

Electrochemical SERS study on well-defined catalytic metal surfaces using hybridized plasmon modes

Katsuyoshi Ikeda,^{a,b} Jian Hu,^a and Kohei Uosaki^{a,c}

^aDivision of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

^bJapan Science and Technology Agency, PRESTO

^cInternational Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan

Surface enhanced Raman scattering (SERS) spectroscopy is normally conducted at a nanostructured surface of coinage metals. This limits application of SERS technique to studying electrocatalyst despite the potential of this technique for in-situ observation. Recently, our group¹⁻⁶ and Prof. Tian's group⁷ have reported on SERS observations on well-defined single crystalline metal surfaces including non-SERS-active Pt-group metals. In these experiments, Au nanoparticles (Au-NPs) are utilized to excite surface plasmons on a smooth metal surface. As a result of plasmon hybridization between Au-NPs and a metal electrode surface, highly localized plasmon modes are built even on non-SERS-active catalytic metal surface, leading to large enhancement of Raman scattering intensity on the electrode surface. Here, this technique is called gap-mode SERS. In the present work, we demonstrate SERS observations of adsorption geometries of arylisocyanides on various catalytic metal monolayers formed on Au(111) electrodes.

Single crystal beads of gold, platinum, and palladium were obtained using the Clavilier method. The (111) facets of these beads were utilized for SERS observation. Pd-modified Au(111) was electrochemically prepared using the underpotential deposition (UPD). Pt-modified Au(111) was obtained by galvanic replacement of Cu-UPD monolayers on Au(111) with Pt²⁺ ions. Pt-Ru alloy modification was conducted using heat decomposition of Pt-Ru bimetallic complex on Au(111). As a model Raman scatterer, 4-chlorophenylisocyanide (CPI) and 4-methylphenylisocyanide (MPI) were utilized to form self-assembled monolayers (SAMs) on these metal surfaces. SERS measurements were conducted using a home-built Raman microscope with a 632.8-nm He-Ne laser light source after Au-NPs were physisorbed on top of the SAMs.

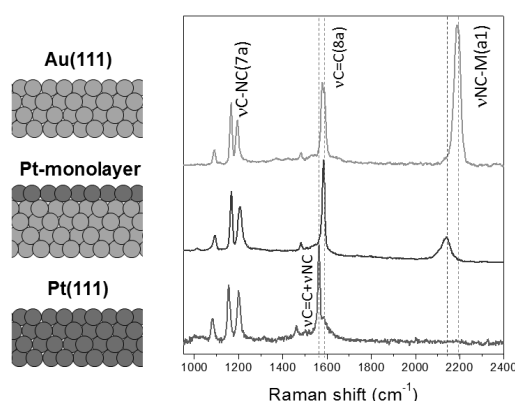


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Figure 1 shows gap-mode SERS spectra of CPI-SAMs on Au(111), Pt_{ML}/Au(111), and Pt(111). The dominant adsorption configuration of CPI was assigned to on-top on Au(111) and three-fold hollow on Pt(111). For Pt_{ML}/Au(111), the obtained spectrum clearly showed that the preferential adsorption was rather similar to that on Au(111), suggesting that the electronic structure of Pt monolayer, which interacts with Au(111), is different from that of bulk Pt.

Figure 2 shows gap-mode SERS spectra of MPI-SAMs on Pt-Ru/Au(111). Because of the spatial inhomogeneity of the Pt-Ru alloy layer, the spectral feature was dependent on the measurement position; typical examples are shown in (a) and (b). In the previous study, we have confirmed that the Pt-Ru alloy layer on Au(111) consisted of monoatomic island structures with the coverage of around 50%. In both spectra, two types of on-top configurations on Au(111) and Pt_{ML}/Au(111) are found at around 2200 and 2150 cm⁻¹, respectively. For Fig. 2(a), there exists an additional νNC mode at 2080 cm⁻¹, which is assigned to on-top adsorption on Ru site. Moreover, one can notice three additional peaks, marked by arrows, which are due to the charge transfer resonance. The result indicates that the electronic structure is significantly different between (a) and (b).

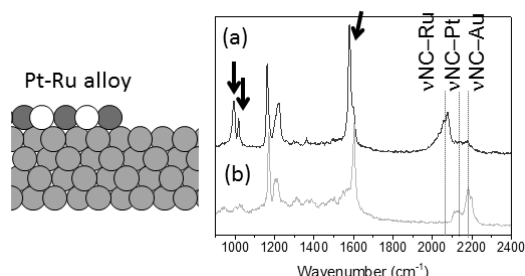


Figure 2: Gap-mode SERS spectra of MPI-SAMs on Pt-Ru/Au(111), measured at different positions, (a) and (b).

In summary, SERS spectra of molecular adsorbates can be measured on atomically controlled metal surfaces. We will also discuss the contribution of step-terrace structures to the adsorption geometry and electrochemical behavior of the molecules on these electrodes.

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