

Metal-enhanced fluorescence: The role of quantum yield, Q_0 , in enhanced fluorescence

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Metal-enhanced fluorescence has attracted enormous research and commercial interest in recent years, due to the ability to significantly enhance fluorescence signatures in the near-field as well as protect fluorophores against photobleaching. In this article, we address one of the major unresolved questions, whether far-field fluorophore quantum yield, Q_0 , has a direct relationship to fluorescence enhancement factors in metal-enhanced fluorescence. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692105>]

Over the last decade, there has been tremendous interest in the use of subwavelength sized metallic nanoparticles to favorably modify far-field observable fluorescence signatures.^{1,2} These interactions can result in enhanced fluorescence intensities,³ much improved fluorophore photostabilities,⁴ and the use of nanoparticles to modify spatial distributions of fluorescence.⁵ While the near-field interactions yielding fluorescence enhancement are known to be complex, this has led to confusions in the literature which have in turn manifested themselves in the incorrect interpretation of the two underlying mechanisms of metal-enhanced fluorescence (MEF). One particular topic has been the role of far-field fluorophore quantum yield and how this lends itself to overall fluorescence enhancement in the far-field. In this paper, we subsequently address this issue and show that in light of the metal-enhanced fluorescence excitation volumetric effects postulated by Geddes and Dragan⁶; then, quantum yield plays little, if any effect, in the enhanced fluorescence of near-field fluorophores, which some authors have suggested is inversely proportional to free space quantum yield,⁷⁻⁹ i.e., $MEF \approx 1/Q_0$.

It is well-known that when a fluorophore radiates into a homogeneous medium in the far-field, the quantum yield of fluorescence is described by¹⁰

$$Q_0 = \frac{\Gamma}{\Gamma + k_{nr}}, \quad (1)$$

where Γ is the fluorophore radiative rate and k_{nr} are the non-radiative rates. The free-space lifetime, τ_0 , is subsequently well-described by¹⁰

$$\tau_0 = \frac{1}{\Gamma + k_{nr}}. \quad (2)$$

However, in the presence of near-field metallic nanoparticles, it has been suggested that the metal-modified fluorophore quantum yield is now described by⁷⁻⁹

$$Q_m = \frac{\Gamma + \Gamma_m}{\Gamma + \Gamma_m + k_{nr}}, \quad (3)$$

where Γ_m is an additional radiative rate, effectively enabling fluorophores to radiate faster near-to plasmonic nanostructures. Interestingly, as Γ_m increases, then the effective quantum yield, Q_m , increases. Similarly, an increased radiative rate also reduces the radiative lifetime of near-field fluorophores,

$$\tau_m = \frac{1}{\Gamma + \Gamma_m + k_{nr}}. \quad (4)$$

As can be seen from Eqs. (3) and (4), an increase in, Γ_m , results in both an increase in the quantum yield and a decrease in lifetime, a condition which is not observed in classical far-field fluorescence, i.e., Eqs. (1) and (2), where for all conditions, both the Q_0 and τ_0 always change in unison. Subsequently, these equations have aided the experimental observations that metal-enhanced fluorescence enhancement factors are inversely proportional to Q_0 .⁷⁻⁹ However, in recent years, Geddes and co-workers have shown that the underlying mechanism of MEF is far more elegant than a simple fluorophore radiative rate modification but is in fact underpinned by two complimentary effects: (1) an enhanced absorption and (2) an enhanced emission component. This interpretation has been experimentally verified by interpretations of the wavelength dependence of metal-enhanced fluorescence,¹¹ as well as numerous reports of plasmonic enhancement of chemiluminescence signatures,^{2,12,13} where clearly, an enhanced electric field component or radiative rate modification is not plausible. These both theoretical and experimental considerations do not, however, explain in themselves, the experimental observations that $MEF \approx 1/Q_0$. However, a recent paper by Geddes and Dragan, which further supports the 2 mechanism MEF model, theoretically suggests that far-field excitation intensity changes the near-field volume of enhancement.⁶ Furthermore, this theoretical consideration implies that far-field excitation irradiance needs to be considered when considering fluorophores of different quantum yield near-to metals, as the natural tendency to shine more light on weakly luminescent species would indeed account for the experimentally observed $MEF \approx 1/Q_0$ dependence. To test this hypothesis, we have subsequently studied fluorophores with the same spectral parameters and under very carefully controlled

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conditions of irradiance and sample geometry. Figure 1 shows the fluorescence emission spectra of two spectrally almost identical fluorophores, namely the low quantum yield Rose Bengal (RB)⁷ and the relatively higher quantum yield Rhodamine B (RhB) fluorophores, both taken from identical sample geometries and using the same laser irradiance. Of particular note is the enhanced fluorescence ratio from silver island films (SiFs), as compared to a control sample, which contains no silver and therefore cannot support MEF. The ratio of the free space quantum yields is ≈ 24 , yet very similar enhancement factors are observed near-to SiFs.

