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ULTRAVIOLET SURFACE-ENHANCED RAMAN SCATTERING FOR DETECTION APPLICATIONS

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14. ABSTRACT

Surface-enhanced resonance Raman scattering with UV excitation has the potential advantage of combining surface and molecular-resonance enhancements for a wide variety of analytes of interest. Nanostructured surfaces of Pd and Pt were formed by electroless deposition on germanium substrates. Ultrathin layers of Al were made by coating thick layers of Al on a microscope slide and partially dissolving them with hydrochloric acid. The substrates were assessed for their ability to enhance the Raman cross sections under UV excitation.

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PREFACE

The work described in this report was performed during the tenure of Erik D. Emmons as a National Research Council Resident Research Associate at the U.S. Army Edgewood Chemical Biological Center. The work was started in July 2008 and completed in June 2011.

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ULTRAVIOLET SURFACE-ENHANCED RAMAN SCATTERING
FOR DETECTION APPLICATIONS

1.   INTRODUCTION

UV excitation provides the potential for combining surface and resonance enhancements for a wide variety of target analyses because all molecules absorb light if the light is of sufficiently short wavelength. Because of the potential for intensity enhancement, the topic of UV surface-enhanced resonance Raman scattering (UV-SERRS) has received significant attention in recent years. UV-SERRS and surface-enhanced Raman spectroscopy (SERS) are being explored as possible techniques to increase the sensitivity and selectivity for detecting chemical, biological, and explosive agents that are a threat to security. Raman spectroscopy, a probe of the chemical bonds in a molecule, has the advantage in that it is highly chemically specific and therefore very useful for identification purposes. However, the scattering cross sections are relatively low (typically $\sim 10^{-30}$ cm^2 with visible excitation), making it desirable to enhance the signals using techniques such as surface and resonance enhancement.

The general conditions for a favorable plasmonic SERS material in a particular wavelength region are that the real part of the dielectric function is negative while, at the same time, the imaginary part is small.[1] The wavelength dependence of the real part of the dielectric function sets the plasmon resonance frequency where the maximum electromagnetic enhancement occurs, while the imaginary part leads to absorption and sets the maximum value of the enhancement.[1-2] Pt, Pd, and Al have favorable dielectric constant values in the UV region of the spectrum. Al appears to be the most promising of the three because it contains the smallest imaginary component of its dielectric constant and, consequently, has the lowest absorption.[1-2] The more commonly encountered SERS active metals (such as Au, Ag, Cu) do not have favorable dielectric function values in the UV region.

UV-SERS is expected to be generally more difficult than SERS with visible light excitation. The coinage (Au, Ag, Cu) and alkali metals have large enhancements in the visible region of the spectrum because their free-electron-like behavior leads to efficient excitation of surface-plasmon resonances, and these metals have small imaginary components of the dielectric constant.[3] The electromagnetic enhancements are expected to be smaller in transition metals because damping due to interband transitions is large.[4] The electronic structures of the coinage and transition metals are different because of the strong mixing of the *d* with the *s* shells in the transition metals, which does not occur with the free-electron metals.[3] Theoretically, the SERS activity of transition metals has been explored. Tian et al.[3] have calculated the SERS enhancement factors for Pt and Ag ellipsoidal nanoparticles. For the geometry used, they found that the enhancement factors for Pt were nearly constant at 10^3 for wavelengths greater than 350 nm, while those of Ag strongly peaked just above 400 nm with a maximum value of 10^7. As a result, Pt does not show any distinct plasmon resonance in this region of the spectrum, but instead, there is a general electromagnetic enhancement of a nonplasmonic nature.[2]

Despite its difficulties, there are several potential advantages to performing SERS measurements using UV excitation ($\lambda < 250$ nm):

- Away from electronic resonances of the analytes, the Raman scattering cross sections scale as v^4. As a result, Raman scattering is inherently more intense in the UV region than in the visible or near-IR regions.

- If the excitation wavelength is close to that of an electronic resonance of the analyte, an additional enhancement of the Raman scattering rates can occur. Because many organic molecules have a high density of electronic resonances in the UV spectral region, resonance enhancement is more likely to occur when compared to visible or near-IR excitation.

- Use of UV excitation ensures the avoidance of fluorescence because of the spectral separation from Raman scattered light of the latter.

- The transition metal substrates may have an advantage over the noble metals in that more molecules may adsorb strongly to them because of the presence of empty d orbitals.[5]

A significant difficulty that must be overcome before SERS can be applied to chemical, biological, and explosives detection is that although it may work well for certain analytes that strongly adsorb on the SERS substrate, SERS is hard to apply generally to any desired analyte that may not bind well to the substrate.

