

Surface plasmon coupled fluorescence from copper substrates

Michael J. R. Previte, Yongxia Zhang, Kadir Aslan, and Chris D. Geddes^{a)}

Institute of Fluorescence, Laboratory for Advanced Medical Plasmonics, Medical Biotechnology Center, University of Maryland Biotechnology Institute, 725 West Lombard St., Baltimore, Maryland 21201, USA

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Previously, we reported the observation of metal enhanced emission from copper nanoparticles. In this letter, we report the observation of surface plasmon coupled fluorescence (SPCF) or emission from thin copper (Cu) continuous films. Using Fresnel calculations to theoretically calculate the reflectance curves for polymethyl methacrylate films doped with sulforhodamine 101, we correlated the minimum reflectance angles for both *s*- and *p*-polarized lights with maximum fluorescence emission. These observations reveal that we can achieve SPCF with copper substrates and possibly design inexpensive copper substrates for fluorescent sensing applications and potentially, fluorescent based electrical signals and circuits. © 2007 American Institute of Physics.

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The coupling of fluorescence emission with metal surfaces was realized with the early observations that fluorescent lifetimes are dramatically affected in the presence of metal surfaces.^{1–5} Currently, we believe that the metal-chromophore interactions or metal-enhanced fluorescence is best understood with the radiating plasmon model (RPM). In the RPM, the excited distal fluorophores nonradiatively transfer their energy to the surface plasmons of proximal metal surfaces, which subsequently reradiate the coupling chromophore emission/quanta.⁶ More recently, we have demonstrated that metal enhanced phenomena are not limited to fluorescence but can also be observed for chemiluminescence,⁷ phosphorescence,⁸ S₂ emission,⁹ and the vibrational structure of a fluorophore.¹⁰ While photophysical studies and applications of metal-enhanced fluorescence have focused primarily on the use of substrates such as silver and gold,^{11,12} we recently reported metal enhanced fluorescence emission of acridine orange from copper nanoparticles.¹³

In addition to metal enhanced fluorescence phenomena, surface plasmon coupled fluorescence¹⁴ (SPCF) or alternatively, surface plasmon coupled emission¹⁵ (SPCE) has become a rapidly progressing area of research.^{16,17} Initial studies in surface plasmon fluorescence capitalized on the enhanced optical field of the resonant excitation of surface plasmons at metal/dielectric interfaces to improve sensitivity and the detection of the free space emission of surface bound fluorescent analyte molecules.¹⁴ Later studies, which are now associated with SPCF, focused on the detection of the surface plasmon coupled emission of bound chromophores.^{18–21} The extent of energy transfer of chromophores to surface plasmons depends on the wavelength of the coupling radiation, the dielectric properties of the metal surface, and the distance of separation between the chromophore and a continuous metal surface (*r*).^{18,19,22–24} When the distance *r* exceeds 300 nm, decay processes occur through far field radiation, while decay processes can couple to surface plasmons at 10–300 nm, and typically, excited state populations decay through lossy surface waves, i.e., quenching, below 10 nm.²⁵ The inherent isotropic fluorescence emission from a population of randomly oriented fluorophores proximal to a metal

surface *directionally emit* by coupling to the surface plasmons of the metal surfaces.^{14,19,21} As a result, it became possible to achieve better detectability of fluorophores at the metal interfaces and facilitate the detection of surface bound biomolecules with SPCF.²⁶

The generation of surface plasmon modes from fluorescent species has been shown for both silver and gold thin metal continuous films.¹⁵ Using the Drude dispersion model, the optical properties of metals such as gold, silver, and copper have been accurately predicted.²⁷ The coupling of light emission from a chromophore to metal surfaces depends on the matching of the wavevector of the incident light (*k*) with the wavevector of the surface plasmons (*k*_{sp}).^{14,23} The wavevector (*k*_{sp}) is the wavevector for the surface plasmon,

$$k_{sp} = k_0 \left(\frac{\epsilon_m \epsilon_s}{\epsilon_m + \epsilon_s} \right)^{1/2}, \quad (1)$$

where ϵ_m and ϵ_s are the real parts of the dielectric constants of the metal ($\epsilon_m = \epsilon_r + i\epsilon_i$) and the sample ($\epsilon_s = \epsilon_r + i\epsilon_i$) above the metal film, respectively. The conditions for surface plasmon resonance excitation are met when

$$k_{sp} = k_x = k_0 n_p \sin \theta_{sp}, \quad (2)$$

where n_p is the refractive index of the prism, λ is the wavelength, ω is the frequency in rad/s, k_0 is the wavevector in free space, and θ_{sp} is the surface plasmon angle. From this equation, it follows that the reflectivity and transmissivity of incident light at the metal/dielectric interface are determined by θ_{sp} .

