Use of silver nanoparticles to enhance surface plasmon-coupled emission (SPCE)

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Abstract

We report that self-assembled monolayers of colloidal silver nanoparticles can increase the intensity of the surface plasmon-coupled emission (SPCE) signal from sulforhodamine 101 (S101). The S101 was spin coated on a glass slide coated with a layer of continuous silver, and a silica layer upon which the nanoparticle layer was self-assembled. Of the various colloid sizes studied, the 40 nm colloids showed both the highest enhancements in the SPCE signal and the largest extent of plasmon coupling, defined as the ratio of SPCE to Free Space signal. Our findings reveal a new technique that can be potentially employed to increase the sensitivity of SPCE applications.
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1. Introduction

The overwhelming majority of fluorescence based experiments today use fluorophores in a dielectric media. These fluorophores are both excited in and radiate into the far-field, i.e. Free Space. However, there is a growing interest in the near-field interaction of fluorophores with metallic nanostructures. These interactions are of interest because they offer an opportunity to modify and control the excited state deactivation pathways and spatial distribution of the emission [1,2]. We have previously reported on the use of metallic surfaces and nanoparticles to modify the emissive properties of fluorophores [1,3–6]. We found that under appropriate conditions, close proximity of fluorophores to silver nanoparticles can lead to increased system (fluorophore–metal) quantum yields and radiative decay rates (enhanced fluorescence intensities), increased photostability and decreased lifetimes [7]. We use a concept based on radiating plasmons called the radiating plasmon model (RPM), and the unified plasmon-fluorophore theory (UPFT) to explain the effects of metals on fluorescence [8–10]. In our studies of fluorophore–metal interactions, we have also demonstrated that resonance interactions can occur between excited fluorophores in close proximity to thin continuous films of metal attached to glass prisms, in addition to particulate films. This resonance interaction results in the generation of surface plasmons and the directional emission of the spectral properties of the excited fluorophores on the glass side. We have termed this phenomenon as surface plasmon-coupled emission (SPCE) [5,6,11–16]. SPCE is inversely related to the widely known phenomenon of surface plasmon resonance (SPR) [5,6,11–22]. SPR is the absorption of light by a thin metal film, usually gold or silver, when the wavevector of the p-polarized incident light matches the wavevector of the surface plasmons at the sample–metal interface [5,6,11–16,18–22]. This wavevector matching only occurs when the light incident on the metal passes through a prism of high refractive index and does not occur if the light is directly incident on the metal through air. The angle of incidence through

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the prism can be adjusted to match the wavevectors and hence resonantly excites the surface plasmons [5,6,18–22]. This angle is called the surface plasmon resonance angle (SPR) for the incident wavelength (θ_{sp}). The reflectivity of the metal film is high except for a small range of angles around θ_{sp} where it sharply drops [5,6,18–22]. In SPCE, the emission is detected at a specific angle, θ_{sp}, instead of being absorbed, where excited fluorophore dipoles in the near-field of the metal, couple to the surface plasmons [5,6,11–16]. This coupling results in the plasmons radiating at the fluorophore emission wavelength at sharply defined angles from the normal on the prism side. Importantly, the angle of SPCE emission is equal to the surface plasmon resonance angle for the emission wavelength [5,6,11–16]. Hence the aforementioned ability to control the optical energy of a population of excited state fluorophores holds potential to be useful in the development of novel high sensitivity devices for downstream fluorescence sensing.

In this Letter, we report a new technique for enhancing the intensity of the SPCE signal by using silver colloidal nanoparticles of varying sizes to increase the coupling efficiency of the excited state fluorophore to the surface plasmons in thin continuous silver films that is attached to a hemicylindrical prism. The colloidal nanoparticles were self-assembled on a thin silica layer (the silica acts as a spacer between the metal film and the fluorophore). Our results indicate that among the three silver colloid sizes tested (20 nm, 40 nm and 80 nm) – (i) all three colloid sizes showed an increase in the observed SPCE signal when compared to the control sample (no colloid layer), with the 40 nm colloids showing the maximum enhancement and (ii) all three colloid sizes showed an increase in the coupling efficiency of the excited state fluorophore with the continuous silver films when compared to the control sample, with the 40 nm colloids showing the maximum coupling efficiency. We define coupling efficiency as the ratio of the SPCE signal to the Free Space signal. These results suggest that colloidal nanoparticles can be used to enhance the coupling efficiency of excited state fluorophores to surface plasmons on smooth metal films, thus leading to significant increases in the intensity of the plasmon-coupled SPCE signal.

