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Spectral shifts in metal-enhanced fluorescence

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We report a 2 nm red shift in the fluorescence spectra observed for Rhodamine 800 dissolved in glycerol on copper substrates as compared to glass reference samples, suggesting a wavelength dependence of metal enhanced fluorescence. The full width half maximum of the blue-red spectra is about 1 nm narrower as compared to the reference sample. We speculate that the observation correlates with a specific interaction mechanism between the Rhodamine 800 transition dipole, the enhanced electric field, and subsequent plasmon coupling, an observation not yet reported.

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Metal-Enhanced Fluorescence (MEF) has attracted significant research interest in recent years, from both a theoretical¹ and practical perspective.^{2,3} From a theoretical perspective, the mechanism of MEF is still under debate, but with significant progress made in the last few years, while the practical applications of MEF are widespread, including applications in imaging, e.g., tip-enhanced near-field optical microscopy,⁴ high throughput analysis,⁵ sensing and in the analytical and life sciences,^{6–8} to name but just a few.

In the vast majority of MEF studies, no spectral shifts or “distortions” are observed, with both the MEF and control sample spectra being reported as identical. However, in this contribution, we show that spectral shifts/distortions can readily be observed in MEF samples, albeit the effect being somewhat minor. Copper films prepared by vapor deposition under controlled conditions, i.e., by carefully controlling the deposition rate and film thickness, allow for the fabrication of morphologies that enhance the fluorescence signature of Rhodamine 800 (Rh 800) up to 4 times in glycerol. The enhanced fluorescence is accompanied by ≈ 2 nm red shift in the enhanced spectra, as compared to an otherwise identical control sample, and further, the Full Width at Half Maximum (FWHM) decreases ≈ 1 nm. While the spectral distortions are relatively small, these observations do impact how we think about and interpret plasmon-coupled and enhanced fluorescence.

Rhodamine 800 and 99.995% pure copper was purchased from AnaSpec, Fremont, CA, USA and from Research and PVD Materials Corporation, Wayne, NJ, USA, respectively. Silicon monoxide, 99.99% pure, methanol, and glycerol were purchased from Sigma-Aldrich, USA. All solvents were of spectroscopic grade. The copper was deposited at a typical rate of 0.1 nm/s on cleaned glass slides, Fisher brand, using an Edwards 360 thermal vapor deposition system equipped with a quartz crystal oscillator to monitor the rate of deposition and subsequently film thickness. The pressure in the vacuum chamber was typically 10^{-6} Torr.

Absorbance spectra were recorded on a Cary 50 Bio UV-Vis spectrograph, Varian, Inc. The Cu film samples were oriented perpendicular to the beam and spectra were

correct for the background signal recorded from an otherwise identical but *uncoated* glass slide. Absorbance spectra on liquid samples were obtained using standard 1 cm quartz cuvettes. Synchronous spectra, i.e., spectra recorded when emission wavelength = excitation wavelength, were obtained on a Cary Eclipse, Varian, Inc., equipped with a plate reader. To minimize background, samples were placed on absorptive neutral density filters before mounted perpendicular to the beam in the plate reader.

Fluorescence spectra recorded from samples in standard 1 cm cuvettes were obtained on a Fluoromax 4P, Horiba, Jobin Yvone, NJ, USA. Emission spectra from samples in a sandwich configuration, i.e., from samples clamped between two SiO₂ slides, were recorded on a HR 2000 spectrograph from Ocean Optics. The samples were excited parallel to the surface normal using a 633 nm Helium Neon laser from JDSU, CA, USA. The excitation power was adjusted using a variable metallic neutral density filter and the power subsequently recorded on a PM100D meter equipped with a silicon photodiode sensor of model S121C from Thorlabs, USA. The excitation beam was focused on the sample using a $f = 50$ mm lens and the emission collected front face at 45° by an optical fiber (1000 μ m core diameter) with a 633 nm edge filter, Semrock, USA, placed in the beam path to block unwanted excitation light from reaching the spectrograph.

Typical absorbance and synchronous scattering spectra recorded for uncoated copper deposited on microscopy glass slides at different thicknesses are shown in Figure 1. As is expected, the absorbance increased with film thickness, and at about 15 nm film thickness (data not shown) the absorbance becomes nearly wavelength independent indicating the formation of a continuous film. The copper Localized Resonance Plasmon Band (LRPB) is centered at ~ 720 nm and is most prominent at 3 nm thickness for uncoated Cu films. The distinct band below 400 nm is most likely related to excitation of inner core electrons (inter-band transitions) and will not directly contribute to the plasmon resonance band or to the MEF phenomenon. It is known that copper undergoes an oxidation reaction when exposed to atmospheric conditions and that the oxidation layer formed on the particle surface disrupts the LRPB characteristics.^{9,10} To protect the Cu from oxidation, a protective layer of SiO_x was

