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SERS at Structured Palladium and Platinum Surfaces

Mamdouh E. Abdelsalam,[†] Sumeet Mahajan,[†] Philip N. Bartlett,*[,†]
Jeremy J. Baumberg,[‡] and Andrea E. Russell[†]

Contribution from the School of Chemistry, University of Southampton, Southampton, SO17 1BJ, U.K., and School of Physics and Astronomy, University of Southampton, Southampton, SO17 1BJ, U.K.

Received February 22, 2007; E-mail: pnb@soton.ac.uk

Abstract: Palladium and platinum are important catalytic metals, and it would be highly advantageous to be able to use surface enhanced Raman spectroscopy (SERS) to study reactive species and intermediates on their surfaces. In this paper we describe the use of templated electrodeposition through colloidal templates to produce thin (<1 μm) films of palladium and platinum containing close packed hexagonal arrays of uniform sphere segment voids. We show that, even though these films are not rough, when the appropriate film thickness and sphere diameter are employed these surfaces give stable, reproducible surface enhancements for Raman scattering from molecules adsorbed at the metal surface. We report SERS spectra for benzenethiol adsorbed on the structured palladium and platinum surfaces of different thicknesses and void diameters and show that, for 633 nm radiation, enhancements of 1800 and 550 can be obtained for palladium and platinum, respectively.

Introduction

Surface enhanced Raman spectroscopy (SERS) is a very sensitive technique. It has been reported that molecules adsorbed on an electrochemically roughened silver substrate produce a Raman spectrum that is, in some cases, a million fold more intense than expected.[1−3] Therefore SERS has been widely used to identify molecules adsorbed at metal surfaces and, for a range of analytical applications,[4,5] to study intermediates in electrochemical reactions[6,7] and to study the structure of the electrode/electrolyte interface.[8,9] Unfortunately, surface enhancement at roughened metal surfaces is only strong on the coinage metals, Ag, Au, and Cu, and this limitation severely reduces the range of applications of SERS. Although the Pt-group metals, e.g., palladium and platinum, have better surface stability and find much wider application as electrodes and catalysts in electrochemistry and surface science, they have been commonly considered as non-SERS-active substrates. There have been considerable efforts over the past 20 years to expand the use of SERS to the Pt-group metals, particularly by the groups of Tian,[10−12] Weaver,[13−16] and Pérez.[17,18]

Tian's group have made extensive studies of surface roughening and surface structuring to create SERS active palladium and platinum surfaces using surface roughening by repetitive potential cycling[10,11,19] and by chemical etching.[20] Low quality SERS and resonance Raman spectra have been reported for adsorbates with a large Raman cross section on roughened platinum surfaces[21] and mechanically polished Pt electrodes.[22] The disadvantage of these roughened surfaces is that they have a wide distribution of surface features that vary in shape and size ranging from nanometers to microns. Thus, it is very hard to judge which feature or size of surface geometry causes the major part of the SERS activity. The observed enhancement is thought to be due to nanoscale "hot spots" of tightly localized plasmons which produce 1000-fold enhancements of the surface electromagnetic field.[23] The presence of this random distribution of hot spots also accounts for the extreme variability of the enhancement from place to place on the surface. Degradation

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[†] School of Chemistry.

[‡] School of Physics and Astronomy.

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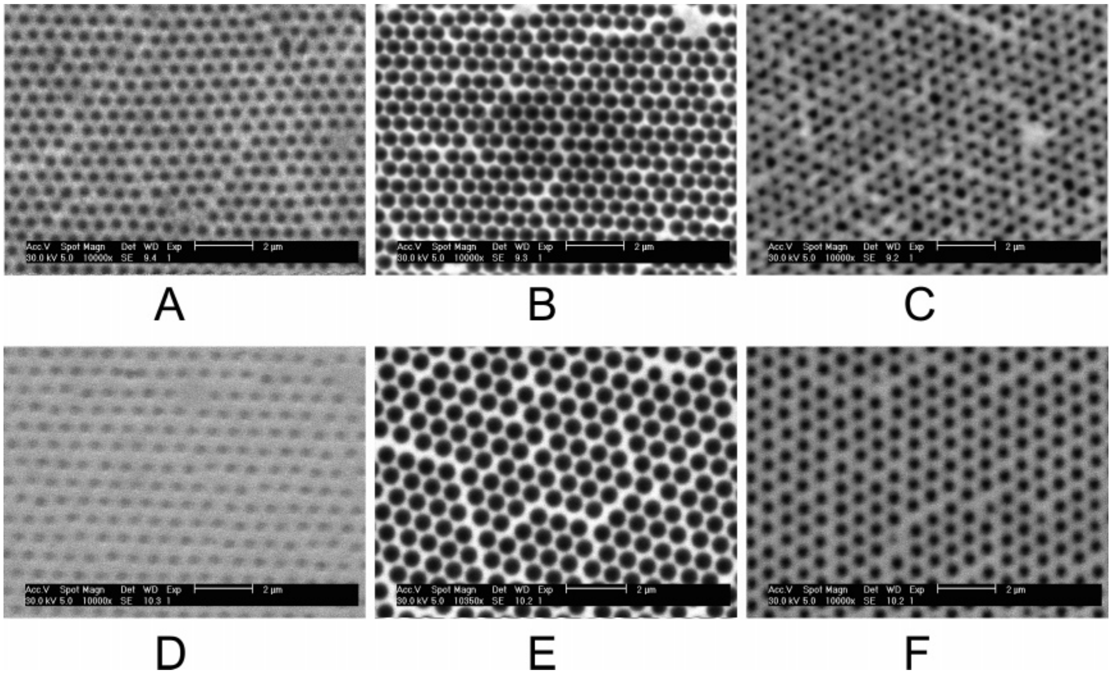