Similarly, Figure 2 shows the emission spectra of dipyrindamole, taken at 2 different pH values and again measured from both SiFs and a glass control sample. The ratio of dipyrindamole free space quantum yield at these 2 pH values is 16 (Refs. 14 and 15) (Figure 1S, supplementary material¹⁷), yet the MEF enhancement factors observed are both ≈ 1.2 . It is worth noting that for both Figures 1 and 2, the sample geometries were identical and the excitation irradiance kept constant. Clearly, metal-enhanced fluorescence enhancement factors are not proportional to $1/Q_0$ as reported by others,⁷⁻⁹

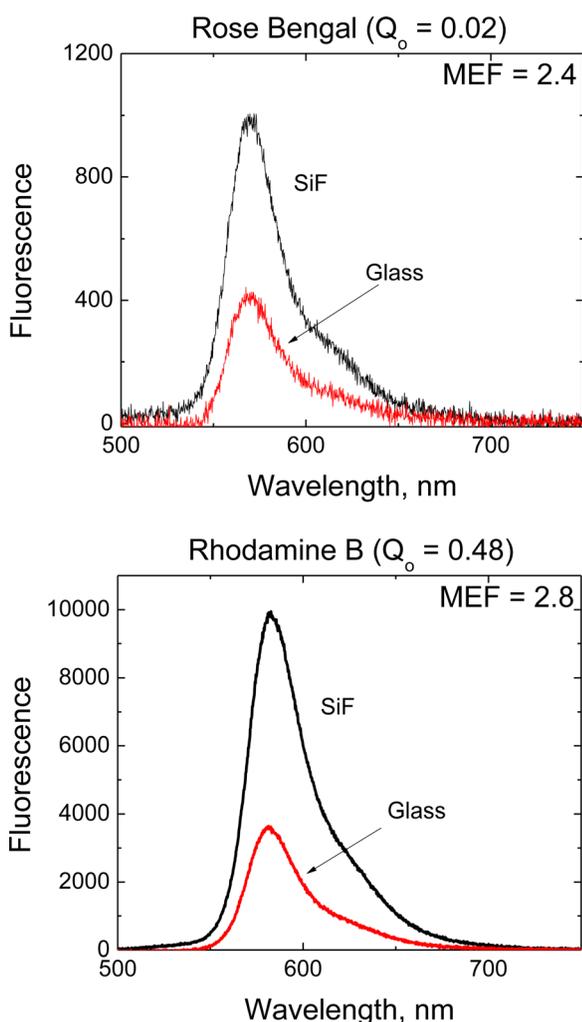


FIG. 1. (Color online) Fluorescence spectra of Rose Bengal and Rhodamine B measured on SiFs and on glass. MEF measured as a ratio of fluorescence intensities from SiFs as compared to that on glass. The ratio of the quantum yields of Rhodamine B to Rose Bengal is $R = Q(\text{RhB})/Q(\text{RB}) = 24$. Excitation was undertaken using a 473 nm CW laser line.

