

Aligned Silver Nanorod Arrays as Substrates for Surface-Enhanced Infrared Absorption Spectroscopy

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Preferentially aligned silver nanorod arrays prepared by oblique angle vapor deposition were evaluated as substrates for surface-enhanced infrared absorption (SEIRA) spectroscopy. These nanorod arrays have an irregular surface lattice and are composed of tilted, cylindrically shaped nanorods that have an average length of $868 \text{ nm} \pm 95 \text{ nm}$ and an average diameter of $99 \text{ nm} \pm 29 \text{ nm}$. The overall enhancement factor for chemisorbed organic films of *para*-nitrobenzoic acid (PNBA) deposited onto the Ag nanorod arrays analyzed by external reflection SEIRA was calculated to be 31 ± 9 compared to infrared reflection-absorption spectroscopy (IRRAS) obtained from a 500 nm Ag film substrate. This enhancement is attributed to the unique optical properties of the nanorod arrays as well as the increased surface area provided by the nanorod substrate. SEIRA reflection-absorbance intensity was observed with both *p*- and *s*-polarized incident radiation with angles of incidence ranging from 25° to 80° . The largest intensity was achieved with *p*-polarization and incident angles larger than 75° . Polarization-dependent ultraviolet/visible/near-infrared (UV/Vis/NIR) spectra of the nanorod arrays demonstrate that the red-shifted surface plasmon peaks of the elongated nanorods may be partially responsible for the observed SEIRA response. The SEIRA detection limit for the Ag nanorod arrays was estimated to be 0.08 ng/cm^2 . Surface-enhanced Raman scattering (SERS) and SEIRA analysis of chemisorbed PNBA utilizing the same nanorod substrate is demonstrated.

Index Headings: Surface-enhanced infrared absorption spectroscopy; SEIRA; External reflection; *p*-Nitrobenzoic acid; PNBA; Nanorod; Nanostructure.

INTRODUCTION

Infrared spectroscopy is a well-established micro-analytical technique. However, this technique suffers from relatively low sensitivity that limits its routine application for trace analysis.¹ Even with this limitation, routine infrared (IR) detection of submonolayer organic films is possible using infrared reflection-absorption spectroscopy (IRRAS) sampling geometries, although hundreds or thousands of scans are normally required to produce monolayer spectra with adequate signal-to-noise ratios (SNR).² The resulting spectra typically have maximum absorbances in the range of a few milli-absorbance units.²

As an alternative to standard IRRAS methods, surface-enhanced infrared absorption (SEIRA) spectroscopy has emerged as a sensitive vibrational technique. SEIRA spectroscopy involves the enhancement of the infrared band intensities for molecules that are either adsorbed on or in close proximity to metal surfaces composed of ideally shaped nanoparticles and is classified as a type of surface-enhanced vibrational spectroscopy similar to the established surface-enhanced Raman scattering (SERS) technique.^{1,3,4} The enhancement

predicted for SEIRA by the local enhanced electric field mechanism can be as large as 10^3 ; however, in practice, most enhancements are in the range of 10 to 100.⁴ Although the intensity enhancements obtainable using SEIRA are much less than the maximum enhancements achievable with SERS (10^8 – 10^{12}), the advantages of SEIRA over unenhanced IR spectroscopy are still significant. The improved sensitivity provided by SEIRA compared to traditional infrared analysis allows for the quantitative and qualitative determination of chemical species in the picogram to microgram range.¹

Surface-enhanced infrared absorption enhancements have predominately been observed for analytes that are physically in contact with a thin ($<15 \text{ nm}$ thickness) metallic film, typically silver or gold, composed of island-like structures. These thin metallic films are traditionally fabricated using physical vapor deposition methods with deposition occurring at normal incidence resulting in anisotropic metallic particles with their long axes lying along the surface of the substrate.^{1,4} Similar to the predictions made by the electromagnetic (EM) theory for SERS,^{5,6} the metallic films providing the best SEIRA enhancements consist of discontinuous particles with oblate (ellipsoidal) geometries having aspect ratios (η) of 2 to 3.^{1,4} The optimum thickness of the metallic films used for SEIRA varies in the literature, but is typically in the range of 4–10 nm.⁷ These films have been formed onto a variety of substrates including glass, CaF_2 , BaF_2 , Ge, Si, KRS-5, KBr, ZnS, and ZnSe, and analyzed in transmission, attenuated total reflection (ATR), and external reflection infrared sampling geometries for a variety of SEIRA applications.^{1,4}

In addition to traditional vapor-deposited metal island films, many different types of nanostructures, such as nanorods, nanowires, and nanobundles, have been used as substrates for vibrational surface enhancement.^{8–10} Although widely utilized as SERS substrates, these types of nanostructured substrates have not been extensively investigated for SEIRA applications. It is feasible to consider, however, based on the similarities between SERS and SEIRA, that these types of nanostructures are potentially SEIRA active. Some researchers who have explored nanofabricated substrates for SEIRA applications include Al-Rawashdeh and Foss,¹¹ who incorporated Au nanorod structures into polyethylene films and obtained SEIRA response from these nanorod structures. Kellner et al.¹² observed the SEIRA response for Au needle films ($<7 \text{ nm}$ total thickness) deposited at grazing angle onto ATR substrates via magnetron sputtering. The enhancement observed for the needle structures was five times greater than the response from an ultrathin (1.2 nm) Au film, although the aspect ratios for the needle structures and the oblate spheroids in the Au film were similar. More recently, Jensen et al.⁷ constructed SEIRA substrates based on a nanosphere lithography technique used

Received 27 December 2005; accepted 11 May 2006.

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by Hulteen and Van Duyn.¹³ Although the total SEIRA enhancement achieved for the PPAs was comparable to traditional island-like metallic films, the type of particle shape used to produce the SEIRA response was quite different from the ellipsoidal shape readily observed in vapor-deposited metal island films.

