Aluminum Film-Over-Nanosphere Substrates for Deep-UV Surface-Enhanced Resonance Raman Spectroscopy

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ABSTRACT: We report here the first fabrication of aluminum film-over nanosphere (AlFON) substrates for UV surface-enhanced resonance Raman scattering (UVSERRS) at the deepest UV wavelength used to date (λex = 229 nm). We characterize the AlFONs fabricated with two different support microsphere sizes using localized surface plasmon resonance spectroscopy, electron microscopy, SERRS of adenine, tris(bipyridine)ruthenium(II), and trans-1,2-bis(4-pyridyl)ethylene, SERS of 6-mercapto-1-hexanol (as a nonresonant molecule), and dielectric function analysis. We find that AlFONs fabricated with the 210 nm microspheres generate an enhancement factor of approximately 104−5, which combined with resonance enhancement of the adsorbates provides enhancement factors greater than 106. These experimental results are supported by theoretical analysis of the dielectric function. Hence our results demonstrate the advantages of using AlFON substrates for deep UVSERRS enhancement and contribute to broadening the SERS application range with tunable and affordable substrates.

KEYWORDS: UV resonance Raman spectroscopy (UVRRS), surface-enhanced Raman spectroscopy (SERS), aluminum plasmonics, film-over-nanosphere substrates

Surface-enhanced Raman scattering (SERS) relies on the electromagnetic (EM) field enhancement by collective oscillations of conduction electrons in metal nanomaterials, known as localized surface plasmon resonance (LSPR). Since the discovery of SERS, the types of substrates that support surface enhancement have been expanded from roughened electrodes to nanoparticles and various solid-support substrates. These substrates, usually made of coinage metals, such as Ag, Au, and Cu, are well characterized and enhance Raman scattering in the visible to infrared wavelength range. The LSPR of Au or Ag nanostructures amplify the inherently weak Raman signal by up to 109. One wavelength region of the spectrum that has remained elusive for SERS enhancement is the deep ultraviolet (DUV). Theoretical calculations predict that metals, such as aluminum (Al), gallium (Ga), indium (In), lead (Pb), tin (Sn), and others with negative real and small imaginary dielectric constants in the UV, are viable materials for SERS. The most common metals used experimentally to attempt UVSERS include Al, Ga, Rh, Ru, Pd. Here, we will focus on the use of Al as a SERS substrate. Previous reports of UVSERS enhancement on Al have achieved enhancement factors (EFs) of ~50 using Al nanoparticle array substrates and 257.2 nm excitation; ~103 on Al nanovoids with adenine excited at 244 nm; and for tip-enhanced Raman spectroscopy, using a silicon cantilever with Al deposited on it, adenine was probed with 266 nm excitation and the calculated EFs were in the 60−200 range.

In addition to harnessing the enhancement due to plasmon excitation in the UV, the excitation of many molecules in the DUV frequency range (190−300 nm) is highly desirable because it results in enhancement due to DUV resonance Raman scattering (UVRRS). UVRRS becomes prevalent when the excitation wavelength falls within an electronic absorption band, exciting a specific chromophore of the target molecule. This excitation, which is in resonance with an electronic transition of the molecule, results in enhancement of the normally weak Raman signal by 2 to 6 orders of magnitude depending on the magnitude of the extinction coefficient of the electronic transition and its excited state line width. Additionally, UV excitation below 250 nm minimizes contaminating fluorescence backgrounds. Combining UVRRS with SERS...
(UVSERRS) allows for highly sensitive and selective enhancement of adsorbed molecules at ultralow sample concentrations. Herein, we present Raman spectra excited at the deepest UV wavelength used to date ($\lambda_{\text{ex}} = 229$ nm) for four analytes on the following: SERS measurements on Ag and Al film over nanosphere (FON) substrates, and resonance Raman measurements on Ag and Al mirrors, quartz, in solution, and in the solid state. To estimate the contribution of the resonance enhancement, we also excited SERS at two different wavelengths ($\lambda_{\text{ex}} = 355$ and 405 nm) where the molecules show minor absorbance (all Raman instrumentation discussed in detail in SI). We additionally employ theoretical arguments to support our experimentally observed enhancements. The data presented here fully characterizes our Ag and Al SERS substrates and allows us to further understand their performance in the deep UV wavelength region.