Figure 1. Scanning electron micrographs of structured palladium films produced using 600 nm diameter template spheres with thicknesses of (A) 160, (B) 250, and (C) 500 nm and of platinum films produced using 700 nm diameter template spheres with thicknesses of (D) 80, (E) 300, and (F) 520 nm. The scale bar is 2 μm in each case.

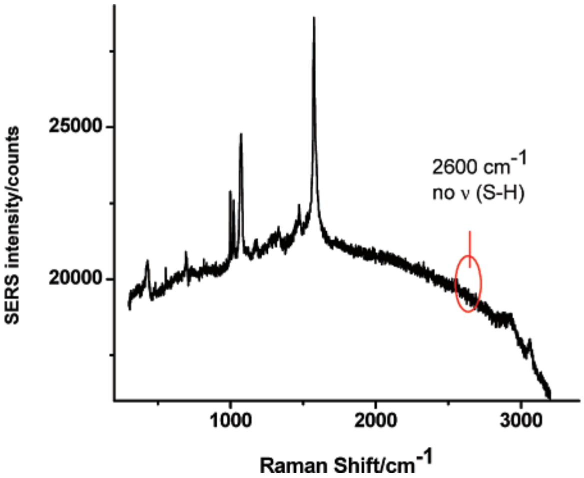

Figure 2. Spectrum of benzenethiol adsorbed on a structured palladium film produced using template spheres of 600 nm diameter and thickness 320 nm. The spectrum was taken using a 633 nm HeNe laser, 3 mW power, single 60 s accumulation.

of the surface enhancement is observed when cleaning of the surfaces is attempted: the sharp nanoscale features that localize the plasmons are easily etched or deformed, and these changes in the surface lead to changes in the surface enhancement.

Exploiting the dependence of the surface plasmon resonance (SPR) of nanoparticles on their size and shape, SERS active surfaces have been made out of nanoparticles of various shapes for a number of metals (Pt, Pd, Ru, and Co) using synthesis procedures mainly based on the reduction of the metal salt or thermal decomposition of organometallic precursors in the presence of surfactants, polymers, and coordinating ligands.[24,25] Triangular and hexagonal nanoplates of palladium have been made by manipulating the reduction kinetics of a polyol process. The SPR properties of these triangular and hexagonal nanoplates have been investigated, and the viability of using them as SERS substrates has been demonstrated.[26] The control parameters of all these syntheses have been largely limited to temperature, the concentration of precursor, and the choice of surfactant or polymer. The ability to control and fine-tune the shape and size has been modestly successful.

Nanoparticles are usually synthesized in solution, and it is very hard to assemble them in a well ordered and controllable way to produce the well-defined electrodes required for *in situ* electrochemical SERS experiments. Nevertheless Tian's group has recently reported the preparation and assembly of platinum nanothorn structures with sharp edges and used these to demonstrate good SERS enhancements.[27]

A further concern when using roughened surfaces or surfaces made from arrays of nanoparticles, where the SERS originates from molecules located at hot spots, is that the environment of the molecules which produce spectra is very different from the environment of the majority of the molecules on the surface and therefore is unrepresentative of the species which are important in electrode or catalytic processes.

Palladium and platinum SERS active surfaces have also been produced using the technique of borrowed SERS. In this case ultrathin films of palladium or platinum are electrodeposited on SERS-active Ag or Au surfaces such as monodisperse Au nanoparticles or roughened surfaces.[10,15,16,28] Tian has recently reported the utilization of the borrowed SERS technique to make SERS substrates using gold core, platinum shell nanoparticles. The shell thickness was one to five monolayers of platinum

