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Sculpting Light by Arranging Optical Components with DNA Nanostructures

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Abstract

DNA nanotechnology has developed into a state where the design and assembly of complex nanoscale structures has become fast, reliable, cost-effective, and accessible to non-experts. Nanometer-precise positioning of organic (dyes, biomolecules, etc.) and inorganic (metal nanoparticles, colloidal quantum dots, etc.) components on DNA nanostructures is straightforward and modular. In this perspective article, we identify the opportunities and challenges that DNA-assembled devices and materials are facing for optical antennas, metamaterials, and sensing applications. With the abilities of arranging hybrid materials in defined geometries, plasmonic effects will, for example, amplify molecular recognition transduction so that single-molecule events will be measurable with simple devices. On the larger scale, DNA nanotechnology has the potential of breaking the symmetry of common self-assembled functional materials creating pre-defined optical properties such as refractive index tuning, Bragg reflection and topological insulation.

Keywords

optical; self-assembly; biological synthesis (assembly)

Introduction

Over the last decades, nanotechnology has allowed us to fabricate novel materials and devices finding applications in all disciplines in science and technology. Nanostructured materials can exhibit striking optical phenomena such as Bragg reflection, (circular) polarization and strong enhancement of electromagnetic fields (hot spots) resulting in nanodevices that can act as highly efficient sensors or as nanophotonic devices.¹ Importantly, the access to these and other intriguing physical phenomena encountered at the nanoscale offers great potential for fundamental research. Taking advantage of several methodologies such as lithography and bulk self-assembly, nanotechnology drives towards finding novel ways of bringing together different nanocomponents to pre-deterministically exploit their interactions. For nanophotonic devices to be functional, structuring or

positioning accuracy of optical components is usually required at a length scale much smaller than the electromagnetic wavelength of interest. For optical wavelengths this implies the necessity to control matter at a scale far below 50 nm. To circumvent current challenges in nanometer-precise placement of individual functional entities with conventional methods, DNA has been successfully employed to arrange optical elements such as colloidal metallic nanoparticles (NPs),² colloidal quantum dots (QDs),³ nanodiamonds,⁴ and fluorophores⁵ with nanometer precision and stoichiometric control.^{6,7} Over the last years, the DNA origami and other DNA self-assembling techniques have evolved as an ideal breadboard to fabricate nanophotonic structures both, static and dynamic (see also the article by Ke *et al.* in this issue). This perspective article will briefly review the main efforts undertaken to self-assemble optical components for nanoantenna-based light funneling, metamaterial applications and nanophotonic sensing devices using the DNA origami technique and along the way describe the main challenges that the technique is facing in the respective areas.

Optical Nanoantennas

Optical antennas were developed for nanophotonic applications in order to control and manipulate light at the nanoscale.⁸ These structures typically consist of an arrangement of metallic nanostructures with an optical response in the visible range associated to the excitation of localized surface plasmons. The collective oscillation of confined electrons in subwavelength sized NPs, or localized surface plasmons, is of great interest in nanophotonic applications due to their quasi-particle nature and their ability to guide and confine light on sub-wavelength space. Initial fabrication efforts exploited mostly electron and ion beam lithography. Despite the success of this approach to focus light to sub-wavelength volumes,⁹ several limitations still remain. Due to the fabrication procedure, lithographic structures are polycrystalline which severely affect the plasmonic resonances, compromising the reproducibility and performance of the optical antennas. However, the main shortcoming is that it is extremely challenging to couple a single quantum emitter to the optical antenna as this commonly involves demanding multi-lithographic steps to position fluorophores or quantum dots at the near field of optical antennas.^{10,11} Alternatively, NP were placed on a metallic layer yielding a mirror geometry, where the spacing between the NP and the metallic layer is controlled by a tunable polymer spacer, but this approach relies on an underdeterministic positioning of the single emitter.^{12–14}

