

The Role of O₂ in SERS-Active Thin Metal Film Photodynamics

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Optical emission from thin Ag films excited by visible light under a non-oxygen atmosphere was analyzed as a function of time and excitation power. The emission behavior under anaerobic conditions was strikingly different from that obtained under an oxygen-containing atmosphere. Specifically, emission intensity increased as a function of time with no photoinduced signal decay. A simple mechanistic model was developed and demonstrated to accurately predict the photodynamic trends observed under both conditions. The model involves oxygen-mediated cyclic production and destruction of photoactive silver clusters on the thin film. The evidence presented here strongly supports the hypothesis that oxygen plays a key role in the “blinking” phenomenon observed on SERS-active Ag films.

Introduction

Understanding the mechanism of enhanced Raman scattering from molecules adsorbed to nanoscale roughened metal surfaces has been a goal since the inception of surface enhanced Raman spectroscopy (SERS).^{1–10} Two theories, electromagnetic and chemical, have prevailed to become the generally accepted descriptions of the extremely large signal enhancements possible with SERS.¹¹ In the lowest concentration SERS experiments, both of these theories involve the presence of SERS “active” sites to provide the amount of signal enhancement necessary to achieve single molecule detection. Electromagnetic active sites are attributed to the interaction of the electromagnetic fields produced at the interstitial sites between noble metal nanoparticles.¹² Chemical active sites, generally characterized as atomic scale defects (e.g., Ag adatoms or clusters), are thought to provide increased coupling between the analyte molecule and the free electrons in the noble metal substrate.^{13,14} Blinking of the Raman signal observed in single molecule (sm) SERS experiments is widely accepted to originate from single molecules undergoing adsorption/desorption cycles or diffusing in and out of these active sites.^{15,16} Our previous publication¹⁷ provided evidence that molecular diffusion might not be solely responsible for the signal fluctuations observed in SERS.

The SERS literature suggests that O₂ plays a crucial role in the underlying mechanism of signal fluctuation observed from SERS substrates. Kudelski and Pettinger¹⁸ reported signal fluctuations of the Raman spectrum of carbon films that had been deposited on electrochemically roughened Ag and Au substrates in the presence of a nonfluctuating pyridine Raman spectrum; these fluctuations were observed only in the presence of O₂.¹⁸ Reaction of O₂ with the carbon chain segments on the surface to form different molecules with varying Raman cross sections was assigned as the cause of the fluctuations. It was determined that dynamic creation of “electromagnetic active sites” could not explain the fluctuations observed for the carbon chain segments because electromagnetic active sites should not be preferentially efficient for carbon chain segments over pyridine. In agreement with these observations, Etchegoin et al. showed that the Raman spectral fluctuations for hemoglobin

molecules¹⁹ and single-stranded DNA²⁰ adsorbed to Ag colloidal particles only occurred when O₂ was present. When hemoglobin was fully deoxygenated in a moderate vacuum (10^{−1} Torr), fluctuations of the spectrum were quenched.¹⁹ Performing experiments under an N₂ atmosphere completely quenched the fluctuations in spectra observed from single-stranded DNA.²⁰ These phenomena were explained by an O₂-mediated resonant charge-transfer interaction that could be affected by thermally induced dynamic changes in the local substrate morphology.²⁰

In addition to influencing the spectral blinking behavior observed from SERS substrates, O₂ also affects other spectral phenomena observed from SERS substrates. Nicolai and Rubim²¹ reported that saturating an electrolyte solution with O₂ caused the irreversible loss of SERS-active sites for Cu and Ag electrodes. Etchegoin et al.²⁰ postulated that O₂ served to activate Raman modes in the SERS spectrum of single-stranded DNA molecules by acting as a “coupler” between the molecule and the metal substrate. Quenching of the broad continuum observed in SERS by O₂ adsorption on cryocondensed Ag films²² and quenching of the SERS spectra of ethylene and ethane on porous Ag and Cu films by adsorption of submonolayer coverages of O₂^{23,24} have been observed by Otto and co-workers. Otto and co-workers²³ also reported that the Raman spectrum of physisorbed O₂ was not detectable from cold deposited porous Ag films, but that Raman “chemical” enhancements of at least the order of 50 had been determined for CO and N₂, even though the relative Raman cross sections of CO, N₂, and O₂ are 0.9:1:1.2. It was suggested that O₂ reacted with the sites of atomic scale roughness necessary to observe chemical enhancement of the Raman spectrum, thus self-blocking the enhancement of the O₂ Raman spectrum.²³ The production of photoluminescent Ag_n clusters on SERS substrates observed by Dickson and co-workers²⁵ and Mihalcea et al.²⁶ has also been attributed to O₂-mediated phenomena.

