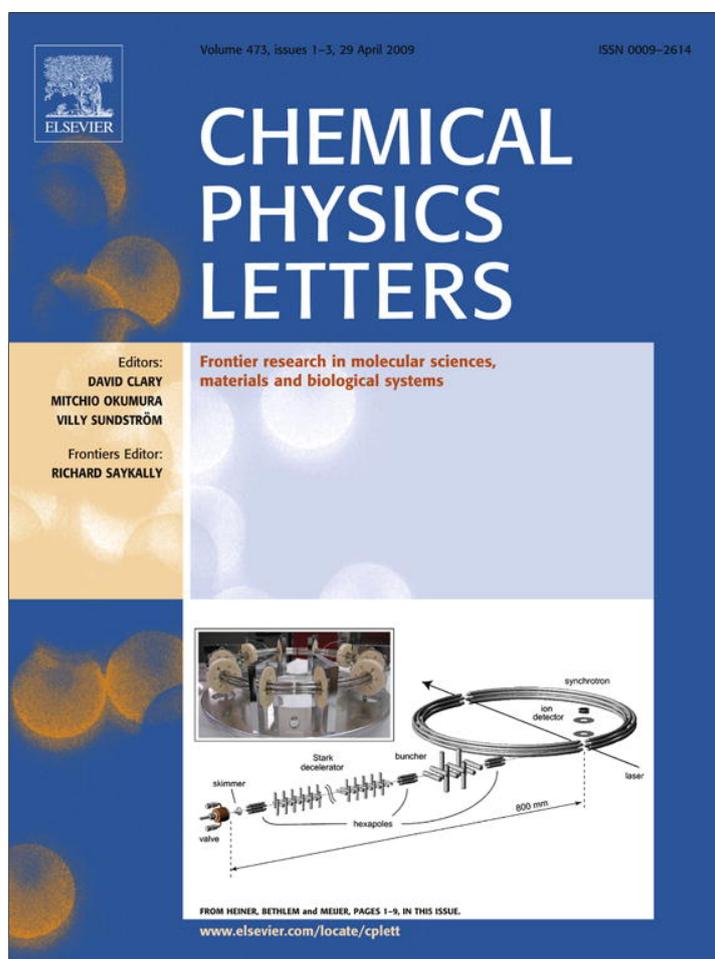


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Directional surface plasmon coupled chemiluminescence from nickel thin films: Fixed angle observation

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ABSTRACT

Directional surface plasmon coupled chemiluminescence (SPCC) from nickel thin films is demonstrated. Free-space and angular-dependent SPCC emission from blue, green and turquoise chemiluminescent solutions placed onto nickel thin films attached to a hemispherical prism were measured. SPCC emission was found to be highly directional and preferentially *p*-polarized, in contrast to the unpolarized and isotropic chemiluminescence emission. The largest SPCC emission for all chemiluminescence solutions was observed at a fixed observation angle of 60°, which was also predicted by theoretical Fresnel calculations. It was found that nickel thin films did not have a catalytic effect on chemiluminescence emission.

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1. Introduction

The interactions of light with surface plasmons in noble metals have been the subject of numerous publications found in the literature. These publications have led to novel bioassay technologies that were either commercialized or in the process of being commercialized with multifarious applications in the Biosciences. One of the most well-known technologies is called surface plasmon resonance (SPR) [1,2], where the quantity of an analyte of interest is monitored by the change in the angle of reflectivity minimum for light incident upon a thin gold film. A fluorescence analog of the SPR technology, called surface plasmon fluorescence spectroscopy (SPFS) [3,4], has recently been developed. In SPFS, fluorescently-labeled biomolecules are employed in the bioassays constructed on the metal surface. The quantity of the biomolecule of interest is monitored by the change in fluorescence emission detected from the sample side (free-space emission) or through a prism (surface plasmon coupled fluorescence, SPCF). In this regard, attomolar sensitivity in immunoassays based on SPFS has been reported [5]. The SPFS technique was also reported for DNA hybridization [6] and protein detection assays [7]. Our research group has also recently reported the proof-of-principle of a technique called surface plasmon coupled chemiluminescence (SPCC) [8], whereby the coupling of chemically excited states to surface plasmons in either silver [9] or zinc [10] metal thin films was observed. Similar to SPCF emission, SPCC emission is observed at specific observation angles from the back of the metal thin films [8]. In addition, due to the preferential coupling of *p*-polarized light to surface plasmons, SPCF and SPCC emission is nearly exclusively *p*-polarized. Subsequently, SPCF and SPCC emission can be visually seen as a

cone, or as a 'ring' from the back of the film when a hemispherical prism is employed [11].