Recently, Ag nanorod arrays produced by oblique angle deposition (OAD) have been reported to produce large SERS responses.⁸ OAD is a type of physical vapor deposition that involves rotating the substrate in the polar direction using a stepper motor.¹⁴ During deposition, the substrate is tilted in such a way that the vapor from the source impinges upon the substrate at incidence angles greater than 75°. This approach produces nanorod arrays that grow preferentially towards the direction of deposition due to adatom diffusion and the shadowing effect. A wide variety of materials can be used to form these nanorod arrays as long as the material used can be evaporated. In addition, the instrumentation required to carry out the OAD process can be any standard thermal evaporation system configured with a unique holder capable of rotation in the polar direction. OAD represents a flexible nanofabrication technique in which one can easily tune the size, shape, density, composition, and arrangement of the nanorod arrays.¹⁴

In this study, aligned silver nanorod arrays produced by the OAD nanofabrication process are investigated as potential SEIRA active substrates. This study represents the first time that long nanorod arrays (average nanorod length = 868 nm) have been used as substrates for SEIRA. These substrates exhibit good SEIRA enhancement factors when used in the external reflection sampling geometry. The experimental variables that govern optimal reflection-absorption spectroscopy for these substrates were investigated. A calibration is also reported that shows the quantitative SEIRA response for nanogram quantities of PNBA deposited onto the surface of the nanorods. Finally, a brief discussion is given about the use of these substrates for dual spectroscopic analysis utilizing both SERS and SEIRA on the same substrate.

EXPERIMENTAL

The Ag nanorods used in this study were fabricated by the OAD method using a custom-designed electron-beam/sputtering evaporation system that has been described elsewhere.⁸ Two different dielectric substrates, glass and CaF₂, were used as the supporting substrate for the deposition of the nanorod arrays. The glass substrates (Fisher Scientific) were typically 1.5 in. × 1.0 in., cleaned with piranha solution and rinsed with deionized water prior to use. Please note that piranha solutions are caustic and energetic. Extreme caution must be taken during handling. The CaF₂ substrates (Spectral Systems) were round 25 mm infrared windows.

The substrates were mounted in the OAD evaporator and tilted using a computerized stepper motor to an angle of 86° between the direction of the vapor and the substrate surface normal. The Ag nanorod arrays were directly deposited onto the substrates resulting in films that were semi-transparent. This semi-transparent structure allowed for SEIRA, SERS, and ultraviolet/visible/near-infrared (UV/Vis/NIR) analysis for a given substrate. Throughout the deposition, the overall thickness of the metal deposited was monitored by a quartz crystal microbalance positioned at normal incidence to the vapor source. The determination of the length, diameter, and density of the nanorods was estimated from the images

acquired with a LEO 982 field emission scanning electron microscope (SEM). Continuous Ag films (500 nm thickness) deposited at normal incidence were produced and used as standard substrates for IRRAS.

The molecular probe used in these studies was *para*-nitrobenzoic acid (PNBA) (Sigma Aldrich, St. Louis, MO). The use of PNBA as the target analyte is based on its historical significance as the first molecule analyzed that exhibited the SEIRA response when cast onto a metallic substrate.³ Since that initial paper, PNBA has been used as a benchmark molecule for comparing SEIRA responses from a variety of metallic substrates.^{1,4} PNBA solutions were made by dissolving PNBA in either ethanol or methanol. Ten microliter (10 μ L) aliquots were then cast onto the Ag nanorod or Ag film substrates for SEIRA and IRRAS measurements, respectively. Due to the fairly destructive nature of the methanol solvent, most samples used in this study were formed from PNBA/ethanol solutions. After dropping the aliquot onto the substrate, the solvent was allowed to evaporate in air, thus forming the cast film. The substrates were then typically rinsed with solvent to remove any physisorbed molecules and dried prior to analysis. The overall PNBA thickness deposited onto the metallic substrates was estimated from the volume and concentrations of solutions used, the surface area of the deposition spot size on the substrate, the estimated surface area of the nanorod substrate, and from assuming a density of bulk PNBA to be 1.61 g/cm³. In these experiments, a monolayer of PNBA is estimated to be \sim 1.7 nm thick and represents a surface coverage of \sim 270 g/cm².¹⁵

All IR spectra were collected using a ThermoElectron Nicolet 4700 Fourier-Transform Infrared Spectrometer equipped with a DTGS detector. The angle of incidence (θ) was varied from 25° to 80° using a variable angle specular reflectance accessory (Thermo Spectra-Tech, Model 500). The polarization was varied using a KRS-5 wire grid polarizer (Specac, England). The states of polarization are defined such that *p*-polarization is the direction of the incident electric field that is parallel to the plane of incidence, while *s*-polarization is the direction of the incident electric field that is perpendicular to the plane of incidence. The *p*-polarized radiation was aligned parallel to the major long axis of the nanorods ($\theta = 0^\circ$), which results in the *s*-polarization being oriented perpendicular to the long axis of the nanorods ($\theta = 90^\circ$). The SEIRA and IRRAS reflectance spectra presented here are reported in absorbance units as $-\log(R/R_0)$, where R_0 and R represent the reflectance of the substrate prior to and after the deposition of the PNBA film, respectively. All spectral manipulation and analysis (baseline correction, band height determination, peak frequency determination) was performed in either the Omnic/Version 7.1a (Thermo Electron Corporation, Madison, WI) or GRAMS 32/Version 5.01 (Galactic Industries Corporation, Nashua, NH) software programs.

Ultraviolet/visible/near-infrared spectra were acquired using a Jasco V-570 UV/Vis/NIR double-beam spectrophotometer specially equipped with two matched rotatable polarizers positioned in the beam paths. For the polarized UV/Vis/NIR spectra, the radiation was polarized so that the incident electric field was either parallel to the major long axis of the nanorods ($\theta = 0^\circ$) or perpendicular to the long axis of the nanorods ($\theta = 90^\circ$).

