学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Investigation of quantum coherence within modal strong coupling systems between localized surface plasmon resonance and Fabry-Pérot nanocavity modes
（局在表面プラズモン共鳴とファブリ・ペローナノ共振器とのモード型強結合系における量子コヒーレンスの研究）

Artificial photosynthesis is a promising approach to convert solar energy into storable chemical fuels. Over the past decades, numerous efforts have been devoted to realizing efficient artificial photosynthetic systems. Among them, Shi et al. demonstrated a modal strong coupling photoanode composed of plasmonic nanoparticles on a Fabry-Pérot nanocavity built with a titanium dioxide semiconductor and an Au mirror. This configuration significantly extended the operational wavelength range into the visible and near-infrared regions and remarkably enhanced the quantum efficiency of water splitting compared with conventional plasmonic photoanodes.

In this study, I employed well-designed Au nanostructures instead of randomly distributed nanoparticles to construct controlled modal strong coupling systems. By precisely tuning their structural parameters, the detailed mechanisms governing modal strong coupling—particularly the role of quantum coherence—were systematically investigated.

Chapter 2 describes the fabrication of modal strong coupling systems composed of Au nanodisks with various particle number densities. Their optical spectra confirmed the achievement of the strong coupling regime. Interestingly, unlike conventional plasmonic structures where absorption increases monotonically with the number of absorbers, both the absorption and near-field intensities of the modal strong coupling structures exhibited saturation behavior with increasing particle number density. Moreover, the splitting energy between the upper and lower branches deviated positively from the classical square-root dependence on particle number density at high values. These unconventional trends motivated further investigation into the role of quantum coherence, discussed in the following chapter.

Chapter 3 explores the apparent quantum coherence in the hot-electron injection process from Au nanodisks into the titanium dioxide layer. The degree of coherence was found to increase with PND for both branches—a dependence absent in conventional plasmonic systems. Combined with photoemission electron microscopy observations, a mechanism of quantum coherence-assisted hot-electron injection was proposed. Under modal strong coupling conditions, plasmonic nanostructures within a certain coherence area can share energy through the nanocavity. This behavior explains both the absorption saturation and the positive deviation of the splitting energy. Furthermore, when fast-damping sites that efficiently inject electrons exist within the coherence area, the shared energy converges toward these sites, enhancing the apparent quantum efficiency. Photoelectrochemical measurements further confirmed that this efficiency enhancement translates into improved single-proton oxidation

reaction performance.

Chapter 4 investigates the dephasing effect by incorporating Au-nanotriangles into Au-nanodisks arrays. Because Au-NTs exhibit faster dephasing than Au-NDs, increasing the percentage of triangles led to a reduction in splitting energy and broadening of both excitation branches. Interestingly, the apparent quantum efficiency showed a branch-asymmetric dependence on the percentage of triangles, suggesting complementary functional roles between Au-nanodisks and Au-nanotriangles mediated by quantum coherence.

Chapter 5 experimentally determined the dephasing times of the mixed structures, revealing a gradual decrease with increasing percentage of triangles for both branches. Notably, under upper-branch excitation, the dephasing time exhibited a drastic drop at high triangle ratios. Near-field simulations showed branch-dependent spatial distributions: under lower-branch excitation, the fields were delocalized across nanostructures, with hot spots concentrated at the sharp tips of Au-nanotriangles—efficient sites for hot-electron generation. Under upper-branch excitation, however, the fields were strongly localized along the edges of Au-nanotriangles, where hot-electron generation is less efficient. These results led to the conclusion that the sharp tips of Au-nanotriangles act as reaction centers, while the long-dephasing Au-nanodisks function as optical antennas. The interplay between coherence-mediated energy sharing and dephasing dynamics gives rise to the observed asymmetric apparent quantum efficiency dependence on the percentage of triangles.

Chapter 6 summarizes the findings and discusses future perspectives. Overall, this work demonstrates that quantum coherence plays a central role in governing energy transfer and hot-carrier dynamics in modal strong coupling systems. A clear understanding of coherence effects—especially the influence of dephasing and near-field distributions—provides a foundation for controlling and optimizing hot-electron transfer. Based on these insights, next-generation modal strong coupling photoelectrodes can be rationally designed to achieve dramatically enhanced efficiencies in artificial photosynthesis, paving the way toward practical and scalable solar-to-chemical energy conversion.