学　位　論　文　内　容　の　要　旨

博士の専攻分野の名称　　博士（情報科学）　　氏名　Zang Xiaoqian

学　位　論　文　題　名

Unique Surface Enhanced Raman Scattering Induced by Plasmon-Nanocavity Coupling and its Application to Elucidating the Mechanism of Enhanced Water Oxidation Under the Strong Coupling Conditions

（プラズモンとナノ共振器のカップリングにより発現する特異な表面増強ラマン散乱とそれを用いた強結合下における水の酸化の増強メカニズム解明）

Noble metal nanoparticles (NPs) such as gold and silver, are of great interest due to their unique optical, magnetic, and electronic properties based on the plasmon resonance. The localized surface plasmon resonance (LSPR) is the collective oscillation of the conduction band electrons at the surface of metal NPs which induces significant electromagnetic field enhancement at the metal NPs surface. Recently, it has been reported that the modal coupling between an LSPR and a Fabry-Pérot (FP) nanocavity mode can enhance the photochemical reactions taking place near the metal NPs. It is great interesting and critical to investigate the enhancement mechanism of plasmon-induced photoelectrochemical (PEC) reaction under the plasmon-nanocavity coupling. In this thesis, the effect of plasmon-nanocavity coupling on the near-field distribution was investigated by a measure of surface-enhanced Raman scattering (SERS). Besides, the plasmon-nanocavity coupling structure was applied to investigate the plasmon-induced water oxidation reaction, which affected by the plasmon-nanocavity coupling, using *insitu* electrochemical surface-enhanced Raman scattering (EC-SERS) measurements.
A plasmon-nanocavity coupling structure consist of Au NPs/TiO_2/Au-film (ATA) was fabricated to investigate the spatial coherence effect by SERS measurements. Compared to the Au NPs/TiO_2 (AT) structures without FP nanocavity, the SERS signal collected on ATA was enhanced by 11 times because of the dramatic near-field enhancement causing by the coupling between LSPR of Au NPs and FP nanocavity resonance. Besides the large near-field enhancement, a spatially homogeneous near-field intensity was observed on ATA, which can be attributed to the coherent coupling between the LSPR of each Au NP and the FP nanocavity. Simulations also showed the homogeneous near-field distribution under the plasmon-nanocavity coherent coupling, which supports our experiment observations.
To investigate the effect of plasmon-nanocavity coupling on the plasmon-induced water oxidation reaction, an Au-Ag alloy NPs/TiO_2/Au-film (AATA) structure was employed, and *insitu* EC-SERS measurements were performed to detect the intermediate species of plasmon-induced water oxidation. The Au-Ag alloy NPs were deposited on TiO_2/Au-film to create a modal strong coupling between the LSPR of Au-Ag alloy NPs and the FP nanocavity resonance. A large splitting energy was observed on the AATA structure which was derived from the large oscillator strength of the LSPR of Au-Ag alloy NPs. The Raman intensity of the Au-O and Au-OH stretching vibrations, which are characterized intermediate species of the plasmon-induced water oxidation on Au-based NPs, were systematically studied at a wide range of electrochemical potentials. Compared with Au-Ag alloy NPs/TiO_2 (AAT) struc-

ture without FP nanocavity, the *insitu* EC-SERS measurement of the intermediate species on AATA electrode showed higher sensitivity. More interestingly, the Raman signals on AATA showed a more negative onset potential than the AAT structures, indicating a much more efficient charge separation on AATA structures that facilitates water oxidation reaction. This enhanced water oxidation efficiency on AATA is likely attributed to the quantum coherence between the Au-Ag alloy NPs through the nanocavity, leading to the accumulation of a large number of holes.

In summary, the near-field intensity distribution, and the water oxidation reaction intermediate on the plasmon-nanocavity coherent coupling structure were investigated by means of SERS measurements. The SERS measurements revealed a large near-field enhancement and spatially homogeneous near-field distribution under the plasmon-nanocavity coherent coupling. Furthermore, the intermediates of plasmon-induced water oxidation were investigated using the plasmon-nanocavity coherent coupling structure by *insitu* EC-SERS measurement. From the EC-SERS measurements, a more negative onset potential of the water oxidation intermediates was observed on AATA, which was attributed the higher near-field enhancement and the efficient plasmon-induced charge separation in the coherent aera under the plasmon-nanocavity coherent coupling.