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Surface-enhanced Raman spectroscopy at non-plasmonic platinum electrodes using long-range surface plasmon modes

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1. Introduction

Surface-enhanced Raman scattering (SERS) is recognized as a powerful spectroscopic method for observing metal/dielectric interfaces such as electrode/electrolyte interfaces, due to the high chemical sensitivity and surface selectivity. However, the applicability of this technique is limited by the degree of the local field enhancement at the interface via excitation of surface plasmons. Thus, coinage metals such as Au and Ag are normally utilized not only for SERS but also for other plasmonic applications because of their Drude-like nature of sp-conduction electrons. On the other hand, platinum group metals (PGMs) have not been used for plasmonic applications because surface plasmons are strongly damped by their localized d-electrons near the Fermi level. Nevertheless, many efforts have been made to increase SERS sensitivity at PGM surfaces because PGMs are one of the most interesting metals with various functionalities such as electrocatalysis; vibrational observation of chemical reactions at a PGM surface should advance the development of highly active catalysts. In order to gain more intensity at highly damping PGM surfaces, the so-called “intensity borrowing” is a common method; for example, when a large number of Au nanoparticles are deposited on a PGM surface, Raman scattering signals are largely enhanced by the sphere-plane type coupled plasmon modes [1]. However, such a nanostructure may influence mass transport, selectivity, and reactivity of electrochemical reactions. For spectroelectrochemistry, it is essential to reduce the plasmon damping without suffering from such a nanoscale effect. In this work, the attenuation of surface plasmons at highly damping Pt surface is reduced using a symmetric slab mode, which is a strongly coupled surface plasmons excited at both interfaces of a thin metal film [2].

2. Results and discussion

Here, we focus on the Kretschmann-type prism-coupled plasmon excitation, which is suitable for electrochemistry. Since the electromagnetic enhancement of SERS intensity is nearly proportional to the forth-power of the local field enhancement, the propagation length of surface plasmons critically determine the enhancement factor in this configuration. In the conventional configuration, surface plasmons are excited at a single-interface of the metal thin film. However, when a metal thin film is bounded on both sides by same dielectrics, surface plasmons can be excited at both interfaces, resulting in creation of two slab modes: short-range surface plasmon (SRSP) and long-range surface plasmon (LRSP) modes. Fig. 1 shows a theoretical calculation of the reflectance at a Pt thin film under the prism-coupled double-interface configuration. A sharp reflectance dip is clearly observed at around the incident angle of 68 degree, which corresponds to the LRSP resonance. This coupled plasmon mode in the double-interface configuration leads to a substantial enhancement of local fields due to the prolonged propagation. Indeed, we experimentally confirmed that Raman scattering signals were significantly enhanced at Pt/aqueous solution interfaces using this strategy.

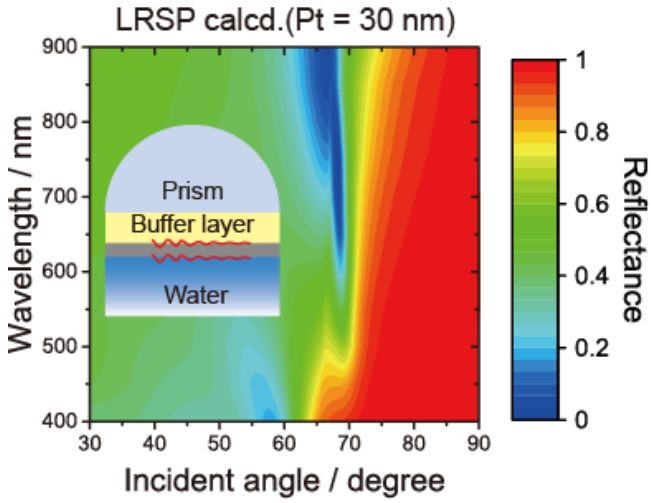

Fig.1. Simulated two-dimensional maps of prism-coupled LRSP resonances at a Pt thin film bounded by solution and buffer layer. The refractive indices of prism, buffer, and solution are 1.46, 1.34, and 1.34, respectively. The thickness of the buffer and Pt layers are 500 and 30 nm, respectively.

3. Conclusion

The strong coupling of plasmon modes enables us to use non-plasmonic PGMs for plasmonic applications such as SERS.

References

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