In our experiments, adenine, tris(bipyridine)ruthenium(II) (Ru(bpy)$_3$), 6-mercapto-1-hexanol (MH), were obtained from Sigma-Aldrich and used as received; whereas, trans-1,2-bis(4-pyridyl)-ethylene (BPE) was recrystallized. We measured UV−visible absorption spectra for 0.125 mM adenine, 0.01 mM Ru(bpy)$_3$,$^2$, 0.01 mM BPE, and 0.5 mM MH with a Cary 5000 UV−vis-NIR spectrophotometer (Agilent). From these measurements, we see that exciting these molecules with $\lambda_{\text{ex}} = 229, 355,$ and 405 nm will probe their Raman spectra in preresonant and nonresonant states (Figure 1A). In particular, MH was included in our measurements at 229 nm as a nonresonant adsorbate example.

FON SERS substrates were used to enhance the UVSERRS signal of the adsorbate molecules investigated. The methodology to create AgFONs is well established,$^{21}$ although not for the wavelength range of interest. We adapted the AgFON methodology for the preparation of Ag and Al FONs used here (see SI for substrate fabrication details). FONs are ideal SERS substrates for several reasons, including low cost, ease of fabrication, and the ability to tune the LSPR $\lambda_{\text{max}}$ to match excitation wavelengths by changing the spheres size or amount of metal deposited. Additionally, we have previously demonstrated that noble metal FONs (Ag and Au) have reproducible enhancement over large areas$^{21}$ and are stable at high temperatures (500 K),$^{22}$ at negative applied potentials (electrochemical)$^{23,24}$ on the shelf for more than 9 months with a protective alumina layer deposited by atomic layer deposition,$^{25}$ in biological fluids,$^{26}$ and in vivo for more than 17 days. $^{27}$

The optical properties of the FONs were measured using a Cary 5000 double spectrophotometer in specular reflectance mode (Varian internal DRA accessory) and are shown in Figure 1B,C. Previous work from the Van Duyne group$^{18}$ on substrates fabricated by nanosphere lithography established that the “ideal” wavelength of maximal signal from the LSPR phenomenon (LSPR $\lambda_{\text{max}}$) is equal to $1/2(\lambda_{\text{ex}} + \lambda_{\text{ vib}})$, where $\lambda_{\text{ex}}$ is the excitation wavelength and $\lambda_{\text{ vib}}$ is the wavelength where the vibrational mode of interest occurs. For the adsorbates being investigated here, the “ideal” LSPR $\lambda_{\text{ max}}$ should fall between 234−238 nm (based on $\lambda_{\text{ex}} = 229$ nm and vibrational modes in the fingerprint region of ~700−1650 cm$^{-1}$). This indicates that the AgFON prepared with 170 nm spheres should provide the highest signal enhancement at $\lambda_{\text{ex}} = 229$ nm, assuming the ideal LSPR condition.