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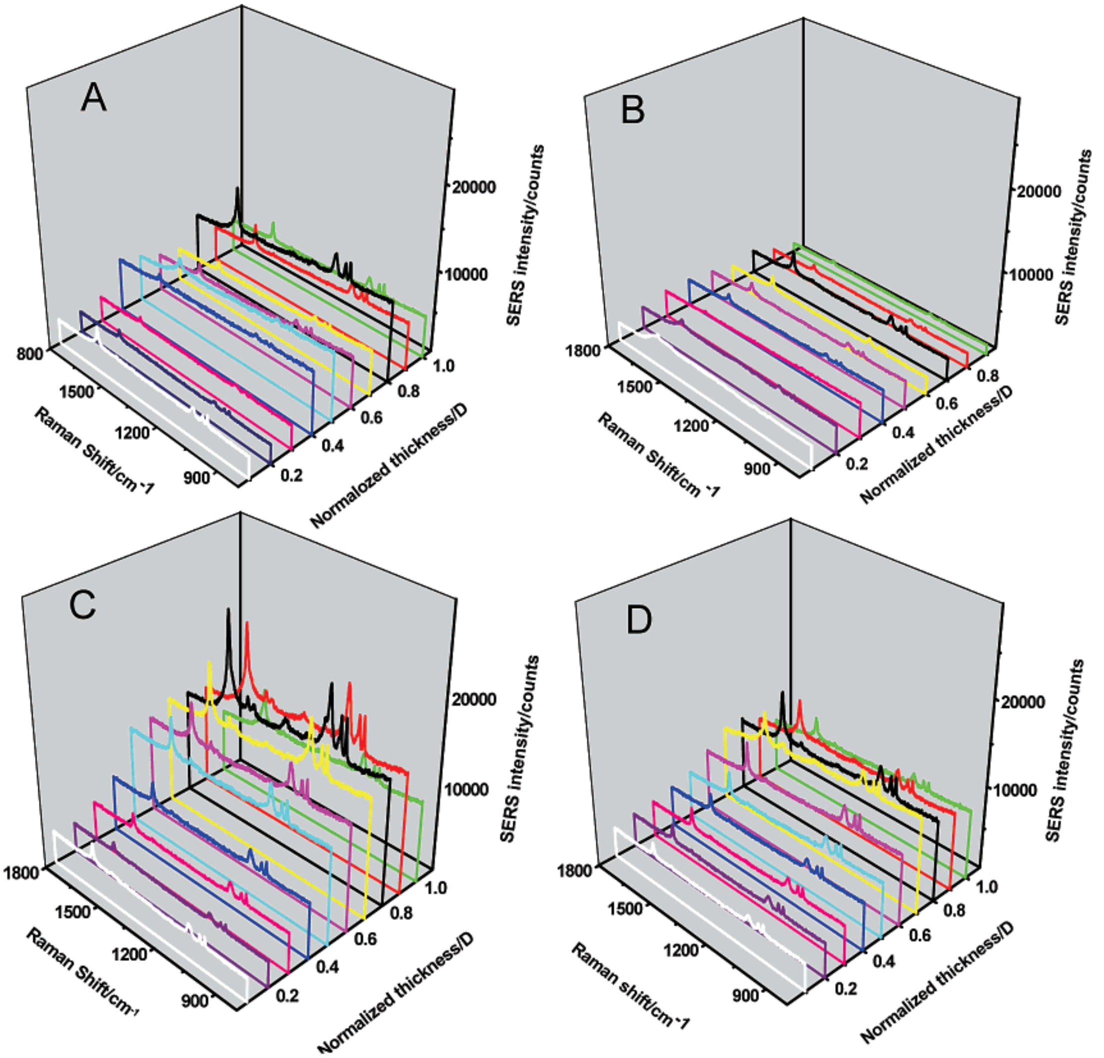

Figure 3. SER spectra of benzenethiol recorded at different film thicknesses for sphere templated Pd films (A) 400, (B) 500, (C) 600, and (D) 700 nm. The spectra were taken with a 633 nm HeNe laser, 3 mW power, single 60 s accumulation.

atoms.[29] In borrowed SERS activity arises from the long-range effect of the electromagnetic enhancement created by the SERS-active substrate underneath. The borrowed SERS activity decreases rapidly with increasing thickness of the overlayer. Consequently the coated film has to be deposited with a thickness of only a few atomic monolayers, and this leads to the potential problem of effects from pinholes where the underlying SERS active substrate is exposed. The experimental difficulty of preparing pinhole free ultrathin films and the possible instability of the film, especially when using them for the *in situ* electrochemical SERS experiments or during prolonged measurements, means that these ultrathin film substrates are not ideal. In addition there are potential problems arising from electronic interactions between the substrate metal and the thin overlayer which could lead to differences between the catalytic behavior of these thin overlayers and the bulk metal.

Thus, despite the success of using roughened surfaces, nanoparticulate arrays, or borrowed SERS approaches, it is still desirable to find new ways to obtain SERS directly from palladium and platinum surfaces. We recently described a new form of nanostructured metal surface in which the plasmon modes can be engineered with precision[30−33] through control of the film thickness and void diameter, and we have shown that for Au and Ag these surfaces show very significant SERS enhancements.[34−37] The plasmons observed on these nanostructured surfaces correspond to localized electromagnetic fields that can be excited by incident light and can be confined strongly in the region of the metal surface. Such surfaces are distinguished from other SERS plasmon substrates by their low surface roughness, by their regularity, and by their sphere

