments or washing steps. However, the majority of salt ions has to be removed from the origami solution⁴⁵ before deposition. They demonstrated the feasibility of the method using various 2D and 3D origami structures, removed the residual salt by spin-filtering,⁴⁵ and spray-coated large areas of glass and silicon substrates. Although one can control the coating procedure at large scales using mechanical masks, the structures are randomly oriented on the deposited areas. However, this technique might become compatible with other methods described in this section.

DNA Origami Plasmonics and Nanophotonics at Interfaces. By combining the DNA-based nanophotonic devices and different techniques to arrange DNA structures on interfaces described in the previous section, one can achieve plasmonic substrates with tailored optical properties. One goal in this direction would be to create metasurfaces using ordered assemblies, but nevertheless, the individual DNA-based objects and their properties should first be characterized.

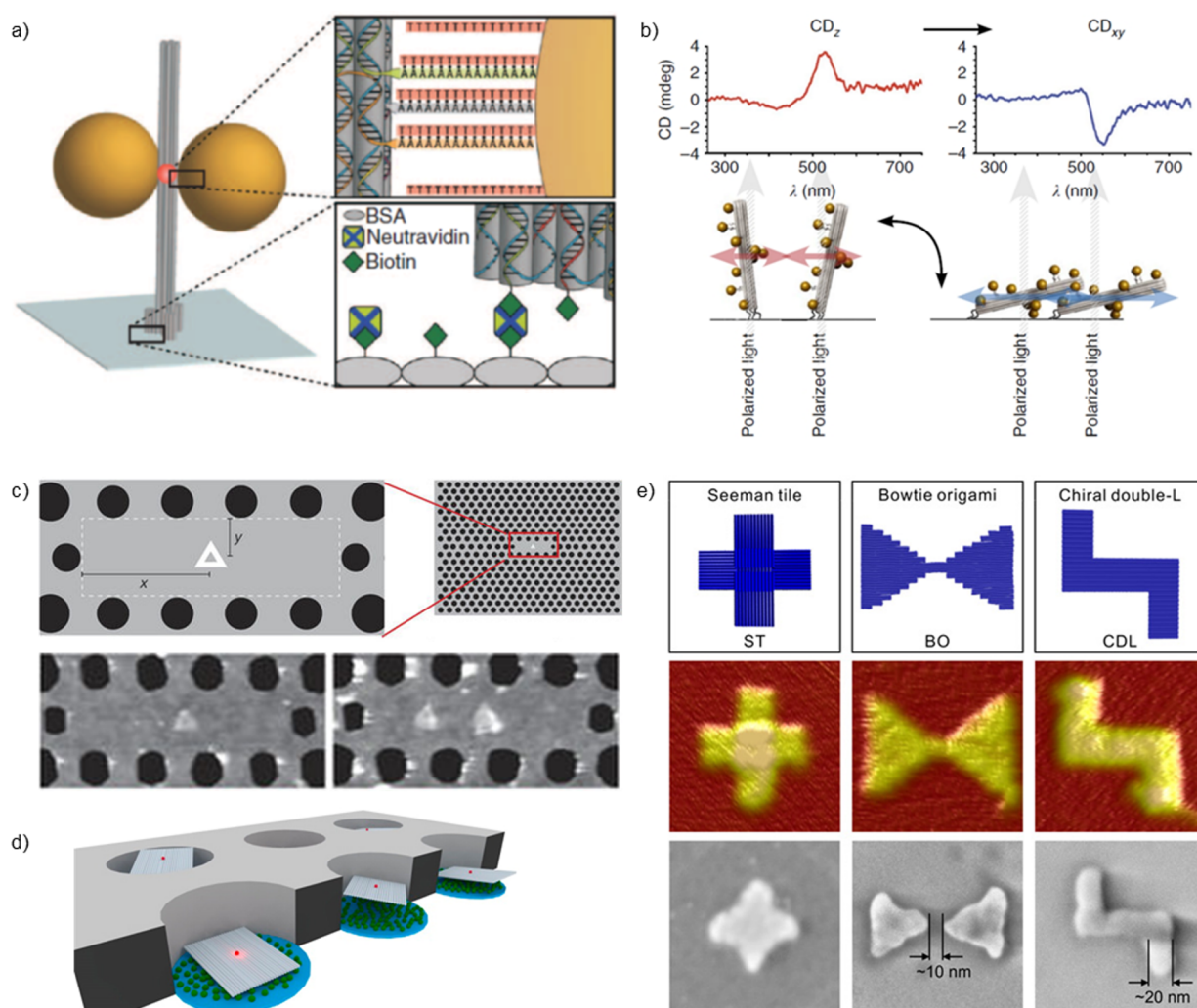


Figure 3. (a) Gold nanoparticles and a rodlike DNA origami form a nanoantenna that is attached to the substrate via biotin–neutravidin interaction.⁷⁵ (b) Chiral plasmonic nanostructures (similar to Figure 1a) arranged onto a substrate to achieve a switchable and directional circular dichroism (CD) effect.¹⁰⁴ (c) DNA origami triangles equipped with fluorophores can be precisely placed into an optical cavity.⁵¹ The number of triangles and their position can be controlled and thus the fluorescence of the “pixel” (inset) in a large array of cavities. (d) DNA origami is used as a nanoadapter to place individual fluorescent molecules in lithographically fabricated metallic zero-mode waveguide.¹⁰⁷ (e) DNA-assisted lithography (DALI).⁵³ DNA origami (top panel) is deposited on a silicon chip (middle panel), and its shape is transferred into a metallic structure on a transparent substrate (bottom panel). Part a is reprinted with permission from ref 75. Copyright 2012 American Association for the Advancement of Science. Part b is reprinted with permission from ref 104. Part c is reprinted with permission from ref 51. Copyright 2016 Springer Nature. Part d is reprinted with permission from ref 107. Copyright 2014 American Chemical Society. Part e is reprinted with permission from ref 53.

