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Author(s)	Yang, Jingyan
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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（ソフトマター科学）　氏　名　楊　婧妍

学 位 論 文 題 名

Stimuli-Responsive Assembly of Gold Nanorods with Uniform Orientation in Polymer Brush Substrates
（ポリマーブラシを足場とした均一配向化金ナノロッドの刺激応答性集合化）

Living organisms exhibit remarkable functionalities, such as molecular transport and homeostasis, driven by sophisticated molecular assembly systems. Examples include the fluid mosaic model of lipid membranes and the dynamic self-assembly of cytoskeletal proteins such as actin and tubulin. These biological systems inspire the design of functional materials. In contrast, inorganic materials typically exhibit limited emergent functions, but advances in nanotechnology have revealed novel properties at the nanoscale, particularly in nanoparticles of noble metals. Metal nanoparticles exhibit unique properties that are invaluable for applications in electrical, optical, and magnetic devices. A notable example is the phenomenon of localized surface plasmon resonance (LSPR) induced by light irradiation in metal nanoparticles such as gold. The characteristics of LSPR are influenced not only by the geometric spatial structure of the nanoparticle ensemble, such as the arrangement of the metal nanoparticles, but also by the shape, size, and composition of the individual nanoparticles. These influencing factors have led to the development of various active plasmonic systems with broad application prospects in chemical and biological sensing, displays, and smart windows. Among gold nanoparticles (AuNPs), rod-shaped gold nanoparticles (AuNRs) exhibit two LSPR modes. The longitudinal axis supports a characteristic and strong plasmon mode (L-LSPR) that appears in the visible-near-infrared region, attracting considerable attention for use in optical antennas, high-sensitivity biosensors, and medical applications, leading to effective utilization of photo-energy. The plasmonic properties of AuNRs are determined by their spatial arrangement, making both assembly (interparticle distance) and orientation control crucial in the design of plasmonic systems. Despite the importance of orientation, most studies have focused on manipulating interparticle distances. Polymer brushes, which are soft materials attached to a solid substrate, possess oriented structures and thus offer significant potential for aligning AuNRs on substrates. However, orientation control using polymer brushes has remained an unexplored frontier. Recently, our research group demonstrated the vertical alignment of AuNRs using polymer (DNA) brushes as a scaffold and achieved reversible orientation changes by modulating environmental pH and salt concentrations. These advances highlight the feasibility of orientation control within flexible polymer brushes. However, achieving unambiguous control over the spatial arrangement of AuNRs, particularly their assembly and disassembly with controlled orientation on solid substrates, remains a formidable challenge. This study aims to achieve stimuli-responsive assembly of AuNRs with uniform orientation using polymer brushes (Scheme 1).

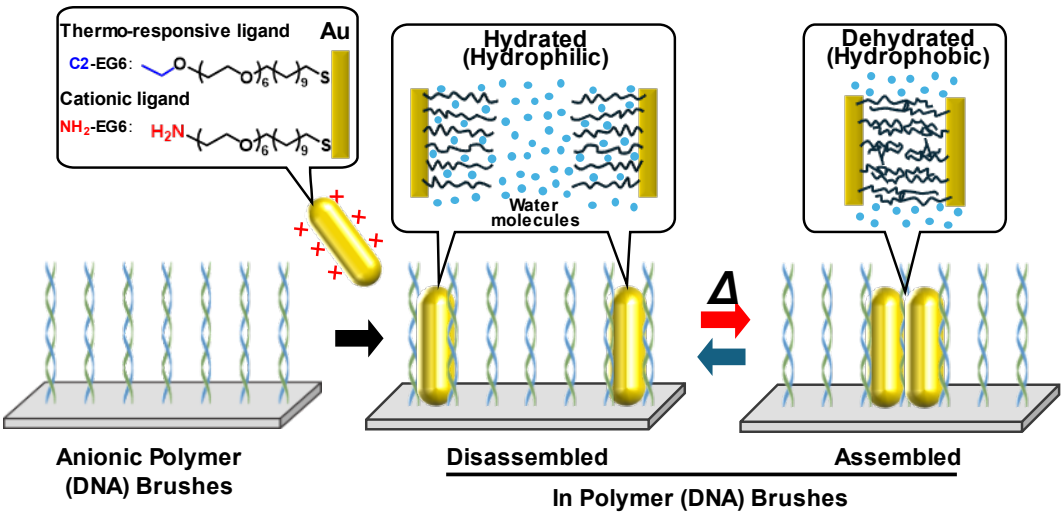
In Chapter 1, I discuss the reversible self-assembly phenomena observed in biological systems and highlight their importance in synthetic materials. In addition, I review the properties of gold nanoparticles and gold nanorods. This chapter also examines previous studies on assembly control of gold nanoparticles and explores the advantages of polymer brushes for flexible control of stimuli-responsive gold nanoparticle assemblies.

In Chapter 2, I prepared temperature-responsive cationic-thermo-responsive gold nanorods (cTR-AuNRs).

To attach the AuNRs to anionic polymer brushes, a cationic charge is necessary. Therefore, I functionalized the AuNRs with different ratios of cationic and thermo-responsive ligands to prepare the cTR-AuNRs and investigated their temperature responsiveness by varying the temperature.

In Chapter 3, I achieved the stimuli-responsive assembly of cTR-AuNRs with uniform orientation using polymer brushes. The thermo-responsive cTR-AuNRs prepared in Chapter 2 were attached to the anionic polymer brushes via electrostatic interaction. I evaluated the attachment orientation of the cTR-AuNRs using extinction spectroscopy and investigated the temperature responsiveness of uniformly oriented cTR-AuNRs by varying the temperature.

In Chapter 4, I summarize this thesis. Using the described method, I successfully achieved the stimuli-responsive assembly of uniformly oriented AuNRs and explored their potential applications in various stimuli-responsive systems. This research paves the way for innovative approaches in the design and application of nanomaterials, particularly in fields requiring high precision and flexible regulation, such as smart sensors and responsive materials.



Scheme 1. Schematic illustration of my doctoral thesis.