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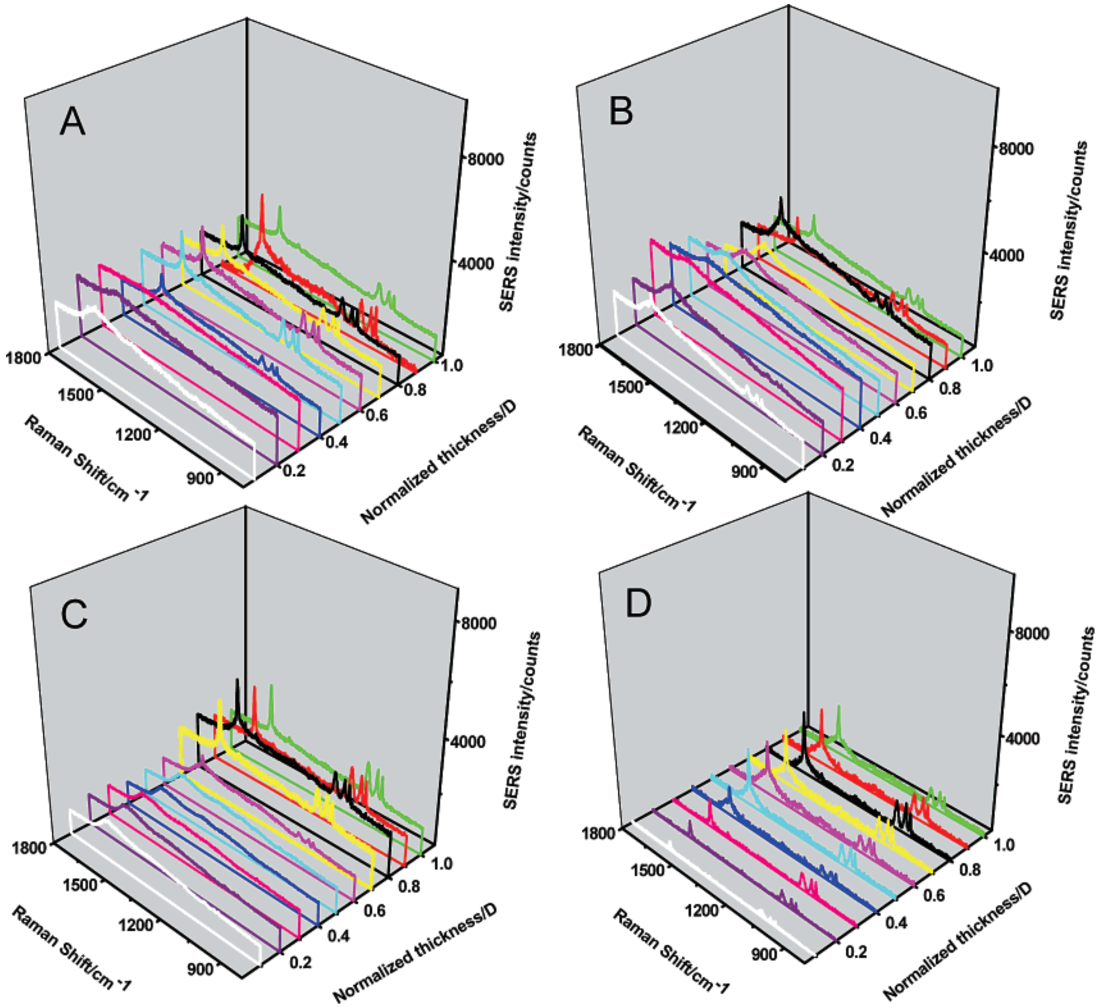

Figure 4. SER spectra of benzenethiol recorded at different film thicknesses for sphere templated Pt films (A) 400, (B) 500, (C) 600, and (D) 700 nm. The spectra were taken with a 633 nm HeNe laser, 3 mW power, single 60 s accumulation.

segment void geometry which allows confinement of localized plasmons within the cavities. Here we extend our work to show that electrodeposition of palladium and platinum through colloidal templates can be used to produce thin ($<1\ \mu$m) films containing close packed hexagonal arrays of uniform sphere segment voids and that these surfaces show surface enhancement for Raman scattering from molecules adsorbed on them which are comparable to or larger than those found for roughened surfaces or borrowed SERS on these metals. The reproducibility of the SERS enhancement across the sample is reported. We also show that this enhancement depends upon engineering the structure of the surface through the choice of template sphere diameter and the thickness of the film for the particular exciting laser wavelength used to record the Raman spectra. Because the films we produce do not have high surface roughness and are stable and reproducible, we believe that they will be useful in studies of electrode processes and catalysis on representative palladium and platinum surfaces.

Experimental Section

The structured palladium and platinum substrates were prepared by electrodeposition of palladium or platinum through a template of self-assembled polystyrene latex spheres onto a suitable conducting surface as described previously.[33,38] In order to avoid any possible borrowed SERS effects all of the structured palladium and platinum films presented here were prepared by electrodeposition onto evaporated palladium substrates. Other experiments using evaporated gold substrates rather than palladium gave identical results.

The evaporated palladium substrates were prepared by evaporating 30 nm of palladium onto 1 mm thick glass microscope slides. The palladium coated microscope slides were then cleaned in isopropanol (analytical grade, Fisher Scientific) in an ultrasonic bath (CE, Ultrawave Limited, Cardiff, UK) for 90 min and then chemically modified with cysteamine (Aldrich) by soaking for 3 days in a 10 mM solution in ethanol (HPLC grade, Rathburn) before assembling the templates (more details can be found in our earlier publication[33]).