The different effects O₂ can have on the optical phenomena observed from SERS substrates indicate that the factors that influence the magnitude of enhancement are more complex than can be accounted for by high electromagnetic fields. Experiments were previously performed to elucidate the photodynamics on native (no adsorbate added) TMFs at various excitation powers under ambient atmospheric conditions.¹⁷ To further

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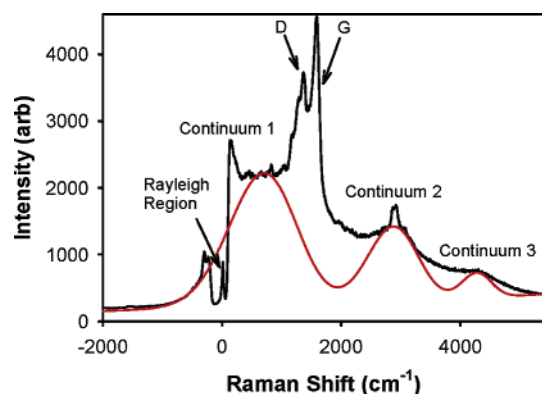


Figure 1. Raman spectrum obtained from a 5 nm TMF with 1 mW excitation power. In this, and all other spectra presented, negative Raman shift is designated anti-Stokes and positive shift represents Stokes. The region of decreased intensity centered about 0 cm^{-1} Raman shift is a result of the notch filter used to filter out the Rayleigh line. Graphitic Raman D (1350 cm^{-1}) and G (1575 cm^{-1}) peaks are indicated by letters. The red line is meant only to guide the eye in identifying the regions that the continua are observed in.

investigate the nature of the blinking observed from SERS-active substrates, TMFs were spectroscopically interrogated under N_2 atmosphere. It was hypothesized that exclusion of O_2 would alter the photodynamics of Ag TMFs in a predictable way. The data presented in this work provide supporting evidence for this hypothesis, and the simple descriptive model previously presented¹⁷ is elaborated upon to explain the photodynamics of these substrates in the absence of O_2 .

Experimental Section

Fused silica cover slips (Esco, S1-UV) were cleaned in a solution of concentrated H_2SO_4 and 30% H_2O_2 in a 2:1 ratio for 30 min. After being rinsed copiously with deionized water, the cover slips were rinsed with high-purity methanol (Burdick and Jackson) and blown dry with N_2 (UHP grade, Airgas). Ag thin films were made using a Denton DV-502 vapor phase depositor. During deposition, the chamber pressure was typically 3×10^{-6} Torr. Ag powder (Aldrich, 99.9+%, 5–8 μm average diameter) was resistively heated in a tantalum foil (Aldrich, 0.05 mm thick, 99.95%) boat. The deposition rate (0.2 $\text{\AA}/\text{s}$) and film thickness were measured with a quartz crystal microbalance (Sycon Instruments, STM-100). Ag films of 5 nm mass thickness were produced for these experiments. All of the images and spectra were obtained using the instrument described in ref 17. During spectral experimentation, the Ag films were mounted in a home-built flow cell with inlet and outlet ports used to admit the purge gas, N_2 (UHP grade, Airgas).

Results

Comparison of Spectra. Figure 1 shows an example Raman spectrum obtained under N_2 at 1 mW power. All of the spectra displayed the same features, varying only in intensity. The spectra exhibited peaks at 1350 and 1575 cm^{-1} corresponding to the D and G peaks from graphitic carbon^{27,28} that most likely originate from carbonaceous contaminants inherent in the vapor deposition process. Under ambient conditions, spectral features were also observed at frequency shifts of ~ 490 and ~ 980 cm^{-1} that could be attributed to AgO or Ag_2O species.^{29,30} Under N_2 , strong carbonaceous Raman peaks appeared for all powers interrogated.

