Fixed-angle observation of surface plasmon coupled chemiluminescence from palladium thin films

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In this letter, the fixed-angle observation of surface plasmon coupled chemiluminescence (SPCC) from palladium thin films is reported. Fresnel calculations predict that light 492–549 nm spectral range can efficiently induce surface plasmon modes in 15 nm palladium thin films. Free-space emission from blue, green, and chartreuse chemiluminescent solutions on palladium thin films was isotropic, while the SPCC emission was highly directional and predominantly *p*-polarized in accordance with the predictions of the Fresnel calculations. In addition, the decay rates of the SPCC and free-space emission were similar, which suggests that palladium thin films have no catalytic effect on chemiluminescence emission. © 2009 American Institute of Physics.
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Surface plasmon coupled chemiluminescence (SPCC) (Ref. 1) is a technique based on the near-field interactions of chemically excited states and surface plasmons in thin metal films. In SPCC, chemiluminescence emission is coupled and emitted in a nearly exclusively *p*-polarized fashion through the back of the metal thin film at a specific observation angle. SPCC emission can be visually seen as a "cone" or as a "ring" from the back of the metal thin film when a hemispherical prism is used. The ring of emission is attributed to the symmetry conditions of the excited state dipoles above the metal thin film in a two-dimensional (2D) plane. Our research laboratory at the University of Maryland Biotechnology Institute has recently demonstrated the use of silver,[1] zinc,[2] nickel,[3] and iron[4] thin films for SPCC. In these series reports, theoretical Fresnel calculations were employed to determine the optimum thickness of the metal thin films: 47, 30, 15, and 15 nm for silver, zinc, nickel, and iron thin films, respectively. Chemiluminescent solutions with emission wavelengths ranging from 492–549 nm, which overlap with the wavelength range of commercially available chromophores, were used to demonstrate the practical application of the SPCC technique. In SPCC, the angle of observation typically shifts as the wavelength of incident light is varied. Subsequently, the adjustment of the position of the detection optics is required, which can significantly increase the experimental error. The efficiency of detection of SPCC emission can be improved while minimizing the experimental error by fixing the observation angle, similar to the traditional fluorescence spectrometer. Despite the availability of a number of different metals for the applications of the SPCC technique, there still is a continued search for metals which afford for both more efficient coupling of the chemiluminescence emission, as well as unique directional properties.

In this letter, the use of palladium thin films for fixed angle of observation of SPCC is presented. The optimum thickness of the palladium thin films for efficient coupling or light in the 492–549 nm spectral range was calculated to be 15 nm including a 10 nm SiO_x protective overlayer using theoretical Fresnel calculations. The SiO_x overlayer was de-posited onto the palladium thin films to protect the metal surface from chemical degradation and to minimize the potential catalytic effect on chemiluminescence emission by the metal. Fresnel calculations predict the reflectivity minimum for incident light in the 492–549 spectral range upon palladium thin films to occur an angle of 50°–55°. Experimental SPCC emission from blue (492 nm), green (509 nm), and chartreuse (549 nm) chemiluminescent solutions on palladium thin films, which occurred at a fixed observation angle of 50°–55°, were found to be in good agreement with reflectivity minimum predicted by Fresnel calculations. SPCC emission from all chemiluminescent solutions was predominantly *p*-polarized, in contrast to the free-space emission where the extent of *s*- and *p*-polarized emission was identical. The decay rates of SPCC and free-space emission for all chemiluminescent solutions were very similar, which suggests that palladium thin films do not have catalytic effect on chemiluminescence emission. The lack of catalytic effect by the palladium thin films is partially attributed to the presence of a SiO_x protective overlayer.

Palladium thin films (15 nm) with an SiO_x overlayer (10 nm) were thermally evaporated onto Silane-prep™ glass microscope slides (Sigma-Aldrich Chemical Corp. Milwaukee, WI, USA) by THINFILMS Inc., NJ, USA. Blue, green, and chartreuse chemiluminescent solutions (Omniglow, West Springfield, MA) used in this study are part of a chemiluminescent kit, which contains the necessary reactants [hydrogen peroxide (oxidizing agent) and diphenyl oxalate for blue emission and diphenyl derivatives for green and chartreuse emission] to produce chemiluminescence. In the chemiluminescent kit, the oxidizing agent and the chemiluminescent dye were encapsulated within different glass tubes inside a plastic tube. A very intense chemiluminescence emission lasting at least 2 h can be observed after the glass tubes were broken and the chemicals were completely mixed. In all the experiments in this study, freshly mixed chemiluminescence solutions were used.

