学　位　論　文　内　容　の　要　旨

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Study on Efficient Water Oxidation under Modal Strong Coupling Conditions
（モード強結合下における水の酸化反応の高効率化に関する研究）

Improving the efficiency of converting the abundant solar energy to the chemical energy is one of the most significant strategies to address the current environmental and energy crisis. For example, the photocatalytic artificial photosynthesis such as water splitting under the irradiation of solar light provides us convenient approaches for energy production and environmental conservation. In recent decades, the concept of photocatalysis combined with localized surface plasmon resonances (LSPRs), which are the collective oscillation of charge carriers at the surfaces of metallic nanoparticles (NPs), has accelerated progress in boosting the photocatalytic activity in visible light and even infrared light. However, it is difficult to harvest visible light effectively with monolayer of metallic NPs. Recently, it was reported that a modal strong coupling between a Fabry-Pérot (FP) nanocavity mode and an LSPR showed a large and broad absorption by optical hybrid modes. In this thesis, essential properties of modal strong coupling between FP nanocavity mode and LSPR was investigated to improve the photoelectrochemical water oxidation under visible light irradiation. Au-NPs/TiO2/Au-film (ATA) structure was employed to achieve the modal strong coupling.

At first, I investigated the particle size effect of Au-NPs on the photoelectrochemical properties under the modal strong coupling condition. The ATA structure was produced based on the technology of sputtering, atomic layer deposition (ALD), thermal evaporation, and annealing, respectively. Au-NPs with various particle sizes were employed for the TiO2 surface decoration and providing the LSPR mode, which could couple with the FP-nanocavity mode of TiO2/Au film. The experimental results illustrated that Au-NPs with a size around 12 nm showed superior properties not only in photoelectrochemical performance but economically friendly. The absorption spectrum of ATA structure exhibited distinct dual bands at wavelength longer than 550 nm when Au-NPs were partially inlaid in TiO2. The photoelectrochemical measurement showed that the ATA structure exhibited obvious photocurrent enhancement. (Chapter 2).

Then, I investigated the hot-electron transfer efficiency on a photoanode under the modal strong coupling conditions by monitoring the photoelectrochemical activities, including IPCE and internal quantum efficiency (IQE) using triethanolamine (TEOA) as an efficient electron donor to sufficiently accelerate the surface reaction. In the presence of TEOA, the IPCEs of the lower branches of hybrid modes formed by the strong coupling were improved as much as 4.0 times, whereas these for upper branches were up to 4.5 time. Furthermore, in the wavelength range 500-800 nm, it the average IQE was calculated to 3

In the ATA structure, however, Au-NPs are partially inlaid inside TiO2 to increase the interaction between the nanocavity and LSPR. The intensified near-field is generated at the bottom of Au-NPs

rather than the surface of TiO2 according to the simulation results. This fact indicates that hot electron and hole pairs are produced and separated at the inlaid interface of Au-NPs/TiO2 inside TiO2. For the photoelectrochemical reactions, the holes must transfer to the surface of TiO2 to participate the oxidation reaction. This migration process of holes has an adverse effect on the photoelectrochemical reactions by inducing the recombination. Therefore, the hot-spot of the near-field should be near the reaction surface for the efficient water oxidation. In order to tailor the near-field distribution, a postdeposited Au on ATA structure was implemented using a facile constant potential electrolysis technique to post deposit Au on ATA photoelectrode (Au@ATA). In Au@ATA structure, a strong near-field is induced at the interface of postdeposited Au and TiO2, where the water oxidation reaction occurs effectively. Consequently, the average IPCE of Au@ATA is approximately 1.3-fold higher than that of ATA. Both simulated and experimental results showed that the interface established in postdeposited Au and TiO2 was significant in improving photoelectrochemical performance (Chapter 4).

In summary, photoelectrochemical properties on the modal strong coupling structure between FP-nanocavity and LSPR under visible light irradiation were investigated using the ATA structure to achieve the efficient water oxidation. The structure of ATA was optimized by varying the size and inlaid depth of Au-NPs. The photoelectrochemical study with the sacrificial electron donor revealed that the hot-electron injection efficiencies of the photoanode under modal strong coupling condition are significantly larger than that of the conventional plasmonic anode. Furthermore, it was found that the near-filed enhancement near the interface of the three-phase boundary between the interface of Au-NPs, TiO2 and aqueous solution was significant in water oxidation on the ATA. Additionally, the enhanced near-field distribution of Au nanostructures can be engineered by simply adjusting their shape and size. It provides the possibility for constructing low-costing artificial photosynthesis systems. These results guarantee the future researches to investigate the mechanism of hot-carrier-induced photoelectrochemical properties.