



# HOKKAIDO UNIVERSITY

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## 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 郭 景春

## 学 位 論 文 題 名

Plasmon-induced photoelectrochemical biosensors using gold nanostructured titanium dioxide  
photoelectrodes

（金ナノ構造担持酸化チタン電極を用いた光電気化学バイオセンサー）

Metallic nanoparticles (NPs) such as gold (Au) and silver exhibit very intense color which is derived from localized surface plasmon resonances (LSPRs). LSPRs are collective oscillations of conduction electrons, which induce large local electromagnetic (EM) field enhancements. EM field enhancement effects are known to induce various optical effects such as surface-enhanced Raman scattering (SERS) and fluorescence enhancement which make it possible to detect small number of molecules. Therefore, SERS and fluorescence enhancement have been applied to highly sensitive biosensors. As the other biosensor using the principle of LSPRs, there is a method which detect a small spectrum shift due to the refractive index change of surrounding medium based on the adsorption of bioanalytes to the surface of AuNPs, which is known as a LSPR biosensor. Although SERS is extremely sensitive and LSPR biosensor is simple, they require relatively large equipment such as laser and spectrometer, and development of small and compact sensor is also demanded. On the basis of the background of biosensors using a principle of LSPRs, a photoelectrochemical (PEC) biosensor in which electronic circuits and detectors can be integrated is proposed in this study by using Au nanostructured titanium dioxide ( $\text{TiO}_2$ ) photoelectrodes. Because the PEC biosensor studied previously relies on the spectrum change of LSPRs based on the refractive index change of surrounding medium, the sensitivity is not expected as similar to LSPR biosensor. In the present study, I proposed the improvement of sensitivity on the PEC biosensor based on the EM field enhancement due to near-field coupling between Au nanostructures on  $\text{TiO}_2$  and AuNPs by connecting using an antigen-antibody reaction of biotin and streptavidin.

To elucidate the influence of near-field coupling between LSPR of Au nanostructures on  $\text{TiO}_2$  photoelectrode and the other optical modes on the PEC responses, I explored the internal quantum efficiency (IQE) of plasmon-induced photocurrent generations as a function of incident wavelength. Namely, the near-field coupling between LSPR and the other optical modes reflects on the PEC response if the IQE spectrum reproduces the near-field spectrum. On the basis of the hypothesis, I employed  $\text{TiO}_2$  photoelectrodes supporting Au nanogratings (AuNGs) because AuNGs/ $\text{TiO}_2$  substrate shows complicated near-field spectra due to the strong coupling between waveguide modes induced by AuNGs and LSPR of AuNGs for the demonstration of performance. Periodic AuNGs were fabricated on  $\text{TiO}_2$  photoelectrodes using electron beam lithography and lift-off processes. Plasmon-induced photocurrent generation was pursued by a conventional PEC measurement using a three-electrode system. It was clearly elucidated that IQE spectrum has successfully reproduced the near-field spectrum predicted by EM simulations based on the finite-difference time-domain (FDTD) method under the coupling

conditions. This paves a new approach to indirectly measure the near-field spectra of coupled plasmonic systems and proves that the near-field coupling reflects on the plasmon-induced photocurrent generation. (Chapter 2).

The photocurrent enhancement by the near-field coupling was studied as a sensitive biosensor for measuring the biotin-streptavidin binding kinetics. In this study, Au nanoislands (AuNIs) loaded single crystal  $\text{TiO}_2$  substrate was used as a photoelectrode. The photoelectrode was then processed by self-assembled thiol-terminated biotin (TTB) molecules. The self-assembled TTB molecules bound on an AuNIs/ $\text{TiO}_2$  photoelectrode successfully detected different concentrations of streptavidin-modified AuNPs solutions based on the PEC measurement owing to the near-field coupling between AuNIs and AuNPs with biomolecules. Furthermore, the real-time monitoring of biotin-streptavidin binding affinities and kinetics by analyzing the PEC sensing characteristics has been also successfully demonstrated. This PEC biosensor could provide a new approach for the specific electrical detection and real-time kinetic measurements for clinical diagnostics and drug development (Chapter 3).

In conclusion, the plasmon-induced photocurrent generation was proved as a useful tool for detecting the biomolecular binding affinity and kinetics. It was clearly confirmed that the near-field coupling between LSPR and the other optical modes reflects on the PEC response, which can be utilized for the highly sensitive detection of bioanalytes. The biosensor for pursuing biotin-streptavidin binding kinetics based on the plasmon-induced photocurrent generation have been successfully improved by the near-field coupling between AuNIs and biomodified AuNPs. These findings provide a powerful tool to detect and determine the binding affinity and kinetics of biomolecular interactions as a compact plasmonic PEC biosensor.