To probe single plasmonic devices, they need to be deposited onto a substrate after their self-assembly in buffer solution. In many reported experimental setups,^{76–78} plasmonic structures were immobilized via electrostatic interactions on a charged substrate (see the previous section). Another commonly used scheme is to take advantage of the strong interaction between biotin and avidin. As an example, Acuna et al.⁷⁵ immobilized a rodlike DNA origami equipped with a AuNP dimer and a single fluorescent molecule in the gap to the substrate by biotin–neutravidin linking (see Figure 3a). The binding and unbinding events of short DNA strands, as well as the conformational dynamics of a Holliday junction in the hot-spot, were visualized in a form of enhanced fluorescence signals in real-time. Recently, a similar system has also been used to characterize single peridinin–chlorophyll *a*–protein complex.⁶⁵

The chiral plasmonic structures similar to the ones designed by Kuzyk et al.⁶¹ can also be immobilized by means of biotin–avidin interaction.¹⁰⁴ Interestingly, upon anchoring of the

structures on the substrate, their CD responses became switchable. When the sample was immersed in buffer, most of the structures were in an upstanding position, but when the buffer was dried, the structures lay horizontally on the surface. Their different relative orientations with respect to the exciting circularly polarized light could induce a change in the CD signal (see Figure 3b).

Another benefit for depositing DNA plasmonic structures on a surface is that they can be combined with materials with which it would be otherwise challenging to assemble in the solution phase. For example, an origami–AuNP dimer–graphene hybrid structure was formed by exfoliating a single layer of graphene on top of an immobilized AuNP nanoantenna.¹⁰⁵ Such a hybrid system has demonstrated superior SERS performance compared to individual components.

Along the lines of using DNA origami as nanoadapters to position nanophotonic components beyond the accuracy of conventional lithography,^{50,96,97,106} Gopinath et al. recently

demonstrated a reliable and controllable coupling of molecular emitters to photonic crystal cavities (PCCs) (see Figure 3c).⁵¹ Because of the high addressability of DNA origami, the location of the dye molecule was sufficiently precise to enable visualization of the local density of states within PCCs with a resolution of about $1/10$ of a wavelength. Moreover, the intensity of the cavity emission could be digitally varied by changing the number of binding sites within a single cavity. Taking the high modularity of DNA origami into consideration, a great number of hybrid nanophotonic applications could be realized with this system.