Templates were assembled from monodisperse polystyrene latex spheres (diameters 400, 500, 600, and 700 nm, Duke Scientific, 1 wt % aqueous suspension). The monolayer template was assembled by the capillary evaporation method to produce a well-ordered hexagonal monolayer of spheres on the palladium coated glass slide.

Palladium or platinum were deposited from 50 mM solutions of ammonium tetrachloropalladate (purity 99.99%, Aldrich) or hexachloroplatinic acid (purity 99.9%, Aldrich). Electrochemical deposition was performed in a thermostated cell at 25 °C using a conventional three-electrode system controlled by an Autolab PGSTAT30. The template-coated palladium substrate was the working electrode with a large area

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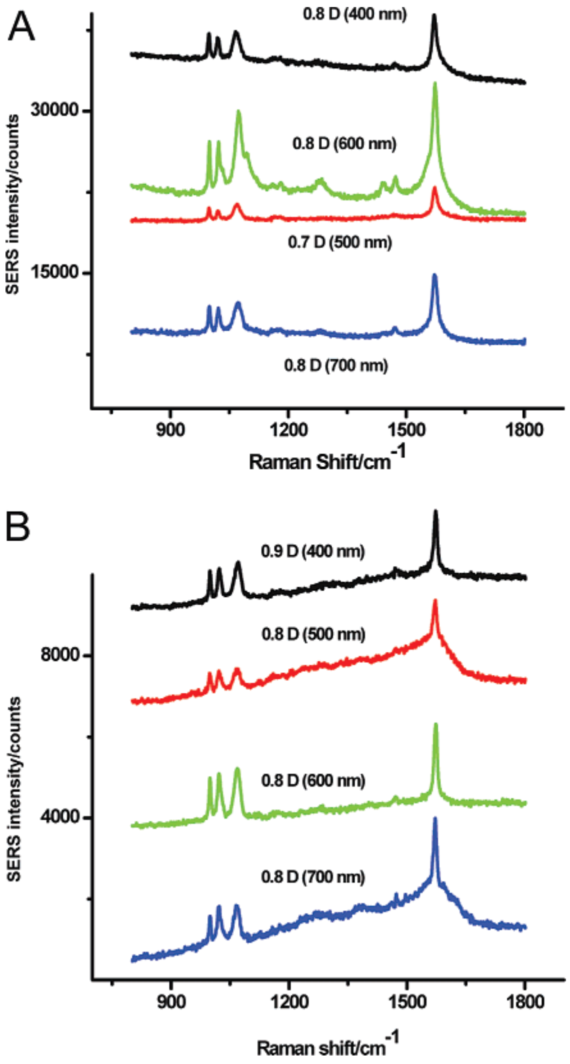

Figure 5. SERS of benzenethiol adsorbed on structured (A) palladium and (B) platinum substrates as a function of sphere diameter. The spectra shown represent the maximum enhancements for each given sphere size; the film thicknesses and template sphere diameters are indicated next to each spectrum.

platinum gauze counter electrode and a homemade saturated calomel (SCE) reference electrode. Palladium and platinum films were deposited under potentiostatic conditions at 0.25 V or 0.05 V vs SCE, respectively. These conditions lead to the deposition of smooth metal films on the template coated substrates. Following electrodeposition, the latex spheres were removed by dissolving in dimethylformamide (DMF, analytical reagent grade, Fisher Scientific) to leave an ordered array of interconnected sphere segment voids.

Electrochemical measurements of the active surface area of the films was carried out by recording cyclic voltammograms in 1 M H_2SO_4. Before each experiment the solution was purged for 15 min with a stream of argon gas to displace dissolved oxygen. The electrochemically active surface areas of the nanostructured palladium films were estimated by integrating the charge passed in the surface oxide stripping peak and using the conversion factor of 424 μC cm^{-2}.[39] For platinum the active surface areas were estimated by integrating the charge associated with the proton adsorption/desorption peaks and using the conversion factor of 210 μC cm^{-2}.[40] All solutions were freshly prepared using reagent-grade water (18 MΩ cm) from a Whatman RO80 system coupled to a Whatman "Still Plus" system.

A Philips XL30 Environmental Scanning Electron Microscope (ESEM) was used to image the structured metal films. All Raman spectra were recorded on a Renishaw Raman 2000 system using a 633 nm HeNe laser with 5 μm diameter spot size and 3 mW power using a single 60 s accumulation unless otherwise stated. Benzenethiol (purity 99.99%, Aldrich) was adsorbed onto the palladium and platinum surfaces by soaking in a 10 mM solution in ethanol for 1 h. The samples were then rinsed with ethanol and left to dry in air for 15 min before measurement. The absence of unbound benzene thiol on the surface was confirmed by the absence in the SER spectra of the −SH band at 2600 cm^{-1}.

The reflectivity of the nanostructured films was measured using an optical microscopy arrangement (BX51TRF Olympus) using an incoherent white light source to illuminate the samples.[33] Images were recorded using a CCD camera (DP2 Olympus). Spectra from selected areas of the sample (50 μm) were recorded at normal incidence using a 20× IR objective with a numerical aperture of 0.40 and a fiber-coupled spectrometer (Ocean Optics, spectral range 300−1000 nm, resolution l nm) placed in the focal plane of the image. All spectra are normalized with respect to that recorded for a flat vapor deposited palladium film or a flat electrodeposited platinum film as appropriate.