Figure 2 shows the SERS spectra of the three resonant adsorbates (columns) on both Ag (2A, 2D, 2G) and Al (2B, 2E, 2H) FONs and mirrors. We find the SERS spectra for BPE, Ru(bpy)$_3^{2+}$ and adenine are shifted from the corresponding normal Raman spectra in solution by 1−30 cm$^{-1}$, which is in good agreement with the frequency shift criteria for SERS (see key factors to consider for characterizing SERS substrates in SI). In Figure 2A, we show the SERS spectra of BPE on AgFONs made from the 170 and 210 nm sphere diameters. We see little enhancement (≤10×) of the Raman spectrum of BPE on the Ag mirror. The spectra are consistent with previously established SERS spectra of BPE$^{12,29}$ with characteristic peaks at 1008, 1200, 1604, and 1640 cm$^{-1}$. On the AgFON 170 nm, the intensities of the 1604 and 1640 cm$^{-1}$ doublet of BPE are enhanced approximately 10 times. On the AgFON 210 nm, the enhancement is larger and the doublet becomes very well resolved, along with other BPE peaks clearly evident (1200 and 1008 cm$^{-1}$). A similar pattern of BPE enhancement is seen on the AlFONs and mirror (Figure 2B). There is little enhancement of the BPE signal on the mirror and AlFON 170 nm, but the enhancement of the AlFON 210 nm substrate is significantly larger. Although the doublet is less well resolved here, the peaks at 1200 and 1008 cm$^{-1}$ are clearly visible. Comparison of the scale bars in Figure 2A,B show that the AlFON achieves ~600 times greater intensity than the AgFON for the BPE SERS signal.
The second column of Figure 2 includes similar comparison between Ag and Al for Ru(bpy)$_3^{2+}$. The SERS spectra for Ru(bpy)$_3^{2+}$ on both metals are comparable to those found in the literature. In Figure 2D, we find that the AgFON 170 nm has approximately 3−5 times higher enhancement than the AgFON 210 nm and the Ag mirror. The AlFON 210 nm has approximately 120 times greater enhancement than the AlFON 170 nm and Al mirror (Figure 2E).

In the case of adenine, third column of Figure 2, the AgFON 170 nm shows a larger enhancement (Figure 2G) than the AgFON 210 nm. We see signal intensities on AgFON 210 nm, which are 10 times less than on AgFON 170 nm and with little signal intensity on the Ag mirror for 1 mM adenine. For Al (Figure 2H), we see once more that the AlFON 210 nm provides greater signal enhancement over the AlFON 170 nm and the Al mirror. In this case, the enhancement of adenine on Al is ∼160 times greater than on Ag. In comparing the spectra of adenine on the Ag and Al FONs with previously published UV SERRS results, we note that the spectra here are different. This illustrates the importance of exciting at deeper UV wavelengths, because we are able to access higher lying excited states than the previous studies, resulting in excitation of different vibrational modes. The differences in the UV resonance Raman spectra of adenine and adenosine from exciting the molecules at different excitation wavelengths (between 200 and 300 nm) have been noted extensively in the literature, and we find that our peaks correspond well with the peak assignments in the literature.

We also note that the spectra of the different molecules are not the same on Al in comparison with Ag. We believe that this could be due to surface selection rules for SERS, which indicate that the Raman modes of the molecule that are oriented perpendicular to the surface will be preferentially enhanced. Additionally, in the case of Ru(bpy)$_3^{2+}$, the spectra on Al highly resemble the...
spectra of 2,2'-bipyridine (Figure 2E), which may be due to an orientation of the adsorbed molecule on the surface that enhances those Raman modes. In addition, the electronic transition excited at 229 nm may be localized on the 2,2'-BPY ligand, thus enhancing these vibrations and containing little metal-to-ligand charge transfer (MLCT) character. For the nonresonant molecule (MH), we were only able to record Raman spectra of the high wavenumber region, because there is little resonance enhancement of the Raman signal (Figure S2).

Up to this point we have been referring to enhancements in terms of increased signal intensity, which provides a general picture of the overall enhancements but does not account for factors such as surface roughness (for FON vs mirror), number of molecules contributing to signal, and so forth. To account for these factors, fully characterize our substrates, and to gain a deeper understanding of the mechanisms influencing the signal enhancement, we calculated the SERS and resonance Raman EFs. We define the enhancement on the FONs as a total EF with contributions from both resonance Raman (RR) and the EM enhancement mechanism of SERS (EF\text{total} = EF_{SERS} \times EF_{RR}; Figure 3). We attribute the enhancement on the mirrors to resonance Raman enhancement. When comparing the enhancement of Ag and Al mirrors for Ru(bpy)$_2^{2+}$, BPE, and adenine, we find a similar order of magnitude of enhancement for each adsorbate (Figure 3). For example, the EF$_{RR}$ for adenine is $\sim 2 \times 10^3$ on Ag mirror and $\sim 1 \times 10^3$ on Al mirror. Achieving similar EFs on the two mirrors supports our assertion that the Raman signals on the mirrors arise from a resonance effect. Additionally, because MH undergoes little resonance enhancement we attribute its entire signal to the EM enhancement effect. Our results show that for MH on AlFON 210 nm the EF$_{SERS}$ is $\sim 2 \times 10^5$ and on AgFON 210 nm the EF$_{SERS}$ is $\sim 4 \times 10^2$. Because of the lack of resonance enhancement, we were unable to collect a signal for MH on either Al or Ag FONs 170 nm or the mirrors.