SPCC and free-space emission measurements were performed using an in-house built experimental setup. The experimental setup contains a hemispherical prism mounted to a stationary stage with a fiber optic assembly that can rotate
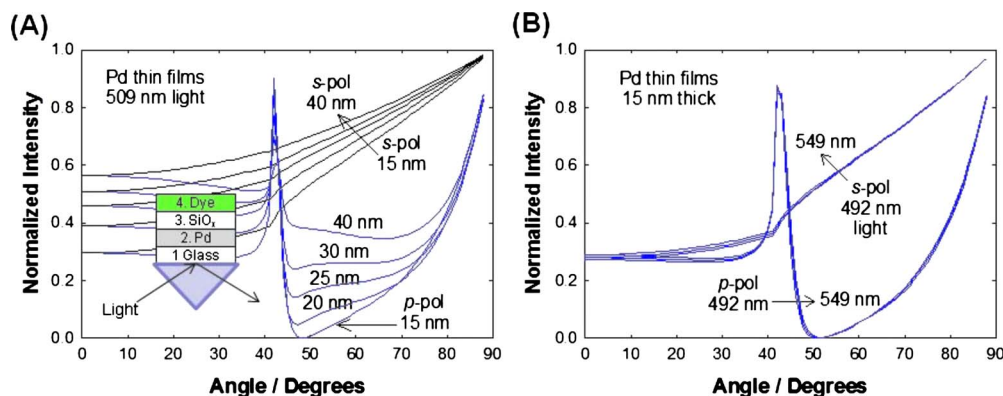
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FIG. 1. (Color online) (a) Four-phase Fresnel reflectivity curves for *p*- and *s*-polarized light at 509 nm for palladium thin film thicknesses, ranging from 15 to 40 nm with a 10 nm SiO$_x$ overlayer. (b) Four-phase Fresnel reflectivity curves for *p*- and *s*-polarized light at 492, 509, and 549 nm for 15 nm palladium thin films with a 10 nm SiO$_x$ overlayer.

360° around the prism. Palladium thin films were placed onto the hemispherical prism after a drop of refractive index matching fluid (glycerol) was added. 50 ml of a chemiluminescent solution was pipetted on the palladium thin films. Subsequently, SPCC (from the back of the hemispherical prism) and free-space emission (above the sample) intensity was collected using an spectrofluorometer (Model No: HD2000+, Ocean Optics, Florida, USA), which is connected to the fiber optic assembly. A polarizer was placed in front of the fiber optic to collect *s*- or *p*-polarized emission.

Theoretical Fresnel calculations were performed using a macroprocedure written for Igor Pro software, which accounts for the different optical properties of each dielectric layer [four-phase: glass, palladium thin film, SiO$_x$, chemiluminescent dye as shown in Fig. 1(a) inset] and their respective thicknesses (palladium: 15 nm, SiO$_x$: 10 nm, dye: 20 nm). Figure 1(a) shows the Fresnel calculations for light 509 nm incident upon a palladium thin film, calculated for various thicknesses (15–40 nm). The initial choice of range of thickness was based on the consideration that thermally evaporated metals form a thin film on solid supports when the thickness of the metal is ≥15 nm.[5] It is also shown that surface plasmons in metal films with a thickness of 50 nm can be effectively induced by light.[6,7] The question whether a metal supports surface plasmons can be answered by the presence of a reflectivity minimum at a certain angle in the reflectivity curves plotted as a result of Fresnel calculations.

The extent of the reflectivity minimum is also indicative of the efficiency of plasmon generation: the lower the intensity value the more efficient is the generation if surface plasmons.[8] In this regard, Fig. 1(a) shows that surface plasmons in 15 nm palladium thin films can be efficiently generated by 509 nm light. As the thickness of the palladium thin films is increased, the efficiency of the generation of surface plasmons is decreased. Subsequently 15 nm thick palladium thin films deemed to be the best surfaces for SPCC applications.