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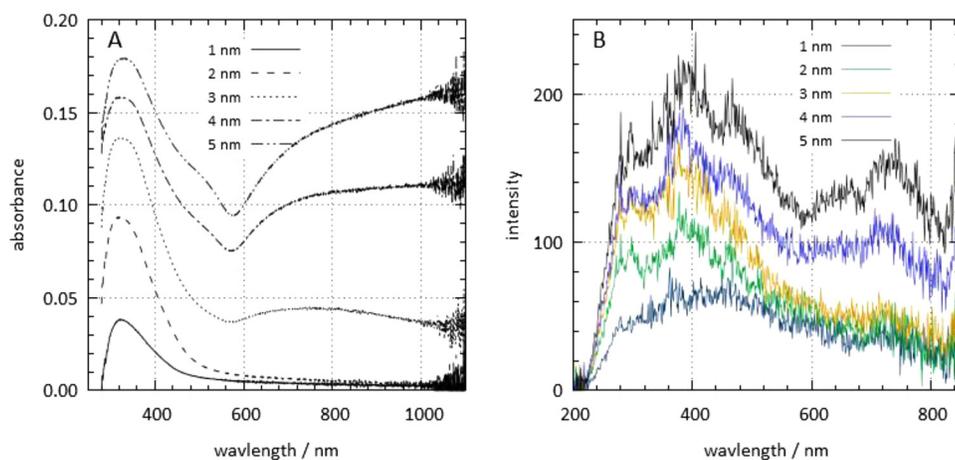


FIG. 1. (a) Absorbance spectra recorded on microscopy slides coated with different thicknesses of Cu. (b) Synchronous scattering spectra, $\lambda_{ex} = \lambda_{em}$, recorded on the Cu slides.

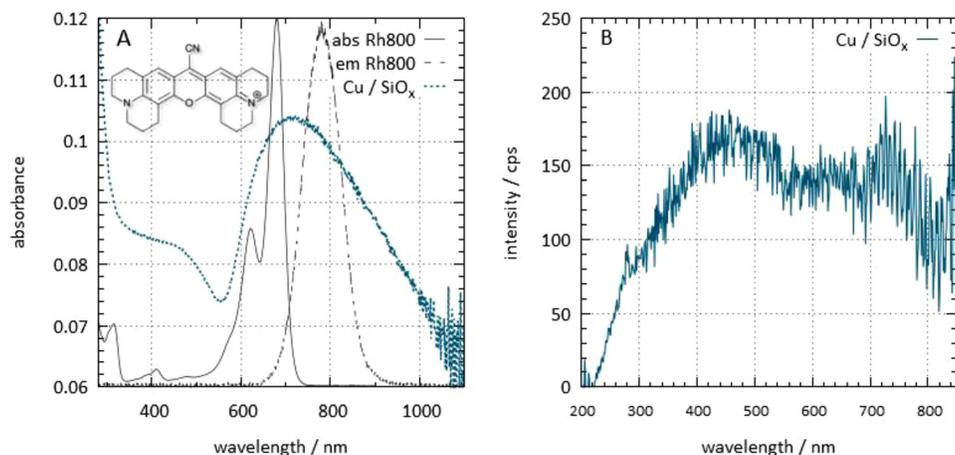


FIG. 2. (a) By coating the 4 nm thick Cu films with a 4 nm layer of SiO_x, it is possible to prevent oxidation of Cu. This protective coating has a large effect on the plasmon band. The absorbance and emission spectra observed for Rh800 dissolved in methanol are also shown. The chemical structure for Rh800 is shown in the inset. (b) Synchronous spectra recorded for the SiO_x coated slides. Note that the films are dry.

deposited on top of the films. This has a profound influence on the absorbance and synchronous scattering band, as shown in Figure 2 for a 4 nm Cu film coated with 4 nm SiO_x. Also shown in Figure 2(a) are the absorption and emission spectra recorded for Rhodamine 800 dissolved in methanol. The absorbance and emission peaks are centered at 680 and 780 nm, respectively, and overlap well with the Cu LPRB band, Figure 2(a).

Unpolarized synchronous scattering spectra, i.e., spectra recorded on a fluorescence spectrophotometer when the wavelength setting on the excitation monochromator, λ_{ex} , equals the wavelength setting on the emission monochromator, λ_{em} , are shown in Figure 1(b). A detailed interpretation of the synchronous scattering spectra is very complex, since it carries convoluted information about both the absorption and scattering processes. It has however been postulated previously by Dragan *et al.*¹¹ that the synchronous scattering spectra is a good indicator of both the magnitude and the wavelength dependence of MEF, as was demonstrated by showing a correlation between the MEF spectra and the synchronous scattering spectra recorded from emissive gold clusters on “Fire in the Hole” (FIH) silver-coated plates. The influence of the SiO_x coating on the synchronous scattering spectra can also be seen from Figure 2(b). Compared with the uncoated Cu films, the signal observed from films coated with a 6 nm SiO_x layer is *less structured* and $\sim 10\%$ lower in intensity. This “loss” is readily explained by the loss in Cu surface plasmons by the SiO_x coating.