2. Materials and methods

Premium quality APS-coated glass slides (75 × 25 mm), silver wire (99.99+% purity) silicon monoxide pieces (99.99% purity), Poly-vinyl alcohol (PVA), 3-aminopropyl-triethoxysilane (APS), and sulforhodamine 101 (S101) were purchased from Sigma–Aldrich (St. Louis, MO). Silver colloidal nanoparticles of 20 nm, 40 nm and 80 nm diameter were purchased from Ted Pella Inc. (Redding, CA). The silver colloids used are citrate stabilized with a net negative surface charge arising from surface carboxylic acid groups [23,24].

Approximately 42 nm of silver was deposited on APS-coated glass slides using an Edwards Auto 306 Vacuum

Evaporation chamber (West Sussex, UK) under high vacuum ($<2 \times 10^{-4}$ Pa). In each case, the metal deposition step was followed by the deposition of 5 nm of silica via evaporation without breaking vacuum. This step served to protect the metal surface from chemical attack, and to provide a means to chemically attach silver colloids. The slides used for silver nanoparticle attachment were then coated with amino groups by dipping the slides in a 1% aqueous solution of APS in ethanol for 30 min at room temperature. The slides were washed extensively with water and air-dried. Approximately 500 μl of each of the silver colloidal solutions were used to coat the surface of separate slides for 24 h, after which the slides were washed extensively with water and air-dried. We have shown previously that differences in the fraction of surface coverage between small and large silver colloids attached on glass surfaces are not significant, and hence it is assumed that the surface nanoparticle coverage is comparable for the three different nanoparticles [24]. All the slides (including the control slide) were then spin coated with a solution of 60 μM
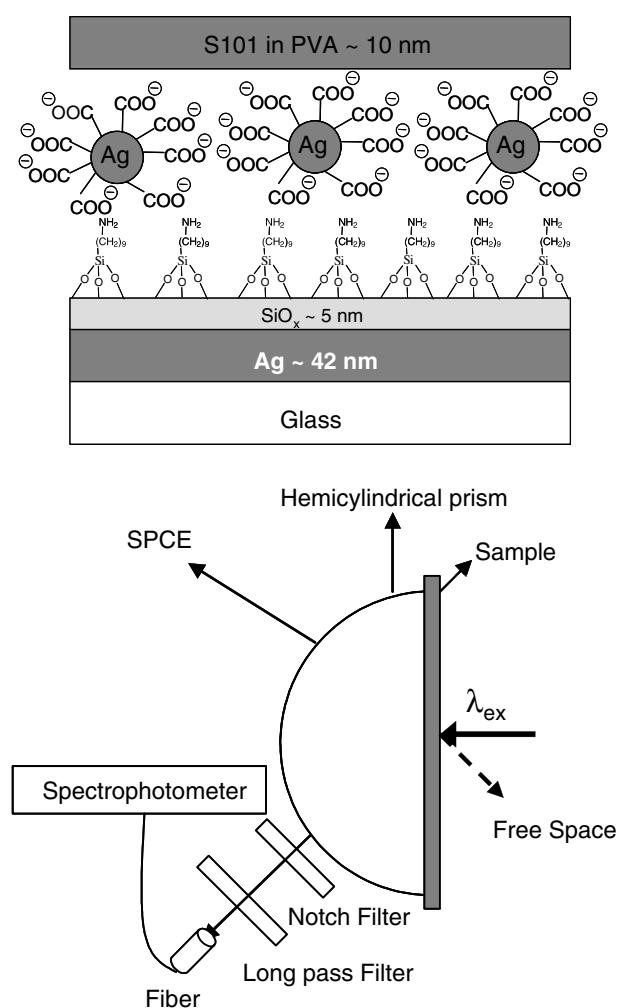

Fig. 1. (Top) Schematic of the configuration of a film of S101 in PVA spin coated on top of silver colloidal nanoparticles assembled on a ~42 nm thick silver film. (Bottom) Geometrical scheme for measurement of angle-dependent emission.

S101 in 0.25% PVA. The S101/PVA film is estimated to be approximately 10 nm in thickness [11]. Fig. 1 (Top) presents a schematic representation of the nanoparticle based silver thin film system.