Broad continuous features underlie all of the spectra obtained. Three distinct regions can be qualitatively observed for these

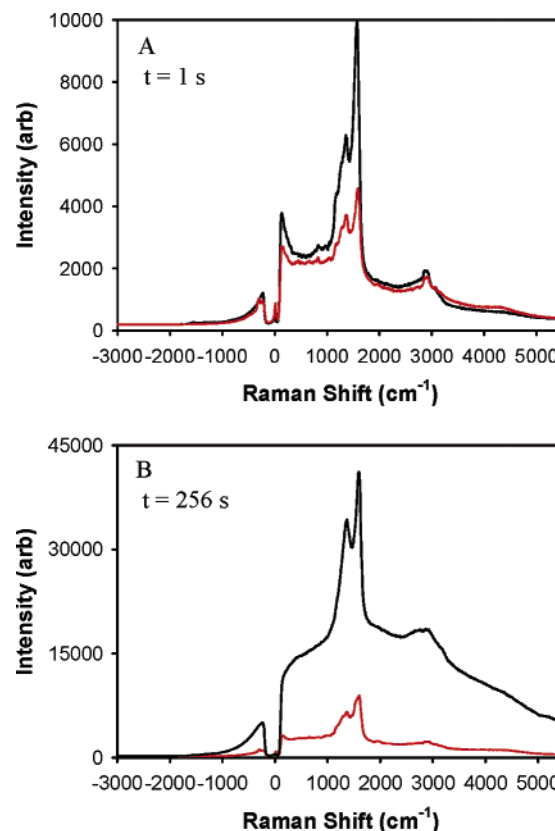


Figure 2. Comparison of spectra obtained with 1 mW excitation power under N_2 (black) and ambient (red) conditions. (A) Spectra obtained after 1 s of continuous excitation. (B) Spectra obtained after 256 s of continuous excitation.

continua, and each is highlighted in Figure 1: the first extends from -1000 cm^{-1} in the anti-Stokes region to approximately 2000 cm^{-1} (continuum 1), one centered about 3000 cm^{-1} (continuum 2), and one centered about 4400 cm^{-1} (continuum 3). These continua were observed for all of the spectra obtained under both ambient¹⁷ and N_2 atmosphere. The Gaussian curves used to fit these regions are meant only to guide the eye. Continuum 1 appears to have a peak very close to the Rayleigh line initially, but this is likely an artifact from the notch filter. Electronic Raman scattering and photoluminescence of the metal substrate have both been postulated to be responsible for the broad spectral bands, but the origin of these bands remains to be conclusively determined.^{22,31–33}

Figure 2 shows a comparison of spectra obtained under ambient and N_2 atmospheres at $t = 1$ s (A) and $t = 256$ s (B) of continuous 1 mW excitation. While the initial spectra were of comparable intensity, after a short period of time the intensity of the spectra obtained under the different conditions is vastly divergent. At this power, both data sets showed an increase in overall intensity with time. However, the increase in intensity observed under N_2 atmosphere is significantly more dramatic than that observed under ambient conditions. The overall intensity of the spectra obtained under N_2 atmosphere was always greater than the intensity of the ambient spectra collected at the same excitation powers, but the same general spectral features were observed in the spectra obtained under both conditions.

Comparison of Images. As with the ambient data sets previously published,¹⁷ the intensity of the Stokes-shifted images obtained under N_2 exhibited an activation process that caused the photoactive area of the image to increase with time. As reported previously, under ambient atmosphere individual

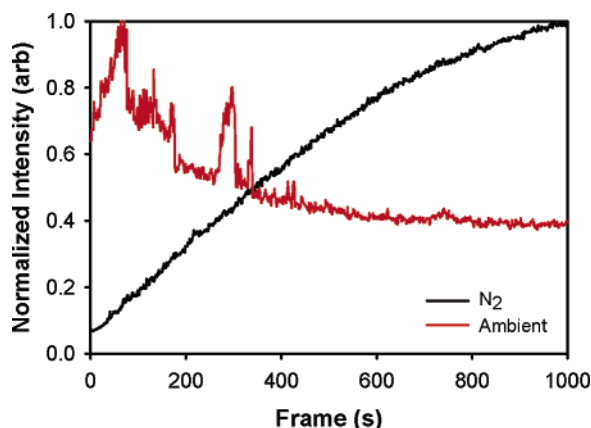


Figure 3. Comparison of the normalized center pixel intensity for images obtained at 3.5 mW excitation power under N₂ and ambient conditions.

blinking regions could be readily distinguished.¹⁷ Under N₂, however, the TMFs did not exhibit blinking behavior for any of the powers interrogated. No significant fluctuations in signal intensity were observed from images at any of the powers interrogated under N₂. Under N₂, the TMFs only showed discrete spots initially. After time, the activation of the surface was such that individual spots could not be resolved with our imaging system.