The reflectivity at the surface below the surface plasmon coupling angle θ_{sp} is very high due to the presence of an evaporated metal layer that acts as a mirror and reflects most of the transmitted light.¹⁴ At just above θ_{sp} , the metal surface acts as a resonator for incident light and gives rise to the resonant excitation of a surface plasmon, which reradiates according to the dispersion curve for surface plasmons.¹⁴ For metals such as copper and gold, the imaginary component of the dielectric, which reflects the damping processes or losses to the metal, is almost an order of magnitude larger than that of silver.²⁷ As a result, the wavevector of the surface plasmon propagates over longer distances and the dispersion curve broadens.¹⁴ Using Fresnel calculations to account for each of the different optical properties of each dielectric layer and their respective thicknesses, surface plasmon resonance con-

^{a)} Author to whom correspondence should be addressed. Electronic mail: geddes@umbi.umd.edu

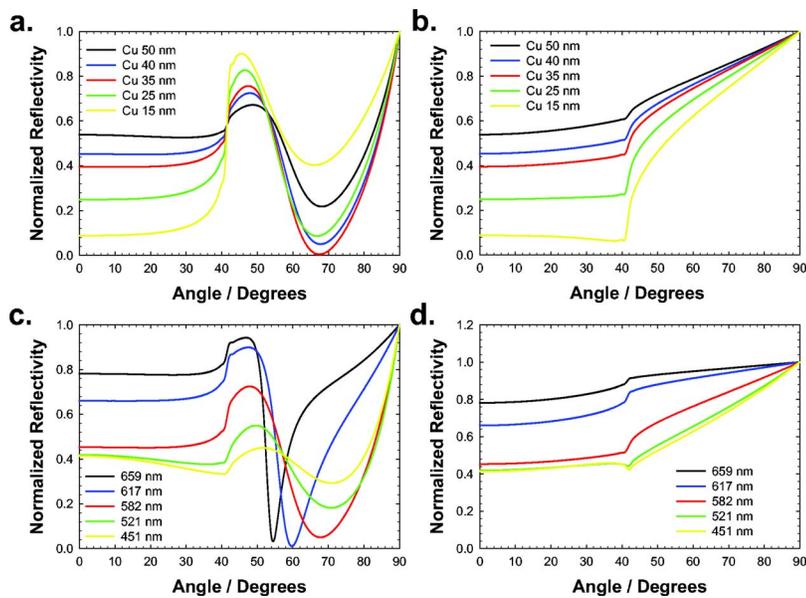


FIG. 1. (Color online) Four-phase Fresnel reflectance curves of (a) *p*- and (b) *s*-polarized 582 nm lights for copper substrates with different thicknesses and a 50 nm polymer film. Four-phase Fresnel reflectance curves of (c) *p*- and (d) *s*-polarized lights of different wavelengths for 40 nm thick copper substrates and a 50 nm polymer film.

ditions can be predicted.²⁸ Since it has been previously shown that surface plasmons can be generated from gold continuous films²⁹ and the optical properties of gold and copper are comparable,²⁷ we demonstrate theoretically and experimentally that SPCF from copper films is possible. Unlike metal enhanced fluorescence from copper nanoparticles, SPCF is highly polarized and directional. In addition to a more cost-effective alternative to gold and silver material for SPCF applications, we believe that this technology can potentially be integrated into technologies that combine fluorescent sensing applications with circuit design.