The metal coated slides containing the samples were attached to a hemicylindrical prism made from BK7 glass ($n = 1.52$) and the refractive index was matched using spectrophotometric grade glycerol ($n = 1.475$) between the back of the glass slide (uncoated side) and the prism. This unit was then placed on a precise 360° rotatory stage that was built in-house. The rotatory stage allowed the collection of light at all angles around the sample chamber, see Fig. 1 (Bottom). The excitation source used is a diode pumped solid state continuous-wave laser, lasing at 532 nm. An Ocean Optics low OH 600 μm diameter optical fiber with NA of 0.22 (Dunedin, FL) used for collecting the SPCE and Free Space signals was mounted on a holder that was fastened on to the base of the rotatory stage. SPCE and Free Space spectra were collected using a model SD 2000 Ocean Optics spectrometer (Dunedin, FL) connected to the optical fiber. The spectra were collected with an integration time of 1 s. Unpolarized, p and s-polarized signal information were collected for the SPCE signal (from 0° to 90° with respect to the front of the prism) and the Free Space signal (from 90° to 180° with respect to the front of the prism). See Fig. 1 (Bottom) for a geometrical scheme for the measurement of angular-dependent emission. All data processing was performed using Origin-Pro 7 from Originlab Corporation (Northampton, MA).

3. Results and discussion

Fig. 2 shows a set of polar intensity plots showing the SPCE and Free Space emission of the S101 for all the samples investigated. Fig. 2a presents the data from the control sample (with no silver colloids), while Fig. 2b–d presents data from the 20 nm, 40 nm and 80 nm colloid sample, respectively. In our experiments we only measured one quadrant in both the SPCE and Free Space case, respectively, as they were representative of the entire 360° angular data. Fig. 2 shows that all the colloid samples show enhanced SPCE emission as compared to the control sample, the enhancement peaking for the 40 nm colloid case. These observations are more clearly revealed in Fig. 3. Fig. 3 (Top) shows the S101 SPCE and Free Space spectra for the control sample and the SPCE spectra at the SPCE peak angle for all the colloid samples. The figure reveals, for the control sample, the SPCE signal is about 5-fold greater than the Free Space signal. Introduction of the 20 nm silver colloids causes a modest increase in the coupled SPCE signal (approximately 1.3-fold increase). When the 40 nm colloids are introduced, we see a significant increase in the coupled SPCE signal, a gain of over 6-fold. The presence of the 80 nm silver colloids also showed an increase in the couple SPCE signal intensity, a gain of approximately 3.5-fold. These enhancement factors are represented in the bar chart presented in Fig. 3 (Bottom).
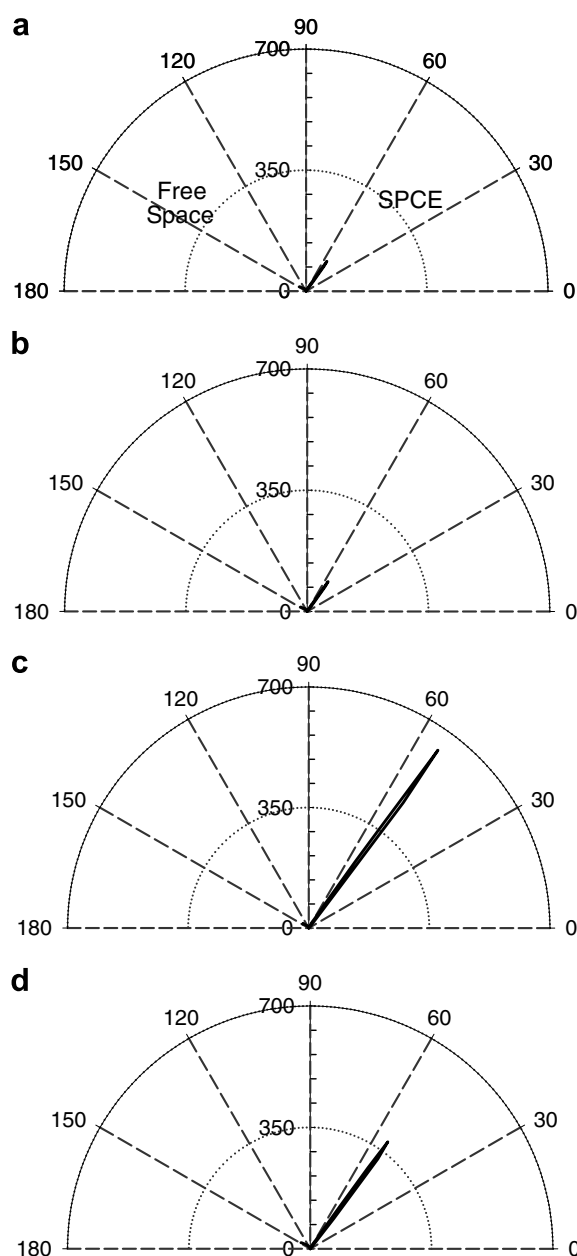