To fully demonstrate the differences in blinking behavior between ambient and N₂ atmospheres, a comparison of the intensities of the center of images obtained with 3.5 mW excitation over time for data sets obtained under N₂ and ambient conditions is presented in Figure 3. The data have been normalized to the highest intensity data point for ease of comparison; however, the raw N₂ data were ~6 times more intense than the ambient data. Under N₂, the intensity increases steadily and shows no fluctuation beyond that which can be ascribed to random noise. The ambient atmosphere data show dramatic fluctuation and an overall signal decay. The absence of blinking behavior in the images obtained from Ag TMFs under N₂ dramatically highlights the role O₂ plays in the blinking phenomenon observed from these substrates in a manner that could not be discerned in the spectral data. The intensity behavior of the TMF under N₂ clearly showed that blinking was not just diminished under N₂ and averaged out by the collection of spectra from so many Ag islands, it was not present.

Although the qualitative behavior of the TMF images at different powers provides some interesting trends, the data are also amenable to quantitative analysis. To directly compare the degree of photoactivity from the TMF surfaces under ambient and N₂ atmospheres, integrated total intensities (I_T) were determined for all of the data sets. I_T was calculated by summing the intensity values for each pixel of the image for each frame of the data set. Figure 4A is a 3-D plot of I_T at various powers for images obtained from a 5 nm TMF under ambient conditions. I_T increased as time progressed for excitation intensities less than 1 mW. A more complicated rise and fall behavior was observed for intensities 1 mW and above and has been described previously.¹⁷

Figure 4B is a 3-D plot of the I_T data obtained with excitation powers from 0.1 to 3.5 mW from 5 nm Ag TMFs under N₂ atmosphere. For all of the data sets, I_T increased in intensity with time and with excitation power. Unlike the behavior observed under ambient conditions, I_T never diminished for these powers over the course of the time scales interrogated (up to

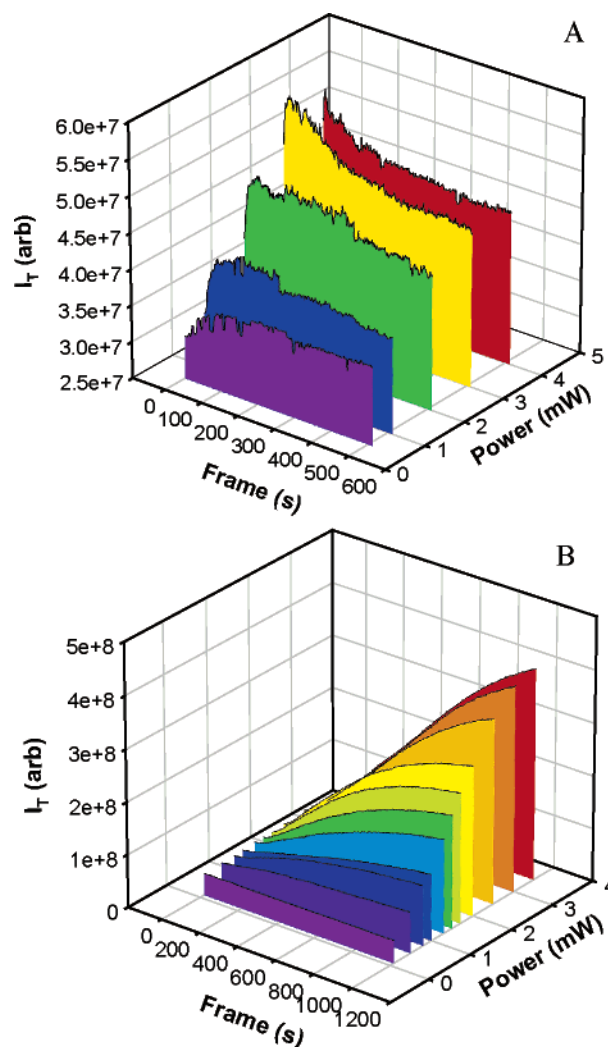


Figure 4. 3-D plots of ambient (A) and N₂ (B) I_T data for various powers.

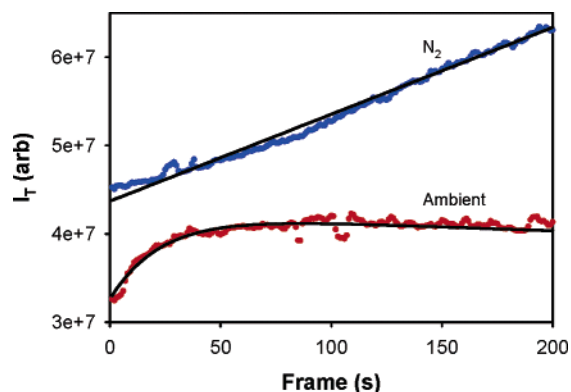


Figure 5. Comparison of I_T obtained at 1 mW excitation power under N₂ and ambient atmospheres. Solid lines are fits to the data (see text for details).