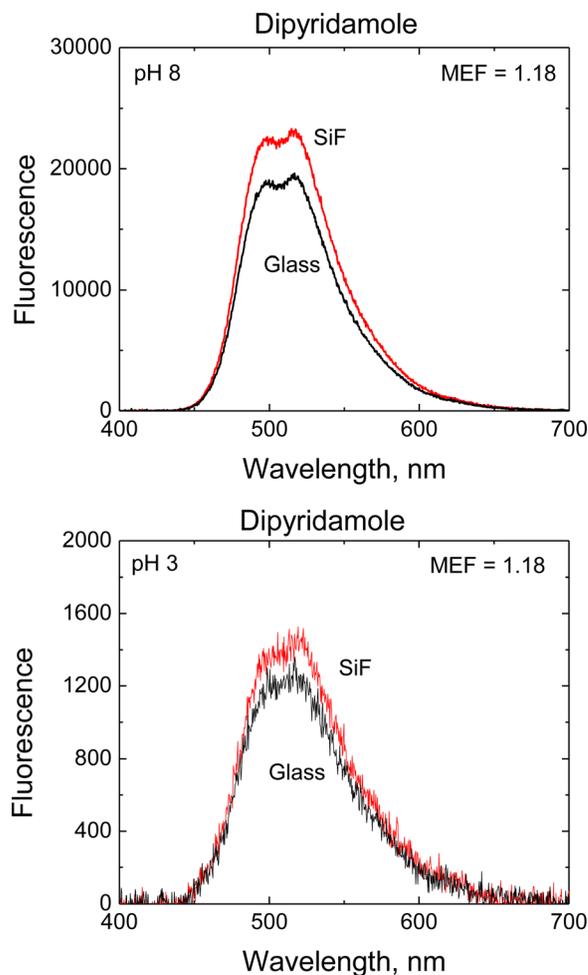


FIG. 2. (Color online) Fluorescence spectra of DIP measured at pH 3 and 8 on SiFs and on glass. The MEF effect has been measured as a ratio of fluorescence intensities on SiFs to that on glass. The ratio of the quantum yields of DIP in two states (pH 8 and pH 3) is $R = 16$. Excitation was with a 405 nm CW laser line.

when identical conditions are employed for all sample types and in particular, the control sample.

To investigate the effects of quantum yield further, we fabricated different sized nanoparticulate SiFs surfaces in a systematic fashion, in line with a recent report by our laboratory.¹⁶ This was undertaken to study whether the lack of quantum yield dependence on MEF was in any way related to the surface density of the SiFs nanoparticles and the subsequent e-field dependence on MEF.¹¹ Figure 3 subsequently shows the MEF enhancement factors as a function of SiFs deposition times (DTs) for both Rhodamine B and Rose Bengal for 2 different laser powers, 1.2 mW and 42 mW. As expected, the MEF enhancement factor increases as a function of DT, in line with a recent report by our laboratory on the e-field dependence of SiFs grown for different times, and the additional complimentary overlap of fluorophore emission spectra with the scattering portion of the SiFs extinction spectrum.¹¹

Most notably, however, is the magnitude of the MEF enhancement factor as a function of laser power. For both the low and high quantum yield fluorophores, the values are very similar, even though the laser powers are 35-fold different, i.e., 42 vs 1.2 mW. These data are contradictory to the

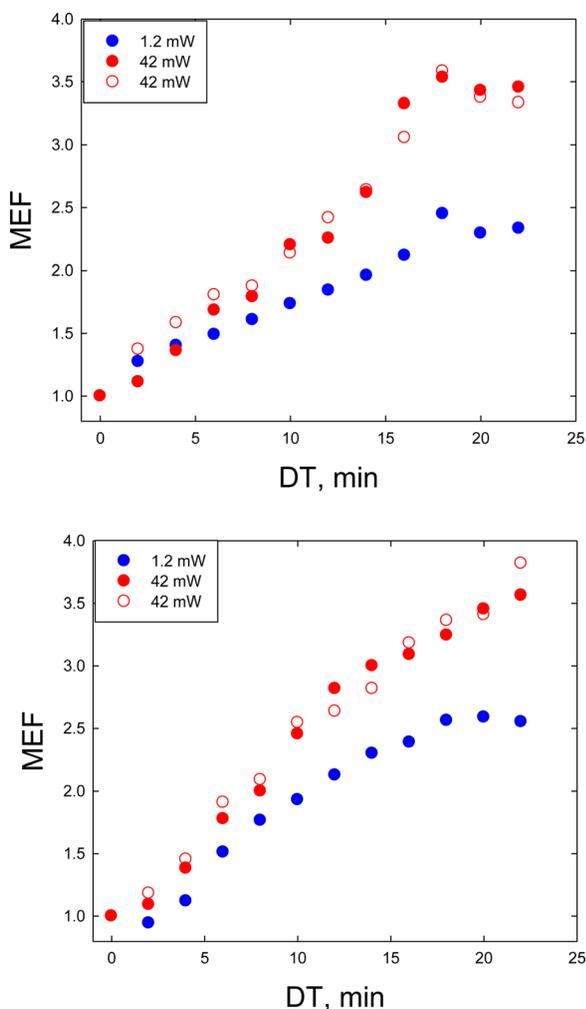


FIG. 3. (Color online) Dependence of the MEF effect upon silver DT and incident laser radiation power (473 nm CW laser line) for RB and RhB. The laser irradiance radiation power was 1.2 and 42 mW.

notion that MEF enhancement factors are proportional to $1/Q_0$ (Refs. 7 and 9) but are, however, in line with the MEF excitation volumetric effects recently postulated by Geddes and Dragan,⁶ which effectively states that larger enhancement factors are observed for greater excitation powers due to an increase in the near-field excitation volume, a property not present for the glass control sample.