Results and Discussion

Structured palladium and platinum surfaces were prepared by electrodeposition through close packed monolayers of polystyrene spheres with diameters between 400 and 700 nm assembled onto evaporated palladium substrates. The thickness of the electrodeposited film was controlled by varying the charge passed during electrodeposition. After deposition the polystyrene template was removed to leave the thin structured films containing a regular hexagonal array of uniform segment sphere voids. These surfaces are strongly colored, the precise color depending on the viewing angle, void diameter, and film thickness.[33] Figure 1 shows typical SEM images of templated palladium and platinum films of various heights grown through templates made from monolayers of 600 nm or 700 nm diameter polystyrene spheres, respectively. The micrographs show that the spherical segment voids left after the removal of the polystyrene spheres are smooth and uniform. The pore mouth diameter and the topography of the spherical cavities change with the film thickness.

Electrochemical measurements of the surface area of these structured surfaces were achieved by measuring the oxide stripping and proton adsorption/desorption charge in acidic solution for palladium and platinum respectively.[39,40] A roughness factor, that is the ratio of the electrochemically determined surface area to the projected area, of 3.65 was obtained for a platinum film made using 500 nm template spheres and grown to 0.5*D* (where *D* is the diameter of the sphere), while a roughness factor of 3.85 was obtained for a palladium film made using 600 nm template spheres and grown to 0.6*D*. The predicted increases in surface area due to the presence of the sphere segment voids within the films, calculated on the basis of the geometry and assuming that the insides of the sphere segment cavities are perfectly smooth, are 2.3 for the palladium film and 1.9 for the platinum film. Thus the modest increases in the experimentally determined surface area are consistent with a smooth, yet sculpted, surface. These results confirm that the templated surfaces do not have high surface roughness compared to the typical values of up to 500 found for the electrochemically roughened surfaces conventionally used for SERS.[11]

The SER spectrum of benzenethiol adsorbed on a structured palladium film (thickness 320 nm, template sphere diameter 600

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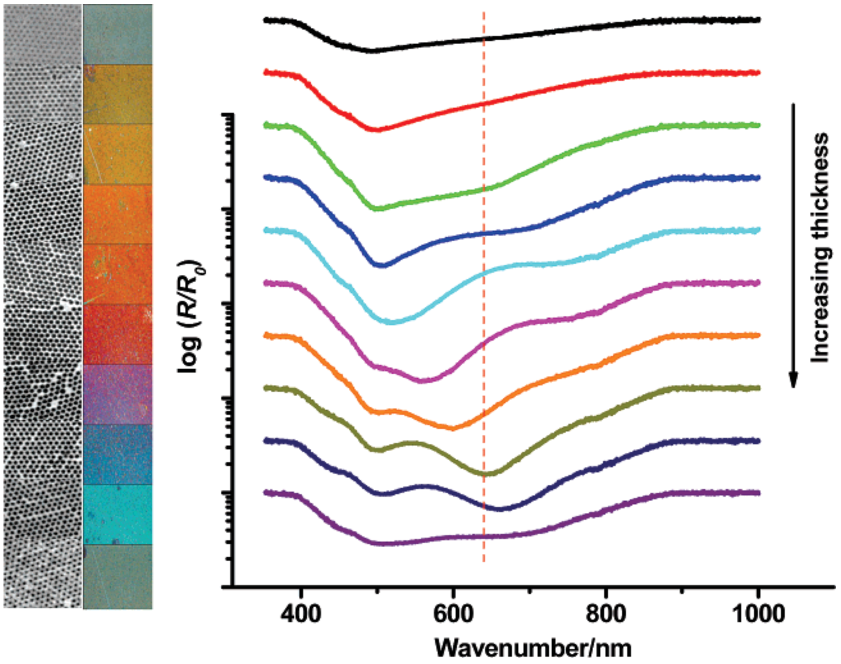

Figure 6. Normal incidence reflectance spectra for a stepped, structured palladium film grown through a 600 nm sphere diameter template together with the corresponding optical and SEM images. The spectra are offset for clarity.

nm) is shown in Figure 2. Similar spectra were obtained using templated platinum films. The spectra agree well with those in the literature for benzene thiol on silver and gold substrates in terms of both band positions and relative intensities.[41,42] The absence of the ν(S−H) stretching vibration peak confirms that the benzenethiol is chemisorbed on the palladium substrate through the Pd−S bond. In control experiments, no SERS spectra are observed for benzenethiol adsorbed on the flat evaporated palladium and platinum substrates or for nonstructured palladium and platinum films electrodeposited on the evaporated palladium substrates under identical conditions. The surface enhancement on the structured palladium and platinum surfaces is reproducible from place to place across the surface. Standard deviations of less than 12.5% were found for spectra ($n = 10$) recorded at different places on the samples. In addition, the structured palladium and platinum surfaces were found to be very stable: the palladium and platinum substrates can be cleaned and reused following the removal of the benzenethiol by electrochemical reduction in 0.5 M KOH solution, and reproducible results were obtained using substrates up to 6 months after cleaning followed by the assembly of a fresh monolayer of the thiol.