The emission spectra recorded for Rh800 dissolved in glycerol and sandwiched between two glass surfaces, the reference, and between a glass and a 4 nm Cu coated slide, the sample, are shown in Figure 3. The excitation source was a HeNe laser at 633 nm (18 mW), which overlaps well

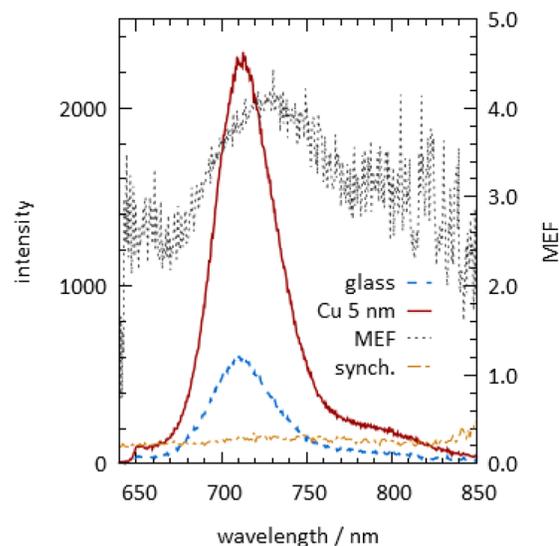


FIG. 3. Spectra recorded for Rh800 dissolved in glycerol and sandwiched between glass slides (control) and between glass copper slides (sample). The calculated MEF response is shown together with the synchronous spectra.

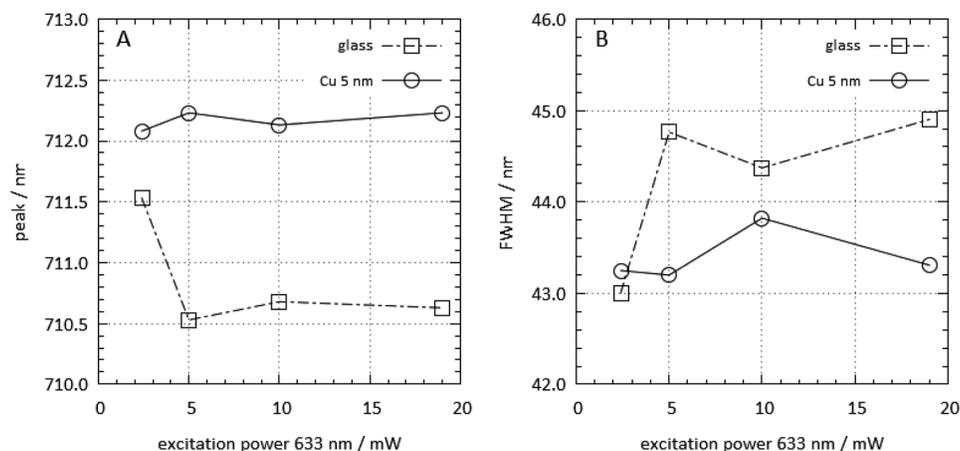


FIG. 4. (a) Peak maxima observed for Rh800 dissolved in glycerol at different excitation powers. The glass sample indicates the control sample and Cu 5 nm, the sample. (b) FWHM observed for Rh800 dissolved in glycerol.

with the Cu localized plasmon resonance band. The calculated MEF spectrum obtained by dividing the sample spectrum with the reference spectrum is also shown, and most surprisingly, is non-linear. The maximum enhancement is observed close to the Rh800 emission peak, $\text{MEF} \sim 4.1$, but decreases with increasing wavelength, i.e., lower energy. It is however interesting to note that the MEF spectra are increasing on the blue side of the Rh800 emission band. This trend has been observed for several other substrate/fluorophore combinations, e.g., Au-protein clusters on silver substrates,¹¹ and observed in our lab for several other chromophores such as fluorescein and carbon dots (data not published).

The observed wavelength dependence of MEF is consequence of a ~ 2 nm redshift of the Rh800 emission band on the Cu substrates, as compared with the glass reference, and further by a ~ 1 nm reduced FWHM. The peak emission wavelength and the FWHM as functions of excitation power for Rhodamine in glycerol are shown in Figures 4(a) and 4(b). In a previous report by Dragan and Geddes,¹² it was reported that metal enhanced fluorescence depends on the excitation power, explained by an power dependent effective excitation volume surrounding the fluorophores, now commonly referred to as the Excitation Volumetric Effect, EVE. A similar increase of MEF with increasing excitation power is also observed for Rh800 and further accompanied by a decrease in FWHM, Figure 4(b).

Taken together, the wavelength dependence of metal enhanced fluorescence, underpinned by a subtle red shifted emission band and narrowing of the FWHM, is strong indicative of a much more complex interaction mechanism between the fluorophores and the localized resonance plasmon band, not hitherto reported and indeed not understood.

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