Rolling up gold nanoparticle-dressed DNA origami into three-dimensional plasmonic chiral nanostructures

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Abstract

Construction of three-dimensional plasmonic architectures using structural DNA nanotechnology is an emerging multidisciplinary area of research. This technology excels in controlling spatial addressability at a sub-10 nm resolution, which has thus far been beyond the reach of traditional top-down techniques. In this paper, we demonstrate the realization of three-dimensional plasmonic chiral nanostructures through programmable transformation of gold nanoparticle-dressed DNA origami. Gold nanoparticles are assembled along two linear chains on a two-dimensional rectangular DNA origami sheet with well-controlled positions and particle spacing. By rationally rolling of the 2D origami template, the gold nanoparticles can be automatically arranged in a helical geometry, suggesting the possibility to achieve engineerable chiral nanomaterials in the visible range.

1. Introduction

Advanced designs of nanomaterials require a large amount of control over the assembly of nanoscale components. Structural DNA nanotechnology, which utilizes the programmability of DNA, offers a compelling approach toward fully addressable nanopatterning [1]. In particular, the DNA origami technique can create arbitrary two- (2D) or three-dimensional (3D) DNA nano-architectures with well-defined sizes, shapes, and spatial addressability. The process involves programmable folding of a single-stranded viral DNA by numerous helper strands. Due to the fact that each individual helper strand can be modified and extended to produce a sequence-dependent surface tag, DNA origami has been utilized as template to assemble functionalized metallic and semiconducting nanocrystals, carbon nanotubes, and biological materials into sophisticated geometries. In addition, DNA origami can carry addressable binding sites at a resolution of ~ 6 nm, which is far smaller than the features obtained using traditional electron-beam lithography. Most remarkably, DNA origami allows for rational organization of nanocrystals in three dimensions, which remains a significant challenge for top-down techniques.

Among a variety of nanocrystals, metallic nanoparticles have been of great interest due to their unique optical properties. A metal nanoparticle supports localized surface plasmons, which are associated with the collective oscillation of the conductive electrons in the nanoparticle. The strong interactions of plasmons in nanoparticle assemblies render possible many useful applications including surface enhanced spectroscopies, subwavelength optical devices, as well as medical diagnostics and therapeutics. Considerable efforts have been devoted to organize metallic nanoparticles into sophisticated plasmonic architectures using DNA origami. Han *et al*. were the first to use DNA origami to assemble multiple gold nanoparticles (AuNPs). These researchers have also demonstrated encapsulation of AuNPs in a DNA origami cage. Pilo-Pais *et al*. created predesigned AuNP assemblies including rings, parallel bars, and H-shapes with DNA origami. In our previous work, we constructed AuNP linear chains that could work as nanolens on triangle DNA origami templates.

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Recently, plasmonic chiral materials have attracted a lot of attention [2]. Natural chiral molecules such as proteins and DNA only exhibit strong optical chirality in the UV range. Theoretical calculations have shown that plasmonic assemblies consisting of metallic nanoparticles that are arranged in chiral geometries such as pyramids, tetrahedrons, and helices, etc. enable a unique way to achieving strong optical chirality in the visible range. At resonance, the dipolar plasmons of individual metallic nanoparticles can be strongly coupled. The collective plasmons that oscillate along a plasmonic chiral structure of certain handedness can lead to different absorption in response to right and left circularly polarized light, i.e., circular dichroism. Over the past several years, different approaches have been directed toward organizing AuNPs into 3D chiral geometries. For example, natural chiral materials such as peptide-amphiphile supramolecules were utilized as scaffolds to directly grow AuNPs through gold nucleation from precursor salt solutions. The geometry of the resulting gold helices, however, are not easily engineerable in that they follow the same morphology of the natural peptide-based materials. Another strategy is associated with self-assembly of DNA tubules through integration of AuNPs. Stacked rings, spirals, and nested spiral tubes were obtained utilizing size-dependent steric repulsion effects among AuNPs. Nevertheless, gold chiral structures of a certain conformation are not readily separated from the product mixture. In 2009, Mastroianni *et al*. demonstrated a chiral grouping of four different-sized gold nanoparticles, which were monofunctionalized with distinct strands of DNA. Due to the substantial size difference, however, the four gold nanoparticles could not be efficiently coupled. Optical chirality in the visible range could therefore not be expected as predicted from the theoretical calculations.

In this Letter, we demonstrate 3D plasmonic chiral nanostructures that are constructed through programmable transformation of AuNP-dressed DNA origami [3]. A 2D rectangular DNA origami template is functionalized with two linear AuNP chains at specific positions. The process is then followed by rationally rolling and stapling the 2D DNA rectangular origami into tubular DNA origami. After rolling, the AuNPs are automatically organized into a 3D helix on the tubular DNA origami. The 3D plasmonic helix composed of nominally identical gold nanoparticles resembles natural chiral biomolecules such as proteins or DNA. Our strategy holds great promise for creation of plasmonic chiral nanomaterials with engineerable optical chirality.

