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A COMPARISON OF SERS AND MEF OF
RHODAMINE 6G ON A GOLD SUBSTRATE

BY
ELIZABETH KOHR

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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OF
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ABSTRACT

Rhodamine 6G is spin-cast onto gold surfaces and the reflectance, emission, excitation, and SERS spectra are reported. Electron microscopy shows that the particle sizes of the gold are uniform for all preparations. Reflection spectra show that the Rh6G aggregates for thicker films and that the gold plasmon band shifts due to the refractive index change on the surface. The intensity of the SERS spectra increases with increasing surface coverage but the rate of change modulates between submonolayer and multilayer surface densities. The emission spectra behave unexpectedly as a function of Rh6G coverage. At submonolayer coverage the emission is relatively strong, decreases as the surface density increases to a monolayer, and then increases as the Rh6G thickness increases. Excitation spectra demonstrate that the emitting species at low surface density is monomeric but for thicker layers the excited state responsible for emission is Rh6G aggregates. For the thicker films, the Rh6G acts as its own dielectric layer for metal enhanced fluorescence of the aggregates.

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PREFACE

This thesis has been prepared in manuscript format. This manuscript has been submitted to the American Chemical Society Journal of Physical Chemistry C and is currently under review for publication.

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MANUSCRIPT

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A Comparison of SERS and MEF of Rhodamine 6G on a Gold Substrate

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INTRODUCTION

The use of plasmonic structures to modulate spectroscopic properties has drawn substantial interest in the last few years. Surface Enhanced Raman Scattering (SERS)¹⁻¹⁷ and Metal Enhanced Fluorescence (MEF)¹⁸⁻³⁵ both exploit the electric field enhancement associated with a plasmon resonance to substantially increase the spectroscopic signal. Despite the mechanistic similarities between SERS and MEF, there are few reports of SERS and MEF on the same structures.^{36,37} This is because most fluorophores are substantially quenched when placed adjacent to a metal surface, so MEF requires that the emitting species be separated from the plasmon source by a few nm. In contrast, SERS does not suffer from this limitation, so enhancement occurs for molecules directly bound to the metal.

Our work has targeted thin films of xanthene dyes for use in sensing applications.^{38,39} One of the best studied of this class of compounds is rhodamine 6G (Rh6G),⁴⁰⁻⁶⁵ which has both a high quantum yield for fluorescence and a large cross section for Raman scattering. Wavelength shifts in the absorbance and emission spectra of Rh6G imply that aggregates form in solution at higher concentrations, as suggested by either exciton⁶⁶⁻⁶⁸ or excimer theory.⁶⁹ In thin films, the same electronic spectroscopic effects are also observed, and are a function of film thickness.⁶⁵ The spectroscopic results indicate aggregation in the excited state (excitons and/or excimers) but we wondered if the aggregation also happened in the ground state of the thin films. Vibrational spectroscopy can be used to answer this question, and SERS on Rh6G was the logical choice to probe the ground state structure.

In this work we report the SERS and MEF spectra of Rh6G thin films on a gold substrate as a function of film thickness. The emission properties of fluorophores as a function of thickness when deposited on nonmetallic substrates has been reported.⁷⁰⁻⁷⁴ No emission was expected for Rh6G on the gold surface since metals typically quench fluorescence. In contrast, Rh6G can be observed in SERS down to single molecule levels when adsorbed to metal nanoparticles.⁷⁵⁻⁷⁷ To our surprise, not only was emission observed, but it demonstrated an unusual behavior with increasing film thickness. The spectroscopic signatures of excited state aggregation were still present, but the typical quenching associated with this was suppressed. The intensities of the emission and Raman spectra paralleled each other as a function of thickness up to a thickness of several monolayers, indicating that the emission enhancement was due to MEF and not a structural reorganization. This conclusion was supported by the observation that the Raman spectra showed no peak shifts as a function of film thickness, which also indicated that there is no ground state aggregation in Rh6G.