Surface-enhanced Raman scattering measurements were performed using a fiber-coupled, confocal Raman microscope

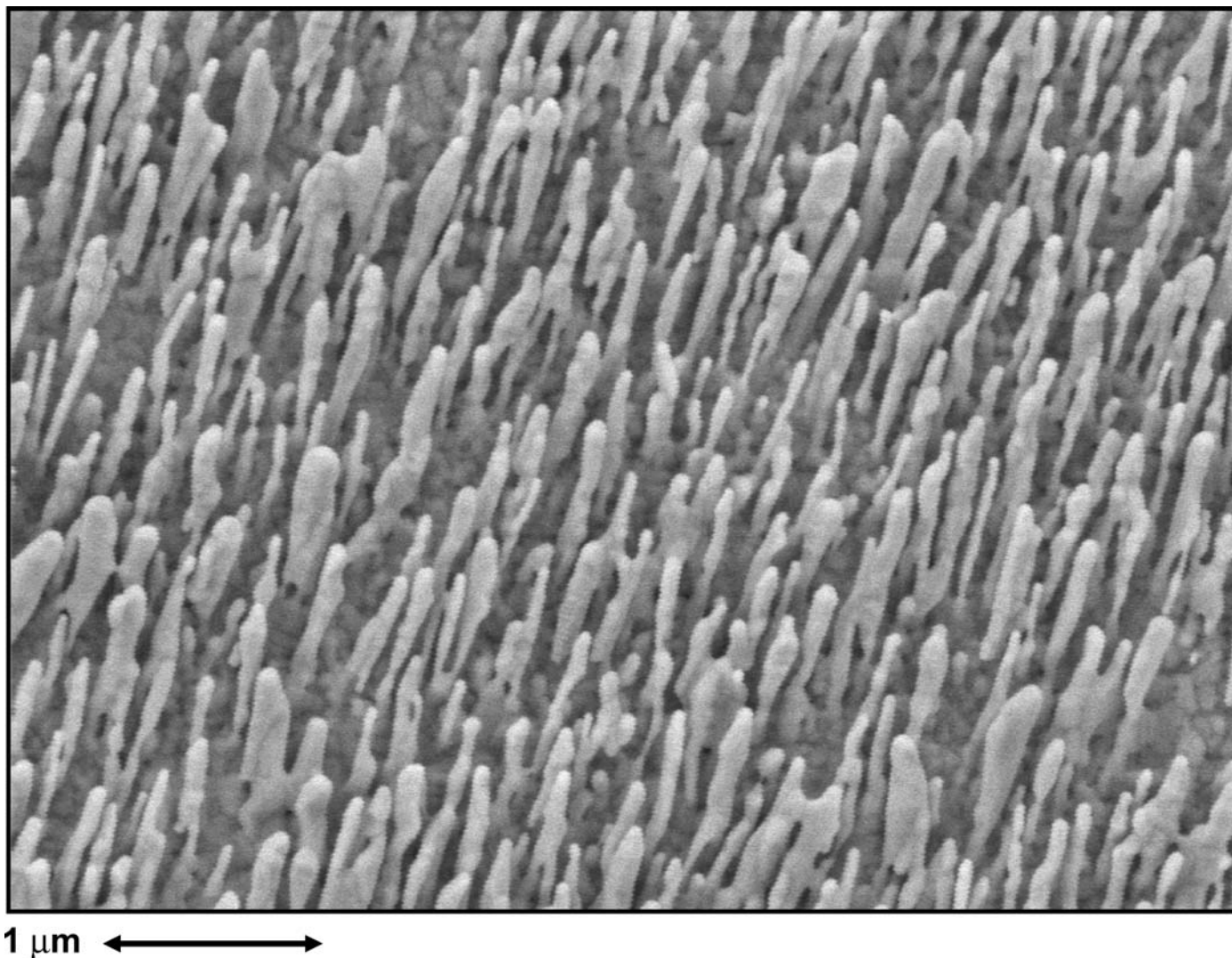


FIG. 1. SEM image of a Ag nanorod array (average nanorod length = 868 nm) deposited onto a glass slide.

interfaced to a charge-coupled device (CCD) equipped spectrograph (Kaiser Optical, Inc., Ann Arbor, MI), as previously described.⁸ A fiber-optic-interfaced 785 nm near-infrared diode laser (Invictus, Kaiser Optical) was used to provide the incoming radiation. The incident laser beam was delivered to the sample by epi-illumination through a 50× microscope objective. SERS spectra were collected from multiple spots on the same sample using single 1-second acquisitions.

RESULTS AND DISCUSSION

Nanorod Characterization and Surface-Enhanced Infrared Absorption Spectra. Figure 1 is a representative SEM image of a Ag nanorod array produced by OAD on the surface of the glass slide. The nanorod array has an irregular surface lattice (i.e., random nucleation sites) and is composed of nanorods of varying length, diameter, and shape. The location of a given nanorod is determined by the initial island site due to adatom nucleation. The shadowing effect encountered with OAD deposition produces nanorods that are preferentially aligned in the same direction, as evidenced from Fig. 1. It is also important to mention that the long axis of these nanorods

extends away from the surface of the substrate with the minor axis on one end lying flat against the substrate. Therefore, the overall substrate surface consists of an irregular pattern of aligned and tilted metal aggregates that have rod-like shapes. While these nanorods are primarily cylindrical, SEM images show that the particles are not perfectly shaped cylinders. The nanorods present in Fig. 1 tend to be irregularly shaped cylinders that are thinner closer to the substrate and expand out in diameter along the length of the nanorod. Some of these nanorods also have corrugations and bifurcations, thus adding to the complexity of their structure.¹⁶

Analysis of the SEM images determined that the average rod length was $868 \text{ nm} \pm 95 \text{ nm}$ with an average diameter of the nanorods equal to $99 \text{ nm} \pm 29 \text{ nm}$, corresponding to an average aspect ratio of 8.8. The density of the nanorods was $13.3 \pm 0.5 \text{ rods } \mu\text{m}^{-2}$ with an average tilt angle of $71^\circ \pm 4^\circ$. This kind of Ag nanorod substrate was previously reported to exhibit large ($>10^8$) SERS enhancements.⁸