Figure 1(b) shows the wavelength dependence of the reflectivity curves plotted by four-phase Fresnel calculations for 15 nm thick palladium thin films. The reflectivity curves for light in the 492–549 nm spectral range are identical and the angle of minimum reflectivity occurs at ≈52°, which implies that SPCC emission measurements within this wavelength range can be made at the same observation angle. At the observation angle of 52° the extent of coupling of *s*-polarized light is predicted to be significantly less than that of *p*-polarized light (≈60% of *s*-polarized light is reflected as compared to virtually 0% of *p*-polarized is reflected, that is all *p*-polarized light is coupled to surface plasmons).

Figure 2 shows the angular-dependent *s*- and *p*-polarized SPCC and free-space emission from blue (492 nm), green (509 nm), and chartreuse (549 nm) chemiluminescent solutions placed on palladium thin films. It is important to note that SPCC and free-space emission measurements were
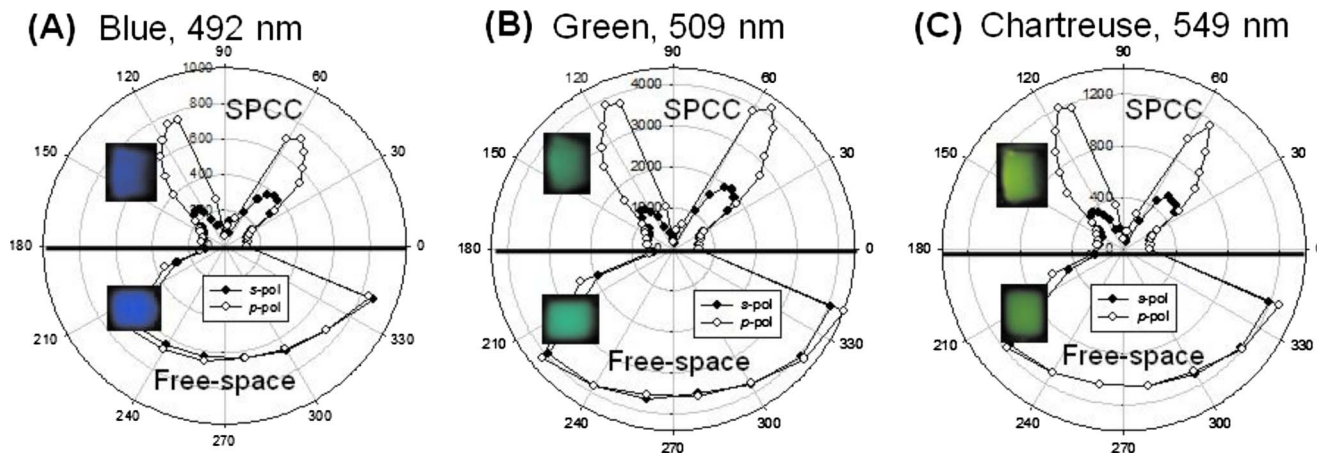

FIG. 2. (Color online) Polar plot of SPCC (0°–180°) and free space chemiluminescence (180°–360°) from palladium thin films with photographs of coupled (top) and free space (bottom) emissions for (a) blue at 492 nm, (b) green at 509 nm, and (c) chartreuse at 549 nm.
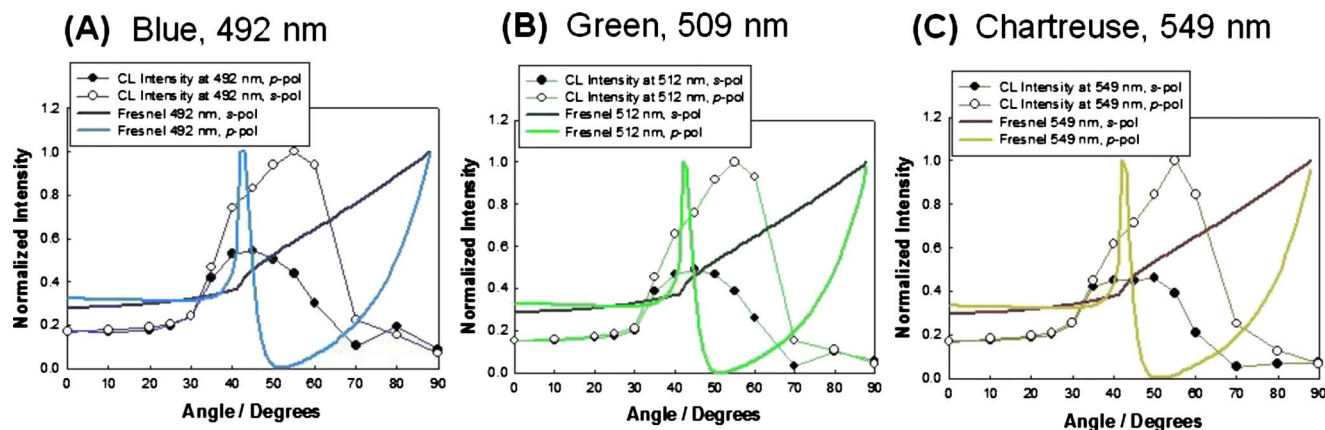
FIG. 3. (Color online) Normalized intensity curves of chemiluminescence emission, *s*-polarized emission, and *p*-polarized emission from 100 μl of dye on 15 nm palladium thin films as compared with the theoretical Fresnel curves for (a) blue at 492 nm, (b) green at 509 nm, and (c) chartreuse at 549 nm.

