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Gold Nanorod Arrays: Excitation of Transverse Plasmon Modes and Surface Enhanced Raman Applications

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Abstract

In this paper we describe a method for the fabrication of gold nanorod arrays and their characterization. The initial requirements were for a robust substrate with strong surface enhancement of Raman scattering with minimal surface contamination. The rods with length up to 20 μm were electrochemically deposited in alumina templates bonded to gold coated silicon wafers. After removal of the template, surface bound cyanide from the deposition process was removed by mild electropolishing. Reflectance and cathodoluminescence measurements revealed transverse dipole and quadrupole plasmon modes. Surface enhancement of 10^6 was determined by taking Raman spectra of self-assembled monolayers of 4-aminothiophenol. The enhancement factor (EF) was found to be independent of nanorod aspect ratio because only the length of the nanorods was varied while their diameter was kept constant and due to the large length of nanorods only the transverse plasmons were excited.

Dedicated to Professor Kohei Uoasaki in recognition of his contributions to electrochemistry and physical chemistry.

Introduction

We were approached with a request to determine the nature of the passive layer formed at a gold surface during gold leaching from thiosulfate solutions. The products of thiosulfate decomposition such as elemental sulfur, sulfides, and polythiosulfonates have characteristic bands in Raman spectra located below 1000 cm^{-1} . Therefore, Raman spectroscopy has the potential to detect the components of the passive layer. In addition, gold is a coinage metal that is known to exhibit surface enhancement of the Raman signal if the gold surface is covered by nanoparticles or is nanopatterned.^{1,2}

The increase in the Raman signal has been attributed to two mechanisms. Chemical enhancement is the result of photon induced charge transfer between the metal nanoparticle and

the molecules chemisorbed on it. This is followed by vibrational relaxation and emission of a photon with a different energy than the incident light. This effect contributes to the signal enhancement by a factor of 10^2 .³

The electromagnetic enhancement is dependent on the wavelength of the incident light and the nanoparticle size, shape, and composition.⁴ When coupling occurs between the metal's conduction band electrons and incident photons, a surface plasmon polariton (SPP) is created.⁵ When the nanoparticle is smaller than the photon wavelength, the SPP is confined and this leads to localized surface plasmon resonance (LSPR).³ The effect of the resonance condition is a distortion of the electron density about the nanoparticle. The distribution of the electric field is not necessarily homogeneous and can be more intense where the particle has more pronounced curvature such as at edges and points.⁶ The electric field impinges on molecules close to the surface and results in a larger induced dipole and Raman signal. Electromagnetic enhancement is usually larger than that of chemical enhancement and together the Raman signal can be enhanced by six orders of magnitude or more for molecules close to or chemisorbed on metal nanoparticles.³

Spherical particles with a diameter less than 100 nm exhibit only a single absorption maximum while oblate spheroids have two. These correspond to transverse and longitudinal plasmon dipole modes where the electron density is distorted about the short and long axes of the nanoparticle respectively.⁷ Excitation of the two modes can happen only if the electric field vector of incident light has a component parallel to the corresponding axis. It is also possible for these plasmon modes to couple when two particles are arranged side by side or end to end. This coupling has been found to become more intense with reduced separation and leads to "hot spots".⁸⁻¹⁰ By increasing the size of metal nanoparticles, the LSPR frequency can be red shifted.^{7,11} In addition,

particles larger than 100 nm in diameter or length may have multi-polar modes appear at shorter wavelengths as size increases.¹² By varying the size, shape, and composition of metal nanoparticles it is possible to change the plasmon resonance frequency and Raman enhancement factor to suit the desired application. If there is a wide distribution of size, shape, and separation of nanoparticles this can result in broader plasmon modes.¹³

The arrangement of nanoparticles in ordered arrays can allow for better control over the size, shape, and distribution of the particles and their optical properties. While there are a number of ways for achieving long range order of nanoparticles, the growth of nanorods in alumina templates is one of the more flexible methods. The growth of such arrays was first demonstrated by Penner and Martin where they produced ultramicroelectrodes in alumina templates for electrochemical studies.¹⁴ Yao *et al.* explored a number of different transition metal nanorod arrays but found that the most significant Raman enhancement was obtained with gold or silver.⁶ After growth of the rods, the alumina template may be left in place or partially removed thereby controlling the length of the gold rods protruding from the template.^{11,15}

