

Transition Metal-Coated Nanoparticle Films: Vibrational Characterization with Surface-Enhanced Raman Scattering

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There is currently considerable interest in the size-dependent chemical, physical, and structural properties of metal nanoparticles, triggered in part by specific applications in catalysis, sensors, and microelectronics. Late transition metals are of great significance in chemical catalysis;¹ for example, Pt-group nanoparticles in the size range 2–10 nm, employed commercially in fuel cells and related applications, exhibit interesting variations in electronic² and coordinative³ properties. The chemistry of such systems is usefully explored by immobilizing them on surfaces, including electrodes. Surface preparative schemes of this type have been developed, in particular, for gold nanoparticles.^{4,5} The attractiveness of gold includes the ability to prepare monodispersed colloidal nanoparticles having a wide diameter range (say, 1.5 to 100 nm),⁶ along with the availability of surface-enhanced Raman scattering (SERS). We have long utilized SERS-active gold surfaces for electrochemical and related applications, exploiting the chemical inertness of this metal.⁷ One strategy utilized extensively in our laboratory is to engender SERS activity for other materials, especially Pt-group metals, by electrodepositing them as ultrathin overlayers on gold.^{8–11} These tactics have been perfected recently, whereby “pinhole-free” Pt-group films even down to 1–2 monolayers (ML) can be prepared with little interference from the underlying substrate.^{9–11} In this communication, we demonstrate how similar tactics can now be harnessed to prepare Au nanoparticle film electrodes modified with uniform Pt-group overlayers. Aside from the intense SERS observed even for weak Raman scatterers chemisorbed on larger (70 nm diameter) particles, providing us with a uniquely sensitive surface vibrational probe, the results point to the broader possibility of utilizing gold nanoparticle templates to prepare nanomaterials having widely varying size, structure, and chemical properties.

We utilize here indium tin oxide (ITO) as the electrode substrate (Delta Technologies, Stillwater, MN), enabling surface plasmon (UV–visible) absorption as well as electrochemical and SERS characterization of the nanoparticle films to be undertaken. The 70 nm gold colloids were prepared, as is conventional,¹² by heating a 1 mM solution of HAuCl₄ to 90 °C and adding 1 mM sodium citrate, then heating the solution to boiling for 20 min and cooling. (The sols are stored at 4 °C.) The average particle diameter, characterized by transmission electron microscopy, can be altered by varying the HAuCl₄ and citrate concentrations. The ITO electrodes (cleaned with aqueous ethanolamine) were modified by immersion into a solution of 3-aminopropyltrimethoxysilane (Aldrich) in 2-propanol, yielding amine-terminated surface functionalities as described in ref 4. Finally, the gold particles were immobilized onto the modified ITO surface by immersion of the latter into the sol for ca. 24 h (cf. ref 13).

Representative cyclic voltammograms obtained (at 50 mV s⁻¹) from -0.3 to 1.25 V vs saturated calomel electrode (SCE) for the resulting gold nanoparticle-modified surfaces in 0.1 M HClO₄ are shown in Figure 1 (dotted traces). The presence of a wide “double-

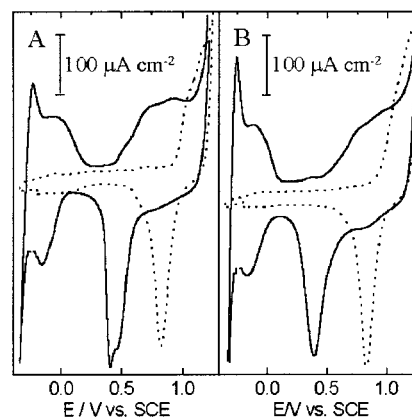


Figure 1. Cyclic voltammograms (50 mV s⁻¹) for gold nanoparticle films on ITO substrates in 0.1 M HClO₄ before (dotted traces) and after (solid traces) coating with 1 ML of (A) Pd and (B) Pt.