There have only been a limited number of attempts to extend SERS beyond the typical coinage metals. Reviews of SERS using transition metals and UV excitation are given in Tian et al.[3,6] It would be advantageous to study SERS using these metals because there are many potential important applications. For example, Pd and Pt are commonly used in catalysis.[7,8] SERS has been observed on some transition metals such as Fe, Ru, Rh, Pd, and Pt, but the enhancement factors observed have been relatively small; they were typically around 10^2-10^4, as opposed to 10^6-10^7 for Au and Ag.[3,5] Studies by a variety of groups, mostly concentrating on visible excitation, have focused on SERS observed from the nanostructured surfaces and colloidal suspensions of these elements.[9-17]

SERS is beginning to be extended to the UV region of the spectrum. Ren et al. observed a weak SERS effect from pyridine and SCN⁻ using roughened Rh, Ru, and Co electrodes with 325 nm excitation.[4,18] However, the enhancement factors were quite low. For example, the enhancement value obtained was only ~100 for SCN⁻ on Rh electrodes.[4] Dörfer et al. used evaporated Al films of thickness less than 100 nm along with 244 nm excitation to observe SERS from crystal violet (CV).[19] Al films with thicknesses less than 100 nm have a reflectance drop below 400 nm due to plasmon excitation, and the reflectance reaches a minimum of 120 nm. As a motivation for this work, Dörfer et al. stated that samples of biological interest such as amino acids have resonances around this region, and as a result deep UV measurements should lead to significant resonance enhancement for biological samples.[19] However, the UV-SERRS spectrum illustrated by Dörfer et al. looks suspiciously like the spectrum of ethanol, despite their claim that they prepared the sample by the drop-and-dry technique from an aqueous solution of CV. More recent works show that Al has attracted increased attention in the field of plasmonics-related research. Chan et al. observed surface

plasmon resonances throughout the visible and UV regions of the spectrum from triangular Al nanoparticles.[1] Porbchii et al. used Al-coated atomic force microscopy tips to perform tip-enhanced Raman spectroscopy.[20] Lackowicz et al. observed metal-enhanced fluorescence from molecules on vapor-deposited Al thin films.[21,22]

Additionally, using gold as a substrate for UV-SERS experiments, two studies were performed. No other groups performing similar studies have been able to observe SERS from gold using UV radiation.[23,24] Wen and Fang observed SERRS spectra of *p*-hydroxybenzoic acid on roughened gold electrodes using 325 nm excitation.[24] Wang and Wu also observed UV-SERS from SCN^- on roughened gold electrodes, again using 325 nm excitation.[23] Both of these efforts using gold focused on the charge-transfer mechanism and the effect of varying electrode potentials on the SERS spectra. Gold, however, is a much more effective SERS active metal in visible than UV light.

In this work, we used Al, Pt, and Pd for preparing SERS substrates. Creighton and Eadon predicted that 10 nm diameter particles of these elements would have absorption maxima in the UV region of the spectrum between 200 and 300 nm.[5] Ultrathin Al substrates were produced by removing material from relatively thick Al coatings on glass slides using hydrochloric acid until the remaining film became semitransparent. Nanostructured substrates of Pd and Pt were produced by electroless deposition of nanoparticles on germanium substrates.

2.   EXPERIMENTAL PROCESS

As mentioned previously, nanostructured substrates of Al, Pt, and Pd were examined for their ability to be used as substrates for SERS with UV excitation. The substrates were examined using Raman spectrometers with excitation wavelengths ranging from 229−262 nm. For the 229 and 244 nm excitations, frequency-doubled Ar^+ lasers were used (Coherent Inc., Santa Clara, CA). For the 262 nm excitation, a pulsed Nd:YLF laser (Crystal Laser, Reno, NV) was used, which was frequency-quadrupled to emit deep UV light. The laser was operated at a relatively high repetition rate (~3.5 kHz) with low-intensity pulses, which reduced photoinduced damage to the samples. The laser light was focused on the sample using a fused silica lens. The Raman scattered light was collected in a backscattering configuration using a 15× long-working-distance reflective microscope objective. This objective was fiber-optically coupled to a Princeton Instruments Acton SP2500 spectrometer (Trenton, NJ) with three gratings and a Pixis 2K back-illuminated UV-enhanced charge-coupled device camera. Long-pass filters (Barr Associates, Westford, MA) were used to reject the Rayleigh scattered light. The 2400 grooves/mm UV optimized grating was used to disperse the scattered light. In addition to excitation with UV light, a JASCO (Easton, MD) Raman microscope system (NRS-3200) was used to examine the substrates with visible excitation. Lasers were available with excitation wavelengths of 532, 633, and 785 nm.
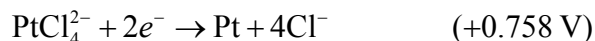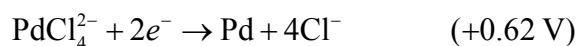
The ultrathin Al films were produced by partially dissolving thicker layers of Al coated on 1 × 1 in. glass microscope slides. The slides were immersed in 1 M solutions of hydrochloric acid for approximately 5−6 h until they were semitransparent. They were then rinsed with copious amounts of ultrapure water (resistivity > 18.2 MΩ·cm) and dried in a stream

of nitrogen gas. The substrates were characterized using UV-visible reflection and absorption spectroscopy. An Ocean Optics (Dunedin, FL) USB2000+XR fiber optic spectrometer was used to cover the range from 200 to 1050 nm. An Ocean Optics DH-2000 deuterium-halogen lamp was used as an illumination source. The specular reflection was recorded using a fiber optic reflection probe. The transmission was also measured, but due to the use of glass substrates, the transmission could not be measured in the deep UV region ($\lambda < 350$ nm).

