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Precise organization of metal nanoparticles on DNA origami template

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ABSTRACT

Nanoscale assemblies of metal nanoparticles in one dimension (1D) to three dimensions (3D) can exhibit novel phenomena that are not observed in the amorphous state. Bottom-up assembly technique is expected to overcome the resolution limit of top-down method and casts a new light on the nanofabrication field. DNA origami, which is mainly used to construct discrete and addressable nanostructures, can be utilized to assemble functional colloidal nanoparticles into delicate geometries with interesting properties. This review aims to summarize the methods that use DNA origami structures as templates to precisely organize metal nanoparticles, such as gold nanospheres (AuNSs) gold nanorods (AuNRs) and silver nanoparticles (AgNPs). The potential applications and the perspective are also discussed.

1. Introduction

As metal nanoparticles possess many intriguing optical and electrical properties that are not observed in bulk materials [1–4], they are arousing increasing interest in the field of nanoscience and nanotechnology. The electron density of metal nanoparticles can couple with electromagnetic radiation of incident light and the plasmons at the surface of metal are confined to the finite volumes, which enable the manipulation of light–matter interactions and provide the opportunity to overcome the diffraction limit. Such plasmon oscillations are also termed as localized surface plasmon resonances (LSPR). Moreover, the plasmonic nanoparticles exhibit various absorption, scattering and coupling properties that are dependent on shapes, sizes and distance between particles. These properties have been widely used for sensing [5–7], medicine diagnosis [8–11], cellular imaging [12,13] and constructing nanoelectronic and nanophotonic devices [14–19]. The photothermal property of the plasmonic nanoparticles can also be applied for cancer therapy [20,21].

The optical properties of plasmonic nanoparticles are strongly affected by their morphologies, chemical composition and dielectric environment. Great theoretical development has been made, including classical electrodynamic and quantum theories, to describe the plasmonic properties of individual metal nanoparticles and their assemblies [22,23]. Computational modeling tools are also available for simulating the plasmon coupling effects of nanoparticle complex [24–26]. The simulation results provide fundamentals for engineering the assemblies of metal nanoparticles experimentally to achieve customized optical properties, in which each plasmonic element is arranged precisely and rationally.

Plasmonic coupling arises significantly only when the center-to-center distance of the particles is less than 1.5 times the particle diameter and it is confined to a small region between the neighboring particles [27]. Towards this goal, two strategies are usually adopted: top-down fabrication and bottom-up self-assembly. Traditional top-down fabrication approaches, such as photolithography and electron beam lithography [28–33], are challenged by their resolution limit and deficient capability of fabricating exquisite 3D architectures. In comparison, bottom-up self-assembly is expected to overcome these limitations and cast a new light on the nanoscience and technology [34–39].

Deoxyribonucleic acid (DNA) is an ideal building block for the construction of sophisticated nanostructures, because of the excellent features such as sequence programmability, specific molecular recognition, the rigidity of the double helix, sequence-independent nanoscale structure, commercial automatic synthesis, versatile chemical modifications and the ability of enzymatic scission and ligation, etc. These properties make DNA one of the promising molecules to organize functional nano-objects, such as metal nanoparticles. Many plasmonic assemblies have been constructed through hybridization of the DNA ligands that were functionalized on the surface of metal nanoparticles, including dimer [40], trimer [41], chiral pyramid [42,43], satellite-like nanoparticle assemblies [44,45] and 3D assemblies [46]. However, there are only very limited kinds of nanoparticle assemblies that could be constructed through direct hybridization between nanoparticle–DNA conjugates.

Rigid DNA scaffolds provide great potential to fabricate well-defined metal nanoparticle assemblies. Metal nanoparticles can be positioned on tile-based DNA nanostructures, such as double-crossover and 4 × 4 tile based 2D lattice. With careful design of the position of the capture strands on DNA-tile nanostructures, complex nanoparticle assemblies were constructed, such as gold

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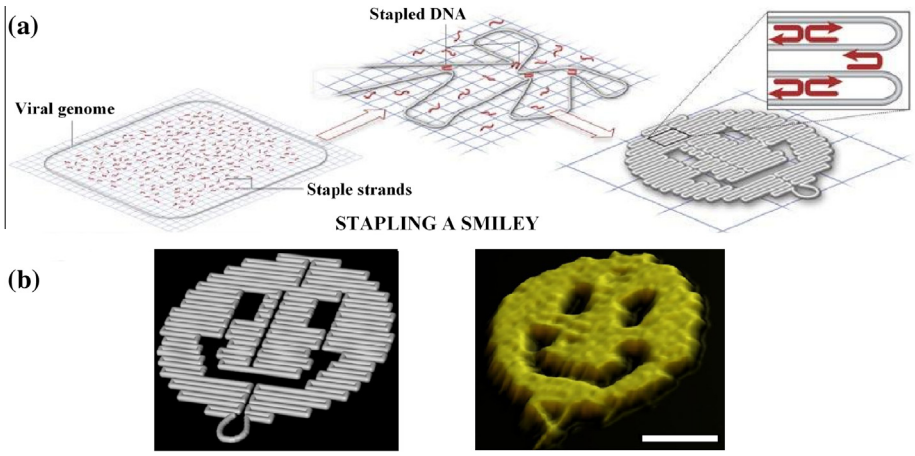

