Nano-Optical Imaging and Application to Nanomaterials

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Studies of local optical properties of molecular assemblies and materials are the keys to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Nano-optical methods, such as scanning near-field optical microscopy (SNOM), enable optical imaging with spatial resolution beyond the diffraction limit of light. Combination of nano-optical techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterial systems. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies. In the past several years, we succeeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

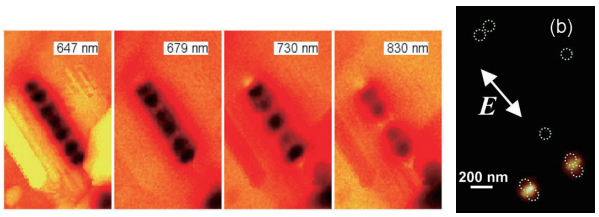

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates the incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

1. Supramolecular Chirality Synchronization in Thin Films of Plasmonic Nanocomposites[1)]

Mirror symmetry breaking (chirality) in materials is a fascinating phenomenon that has practical implications for various optoelectronic technologies. Chiral plasmonic materials are particularly appealing due to their strong and specific interactions with light. In this work we broaden the portfolio of available strategies toward the preparation of chiral plasmonic assemblies, by applying the principles of chirality synchronization—a phenomenon known for small molecules, which results in the formation of chiral domains from transiently chiral molecules. We report the controlled co-crystallization of 23 nm gold nanoparticles and liquid crystal molecules yielding domains made of highly ordered, helical nanofibers, preferentially twisted to the right or to the left within each domain. We applied our recently developed precise far-field circular dichroism (CD) microscopy to this system and confirmed that such micrometer sized domains exhibit strong CD signals, even though the bulk material is racemic. We further highlight the potential of the proposed approach to realize chiral plasmonic thin films by using a mechanical chirality discrimination method. Toward this end, we utilized a rapid CD imaging technique based on the use of polarized optical microscopy, which enabled probing the CD signal. The method allows us to extend intrinsically local effects of chiral synchronization to the macroscopic scale, thereby broadening the available tools for chirality manipulation in chiral plasmonic systems.

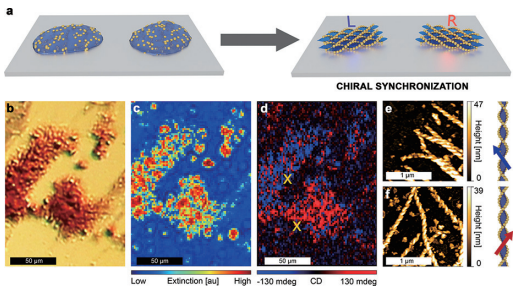

Figure 2. Micrometer-scale circular dichroism measurements of the helical Au nanoparticle assemblies.[1)] (a) Graphical representation of the chiral synchronization process. (b) Optical micrograph, (c) extinction intensity map at 550 nm, and (d) CD map at 550 nm from the same region of the sample. (e) AFM height map of a selected region from a left-handed and (f) a right-handed domain, with graphical models of the helical nanofilament. ©ACS 2020

2. Directional Supramolecular Polymerization to Form Nanofibers in a Microflow Reaction System[2,3)]

Directional chain reactions are common self-assembly processes in nature. However, it has been challenging to achieve such processes in artificial one-dimensional self-assembling systems. In this work, we conducted supramolecular polymerization of perylene bisimide derivatives to form nanofibers. With selectively activating one end of a supramolecular polymer during its growth in a microflow channel, it realized directional supramolecular polymerization. The dependency of the aggregation efficiency on the flow rate suggested that the shear force facilitated collisions among the monomers to overcome the activation energy required for nucleation. By introducing a solution containing both monomer and polymer, we investigated how the shear force influenced the monomer–polymer interactions. In situ fluorescence spectra and microscopic absorption linear dichroism measurements in the microflow system revealed that growth of the polymers was accelerated only when they were oriented under the influence of shear stress. Upon linear motion of the oriented polymer, polymer growth at that single end became predominant relative to the nucleation of freely diffusing monomers. This strategy—friction-induced activation of a single end of a polymer—should be applicable more generally to directional supramolecular block co-polymerizations of various functional molecules, allowing molecular heterojunctions to be made at desired positions in a polymer.

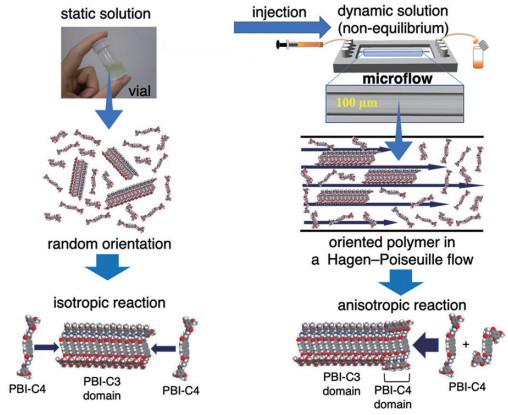

Figure 3. Comparison of general isotropic supramolecular polymerization in a vial (left) and the directional anisotropic supramolecular polymerization in a microflow system (right).[2)] In the microflow system, the forward-facing terminus of the highly aligned polymer reacts with monomers, thereby leading to anisotropic elongation. ©ACS 2021

3. Optical Trapping of Chiral Metal Nanoparticles

Optical trapping experiments of chiral metal nanoparticles with circularly polarized light were conducted. The analysis of the data to reveal the origin of dissymmetry in optical force is now in progress.

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