Pt and Pd nanostructured substrates were produced by electroless deposition of nanoparticles on a germanium substrate. In the electroless deposition technique, metal ions in solution are spontaneously reduced on an appropriate substrate, and nanoparticles of the metal are subsequently deposited. For example, if a germanium wafer is immersed in a silver nitrate solution, silver nanoparticles will plate on the surface. For the electroless deposition to occur, the reduction potential of the substrate needs to be smaller than that of the metal. This is the case for Pt and Pd ions, as shown in the following reactions:[25]

$$Ge \rightarrow Ge^{4+} + 4e^- \qquad\qquad (-0.124\,\text{V})$$

and

$$PdCl_4^{2-} + 2e^- \rightarrow Pd + 4Cl^- \qquad\qquad (+0.62\ \text{V})$$

$$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^- \qquad\qquad (+0.758\ \text{V})$$

This technique was used by Brejna et al. to produce silver and gold substrates for use in surface-enhanced Raman spectroscopy.[26] Other works have also been published on the application of electroless deposition to produce substrates for SERS and surface-enhanced IR absorption spectroscopy.[27-30] In the present work, nanostructured substrates of Pt and Pd were produced by immersing germanium substrates in 10 mM aqueous solutions of K_2PdCl_4 or K_2PtCl_4. The germanium substrates were first polished with 1 and 0.05 μm alumina, then cleaned with ethanol and ultrapure water, and finally dried in a stream of nitrogen. The UV-visible reflection spectra were also examined using the setup described in the previous paragraph.

3. RESULTS AND DISCUSSION

The substrates were tested using a variety of analytes including 1,2-bis(4-pyridyl)ethylene (BPE), CV, and rhodamine 6G perchlorate (R6G). The substrates were either immersed in a dilute solution of the analyte and then rinsed and dried or the analyte was spin-coated onto the substrate. BPE, CV, and R6G are standard SERS analytes that bind strongly to gold and silver. These analytes have been used in studies with other metals. The UV-visible absorption spectra are shown in Figure 1. These spectra were obtained at concentrations of 0.01 mg/mL in a 1 cm path length cell. Ethanol was used as a solvent for the BPE and R6G samples, while ultrapure water was used for the CV samples. The main panel shows the absorbance in the UV region, and the inset shows an expanded view covering the visible region. These analytes show significant absorption in the UV region of the spectrum and, therefore, show resonance enhancement of some of the Raman bands (illustrated in Figure 2). These spectra were obtained at a concentration of 0.25 mg/mL with 244 nm excitation in solution (no substrate present). Despite the low concentration, the analyte peaks are of comparable intensity to the solvent peaks.
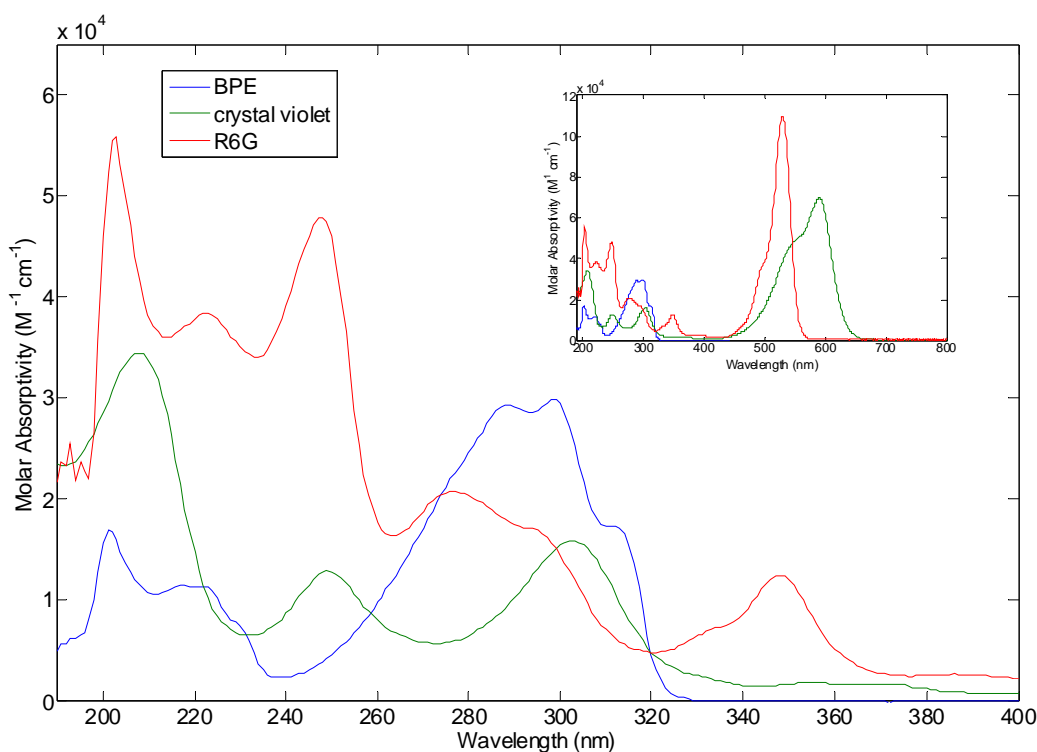