Figure 2 displays representative external reflection SEIRA and IRRAS spectra for 1.67 μg of deposited PNBA that has been rinsed with copious amounts of ethanol on the Ag nanorod substrate and the 500 nm Ag film substrate, respectively. It is estimated that 1.67 μg of deposited PNBA

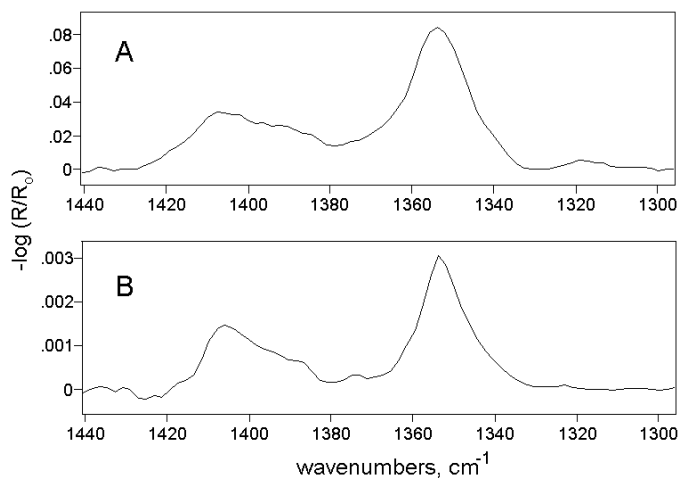


FIG. 2. External reflection-absorption IR spectra of 1.67 μg of PNBA deposited onto Ag substrates. It is estimated that 1.67 μg of deposited PNBA corresponds to a 0.5 nm PNBA film on the Ag nanorod array and a 2.0 nm PNBA film on the 500 nm Ag film substrate. (A) External reflection SEIRA spectrum (32 scans) of PNBA on a Ag nanorod (average nanorod length = 868 nm) substrate. (B) IRRAS spectrum (500 scans) of PNBA on a 500 nm Ag thin film substrate. Both the SEIRA and IRRAS spectra were collected in the external reflection geometry at an 80° angle of incidence and p -polarization.

results in a 2.0 nm PNBA film on the 500 nm Ag film substrate and a 0.5 nm PNBA film on the nanorod array. The difference in the estimation of the PNBA film thickness for the same amount of deposited analyte is attributed to the increased surface area of the nanorod substrate. Both spectra were acquired in the external reflection mode with p -polarized radiation at an angle of incidence of 80° . The external reflection SEIRA spectrum of PNBA (Fig. 2A) was acquired with a total of 32 scans, while the IRRAS spectrum of PNBA (Fig. 2B) required a total of 500 scans in order to achieve comparable signal-to-noise ratio (S/N). The only spectral differences observed between the external reflection SEIRA and IRRAS spectra in Fig. 2 are the slight variations in the relative intensities and the bandwidths. Also note that the plotted absorbance scale of the external reflection SEIRA spectrum in Fig. 2A is a factor of ten larger than the absorbance scale of the IRRAS spectrum in Fig. 2B, indicating the relative magnitude of the surface enhancement produced by the Ag nanorod arrays.

The IR bands observed in Fig. 2 and the interpretation of the orientation of PNBA on the surface of the nanorod substrate are the same as previously reported for chemisorbed monolayers of PNBA deposited onto silver films monitored both with SEIRA and IRRAS.^{1,15,17,23} The spectral bands observed in Fig. 2 more closely resemble the spectral bands of p -nitrobenzoate (PNBA⁻) than bulk p -nitrobenzoic acid. The spectral band at 1410 cm^{-1} observed in both spectra in Fig. 2 is assigned to the symmetric COO⁻ stretching mode. This indicates that the PNBA molecule deprotonates and chemisorbs to the surface of the silver metal through the carboxyl group. The strongest band observed in both the external reflection SEIRA and IRRAS spectra in Fig. 2 is the 1350 cm^{-1} band, which is assigned to the symmetric NO₂ stretching mode.¹⁵ The surface selection rule for IRRAS on metallic surfaces states that only vibrations with dipole moment derivative components that are perpendicular to the surface will be observed.^{18,19} Osawa and coworkers^{15,17,23} in separate papers have concluded, based on

this selection rule and the similarity of the results obtained for SEIRA and IRRAS for similar PNBA films, that chemisorbed PNBA is oriented with its long axis (C_2 symmetry axis) perpendicular to the surface. This molecular orientation results in observation of only the symmetric stretches (A_1 modes in C_{2v} symmetry) for PNBA⁻. These authors have stated that the surface selection rule applies for SEIRA, although other researchers have provided examples that prove that this assumption should not be made in all cases.^{4,20,21} In this present study, however, the surface selection does appear to apply for the external reflection SEIRA spectra of chemisorbed PNBA on the silver nanorods.

The intensity of the spectral peak at $\sim 1350\text{ cm}^{-1}$ assigned to the symmetric NO₂ stretching mode, $\nu_s(\text{NO}_2)$, was used in the calculation of the average overall enhancement factor for external reflection SEIRA relative to IRRAS for cast PNBA films. For the PNBA spectra shown in Fig. 2, the overall enhancement factor for the Ag nanorod array compared to the 500 nm Ag film substrate is 31 ± 9 . This enhancement is attributed to both the increased surface area and the unique optical properties of the nanorod array. Based on the density of the nanorods within the array, the surface area of the nanorod array is estimated to be about four times larger than the surface area of the continuous Ag film assuming that each nanorod in the array is cylindrical in shape. Due to the increased surface area provided by the nanorod array, more sites are available for chemisorption on the metal when the same amount of PNBA is deposited, which leads to greater SEIRA response. Since optimum SEIRA enhancements arise from molecules that are in close proximity to the metal surface, having a substrate with an increased metal surface area represents an important advantage for thin film studies. In contrast, when normalizing for the increased surface area of the nanorod array compared to the continuous metal film, the average external reflection SEIRA enhancement factor attributed solely to the optical properties of the nanorod array is 8 ± 2 compared to the IRRAS obtained from the 500 nm Ag film substrate. Although less than the external reflection SEIRA enhancement factor reported by Osawa et al.²³ for PNBA deposited onto a 5 nm silver layer on BaF₂, this enhancement is still significant based on the fact that the observed SEIRA enhancement obtained from the nanorods arises from non-traditionally shaped nanostructures. Note that only nanorod arrays with average nanorod lengths of 868 nm were investigated in this study, since these substrates were shown to provide optimal SERS response.⁸ Current research efforts are focused on optimizing the SEIRA enhancement through the manipulation of the geometric and structural properties of the nanorod arrays while attempting to understand and determine how nanostructure design influences the observed SEIRA response.