EXPERIMENTAL

A plating bath that was 0.025 M tin(II) chloride and 0.07 M trifluoroacetic acid in 50/50 methanol/water, an ammoniacal silver nitrate solution, and an aqueous plating bath of 7.9×10^{-3} M sodium gold sulfite, 0.127 M sodium sulfite, and 0.625 M formaldehyde were prepared, all in accordance with Whelan, et al.⁷⁸ The sodium gold sulfite solution was also prepared in accordance with Whelan, et al.⁷⁸ Silicon chips were cut into squares of approximately 1.0 cm^2 . The silicon chips were sonicated in 95% ethanol, then distilled water, each for 15 minutes. For the drying step, the chips were left to air dry. Rhodamine 6G (Rh6G) solutions were prepared by dissolving 0.2394 g of Rh6G and diluting to approximately 40 mL. This was left to warm overnight and was later diluted to 50.00 mL to give a concentration of 1.0×10^{-2} M. Serial dilutions were made of this solution resulting in concentrations of 7.5×10^{-3} , 5.0×10^{-3} , 2.5×10^{-3} , 1.0×10^{-3} , 7.5×10^{-4} , 5.0×10^{-4} , 2.5×10^{-4} , and 1.0×10^{-4} M. The solutions were all kept in aluminum foil to prevent exposure to light. Each silicon chip was spun-cast for 45.0 s at 1200 rpm (acceleration of 1080 s^{-2}) immediately after a 50 μL volume of Rh6G solution was deposited on each chip.

The morphology of the substrates was studied by a TESCAN Field Emission Mira III LMU (Czech Republic) at an accelerating voltage of 5 kV. The energy dispersive X-ray spectroscopy (EDS) measurements were done on Bruker Quantax EDS with XFLASH 5010 detector attached to a field emission scanning electron microscope MIRA II LMH. The reflection spectra were obtained using a Filmetrics F40 microscope with a tungsten-halogen light source from 400-1000 nm. Raman

spectra were obtained on an Agiltron PeakSeeker spectroscope with a 785 nm laser and an integration time of 30 seconds. Fluorescence measurements were made on a Horiba (JobinYvon) Fluorlog spectrometer at a 60° angle with slit widths of 2.0 nm for the light source and detector. The integration time was set to 1 s and wavelength increments to 1 nm. The samples were irradiated with a xenon arc lamp excitation source at a wavelength of 525 nm. The emission range was set to 535-800 nm. Excitation spectra were collected with fluorescence monitoring at 555 nm and 610 nm with two excitation ranges for each. For the monitoring at 555 nm the excitation ranges were 300-545 nm and 565-800 nm. For the monitoring at 610 nm the excitation ranges were 310-600 nm and 620-800 nm.

RESULTS AND DISCUSSION

Deposition of gold onto the silicon substrate followed the procedure previously reported.⁷⁸ The gold surfaces were coated with Rh6G using spin-casting, using conditions previously used to coat glass.⁶⁵ Direct measurement of the thickness of the Rh6G layer using optical or AFM methods proved to be ineffective. When spin-casting Rh6G onto glass the relationship between solution concentration and coating thickness was markedly nonlinear.⁶⁵ For example, when $[\text{Rh6G}] = 1 \times 10^{-4} \text{ M}$, $t_{\text{Rh6G}} \sim 1 \text{ nm}$, when $[\text{Rh6G}] = 1 \times 10^{-3} \text{ M}$, $t_{\text{Rh6G}} \sim 3 \text{ nm}$, and when $[\text{Rh6G}] = 1 \times 10^{-2} \text{ M}$, $t_{\text{Rh6G}} \sim 45 \text{ nm}$. We expected similar, but not identical, behavior for spin-casting onto the gold substrate. For the remainder of this paper reference will only be made to the spin-casting concentration.

Figure 1. SEM micrographs of A) Au with no Rh6G; B) Au spin-cast with 1×10^{-4} M Rh6G; C) Au spin-cast with 1×10^{-3} M Rh6G; D) Au spin-cast with 1×10^{-2} M Rh6G. The scale bars are 1 μm for each image.

Figure 1 shows the SEM images of samples covered with different thicknesses of Rh6G. Each sample shows the same features: grains that are less than 100 nm in size that cover the whole surface with a few particles that are 0.5 to 1 μm in diameter. Both of these features are attributed to the gold coating, which mainly coats the

substrate as small grains but there are a few particles that grow to larger size. There are no morphological features that can be assigned to the Rh6G. This is reasonable since the Rh6G is expected to be less than 50 nm thick for all of the coating conditions used. However, the EDS spectra, shown in Figure 2, indicate the presence of the Rh6G. The primary elements observed are Au and C with smaller peaks for Si and O. As the Rh6G coating becomes thicker, the intensity of the Au peak decreases, and the C peak increases. This confirms that the Rh6G is present but does not affect the morphology of the substrate.