6000 s, data not shown). To more concisely highlight the difference in photoactivity for these substrates in the presence and absence of O₂, I_T obtained with 1 mW excitation power under ambient and N₂ atmospheres is displayed in Figure 5.

Discussion

When viewed in the context of significant blinking observed under ambient atmospheric conditions, the absence of blinking and constant rise in intensity observed from Stokes-shifted

images and spectra obtained under a N₂ atmosphere strongly suggest that blinking is dependent on an O₂-mediated mechanism and that the decay of photoactivity observed under ambient conditions is also O₂ dependent. All of the data taken together suggest photoinduced processes that both produce (under ambient and N₂ conditions) and destroy (under ambient conditions) an emitting species that can serve as a SERS-active site.

One possible explanation for the role of O₂ involves cyclic reactions with Ag to produce and destroy Ag clusters. Metal clusters have been postulated to be the origin of the active sites necessary for the largest enhancement of the SERS signal nearly since the advent of the technique. Described as areas of atomic scale roughness provided by atomic surface defects,¹⁴ metal cluster active sites are thought to either provide sites for enhanced chemisorption, which in turn can "improve the coupling between photons and free electrons in the metal,"³⁴ or to facilitate photon driven charge transfer, which allows for a resonance enhancement of the adsorbed molecule.¹⁴

Watanabe et al. demonstrated quenching of SERS by addition of S₂O₃²⁻ to the electrolyte solution of a Ag electrode.⁷ The loss of SERS under these conditions was ascribed to the permanent loss of active site species on the Ag electrode surface from the formation of a complex between Ag⁺ and S₂O₃²⁻ that could be dissolved in water. Stabilization of Ag⁺ active sites on Ag electrodes and decreased quenching of the SERS signal from application of a cathodic potential by adsorption of trace amounts of Cu atoms were reported by Moerl and Pettinger.⁶ In support of Ag clusters as SERS-active sites, Furtak and co-workers observed the following: (1) SERS activation of a Au substrate on which electrochemically controlled monolayers of Ag had been deposited,³⁵ (2) the thermal quenching of the SERS signal from KCl electrolyte on a Ag electrode attributed to the thermal dissociation of Ag–adatom–Cl⁻ surface complexes,³⁴ (3) more than one molecule can populate a SERS-active site and that these active sites compose less than 3% of the substrate surface as evidenced by the deactivation of Ag surface defects by thallium deposition,¹³ and (4) low-frequency Raman peaks that could be attributed to Raman-active modes of Ag_n⁺ clusters.^{36,37}

The continuous increases in intensity of the Raman peaks observed from the carbonaceous contaminants under N₂ atmosphere, and at low powers under ambient conditions, imply that the number of active sites on the surface increases with time under these conditions. Ag TMFs are composed of stationary Ag islands that are separated by distances of approximately 5 nm.³⁸ Atomic force microscopy experiments performed to elucidate the effect of laser excitation on the EM enhancement of TMFs indicated that a change in substrate morphology was not responsible for the trends observed. Laser-induced morphological changes will be addressed in a subsequent manuscript.³⁹ The increase observed in the continuum signal may be due to photogeneration of Ag clusters, which have been widely reported to display a broad photoluminescent response.^{25,40,41}

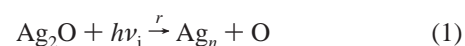
While not necessarily native to the synthesis of SERS substrates, Ag clusters have been widely reported to result from photoreduction of Ag oxide species present on the surface of Ag SERS substrates and from Ag oxide SERS substrates.^{25,42–44} As previously described, Dickson and co-workers confirmed the presence of silver oxides on TMF surfaces by XPS and postulated that metal clusters are generated by photoreduction of Ag₂O on the surface.²⁵ Ag₂O colloidal particles have been demonstrated to be activated for SERS by photochemical

reduction of Ag₂O to Ag_n by Xiao et al.⁴⁵ Finally, Mihalcea et al. observed fluorescence from Ag_n produced by photoactivation of reactively sputtered Ag oxide layers.²⁶

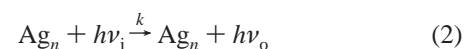
Based upon observation of the photoactivation of Ag TMF substrates under ambient and N₂ conditions, intermittent Raman spectral fluctuations in the presence of O₂,¹⁷ the absence of spectral fluctuation under N₂ atmosphere, and the apparent lack of reactions that decay the photoactivity of the surface under N₂, it is hypothesized that blinking is due to a cyclic, O₂-mediated process. Because Ag_n clusters can be created and deactivated on TMFs in the presence of O₂ and because Ag_n clusters are thought to be a possible origin of the active sites necessary for the chemical enhancement mechanism of SERS, it is hypothesized that the O₂-mediated cyclic photochemistry of Ag_n clusters is the mechanism that gives rise to blinking in SERS.