taken at observation angles between 0° and 180° (back of the hemispherical prism) and 180°–360° (sample side). SPCC emission from all chemiluminescent solutions was predominantly *p*-polarized and highly directional at an observation angle 55° and 115°. The occurrence of two observation angles for the maximum value of SPCC emission can be attributed to the symmetry conditions of dipoles above the palladium thin film in a 2D plane. *p*-polarized SPCC emission is 3, 4, and threefold larger than *s*-polarized emission for blue, green and chartreuse chemiluminescence, respectively. On the other hand, free-space emission from all chemiluminescent solutions is isotropic and the extent of *s*- and *p*-polarized free-space emission are identical, which is due to the decay of chemically induced excited states of the randomly oriented chemiluminescent species. The real-color photographs of SPCC and free-space emission for all chemiluminescent solutions are identical in color and spectra (data not shown), which indicates that SPCC emission is from the overlaying chemiluminescence solution.

The qualitative comparison of the experimental SPCC emission data (observation angle for SPCC and the extent of coupling of *s*- and *p*-polarized emission) for all three chemiluminescent solutions with the predictions made by Fresnel calculations (angle of minimum reflectivity and the extent of *s*- and *p*-polarized light) is shown in Fig. 3. The reflectivity curves for light at 492, 509, and 549 nm predict a reflectivity minimum at ≈52°, that is, surface plasmons can be efficiently generated by light at 492–549 nm spectral range. Experimental SPCC emission intensity for all chemiluminescent solutions with emission intensity peaks at 492, 509, and 549 nm occur a maximum at ≈55°, in very close agreement with the angle of minimum reflectivity predicted by Fresnel calculations. The reflectivity curves also show that the extent of coupling of *p*-polarized light is predicted to be significantly larger than the extent of *s*-polarized light at ≈52°. Experimental SPCC emission data show that the extent of coupling of *p*-polarized SPCC emission is significantly larger than the extent of coupling of *s*-polarized SPCC emission at ≈55°.

The potential catalytic effect of palladium thin films on the chemiluminescence emission is investigated. In this regard, the decay rates of SPCC and free-space emission intensity over 10 min for all three chemiluminescence solutions were measured on palladium thin films (data not shown). It

was found that the decay rates for SPCC and free-space emission very similar, implying that palladium thin films do not have catalytic effect on chemiluminescence emission. It is important to remind that in all the experiments carried out in this study a 10 nm SiO_x overlayer was present on the palladium thin films. The presence of a SiO_x overlayer afforded for protection of palladium thin films from chemical degradation by components of the chemiluminescent solutions.

In conclusion, SPCC emission from chemiluminescent solutions emitting in the 492–549 nm spectral range placed in close proximity to palladium thin films is demonstrated. Theoretical Fresnel calculations predicted the most efficient generation of surface plasmons occurs in 15 nm thick palladium thin films. Fresnel calculations also predicted that the reflectivity curves for light at 492–549 nm wavelength range is identical and the angle for minimum reflectivity is 52°, which implied that the maximum SPCC emission from chemiluminescent solutions at this wavelength range can be observed at a fixed angle. Experimental SPCC emission was indeed at a maximum at the observation angle of 55°, in close agreement with the predictions of Fresnel calculations. The experimental SPCC emission was also predominantly *p*-polarized as predicted by Fresnel calculations. The investigation of potential catalytic effects by palladium thin films revealed that there is no catalytic effect on chemiluminescence emission by palladium thin films.

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