論 文 の 内 容 の 要 旨

論文題目　DNA-Guided Anisotropic Self-Organization of Spherical Nanoparticles
（DNAが誘導する球状ナノ粒子の構造異方的な自己組織化）

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Chapter 1: General Introduction

Nanoparticles exhibit unique physical and chemical properties and have been applied to electronic, magnetic, and optical devices. Among a variety of metallic nanoparticles, gold nanoparticles (AuNPs) have widely been used. Various biomolecules have been successfully immobilized onto the AuNP surface. DNA-modified AuNPs (DNA–AuNPs) have been considered a powerful tool for biosensing and also a versatile building block for self-assembled functional materials. Current attention to AuNP assemblies is attracted by their collective properties. Self-assembly is a straightforward strategy to produce AuNP assemblies in a highly controllable and designable way. Among them, two-dimensional (2D) AuNP arrays have witnessed tremendous progress in synthesis and characterization. To fabricate the 2D AuNP arrays, methodologies such as Langmuir–Blodgett method and photolithography have been widely applied, whereas some defects still exist. As a new methodology, the base-pairing specificity of DNA sequences should be a useful tool.

In 2003, Maeda and coworkers found that fully matched double-stranded (ds) DNA–AuNPs aggregated spontaneously at high ionic strength (Figure 1).[1] Notably, this aggregation was strongly inhibited when the surface-grafted dsDNA had a single-base mismatch or protrusion at the distal end. Nucleobase stacking is considered an origin of drastic reduction of colloidal stability of the fully matched dsDNA–AuNPs. In the current study, the author exploited this non-crosslinking aggregation to induce anisotropic self-organization of the DNA–AuNPs. To construct DNA–AuNP assemblies that undergo structural changes with high sensitivity to single-base difference, the author established a hierarchical self-organization strategy with two steps.[2] First, the DNA–AuNPs were immobilized onto a long ssDNA template by using the DNA hybridization to precisely produce linear precursors. Next, the non-crosslinking aggregation was

implemented in order to program the self-organization performance. By this methodology, the author succeeded in constructing an anisotropic structure from isotropic sphere AuNPs. Besides, two-dimensional AuNP arrays with highly regulated arrangement has also been created through the self-organization of the long AuNP chains. Emphasis is placed on the fact that the structural changes exhibited high sensitivity to single-base difference.

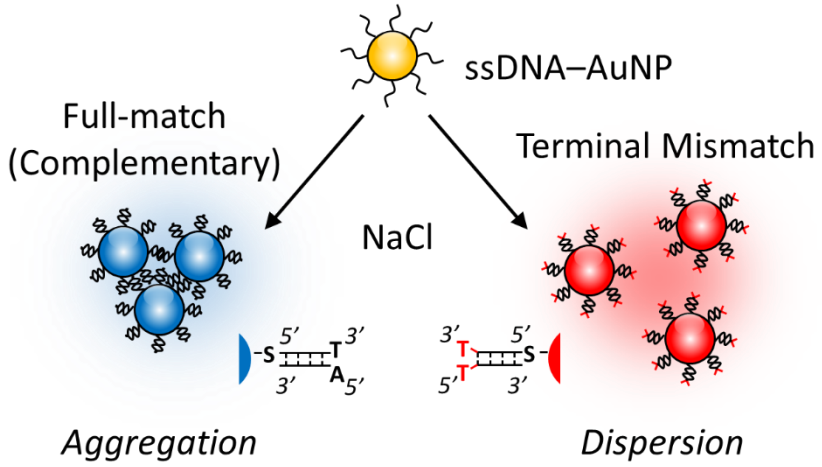

Figure 1. Non-crosslinking aggregation of DNA–AuNPs.

Chapter 2: DNA-Guided Anisotropic Self-Organization of AuNPs

This chapter describes a strategy to produce an anisotropic assembly from isotropic particles (Figure 2).[3] To generate the anisotropy, local-structure-sensitive colloidal stability of dsDNA–AuNPs was exploited; fully matched particles were spontaneously aggregated at high ionic strength, whereas terminal-mismatched particles continued to stably disperse. Initially, linear trimers were prepared by aligning both the fully matched and terminal-mismatched dsDNA–AuNPs on a DNA template in a strictly defined order. Then, the non-crosslinking assembly was induced for the obtained trimers to achieve anisotropic self-organization of the AuNPs. The systematic investigations revealed that the identity of the central particle determined the structural anisotropy. The trimers containing the terminal-mismatched or fully matched particle at the center selectively assembled in an end-to-end (Figure 2a, top) or side-by-side manner (Figure 2a, bottom), respectively. Further, similar trimers having a central terminal-mismatched particle larger than the peripheral fully matched particles formed assemblies that had small particles between the large particles (Figure 2b, top). By contrast, the trimers with a central fully matched particle larger than the peripheral terminal-mismatched particles formed an assembled structure in which the large particles were surrounded by the small particles (Figure 2b, bottom). The anisotropy was programmable by the rule that an attractive force emerged only between the fully matched particles. This methodology could be useful to fabricate nanodevices.