Experimentally, the AlFON 210 nm proved to be the most highly enhancing substrate, generating total EFs in the $10^5$--$10^7$ range, whereas the other FONs generated total EFs of $10^2$--$10^4$ (Figure 3). This is in disagreement with our hypothesis that the AlFON 170 nm would be the most highly enhancing substrate based on the “ideal” LSPR $\lambda_{\text{max}}$ equation determined by McFarland et al. (2005). However, this disparity may be explained by the fact that the “ideal” LSPR equation was developed for periodic particle arrays (PPA), which are more highly ordered substrates than FONs. The less well-ordered structure of the FONs is due to different shapes and nanostructures on the FON surface which means the near fields the molecules are experiencing are probably very different than the “ensemble” LSPR, or far fields, collected via UV-vis absorption spectroscopy. Consequently, we report here the first fabrication of FONs with Al, demonstrate that the behavior of FONs fabricated with different metals cannot be generalized, and we establish that we cannot determine optimal enhancement based solely on sphere size and LSPR $\lambda_{\text{max}}$.

In Table 1, we outline the total enhancements for each molecule on AlFONs 210 nm, as well as the enhancements due to the EM mechanism (EF$_{SERS}$) and resonance Raman (EF$_{RR}$).

![Figure 3. Ensemble averaged enhancement factors at 229 nm for the four adsorbates investigated, Ru(bpy)$_2^{2+}$, BPE, Adenine, and MH, on Ag and Al FONs and mirrors. The mirrors show the resonance Raman enhancement. AlFON 210 nm results in the largest total enhancement $\sim 3 \times 10^7$ for BPE and SERS enhancement $\sim 2 \times 10^5$ for MH. The error bars reflect standard deviation in signal intensity for multiple peaks on each substrate for 6–12 spectra per substrate.](Image)

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Table 1. Ensemble Averaged Enhancement Factors for Each Molecule on the AlFON 210 nm Broken down by Total EF, EF Due to Resonance Raman Effect (EF$_{RR}$) and EF Due to Electromagnetic Enhancement Mechanism of SERS (EF$_{SERS}$)

To probe further into the behavior of the Ag and Al FONs, we use the optical constants from Johnson and Christy for Ag and from Palik for Al in an analysis of the dielectric functions to explain the observed enhancements (Figure 4). Notably, an LSPR can only be supported when the real part of the dielectric function is negative (Figure 4A, bottom), suggesting that Al will be “plasmonic” in the UV while Ag will not be. Additionally, we use the dielectric functions to calculate a plasmon quality factor ($Q_{\text{SPP}} = \alpha_{\text{max}}^2/\epsilon_{\text{r}}$), which describes the field confinement of the surface plasmon polariton and which is optimized at each wavelength with respect to particle shape (Figure 4B). Comparisons with experiment show that the relationship between EF and $Q_{\text{SPP}}$ varies as $\text{EF} = \alpha_{\text{max}} \times Q_{\text{SPP}}$, where $\alpha_{\text{max}}$ is a geometry-dependent prefactor. We have previously determined the $\alpha$-factor to be 10.5 for Ag immobilized nanorod arrays (AgINRA) substrates, which are similar to FONs except that in the INRA nanorod-type structures are developed on the surface of the deposited sphere mask. The original work included experimental results collected with laser excitations at 633, 785, and 1064 nm. We have added two additional data points at 488 and 532 nm with the original $Q_{\text{SPP}}^2$ determination (Figure 4B).
In Figure 4C,D (and Figure S3), we plot the $Q_{SPP}^2$ results for pure Ag, pure Al, and an approximate result for Al coated with Al$_2$O$_3$. Previous results suggest that the optimal enhancement by Al with a native Al$_2$O$_3$ coating (Al-Ox) is $\sim 167$ times less than that for Al, so we implement 167 as a first approximation to $1/\alpha$. Figure 4C shows that the EFs measured for Ru(bpy)$_3^{2+}$ on AlFONs 170 nd 210 nm at $\lambda_{ex} = 229$ nm fall between the Al and Al-Ox quality factors, indicating consistency with this crude EM enhancement factor at lower wavelengths (see Figure S3 for Adenine and BPE).

