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Plasmonic applications of lossy transition metals

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1. Introduction

In the field of plasmonics, noble metals such as Au or Ag have been frequently utilized due to their strong plasmon resonance features arising from the Drude-like property of sp-electrons. On the other hand, transition metals such as platinum-group metals (PGMs) are usually not considered as a plasmonic material because of their weak plasmon resonances damped by localized d-electrons. It is, however, known that transition metals exhibit various unique functionalities due to the d-electrons. Therefore, if such functionalities are combined with plasmonic nano-systems, plasmonics may be extended to various research fields and applications.

2. Plasmon enhanced spectroscopy on Pt surfaces

Surface enhanced Raman scattering (SERS) is recognized as a powerful vibrational spectroscopic method for studying molecular adsorbates on a metal surface. However, this technique is applicable only on noble metal surfaces with nanometric structures because the signal enhancement is induced by excitation of surface plasmons. In the fields of electrocatalysis and surface science, SERS observations on lossy PGMs with atomically defined surfaces to develop highly active electrocatalysts; PGMs often exhibit high catalytic activities for various electrochemical reactions and their activity is known to be sensitive to the surface structure on the atomic scale. SERS observation on an atomically defined model surfaces can be possible when sphere-plane type nano-gap structures are formed on a single crystalline metal surface. Using this technique, we have reported that SERS spectra of molecular adsorbates are clearly dependent on crystal orientations on both Au [1,2] and Pt electrodes [3], which information are easily hindered in conventional SERS studies on roughened metal surfaces. The spectral difference is not only due to the difference in the adsorption geometry but also due to the difference in the electronic structure at metal-molecule interfaces.

Figure 1 shows SERS spectra of self-assembled monolayer of 4-chlorophenyl isocyanide model molecules, measured on Pt single crystal surfaces of various orientations [3]. There appear three types of adsorption geometries having different frequencies of νNC vibrations: atop, bridge, and hollow configurations. The origin of the crystal orientation dependence of the adsorption configuration was well explained by considering the atomic arrangements of these surfaces. Moreover, the frequency of νNC(atop) was dependent on these surfaces. This peak

shift was well explained by the difference of the d-band center among these surfaces. This result clearly indicates that SERS can be a powerful tool even on lossy PGM surfaces especially when their surfaces are atomically defined.
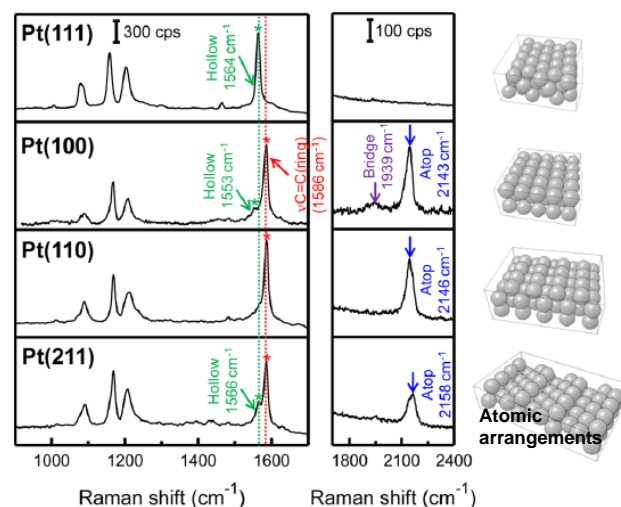

Figure 1. Crystal orientation dependence of SERS spectra of phenyl isocyanide monolayers, measured on Pt single crystals with various orientations.

3. Tuning of plasmon resonances using hydrogen uptake into Pd nanostructures

Pd can absorb hydrogen into the crystal lattice, resulting in formation of palladium hydride, PdH. Since optical constants of PdH are different from those of Pd, one can expect that plasmon resonance energy can be tuned by hydrogen uptake [4]. In principle, dynamic tuning of plasmon resonances is quite difficult because the resonance energy is characterized by size and shape of metal nanostructures. We have fabricated Pd-Ag layered nanostructures, which exhibit strong resonance intensity and large tunability simultaneously. Moreover, photo-induced variation of plasmon resonances will be demonstrated on the basis of the hydrogen-induced tuning.

References

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