

New Strategies for Surface-Enhanced Raman Scattering at Transition-Metal Interfaces: Thickness-Dependent Characteristics of Electrodeposited Pt-Group Films on Gold and Carbon

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The surface-enhanced Raman scattering (SERS) properties of rhodium films electrodeposited onto a SERS-active gold substrate are examined as a function of overlayer thickness, using carbon monoxide and thiocyanate as chemisorbate probes in aqueous solution. Although the adsorbate Raman signals obtained for ultrathin (≤ 10 monolayers, ML) Rh layers emanate from the gold template, a significant or even dominant SERS component for thicker films is identified as arising instead from the transition-metal overlayer *itself*. The latter contribution was diagnosed and characterized from similar experiments undertaken using SERS-inactive gold and carbon substrates, and from the observation of comparable Raman enhancements obtained with green (514.5 nm) as well as red (632.8 nm) excitation. While the surface enhancement factors for these layers, of the order of 10^3 , are markedly less than those obtained for ultrathin films on SERS-active gold, the signals even for very weak Raman scatterers (such as adsorbed hydrogen) on palladium and platinum, as well as rhodium, electrochemical interfaces are detectable with a confocal Raman spectrometer. The broad-based potential utility of such films for the detailed vibrational characterization of transition-metal ambient interfaces is also pointed out.

Introduction

Over the last twenty years, surface-enhanced Raman scattering (SERS) has become an increasingly important means of characterizing adsorbates on metal surfaces in ambient, especially electrochemical, environments.¹ While the unique surface selectivity, sensitivity, and liberal selection rules of SERS enable remarkably rich vibrational spectra to be obtained for a myriad of adsorbates, its apparent restriction largely to the “coinage metals” (Cu, Ag, Au) has limited severely the breadth of practical chemical applications. Given the key importance of transition metals in interfacial chemistry, catalysis, and materials science, it is of great interest to elucidate means by which substantial surface Raman enhancements can be imparted to such materials.

Both our laboratories have been devising strategies toward this goal. Some time ago, the Purdue group found that ultrathin (2–5 monolayer, ML) electrodeposits of Pt-group metals on mildly roughened (SERS-active) gold produces intense SERS for chemisorbates bound to the overlayer metal.² This “overlayer-film” strategy is based on the expectation from electromagnetic theory that substantial Raman enhancements should be engendered even for molecules separated spatially from a SERS-active substrate,^{3,4} although the signals should attenuate sharply with increasing “spacer” film thickness.⁵ A limitation of this procedure originally was that the presence of exposed gold sites (“pinholes”) can trigger spectral and electrochemical interferences from the underlying substrate.² Recently, however, modified electrodeposition procedures were devised, yielding

essentially pinhole-free films of Pd, Rh, Pt, and Ir that are nonetheless sufficiently thin to exhibit near-optimal SERS characteristics.^{6,7} The Xiamen group have instead explored strategies aimed at generating SERS for the transition metals *themselves*.^{8–11} Specifically, creation of suitable surface roughness by repetitive potential cycling,⁸ chemical etching,⁹ or electrodeposition of very thick ($\sim 100 \mu\text{m}$) metal films¹⁰ was found to yield Raman scattering enhancements.¹¹ The observed signal increases beyond those expected for the adsorbate on a planar surface can be attributed in part to large “roughness factors”, R , for which, at least for electrochemically roughened Pt,^{8b} typically $R \sim 20$ –200. However, the measured signals for adsorbed pyridine are also indicative of substantial increases in the Raman scattering cross-sections (the per molecule “surface enhancement factor”, SEF), so that $\text{SEF} \approx 10$ –100; i.e., relatively weak yet significant SERS is evident.^{8b} While these surface enhancements are much smaller (by at least 10 – 10^2 fold) than for thin Pt-group overlayers on SERS-active gold, the signals are nonetheless readily detectable using a confocal Raman spectrometer, as employed by the Xiamen group.^{8–11}

The study described herein was initiated with the goal of examining the SERS characteristics of the Pt-group films utilized by the Purdue group as a function of overlayer thickness, employing the Xiamen spectrometer. The very high sensitivity of this instrument enables a range of thicker metal films to be examined, also offering comparisons with the SERS-active transition-metal surfaces explored by the Xiamen group. The test overlayer system selected initially was rhodium with carbon

monoxide as the chemisorbate probe. This choice was prompted by earlier studies by the Purdue group;⁶ CO constitutes a simple yet environment-sensitive adsorbate whose surface concentrations can be determined by simple faradaic means.¹² The weak Raman-scattering properties of CO also provide a stringent test of the practical applicability of SERS to transition metals, especially given the archetypical importance of this chemisorbate in surface vibrational spectroscopy. Spectra were also obtained for adsorbed thiocyanate and atomic hydrogen, the former being utilized to obtain SEF estimates for the overlayer surfaces (vide infra).