Figure 2. EDS spectra of Au coated with Rh6G. The inset shows the integrated area of the C and Au peaks as a function of Rh6G concentration.

Figure 3. Reflectance spectra of Rh6G coated on gold for different surface coverages.

Figure 3 shows the reflection spectra for Rh6G on gold for several surface coverages. The Au surface has a reflection minimum at ~ 480 nm, consistent for all preparations, and indicative of a pure gold surface with relatively large particle size.⁷⁹ As the thickness of Rh6G is coated onto the surface, several spectral responses can be noted. First, as expected, the reflection from the gold is reduced as the Rh6G thickness increases. At the thinnest coverage, this is the only change that is observed – no feature associated with absorption by Rh6G is measurable. At intermediate thicknesses, a broad feature grows in, centered at about 590 nm. Finally, the thickest films show three peaks at 530, 575, and 630 nm. The peaks at 530 nm and 575 nm are assigned to monomeric and aggregated Rh6G respectively, consistent with the literature.⁴⁰⁻⁶⁵ The absorption located in the 590 – 630 region is assigned to the plasmon shifted gold resonance.

Figure 4 shows the background corrected Raman spectra of Rh6G coated onto Au as a function of the concentration used in the spin-casting solution. (The SERS spectra all have a fluorescence background, especially for thicker films.) As expected in a SERS response, as the film becomes thicker, the intensity of the Raman peaks increases. Three peaks at 1314, 1363, and 1512 cm^{-1} were fit to a Gaussian lineshape for each sample. As the film thickness increased, there was no substantial change in either the peak maxima or peak width (all fits agreeing within ± 1 cm^{-1} , less than the 4 cm^{-1} resolution of the measurement), indicating that there is no coupling between Rh6G molecules in the ground state. However, the intensity change as a function of surface coverage shows two regions, as indicated by the lines in Figure 4B. The break

occurs where the surface density of Rh6G molecules is expected to transition from a monolayer to multilayers.

Figure 4. **A**, Top: Background corrected SERS spectra of Rh6G on Au as a function of the solution concentration used in spin-casting. **B**, Bottom: Peak intensity of selected peaks as a function of Rh6G concentration used in spin-casting. The lines are guides for the eye.

Figure 5. Emission spectra of Rh6G on Au as a function of the solution concentration used in spin-casting. Excitation was done at 525 nm. Inset: Total area under the emission spectrum as a function of Rh6G concentration used in spin-casting.

Figure 5 shows the emission spectra of Rh6G as a function of surface coverage. The thinnest film (created using a 1.0×10^{-4} M solution for spin-casting) has a maximum at 555 nm. As the film thickness grows the emission intensity initially decreases and the wavelength maximum shifts to lower energy. This is consistent with what has been reported previously on glass.⁶⁵ However, with further addition of Rh6G, the emission intensity begins to increase and the maximum wavelength continues to shift to lower energy.

Table 1. Deconvoluted parameters for the emission spectra of Rh6G on gold and glass (from reference 65). λ is the wavelength maximum (in nm) and Γ is the full-width-at-half-maximum (in nm). The uncertainty in λ and Γ are both ± 2 nm.

[Rh6G]	λ_1	Γ_1	λ_2	Γ_2	λ_3	Γ_3	λ_4	Γ_4
Gold	556	19	577	43	603-615	25	640-656	60
Glass	550	16	573	21	600	35	650	47
Assignment	Monomer		Excimer		Exciton		Aggregate	

Each emission spectrum was deconvoluted into two or three Gaussian peaks, as needed, to give an acceptable fit. For the films with the two lowest surface coverages only two peaks were required: one with a narrow lineshape with a maximum at 556 nm and a second broader peak located at 577 nm. The intensity and lineshape are similar to what was reported for thin films of Rh6G on glass,⁶⁵ so the peaks are assigned to monomers (556 nm) and excimers (577 nm). The intensity of the emission spectra at low surface coverage is surprising since a metal surface typically induces quenching of an adjacent fluorophore. As the surface coverage increases a third peak is required to fit the emission spectra. The maximum of this third peak varies between 603 and 615 nm for different film thicknesses, but the linewidth remains constant at 25 nm. This peak is assigned to an exciton emission. Finally, for the thickest films the feature at 556 nm is no longer detectable and a new peak arises, observed as a broad shoulder, with a maximum in the range of 640 – 656 nm, assigned to aggregates or crystallized Rh6G. All of these assignments are summarized in Table 1.