In this Letter, the use of nickel thin films for fixed angle of observation of SPCC is demonstrated. Free-space and SPCC emission from blue, green and turquoise chemiluminescent solutions, which have an emission peaks at 492, 509 and 549 nm respectively, were measured using a rotating stage equipped with a fibre optic detection system. The optimum thickness of the nickel thin films for effective coupling of light at these wavelengths was determined to be ≈ 15 nm, using theoretical Fresnel calculations. A 10 nm SiO₂ overlayer was also used to protect the nickel surface. Experimental SPCC emission for all the chemiluminescence solutions, which occurred at a fixed angle due to broad wavelength/angle of reflectivity of the metal, was found to be in good agreement with the results of the Fresnel calculations. The observation angles for SPCC emission (492–549 nm) from silver thin films were also calculated and were found to shift as a function of wavelength, in contrast to nickel thin films. To investigate whether nickel thin films have a catalytic effect on the chemiluminescence emission, the decay rates of both free-space and SPCC emission were calculated from time-dependent emission intensity measurements. It was found that the decay rate of the free-space and SPCC emission were very similar, which strongly suggests that nickel thin films have no catalytic effect on chemiluminescence emission. Our findings suggest that 15 nm thick nickel films can be potentially useful for high-sensitivity chemiluminescence-based applications, such as enzyme-linked immunosorbent assays (ELISA), operating at a fixed angle observation.

2. Materials and methods

Silane-prep™ glass microscope slides were purchased from the Sigma-Aldrich Chemical Company (Milwaukee, WI, USA). Nickel

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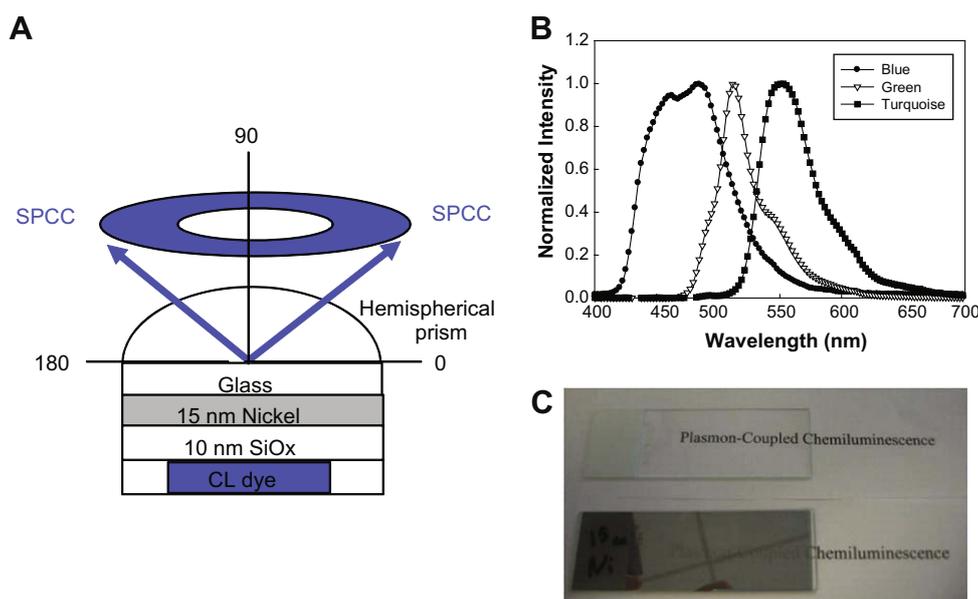


Fig. 1. (A) Experimental configuration of surface plasmon coupled chemiluminescence (SPCC). (B) Normalized spectra of blue, turquoise, and green coupled chemiluminescence through the prism. (C) Photographs of 15 nm nickel thin films compared to a blank glass slide. The text below the slides demonstrates the transmission of the films.

thin films (15 nm) with a 10 nm thick SiO₂ overlayer were deposited onto silane-prep™ glass microscope slides by AccuCoat Inc., Rochester, NY, USA. Blue, green and turquoise chemiluminescent solutions were purchased from Omniglow (West Springfield, MA). These solutions are part of a chemiluminescent kit that contains reactants (hydrogen peroxide and diphenyl oxalate) to produce chemiluminescence emission, which were encapsulated within different glass tubes inside a plastic tube. A very intense chemiluminescence emission, lasting ≈2 h, was observed after the glass tubes were broken and the chemicals were completely mixed.

SPCC and free-space emission from chemiluminescent solutions on nickel thin films were measured according to the following procedure: nickel thin films were placed on a hemispherical prism that is attached to a rotary stage equipped with a fibre optic and fluorometer (Model HD2000, Ocean Optics, Inc., Florida, USA). Freshly mixed (70 μl) chemiluminescent solutions were placed on the nickel thin films and the chemiluminescence emission spectrum and emission intensity at observation angles of 0–360° were recorded. The decay rates of free-space and SPCC emission were recorded at 270° and 60°, respectively (Fig. 1A).

3. Results and discussion

Fig. 1B shows the chemiluminescence emission spectrum for blue,¹ green and turquoise chemiluminescent solutions used in this study. Each chemiluminescent solution has an emission peak at different wavelengths of the spectrum: blue: 492 nm; green: 509 nm and turquoise: 549 nm. It is important to note that these wavelengths are very similar to those observed for commercially available chemiluminescence bioassays. Subsequently, one can potentially employ the SPCC technique in bioassays using this chemiluminescence technology. Fig. 1C shows the real-color photographs of a nickel thin film deposited onto a glass support and also a blank glass support respectively, demonstrating the semi-transparent nature of the nickel thin films.

¹ For interpretation of color in Figs. 1–6, the reader is referred to the web version of this article.

Fig. 2A shows the angular-dependent SPCC (0–180°, back of the prism) and free-space (180–360°, sample side) *p*- and *s*-polarized emission measured at 492 nm from the blue chemiluminescent solution placed on the nickel thin films. An isotropic free-space emission is observed from the sample side, which is typical for free-space dipoles [7,8,11]. In addition, the extent of *s*- and *p*-polarized free-space emission was identical, as expected for free-space emission, which is simply the result of the decay of chemically excited states of the randomly oriented chemiluminescent solutions. On the other hand, the SPCC emission is highly *p*-polarized and highly directional. A maximum SPCC *p*-polarized emission is detected at observation angles of 60° and 110°. The observation of maximum SPCC *p*-polarized emission at two angles is due to the symmetry conditions of the dipoles above the metal [7,8,11]. Since the same hemispherical prism and nickel thin films are used for all the chemiluminescent solutions in this study, the SPCC emission has a maximum at two observation angles (in the 2D plane) for all the chemiluminescent solutions. In comparison, SPCC *s*-polarized emission is significantly less (≈1/3rd) that of the *p*-polarized emission and is observed over a wide-range of angles (35–70° and 110–145°, Fig. 2A).

The comparison of the experimental observations with the predictions of the theoretical Fresnel calculations was also made, and is shown in Fig. 2B. In this regard, Fresnel calculations for *s*- and *p*-polarized light at 492 nm (corresponds to a maximum emission peak of the blue chemiluminescent solution) were undertaken and plotted side-by-side with the experimental data. In addition, total chemiluminescence emission (measured separately without a polarizer) is measured and all the experimental data is normalized to the largest value of the total emission. Total chemiluminescence emission is the sum of *s*-, *p*-polarized SPCC emission and background light. Fig. 2B shows that *p*-polarized SPCC emission has a maximum value at an observation angle of 60°, which corresponds to the angle where the 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 surface plasmon coupled and thus is directional. In addition, the real-color photographs of total free-space and SPCC emission (Fig. 2A) are identical in color (and

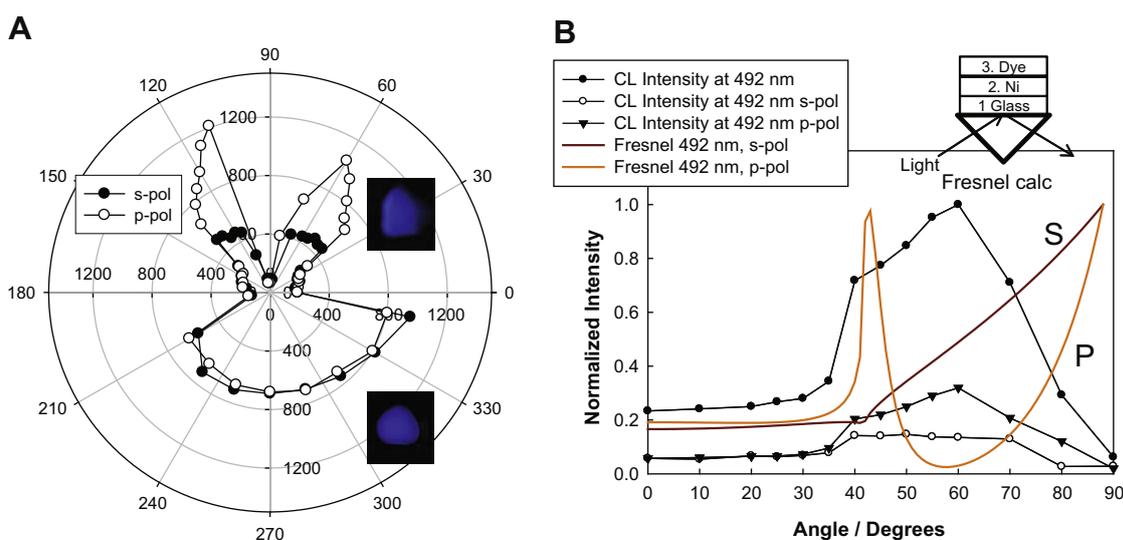


Fig. 2. (A) Polar plot of blue SPCC (0–180°) and the free-space chemiluminescence (180–360°) with photographs of coupled (top) and free-space (bottom) emissions. (B) Normalized intensity curves of blue chemiluminescence emission, s-polarized emission, and p-polarized emission from 100 μ L of chemiluminescent solution on a 15 nm nickel thin films compared with the theoretical reflectivity Fresnel curves.

spectra (data not shown)), which indicates that SPCC emission is indeed from the blue chemiluminescence solution. As described earlier s-polarized SPCC emission is observed over a 30° range.

It is important to comment on the utility of Fresnel calculations for SPCC. Fresnel calculations are performed for incident light that enters the prism and induces surface plasmons in metal thin films placed on the prism itself. In this regard, Fresnel calculations are typically employed in the SPCF technique [3,11], where the incident light is used to excite near-field fluorophores. Using Fresnel calculations, the optimal thickness of the nickel thin films was previously determined to be ≈ 15 nm for SPCF [12]. Since both SPCC (chemically induced electronically excited states) and the SPCF (optically pumped electronically excited states) techniques involve the interactions of excited states of solutions with surface plasmons, the same metal thin films can be employed in both techniques. In this regard, the theoretical Fresnel calculations are a

useful predictive tool for applications based on the surface plasmon coupled phenomena.

Fig. 3A shows the angular-dependent SPCC, free-space, and p- and s-polarized emission measured at 509 nm from the green chemiluminescent solution placed on thin nickel films. Similar to SPCC emission from the blue chemiluminescence solution, SPCC emission from the green chemiluminescence solution is highly p-polarized (3-fold larger than s-polarized emission) and highly directional: a maximum SPCC p-polarized emission is detected at observation angles of 70° and 110° in the 2D plane. Free-space emission from green chemiluminescence solution is observed to be isotropic and the extent of s- and p-polarized emission is similar. Fresnel calculations for the interaction of light at 509 nm with 15 nm thick nickel films were undertaken and plotted together with the corresponding experimental data, c.f. Fig. 3B. Fig. 3B shows that largest SPCC emission from the green chemiluminescence

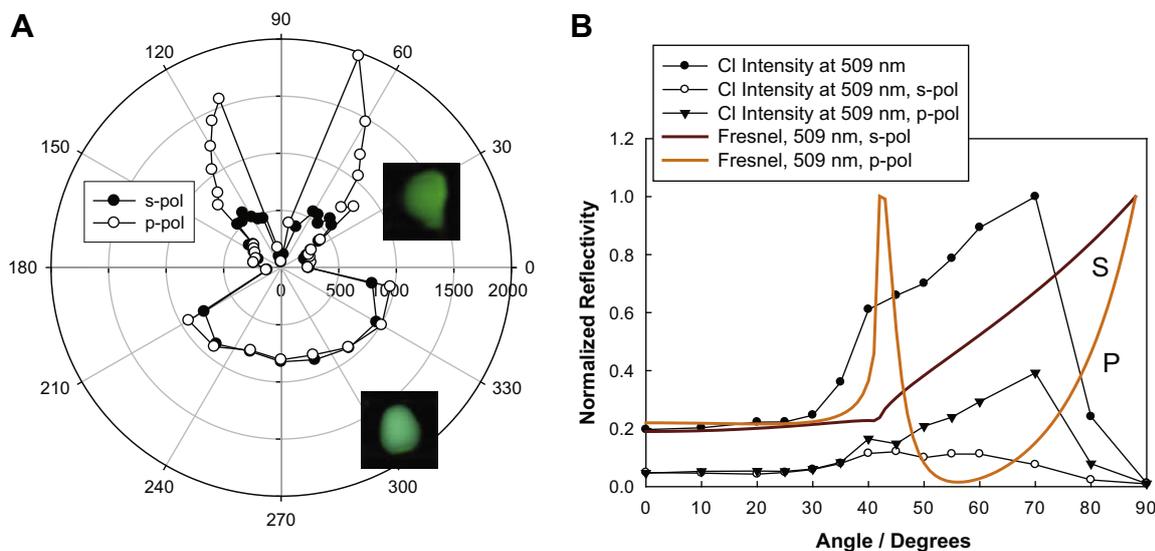


Fig. 3. (A) Polar plot of turquoise SPCC (0–180°) and free-space chemiluminescence (180–360°) with photographs of coupled (top) and free-space (bottom) emissions. (B) Normalized intensity curves of turquoise chemiluminescence emission, s-polarized emission, and p-polarized emission from 100 μ L of dye on a 15 nm nickel thin films as compared with the theoretical Fresnel curves.

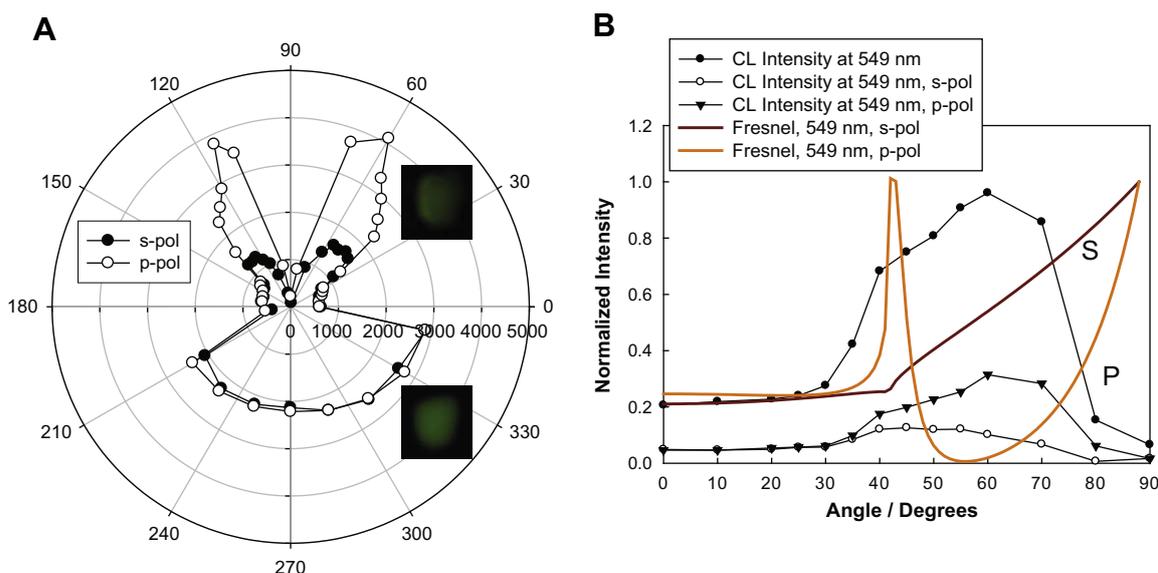


Fig. 4. (A) Polar plot of green SPCC (0–180°) and free-space chemiluminescence (180–360°) with photographs of coupled (top) and free-space (bottom) emissions. (B) Normalized intensity curves of green chemiluminescence emission, *s*-polarized emission, and *p*-polarized emission from 100 μL of dye on a 15 nm nickel thin films as compared with the theoretical Fresnel curves.

solution is observed at an angle of 70°, and is preferentially *p*-polarized, as predicted by Fresnel calculations. Once again, the extent of coupling of the *s*-polarized emission was significantly less than the extent of coupling of the *p*-polarized SPCC emission. The real-color photographs of total free-space and SPCC emission (Fig. 3A) appear to be identical in color and indeed spectral shape (data not shown), which indicates that the SPCC emission originated from the green chemiluminescence solution.

Fig. 4A shows the angular-dependent SPCC, free-space, *p*- and *s*-polarized emission measured at 549 nm from the turquoise chemiluminescent solution also placed on the nickel thin films. Similar to SPCC emission from the blue and the green chemiluminescence solutions, SPCC emission from the turquoise chemiluminescence solution is highly *p*-polarized (≈ 2.5 -fold larger than *s*-polarized emission) and highly directional. A maximum SPCC *p*-polarized emission from the turquoise chemiluminescent solution is detected at observation angles of 60° and 115°. Free-space emission from the turquoise chemiluminescent solution was also isotropic and was not preferentially polarized. Fig. 4A shows that the real-color photographs of total free-space and SPCC emission appear to be identical in color (and spectra (data not shown)), providing additional evidence that SPCC emission originates from the turquoise chemiluminescence solution. The angular-dependent turquoise chemiluminescence emission was also overlaid with the results of the Fresnel calculations undertaken for 549 nm (corresponding to the emission peak of the turquoise chemiluminescent solution) and 15 nm nickel thin films (Fig. 4B). Fig. 4B shows that there is a good agreement between the angle of minimum reflectivity predicted by Fresnel calculations and the angle where the largest SPCC emission was observed.

It is interesting to further comment on the directional chemiluminescence emission shown in Figs. 2–4. It is known that fluorophores which are *p*-oriented with respect to the surface are readily coupled, with *s*-oriented molecules either not coupling or indeed coupling but, to a much weaker extent [13]. For the chemiluminescence solutions studied here on nickel thin films, this also appears to be the case, Figs. 2–4, with a very weakly coupled *s*-polarized emission, thought due to the partially cancelled mirror dipole in the metal film (Fig. 5). In contrast *p*-oriented chemiluminescence molecules (perpendicular to the film surface) are both

coupled efficiently and indeed thought to show a net increase in the surface induced dipole (Fig. 5).

For 15 nm nickel thin films, the reflectivity minimum for the wavelengths studied are both approximately constant and quite broad with respect to collection angle (Fig. 5A). This suggests that for a broad range of wavelengths, a fixed experimental collection geometry could be used, simplifying the collection optics. Fig. 5C shows how *p*-oriented dipoles for the chemiluminescence dyes are thought to produce the cone of emission from the back of the films, as viewed from the top, i.e. *z*-axis. Interestingly, the chemiluminescence emission cone is likely to be broader in angle, as compared to the well studied silver films, which show angle shifts as a function of wavelength (Fig. 5B).

It is also interesting to comment on how the volume/thickness of the coupling dipoles (chemiluminescence solution) can influence the observation angle of SPCC and/or the free-space and coupled emission intensity. It is known that dipoles within 10 nm of the surface show a decreased emission [13], where as free-space emission is dominant above 500 nm from the surface. At in-between distances such as for $\lambda/2$ the chemiluminescence emission, the *s*-oriented dipoles (parallel) will show an increased free-space emission, while the *p*-oriented molecules (perpendicular) will show decreased free-space emission and an increased SPCC. It is this behavior which is well known to cause the oscillatory behavior for dipoles in front of mirrors [14]. For our approximately 1 mm chemiluminescence solution thickness, only a small fraction of the total light was coupled, as evidenced by the large free-space chemiluminescence intensity. For ELISA based assays, where both chemiluminescence substrates and dipoles are located close to surfaces (typically <100 nm), then a significant fraction of the total emission would be expected to couple and be highly polarized and directional.

Finally, metals are known to catalyze chemiluminescence reactions resulting in increased emission and thus faster kinetics of chemical reactions. Subsequently, to investigate whether nickel thin films catalyze reactions that lead to enhanced chemiluminescence emission, the decay of free-space emission (at 270°, Fig. 1A) and SPCC emission (60°, Fig. 1A) intensity over time was measured. Fig. 6 shows the free-space and SPCC emission decay curves for the blue, green and turquoise chemiluminescence solution. The curves

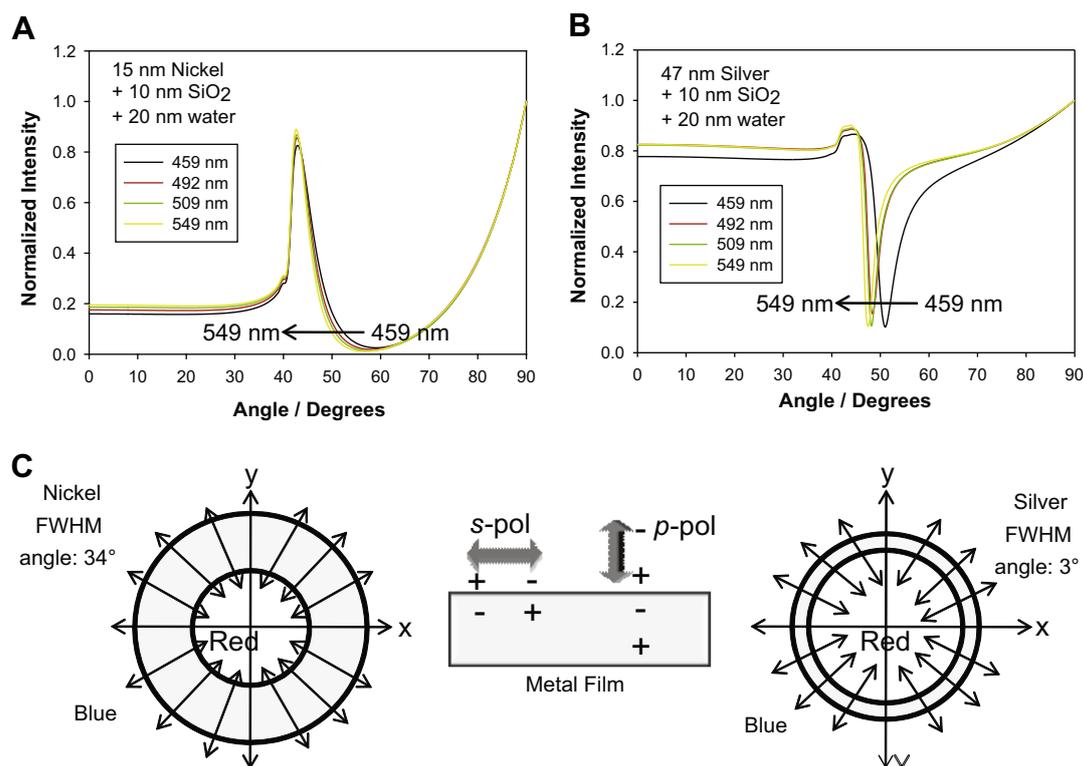


Fig. 5. Fresnel reflectivity curves for *p*-polarized light incident upon (A). 15 nm nickel thin films and (B) 47 nm silver thin films. (C) ‘Cone’ of SPCC from nickel and silver thin films as seen from the *z*-axis (looking down). Depiction of *s*- and *p*-polarization of SPCC is also shown. FWHM-full width half maximum.

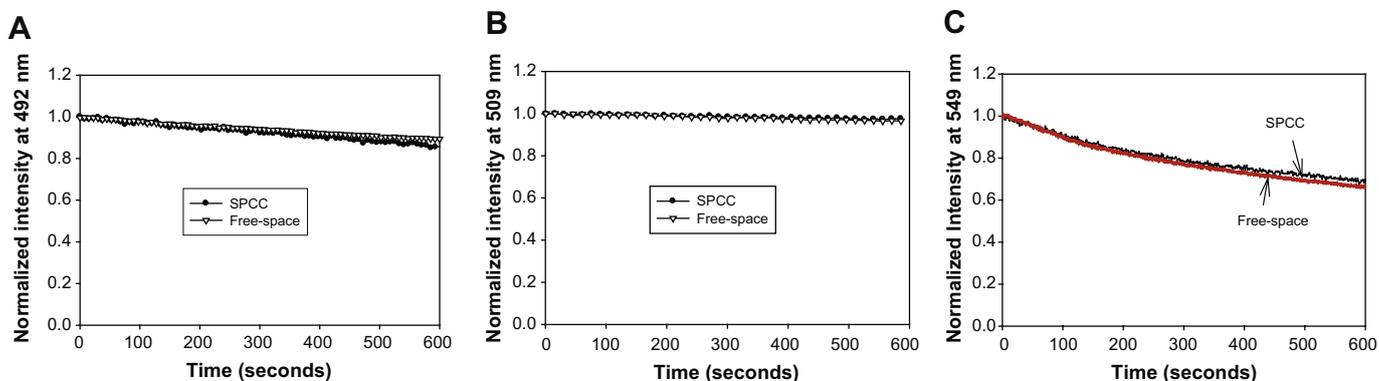


Fig. 6. The free-space and SPCC emission decay curves for the (A) blue, (B) green and (C) turquoise chemiluminescence solutions.

Table 1
SPCC and free-space decay rates for blue, turquoise, and green chemiluminescence solutions.

Emission wavelength (nm)	Coupled rate <i>k</i> (s ⁻¹)	<i>R</i> ²	Free-space rate <i>k</i> (s ⁻¹)	<i>R</i> ²
492	0.0061 ± 0.0001	0.999	0.0047 ± 0.0002	0.998
509	0.0021 ± 0.0003	0.999	0.0021 ± 0.0002	0.999
549	0.029 ± 0.001	0.998	0.027 ± 0.002	0.999

for all the chemiluminescence solutions could be fitted well to a single-exponential decay function (1st order kinetics) which closely describes the chemical reactions that lead to chemiluminescence emission. The calculated values of the decay rates are tabulated in Table 1. These values show that free-space emission and SPCC emission rates are very similar, that is, nickel thin films do not have a catalytic effect on these chemiluminescence reactions. This can be partly attributed to the fact an SiO_x overlayer,

prevented the direct contact between the chemiluminescent solutions and the nickel thin films.

4. Conclusions

The first observation of directional surface plasmon coupled chemiluminescence from nickel thin films is demonstrated. Chemiluminescence emission from blue (492 nm), green (509 nm) and tur-

quise (549 nm) was found to induce surface plasmons in 15 nm thick nickel films, which was subsequently emitted (preferentially *p*-polarized) through the back of the nickel films at observation angles of 60° and 110°. The extent of coupled *p*-polarized emission was ≈3-fold larger than the extent of coupled *s*-polarized emission. Free-space emission from all the chemiluminescence solutions was isotropic and did not have preferential polarization, as expected. It was also found that nickel thin films did not have any catalytic effect on the chemical reactions that lead to enhanced chemiluminescence emission. Finally, the use of nickel thin films affords for the potential construction of SPCC-fixed angle geometry devices for a wide-range of chemiluminescence emissions and applications, as compared to the use of other metals (Fig. 5), which have much narrower and sharper angular-dependencies as a function of wavelength.

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