Intriguingly, the results indicate a progressive transition from SERS arising from the gold substrate to that emanating instead from the rhodium overlayer itself as the film thickness is increased over the range 5–200 ML. This deduction was made from Raman measurements for Rh films deposited on SERS-inactive smooth gold and glassy carbon substrates, along with variations in the excitation wavelength. Some results are also noted here for Pd and Pt films. Aside from providing information on the SERS properties intrinsic to the transition-metal as distinct from the coinage-metal substrate, the findings underscore the practical utility of Raman spectroscopy for the vibrational characterization of ambient transition-metal interfaces.

Experimental Section

Details of the experimental arrangements used for electrochemical SERS at Purdue and Xiamen are given in refs 13 and 8, respectively. The former utilized a SPEX Triplemate spectrometer with a CCD detector, and utilized 647.1 nm Raman excitation. The latter employed a LabRam I confocal microprobe system (Dilor Inc.), with 12 mW excitation either at 632.8 or 514.5 nm. The protocol used to prepare the rhodium films on SERS-active gold is outlined in ref 6a. The same constant-current electrodeposition procedure, at 0.1–0.2 mA cm⁻² from 20 mM RhCl₃ in 0.1 M HClO₄, was also utilized on smooth (mechanically polished) gold and glassy carbon disk substrates. The Pd and Pt films were prepared as noted in ref 6a. The gold and carbon electrodes were 0.1 and 0.2 cm² disks, respectively, sheathed in Teflon. All electrode potentials are reported versus the saturated calomel electrode (SCE).

Results and Discussion

Of central interest here are the Raman spectral intensities for saturated CO adlayers formed on rhodium overlayers in CO-sparged 0.1 M H₂SO₄ as a function of film thickness. The thickness, in equivalent monolayers (ML), was estimated from the cathodic deposition charge by presuming layer-by-layer hexagonal atomic packing as noted in refs 6a and 7b (footnote 20). (Limitations to this assumption are considered below.) As in ref 6a, progressively larger film thicknesses were examined by depositing sequentially the desired amount, the adsorbed CO being removed by a potential cycle in 0.1 M H₂SO₄ between -0.2 and 0.6 V. Essentially the same results were obtained if a given film thickness was formed incrementally in this fashion or by a single deposition step.

A pair of typical SER spectra in the C–O stretching (ν_{CO}) frequency region for 5 and 40 ML Rh films on electrochemically roughened (SERS-active) gold at 0 V are shown in Figure 1A. The laser excitation was at 632.8 nm, with a 30 s spectral acquisition time. (Other spectral measurement details are as described in ref 8.) The red excitation wavelength is well-known to engender intense SERS on gold surfaces. A strong ν_{CO} band at 2045 cm⁻¹ and a weaker feature at ca. 1910 cm⁻¹ are evident, due to atop and bridging CO, respectively.¹⁴ These bands are