In order to determine the ideal thickness of copper continuous films to couple emission from sulforhodamine 101 (emission max ~ 590 nm), we calculated the reflectivity curves with Fresnel calculations for a polymer film 50 nm thick doped with sulforhodamine 101 dye on continuous copper films. Optical constants (n and k) for copper at 582 nm were used to predict the necessary thickness of copper continuous films to generate surface plasmon coupled emission [Figs. 1(a) and 1(b)].²⁷ At the resonance angle θ_{sp} for 582 nm light, 35 nm Cu films yield the minimum reflectivity for *p*-polarized light and subsequently, the maximum plasmon coupled emission [Fig. 1(a)]. While the minimum reflectivity for *p*-polarized light at plasmon resonance for copper substrates was found to be 35 nm [Fig. 1(a)], the reflectivity of *s*-polarized light was less for 40 nm films than 35 nm films [Fig. 1(b)]. We chose to implement 40 nm films in order to optimize both *p*-polarized coupling of 582 nm and minimize the coupling of *s*-polarized emission. In addition, we calculated the reflectivity curves for multiple wavelengths to determine the fluorophores that will most efficiently couple to the copper films [Figs. 1(c) and 1(d)]. We observed that the reflectivity curves for *p*-polarized light are narrower and steeper as the emission is redshifted.

With these results, we sought to correlate the theoretical evidence with experimental evidence that SPCF is possible using copper substrates. Copper continuous 40 nm thick films were deposited with a deposition rate of 0.1 Å/s using thermal vapor deposition (model 306, Edward). During the deposition process, the thickness of the films was monitored with an Edmunds FTM6 film thickness monitor. Samples were imaged using atomic force microscopy (AFM)

(Molecular Imaging Picoplus Microscope) at a scan rate of 1 Hz with 512×512 pixel resolution in tapping mode and the average film thickness was determined to be 40 nm (data not shown). Sulforhodamine 101 sulfonyl chloride was dissolved in a 50:50 mixture of chloroform and ethanol to a final concentration of 1 mM and then diluted in 8% PMMA stock solutions that were prepared in chloroform. Final dye/PMMA solutions were mixed at 0.8% PMMA and $2 \mu\text{M}$ sulforhodamine 101 sulfonyl chloride. $40 \mu\text{l}$ of PMMA dye

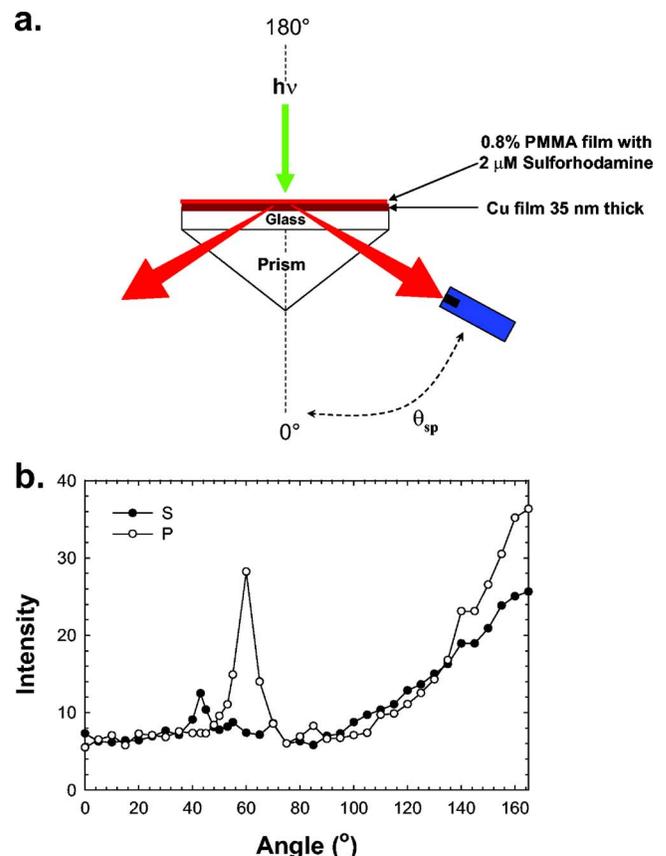


FIG. 2. (Color online) (a) Experimental geometry and detection scheme for copper SPCF experimental results. (b) Angular distribution of *s*- and *p*-polarized free space and SPCF emissions of $2 \mu\text{M}$ sulforhodamine 101 in 0.8% PMMA on copper films 35 nm thick.