The Effect of Incident Angle and Polarization. We have investigated the effect of the polarization of the incident radiation as well as the incident external reflection angle on the SEIRA intensity, since both have been shown to affect the observed response.¹ Figure 3 represents a plot of the absorbance for the 1350 cm^{-1} band for a 0.5 nm thick PNBA film deposited onto the Ag nanorod substrate versus the angle of incidence and polarization state of the incoming radiation. Figures 3A and 3B represent p -polarized and s -polarized incident radiation, respectively. Incidentally, the nanorods were aligned parallel to the plane of incidence because this orientation provided the largest SEIRA responses.

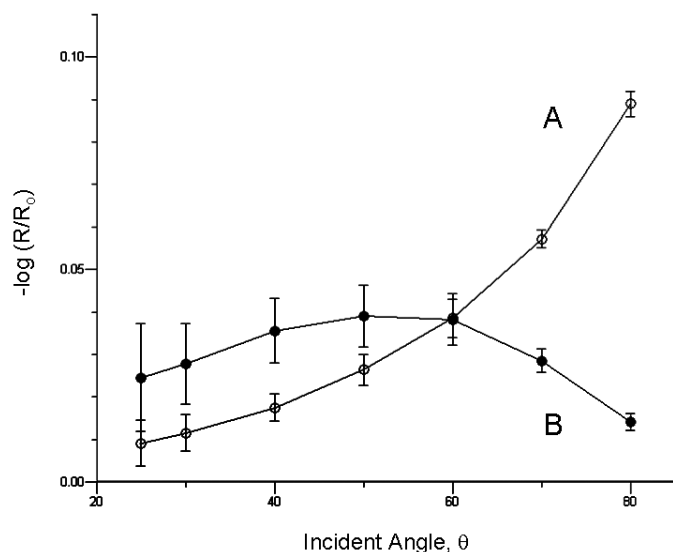


FIG. 3. External reflection-absorption SEIRA intensity of the 1350 cm^{-1} symmetric NO_2 stretch from a 0.5 nm thick chemisorbed PNBA film on the surface of the Ag nanorod/glass substrate as a function of angle of incidence and polarization state of the incoming radiation. (A) p -Polarization (open circles). (B) s -Polarization (closed circles).

Figure 3 shows that the SEIRA absorbance of the PNBA 1350 cm^{-1} band increases for p -polarized light as the angle of incidence increases, while the s -polarized absorbance reaches a maximum value at $\sim 50^\circ$ before decreasing at grazing incident angles. The large standard deviation in absorbance at lower angles of incidence ($<40^\circ$) is attributed to the difficulty in acquiring data with the reflection accessory.

As is evident in Fig. 3, significant reflection-absorbance intensity is observed for both p - and s -polarizations at all angles of incidence, which is contrary to the conditions predicted for IRRAS at grazing incidence on a planar isotropic metallic surface.^{18,19,22} However, the prediction that p -polarization should provide the strongest signal at high angles of incidence is still observed in the Ag nanorod substrates. The appreciable signal observed for both p - and s -polarization indicates that symmetric vibrations aligned both perpendicular and parallel to the nanorod surface are observed. This is attributed to the various shapes of the nanorods and the orientation of the chemisorbed molecules on the surfaces of these nanorods. The unexpected magnitude of the absorbances obtained with both polarizations is attributed to the fact that the Ag nanorod substrate, as previously mentioned, is quite irregular and is composed of varying cylindrically shaped nanorods that contain numerous bifurcations and protrusions. Therefore, the Ag nanorod array has a very anisotropic structure. The anisotropy of the substrate will introduce a cross-polarization effect during the reflectance measurement. Therefore, it is not surprising that the Ag nanorod substrates produce a different SEIRA polarization response than does a continuous isotropic metal film.

Due to the porous nature of the nanorod array, a possible interaction of the incident radiation with the underlying dielectric substrate was also considered. Previous external reflection SEIRA work for thin organic films deposited onto thin ($<10\text{ nm}$) vapor deposited silver or gold films on dielectric substrates reported appreciable response for both p - and s -polarization off of the Ag film/dielectric substrate along with

a characteristic inversion of the spectral bands occurring for p -polarization with an angle of incidence near the Brewster angle for the dielectric substrate.²³ In this same study, for s -polarized radiation, negative absorbance was observed at all angles of incidence.²³ Negative absorbance and the characteristic spectral band inversion for p -polarization were not observed in our experiments. Specifically, only positive absorbance was observed for both p - and s -polarization. This indicates that although our substrate is semi-transparent, the interaction of the incident radiation with the underlying substrate is negligible.

It was determined that the direction of the nanorods, tilted either towards or away from the incident radiation, does not affect the observed SEIRA response or the spectral band shapes and intensities for the chemisorbed PNBA as long as the long axis of the nanorod is parallel to the plane of incidence and parallel to the incident electric field. If the nanorods were placed perpendicular to the plane of incidence in either direction, spectra similar to the p -polarized data were observed when using s -polarization, which in this configuration would now be oriented along the long axis of the nanorod. Although the spectra appeared similar, the overall magnitude of the absorbances were almost an order of magnitude smaller in intensity. In general, for both p - or s -polarization, if the incident electric field was positioned perpendicular to the long axis of the rod, slight band asymmetry, reduced absorbances, and lower signal-to-noise was observed.