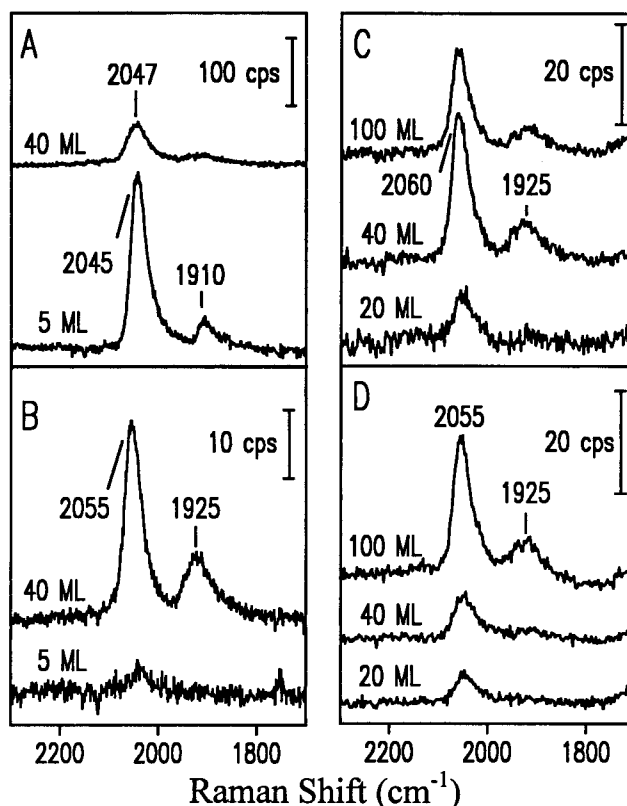


Figure 1. Representative surface Raman spectra in the C–O stretching region for saturated CO adlayers on electrodeposited rhodium films of thickness indicated (in monolayers, ML) at 0 V vs SCE in CO-saturated 0.1 M H₂SO₄ on (A) roughened (i.e., SERS-active) gold; (B) smooth gold, both at 632.8 nm excitation; (C) smooth gold; and (D) glassy carbon, both at 514.5 nm excitation. Spectral acquisition time are 30 s for A, and 90 s for B, C, and D. Note that cps represents counts per second.

accompanied by Rh–CO stretching ($\nu_{\text{Rh–CO}}$) vibrations at 445 and (as a shoulder) 350 cm⁻¹, respectively^{6a,14} (not shown). The ν_{CO} band frequencies vary significantly (by 10–20 cm⁻¹) with film conditions, especially for increasing thickness, due undoubtedly to differences in the microscopic Rh surface structure. (Note that comparable ν_{CO} frequency variations are seen at a given potential for saturated CO adlayers on the three low-index rhodium surfaces by using in-situ infrared spectroscopy.¹⁵) Identical SER spectra were obtained over the potential region, -0.2 to 0.2 V, lying between cathodic hydrogen evolution and CO electrooxidation, except that the ν_{CO} frequencies blueshift, as usual,¹⁵ by 30–40 cm⁻¹ V⁻¹ toward higher potentials.

As exemplified by Figure 1A, the SERS band intensities are seen to decrease monotonically with increasing film thickness. A semilogarithmic plot of the atop ν_{CO} band intensity, I , versus the Rh film thickness, d , on SERS-active gold as obtained in Xiamen is shown as the filled circles in Figure 2. For comparison, a typical set obtained for ostensibly the same electrochemical conditions at Purdue is also shown (crossed squares). Both data sets are normalized to the signal intensities, I_0 , for the thinnest, 5 ML, film. While the latter data set exhibits a somewhat larger log $I - d$ dropoff, this is probably due (at least partly) to a more optimal preparation of the SERS-active substrate yielding larger I values for the ultrathin films. (The Au SERS activity is notoriously sensitive to the precise roughening protocol.¹⁶) While the Raman intensities are only reproducible typically to ca. ± 25 –50%, the log I vs d plots shown in Figure 2 are typical “average” results from several

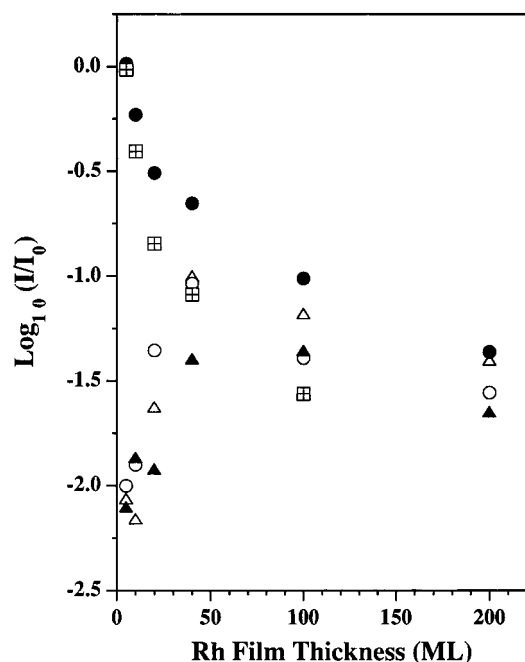


Figure 2. Semilogarithmic plots of Raman intensity, I , of atop ν_{CO} band for adsorbed CO on Rh overlayers as a function of equivalent film "thickness" (monolayers, ML). Key to substrates and excitation wavelengths: filled symbols, roughened (SERS-active) gold; open symbols, smooth (SERS-inactive) gold; circles, 632.8 nm, triangles, 514.5 nm. Crossed squares refer to data on roughened gold substrates obtained instead at Purdue. (see text).

