

Supporting Materials:

In order to reduce the interference of the bulk solution signal to the surface signal, a Raman instrument with confocal configuration was used in this study. The laser power on the sample is about 5 mW. The spectra given in Figure 1 were obtained by subtracting the spontaneous Raman spectrum of the measuring solution.

The applied current or potential during the roughening and SERS measurements were controlled by a PAR 173 potentiostat (EG&G). Square-wave form was initiated by a GFG-8016G function generator (Good Will Instrument, Co. Ltd.). Cyclic voltammograms were recorded with a CHI631A electrochemical workstation (CH Instruments, Inc.).

A Rh rod (diameter, 1 mm) of 99.9% purity (Aldrich) was purified by cycles of melting the rod and dissolution of the impurities in aqua regia until no "cloud" can be found in the bead. The bead is then sealed into the Teflon sheath and polished to form the Rh working electrode of disk shape. The final diameter of the rhodium surface is about 2.2 mm. The Rh electrode with reasonably good SERS activity could be obtained by the following method in 0.5 M H₂SO₄: First, the smooth Rh electrode was electrochemically cleaned by potential cycling between -0.25 to +0.8 V at a rate of 0.5 V s⁻¹; next, a pulsed current with the cathodic and anodic current densities of -950 and +1600 mA cm⁻² and a frequency in the range of 200 to 800 Hz was applied to the electrode for a desired time (a typical time is ca. 2 min); afterward, the electrode was reduced at -0.2 V; and finally, it was stabilized by potential cycling using the same condition as the first step.

So far we still have not been able to develop an ideal roughening method for obtaining SERS from massive Ru electrodes. Therefore, in this study, we generated the SERS Ru electrode by electrodeposition of Ru over a massive Ru electrode. After polished with Al₂O₃ down to 0.3 μm till mirror finish and cleaned with sonication, the massive Ru electrode was electrochemically cleaned using the same procedure as that for Rh. Then the well-cleaned Ru electrode was controlled at -0.3 V for deposition in 5mM RuCl₃ + 0.1 M HClO₄ for 2000 s. An electrochemical stabilization treatment was applied to this electrode using the same procedure as described in the first step until reproductive cyclic voltammograms were obtained. The increase in the surface area is about 400 for Ru and 2 for Rh compared with their geometric areas.

In the present studies, a large platinum ring served as the counter electrode. The reference electrode was a saturated calomel electrode (SCE); all potentials are given with respect to SCE. All chemicals used were analytical grade reagents and the solutions were prepared using Milli-Q water.

The solution used in the study of pyridine adsorption contains 0.1 M NaClO₄ and 0.01 M pyridine. The spectra acquisition time is 20s. The experiment was done by moving the potential negatively from the open circuit potential. In the case of SCN⁻ study, the solution is 0.01 M NaSCN + 0.1 M NaClO₄ and the acquisition time is 200 s. The experiment was done by moving the potential positively.

The averaged surface enhancement factor is defined as $SEF = \frac{I_{surf} / N_{surf}}{I_{bulk} / N_{bulk}}$. I_{surf} stand for the intensity of

adsorbate such as SCN⁻ and I_{bulk} for the same molecule recorded from the solution phase. Both of the intensity can be directly obtained from the experiment, for example, $I_{bulk} = 280 \text{ cps.cm}^{-1}$ and $I_{surf} = 51 \text{ cps.cm}^{-1}$ when the applied potential was hold at -1.2 V. N_{surf} is the number of the surface adsorbed SCN⁻ within the laser illumination spot, which can be expressed as $\sigma A R$, where A is the surface area of the illumination spot, σ the average area occupied by one adsorbed SCN⁻, and R the roughness factor of the Rh electrode. In the present study R was obtained experimentally as 2.1. σ was calculated based on the adsorption model of a saturated monolayer of SCN⁻ on Rh (111) surface. As the radius of the Rh atom is 1.83 Å, $\sigma = \frac{1}{2} \times (2 \times 1.83 \times 10^{-10})^2 \text{ m}^2$. N_{bulk} is the molecule number of the solution SCN⁻ in the laser illumination volume. For a confocal Raman microscope, it is relatively complicate to get this value. We have described the calculated idea and routine in our previous paper (*Surf. Sci.* 406 (1998) 9-22). Accordingly we can obtain $SFE = 315$. The value is close to that we obtained from the CO system (ca. 500). Overall, the surface enhancement factor of UV-SERS for the small molecules adsorbed on the Rh electrode is about 2 orders of magnitude under the excitation line of 325 nm.