Plasmonics is the subfield of photonics that has benefited most from the versatility that DNA nanotechnology can provide. One advantage of using the pre-programmability of DNA is to serve as a modular template, capable of exploiting the synergy of bringing together two or more components including colloidal NPs and single quantum emitters. DNA can serve to design optical properties when bringing together two or more nanocomponents. Early examples include quenching of fluorophores^{15,16} and QDs¹⁷ due to nearby gold NPs, and formation of molecular excitons between individual fluorophores due to proximity effects.¹⁸ A noteworthy use of DNA is its ability to finely control the interparticle distance between colloidal metallic NPs, permitting the fabrication of plasmonic nanocavities with tailored plasmon resonance. The gap within the NPs contains a region of enhanced field, which is well below the diffraction limit, the so-called “hot spot.” In the weak coupling regime, these plasmonic nanocavities can serve as optical antennas and can be used to enhance

Fluorescence intensity,^{19–24} photostability,²⁵ and Raman spectroscopy signals, ^{26–32} as well as Förster resonance energy transfer.^{33,34} Additionally, the interaction with plasmonic antennas affect the photophysical rates³⁵ and can mediate the emission of single quantum sources³⁶ as well as it can increase the spontaneous emission intensity and emission rates, desired for high speed optical devices.¹³ The central advantage inherent to DNA templates used for assembling nanoparticle antennas is the possibility to also precisely and selectively position molecules of interest in the hot spot. This enables the development of sensitive devices operating at the single-molecule level and will foster research on molecular interactions in nanometer and potentially even sub-nanometer plasmonic cavities. Besides plasmonic antennas,^{37,38} the DNA origami's ability to position different species with nanometer precision and stoichiometric control has been exploited for light funneling applications in which light is guided and controlled through a series of resonance energy transfer processes (FRET) between different fluorophores⁵ and even synthetic polymer wires.^{39,40} This approach constitutes a major step towards the self-assembly of artificial light harvesting devices^{41–44} which could be further enhanced in combination with plasmonic antennas⁴⁵ placed in DNA origami structures.

In the strong coupling regime, plasmonic nanocavities can be used to coherently exchange energy between a plasmon and an exciton. Under this condition, the individual components can no longer be treated separately but rather as a new set of degenerate eigenstates which display a characteristic Rabi splitting on the farfield extinction spectra and Rabi oscillations on the lifetime decay.⁴⁶ Plasmonic nanocavities displaying strong coupling can be exploited for single photon sources via the photon blockade effect,⁴⁷ and for the fabrication of lasing devices based on the cavity's coherent emission. As the coupling strength ($g \sim 1/\sqrt{V}$) of optical cavities is limited by their mode volume (V) the diffraction limit governs the sizes of conventional cavities. Using plasmonics combined with DNA nanotechnology, it is possible to fabricate systems of NPs with small enough mode cavity volumes to achieve strong coupling at room temperature when excitons are placed within them.

To further promote coherent coupling, it is desired to increase the field confinement by reducing the mode volume on the plasmonic cavity.

Although DNA offers base-pair precision, the proximity between two NPs can be influenced by the in-solution behavior of the molecules coating the NPs, or the particles are forced to touch due to capillary effects when dried on a substrate. Counter ions to reduce repulsion,⁴⁸ or using a DNA sheet as a spacer are possible venues to control the spacing gap. Adsorbed on a substrate, plasmonic heating to dehydrate the DNA spacer has helped to reduce the gap further in a controlled manner.²⁹ Small mode volume cavities encounter yet another challenge, in that their plasmon resonance is highly susceptible to NP inhomogeneities and size variation. Protrusions of the NP facets towards the nanometer-size gap can greatly red-shift the spectra. Current efforts to achieve such small gaps make use of ultrasoft colloidal NPs.⁴⁹