replicate experiments. Interestingly, the $\log I - d$ slope decreases progressively toward higher d , indicating that the incremental degree of SERS attenuation becomes progressively milder for thicker films. This finding is surprising on the basis of simple EM predictions and some experimental observations.^{3,5,6a}

An intriguing as well as unexpected source of the mild $I - d$ attenuations observed for thicker Rh films, say $d \geq 40$ ML, became evident upon performing corresponding Rh thickness-dependent Raman measurements on a *smooth* (i.e., mechanically polished) gold substrate. Unlike electrochemically roughened gold, the smooth substrate should be virtually SERS-inactive. Indeed, Raman spectra for ultrathin Rh films (≤ 10 ML) on smooth gold yield barely detectable ν_{CO} signals (bottom spectrum, Figure 1B). However, increasing the Rh thickness yielded sharply enhanced Raman signals, the intensities peaking at about 50 ML before tailing off more mildly toward larger d values, as illustrated by the open circles in Figure 2. Comparison between the corresponding I values obtained for the Rh films on roughened and smooth gold (filled versus open circles, Figure 2) shows that the latter converge toward the former intensities for $d \geq 50$ ML. This suggests that the SERS activity of the gold substrate, while clearly responsible for substantial (at least 100-fold) Raman enhancements with the ultrathin Rh films, provides a decreasingly important, and even minor, contribution to the Raman signals observed for relatively thick (say 100–200 ML) overlayers. (Note that the degree of roughening engendered for the SERS-active gold substrate itself yields only minor changes in R , less than 1.5–2-fold, compared to the "smooth" surface.^{6a,16}) Consequently, then, it appears that a major and possibly even the dominant contribution to the enhanced SERS signals under these conditions arises from the Rh film *itself*, rather than from the underlying gold template.

Persuasive evidence confirming this contention was obtained from two further types of measurements. First, corresponding

Rh thickness-dependent Raman spectra were obtained for CO on both roughened and smooth gold as before, but using 514.5 nm excitation. In contrast to 632.8 nm light, such green excitation is known to yield only weak or even negligible SERS on gold,¹⁷ thereby essentially eliminating the "substrate" contribution to the surface Raman signals. Significantly, while readily detectable ν_{CO} signals were obtained, the $I - d$ behavior using 514.5 nm excitation was found to be *essentially the same* on smooth and roughened gold substrates. Examples of ν_{CO} spectra for three film thicknesses on smooth gold are shown in Figure 1C. These data for smooth and roughened gold, plotted as open and filled triangles in Figure 2, are seen to be closely similar to the $\log I - d$ behavior observed on smooth gold using 632.8 nm excitation. Note that the I values for green and red excitation refer to equal laser intensities and spectrometer throughput. This finding therefore indicates that the $I - d$ dependence observed both with 514.5 and 632.8 nm excitation on smooth gold, and also with the former on roughened gold, arises entirely from a Raman enhancement mechanism associated with the Rh overlayer.

The second piece of evidence along these lines is obtained from corresponding film thickness-dependent measurements on glassy carbon. This substrate was chosen in view of its inability to engender SERS, along with previous Raman measurements by the Xiamen group for thicker electrodeposited transition-metal films on carbon.¹⁰ Representative Rh thickness-dependent ν_{CO} spectra are shown using 514.5 nm excitation on carbon in Figure 1D, to be compared with the corresponding data on smooth gold given in Figure 1C. Comparable ν_{CO} spectra were obtained on carbon and gold substrates, although the Raman intensities exhibit a slightly different dependence on the overlayer thickness, the signal intensities on carbon approaching a plateau toward large d values (100–200 ML). While similar results were obtained on carbon using 632.8 nm light, the d -dependent Raman intensities exhibit instead a broad maximum around 100 ML. The observed variations in the Raman intensity of the $\nu_{\text{Rh-CO}}$ modes with Rh film thickness, the substrate, and the excitation wavelength were all found to be essentially the same as for the ν_{CO} chromophore.