layer” region below ca. 0.6 V and the anodic formation and cathodic removal of oxide at higher potentials are familiar features of gold electrochemistry. The solid traces in Figure 1A,B are corresponding voltammograms obtained after the deposition of 1 ML of palladium and platinum, respectively, using essentially the procedure described in ref 11, as follows. First, an underpotential deposited (upd) monolayer of copper was formed on the nanoparticle film by holding the potential at 0 V in 0.1 M H₂SO₄ containing 1 mM CuSO₄. The electrode was then transferred to a solution of 5 mM Pd(II) or Pt(II) salt (from PdCl₂ and H₂PtCl₄, respectively) in deaerated 0.1 M HClO₄ for 10 min, then rinsed and immersed in the voltammetric cell. The procedure involves spontaneous redox replacement of the Cu layer by the Pt-metal,¹¹ similar to that described in ref 14. The value of this method is that it provides epitaxial Pt-group layers on the Au nanoparticles.

Significantly, the resulting cyclic voltammograms provide clear evidence that the Au nanoparticle surface is modified essentially entirely by the transition metals. Thus the anodic–cathodic current profile, comprised of near-reversible peaks associated with hydrogen desorption–adsorption and the irreversible features corresponding to the formation and removal of surface oxide, are characteristic of conventional Pd and Pt surfaces¹⁵ even though only monolayer-level films are apparently present (Figure 1A,B). In particular, the presence of the transition metal oxide reduction peak at ca. 0.4 V, along with the near-absence of the corresponding gold oxide feature at ca. 0.85 V, shows that few exposed Au sites remain. The further addition of Pd or Pt, either by direct electrodeposition^{9a} or by repeating the Cu upd–redox replacement cycle, removes all traces of the Au reduction peak, while the transition metal voltammetric features are altered to only a minor extent.

The charge density for H adsorption–desorption can also be used as an approximate measure of the effective nanoparticle film surface area. Typical values of ca. 300–400 μC cm⁻² (geometric surface

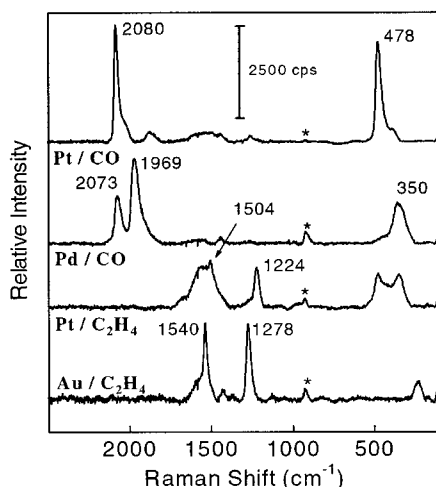


Figure 2. Representative SERS spectra for carbon monoxide and ethylene chemisorbed on Pt- and Pd-coated, and unmodified, Au nanoparticle films, as indicated (see text for details). Peaks identified by an asterisk are due to solution perchlorate. Raman excitation was at 647.1 nm.

area) were obtained, slightly larger than that observed for planar Pt-group surfaces (ca. $250 \mu\text{C cm}^{-2}$). Evidently, then, the Au nanoparticles form dense arrays on the modified ITO substrate. The surface plasmon characteristics of these films are also of interest. Briefly, the 70 nm nanoparticle films exhibit a plasmon absorbance peak at 535 nm. Coating even 1 ML of Pt or Pd yielded a detectable (ca. 5–10%) decrease in the peak absorbance, together with some band broadening toward longer wavelengths (cf. ref 16).