Figure 1. UV-visible absorption spectrum of BPE, CV, and R6G. The main panel shows the absorbance in the UV region of the spectrum, while the inset shows the absorbance throughout the UV and visible regions.
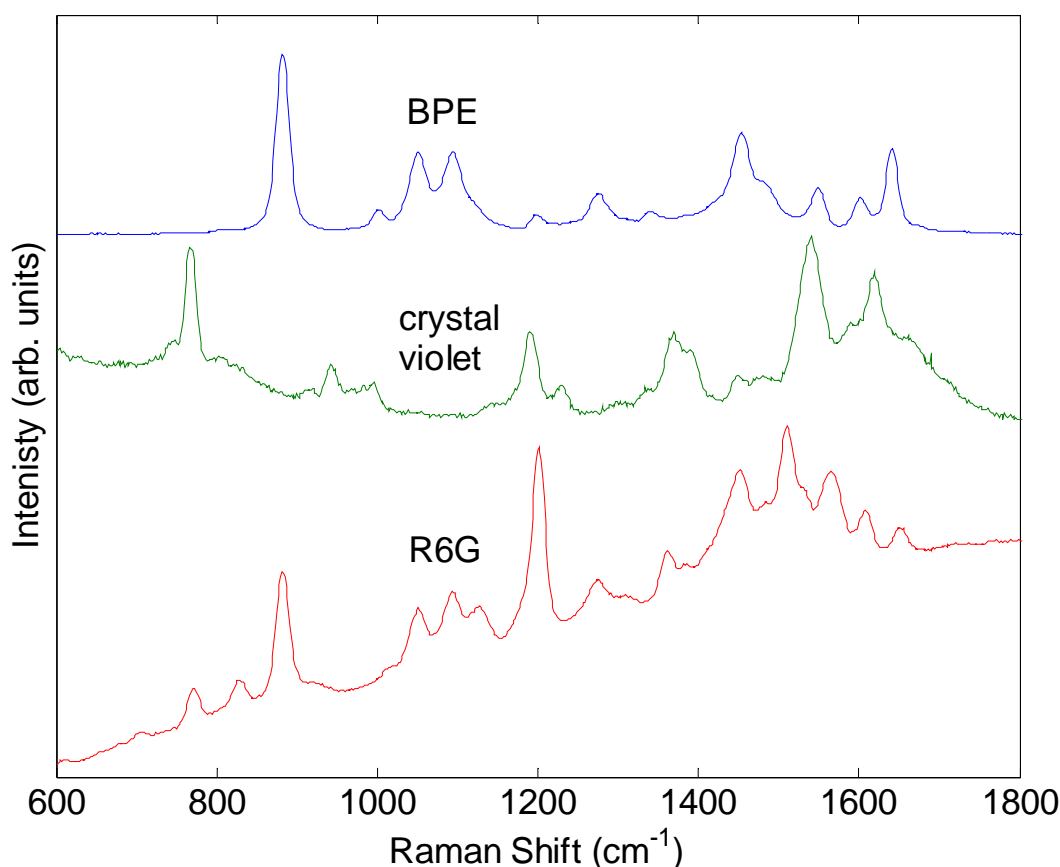
Figure 2. UV resonance Raman spectrum of BPE, CV, and R6G under 244 nm excitation in the solution phase. The samples were measured at a concentration of 0.25 mg/mL.

BPE, CV, and R6G were used to evaluate the UV-SERRS activity of the substrates that were formed. These measurements were obtained with 244 nm excitation with ~50 mW of laser power. Because of the potential intensity of the UV laser beam to cause photodegradation of the substrate and the analytes, the substrates were spun under the laser beam at the rate of a few hundred revolutions per minute. Additionally, the spinning substrate was manually translated during the measurements so that a spiral pattern of concentric circles was traced.

First, results for the ultrathin Al films will be discussed. As previously mentioned, these substrates were formed by immersion in 1 M HCl solutions for ~5−6 h. The procedure was not highly reproducible, so a variety of different thicknesses of Al were produced when different slides were processed. In addition, there were gradients in the thicknesses at different places in an individual slide. The absorbance and reflectance spectra are shown in Figure 3. The reflectance spectra were measured at spots in the four different regions of the substrate, illustrating the variations of the thickness with position. The reflectance spectra were measured relative to the reference signal from a thick, unprocessed Al slide. Figure 3 shows a

decreased reflectance of the ultrathin Al film substrates in the UV region of the spectrum, possibly indicating a plasmon absorbance band.
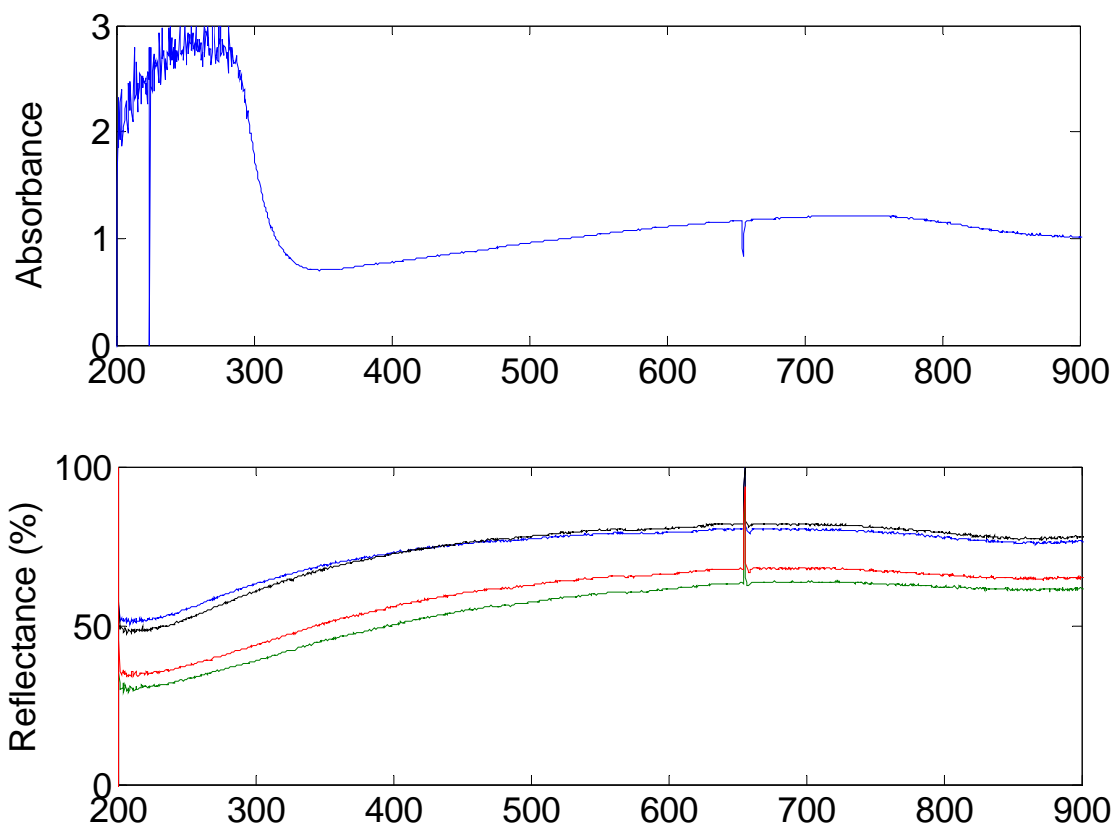