We also measured experimental SERS spectra of Ru(bpy)$_3^{2+}$ excited at 355 and 405 nm on Ag and Al FONs (Figure S4). For both excitation wavelengths (355 and 405 nm), AgFONs perform better than AlFONs. Including these data points on our theoretical plots shows that the $Q_{SPP}$ is less accurate at 355 and 405 nm on AlFON 300 nm, where the experimental EFs are higher than those values predicted for pure Al (Figure 4D). For the Ag 170 nm sphere, we show that the theory matches the experimental EFs well at 355 nm, while on the Ag 280 nm sphere the experimental EF is higher than the predicted value. At 405 nm the EFs on Ag 170 nm are slightly less than those predicted by $Q_{SPP}$, while on Ag 280 the value is significantly higher.

For Ag, as the excitation wavelength drops below 400 nm, the enhancement drops off rapidly, as is to be expected given that interband transitions (and therefore plasmon damping) is important below $\sim 325$ nm. For Al, the EFs increase in going from 200 to 400 nm and reach values greater than $\sim 10^5$. In Figure 4A, there is also an important dip in the real component of Al dielectric function near 800 nm that arises from interband transitions, but this prediction of the theory has not been tested here. From this analysis of the dielectric functions, it is clear that Al provides consistent enhancement throughout the UV, whereas Ag provides strong enhancement in the visible that drops off rapidly below 350 nm. The $Q_{SPP}$ provides good agreement with the EFs observed for the 170 and 210 nm AlFONs (at $\lambda_{ex} = 229$ nm), as well as for the 170 nm AgFONs (at $\lambda_{ex} = 355$ nm), however this metric underestimates the enhancement observed for the 280 nm Ag and 300 nm AlFONs. These differences are likely due to nanoscale variation in the FONs, as well as near-field versus far-field effects not captured by the simple $Q_{SPP}$ EF metric.

In conclusion, the present work demonstrates for the first time fabrication of AlFONs and excitation of combined resonance Raman and SERS at the deepest UV wavelength to date ($\lambda_{ex} = 229$ nm). We confirm that AgFONs support plasmonic enhancement at wavelengths greater than 400 nm, while below 400 nm we see only contributions from resonance enhancement. We also demonstrate both experimentally and theoretically that AlFONs provide electromagnetic enhancement in the 200–400 nm range. The magnitude of the enhancement is $10^3$–$10^5$. However, when combined with the resonance effect, the total enhancement of the AlFONs is in the $10^5$–$10^7$ range, depending on the resonance enhancement of the molecule being probed, which is comparable to or greater than previously reported enhancement factors.7,9,19 We demonstrate that BPE on the AlFON 210 nm provides the largest total enhancement at the deepest UV wavelength used to excite SERS spectra to date.

As this is the first report on the fabrication of AlFONs, there is room for optimization of the substrates. We continue to work on characterizing various nanosphere sizes and deposition conditions to expand the use of AlFONs across a range of UV wavelengths. By combining the advantages of UV resonance Raman with SERS, there is great potential for these FONs to be applied in the collection of SERS spectra at ultralow concentration, using label-free samples in a variety of fields including materials research, biological and chemical applications, and catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b04296.

†Raman instrumentation; substrate fabrication; nonresonant Raman spectra of mercaptotetanol; key factors to consider for characterizing SERS substrates; enhancement factor calculations; relationship between EF and $Q_{SPP}^2$ for Ag and Al FONs incubated with BPE and adenine; experimental SERS spectra for Ru(bpy)$_3^{2+}$ excited at 355 and 405 nm on Ag and AlFONs (PDF)

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