Of central interest here are the chemisorbate vibrational characteristics on the transition metal-coated nanoparticles as revealed by SERS. Figure 2 contains illustrative spectra obtained at -0.2 V vs SCE in 0.1 M HClO_4 for carbon monoxide and ethylene bound to the Pt- and Pd-coated films. As in our earlier studies of conventional Pt-group overlayers,^{9a,9i,17} these chemisorbrates were chosen in view of the sensitivity of their vibrational features to the surface structure and metal composition. The top spectrum, for CO on the Pt-coated nanoparticles, displays the hallmarks of predominantly atop coordination, with C–O stretching (ν_{CO}) and metal–CO stretching ($\nu_{\text{M–CO}}$) bands at 2080 and 478 cm^{-1} , with minor features (1870 , 350 cm^{-1}) arising from corresponding modes for bridging CO.^{9a,17} Two features of this spectrum are noteworthy here. First, there is a complete absence of the ca. 2120 cm^{-1} ν_{CO} feature diagnostic of CO bound to residual Au sites,^{9a} indicating further the essentially “pinhole-free” nature of the 1 ML Pt coating. Second, both the atop ν_{CO} and $\nu_{\text{M–CO}}$ features display remarkably high SERS intensities, about 10-fold higher than those for the corresponding Pt overlayers on conventional (planar) gold electrodes.¹¹

Similar remarks apply to the corresponding SER spectra for CO on Pd-coated nanoparticles, shown underneath in Figure 2. In this case, bridging rather than atop CO coordination predominates, the former exhibiting ν_{CO} and $\nu_{\text{M–CO}}$ modes at ca. 1970 and 350 cm^{-1} , respectively, again consistent with the behavior of the macroscopic planar electrodes.^{9a,11} Both CO adlayers exhibit increasing ν_{CO} (and slightly decreasing $\nu_{\text{M–CO}}$) frequencies as the potential is made more positive (cf. ref 9a), the SERS signals attenuating sharply above 0.5 V due to CO electrooxidation.

The bottom two SER spectra in Figure 2 refer to ethylene bound to the Pt-coated and unmodified Au nanoparticle films, as indicated, at 0 V in 0.1 M HClO_4 . The latter exhibits vibrational bands at 1278 and 1540 cm^{-1} , characteristic of coupled C=C stretch

[$\nu(\text{C}=\text{C})$] and CH_2 scissors [$\delta(\text{CH}_2)$] modes.¹⁷ The corresponding spectrum on Pt exhibits similar bands, but red-shifted to 1224 and 1504 cm^{-1} , similar to conventional Pt surfaces.¹⁷ Significantly, the latter spectrum exhibits no 1278 cm^{-1} component, indicating again the lack of residual Au binding sites even with a 1 ML Pt film. Admittedly, the ca. 1500 cm^{-1} C_2H_4 band on the Pt-coated nanoparticles is contained within a broader band envelope in the 1400 – 1700 cm^{-1} region. The latter feature and the low-frequency bands at ca. 300 and 500 cm^{-1} (Figure 2) are often seen for the nanoparticle films in the absence of added chemisorbate, and probably arise from citrate and/or decomposition products.

Similar experiments were also undertaken for films composed of 13 nm diameter nanoparticles. However, the SERS intensities are much (at least 100-fold) weaker than for the aforementioned 70 nm particles. While SER spectra have been reported earlier for very strong Raman scatterers bound to 12 nm Au arrays,^{4a} it is important to recognize that the present chemisorbrates provide a much more stringent test of the intrinsic SERS activity of the Pt/Pd-modified nanoparticles.

Overall, the present results demonstrate a straightforward preparation of nanoparticle films exhibiting well-defined electrochemical and adsorbate vibrational properties which reflect only the chemical nature of the Pt-group coating, yet maintaining SERS activity, and therefore presumably the morphology, of the gold template. This characteristic is distinct from several other “core–shell” nanoparticle synthetic strategies reported recently,¹⁸ which typically yield composite (e.g., alloy) properties. Given the availability of well-developed strategies for preparing monodispersed gold nanoparticle films, together with the diversity of overlayer materials (metals, semiconductors, etc.) that can be electrodeposited on gold,¹⁰ there is clearly tremendous scope for generating a myriad of nanomaterials by the present means.

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