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学 位 論 文 内 容 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)

Efficiency utilization of solar energy is recognized as one of the paramount issue for the energy crisis. Although plenty of work, e.g. molecular photocatalyst, photovoltaic solar cell, or metal nanostructured photocatalysis, has devoted in this area, the utilization efficiency of visible light still needs to be improved. Localized surface plasmon resonance (LSPR) has been demonstrated as one of the promising candidate to increase the photon conversion efficiency. Because of the typical characteristics, the utilization of photons could be enhanced dramatically due to the nanoscale localization of the concentrated light energy. The plasmon induced enhancement of electric field also plays a crucial role for the broad photocatalysis applications. In addition, plasmon excitation generates the excited electrons and holes which can lead to the efficient multiple electron transfer. However, at the present stage, the efficiency of the photoenergy conversion induced by plasmon is relatively low due to the limitation of the absorption characteristics. And also, the detailed reaction mechanism of plasmon-induced multiple electron transfer is still under investigation. From these backgrounds, it can be considered that the enhancement of light-matter interaction, resulting in the improvement of the various photon energy utilization, and the detailed understanding of the reaction mechanism should be important for the realization of innovative future plasmon-based photo conversion devices.

In this thesis, by the use of structural control of metal nanostructure, the improvement of the interaction between electrons in materials and energy of photons has been conducted for effective plasmon-driven electron transfer reactions. Additionally, through the photoelectrochemical and spectroscopic measurements, the detailed understanding of the intrinsic principle of plasmon driven electron transfer have been also clarified successfully.

Chapter 1 gives a general introduction of the definition and properties of LSPR. The application of plasmonic catalysis was introduced. The concept of oxygen evolution reaction (OER) and well-established catalysis for OER were also introduced since, in this thesis, I mainly focus on plasmon-induced OER process.

In chapter 2, as one of the representative ways to improve the light-matter interaction, the strong coupling between MoS_2 and plasmon energy on silver nanoparticles was investigated. By tuning the layer number of MoS_2, the peak splitting indicating the formation of the strong coupling

could be observed. The active control of the coupling state has also been achieved by the electrochemical potential control.

In chapter 3, the influence of localization properties of plasmonic modal strong coupling on the Fermi level was investigated for the clarification of the electronic structure of the electrode during OER. The modal strong coupling is formed on the TiO_2 electrode sandwiched by Au film and Au nanoparticles. Surface enhanced Raman scattering (SERS) spectroscopy of graphene was adopted to measure the electrochemical potential of the Fermi level quantitatively. Through the graphene-based electrochemical SERS observations, the relationship between the Fermi level and the catalysis performance has been firstly revealed.

In chapter 4, the pH dependent catalysis performance of OER on Au nanostructures supported on TiO_2 electrode was investigated. Based on the result of pH dependent on the photocurrent values, the high efficient catalyst performance was observed especially under neutral condition. The origin of it was demonstrated by observation of an intermediate species which appears at high overpotential of electrocatalysis on OER process.

In chapter 5, enhancing the catalysis performance of Au / TiO_2 electrode for OER was conducted by depositing $Ni(OH)_2$ by electrochemical method. The optimization of deposited layer number of $Ni(OH)_2$ was determined. The catalysis performance on this electrode exhibits relatively high performance under weakly basic condition close to neutral, which is totally different with that of electrocatalysis of OER at ordinary Ni catalysis. The reaction mechanism of such behavior was investigated by isotope effect of heavy hydrogen (D) and heavy oxygen (^{18}O). Both isotope effect of D and ^{18}O of plasmonic Ni catalysis are lower than those of electrocatalysis on Ni indicating the acceleration of reaction by plasmon. By the comparison with the common Ni electrocatalyst, the information of the rate determining step of the plasmon-induced reaction has been clarified.

In conclusion, this thesis demonstrated the efficient electron transfer process driven by plasmon. The available range of solar spectra could be extended by strong coupling between different emitter and cavity mode. Influence of high localization effect of plasmonic system on the reaction rate was observed. It has been demonstrated that these unique effects of plasmonic system can be applied to OER system. The enhancement of catalysis performance was achieved and the reaction mechanism was also clarified. The present work successfully proposed a new pathway to fulfill the efficient electron transfer and establish the high efficient plasmon-based photovoltaic devices beyond the current limitation in future.