To understand further the trends in Figure 3, i.e., greater MEF enhancement factors vs DT, we performed synchronous excitation/emission scans on the SiFs substrates. The advantage of this approach is the visualization of the trends in the scattering portion of the nanoparticle extinction, which is known to partly contribute to MEF enhancement factors,^{2,11} due to its spectral overlap with the emission spectra of fluorophores. As can be seen from Figure 4 (and Figure 2S (supplementary material¹⁷)), the scattering portion of the extinction spectrum readily increases in the red portion of the visible spectrum, in line with the increasing MEF enhancement trends observed in Figure 3, and the postulated wavelength dependence of MEF (Ref. 11) by our group. We have subsequently deconvoluted the synchronous excitation/emission scan data (Figures 3S (supplementary material¹⁷)) and readily show that the absorption and scattering components of the SiFs extinction spectrum are consistent with

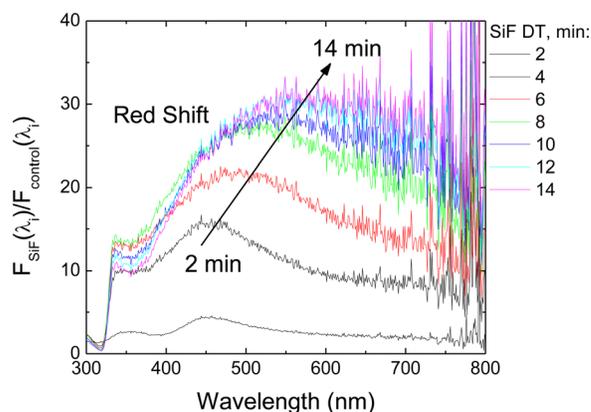


FIG. 4. (Color online) Elastic reflection/scattering spectra collected from SiFs surface as a function of DT. Spectra were normalized with respect to the spectrum from the control surface (i.e., no SiFs deposition). The spectra were recorded in synchronous mode, and the wavelength of emission registration was equal to the wavelength of excitation. Silver DT was varied from 2 min to 14 min.

those calculated from Mie theory for the same size particles (Figure 3 right (supplementary material¹⁷)).

In conclusion, in this paper, we have studied the effect of fluorophores' far-field quantum yield on the dependence of metal-enhanced fluorescence. As we have shown, the MEF enhancement factor can be modulated by changing the surface properties comprised of metallic nanoparticles, which alter the surface electric field distributions² and contributions from the nanoparticle scattering portion of the extinction spectrum.¹¹ However, there is no direct evidence that MEF is inversely proportional to free space quantum yield as suggested by others.⁷⁻⁹ Further, previous observations by others can readily be explained by changes in the near-field excitation volume⁶ and the need to shine more light on weakly fluorescing samples. Given the widespread utility and interest in the MEF phenomenon, then our findings are fundamentally important to our collective continued understanding of MEF.

At present, the analytical functions describing absolute enhancement of fluorophores in the near-field are not fully understood/realized, but it is clear from ongoing works that:

- excitation source irradiance,
- near-field volume, i.e., number of fluorophores in the near-field,
- distance of fluorophores from the metallic nanoparticles,
- overlap of the nanoparticle extinction spectra with both the absorption and emission components of the fluorophore.

all play a critical role in realizing enhanced near-field intensity. Given the widespread utility and interest in the MEF phenomenon, then our findings are fundamentally important to our collective continued understanding of MEF.

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- ¹⁷See supplementary material at <http://dx.doi.org/10.1063/1.3692105> for fluorescence spectra of dipyridamole (DIP) at different pH in solution, absorption and reflection/scattering spectra of SiFs for three different SiFs density, for deconvolution of the plasmon optical absorption spectra and plasmon reflection/scattering spectra on plasmon absorption and scattering components and Mie theory simulation of extinction, scattering and absorption components of the plasmon resonance band of the silver nanoparticle.