Fig. 2. Polar intensity plots showing surface plasmon-coupled emission (SPCE) and Free Space emission of S101 in PVA on ∼42 nm silver films with: (a) control, no Ag colloid, (b) 20 nm Ag colloid, (c) 40 nm Ag colloid and (d) 80 nm Ag colloid. Only one quadrant in both the Free Space and SPCE region is presented for clarity.

It should be noted that the SPCE peak angle for all the samples tested (including the control) remained approximately constant at 52° (and drops off sharply at other angles), and we did not observe any noticeable change in the angular broadness of the SPCE signal. Another interesting observation is shown in the inset in Fig. 3 (Top), where we see the SPCE signal from the 40 nm colloid sample is completely p-polarized. This was observed for the other colloid samples and the control sample. This suggests that the SPCE enhancements observed from the colloid-based samples are not due to enhanced direct transmission
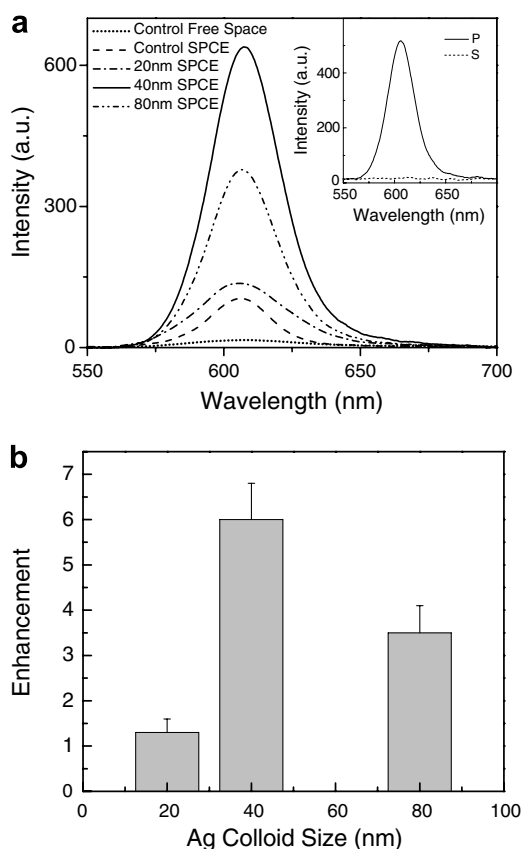
Fig. 3. (Top) Emission spectra from S101 in PVA on ~42 nm silver films with no Ag colloid (control), and with 20 nm, 40 nm and 80 nm Ag colloid. (Inset) S101 emission data from 40 nm Ag colloid sample showing SPCE signal to be completely p-polarized. (Bottom) Enhancement factor for SPCE signal as a function of Ag colloid size. The enhancement factor is defined as the ratio of the SPCE signal of the colloid sample to that of the SPCE signal of the control sample.

of fluorescence, but rather might be due to increased electromagnetic coupling efficiency between the excited state fluorophores and smooth metal films that is mediated by the silver nanoparticles. These findings are in direct agreement with a recent report of enhanced phosphorescence signatures near colloid coated continuous thin metal films [17]. We believe that in addition to direct fluorophore excitation of the surface plasmon polaritrons (SPP) on the smooth metal surface, the excited state fluorophores also create localized surface plasmons (LSP) on the nanoparticles which subsequently couples with the SPP's on the metal film thus resulting in an enhanced electromagnetic field near to the metal film surface. This enhanced field subsequently radiates the spectral properties of the fluorophore in the far-field through the prism side. We have recently published a systematic study investigating the effect of the separation of the fluorescent dye from the continuous silver film using dielectric spacers which show experimental observations that agree with theoretical predictions [15]. This Letter shows that the SPCE signal progressively increases from a spacing of 0–17 nm from the silver surface, peaks at 17 nm, and then progressively

decreases in intensity at higher separation distances. Hence we believe that the silver nanoparticles in this study were not acting merely as spacer layers that lead to the varying enhancements observed, otherwise we would expect to observe a maximum SPCE signal for the 20 nm silver nanoparticle instead of the 40 nm particles as reported here.

Another strong indication for increased coupling between the excited state fluorophores and SPPs on the continuous metal surface can be obtained by measuring the ratio of the coupled SPCE signal to the Free Space signal for the samples as shown in Fig. 4. Fig. 4a–d shows the SPCE spectra and the Free Space spectra for the control, 20 nm, 40 nm and 80 nm colloid sample, respectively. Fig. 4e is a bar chart that shows the ratio of the intensity of the SPCE to the Free Space signal for all the samples studied. Note that the 0 nm colloid size shown in Fig. 4e represents the control sample, and the ratio of the signals is approximately 6.5. In this figure, we clearly see that introduction of the self-assembled colloidal nanoparticle layer leads to an increase in the ratio of SPCE to Free Space signal when compared to the control. Similar to the SPCE intensity enhancements, the SPCE to Free Space signal ratio only slightly increases with the 20 nm colloid sample to approximately 9. With the 40 nm colloid sample this ratio dramatically increases to 36 before falling off to approximately 13.5 for the 80 nm colloid sample. It is interesting to see that there is qualitative agreement between Figs. 4e and 3 (Bottom), i.e. an increase in the SPCE signal is accompanied by an increase in the ratio of the coupled SPCE to Free Space emission. We believe that nanoparticle-mediated enhancement of SPCE is similar to the nanoparticle-enhanced SPR phenomenon [18–22]. Several groups have reported large perturbations in the observed SPR curves due to the interaction of a metal nanoparticle layer with the continuous metal film that is used as the SPR substrate [18–22]. Among the many theories that have been presented to explain this effect, a principal one involves the electromagnetic coupling between LSP's on the nanoparticles and the SPP's on the metal films [18–21]. The Free Space emission shown in Fig. 4 is the far-field emission of the fluorophores into space. On the other hand, the SPCE emission shown in Fig. 4 is the result of the resonance interactions between surface plasmons in the continuous silver film and excited state fluorophores in the near-field of the silver [5,6,11–16]. This resonance interaction leads to emission by the surface plasmons into the prism side. Strict wavevector matching conditions dictate the sharp angular distribution of the SPCE signal (the SPCE signal is not a direct transmission of the fluorescence through the silver film) [5,6]. We believe the introduction of the silver nanoparticles increases the electromagnetic coupling of the excited state fluorophores with surface plasmons on the continuous silver film. Hence an increase in excited fluorophore–silver film coupling can be expected to lead to a decrease in Free Space emission as more of the excited state molecules will be coupling to the surface plasmons in the silver film. Hence in Fig. 4, the 40 nm par-
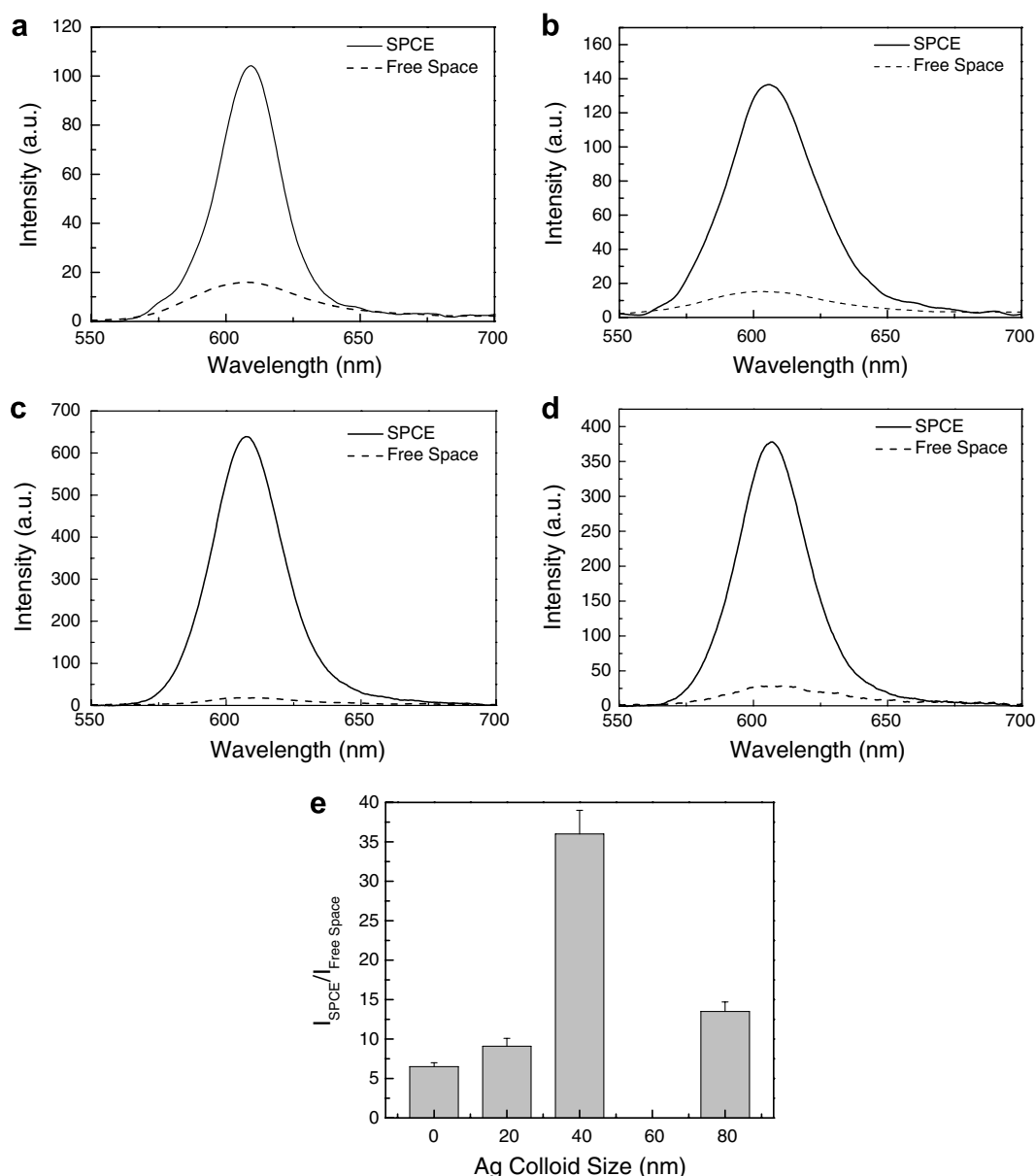
Fig. 4. Surface plasmon-coupled emission (SPCE) spectra and Free Space emission spectra from S101 in PVA on ~42 nm silver films with: (a) control, no Ag colloid, (b) 20 nm Ag colloid, (c) 40 nm Ag colloid, (d) 80 nm Ag colloid and (e) ratio of intensity of SPCE signal to Free Space signal for all the samples. Note 0 nm colloid size denotes the control sample.

