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Gold Nanoparticle Self-Similar Chain Structure Organized by DNA Origami

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Recently, assemblies of well-defined metal nanostructures have attracted much interest because they generate high local-field enhancement when excited at their plasmon resonance. This has in turn led to new ideas for detectors, optical waveguides, and resonators as well as applications in sensing, spectroscopy, and microscopy.[1,2] These plasmonic structures generally require the fabrication of materials with nanoscale dimensions, preferably with sizes and spacings less than 10 nm. Here we demonstrate a method that uses DNA origami to organize different-sized Au nanoparticles to form a linear structure with well-controlled orientation and <10 nm spacing. This structure could be used to generate extremely high field enhancement and thus work as a nanolens.

Theoretical study has shown that a self-similar linear chain of several metal nanospheres with progressively decreasing sizes and separations could generate large field enhancements.[3] The structural requirements present a difficult experimental challenge in that the metal nanospheres must be precisely oriented with spacings of only a few nanometers. DNA-templated nanofabrication methods are thus of great interest for this application, since such methods are capable of reaching down to this size scale, while top-down methods such as electron-beam lithography generally are not. The use of DNA to organize nanoparticles was originally demonstrated by Alivisatos[4] and Mirkin.[5] Other groups have used stiff DNA motifs to organize nanoparticles in a well-designed fashion to form 1D and 2D arrays.[5–8] Bidault and co-workers recently reported a plasmon-based nanolens consisting of three different-sized Au nanoparticles (AuNPs) assembled on a DNA template.[9] Their method used only a DNA duplex as the template, so the orientation and distance between nanoparticles was hard to control. Our previous research has demonstrated the construction of well-defined linear chains of three AuNPs on a DNA triple-crossover template.[10] However, a linear chain of six metal NPs with progressively decreasing sizes and separation that was predicted to show the highest field enhancement could not be effectively generated by any of the previous methods, even the bivalent thiol−gold conjugation strategy reported by Sharma et al,[8] because of the significantly increased number of particles being assembled.

We have designed a strategy that uses the scaffolded DNA origami method developed by Rothemund[11] to organize six AuNPs. The schematic drawing is illustrated in Figure 1a. First, we designed different DNA sticky-ends on the triangular DNA origami template at specific locations. These sticky-ends were designed by extending the sequence from selected staple strands of the DNA origami structure. After hybridization of the triangular DNA origami template, all of these sticky-ends are displayed on one side of the origami template surface. We chose to use three identical-sequence sticky-ends to localize each individual AuNP. We thus used a total of 18 sticky-ends to organize

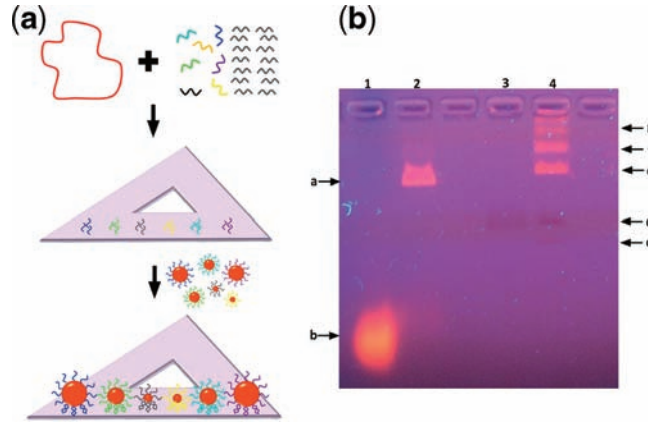

Figure 1. (a) Schematic drawing of the assembly of six different AuNPs on a triangular DNA origami template through DNA hybridization. First, the long scaffold strand (red) hybridizes with designed staple strands to form the DNA origami template with different binding sites on one side of the origami surface. Different AuNPs covered with corresponding DNA strands then bind to the designed locations through complementary strand hybridization. (b) Ethidium bromide-stained agarose gel of assembled DNA origami/AuNP products.

six different AuNPs. Six AuNPs fully covered by corresponding thiolated complementary DNA strands were then assembled on the designed position of the DNA origami structure through complementary strand hybridizations. The spacing between particles was controlled by the position of these sticky-ends. Each AuNP was bound by three DNA linkages to the DNA origami template.

To assemble the AuNPs on the template, we first prepared the DNA origami template and purified the assembled origami structure from extra staple strands by filtration through a size-exclusion column (see the Supporting Information). At the same time, we incubated the different-sized AuNPs (15, 10, and 5 nm) with the corresponding thiolated DNA strands in a [DNA]/[AuNP] ratio of >200:1 for 40 h. Subsequently, unbound DNA was removed by column filtration as well. Freshly purified AuNP−DNA conjugates and DNA origami templates were annealed again from 37 to 20 °C slowly at a 1:1 ratio. The assembled DNA origami/AuNP products were analyzed by agarose gel electrophoresis (Figure 1b). Lane 1 contained the mixture of staple strands, which is shown as band b. Lane 2 contained the assembled DNA origami, which appeared as the clear major band (band a). Lane 3 contained 15 nm AuNPs fully covered by thiolated DNA. Lane 4 contained the annealing product, which runs as multiple bands. Judging from the band positions in lanes 1, 2, and 3, we concluded that band c was extra 10 nm AuNP−DNA conjugate and band d was extra 15 nm AuNP−DNA conjugate. We assumed that band e was the desired product, which is the complex of one DNA origami template with six AuNPs attached to it. The yield of band e was ∼50%. We assumed that band f was the dimer of DNA origami linked by