Time-Dependent Model. A simple kinetics model for the production and destruction of luminescent species has previously been proposed to account for the trends in intensity and temporal fluctuations in intensity and is elaborated here.¹⁷ Assuming that the excitation–emission process is fast with respect to both the production and the destruction of Ag_n (reasonable under the high photon fluxes used in this work), the general trend in emission intensity would depend on which of the two processes, production or destruction, dominates the concentration of Ag_n on the surface. A general mechanism for the photoproduction of luminescent Ag_n clusters from oxides on a TMF surface is:

Production of Ag Clusters



Excitation/Emission for Ag Clusters



Loss of Emitting Species



Equation 1 describes the photochemical conversion of Ag₂O (present on the surface from oxidation of the Ag islands by atmospheric O₂) to Ag cluster species (Ag_n). Excitation of Ag_n by incident light, $h\nu_i$, and subsequent emission of frequency-shifted light, $h\nu_o$, is described by eq 2. Production of Ag_n with electronic resonance at the excitation wavelength may require diffusion and combination on the surface. However, diffusion of clusters on the surface, with potential subsequent formation of larger or new nonactive clusters, does not account for the blinking in the frequency-shifted emission because blinking is not observed under the same excitation powers in the absence of atmospheric O₂. Because decay in the photoactivity of the Ag TMFs is observed under ambient conditions but not under N₂ atmosphere, a Ag_n deactivation channel involving reaction with O₂ is proposed (eq 3). Ag_n can also react with O₂ to reform Ag₂O, deactivating Ag_n as a SERS-active site and for luminescence, but providing a species that can be reconverted to a photoactive Ag_n species. This cyclic reaction of Ag_n with O₂ may account for the blinking observed from these substrates. Because the reaction of Ag_n with O₂ can proceed in different ways, the product of this reaction is nonspecific, and could be ascribed to Ag₂O, AgO, or some other Ag oxide species that is not photolabile.

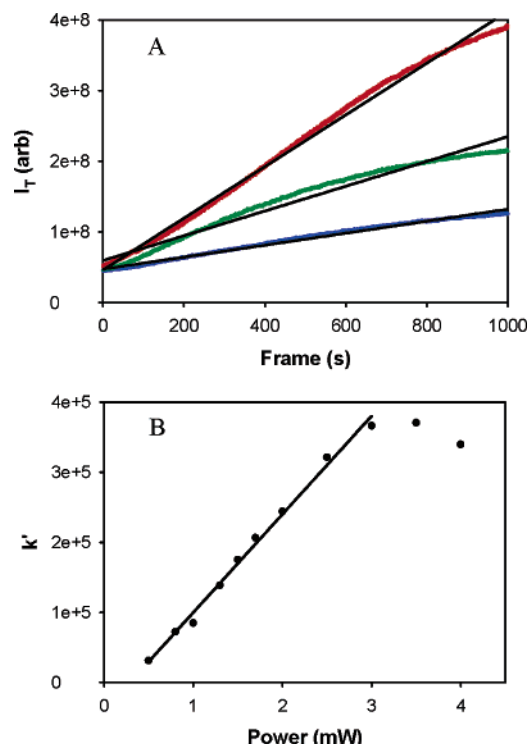


Figure 6. (A) Linear fits (black) of eq 6 to representative N₂ I_T data. 1.0 mW data (blue): $R^2 = 0.99$, $k' = (8.48 \pm 0.03) \times 10^4$. 1.5 mW data (green): $R^2 = 0.97$, $k' = (1.75 \pm 0.01) \times 10^5$. 3.0 mW data (red): $R^2 = 0.99$, $k' = (3.66 \pm 0.008) \times 10^5$. (B) Pseudo-first-order rate constants (k') obtained from linear fits to N₂ I_T data for various powers.

The rate expression for the proposed role of oxygen in the production and destruction of Ag clusters is:

$$\frac{d[\text{Ag}_n]}{dt} = r[\text{Ag}_2\text{O}][h\nu_i] - f[\text{Ag}_n][\text{O}_2] \quad (4)$$

where r is the rise constant and f is the fall constant. As detailed in ref 17, the integrated rate law in terms of measured emitted intensity is:

$$I_T = \frac{Mr}{(f-r)}(e^{-rt} - e^{-ft}) \quad (5)$$

The rise/fall intensity behavior from TMFs in the presence of O₂ is well fit by eq 5, as shown in Figure 5.