The presence of the aluminum oxide lends mechanical support to the array but also affects the optical properties of the substrate. It has been noted that the periodic nature of the pores leads to interference fringes in the UV-Vis absorbance spectrum.^{16,17} The dielectric of alumina also modulates the transverse and longitudinal plasmon resonance, red shifting these modes (with respect to air) but also making them more intense.^{13,15} The removal of the template exposes more nanorod surface area to the probe molecule and this can increase the SERS signal.¹⁸ As the AAO is etched away, the rods are less supported and will sometimes bend so that there is a small gap between adjacent tips. This results in coupling between the transverse modes as mentioned above.⁹⁻¹¹ Ideally these hot spots are evenly spaced across the substrate surface but in reality the

distribution is non-homogeneous¹⁹ and this leads to broader plasmon peaks.¹⁵ If the template is completely removed the rods are unsupported and become disordered, thereby changing their optical properties and Raman enhancement.^{11,15,18,19}

Arrays of metal nanorods also allow for the exploration of the dependence of the plasmon modes on the polarization and angle of incident light. S-polarized light is able to stimulate the transverse plasmon mode at all angles of incidence.^{13,17,20} With P-polarized light at small angles of incidence, only the transverse mode is excited^{13,17,20} but the longitudinal mode can also be probed by increasing the angle of incidence.^{13,15,17,20} At a glancing angle of incidence there is an equal contribution from both transverse and longitudinal modes though this also leads to red-shift and broadening due to coupling.^{13,17,20}

During gold leaching, the nanoparticles are dissolved as a function of leaching time.²¹ Therefore the surface enhancement changes and the intensity of Raman bands decreases or the bands disappear. To apply SERS to study the surface composition of gold during its dissolution one needs to design a special type of nanostructure. In this paper we demonstrate that this could be achieved using gold nanorod arrays.²²⁻²⁴ During leaching of the gold nanoarray the dissolution takes place only from the top of the gold nanorods exposed to the leaching solution, because only this fragment is exposed to reagents (oxygen, thiosulfate) diffusing from the bulk of the solution. The reagents initially present inside the array are depleted during the initial stage of the dissolution. Consequently, the width of the nanorods remains constant and only their length changes during the remaining time of the dissolution experiment. When the length of nanorods exceeds one micrometer and the diameter is in the range of nanometers, the excitation of longitudinal plasmons is shifted far into IR region while the transverse plasmons can be excited by visible light.²⁵ In this way one is able to produce a durable substrate that exhibits strong and

steady enhancement throughout the course of spectroelectrochemical experiments. Although there can be variation in surface enhancement across the surface of a given substrate, each leaching experiment monitored a single site over the course of several hours and for this reason, the enhancement did not change. Since gold is continuously dissolved and hence the surface is continuously renewed the beam damage to the film is not a concern in that case. This strategy eliminates the need for internal standards for quantification of spectral data as is the case for shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).²⁶

The goal of this paper is to describe the preparation of the nanorod electrodes for SERS studies and their plasmonic properties. The fabrication method is low cost and simple when compared with other methods requiring the deposition and anodization of aluminum films on solid supports.²⁷ The use of commercial alumina templates also allowed us to investigate gold nanorods with dimensions larger than most literature reports. We show that the enhancement factor is not affected by the length of the rods and that this is advantageous from the point of view of analytical applications. This type of substrate found a unique application in studying the structure of a film formed on gold during gold leaching in thiosulfate solutions. However, it may also find applications in other studies where the SERS active substrate may undergo dissolution.

Methods

All polytetrafluoroethylene (PTFE) was cleaned with fresh piranha solution ($3\text{H}_2\text{SO}_4:1\text{H}_2\text{O}_2$) while glassware was cleaned with 100°C concentrated acid ($3\text{H}_2\text{SO}_4:1\text{HNO}_3$). Milli-Q water was used for rinsing as well as for preparation of all aqueous solutions. All chemicals were reagent grade and used without further purification. All electrochemical experiments used a HEKA PG590 potentiostat controlled and monitored by a National Instruments data acquisition board (PCI 6052E).