Consequently, then, it is clear that the Rh overlayer itself can engender readily detectable chemisorbate Raman signals that, although being at least ca. 20-fold weaker than the optimal levels induced by the SERS-active gold substrate with red excitation, are also present at comparable levels when using 514.5 nm excitation. It is instructive to obtain at least approximate estimates of the surface enhancement factors, SEF, that characterize the Rh films. This requires the use of chemisorbates for which corresponding bulk-phase Raman spectra can also be obtained. Although not feasible for CO, thiocyanate provides a suitable small-molecule chemisorbate for this purpose.^{8a,18} With this objective in mind, Raman spectra were obtained for saturated NCS^- layers on the rhodium overlayers under the same conditions as described above for CO. The electrolyte used was typically 10 mM $\text{NaNCS} + 0.1$ M NaClO_4 . Illustrative spectra in the C–N stretching (ν_{CN}) region for 40 and 100 ML Rh films on smooth gold using 514.5 and 632.8 nm excitation are shown in Figure 3A and B, respectively. While several other thiocyanate vibrational features are evident in SERS,¹⁸ the ν_{CN} band is the most characteristically environment-sensitive mode for our purpose. The dependencies of the ν_{CN} band intensity on the variables already considered (i.e., Rh film thickness, smooth versus roughened Au and C substrates, and excitation wavelength) were again closely comparable to those observed for chemisorbed CO.

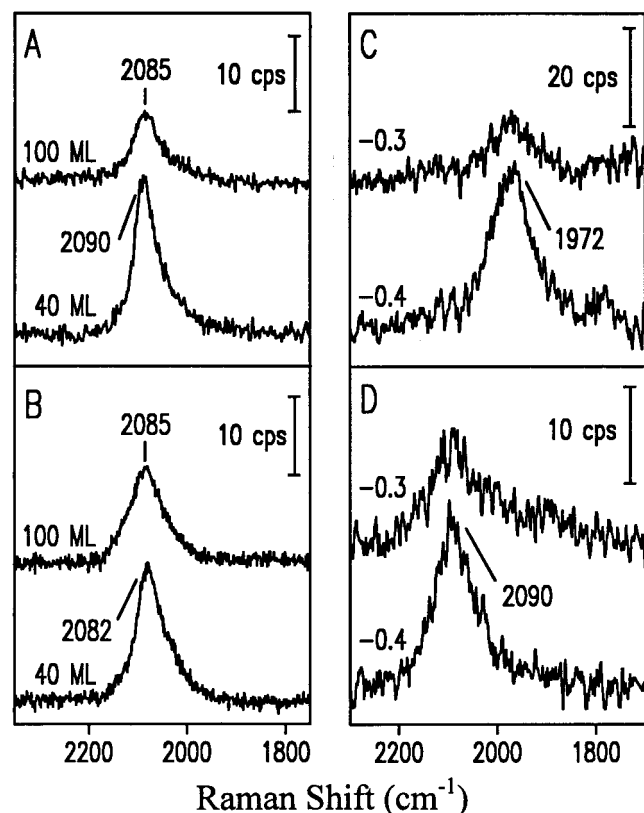


Figure 3. (A, B) Representative surface Raman spectra in the C–N stretching region for saturated thiocyanate adlayers on 40 and 100 ML rhodium films on smooth gold at -0.3 V vs SCE in 10 mM NaNCS + 0.1 M NaClO₄, using (A) 514.5 nm, (B) 632.8 nm excitation, both with acquisition time = 90 s. (C, D) Surface Raman spectra in the metal–H stretching region for adsorbed hydrogen on (C) Rh and (D) Pt film on roughened (i.e., SERS-active) gold in 0.1 M H₂SO₄ at indicated electrode potentials. Films were ca. 5 ML thick, with 632.8 nm excitation.

Values of the surface enhancement factor, SEF, for the saturated thiocyanate adlayers were deduced by comparing these SERS data with corresponding normal Raman ν_{CN} intensities for thiocyanate solutions (0.01 – 0.5 M), largely as described in ref 8b. Briefly, the surface concentration for the (saturated) thiocyanate adlayers on rhodium was presumed to be 8×10^{14} ions cm^{-2} , as derived from packing density considerations. As usual, the SEF values are defined as the ratio of the Raman cross sections for the adsorbed versus the free solution-phase species. If the metal surface is considered to be planar (i.e., $R \approx 1$, vide infra), we obtain the following SEF values with adsorbed thiocyanate: For 5 and 40 ML Rh on roughened Au, $\text{SEF} = 5 \times 10^4$ and 4×10^3 , respectively, with 632.8 nm excitation; and $\text{SEF} = 50$ and 1.2×10^3 , respectively, for 514.5 nm excitation. As noted in ref 8b, there is some justification for including the surface roughness factor in the SEF calculation, hence accounting for the anticipated larger number of chemisorbate molecules available for Raman scattering, although it is unclear what fraction (or type) of the additional surface sites actually contribute to the observed SERS signals. This adjustment is unimportant for the ultrathin Rh films on roughened gold, for which $R \leq 2$; i.e., the surfaces approach microscopic planarity. However, voltammetric measurements for the thicker films indicate that R increases significantly with increasing d , by ca. 4-fold and 10-fold for the 40 and 200 ML Rh films, respectively. (These R values were deduced most directly from the anodic charge contained under voltammograms for oxidizing

