Electrochemical SERS study on well-defined catalytic metal surfaces using hybridized plasmon modes  
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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 group a,b and Prof. Tian’s group 1 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. Pt-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 Pt ions. Pt-Ru alloy modification was conducted using heat treatment of Au-NPs on Au(111) and Pt-Ru alloy modification was conducted using heat treatment of Au-NPs on Au(111) and 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 controbution of step-terrace structures to the adsorption geometry and electrochemical behavior of the molecules on these electrodes.

References: