Surface plasmon coupled chemiluminescence from iron thin films: Directional and approaching fixed angle observation

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We report the observation of surface plasmon coupled chemiluminescence (SPCC) from iron thin films. Theoretical Fresnel calculations were employed to determine the optimum thickness of iron thin films to be 15 nm, which is assessed by the value of minimum reflectivity curves for incident light upon the thin film. An overlayer 10 nm thick SiO_2 was used to protect the iron thin films from oxidation by air or physical changes induced by chemiluminescent solutions. SPCC emission from blue, green, and chartreuse chemiluminescent solutions on iron films can be observed at a fixed angle of 60° for all the chemiluminescent solutions, while free-space emission was isotropic. Iron thin films do not have a catalytic effect on chemiluminescence emission. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3160300]

I. INTRODUCTION

Chemiluminescence is a very useful analytical technology for the quantitative detection of biomolecules of interest.[1] Chemiluminescence emission, which is a result of chemical reactions between an organic dye and an oxidizing agent in the presence of a catalyst, is the primary approach in this technology. Chemiluminescence emission occurs as the excited organic dyes, which are chemically excited, decay to the ground state. The duration and the intensity of the chemiluminescence emission are mostly dependent on the properties of the chemical reagents present in the reaction solution. Despite the usefulness of the chemiluminescence technology, chemiluminescence emission is isotropic (emission in 360°), the efficiency of detection of chemiluminescence therefore limited by the detection optics and the degree to which isotropic emission can be collected. Subsequently chemiluminescence technologies still require much needed improvements in the efficiency of detection of chemiluminescence emission.

Surface plasmon coupled chemiluminescence (SPCC), a phenomenon based on the interactions of chemiluminescence emission and metal thin films, was recently introduced to improve the efficiency of detection of chemiluminescence emission.[2,3] In SPCC dipoles induce surface plasmon modes in the thin metal film. Since the emission from the *s*-oriented dipoles is canceled out and the emission from the *p*-oriented dipoles is enhanced by the surface plasmons, the coupled emission is predominantly *p* polarized. The SPCC emission is emitted at a certain observation angle from the back of the metal thin film. The observation angle for SPCC typically overlaps with the angle where the metal thin film has a reflectivity minimum, which also corresponds to the angle of incidence of light to the metal, for surface plasmon resonance (SPR) to occur. To this end, theoretical Fresnel calculations afford for the prediction of the interactions of light with any surface plasmon supporting metal, and indeed, the angle of reflectivity minimum can be precisely predicted. Since the first demonstration of SPCC with silver thin films,[3] other surface plasmon supporting metals, such as zinc, have been reported.[4]

In this work, we present the results of our detailed investigation of highly directional SPCC emission at a fixed observation angle from iron thin films. Theoretical Fresnel calculations were used to predict the optimum thickness of the iron thin films and the interaction of light at different wavelengths with the films. Free-space and SPCC emissions from blue, green, and chartreuse chemiluminescent solutions on iron films were measured on an experimental setup built in-house. It was found that SPCC emission is highly directional and can be observed at an angle of 60° for all the chemiluminescent solutions. A good agreement between the theoretical Fresnel calculations and experimental data was also observed. It is also shown that iron thin films do not have a catalytic effect on chemiluminescence emission, suggesting that iron thin films are ideal substrates for observing directional chemiluminescence emission.

II. EXPERIMENTAL

A. Materials

Silane-prep™ glass microscope slides were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Iron thin films (15 nm) with a 10 nm thick SiO_2 overlayer were deposited onto Silane-prep™ glass microscope slides by THINFILMS Inc., NJ.

B. Preparation of chemiluminescence solutions

Blue, green, and chartreuse chemiluminescent solutions were purchased from Omniglow (West Springfield, MA). These solutions are part of a chemiluminescent kit that contains reactants [hydrogen peroxide (oxidizing agent) and diphenyl oxalate (blue emission] and diphenyl derivatives for green and chartreuse emissions to produce chemilumines-

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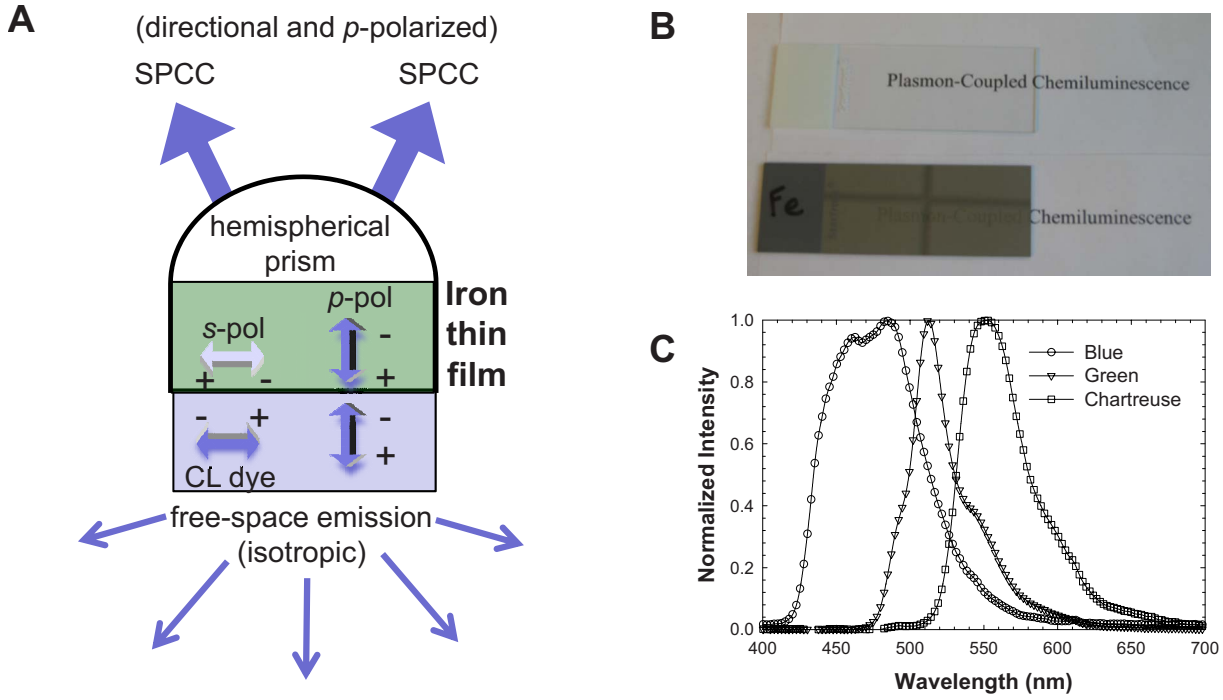

FIG. 1. (Color online) (a) Schematic depiction of SPCC from iron thin films. (b) Photographs of 15 nm iron thin films as compared to a blank glass slide. The printed text "Plasmon-Coupled Chemiluminescence" below the slides demonstrates the semitransparent nature of the films. (c) Normalized spectra of blue, green, and chartreuse emissions. CL: chemiluminescent.

cence. The oxidizing agent and the chemiluminescent dye were encapsulated within different glass tubes inside a plastic tube. A very intense chemiluminescence emission was observed after the glass tubes were broken and the chemicals were completely mixed. Freshly mixed chemiluminescent solutions were used for all the experiments.

C. Surface plasmon coupled chemiluminescence and free-space emission measurements

Iron thin films were placed onto a hemispherical prism that was attached to a stationary stage. A fiber optic assembly that can rotate 360° at a fixed distance to the hemispherical prism was mounted around the stage. 50 μl of the chemiluminescent solution was placed onto the iron thin films and SPCC (from the back of the iron thin films) and free-space emission intensities at observation angles of 0°–360° were collected using a spectrofluorometer (model No HD2000+, Ocean Optics, USA), which is connected to the fiber optic assembly. Polarizing filters were used in front of the collection fibers which are nonpolarization maintaining. The polarization was therefore intensity based and selected from an appropriate choice of the polarizing filter before the spectrofluorometer.

SPCC emission spectra of all chemiluminescent solutions were measured from the back of the iron thin films at an observation angle of 55°. The decay of SPCC and free-space emissions versus time was measured at observation angles of 55° and 270°, respectively.

D. Fresnel calculations

Fresnel calculations were performed by executing a macroprocedure written for the commercially available IGOR PRO 6 software (WaveMetrics, Portland, OR). The optical properties of dielectric layers [four phases: (1) glass, (2) iron thin film, (3) silicon dioxide, and (4) chemiluminescent dye] and their respective thicknesses (iron: 15 nm; silicon dioxide: 10 nm; dye: 20 nm) were used in the calculations.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the schematic depiction of the SPCC phenomenon. In SPCC, *p*-polarized emission (and *s*-polarized emission) from chemiluminescent solutions induce/couple to surface plasmons in iron thin films, and SPCC is subsequently emitted from the back of the iron thin films at a specific observation angle. The observation angle occurs at the reflectivity minimum of the iron thin films, which can be predicted by theoretical Fresnel calculations. In addition, free-space emission from the sample side is also measured for the comparison of the directionality and polarization of the SPCC emission. It is also important to note that due to symmetry conditions in a two dimensional (2D) plane, SPCC emission is observed at two angles (a cone is observed in three dimensions), as indicated by the arrows [Fig. 1(a)]. The real-color photographs of an iron thin film deposited onto a glass support and also a blank glass support are shown in Fig. 1(b), respectively. Iron thin films appear as semitransparent films, where the printed letters on a paper are still legible in the background. Figure 1(c) shows the chemiluminescence emission spectrum of blue, green, and chartreuse chemiluminescent dyes, where an emission peak is observed at 492 nm for blue, 509 nm for green, and 549 nm for chartreuse emission. These emission wavelengths are subsequently used to collect free-space and SPCC emissions at various observation angles (0°–360°).

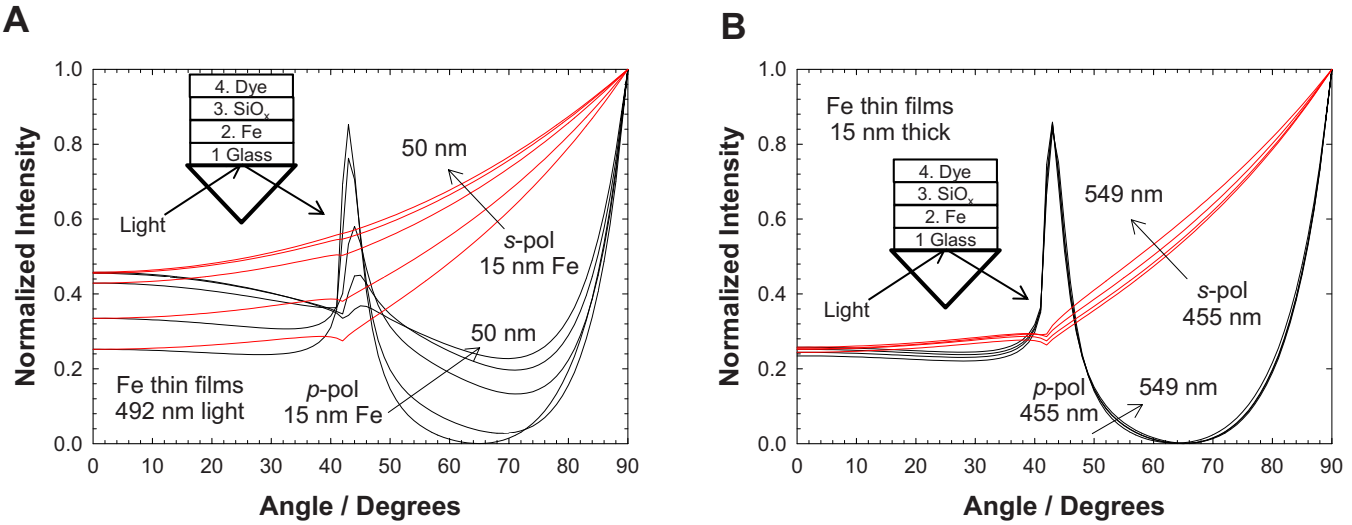

FIG. 2. (Color online) (a) Four-phase Fresnel reflectivity curves for *p*- and *s*-polarized lights at 492 nm for iron thin film thicknesses of 15, 20, 30, 40, and 50 nm with a 10 nm SiO_x overlayer. (b) Four-phase Fresnel reflectivity curves for *p*- and *s*-polarized lights at 455, 492, 509, and 549 nm for 15 nm iron thin films with a 10 nm SiO_x overlayer.

The theoretical investigation of the optimum thickness of iron thin films for SPCC was undertaken using Fresnel calculations. Figure 2(a) shows the Fresnel calculations for light 492 nm incident upon an iron thin film, calculated for various thicknesses (15–50 nm). It is important to note that the initial choice of the range of thickness is based on the results of the previous studies,[5] which have shown that 15–50 nm thick metal thin films readily support surface plasmons.[5] The reflectivity curve for *p*-polarized light at 492 nm has the lowest value of normalized intensity at 65°, which is an indicator of efficient surface plasmon generation, for 15 nm iron thin films. As the thickness of the iron thin films is increased, the predicted efficiency of surface plasmon generation is decreased. Subsequently, 15 nm thick iron films are concluded to be the best candidate for the SPCC phenomenon. It is also important to note that the extent of coupling of *s*-polarized light is predicted by Fresnel calculations to be significantly less than the extent of coupling of *p*-polarized light [Fig. 2(a)].

Subsequently, the wavelength dependence of the reflectivity curves for 15 nm iron thin films was investigated. In this regard, four-phase Fresnel calculations were undertaken for light at 455–549 nm and plotted as a function of angle [Fig. 2(b)]. Figure 2(b) shows that the angle of reflectivity is at a minimum at 65° and the reflectivity curves are identical for light in the 455–549 nm wavelength range. This accounts for the SPCC measurements for all chemiluminescent solutions to be realized at a fixed angle (65°). In addition, Fresnel calculations predict that the extent of coupling of *s*-polarized light becomes slightly less as the wavelength is increased, effectively increasing the polarization ratio (p/s) of the coupled emission. It is also important to note that the 455–549 nm wavelength range corresponds to the wavelengths of emission peaks for the chemiluminescent solutions [Fig. 1(c)].

It is informative to discuss the relevance and usefulness of Fresnel calculations in SPCC. Fresnel calculations are originally derived for the prediction of interactions of light with surface plasmons in metals, which are typically used in the SPR technique.[6,7] It is also known that surface plasmon modes in metal thin films can be generated by excited states of the fluorescent species in close proximity, i.e., in the near field,[8] and thus Fresnel calculations have been additionally used in another technique, called surface plasmon fluorescence spectroscopy (SPFS). It is important to note that in SPFS an external light source is required to excite fluorescent species (optically pumped electronically excited states). Subsequently, the excited states induce and couple to surface plasmons within several hundred nanometers. The coupled emission is in turn emitted from the back of the metal thin films at a specific angle, where the reflectivity of light is at a minimum. In a similar fashion, the coupling of chemiluminescence emission (chemically induced electronically excited states) to surface plasmons occurs, resulting in the emission of SPCC from the back of the thin films. Thus, one can use the theoretical Fresnel calculations as a predictive tool for applications based on surface plasmon coupled phenomena.

Figure 3 shows angular-dependent SPCC (0°–180°, back of the hemispherical prism) and free-space (180°–360°, sample side) *p*- and *s*-polarized emissions from the blue [at 492 nm, Fig. 3(a)], green [at 509 nm, Fig. 3(b)], and chartreuse [549 nm, Fig. 3(c)] chemiluminescent solutions. A highly *p*-polarized and highly directional SPCC emission is observed for all chemiluminescent solutions. *p*-polarized SPCC emission was maximum at observation angles of ≈60° and 110°. The observation of maximum SPCC *p*-polarized emission at two angles can be explained by the symmetry conditions of the dipoles above the iron thin films in a 2D plane.[3,9,10] Since the same hemispherical prism and iron thin films are used for all the chemiluminescent solutions (separate measurements) in this study, the SPCC emission has a maximum at two observation angles (in the 2D plane) for all the chemiluminescent solutions studied. In comparison, SPCC *s*-polarized emission is significantly less (≈1/2–1/4) that of the *p*-polarized emission, as predicted

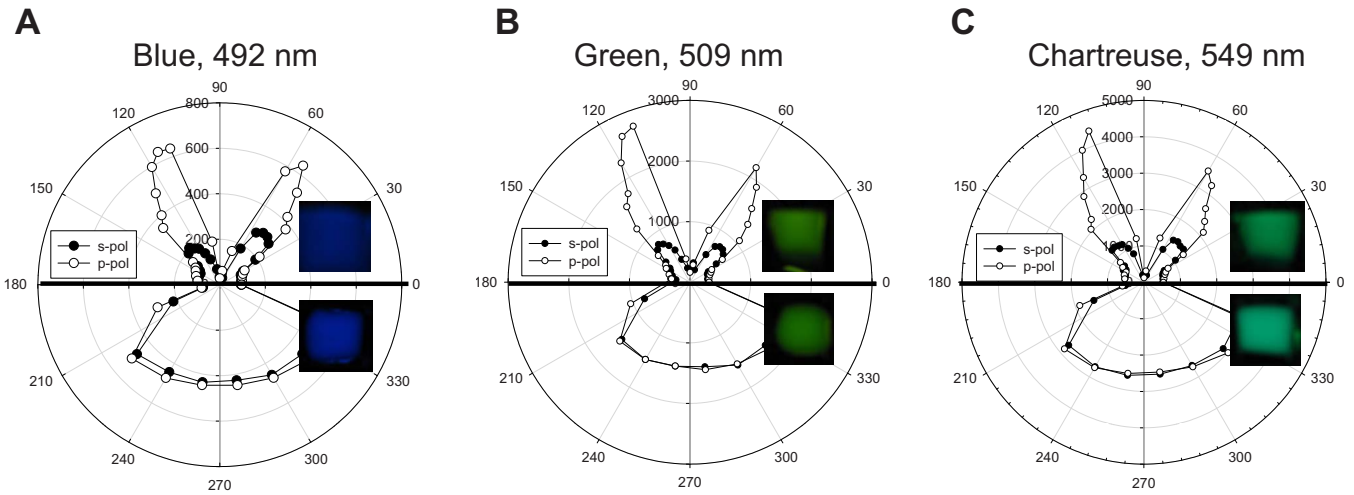

FIG. 3. (Color online) Polar plot of SPCC (0°–180°) and free-space chemiluminescence (180°–360°) with photographs of coupled (top) and free-space (bottom) emissions for (a) blue at 492 nm, (b) green at 509 nm, and (c) chartreuse at 549 nm.

by the Fresnel calculations. In contrast, free-space emission from the sample side was isotropic, which is typical for free-space rotationally averaged dipoles.[3,9,10] The extent of *s*- and *p*-polarized free-space emission was identical, which is due to the decay of chemically induced excited states of the randomly oriented chemiluminescent species. The real-color photographs of free-space and SPCC emissions for all three chemiluminescent solutions are identical in color [and spectra (data not shown)], which indicates that SPCC emission is indeed from the overlaying chemiluminescence solution.

Subsequently, the comparison of the experimental observations for all the chemiluminescent solutions with the predictions of the theoretical Fresnel calculations can be made, which are shown in Fig. 4. The side-by-side comparison was made by plotting the normalized reflectivity curves for *s*- and *p*-polarized lights at 492, 509, and 549 nm (in separate graphs) with the normalized SPCC emission intensity [*s*- and *p*-polarized emissions collected without a polarizer (all)]. Figure 4 shows that *p*-polarized SPCC emission has a maximum value at an observation angle of 60°, which corresponds to the angle where the metal reflectivity is a minimum, as predicted by Fresnel calculations. Similarly, total chemiluminescence emission has a maximum value at 60°, which implies that the measured chemiluminescence emission is coupled to surface plasmon and is directional. Fresnel calculations show that for *s*-polarized light at 492, 509, and 549 nm, the extent of coupling is predicted to be larger at observation angles of 0°–50° and is predicted to get smaller at observations angles of 50°–90°, see Fig. 4. Figure 4 also shows that the extent of coupling of the measured *s*-polarized emission is greater at observation angles of 40°–60° for all chemiluminescent solutions and is significantly less than that for *p*-polarized emission at 60°.

It is well known that chemiluminescence reactions can be catalyzed by the ionic form of several metals (e.g., copper) that results in chemiluminescence emission.[11–13] In this regard, it is important to investigate the possible catalytic effect of iron thin films on the chemiluminescence emission. It was thought that if the iron thin films indeed had a catalytic effect on the chemiluminescence emission, the decay of the emissions of free space, SPCC, and a solution on simple glass slides would be significantly different. Figure 5 shows the SPCC and free-space emissions on iron thin films and on a glass slide at 549 nm for chartreuse chemiluminescence measured at 60°, 270°, and 90°, respectively. The decay curves for other chemiluminescent solutions were also mea-

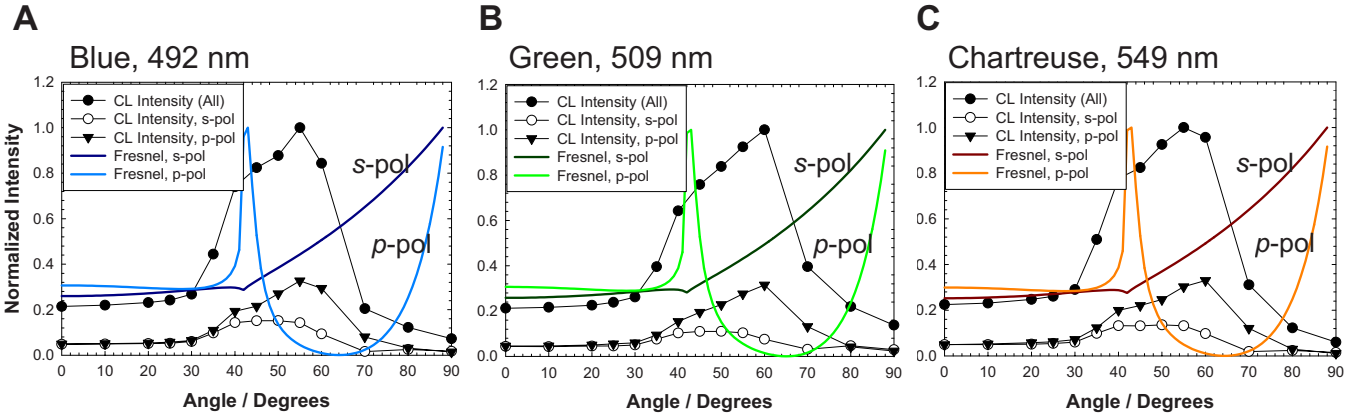

FIG. 4. (Color online) Normalized intensity curves of chemiluminescence emission, *s*-polarized emission, and *p*-polarized emission from 100 μl of dye on 15 nm iron thin films as compared with the theoretical Fresnel curves for (a) blue at 492 nm, (b) green at 509 nm, and (c) chartreuse at 549 nm.

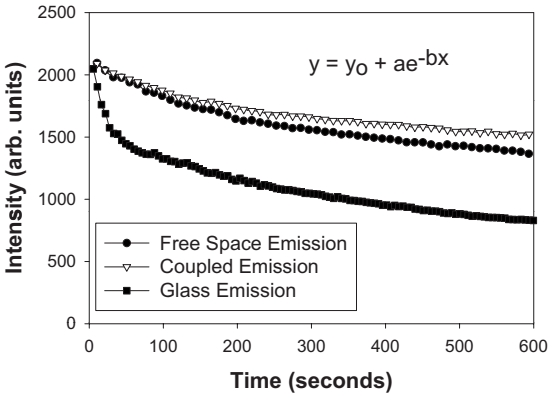

FIG. 5. The free-space and coupled emission decay curves for chartreuse chemiluminescence, measured at 549 nm.

sured (data now shown). The curves for all the chemiluminescence solutions were fitted to a single-exponential decay function, which closely describes the chemical reactions that lead to chemiluminescence emission. The calculated values of the decay rates are shown in Table I. These values show that the emission rates are very similar, surprisingly so given the error and difficulties in measuring decay rates for small volumes of fluid. Subsequently, one can conclude that iron thin films (in the configuration used in this study) do not have a catalytic effect on these chemiluminescence reactions. It is also important to note that a 10 nm thick SiO_x continuous overlayer was present on top of the films, which prevented the direct contact between the chemiluminescent solutions and the iron thin films, so the absence of a catalytic effect is not too surprising.

IV. CONCLUSIONS

SPCC from iron thin films is presented. The optimum thickness of iron thin films was predicted by theoretical Fresnel calculations to be 15 nm based on the maximum value of the reflectivity minimum. Fresnel calculations also predicted that chemiluminescence emission at 455–549 nm wavelength range should couple to iron thin films, which can be observed at a fixed angle of 65°. Experimental measurements of chemiluminescence emission from blue, green, and chartreuse chemiluminescent solutions placed on iron thin films showed that the chemiluminescence emission coupled to iron thin films (SPCC) and were subsequently emitted at an observation angle of ≈60° from the back of the film. SPCC emission was also predominantly *p* polarized. Free-space emission showed no preferential polarization and angular dependence as expected. The comparison of the experimental results and the theoretical Fresnel calculations revealed that both were in good agreement. The investigation of the decay of free-space and SPCC emission from iron thin films revealed that there is no catalytic effect on chemiluminescence emission by iron thin films. Finally, iron thin films afford for the opportunity to make SPCC measurements for a wide range of wavelengths at fixed angle geometry, negating the need to make adjustments to the detection optics.

TABLE I. SPCC and free-space decay rates for blue, chartreuse, and green chemiluminescence solutions.

	Coupled rate (Fe) k (s^{-1})	Free-space rate (Fe) k (s^{-1})	Glass rate k (s^{-1})
Blue	0.0031	0.0025	0.0042
Green	0.0045	0.0043	0.0040
Chartreuse	0.0022	0.0027	0.0052

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