The effect of film thickness on the SERS intensity for 400, 500, 600, and 700 nm sphere templated substrates is shown in Figures 3 and 4. These spectra were obtained using films that were grown with a series of steps in thickness by withdrawing the substrate in a series of steps (each ~500 μm) from the solution during electrodeposition. In this way the film height was systematically increased in steps from 0 to 1*D*. It is clearly evident that the SERS intensity varies with the film thickness and the template sphere size indicating that the precise geometry of the structured film is an important factor in determining the enhancement. These results agree well with results previously obtained for templated gold substrates.[34−36] For palladium and platinum surfaces made using various sphere sizes and using 633 nm excitation, the maximum enhancement always occurs between 0.7 and 0.9 *D*, the precise value depending on the template sphere diameter. For all the palladium and platinum samples investigated, the most intense SERS spectra for adsorbed benzenethiol obtained using 633 nm excitation are shown in Figure 5 (the normalized film thicknesses are quoted next to each spectrum). For both palladium and platinum the largest SERS enhancements were obtained with 600 nm sphere-templated nanovoid film at around 0.8 *D*. Enhancement factors were calculated for both palladium and platinum films using the method described in the literature assuming a surface coverage of 0.45 nmol cm^{-2} for benzenethiol on platinum and the surface roughness of 3.0.[11,43] The calculated values for palladium and platinum are 1800 and 550, respectively. The enhancement factors reported here on the structured palladium and platinum surfaces are reproducible from place to place across the surface and from sample to sample when prepared under identical conditions. Xia et al. have reported an enhancement factor of 1.3 × 10^4 for 4-mercaptopryidine adsorbed on Pd nanoboxes. The enhancement critically depends on the way in which the nanoboxes aggregate upon drying, and therefore the enhancement changes significantly from sample to sample and from place to place within the same sample.[44] For pyridine adsorbed on the electrochemically roughened Pd Tian *et al.* have reported an enhancement factor of 1800.[45] For platinum Tian has reported an enhancement factor as high as 2000 for adsorbed pyridine on a platinum nanothorn substrate.[27] Among all the samples prepared in our study the smallest enhancements were

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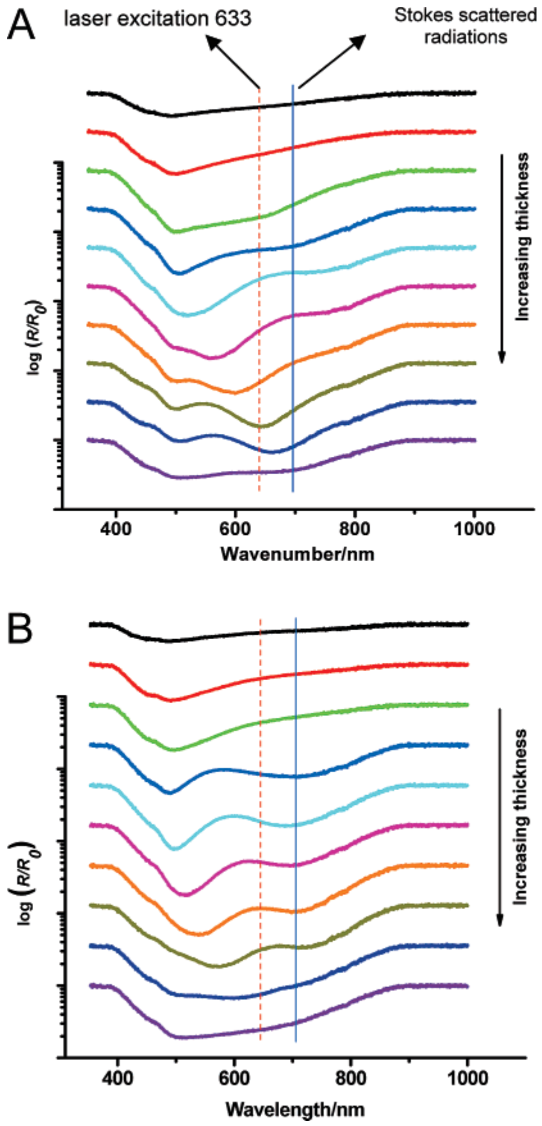

Figure 7. Reflectance spectra of graded in thickness palladium substrates made using (A) 600 and (B) 500 nm template spheres. The dashed red line denotes the ingoing laser excitation at 633 nm and the solid blue line denotes the out coming radiation at 703 nm corresponding to the 1570 cm^{-1} SERS band of benzenethiol.

obtained with the 500 nm sphere templated structures, with enhancements of 500 for palladium and 200 for platinum.