It has been reported for SERS applications utilizing various nanostructured substrates that there is a polarization dependence of the SERS effect relative to the direction of the nanostructure.¹⁶ For isolated nanostructured particles, the maximum SERS signals were produced when the polarization was oriented along the long axis of the nanostructure.^{24,25} However, for several SERS substrates utilizing nanobundles and nanowires, the maximum SERS intensity is observed for radiation that is perpendicular to the nanostructure's long axis.²⁶ Recently, we have also measured the polarized SERS and UV/Vis/NIR spectra for Ag nanorod arrays produced by OAD and observed that the anisotropy of the SERS polarization was different from that of the polarized UV/Vis/NIR absorbance.¹⁶ The maximum SERS intensity was observed in the polarization direction perpendicular to the long axis of the Ag nanorods, while the UV/Vis/NIR absorbance was strongly polarized along the direction of the long-axis of the nanorod array. The SERS anisotropy was primarily attributed to the lateral arrangement of the three-dimensional tilted nanorod lattice in which highly localized plasmon modes are created by strong electromagnetic coupling between adjacent metallic nanorods. In the current study, the strongest SEIRA response was achieved when the polarized radiation's electric field was aligned along the long axis of the nanorod structure. This supports the notion that the red-shifted surface plasmon of the elongated nanorod array is a contributor to the observed SEIRA response.

Figure 4 shows the polarization-dependent UV/Vis/NIR spectra of the Ag nanorod substrate (average nanorod length = 868 nm). For polarized radiation with the incident electric field parallel to the long axis of the nanorods ($\theta = 0^\circ$), a broad, intense absorbance feature corresponding to the longitudinal plasmon mode appears at visible wavelengths greater than 400 nm and continues into the NIR spectral region. When the incoming electric field is perpendicular to the long axis of the nanorods ($\theta = 90^\circ$), the absorbance of the broad Vis/NIR

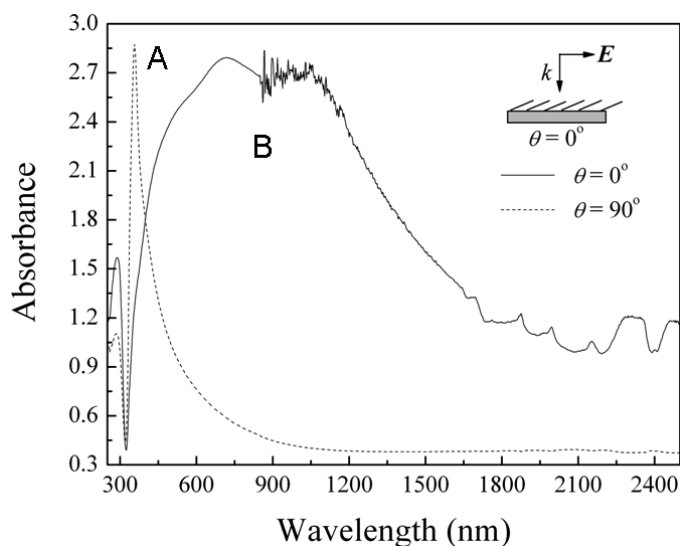


FIG. 4. Polarized UV/Vis/NIR absorbance plot of the Ag nanorod/glass substrate (average nanorod length = 868 nm). (A) Radiation polarized perpendicular to the long axis of the nanorods ($\theta = 90^\circ$). (B) Radiation polarized parallel to the long axis of the nanorods ($\theta = 0^\circ$).

feature decreases, while a sharp UV peak is present at 357 nm. This sharp peak can be attributed to the transverse plasmon mode of the nanorod array. These results support the conclusions made by Al-Rawashdeh and Foss¹¹ for surface plasmons of nanorod structures. The longitudinal, red-shifted plasmon bands are believed to be partially responsible for the large SEIRA enhancements achieved when *p*-polarized radiation was aligned along the length of the nanorod even though the longitudinal plasmon mode peak wavelength is non-resonant with the mid-infrared radiation used in this SEIRA study.

The Effect of the Dielectric Constant of the Underlying Substrate. The semi-transparent nature of the Ag nanorod/glass substrate was problematic in the external reflection infrared sampling geometry due to the presence of absorption peaks assigned to the glass, which prevented the observation of some of the chemisorbed analyte spectral bands in the fingerprint region. Figure 5A illustrates an uncorrected external reflection SEIRA spectrum of a 0.5 nm PNBA film deposited onto a long Ag nanorod array deposited onto a glass substrate. The spectral region between 1250–850 cm^{-1} in Fig. 5A is dominated by the background absorption of the glass substrate. To eliminate this background, CaF_2 was chosen as the base substrate for the nanorod deposition. As shown in the uncorrected spectrum in Fig. 5B, the Ag nanorods deposited on CaF_2 allow the region between 1600–700 cm^{-1} to be observed without interference from the underlying substrate. The only exception is the sharp feature around 620 cm^{-1} , which may be attributed to the reststrahlen band of CaF_2 .

Figure 5 also shows that a CaF_2 substrate allows us to observe additional spectral features for the PNBA film. In particular, the A_1 modes of PNBA at 1107, 1014, 864, and 825 cm^{-1} are enhanced on the Ag nanorod/ CaF_2 substrate. The 1107 cm^{-1} and 1014 cm^{-1} bands are attributed to the symmetric in-plane stretching/bending modes of the benzene ring, and the band at 825 cm^{-1} is assigned to the symmetric O–N–O deformation mode of the NO_2 group.