Metamaterials

In contrast to bulk materials, where the optical response is determined by the chemical composition, metamaterials gain their optical properties that are often not found in nature from structuring the material or from the arrangement of optical entities on a sub-wavelength scale. Using the pre-programmable assembly of nanocomponents, DNA nanotechnology can offer alternative solutions to current challenges encountered in the field of metamaterials, such as providing flexible substrates for dynamic materials, combinatorial freedom of optically active materials, nanometer-precise positioning and overcoming limits of scalability and lithographically-built 3D materials. DNA templates have already been used to fabricate individual plasmonic meta-atoms with custom-tailored light properties. The first optically active plasmonic DNA objects consisted of gold NPs arranged in a left- or right-handed helical conformation along tubular DNA helices, displaying preferential absorption of a given circular polarized light handedness.^{50,51} Thereupon, DNA-templated chiral structures have been programmed to display switchable reconfiguration via drying and hydration cycles,⁵² DNA strand-displacement⁵³, light driven radiation,⁵⁴ and changes in pH.⁵⁵ The design flexibility provided by DNA nanotechnology allows the spectral tuning of multiple plasmon modes, displaying interesting signatures on the farfield spectra, such as magnetic⁵⁶ and Fano resonances.⁵⁷ The Fano asymmetric lineshape is a consequence of the constructive and destructive interference of the light pathways within the nanophotonic device and is highly sensitive to environment changes making them ideal for sensing applications.⁵⁸

Often-cited applications of metamaterials are the development of cloaking devices and perfect lenses. Applications that are much closer on the horizon include optoplasmonic devices such as high-performance optical filters and absorbers, light funnels or optical waveguides. When using plasmonic particle arrangements, one general obstacle are the plasmon propagation losses limiting the performance and ultimately the realization of all optoplasmonics devices. One promising alternative is to use novel hybrid structures such as two gold NP coupled via a non-dissipative plasmon mediated by a silver NPs chain.⁵⁹ Alternatively, one could take advantage of the spatial arrangement that DNA provides to fabricate NPs with topological protected states. Certain topologies could offer spectral dependent activated hot spots,⁶⁰ providing a venue to realizing opto-plasmonic devices. Other promising efforts to circumvent propagation losses in metals simply make use of dielectric materials.⁶¹

Ultimately, DNA offers unparalleled capabilities to self-assemble 3D crystals with engineered geometries, capable to host nanocomponents within the crystal structure.^{62–65} A current challenge for the formation of DNA-mediated crystals is the growth of lattices with low defects, however, impressive assemblies have been achieved. It is now up to experimentalists and theoreticians alike to identify and realize 3D arrangements – periodic, glass-like, anisotropic, or fully isotropic – of optical nanocomponents to design materials and devices with unprecedented optical properties arising from the combination of materials and / or their spatial patterning. In parallel, 2D metasurfaces hold great potential for the development of functional surfaces such as flat lenses due to their capabilities to miniaturize conventional optics operating in the visible regime.⁶⁶ A possible route to achieve such goals

is to integrate the rational engineering and self-assembly capabilities of DNA to arrange metallic components with existing top-down technologies.^{67–69}

Sensing

Sensing involves the recognition of an analyte and the transduction of the recognition event by a physical mechanism. Plasmonic nanoparticles have long been used to detect binding events of ligands on their surface. The most straightforward transduction mechanism was a change in the scattering spectra when plasmonic nanoparticles aggregate or, more subtly, when the refractive index of the environment is altered by the binding event.⁷⁰ This approach is in analogy to surface plasmon resonance measurements on flat surfaces but could be carried out with little effort in solution and even on the single particle (single dimer) level and led to the detection of single molecules.⁷¹ The sensitivity of this label free approach depends on the electric field intensity where the analyte is binding. With DNA nanotechnology, it is possible to selectively place such binding sites at the hotspots of gap nanoantennas and thus increase sensitivity and robustness of the assay as no analyte binds outside the hotspot. If fluorescence is used for optical transduction, the sensitivity of assays might be enhanced by the factor of fluorescence enhancement that has been shown to reach three to four orders of magnitude. Besides the sensitivity enhancement, signals of a few or even single molecules might become so bright that they could be detected with simple point-of-need devices even including slightly modified smartphones (see figure 3).⁷² Even larger enhancement factors can be reached by surface enhanced Raman scattering based detection also enabling single-molecule detection. While a sheet of DNA between two nanoparticles can create an explicitly well-defined hotspot, it might become more challenging to still place capturing ligands between the nanoparticles in a sub 10 nm gap. Other transduction mechanisms could be explored when the binding event goes along with larger conformational changes. Changes of optical activity could here be exploited to detect nucleic acid binding.^{53,73,74} Other possibilities include the conversion of a DNA walker into a fluorescence amplification device.⁷⁵