To relate the dependence of the SERS enhancement to the geometry of the structured film, reflectance spectra were recorded for the palladium and platinum surfaces as a function of film thickness at the same positions on the graded substrates at which the SERS were measured. Reflection spectra for a templated palladium film are shown in Figure 6 together with corresponding optical and SEM images (similar results were obtained for platinum). The optical images show the striking range of colors of the film when viewed at normal incidence, changing from gray-green through red, orange, and blue, and then back to gray-green as the film thickness increases from 0 to 1*D*. The corresponding SEM images show the associated change in pore mouth diameter. Individual reflection spectra are plotted on a log scale (off-set from one another for clarity) with the sample thickness increasing from top to bottom. Dips in reflectivity, corresponding to localized Plasmon absorption, are observed which shift to progressively longer wavelengths as the film thickness increases, causing the dramatic changes in the observed color of the sample.

The features observed in the reflectance are similar to those previously reported for gold and silver.[33] We have recently shown that the absorbance features observed in the reflectance spectra of template structured gold surfaces can be described in terms of the relative contributions of the various plasmon modes.[34−37] When the film is very thin the surface takes the form of an array of shallow dishes, ordered in a close packed hexagonal lattice, with the top surface consisting of flat areas of metal separating the dishes. Plasmons freely propagate on the flat surface and multiply scatter off the rims of the dishes resulting in plasmonic band gaps following a Bragg dispersion.[46] As the film thickness increases the surface becomes strongly corrugated, and in addition to the (Bragg) surface plasmons travelling across the top surface, other plasmons are trapped within the spherical cavities. For fully spherical voids, i.e., if the top surface were to close over, the electromagnetic solutions to an isolated spherical dielectric cavity within an infinite expanse of metal correspond to Mie scattered modes from a sphere.[47] These are calculated from Maxwell's equations expanded in spherical coordinates, by matching boundary conditions at spherical coordinates; more details can be found in our recent paper.[31] The Mie and Bragg modes interfere with the incoming light, and this interference produces the series of absorbance features observed in the reflectance spectra of the thicker films. In recent studies we have used angle-resolved reflectivity measurements of templated gold films to allow us to fully map the spectral and angular dispersion of the different types of plasmons and their interactions.[31] Moreover we were able to map the SERS signal intensity at different angles of both the incident pump laser and the Stokes scattered photons and thus clearly demonstrated the role of resonant plasmon enhancement for both the incoming and outgoing light on the SERS signal intensity.[34] Sharp enhancements occur when the laser is scanned through a plasmon resonance (ingoing) and also when individual Raman scattered lines coincide with plasmon resonances (outgoing); the Stokes scattered photons are not emitted isotropically from the templated structure but come out at particular angles. Consequently, to achieve maximal surface enhancement templated substrates have to be carefully designed bearing in mind not only the wavelength of the exciting laser but also the geometry and numerical aperture of the spectrometer.

Comparing the SERS enhancement for the palladium and platinum samples, the 500 nm sphere templated films gave the smallest SERS enhancement while the 600 nm sphere templated films gave the largest enhancement. This can be rationalized by comparing their reflectance spectra, Figure 7. The SERS enhancement depends on the matching of the incident and exiting radiation with plasmons on the substrate. The wavelengths corresponding to the laser excitation, 633 nm (red line), and Stokes scattered photons for the 1571 cm^{-1} SERS peak at 703 nm (blue line), are shown in Figure 6. As can be seen, for the 600 nm sphere templated films both the wavelength of the excitation laser and the Stokes scattered photons overlap with a strong absorption feature in the reflectance spectra for the thicker film. Therefore a large SERS signal is expected. For

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the 600 nm sphere templated film this overlap is maximized for film heights of $\sim 0.8D$. In contrast, in the case of the 500 nm sphere templated films the incident and Stokes scattered radiation do not match well with the strong plasmon absorptions in the spectra, and consequently these surfaces are expected to produce much smaller surface enhancements. This analysis is somewhat simplistic, since it does not take into account any variation in the strength of the enhancement for the different types of plasmon (Bragg or Mie) or the full angular dependence of the reflectance spectra and the collection angle (numerical aperture) of the spectrometer. A more detailed analysis is beyond the scope of the present paper but will be the subject of a future publication.

Conclusions

In this study we have shown that the templated electrodeposition technique can be used to produce structured Pd and Pt films that give SERS active substrates with significant signal enhancements. An advantage of the structured surfaces reported here is that both the template sphere diameter and the film thickness can be varied to allow control over the optical properties of the substrates. The surfaces can therefore be precisely tailored to tune the surface plasmon modes to match the requirements of the SERS experiment. The maximum surface enhancement was obtained when the incident and Stokes scattered radiation match plasmonic resonances of the surface. The enhancements observed for the structured palladium and platinum surfaces reported here are reproducible from place to place on the sample (unlike SERS substrates produced by electrochemical roughening or colloidal nanoparticles). The structured surfaces are smooth, uniform, and very stable (unlike the SERS substrates produced by ultrathin films), and exceptionally these surfaces can be cleaned and reused. Given the relative ease of preparation and the robust and reproducible nature of these surfaces, we believe that they have great promise for applications in electrochemistry and analysis.

Acknowledgment. We thank Suzanne Cintra and Robin Cole for assistance with the Raman and reflectance spectrometers and the EPSRC (Grant number EP/C511786/1) for funding this work.

JA071269M