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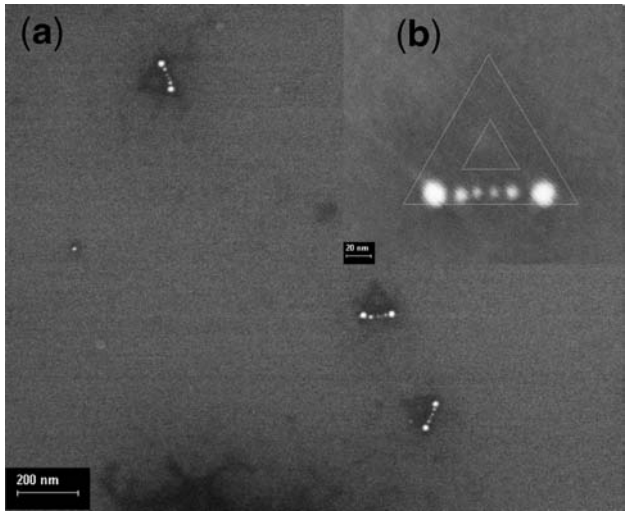

Figure 2. SEM images of six-AuNP linear structures organized by triangular DNA origami. (a) SEM image of three assembled structures. The triangular shape of the DNA origami templates is visible as darker color. (b) Zoom-in image of one assembled origami−AuNP structure. The superimposed triangle shows the position of the DNA origami template.

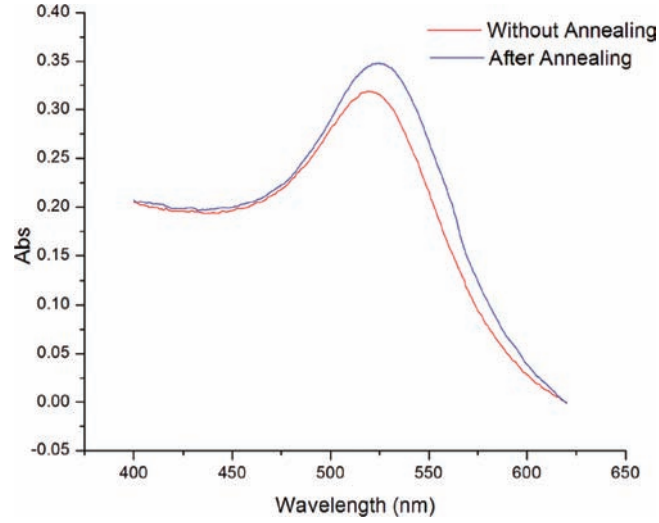

Figure 3. UV−vis absorbance spectrum of AuNP/DNA origami mixtures without annealing (red) and after annealing (blue). The plasmon band peak shifts from 521 (red) to 526 nm (blue) upon annealing.

AuNPs and band g an agglomerate of multiple origami and AuNPs. The structures from these bands were cut and purified from the gel and analyzed by scanning electron microscopy (SEM). The SEM images were consistent with our assumptions. Figure 2 shows the images from the target band e sample. In Figure 2a, the self-similar chain structure of six Au nanoparticles is clearly demonstrated. The DNA origami template's shape is also visible as a black triangle. The average center-to-center distance of two 15 nm particles was 90 nm, which is consistent with our design. Figure 2b shows a close-up image of one assembled complex. Upon zoom-in during SEM scanning, the DNA template cannot be seen clearly because of deposited contamination material from the SEM chamber. The superimposed triangle shape is labeled on the image to indicate the position of the template. We sometimes observed ± 2 nm differences from the designed values of the gap sizes between particles, which were mainly due to the 10% size dispersion of the AuNPs. More SEM and TEM images can be seen in the Supporting Information.

The UV−vis spectrum was measured for the AuNP/DNA origami mixtures without annealing and after annealing, as shown in Figure 3. A plasmon band shift from 521 to 526 nm was observed, indicating that there is plasmonic interaction among the assembled AuNPs in the annealed solution. More systematic photonic studies of the AuNP size- and distance-dependent effects are needed in order to establish important parameters that could achieve stronger plasmonic coupling.

In the first design, we used three DNA strands to capture each AuNP in order to achieve accurate control of the spacing between adjacent NPs. A control experiment with only two linkages on each NP was also performed. The SEM images are shown in Figure S7 in the Supporting Information. Missing particles, inaccurate positioning, and misalignment of the AuNPs were observed. This indicates that of the use of three DNA capture strands for each AuNP is important to improve the assembly yield and accurate spatial control of the NPs.

In summary, we have demonstrated the successful fabrication of six-nanoparticle self-similar chain structures that could possibly be used as a photonic nanolens to generate high local electromagnetic field enhancements within the central gap. DNA origami was used here to precisely organize these different particles to form the linear chain with gap sizes of <10 nm. The design using three DNA hybridizations to link one particle generates stronger and more precise bindings than that using two DNA linkages. We have demonstrated for the first time that a large DNA structure (DNA origami) and multiple metal nanoparticle complexes can be assembled and purified from a gel with reliable yield. We expect that the rationally designed DNA origami template could be further modified and used to precisely organize multiple components such as magnetic nanoparticles, which could function as basic logic building blocks, or different metal nanoparticles, quantum dots, and proteins to construct more complex nanostructures with more functionality.

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Supporting Information Available: Additional synthesis and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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