The overall enhancement factor calculated for a 0.5 nm PNBA film on a Ag nanorod/ CaF_2 substrate after rinsing with

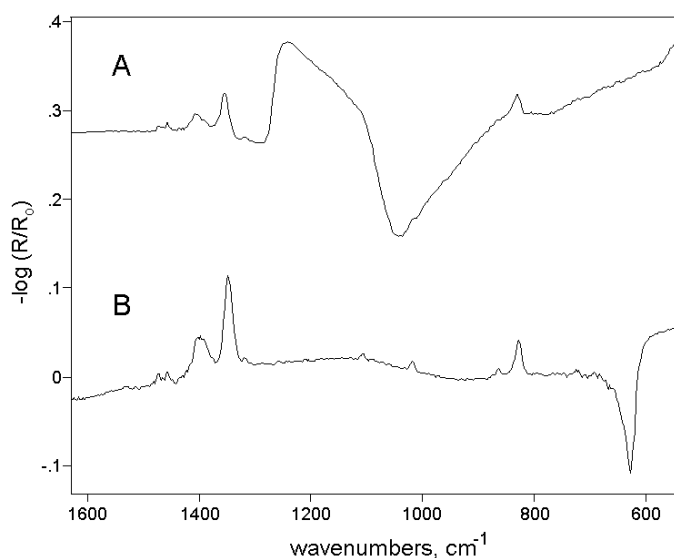


FIG. 5. External reflection SEIRA spectra of a 0.5 nm thick PNBA chemisorbed film on a Ag nanorod film (average nanorod length = 868 nm) deposited on different dielectric substrates. (A) SEIRA spectrum of PNBA on a nanorod/glass substrate. (B) SEIRA spectrum of PNBA on a nanorod/ CaF_2 substrate.

ethanol with *p*-polarization and an incident angle of 80° is 41 ± 13 compared to the same PNBA sample deposited onto a 500 nm Ag film monitored with IRRAS. This represents approximately a 33% increase in the SEIRA response for PNBA films chemisorbed to Ag nanorod arrays deposited onto CaF_2 compared to glass substrates. Jensen et al.⁷ calculated that a metallic oblate spheroid directly in contact with various underlying substrates (mica, silicon, germanium) should have a surface plasmon resonance that would red-shift and increase in magnitude as the dielectric constant (ϵ) of the underlying substrate is increased. The observed increase in SEIRA response for PNBA films formed on nanorods deposited onto CaF_2 ($\epsilon = 7.4$) compared to silica glass ($\epsilon = 3.8$) may be attributed to the increasing dielectric constant of the underlying substrate.

The Effect of Solvent and the Long-Term Stability of the Nanorod Substrates. Upon rinsing the nanorod substrate with ethanol, a slight decrease in the SEIRA response was observed for the chemisorbed PNBA film. This is attributed to a disruption of the surface lattice of the nanorod substrate, which was visibly apparent after rinsing. To observe the extent of disruption based on the solvent used, PNBA films were formed from methanol solutions onto the nanorod substrates. The average enhancement factors for external reflection SEIRA were 11 ± 3 after rinsing with methanol. The use of methanol visibly appeared to damage the surface of the nanorod substrate to a greater extent. The overall decrease in the enhancement factor compared to PNBA films formed from ethanol solutions is attributed to a greater disruption of the surface lattice of the nanorod substrate caused by the use of the more polar solvent. Therefore, in order to maintain an optimum SEIRA response for these substrates, careful selection of the solvent is a crucial experimental variable that will ultimately dictate the magnitude of the observed SEIRA response.

It is important to consider the effect of surface oxidation on the SEIRA response when considering substrates composed of silver and other metals that readily oxidize when exposed to

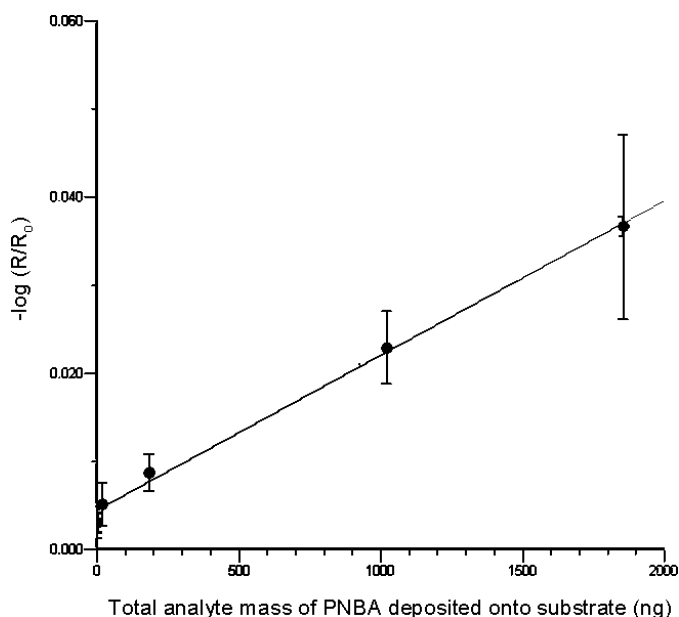


FIG. 6. Calibration plot of the observed SEIRA response versus the amount of deposited PNBA in nanograms. $R^2 = 0.998$.

atmospheric conditions. Due to the short-range enhancement that is observed for SEIRA measurements, the presence of an oxide layer on the metal surface will reduce the overall SEIRA response.¹ For the Ag nanorod substrates, the enhancement factors observed for chemisorbed PNBA deposited films formed immediately after vapor deposition and chemisorbed PNBA deposited films formed on nanorod substrates that had been stored in ambient conditions for four weeks or more were comparable. Therefore, it appears that these silver nanorod substrates are fairly stable over time.