ticle sample shows the highest ratio of SPCE to Free Space signal followed by the 80 nm and 20 nm particle samples, respectively. The nanoparticle-enhanced SPR effect has been used to significantly increase SPR sensitivity and hence expand the use of SPR based biosensing to a wide range of biochemical interactions [20]. Analogously, we expect nanoparticle-enhanced SPCE to also significantly increase SPCE sensitivity and thus establish SPCE as a viable tool for biological applications.

4. Conclusions

We conclude that colloidal silver nanoparticles self-assembled on top of continuous silver films can be used to increase the coupling efficiency of the excited state fluorophores to the surface plasmons in silver films, and thereby significantly enhance the SPCE signal. Of the various sizes of colloids tested, 40 nm colloids showed the greatest enhancement of the SPCE signal and highest ratio of coupled SPCE to Free Space signal. This indicates that for the given experimental configuration and colloid sizes tested, the self-assembled 40 nm silver colloid layer most effectively mediated the coupling of the excited state fluorophores with surface plasmons on the silver films. Importantly, these substrates are easy to prepare and do not require expensive nanofabrication techniques. Hence we can postulate that this setup can lay the foundations for creating improved SPCE substrates that can be employed

in myriad biological assays to increase signal collection efficiency and hence the sensitivity of such assays.

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