Conclusions and Perspective

For DNA nanostructures to become more applicable in material research, we see highly interesting challenges on the small and on the long length-scale: On the small scale, the interface of chemistry and DNA nanotechnology could be improved as DNA building blocks are more than one order of magnitude larger than the single-bond precision achieved in synthetic chemistry. On the large scale, self-assembly becomes less efficient due to the shallow hierarchy of bonds as well as to the increased time of assembly associated with objects of increasing size. Nevertheless, the capabilities of using DNA to pre-program the self-assembly of hybrid optical nanocomponents has already proven successful, however, a plethora of optical phenomena still remains to be explored using DNA nanotechnology. For example, non-linear optics is a tackling point where DNA can offer viable alternatives to conventional lithography. The resulting high confinement from DNA plasmonic nanocavities along with the placement of hybrid components to offer symmetry breaking can be used to produce high order harmonic generation. In combination with gain media plasmonic lasers, so-called spasers, superradiant lasers and other devices relying on cooperative effects can be

pursued. DNA-assembled 2D and 3D materials could help close the gap between the resolution limits of lithography and the requirements for materials that exhibit novel function in the optical frequency window. It remains to be seen if DNA can reach enough maturity to provide useful opto-plasmonic devices, but for now it certainly adds to the toolbox of current nanotechnologies.

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Philip Tinnefeld is full professor for physical chemistry at Ludwig-Maximilians-Universität (LMU) München. During previous stations in the physics department of LMU and as professor for biophysical chemistry at TU Braunschweig, he was involved in the development of the superresolution techniques dSTORM, Blink Microscopy and DNA PAINT and discovered the ROXS photostabilization formula. In recent innovations, Philip Tinnefeld used DNA nanotechnology for self-assembled molecular devices including calibration nanorulers, nano-adapters, optical signal amplifiers and molecular force clamps. He is initiator and mentor of GATTAquant, the first company commercializing DNA origami applications.

Tim Liedl

Tim Liedl is Professor for experimental physics at the Ludwig-Maximilians Universität. During his undergraduate studies he worked on the development of hydrophilic coatings for fluorescent semiconductor nanoparticles. He obtained his Ph.D. in physics at the Ludwig-Maximilians Universität studying DNA-based nanodevices and switches, which are driven by chemical oscillations. For his postdoctoral studies he visited the Dana-Farber Cancer Institute / Harvard Medical School where he co-developed 3D DNA-origami method. The research of Tim Liedl is multi-disciplinary and exploratory positioned at the interface between nanoscience, plasmonics, synthetic biology and cell-biology. Its current focus lies on the application of DNA-based nanostructures in biology and on self-assembled plasmonic materials.

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Figure 1. DNA-mediated plasmonic nanostructures

used to sculpt light displaying static (a) and reconfigurable (c,d) circular dichroism, (b) enhanced fluorescence, (d) strong coupling between plasmon and exciton and (e) photonic crystal.

Figure 2. DNA as a building material for Nanophotonics.

DNA templates are used to assemble a great variety of nanophotonic structures that span across optical Antennas, metamaterials, and sensing.

Figure 3. Point-of-need devices.

The high confinement offered by DNA plasmonic nanocavities can serve to detect signals with simple devices such as slightly modified smartphones.