Comment on "Theoretical study of single molecule fluorescence in a metallic nanocavity" [Appl. Phys. Lett. 80, 315 (2002)]

Hongxing Xu[a)]
Division of Solid State Physics, Lund University, Box 118, S-22100, Sweden and Institute of Physics, Chinese Academy of Science, Beijing 100080, China

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In a recent letter, Enderlein,[1] reported enhanced single molecule fluorescence in a nanometric metal-coated dielectric bead. The enhancement of the fluorescence can be more than one order of magnitude for a thin silver coating layer down to 5 nm. They have used the standard numerical method for the calculations, but the size-dependent dielectric function for the thin silver layer was not included in the calculations. It is well known that the dielectric function of a small metal particle will become size dependent when the size of the metal particle is much smaller than the electron mean-free path of the bulk metal.[2] The electron mean-free path for bulk silver is about 57 nm, which is one order of magnitude more than the thickness of the silver coating layer in Ref. 1. In this case, surface-electron collisions will give a dominating contribution to the damping mechanism of the plasmon response of the silver shell rather than electron-electron collisions. The larger damping as a result of more frequent electron-surface collisions diminishes drastically the field enhancement inside the nanocavity of the silver shell. Hence, the results in Ref. 1 will not be reliable.

Except for the electron-electron collision with a frequency Γ in metal nanostructures, the electron-surface collision frequency in the simple Drude theory is $\Delta\Gamma = V_F/\bar{x}$, where V_F is the Fermi velocity and $\bar{x}$ is the electron mean path of the electron-surface collision. For complex metal nanostructures, the exact value of $\bar{x}$ is not obviously determined. For a spherical metal nanoshell, Averrit *et al.*[3] just simply took the shell thickness as the value of $\bar{x}$. But the tangential path can be larger than the shell thickness. In order to calculate $\bar{x}$, we use the following mathematical description. A random electron free path x of the electron-surface collision can be either a line connecting the inner surface and the outer surface of the shell, or a line with two ends on the outer surface only. For the former case, $x = r_2 \cos\theta - \sqrt{r_1^2 - r_2^2 \sin^2\theta}$ $(\sin\theta \leqslant r_1/r_2)$, and for the latter case $x = 2r_2 \cos\theta$ $(\sin\theta > r_1/r_2)$, where θ is the angle between x and the radius at the end on the outer surface, r_1 and r_2 are the radii of the inner and outer surfaces of the shell, respectively. Then, $\bar{x}$ can be calculated,

$$\bar{x} = \int_0^{\pi/2} x \sin\theta d\theta. \tag{1}$$

Similar to the size-dependent dielectric function of small metal particles with a substitution of the bulk collision frequency Γ_0 to the modified collision frequency $\Gamma_0 + \Delta\Gamma$ in the Drude term,[2] the dielectric function of the shell can be modified as

$$\varepsilon(\omega,\bar{x}) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_0} - \frac{\omega_p^2}{\omega^2 + i\omega(\Gamma_0 + \Delta\Gamma)}, \tag{2}$$

where $\Gamma_0 = V_F/l_0$ and l_0 is the bulk electron mean-free path, and ω_p is the Drude-type bulk-plasma frequency.

In Ref. 1, $\varepsilon_{bulk}(\omega) = n_m(\omega)^2 = -14.568 + 1.2i$ at 635 nm for silver. For the silver shell with $r_1 = 25$ nm and $r_2 = 30$ nm, which parameters correspond to the highest enhancement factor in Fig. 4 of Ref. 1, we obtain $\bar{x} = 12.6$ nm, and $\varepsilon(\omega,\bar{x}) = -14.523 + 2.025$i. $V_F = 1.39 \times 10^6$ m/s and $\hbar\omega_p = 9.2$ eV for silver are used here. Although the real part of the modified dielectric function $\varepsilon(\omega,\bar{x})$ is not dramatically changed, the imaginary part of $\varepsilon(\omega,\bar{x})$ increases about 70% more than in $\varepsilon_{bulk}(\omega)$. A large damping effect that diminishes the field enhancement can be expected from the fundamental electromagnetic theory. Moreover, the absorption of the metal shell will increase significantly, roughly about 70% as well. Hence, the results about the fluorescence intensity enhancement in Ref. 1 should be overestimated. The investigations of the influences to the fluorescence lifetime and the photostability are thus not correct either.

As the author of Ref. 1 claimed, the results presented in Ref. 1 can be important for the design of a new class of fluorescent labels with significantly higher photostability and increased fluorescence intensity. In order to help experimentalists achieve the true features of designed fluorescent labels, we hope the author of Ref. 1 should reestimate the original results with the correction of the size-dependent dielectric function of the thin silver shell in their reply.

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[1] J. Enderlein, Appl. Phys. Lett. **80**, 315 (2002).
[2] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, New York, 1995).
[3] R. D. Averitt, D. Sarkar, and N. J. Halas, Phys. Rev. Lett. **78**, 4217 (1997).

[a)]Electronic mail: hongxing.xu@ftf.lth.se