2. Experiment

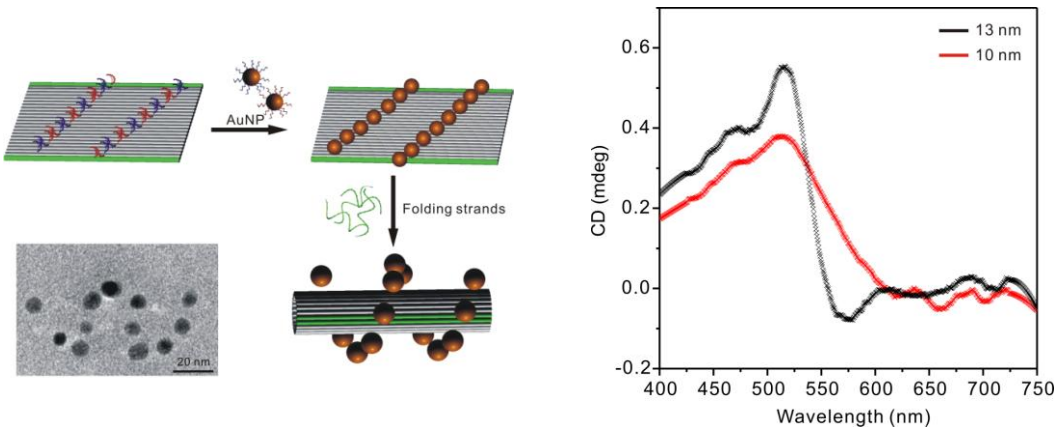

Fig 1. Left: Illustration of the experimental scheme. AuNPs covered with corresponding DNA strands are assembled at the predesigned locations on the origami sheet through complementary strand hybridization. The sequence of the two long sides of the rectangular DNA origami (in green) is modified to be complementary to that of the folding DNA strands. Addition of the folding strands leads to the rolling and subsequently stapling of the 2D rectangular origami sheet into a hollow DNA origami tube. As a result, the AuNPs are automatically arranged into a 3D helix. Right: Measured CD spectra of the assembled AuNP helices. The red and black lines represent 10 nm and 13 nm AuNP helices, respectively.

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Fig. 1 shows the illustration of the experimental scheme. A rectangular DNA origami template composed of 24 DNA helices was first prepared following the scaffolded DNA origami method developed by Rothemund. The dimensions of the 2D origami were $90 \times 60 \times 2$ nm^3. DNA capture strands with carefully designed sequences were extended from the rectangular DNA template at specific positions. After hybridization of the rectangular DNA origami template, all of these capture strands were displayed on one side of the template. We had altogether 15 binding sites that were arranged along two parallel lines as shown in Fig. 1. At each binding site, three identical-sequence capture strands were used to precisely localize one single AuNP (10 nm). In order to avoid nonspecific binding, different-sequence capture strands (in red and blue) were placed alternatively at the binding sites. The AuNPs were functionalized with corresponding complimentary DNA strands. The spacing (16 nm) between the individual AuNPs along each chain was controlled by the positions of the capture DNA strand groups. The sequence of the two long sides of the rectangular DNA origami (in green) was modified to be complementary to that of the folding DNA strands. Upon the addition of the DNA folding strands, the rectangular origami sheet started to roll up. Eventually, the two long sides of the 2D DNA origami sheet were stapled together, giving rise to a hollow DNA origami tube. As a result, the gold nanoparticles were arranged in a helical geometry on the hollow origami tube as illustrated in Fig. 1.

In order to characterize the optical response of the AuNP helices, circular dichroism (CD) measurements were carried out in a $1\times$TAE/Mg^{2+} buffer with a quartz cuvette (0.2 cm path length) using a J-810 Circular Dichroism Spectrometer. The wavelength range is from 400 nm to 750 nm and the scanning rate is 50 nm/min. As shown by the red curve in Fig. 1, the CD spectrum of the 10 nm AuNP helices exhibits the characteristic peak-dip CD line shape in the vicinity of the plasmonic resonance of the AuNPs (~525 nm), demonstrating the plasmonic chiral response of our structure. Taking a further step, we have also fabricated left-handed 13 nm AuNP helices (see supporting information), which give rise to much stronger CD signals due to the stronger oscillator strength of the larger AuNPs (black curve).

3. Conclusion

In conclusion, we have introduced a unique and simple way to constructing 3D AuNP helices using DNA origami. 2D rectangular DNA origami was utilized to precisely organize AuNPs at well-defined binding sites along two linear chains. 3D AuNP helices were obtained by rationally rolling and stapling the 2D rectangular origami sheets. The structural configuration of the 3D AuNP helices such as the diameter and axial length could be tuned by modifying the width, length, and stapling position of the rectangular DNA origami template. The pitch of the 3D AuNP helices could be adjusted by varying the AuNP chain number on the origami. Furthermore, the coupling strength between the AuNPs could be increased through Au or Ag electroless deposition in that it can enlarge the size of the AuNPs and simultaneously can reduce the AuNP spacing on the DNA origami. This would lead to fully engineerable plasmonic chiral nanomaterials.

Our strategy opens up a number of possibilities to realize programmable 3D plasmonic structures with desired optical properties. We envision that 3D plasmonic helices with high yield and homogeneity could exhibit strong optical chirality in the visible range. These 3D chiral nanomaterials might enable a new generation of 3D plasmon rulers in that CD spectra are notably sensitive on 3D conformational changes. For example, subtle spatial changes could be reported in real time by monitoring the CD spectrum change resulting from the binding or cleavage of a specific staple strand on the origami by enzymes or proteins. Also, rationally designed DNA origami templates could be further modified to precisely organize multiple components in three dimensions including different metallic nanoparticles, magnetic nanoparticles, quantum dots, and proteins for various functionalities and applications.

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