Silicon wafers (MEMC Electronic Materials, WAFVY87) were sputter coated with 5 nm of titanium and 10 nm of gold in a Kurt J. Lesker AXXIS physical vapour deposition system. Anodized aluminum oxide (AAO) filter discs (Whatman 0.2 μm Anodisc 13) were bonded to the gold coated wafers with four 0.1 mm^3 pieces of low density polyethylene (LDPE) by heating in an oven at 170° C for 15 minutes.

The electrodeposition of gold nanorods was carried out in a glass three electrode cell with a Ag/AgCl reference electrode, gold wire counter electrode, and the AAO-wafer as working electrode. An electrolyte of 0.1 M $\text{KAu}(\text{CN})_2$ and 0.1 M KCN was used with pH adjusted to 10 with HClO_4 to prevent dissolution of the template. The solution was de-aerated with argon for 30 minutes and a potential of -0.95 V was applied to the working electrode for 5-20 hours. The alumina template was dissolved with 1 M NaOH and the substrate was rinsed with water. Electropolishing was done with stirring in an open beaker containing 3 M HNO_3 , a platinum counter electrode, and a Ag/AgCl reference electrode. A potential of +1.3 V was applied to the substrate for 60 seconds, then +1.1 V for 60 seconds, and finally transferred to water for 60 seconds. This was repeated three times. Water was removed from the samples by using a custom built critical point dryer.^{28,29} Scanning electron microscopy (SEM) images were collected with a FEI Inspect S50.

Reflectance measurements were collected with an ORIEL 66184 ATH 150W lamp, ORIEL 1/8m cornerstone T4000 monochromator, Thorlabs 32mm Glan-Thompson calcite polarizer, and Thorlabs DET210 Si photodiode detector. Nanorod reflectance data was corrected for dark current and normalized with respect to reflectance measurements taken from smooth gold slides to account for detector sensitivity.

Cathodoluminescence (CL) data was obtained using a Hitachi S570 SEM with a Linos Optics aluminum parabolic mirror mounted above the sample stage. A 1 mm hole allowed for the passage of the electron beam from the source to the sample. The light collected by the mirror was directed to a 20 mm diameter fused silica window (Allectra) in the SEM chamber. An aluminum mirror (Edmund Optics) switched the path between a photomultiplier tube (R649 PMT) and a monochromator/CCD (Jobin Yvon Triax 320, Spectrum One). Control and monitoring of the setup was done using a National Instruments PCI 6251 data acquisition card with IgorPro software. A detailed description of the cathodoluminescence setup can be found in Ma *et al.* 2014.³⁰

Enhancement factor was determined by using the 1588 cm^{-1} peak of 4-aminothiophenol (4ATP).^{31,32} The substrates were immersed overnight in a solution of 5 mM 4ATP in methanol and then rinsed with methanol and water. Reference spectra of bulk 4ATP were taken with 100% laser power while Raman spectra of the nanorod samples were obtained at 1% laser power (785 nm, 300 mW, Renishaw RL785 laser) with a Renishaw RM2000 Raman spectrometer equipped with a Leica 63X water immersion lens.

Results and Discussion

Our first attempts at making a gold nanorod array used just a 100 nm thick layer of vapour deposited gold on alumina discs, but these substrates were unusable once the template had been removed. The bonding of the conductive support and template was developed to produce a more robust array. A similar approach was taken by Ponrouch *et al.* where a solid conductive backing and template were clamped together.³³ The advantage of using LDPE as an adhesive is that the deposition process can be monitored visually and adjusted as needed. Typically, the sample becomes yellowish as a smooth gold layer is deposited on the conductive surface in the space

between the wafer and template. As gold begins to fill the pores, the sample takes on a dark appearance. If the rods overgrow the template, the sample becomes yellow-orange.