Fig. 1. (a) Schematic illustration of the basic principle of DNA origami technique. Adapted with permission from Ref. [57]. Copyright 2010. Macmillan Publishers Ltd. (b) AFM micrographs of the assembled smiley structures. The scale bar is 100 nm. Adapted with permission from Ref. [58]. Copyright 2006. Macmillan Publishers Ltd.

nanoparticles 2D array [47,48]. Through substitution of DNA strands in the array with single-DNA-conjugated metal nanoparticles, aligned metal nanoparticle chains [49], metal nanoparticle 2D array [50] as well as spiral chains and double helices [51] can be produced. However, the metal nanoparticles assembled on DNA-tile templates typically included several assemblies that differed in nanoparticle number. It is challenging to obtain assemblies with identical number of nanoparticles. It is difficult to use traditional DNA-tile assembly to produce DNA array with uniform and finite size. Recently, rationally designed DNA tiles can be used to construct 2D or 3D finite size nanostructures which may be utilized for delicate particles assemblies [52–56].

DNA origami technique, which was first demonstrated by Paul W.K. Rothemund in 2006 [57,58], is mainly used to construct discrete and well-arranged nanostructures (Fig. 1). This assembly technique is to fold a long viral single-stranded DNA (scaffold strand) with the help of hundreds of appropriately designed short single strands (staple strands). Almost any arbitrary 2D [58–60] and 3D [61–67] DNA nanostructures with well-defined sizes, shapes, and fully spatial addressability can be constructed through DNA origami technique. Instead of purified DNA strands which are usually required for traditional tile assembly, crude staple strands can be directly used for annealing without purification. Thus, much time and effort can be saved. For regular DNA origami structures, the yield can reach above 80% with just several hours annealing. Because all staple strands are unique in both sequence and position, they can be spatially distinguished at a resolution of ~6 nm. Nanoscale materials such as metal nanoparticles [14,68–70] or semiconducting nanocrystals [71–74] functionalized with complementary sequences can be anchored via hybridization with the protruded capture strands. A more direct approach to arrange nanoparticles on DNA origami is to replace one of the staple strands with the DNA modified nanoparticles and to position the nanoparticles during the folding of the scaffold [75]. In this review we aim to describe the use of DNA origami as a template to precisely organize metal nanoparticles, including AuNSs, AuNRs and AgNPs. The detailed protocols will be highlighted.

2. Functionalize metal nanoparticles with DNA

Thiolated oligonucleotide strands can be conjugated to the surface of specific metal nanoparticles, serve as negatively charged ligands to keep the nanoparticles from aggregation, and provide sequence-specific recognition for nanoparticles assembly. The functionalization reaction can be influenced by several factors. First of all, for the metal nanoparticles with larger size, increased amount of DNA or stabilizer molecules was necessary for stabilization of DNA–metal nanoparticle conjugates in the saline [76]. With regard to the DNA sequence, it is reported that adenine had the strongest affinity to the surface of gold nanoparticles, while the affinity of thymine to gold surface was weakest among the four nucleotides [77]. Due to the weaker interaction of the thymine with the gold surface, higher coverage of thiolated poly(thymine) oligonucleotides on the surface of gold nanoparticles could be attained [78]. Based on the stronger affinity of adenine to gold surface, it was also demonstrated that poly(adenine) can serve as an effective anchoring block for preferential binding with the gold nanoparticles surface, instead of the thiolated oligonucleotide strands [79]. The buffer conditions, particularly the salt concentration and the pH value, play an important role in the functionalization. On one hand, higher salt concentration could increase the oligonucleotide loading, because salt reduced the charge repulsion between DNA and the capping ligand (citrate or BSPP) on gold nanoparticles [76]. The salt concentration of the buffer should be increased progressively within tens of hours, because the high concentration of salt could also result in the aggregation of metal nanoparticles. On the other hand, the buffer with low pH value could tremendously accelerate the conjugation reaction between the thiolated DNA and gold nanoparticles [44,80]. In the citrate buffer at pH 3.0, adenine and cytosine were both positively charged, which could reduce the charge repulsion between negatively-charged AuNPs and DNA molecules and allow fast adsorption. The reaction between thiolated oligonucleotide strands and gold nanospheres only required a few minutes, compared to the salt-aging method that took more than 40 h. Not only the gold nanospheres, but the gold nanorods could be functionalized with DNA molecules through this low pH-assisted method [44]. Besides the factors mentioned above, the functionalization is also influenced by reaction temperature: too high temperature (>70 °C) will reduce the stability of metal nanoparticles to be modified, and desorb the thiolated DNA from the gold nanoparticle surface [81].

Both monovalent and polyvalent surface functionalizations with DNA have been employed for assembling metal nanoparticles. When thiolated DNA strand is incubated with metal nanoparticles (e.g., Au, Ag or Pt) with 1:1 molar ratio in buffer solution, the modified products are usually a mixture containing single-, double- and multiple-strands-attached nanoparticles. Single-strand-modified metal nanoparticles can be obtained through purification with gel electrophoresis [82] or anion-exchange high