Shape-dependence of Gold Nanoparticle in Enhanced Sensitivity of Surface Plasmon Resonance Sensing

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Surface plasmon resonance (SPR) spectroscopy is an effective method for the detection of biochemical changes occurred at the surface of a thin noble metal film. However, sensitivity of SPR is limited by small shifts in both angle and reflectance. The coupling of SPR with gold (Au) nanoparticles has been proposed in order to enhance the sensitivity of SPR. It is well known that the curved surface of nanoparticle has their own localized surface plasmons (LSP) due to the collective oscillations of free electrons. Therefore, additional surface plasmon polaritons (Au film) - LSP (Au nanoparticle) interactions result in the enhancement (large perturbation) in the sensitivity of SPR measurements. To our knowledge, however, no clear proof about the geometrical effect (shape-dependence) of Au nanoparticle has been reported so far. In this study, shape-dependence of Au nanoparticle coated on the thin film for the amplified surface plasmon resonance response is reported. Spherical and rod-like nanoparticle were prepared by Frenz method and seedmediated method, respectively. SPR substrate was prepared by the sequential thermal evaporation of a thin adhesion layer of Cr (5 nm) and Au (50 nm) layer. Au films were modified with 1,6-hexanedithiol (HDT), which produced a self-assembled monolayer. An Au coated substrate with the HDT monolayer was immersed for 12 hr into the spherical Au nanoparticle solution and rod-like particle solution. SPR measurements were carried out using a home-made instrument. Adsorption of Au nanoparticles on the surface of Au film result in dramatic and shape-dependent shifts in surface plasmon angle and minimum reflectance. The extent of this enhancement is largely dependent on the particle geometry. From the in situ SPR kinetics measurements of nanoparticle adsorption, it is observed that the shape of Au nanoparticle has a critical role in the kinetics of signal change. These results indicate that the selection of nanoparticle shape improves both sensitivity and kinetics of SPR.

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Figure 1. Representative TEM images of as-made spherical Au nanoparticle (left) and rodlike nanoparticle (right).



Figure 2. *In situ* SPR measurements for the deposition of spherical Au nanoparticles and schematic representation of multi-layer assembly (bottom).



Figure 3. *In situ* SPR measurements for the deposition of rod-like Au nanoparticles and the corresponding scheme (bottom).