In addition to relying just on the pattern with the same outline as DNA origami, circular openings in a metallic film can also host DNA origami adapters with size-selectivity. In the work of Pibiri et al.,¹⁰⁷ individual dye molecules were placed inside a so-called zero-mode waveguide (ZMW) (see Figure 3d). In this way, the ZMW usage was optimized, and the photophysical properties of dyes were improved compared to stochastically immobilized molecules.

DNA objects can also be used as templates or stencils for producing accurate objects from different materials. One such example is creating custom-shaped features from inorganic oxides using DNA origami as a template.¹⁰⁸ In this approach, Surwade et al.¹⁰⁸ deposited DNA origami structures on a silicon oxide substrate, and by employing a chemical vapor deposition procedure, they created either oxide layers with DNA-origami-shaped openings or oxide shapes that have inherited the original origami shape (positive- and negative-tone patterns). To further employ this high-resolution and parallel substrate-based technique, Shen et al.⁵² showed that these origami-shaped openings in the grown oxide layer can be used as a mask for further lithography steps followed by metal evaporation. They demonstrated the versatility of the approach by fabricating gold, silver, and copper nanostructures having original DNA origami shapes (crosses and rectangles) on the silicon substrate. Later on, Shen et al.⁵³ generalized the method to other substrates by fabricating, for example, gold bow-tie antennas and chiral gold shapes onto silicon nitride and sapphire (Figure 3e). The authors demonstrated that, by their DNA-assisted lithography (DALI) method, it is possible to produce transparent substrates with CD properties and a SERS capability for molecular diagnostics. In this work, individual metallic cross-shapes and antennas were also characterized, and these structures showed the plasmonic resonances at the visible wavelength range. However, the main drawback of this technique is that the metallic structures are randomly oriented on the substrate. Nevertheless, this method is compatible with the approaches presented by Gopinath et al.,⁵⁰ and therefore parallel and large-scale patterning of plasmonic substrates with high resolution may become possible.

DNA origami has also been used in optical nanocavity fabrication and characterization. Chikkaraddy et al.¹⁰⁹ constructed a nanocavity with <5 nm gap between a Au film and a AuNP. In such a device, a DNA origami plate between the two components has been employed not only to attach the AuNP to a substrate but also to precisely position Cy5 molecules with a nanometer-level lateral resolution. This enabled the precise mapping of the local density of optical states (LDOS) inside the nanocavity.

CONCLUSIONS

Although there are a plethora of examples of plasmonic structures that are assembled using DNA,^{46,48,49} so far only a

few examples of DNA-based plasmonic interfaces or prototypes and approaches aiming toward DNA-assisted metasurfaces have been reported. However, despite all the challenges ahead, the future seems promising. As the cost of a single gram of mass-produced DNA origami has been reduced to 200 dollars,¹⁰ this means that covering a square meter of the substrate would cost only approximately 20 cents.¹⁰⁶ This kind of vast area patterning may become possible by employing the presented methods to organize single DNA structures at interfaces or in 3D.⁹¹ Nevertheless, another route to achieve higher-order systems also exists, since approaches to create larger and larger DNA origami have recently been reported.^{15,16} This progress may lead to mass production of plasmonic DNA nanoantennas for sensing and intriguing optical metasurfaces consisting of miniature light scatterers.^{110,111}

In general, using DNA origami as a bridge between bottom-up and top-down fabrication methods may help to go beyond the resolution limit of conventional lithography and solve the challenges of nanofabrication. This way it would be possible to achieve a whole class of novel hybrid materials with tunable optical and electronic properties.^{107,111} In addition to providing alternative approaches for solid-state nanofabrication, wet chemistry and structural DNA nanotechnology meet at the interface where DNA structures can be used in the fabrication of inorganic nanoparticles.^{22,53,112–114} Integrating these components into larger devices remains a challenge, but by merging the subfields with the help of DNA nanotechnology, we believe that the current achievements present just the beginning of a flourishing era of DNA-origami-based nanophotonics.

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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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