学位論文審査の要旨

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学　位　論　文　題　名

Studies on plasmon-driven efficient multi-electron transfer reactions at electrified interfaces

（電気化学界面におけるプラズモン誘起高効率多電子移動反応に関する研究）

The effective utilization of solar energy for chemical reactions has been regarded as the challenging issue in the photochemistry field. For that, various systems, such as the molecular and semiconductor catalysts have been established for the highly efficient photo energy conversion. However, it can be said that several points, such as the utilization of lower energy photon or the control of photon absorption efficiency, should be improved. Localized surface plasmon resonance (LSPR) which is the collective oscillation of free electrons in the metal nanostructures induced by the visible light illumination could be an effective tool. Under the plasmon excitation, enhanced electromagnetic field is generated at the vicinity of metal nanoparticles, leading to the unique optical response property. During the decay process of plasmon excitation, hot carriers can be generated and be used for multi-electron transfer reactions. However, although much effort has been done in this field, the detailed understanding of the plasmon-induced multi electron transfer reactions is still under discussion. From these backgrounds, the purpose of my thesis is to improve the light-matter interaction for the improvement of various photon energy utilization and to understand the reaction mechanism on the plasmonic electrode for the future innovative photovoltaic devices.

This thesis consists of 6 chapters.

In Chapter 1, the basic concept of plasmonic photon energy utilization was given. Oxygen evolution reaction (OER) and the effective catalysts for this reaction have been introduced. The current research status about the plasmonic OER has also been introduced. Based on the backgrounds and general problems in the field, the aims of this study were proposed.

In Chapter 2, the electronic interaction between two-dimensional molybdenum disulfide (MoS_2) and silver plasmonic structures was investigated. The formation of the strong coupling regime between them has been confirmed via the dark-field scattering measurements. In addition, it has been revealed that not only the layer number of MoS_2 but also the electrochemical potential tuning

enabled to actively tune the light-matter interaction. In summary, the strong interaction between plasmon and material has been achieved for the efficient light energy usage.

In chapter 3, the utilization of photon with lower energy and the enhancement of photon confinement were investigated using a plasmonic electrode consisting of Au film / TiO_2 / Au nanoparticles (ATA), leading to the formation of the modal strong coupling between the LSPR mode and Fabry–Pérot nanocavity mode. The intrinsic electronic structure of ATA was probed via the graphene based electrochemical surface enhanced Raman scattering (SERS) spectroscopy. This is because that the wavenumbers of G and 2D bands for graphene layer reflects the Fermi level of the electrode. Through the comparison of SERS spectra, the different electronic structure depending on the OER performance has been revealed. It was also clarified that the highly localization of photon energy realized by the modal strong coupling contributed to the improvement of the reaction activity.

In chapter 4, the OER on plasmonic Au / TiO_2 electrode was investigated. Generally, the catalysis performance under basic condition becomes higher compared to other pH condition on the conventional OER catalyst. However, it has been found that the highest reaction activity could be obtained under the neutral condition. This result indicated that the reaction mechanism on the plasmonic electrode was totally different from that on conventional metal catalysis.

In chapter 5, the enhancement of OER performance has been achieved by depositing nickel on Au / TiO_2 electrode. The reaction mechanism for the multi electron transfer process has been also investigated through the pH dependence and the isotopic effect. From the comparison of the isotopic effect on both plasmonic and conventional electrode under base and neutral conditions, the plasmon-accelerating reaction step has been firstly revealed. It is also important that, especially under neutral condition, the characteristic molecular process on the plasmonic electrode for the efficient multi electron transfer process has been successfully clarified.

In Chapter 6, the general conclusion of my thesis was given.

To summarize, the current thesis has demonstrated the efficient electron transfer process driven by the plasmon excitation. The effect of strong localization of plasmon on the reaction rate was also observed. Electronic structure of plasmonic system was clarified for understanding the effective reaction performance. Additionally, not only the enhancement of reaction activity but also the reaction mechanism has been demonstrated. Based on these achievements, it is sure that the insights obtained through the current investigations would have the great possibility for the realization of the high-performance future photovoltaic devices. Therefore, the author, Ms. Yuchung Wang, should be deserved as a doctoral degree from Hokkaido University.