In the absence of O₂, the destruction channel is eliminated and the rate expression for production of Ag_n is given by:

$$\frac{d[\text{Ag}_n]}{dt} = r[\text{Ag}_2\text{O}][h\nu_i] \quad (6)$$

Because the activity of Ag₂O_(s) is 1, the integrated rate law reduces to a simple first-order expression with respect to $h\nu_i$:

$$[\text{Ag}_n] = [\text{Ag}_n]_0 + k[h\nu_i]t \quad (7)$$

As detailed in eq 2, the integrated intensity (I_T) is proportional to the concentration of Ag_n on the TMF surface; therefore, eq 7 can be rewritten in terms of intensity:

$$I_T = I_{T\text{initial}} + k't \quad (8)$$

where k' is a pseudo-first-order rate constant. Equation 8 can be used to fit $I_T(t)$. According to eq 8, in the absence of O₂ a linear rise in I_T as a function of time is predicted as the

concentration of the emitting species increases with excitation intensity, which is substantially different from the behavior observed in the presence of O₂.

Representative examples of eq 8 fits to $I_T(t)$ are shown in Figure 6A. This simple model accurately predicts the trend for excitation powers ranging from 0.1 to 3.5 mW fairly well, which is consistent with the hypothesis that O₂ is responsible for the destruction of photoactive species observed under ambient conditions. As a further test of the linear dependence for the photoactivation process on excitation power, the pseudo-first-order rate constants extracted from the slope of fit to I_T as a function of time were analyzed as a function of power (Figure 6B). The trend is linear up to approximately 3 mW. At higher powers, as shown in Figure 6B, the dependence deviates from linearity. This simple model does not address deviations at high excitation powers; the nonlinear regime will be addressed in a subsequent manuscript.

Conclusions

Evidence to support our hypothesis that O₂ plays a critical role in the photodynamics observed on native SERS-active surfaces was presented. In the presence of O₂, the integrated intensity from Ag TMFs decays with time. When ambient gas-phase O₂ is purged from the surface, the integrated intensity rises continuously. A simple model involving the cyclic production and destruction of photoactive Ag clusters was developed and demonstrated to accurately describe integrated intensity behavior as a function of time under both sets of atmospheric conditions. While these trends have been studied on SERS-active thin silver films, the photodynamics should be equally applicable to SERS-active Ag colloids.

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References and Notes

- (1) Otto, A. *Appl. Surf. Sci.* **1980**, 6, 309.
- (2) Otto, A. *J. Electron Spectrosc. Relat. Phenom.* **1983**, 29, 329.
- (3) Otto, A. Surface-Enhanced Raman Scattering: "Classical" and "Chemical" Origins. In *Topics in Applied Physics*; Cardona, M., Guntherodt, G., Eds.; Springer-Verlag: New York, 1983; Vol. 4, p 289.
- (4) Otto, A. *Indian J. Phys.*, B **2003**, 77B, 63.
- (5) Pettinger, B.; Tadjeddine, A.; Kolb, D. M. *Chem. Phys. Lett.* **1979**, 66, 544.
- (6) Moerl, L.; Pettinger, B. *Solid State Commun.* **1982**, 43, 315.
- (7) Watanabe, T.; Kawanami, O.; Honda, K.; Pettinger, B. *Chem. Phys. Lett.* **1983**, 102, 565.
- (8) Moskovits, M. *Rev. Mod. Phys.* **1985**, 57, 783.
- (9) Gersten, J.; Nitzan, A. *J. Chem. Phys.* **1980**, 73, 3023.
- (10) Etchegoin, P.; Cohen, L. F.; Hartigan, H.; Brown, R. J. C.; Milton, M. J. T.; Gallop, J. C. *J. Chem. Phys.* **2003**, 119, 5281.
- (11) Campion, A.; Kambhampati, P. *Chem. Soc. Rev.* **1998**, 27, 241.
- (12) Michaels, A. M.; Jiang, J.; Brus, L. *J. Phys. Chem. B* **2000**, 104, 11965.
- (13) Furtak, T. E.; Roy, D. *Phys. Rev. Lett.* **1983**, 50, 1301.
- (14) Otto, A.; Billmann, J.; Eickmans, J.; Erturk, U.; Pettenkofer, C. *Surf. Sci.* **1984**, 138, 319.
- (15) Jiang, J.; Bosnick, K.; Maillard, M.; Brus, L. *J. Phys. Chem. B* **2003**, 107, 9964.
- (16) Bjerneld, E. J.; Johansson, P.; Kall, M. *Single Mol.* **2000**, 1, 239.
- (17) Jacobson, M. L.; Rowlen, K. L. *Chem. Phys. Lett.* **2005**, 401, 52.
- (18) Kudelski, A.; Pettinger, B. *Chem. Phys. Lett.* **2000**, 321, 356.
- (19) Etchegoin, P.; Liem, H.; Maher, R. C.; Cohen, L. F.; Brown, R. J. C.; Milton, M. J. T.; Gallop, J. C. *Chem. Phys. Lett.* **2003**, 367, 223.
- (20) Etchegoin, P.; Liem, H.; Maher, R. C.; Cohen, L. F.; Brown, R. J. C.; Hartigan, H.; Milton, M. J. T.; Gallop, J. C. *Chem. Phys. Lett.* **2002**, 366, 115.
- (21) Nicolai, S. H. A.; Rubim, J. C. *Vib. Spectrosc.* **1994**, 7, 175.
- (22) Akemann, W.; Otto, A. *Surf. Sci.* **1994**, 309, 1071.
- (23) Pettenkofer, C.; Eickmans, J.; Erturk, U.; Otto, A. *Surf. Sci.* **1985**, 151, 9.