Initial work on the fabrication of gold nanorod arrays was done using commercial plating solutions but this was discontinued due to batch inconsistency and problems with surface contamination.²²⁻²⁴ A non-toxic thiosulfate-sulfite gold plating solution was also tested but it was not possible to grow rods in the template.³⁴ Although less desirable to work with, a $\text{KAu}(\text{CN})_2$ based electrolyte proved to be highly reliable with some minor surface contamination issues.

In the electrodeposition process there are two distinct regimens. First the gap is filled over the course of 2-3 hours (Figure 1A) depending on the separation between wafer and template (typically 5-10 μm). The second phase (Figures 1B, 1C) begins with the filling of the pores although there is no change in the measured current that signals this transition. The rod length is controlled by varying applied potential and deposition time. The onset of hydrogen evolution at -1.0 V vs. Ag/AgCl limits the use of more negative potentials to accelerate the process though the formation of H_2 gas bubbles in the pores does make it possible to form tubes rather than rods.

The nanorods are uniform in height and have an average diameter of 282 nm (Figure 1C, 1D). The width of nanorods is quite large relative to samples investigated earlier in the literature¹¹ but the samples still have large surface enhancement. Wider nanorods have the advantage taking longer to dissolve in leaching experiments. In addition they are sturdier and less susceptible to coalesce after removal of the aluminum template. When samples are subjected to critical point drying the rods are separated by a gap of 127 nm (Figures 2A) but form clusters separated by large gaps when water evaporates in an uncontrolled manner (Figures 2B). Turbulence in solution may also play a role in determining separation distance.

Figure 1. A) The electrodeposition of gold in the gap between the gold coated silicon wafer and the alumina template. B) After the gap has been filled, gold nanorods begin to be deposited in the pores and continue until the desired length is reached (C). D) Side image of gold nanorod substrate showing a gap thickness of 9.2 μm and rods 3.9 μm long.

Figure 2. Top images of gold nanorod substrates. A) well separated rods, B) aggregates formed by capillary force during drying. Due to aggregation the clusters of rods appear slightly tilted in this image. Broken rods can be seen lying on the surface in both images.

Electrodeposition of gold to form the nanorod arrays leads to the unintended consequence of adsorbed cyanide species as seen in the SER spectrum (Figure 3). The CN stretch has an intense, narrow peak at 2125 cm^{-1} while the $\nu\text{Au-C}$ and δAuCN modes are observed at 378 cm^{-1} and 290 cm^{-1} respectively.³⁵ Theoretical studies have shown that adsorption of CN leads to a shortening of the triple bond and that this effect is more pronounced with attachment through the carbon as opposed to the nitrogen.³⁶ As a consequence of this, DFT calculations predicted the νCN mode of Au-CN to be 45 cm^{-1} greater than Au-NC.³⁷ Experimental work has shown that the CN peak position is dependent on the applied potential with Au-CN being favored at more positive potentials and Au-NC being favoured at more negative potentials.³⁸⁻⁴¹ Our results suggest that CN has been adsorbed through the carbon. *In situ* STM work has noted some adsorption of CN but suggests that the surface is primarily composed of a Au-CN adlattice where the CN bond is parallel to the surface.^{42,43} This model does not seem to be consistent with our SERS results or those reported in the literature since the CN bond would be orthogonal to the electric field of the LSPR.

Surface bound CN presents two problems for SERS experiments. First is that the presence of cyanide modifies the gold surface and may lead to a significantly altered chemical environment. The second concern is that the presence of CN vibrational peaks may overlap or obscure spectral features of interest. For these reasons a number of different cleaning methods were tested. Mild electropolishing (as described in the methods section) proved to be the most effective at removing surface contaminants and did not damage the nanorods. The use of HCl, HClO₄, or NaOH instead of HNO₃ lead to an intense peak at 267 cm^{-1} which can be assigned to the Au-S stretch of adsorbed sulfur contaminants contained in the reagents. Incomplete removal of the

gold oxide formed at +1.3 V during the electropolishing step resulted in a strong peak at 550 cm⁻¹

1.