Figure 3. Transmission (upper panel) and reflectance (lower panel) spectra of ultrathin Al films. The four spectra shown in the reflectance panel are from different quadrants of the substrate. A spike is present near 660 nm due to a saturation effect of an intense line in the deuterium-halogen lamp.

Tests of these substrate types are shown in Figures 4 and 5. Figure 4 illustrates the spectra with BPE. Note that in the spectra obtained with 244 nm excitation of the planar substrates measured throughout this work, interfering peaks from gaseous oxygen and nitrogen molecules are observed at 1556 cm^{-1} and 2331 cm^{-1}, respectively. Analytes were deposited on the substrates by spin-coating. A volume of 1 mL of BPE in ethanol was placed on top of the substrate and the substrate was spun to 2800 rpm. Progressively higher concentrations were sequentially deposited on the substrates. It was not possible to observe spectral features at concentrations significantly below 0.1 mg/mL for BPE. This process was performed on both a processed and an unprocessed slide to provide a baseline. The signal levels were comparable for the processed and unprocessed slides, albeit with a relatively large amount of scatter. Therefore, it was not possible to observe any SERS enhancement. A similar analysis was performed using R6G as a test analyte, as shown in Figure 5. In this case, it was possible to observe the R6G at a lower concentration of near 0.01 mg/mL in the spin-coated solution. However, the signal levels were again comparable on both slides.
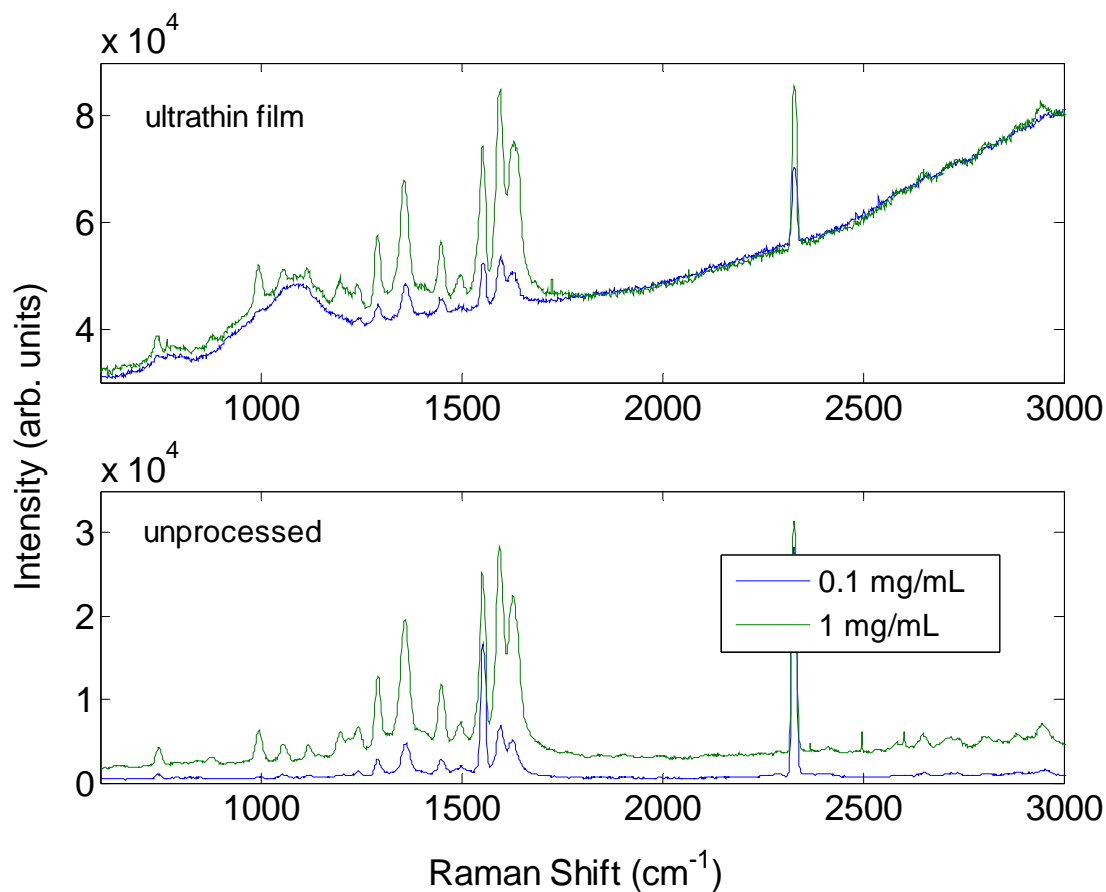
Figure 4. Spectra of BPE on processed (upper panel) and unprocessed (lower panel) Al substrates. The upper panel shows the spectra on an ultrathin film, while the lower panel shows the spectra on an unprocessed Al slide. Broad background features are present in the spectra for the ultrathin Al slides, which are believed to be due to the underlying glass substrate.
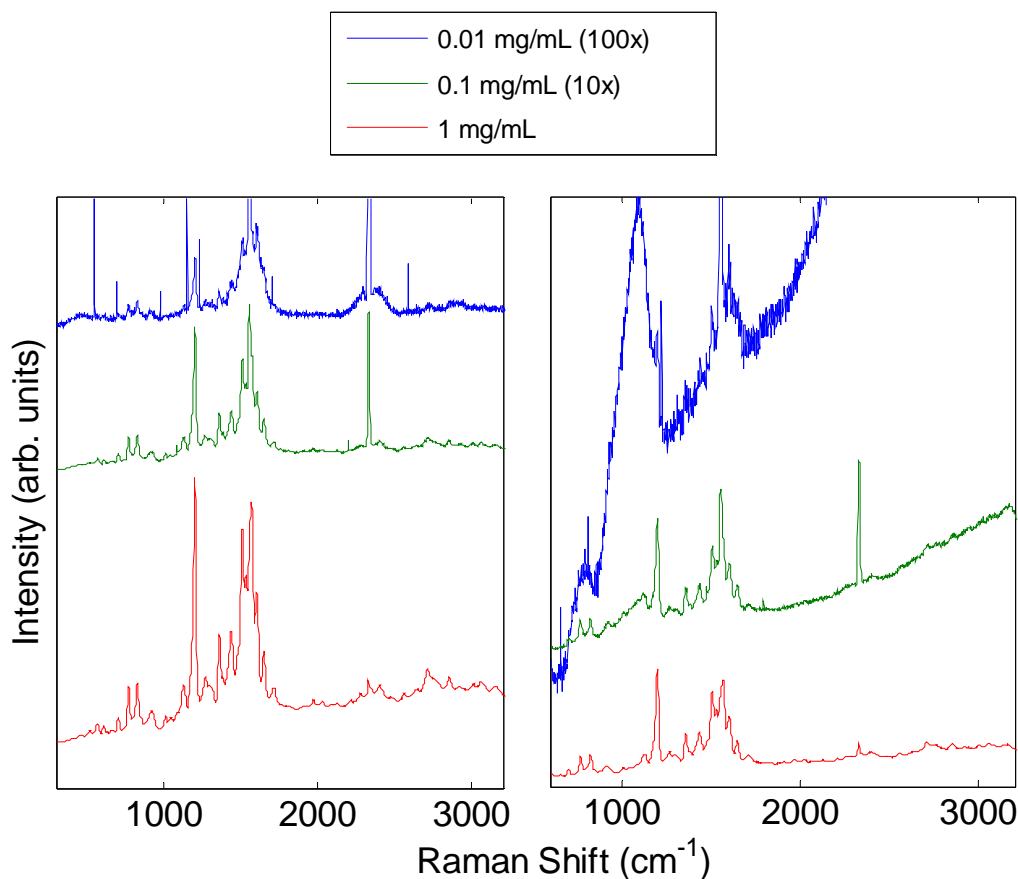
Figure 5. Spectra of R6G on processed (right panel) and unprocessed (left panel) Al substrates.