- (24) Erturk, U.; Pettenkofer, C.; Otto, A. *J. Electron Spectrosc. Relat. Phenom.* **1986**, 38, 113.
- (25) Peyser, L. A.; Vinson, A. E.; Bartko, A. P.; Dickson, R. M. *Science* **2001**, 291, 103.
- (26) Mihalcea, C.; Buchel, D.; Atoda, N.; Tominaga, J. *J. Am. Chem. Soc.* **2001**, 123, 7172.
- (27) Tuinstra, F.; Koenig, J. L. *J. Chem. Phys.* **1970**, 53, 1126.
- (28) Tsang, J. C.; Demuth, J. E.; Sanda, P. N.; Kirtley, J. R. *Chem. Phys. Lett.* **1980**, 76, 54.
- (29) Waterhouse, G. I. N.; Bowmaker, G. A.; Metson, J. B. *Phys. Chem. Chem. Phys.* **2001**, 3, 3838.
- (30) Iwasaki, N.; Sasaki, Y.; Nishina, Y. *Surf. Sci.* **1988**, 198, 524.
- (31) Birke, R. L.; Lombardi, J. R.; Gersten, J. I. *Phys. Rev. Lett.* **1979**, 43, 71.
- (32) Eesley, G. L. *Phys. Rev. B: Condens. Matter* **1981**, 24, 5477.
- (33) Heritage, J. P.; Bergman, J. G.; Pinczuk, A.; Worlock, J. M. *Chem. Phys. Lett.* **1979**, 67, 229.
- (34) Macomber, S. H.; Furtak, T. E. *Solid State Commun.* **1983**, 45, 267.
- (35) Loo, B. H.; Furtak, T. E. *Chem. Phys. Lett.* **1980**, 71, 68.
- (36) Roy, D.; Furtak, T. E. *Chem. Phys. Lett.* **1986**, 124, 299.
- (37) Roy, D.; Furtak, T. E. *Phys. Rev. B* **1986**, 34, 5111.
- (38) Roark, S. E. Characterization of sers-active silver-island films using atomic force microscopy. Ph.D. Thesis, University of Colorado, 1995.
- (39) Jacobson, M. L.; Corbman, J. D.; Rowlen, K. L. *J. Phys. Chem. B*, manuscript in preparation.
- (40) Konig, L.; Rabin, I.; Schulze, W.; Ertl, G. *Science* **1996**, 274, 1353.
- (41) Rabin, I.; Schulze, W.; Ertl, G. *J. Chem. Phys.* **1998**, 108, 5137.
- (42) Buchel, D.; Mihalcea, C.; Fukaya, T.; Atoda, N.; Tominaga, J.; Kikukawa, T.; Fuji, H. *Appl. Phys. Lett.* **2001**, 79, 620.
- (43) Kotz, R.; Yeager, E. *J. Electroanal. Chem.* **1980**, 111, 105.
- (44) Peyser, L. A.; Lee, T.-H.; Dickson, R. M. *J. Phys. Chem. B* **2002**, 106, 7725.
- (45) Xiao, Y.; Li, Y. S.; Swihart, G. H. *Talanta* **2002**, 58, 755.