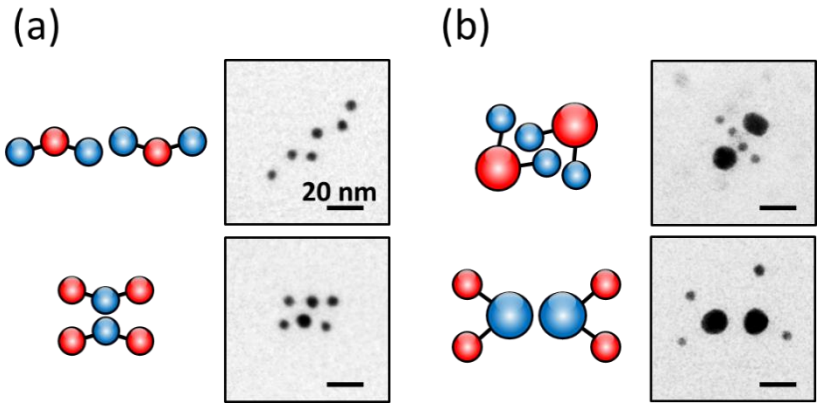

Figure 2. Programmed anisotropic self-assembly of nanoparticles. Blue and red spheres represent the fully matched and terminal-mismatched dsDNA–AuNPs, respectively.

Chapter 3: DNA-Guided Formation of 2D AuNP Arrays

Nanoparticle arrays exhibit collective physical and chemical properties, which are potentially applicable to various nanodevices, such as data storage media and biosensors. This chapter describes a spontaneous method of constructing 2D nanoparticle arrays from precursory 1D chains of DNA-modified nanoparticles (Figure 3).[4] The single-stranded (ss) DNA–AuNPs were hybridized to a long repetitive ssDNA synthesized with rolling circle amplification to produce the precursory AuNP chains. Transmission electron microscopy revealed that the chains of fully matched dsDNA–AuNP underwent shrinkage and folding during evaporation to afford the 2D nanoparticle arrays. By contrast, the terminal-mismatched dsDNA–AuNP chains maintained the linear shape. Noticeably, the chains of long dsDNA–AuNP with short interparticle spacing formed the nanoparticle arrays with anisotropic interparticle spacing. The present approach could be useful for readily aligning nanoparticles on the substrate surface.

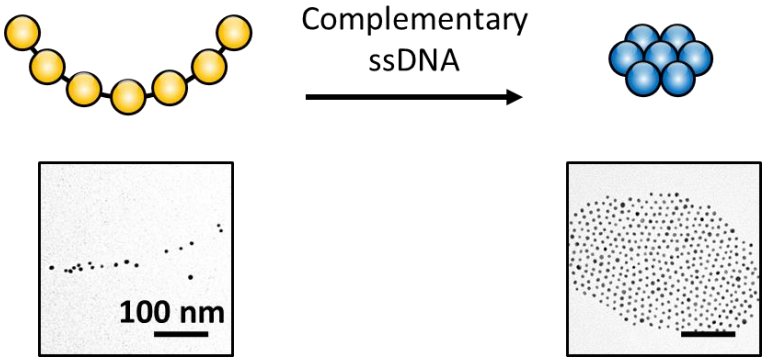

Figure 3. Folding of nanoparticle chains into 2D arrays. Yellow spheres represent the ssDNA–AuNPs.

Chapter 4: Conclusion and Outlook

In the present work, the author has tried to develop a novel methodology to produce anisotropic structures from isotropic nanoparticles; namely, spherical AuNPs were successfully assembled into anisotropic 2D structures by employing DNA. All anisotropic structures obtained in this study were simply deduced from the rule that an interparticle attractive force emerged only between the fully matched dsDNA–AuNPs. This rule was in line with the working hypothesis that interparticle attraction in the non-crosslinking assembly arose from the blunt-end stacking. It is imperative to note that this methodology exhibited extremely high selectivity, which was stimulated by only a single nucleotide substitution. Such local structural changes led to entirely opposite colloidal behaviors, which were expected to be useful for device fabrication.

However, there are several challenges that need to be overcome for future practical applications. First, various types of nanoparticle should be applied to the current methodology. Second, the present methodology should be improved to work in an aqueous phase for generating anisotropic 3D structures. The author believes that these two improvements will be harnessed to fabrication of various advanced nanodevices on the basis of the current methodology.

References

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