Figure 3. Untreated nanorod substrates display a prominent CN peak at 2125 cm⁻¹ and smaller peaks at lower wavenumbers. SER spectra of electropolished samples are devoid of contaminant peaks. Spectra acquired with 3 mW laser power, one scan, accumulation time 10 seconds.

Visually the substrates are homogeneously brown though there can be some variation in the shade from sample to sample. The exact nature of the plasmon resonances was probed with specular reflectance spectroscopy and cathodoluminescence measurements.

Figure 4 shows specular reflectance spectra taken with four different angles of incidence using S- and P-polarized light (Figures 4A & 4B). Specular reflectance intensity is significantly greater

at high angles of incidence due to reduced interaction of incident light with the length of gold nanorods. There are minor differences between the shape of the spectra recorded using S- and P-polarized light. They display a strong minimum at ~ 720 nm and at small angles of incidence weak minima (inflections) at ~ 560 nm and ~ 450 nm. With P-polarized light, the reflectance minima around 720 nm shift to shorter wavelength with increasing angle of incidence however, with S-polarized light the minimum was independent of the angle of incidence. The minimum at ~ 450 nm can be assigned to inter-band transitions (from the top of d band to the Fermi level).^{44,45} McMillan *et al.* performed specular reflectance experiments on an array of gold nanoparticles of apparently much smaller size (dimensions of nanoparticles are not given in that paper).¹⁷ They observed two absorption minima at 550 nm and 720 nm that were assigned to transverse and longitudinal resonances, respectively. However, their spectra change significantly with the photon polarization and for S-polarized light the absorption minimum at 720 nm was not observed. Clearly, the optical behaviors of short and long nanorods are different. Since the diameter of our nanorods is large, multipole excitation should be observed as explained by Evlyukhin *et al.*¹² Consequently, we assign the minimum at ~ 720 nm to the transverse dipole mode and the minimum at ~ 560 nm to the transverse multipole mode.

Figure 4. Specular reflectance spectra taken at different angles of incidence. Scaling factors for the different angles of incidence are indicated in parenthesis. A) S-polarized light (S15° X25, S30° X20, S45° X2), B) P-polarized light (P15° X35, P30° X30, P45° X15).

Cathodoluminescence experiments were performed to confirm the interpretation of the specular reflectance spectra. A 15 keV electron beam of a scanning electron microscope was focused onto the gold nanorod sample. The impinging electrons produce transition radiation and excite SPP.⁴⁵ The transition radiation is the result of the temporally varying dipole moment produced when an electron combines with its image charge at the metal interface. Transition radiation causes a very broad background in the cathodoluminescence spectra.⁴⁶ Excited SPP can couple to light by momentum transfer by scattering at the boundaries of the nanorods leading to distinct peaks in the cathodoluminescence spectra.

Figures 5A and 5B correlate the SEM image of the top of the array and the cathodoluminescence map of the array. To obtain the cathodoluminescence map, the intensity of the emitted cathodoluminescence is recorded while scanning the electron beam over the sample. Moderate intensity was found when the beam hit the top of the nanorods while at the lower edge of the nanorod array, where the sides of the nanorods were also irradiated, a significantly higher intensity was found (Figure 5B).

Figure 5C plots the cathodoluminescence spectra taken from the two positions on the array marked in Figure 5A. The shape of the spectra is independent of the position from which they were collected and revealed a broad maximum with weak inflections between 500 and 1000 nm. Below ca. 500 nm only transition radiation contributes to CL since SPP are strongly damped, mostly due to excitation of gold interband transitions (Figure 5C). At longer wavelengths (i.e. >900 nm) the sensitivity of the detector strongly decreases, hence the CL probably extends

farther into the IR. The width of the cathodoluminescence spectrum and its structure implies the simultaneous excitation of various plasmon modes by the impinging electrons. We expect that in addition to the transverse modes, higher order longitudinal modes are also excited. The overlap of these modes forms a wide band in the CL spectrum.

Figure 5. Secondary electron (A), and cathodoluminescence (B) images of gold nanorods. (C) Cathodoluminescence spectra corresponding to positions (1) and (2) indicated on the SEM image.