Figure 6 presents an example of Pd nanostructured film formed by electroless deposition on a germanium substrate. The Pd substrates are discussed because the Pd films and nanoparticles bind more strongly and form a more regular surface on germanium than those of Pt. The reflectance spectrum is also shown in Figure 6. This substrate was formed by immersing a polished germanium substrate in a 10 mM aqueous solution of K_2PdCl_4 for 3 min. The reflectance spectrum shows a general decrease in the reflectance as the wavelength decreases, but no clear evidence of plasmonic behavior. Figure 7 shows Raman spectra of R6G, spin-coated on one of the substrates. One 50 μL droplet was placed on the substrates instead of the 1 mL droplet used with the 1×1 in. Al slides, because the Pd substrates were circular and 1 cm in diameter. The substrates were then spun up to 2800 rpm. On these substrates, a lesser amount of R6G could be detected (down to 0.001 mg/mL). It is not completely clear whether this was due to surface enhancement or if the R6G binds more strongly to Pd than Al, resulting in normal resonance Raman spectra. A comparison test between a surface with a thick Pd film and a surface that is not nanostructured is warranted. However, regardless of the results, it is seen that in this case excitation with 244 nm light is very sensitive. Indeed, some previous work has shown that it is possible to detect Raman spectra from monolayers of analytes even without enhancement,[31-32] which may be the case here.
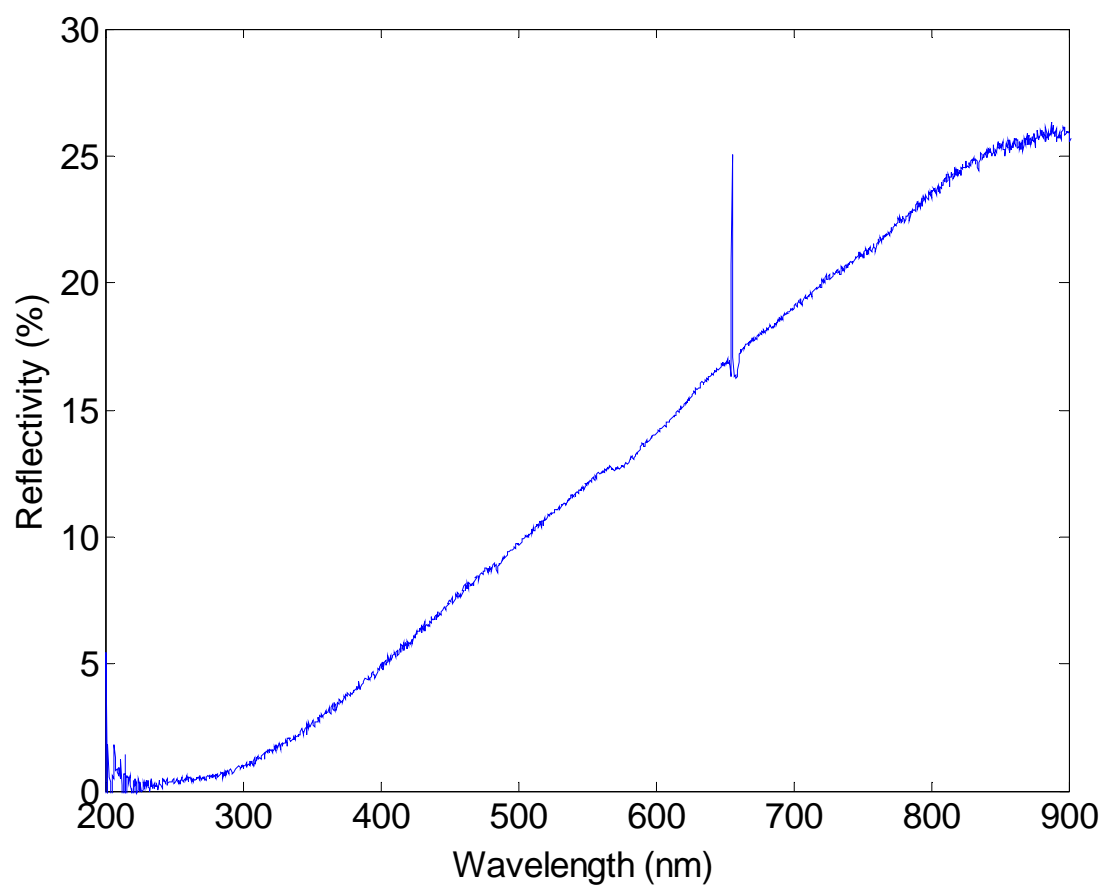
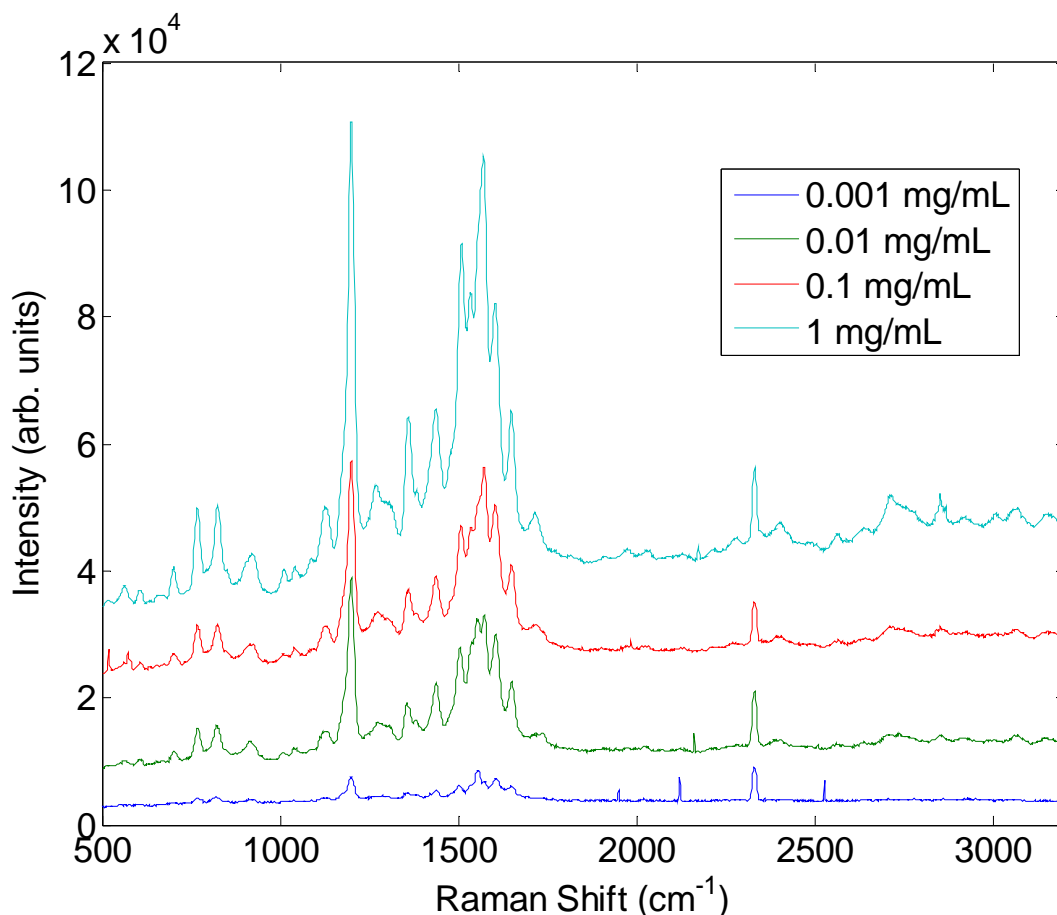Figure 6. Reflection spectrum of an electrolessly deposited nanostructured film of Pd.