saturated CO adlayers, following N₂ purging to remove solution CO).¹⁹ Taking such surface roughness into account in the enhancement calculations will lower the above “formal” SEF estimates by the factor R . Nevertheless, in either case the SEF estimates for the Rh overlayers under conditions where the gold substrate contributes little (or nothing) to the observed surface enhancement are clearly substantial, for example, at least ca. 500 for 40 ML films on smooth Au at 632.8 nm. It is therefore evident that the present Rh films yield remarkably large Raman enhancements.

Given the obvious practicality of the Rh overlayer surfaces as Raman-active electrochemical substrates, it is of interest to ascertain if the approach can also be utilized with other transition metals, together with exploring the diversity of adsorbates whose in-situ vibrational properties are now accessible by this means. Such studies are underway. Electrodeposited palladium films on smooth gold were found to yield readily measurable Raman signals for chemisorbed CO, indicating that surface enhancements can arise from Pd overlayers themselves in a fashion similar to rhodium. Some preliminary measurements have also been undertaken for atomic hydrogen adsorbed on thin Rh, Pd, and Pt overlayers, following earlier Raman studies for this system on roughened Pt electrodes by the Xiamen group.^{8c,d} Examples of Raman spectra obtained in the metal–H stretching region on Rh and Pt films in 0.1 M H₂SO₄ are shown in Figure 3C and D, respectively. Both these films, on SERS-active gold, are sufficiently thin (ca. 5 ML) so to yield near-optimal Raman activity. Even though the acquisition times are relatively short (20 and 40 s on Rh and Pt, respectively), metal–H vibrational bands are readily discernible at electrode potentials close to the onset of cathodic H₂ evolution. Weaker yet still detectable metal–H bands were obtained for thicker films, where the transition metal provides a substantial contribution to the SERS. While similar to those reported earlier on roughened Pt, the Raman signals in Figure 3D are again markedly stronger, reflecting again the near-optimal SERS properties of the ultrathin films on roughened gold.^{6a} This emphasizes further the value of the ultrathin transition-metal films when combined with high-sensitivity Raman instrumentation for readily obtaining surface vibrational data even for very weak Raman scatterers.

It remains to consider likely reasons for the remarkable surface enhancements observed here for rhodium using both red and green excitation. Although the indicated occurrence of SERS for transition metals on the basis of the electromagnetic (EM) model might appear surprising, earlier calculations along these lines predicted substantial enhancements for larger (ca. 100 nm) Pt-group particles, typically 10^2 or even greater, with green and especially red excitation.²⁰ Possibly related surface enhancements of second harmonic generation have been reported on Pt surfaces.²⁴ While it is certainly feasible that “chemical”, especially adsorbate/surface charge transfer (CT) resonance, mechanisms may also contribute to the present SERS, the observed ability to engender readily measurable Raman signals for chemically diverse adsorbates at multiple excitation wavelengths argues against the dominant importance of such effects.^{21,22} Particularly in the context of EM mechanisms, it would obviously be desirable to ascertain the size and shape of the transition-metal particles responsible for SERS. Scanning electron microscopy of the present Rh films reveals the extensive presence of roughness features around 100 – 200 nm in diameter. Given the availability of methods for preparing arrays of transition-metal particles using lithographic techniques,²³ Raman experiments utilizing controlled-geometry surface morphologies should be feasible.

It is now clear that a combination of the present surface electrodeposition tactics with sensitive new-generation Raman spectrometers offers a potent and increasingly versatile means of extracting detailed vibrational information for adsorbates at electrochemical and other ambient transition-metal interfaces. The widening range of surface chemical applications having made feasible by such tactics, involving reactive as well as stable adsorbate systems, appears destined to exert an important impact in interfacial science.

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