Figure 6 compares the intensity of the cathodoluminescence to the specular reflectance represented as $\log(1/R)$. In this representation the maxima of the $\log(1/R)$ curve correspond to the efficient excitation of LSP by the incident light. The cathodoluminescence spectrum exhibits a wide maximum centered at about 680 nm, which comes close to the maximum of the $\log(1/R)$ curve. Furthermore, the shoulder of the $\log(1/R)$ curve at 560 nm is reproduced in the CL spectrum. The $\log(1/R)$ maxima at 720 nm and 560 nm are therefore in accordance with the excitation of transverse LSP in the nanorods. No significant CL emission was found at 450 nm,

where a strong maximum is found in the $\log(1/R)$ curve (Figure 6). As stated earlier we infer that the $\log(1/R)$ maximum at 450 nm has to be attributed to the optical properties of the gold surface rather than to the excitation of multipole LSP. Obviously the excitation of the SPP by light or electrons strongly differs. Electrons are able to simultaneously excite a variety of plasmon modes. With excitation by S-polarized light, where the electric field is always oriented in the transverse direction of the nanorods, transverse plasmons can be selectively excited. The broadness of the plasmon modes observed in the reflectance and cathodoluminescence spectra is likely due to variation in the size, shape, and spacing of the gold nanorods.¹³

Figure 6. Comparison of specular reflectance (S-polarized, 15°) represented as $\text{Log}(1/R)$ and cathodoluminescence (position 2, Figure 5A,C).

Clean nanorod substrates were tested by measuring the SER spectra of self-assembled monolayers (SAM). The test molecule, 4ATP, was chosen because it has been well characterized and is known to form ordered layers.⁴⁷⁻⁴⁹ 4ATP also has a large scattering cross section and a distinctive spectral profile that makes an unambiguous identification possible.

Raman and SER spectra of 4ATP (Figure 7) were very similar to those reported in the literature. Some papers have presented bulk spectra with peaks at 1140 cm^{-1} $\delta(\text{CH})$, 1390 cm^{-1} $\nu(\text{CC}) + \delta(\text{CH})$, and 1430 cm^{-1} $\nu(\text{CC}) + \delta(\text{CH})$ though these were absent in our spectra.^{31,48-50} The appearance of these peaks has been attributed to the dimerization of 4ATP to form bis(4-aminophenyl) disulfide, a process that is accelerated at elevated temperature and on the surface of gold.⁵¹ The 400 mW 1064 nm laser used by Mainu *et al.* is an order of magnitude more powerful than the laser sources used by other researchers and may explain the presence of these peaks in their bulk spectra of 4ATP.⁴⁹

Most SERS studies of 4ATP do show signs of bis(4-aminophenyl) disulfide with peaks at 1140 , 1390 , and 1430 cm^{-1} .^{31,48-50,52,53} Mohri *et al.* suggested that the reaction is initiated by adsorption of 4ATP on gold and oxidation to the thiolate.³⁹ When this species desorbs it is able to form the disulfide bond giving rise to bis(4-aminophenyl) disulfide.³⁹ It was also found that the rates of adsorption and desorption are proportional to temperature.³⁹ Plasmonic heating at gold nanostructures⁴² would seem to create the ideal conditions for this reaction to happen. The absence of peaks characteristic of bis(4-aminophenyl) disulfide in our spectra can be explained by the low laser power employed (3 mW). Laser power of 50% or 100% could not be used in our SERS experiments because of detector saturation and concern that local heating would degrade the surface species.

The similar profile of our bulk and surface enhanced Raman spectra suggests that the adsorbed molecule is oriented perpendicular to the surface where most vibrational modes are parallel to the electric field of the LSPR. This is consistent with STM results where the unit cell was found to be $(\sqrt{3} \times \sqrt{3})R30^\circ$ and the coverage was $1/3$ suggesting a vertical orientation.⁴⁷ Near-edge X-ray absorption fine structure (NEXAFS) data also suggested a vertical orientation.⁵⁴ Our spectra make it possible to determine the enhancement effect of the nanorod arrays by comparing the intensity of peaks common to both the bulk and SERS measurements.