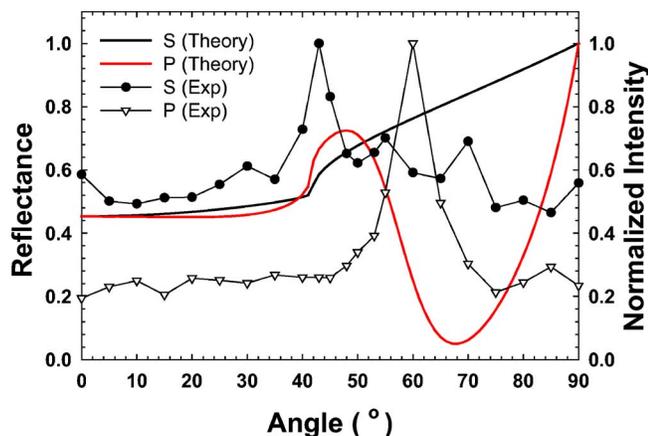


FIG. 3. (Color online) Four phase Fresnel reflectance curves of *s*- (black line) and *p*- (red dashed line) polarized 582 nm lights for 35 nm thick copper substrates with 40 nm polymer film (dashed red). Experimental normalized fluorescence intensity for *s*- (solid circles) and *p*- (open triangles) polarized from 2 μ M sulforhodamine in 0.8% PMMA films on 35 nm thick copper substrates (dotted lines).

solutions were spin coated on copper substrates to create 50 nm thick PMMA/dye films. The thickness of the PMMA films were estimated according to previously published data that describe the relationship of polymer percent composition and film thicknesses.³⁰ In addition, AFM measurements were performed to confirm that the PMMA film thickness was 50 nm (data not shown). Samples were excited using a reverse Kretschmann configuration that has been previously described.³¹ All angular emission measurements were made with an Ocean Optics HD2000 spectrofluorometer and a 600 mm fiber that was mounted on a rotation stage that could be rotated 360° around the sample [Fig. 2(a)].

From these results, we show the angular distribution of both *p*- and *s*-polarized emissions from the PMMA films doped with sulforhodamine 101 [Fig. 2(b)]. With these results, we observed that the free space emission was predominantly isotropic but did show a gradual increase in the *p*:*s*-polarization ratio before reaching a maximum of about 1.39 [Fig. 2(b)]. On the other hand, the normalized *p*- and *s*-polarized SPCFs are accurately predicted from the Fresnel calculations for 40 nm films at 582 nm (Fig. 3). Although it appears that the minimum of Fresnel reflectivity curve is slightly shifted to a larger angle than the fluorescence maximum, we believe that this result is reflective of the emission plot being taken from the maximum emission wavelength of the sulforhodamine 101 dye which is 590 nm. To support this supposition, we note that at longer wavelengths, the Fresnel curve becomes narrower and the minimum shifts to smaller angles [Fig. 1(c)]. Since the calculations for the overlay plot were undertaken for 582 nm (Fig. 3), it is likely that the minimum angle would more precisely match if it was performed with the optical constants at 590 nm [Fig. 1(c)]. In this regard, we expect that the Fresnel reflectivity curves can accurately predict the angular distribution of coupled fluorescence on copper substrates from fluorophores with different spectral properties.

In conclusion, we report the observation of SPCF from continuous copper films. The results reported here are consistent with reflectivity curves that are theoretically predicted using Fresnel calculations. From these calculations, we observe that red fluorophores likely couple more efficiently to copper substrates. With these observations, we have intro-

duced a means to create polarized and directional fluorescence from copper substrates. While we did not perform a direct experimental comparison to SPCF from gold films, the reflectivity curves for gold and copper continuous films at 582, 617, and 669 nm are similar (data not shown). Subsequently, we predict that the extent and wavelength dependence of coupled fluorescence is similar. Recently reported technologies have shown that optical signals can be transduced into electrical ones using plasmon resonances in gold nanostructures.³² Since copper films are capable of sustaining resonant plasmon oscillations induced by close proximity coupled dipoles, the transduction of fluorescence signals into electrical ones (and vice versa) is potentially feasible through the excitation of chromophores bound to the surfaces of copper nanostructures. Using the more cost-effective copper substrates with higher electrical conductivities, we believe that this work can provide a cost-effective alternative to create fluorescent based electrical signals and circuits.³²

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