Figure 7. Raman spectra of R6G spin-coated on an electrolessly reduced Pd substrate. Successively higher concentrations were added to the substrate.

An investigation with gold substrates was performed (shown in Figure 8). A gold substrate is not expected to have the same effect as UV-SERS, but analytes such as BPE and R6G are known to bind strongly to it. This gold substrate was produced by a similar electroless deposition technique as used to produce the Pd substrates. In this case, the germanium disc was immersed in a 5 mM aqueous solution of $HAuCl_4$ for 10 min. It was then soaked in an ethanolic BPE solution and dried. The spectral intensity was examined using 785 and 244 nm excitations. A strong SERS signal was observed with 785 nm excitation, as expected for gold SERS substrates (right panel). These substrates were then examined with 244 nm excitation. Evidence of BPE was detected in the spectra obtained at 244 nm (left panel), although the spectra exhibited somewhat different relative intensities of the peaks. Because gold is not expected to have enhancement in the UV region, this seems to point to the ability of normal UV resonance Raman spectroscopy to detect very small amounts of material. The experimental setups show several advantages for 244 nm excitation for detecting these small amounts of material. Due to the normal v^4 dependence of Raman cross sections, the cross sections are ~100 times larger at 244 nm than at 785 nm. The resonance enhancement effect adds an additional unknown but possibly large enhancement. There are instrumental issues in the current setup that could also lead to larger signal levels. For example, a larger numerical aperture objective and

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larger laser powers were used at 244 nm excitation. These effects could partially make up for the loss of SERS enhancement, which is typically 10^6 for gold substrates. A possible valuable area of research could be the study of UV resonance Raman spectroscopy of self-assembled monolayers that are carefully prepared to determine the sensitivity of UV resonance Raman spectroscopy more efficiently.
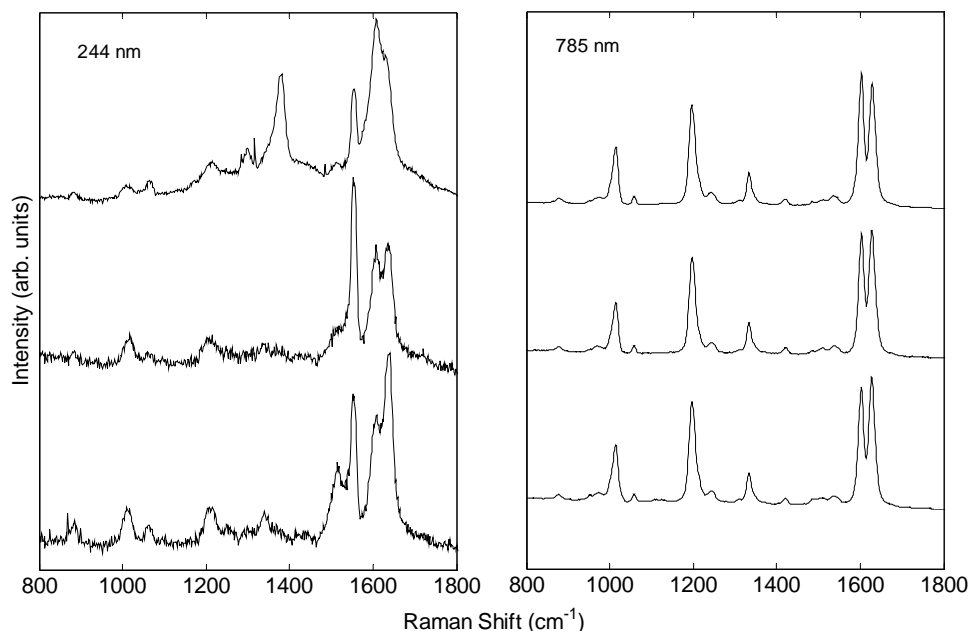

Figure 8. Raman spectra under 244 (left panel) and 785 nm excitation (right panel) of an electrolessly reduced Au substrate exposed to BPE.

4.   CONCLUSIONS

        The use of nanostructured substrates of Al, Pd, and Pt was explored for their potential to act as enhancing substrates for UV-SERS. Although a UV-SERS enhancement effect was not definitively seen, large signal levels were observed. However, there appears to be significant merit in using Raman spectroscopy with UV excitation for chemical detection, regardless of the presence or absence of surface enhancement. More detailed studies of the limits of detection of small layers of material on surfaces with UV excitation are warranted. Future studies should be performed with self-assembled monolayers of materials or inkjet-printed samples.

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