Figure 7. Surface enhanced Raman spectrum of 4-aminothiophenol monolayer on gold nanorod array substrate shows most peak positions redshifted with respect to the bulk compound. Bulk spectrum acquired with 300 mW laser power, SERS spectrum acquired with 3 mW laser power. Accumulation time was 10 seconds, one scan.

Table 1. A comparison of surface enhanced Raman 4ATP peak positions with bulk and literature references.³⁶

bulk (cm ⁻¹)	SERS (cm ⁻¹)	reported (cm ⁻¹)	assignment
1007	1005		$\gamma\text{CC} + \gamma\text{CCC}$
1087	1079	1087	vCS
1177	1177	1176	δCH
1494	1487	1492	vCC+ δCH
1593	1588	1593	vCC
1618		1616	δNH

Enhancement factor could be found by comparing the 1588 cm⁻¹ (vCC) peak intensities of the bulk and SER spectra. The number of molecules contributing to the signal collected in the bulk measurements was calculated from the focal volume of the Raman microscope. The number of molecules probed in SERS experiments was determined from the surface area of the nanorods in the focal volume and 4ATP surface coverage. Enhancement factor is defined by the ratio of intensity (I) to number of molecules probed (N):

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{bulk}/N_{bulk}}$$

The enhancement was determined taking into account the microscope probe volume. The rods have a diameter of 282 nm and were grown to lengths of 1.1 to 23.9 μm . The microscope collects light from a volume of 5.5 fL and the total depth probed is 1.2 μm . When the microscope is brought into focus on the top of the rods, light is collected from the 600 nm space above the rods and the 600 nm below occupied by the rods and surrounding medium (water in our experiments). The SERS intensity and enhancement factor are plotted as a function of the aspect ratio of the nanorods in Figure 8.

Figure 8. Raman intensity of 1588 cm^{-1} peak and surface enhancement observed for rods of variable length. The EF was calculated by considering only the surface area of the rods in the focal volume and appears to be independent of aspect ratio. The error bars represent standard deviation from five measurements taken from five different locations on the sample.

Figure 8 shows that there is no correlation between enhancement factor and aspect ratio. This result can be explained by the geometry of the Raman microscope. The angle of incidence of light reaching the substrate relative to the long axis of the nanorods is $0\text{-}30^\circ$. This fact along with the close spacing of the rods means that only the transverse mode is probed when using nanorod

arrays. With the exception of one outlying point the spread of the data is comparable to the error bars that represent differences in the enhancement at different location of the same sample. Liao *et al.* noted that most of the Raman signal produced at the rod tips results from coupling of the transverse modes resulting in hot spots.¹¹ The variation of SERS intensity and EF may be explained as the result of variation in rod spacing which has been shown to have a significant impact on electric field strength at the rod tips.^{11,13,15,19}

There are several implications for these findings. First, there should be no change in enhancement with rod length. This is important in the use of gold nanorod arrays to study the leaching of gold where a significant amount of metal may be removed from the substrate as the experiment progresses. With this constant enhancement at a given site, it is possible to directly compare spectra taken at any time point without the use of internal standards.¹⁵ Secondly, SERS substrates with large EF could also be fabricated with very short nanorods. Lastly, it should also be possible to achieve greater surface enhancement. This could be done by changing the alumina template pore diameter and resulting rod diameter. The other approach is to use a laser source more closely matching the plasmon resonance frequency. Damm *et al.* were able to match the transverse plasmon mode with a 532 nm laser source^{15,19} while Liao *et al.* found that a 488 nm source was ideal for gold nanorod arrays with a transverse plasmon mode that ranged from 460 to 550 nm.¹¹ The reflectance and cathodoluminescence results suggest that for our samples a 720 nm laser may result in greater enhancement but this source was not available to us.

Conclusions

We have developed a simple method for the fabrication of gold nanorod arrays using readily available reagents. These substrates are clean, robust, and uniform. The enhancement factor has been found to be 10^6 and does not depend on aspect ratio due to the angle of incidence of the

excitation source. These SERS active substrates are suitable for application in studying SAMS, biomimetic systems, and gold leaching.

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