Surface-Enhanced Infrared Absorption Detection Limits for *Para*-Nitrobenzoic Acid. We have determined the detection limit for PNBA on the surface of the Ag nanorod/glass substrate to be 0.08 ng/cm². PNBA samples were prepared by sequential deposition and analyzed by external reflection SEIRA. Figure 6 represents the calibration curve for these depositions. The calibration is linear with a coefficient of determination (R^2) equal to 0.998. This graph shows that quantification of PNBA was possible down to ~ 1 ng of deposited PNBA analyte. This amount of analyte corresponded to a SNR between 2 and 4 for the 1350 cm⁻¹ band of PNBA in the SEIRA spectra for the replicates analyzed. Taking into account the deposition spot size and the increased surface area of the nanorod array, 1 ng of deposited PNBA corresponds to a film that is roughly 0.08 ng/cm². The linear response of absorbance versus concentration was observed up to the highest concentration investigated (133 ng/cm² of PNBA), which is estimated to be a film with total thickness around ~ 0.8 nm (0.5 monolayers). In similar work, Osaka and Ataka²⁷ showed a linear increase of surface-enhanced absorbance with increasing thickness of the analyte film up to a total coverage between 2 and 3 monolayers. Kellner et al.¹² and Johnson et al.²⁸ also reported similar behavior for films that were less than two monolayers of PNBA deposited onto thin metallic films. Therefore, the linear behavior of the SEIRA response obtained from these nanorod arrays is similar to these previous reports. It should be noted that for the calibration, the deposited PNBA was not rinsed after each deposition. The variability in the

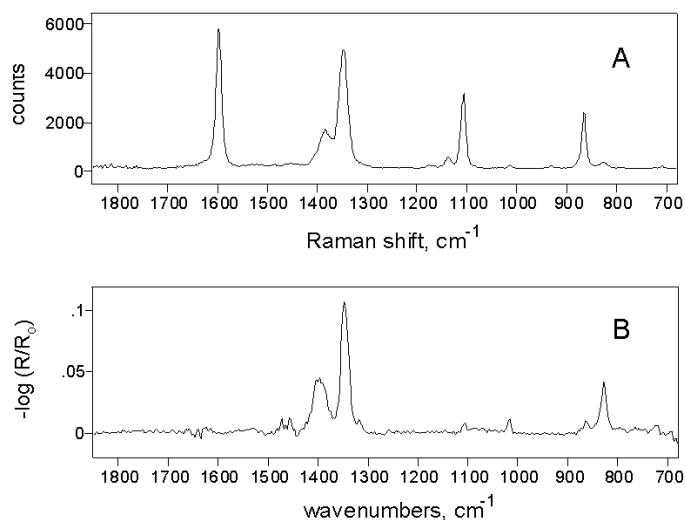


FIG. 7. Surface-enhanced vibrational spectra for a 0.5 nm thick chemisorbed PNBA film on the same Ag nanorod/glass substrate. (A) SERS. (B) External reflection SEIRA.

absorbances measured for the larger amounts of deposited PNBA in the calibration plot may be the result of the disruption of the nanorod array from the solvent used as multiple depositions were performed in a sequential manner on the same substrate.

Dual Surface-Enhanced Raman Spectra and Surface-Enhanced Infrared Absorption Spectra of *Para*-Nitrobenzoic Acid. Figure 7 represents dual surface-enhanced vibrational analysis of a 0.5 nm PNBA film chemisorbed onto the Ag nanorod/glass substrate analyzed by both SERS and SEIRA, respectively. The applicability of the Ag nanorod substrate for both SEIRA and SERS spectroscopies allows each technique to provide complementary spectral information. This dual SERS/SEIRA analysis approach has been previously reported for monolayers deposited on silver, gold, and copper vapor deposited substrates.²⁹

The spectral assignments for the external reflection SEIRA spectrum observed in Fig. 7 are the same as those previously discussed. The most intense spectral bands observed in the representative SERS spectrum for the PNBA monolayer in Fig. 7 are at 863, 1106, 1134, 1348, 1395, and 1600 cm⁻¹. Similar to IRRAS at grazing incidence, SERS has a surface selection rule that states that vibrations from adsorbed molecules on the surface of the roughened metal with polarizability tensor components perpendicular to the surface along the surface normal will be preferentially enhanced. The SERS spectral bands at 863 and 1395 cm⁻¹ are assigned to the COO⁻ bending and symmetric stretching vibration, respectively. This implies once again that PNBA binds through the carboxylic acid to the surface of the metal. The 1348 cm⁻¹ band is assigned to the symmetric stretch of the NO₂ group. Even though this moiety is furthest away from the surface, its alignment along the surface normal produces a strong observable SERS band for this group. The vibrations observed at 1106 and 1134 cm⁻¹ are assigned to the C-H in-plane bending modes. The strong singlet centered at 1600 cm⁻¹ is assigned to the C-C stretching of the benzene ring present in the PNBA molecule. All assignments were made from literature values.³⁰

Based on these assignments and their relative strengths, it can be assumed from the SERS data that the PNBA molecule is

oriented along the surface normal perpendicular to the substrate surface. These results thereby confirm the conclusions made from SEIRA for the same chemisorbed film. In addition, the C–C stretching band at 1600 cm^{-1} is an example of a vibration that has strong SERS polarizability but is SEIRA inactive due to a small IR dipole moment. The combination of SERS and SEIRA for the same analyte adsorbed onto the same substrate improves upon the usefulness of each of these techniques by providing a more complete surface-enhanced spectroscopic analysis of a given sample.

CONCLUSION

Aligned silver nanorod arrays fabricated by oblique angle vapor deposition represent a new substrate design for SEIRA applications. When used in an external reflection sampling geometry, the overall enhancement for these arrays for the same amount of deposited sample is ~ 30 compared to standard IRRAS methods. This overall enhancement is attributed to the unique optical properties and the increased surface area of the nanorod array substrates. It is believed that a red-shifted surface plasmon of the nanorod array is a contributor to the observed SEIRA enhancement response. This plasmon arises from the unique shape, size, and lattice constants of the nanorod array. Dual Raman-IR surface-enhanced vibrational analysis is possible using this substrate design. The flexibility and ease of use of the OAD process opens up numerous possibilities for the fabrication of novel nanostructured substrates with geometries optimized to provide maximum SEIRA responses.

ACKNOWLEDGMENTS

C.L.L. would like to thank Dr. Douglas Elmore for many helpful discussions. C.L.L. and S.A.J. are supported by a grant from the University of South Carolina Research and Productive Scholarship Fund. S.B.C. and Y.P.Z. are supported by NSF grant ECS-0304340. S.S. and R.A.D. are supported by NIH grant EB001956.

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