The total intensity of the emission spectra as a function of surface coverage is remarkable. As shown in the inset in Fig. 5, the emission intensity is high for the thinnest film and then decreases substantially as the surface density increases. At approximately one monolayer coverage the total emission intensity reaches a minimum. Then, as multiple layers accumulate, the intensity increases up to a maximum when the film thickness is estimated to be ~10 nm. For thicker films, which should be dominated by aggregates and crystallites, the emission slowly decreases as the films get thicker. In contrast, the intensity profile on glass as a function of film

thickness shows high emission for surface coverages less than one monolayer, but is substantially quenched for thicker films.

The rise in emission intensity of films of Rh6G which are a few monolayers thick is attributed to MEF, where the Rh6G is acting as its own dielectric. In this interpretation, the enhanced fluorophore is the aggregate structure, not isolated Rh6G molecules. The maximum MEF response is found when the Rh6G is ~ 10 nm thick, which is consistent with previous studies of the optimum dielectric thickness for MEF.⁸⁰⁻⁸² A comparison of the Rh6G emission intensity for films created from a 5×10^{-3} M solution on glass⁶⁵ vs gold implies an enhancement factor of ~ 10 . The overlap between the shifted gold plasmon resonance and the aggregate emission peak is likely responsible for the electric field enhancement that causes the MEF response.

Figure 6. Normalized excitation spectra for selected films of Rh6G spin-cast onto Au. The molarities indicate the concentration of Rh6G used in spin-casting. Left: emission detected at 555 nm. Right: emission detected at 610 nm.

Figure 6 shows the normalized excitation spectra of Rh6G for several surface coverages. When the emission is detected at 555 nm, i.e. emission from the monomer excited state, the excitation spectra all have maxima at 534 nm, except for the thickest film (cast from $[\text{Rh6G}] = 1 \times 10^{-2}$ M), which has a maximum in the range of the

detection wavelength. The absorption maximum of Rh6G on glass at 527 nm is associated with the monomer, consistent with the emission spectra. The thick film, with an excitation maximum of 555 ± 10 nm indicates absorption from aggregates and the lineshape, displays little absorption in the monomer region. To better understand this behavior, the excitation spectra were also measured using detection at 610 nm, which selects for both exciton and aggregate excited states. Under these measurement conditions the excitation spectra exhibit two general profiles. For low surface coverages the excitation maximum is at 534 nm, again indicative of absorption by monomer. In contrast, for films greater than a monolayer thickness, the excitation spectra have a maximum at 556 nm, are very broad, and have significant absorption at 534 nm. This is consistent with absorption associated with monomer, exciton, and aggregates. However, the energy absorbed by the monomer at these multilayer thicknesses is transferred to exciton or aggregate excited states.

Scheme 1 summarizes the observations. At low Rh6G coverages the emission signal is strong, arising from monomers, and the SERS signal is weak, because of the low number density. At monolayer coverage the emission spectrum is quenched, probably because of self-quenching and influence from the underlying gold surface. In contrast, the SERS signal is strong. Finally, at multilayer coverage both the emission

and SERS exhibit strong signals. The emission signal is enhanced because the fluorophores are sufficiently distant from the surface to allow MEF to occur, but the emission is from aggregate states, not monomers. The SERS signal is strong for two reasons: a large number density and electric field enhancement from the gold surface. The emission enhancement decreases at thicker films while the SERS intensity is still increasing. This change occurs because $I_{\text{emission}} \propto E^2$ while $I_{\text{SERS}} \propto E^4$, where E is the electric field, so that the SERS effect extends to thicker films than MEF.

CONCLUSION

Rh6G coated on gold has a complicated spectroscopic behavior as a function of coating thickness. The gold particles are synthesized to give reproducible sizes so that observed changes are not a result of the underlying gold layer. For submonolayer coverage, the structure of the Rh6G is primarily monomeric, as indicated by the emission spectrum. The emission, excitation, and SERS spectra all demonstrate changes as the film thickness exceeds a monolayer. In the case of SERS, this is observed as a change in the slope of the intensity vs coverage, with the change in slope occurring at about a monolayer thickness. For the fluorescence spectra, there are multiple changes observed as a function of Rh6G thickness. For submonolayer coverage, the emission intensity is high and arises from monomer excited state, but decreases substantially as the thickness increases. Surprisingly, with further coverage by Rh6G, the emission intensity increases, but the source of the emission is the aggregate excited state. The enhancements in both SERS and MEF rely on the electric field created by the underlying gold substrate.

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