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Studies on Plasmonically-powered Processes for Electronic Excitation

(プラズモニック電子励起プロセスに関する研究)

Efficient harvest of light energy is one of the environment-friendly ways to meet the increasing energy demand of human being in a low-carbon society. Conversion of light energy to chemical energy can be realized via photoelectrochemical processes, making the energy transport and storage convenient. Recent attempts to improve the efficiency of photoelectrochemical processes have focused on the optimization of light-matter interaction. However, the light-matter interaction, e.g. the light absorption defined by quantum efficiency, for a given photosensitive material, are limited by the intrinsic electronic structure of the material. Localized surface plasmon resonance (LSPR) provides an unprecedented way to control light-matter interaction. Typical features of the LSPR include the apparent enhanced absorption cross-sections due to enhanced optical near-field intensity. Addition to the feature, recent finding on LSPR excitation suggests possibility on breaking a limit of light absorption via the modification of the selection rule at photo-excitation of electrons and holes due to huge gradient of LSPR field highly localized in nano-space. These features improve the light-matter interaction in a wide range, such as the efficiency of hot carrier generations and injections. Surface-enhanced Raman spectroscopy has been regarded as one of the powerful methods to monitor changes in the optical response of matter, providing rich information for optimizing the photoexcitation process.

In this thesis, I investigated the photo absorption, scattering, and hot carrier generation in the presence of LSPR under electrochemical circumstances, defined as the plasmonically-powered processes. The systems showing the plasmon-induced exotic electronic transitions were designed, constructed, and interrogated to realize the formation of hot carriers with very characteristic electrochemical potential for chemical reactions.

Chapter 1 gives a general introduction on LSPR and its effects on hot-carrier generation and injection. The typical up-to-date results on electrochemical potential of hot carriers and plasmon-modified photoexcitation are also introduced.

In chapter 2, effects of plasmon modes on the electrochemical polymerization of pyrrole is investigated. The charge transfer efficiency is found to be dependent on the shape of metal nano-structures. The findings demonstrate the relation between plasmon mode,

excitation wavelength and the shape of metal. It shows the possibility to carry out chemical reactions on a specific metal structure with a variety of photon energies and remotely control the reaction sites with nanometer preciseness.

In chapter 3, the plasmon thermal effects on the excitation process is investigated. It is found that the intense pulse laser leads to the shape transformation of Au nanorods and further peeled off the TiO₂ substrate under resonance condition. The findings show that the stability of plasmonic metal nanostructures is critical in plasmon-induced chemical reactions.

In chapter 4, the Raman spectra of Au-covered graphene under resonance illumination were measured with increasing laser power. The D-to-2D band intensity ratio in the lower power regime suggests the reshaping of Au nanodimers; while the ratio in the higher power regime indicates the irreversible oxidation of graphene. Thus, attention should be to the chemical stability of target materials for the plasmonically-powered processes.

In chapter 5, plasmon effects on the Raman spectra of graphene were investigated. A single G band around 1600 cm⁻¹ split into three bands when the laser frequency is in resonance with the localized surface plasmon. According to their distinct behaviors under electrochemical control, the appearance of new bands in a defect-free single-layer graphene is ascribed to the plasmon-assisted electronic transition, in which confined photons have large enough wavevectors to excite non-zero momentum transitions. Furthermore, Raman spectra of graphene at electrochemical high doping proved the suppression of the quantum interference of electronic excitation by LSPR. The finding proves the non-vertical electronic transitions have potential to change the electrochemical potentials of hot electrons and holes.

In conclusion, this thesis proves plasmon effects on the photoelectrochemical processes. The spectral range of photo-response of material could be extended via excitation of different plasmon modes. Most importantly, new photoexcitation pathways are enabled by LSPR effect. This not only changes the optical response of the target materials but also tunes the electrochemical potentials of hot electrons and holes. Therefore, drastic improvements in the efficiency and the diversity of photoelectrochemical reactions could be realized by the newly developed method based on the present finding.