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Ultra-Amplification of Surface Plasmon Coupled Emission Using an Engineered Graphene-Silver Thin Film Hybrid

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Abstract: We report the selective ultra-amplification of the Surface Plasmon Coupled Emission by synergistic plasmon coupling on incorporating a novel hybrid thin film stacking of graphene on silver.

Introduction:

Fluorescence emission serves as the basis for detection in numerous assays developed in the biological sciences, biotechnology and medical diagnostics. However fluorescence methods have certain limitations that restrict its sensitivity and rapid detection levels. The techniques used so far, rely on detection of fluorescence that is isotropic in nature with emission in all directions from the point source referred to as, free space emission. This would result in poor collection efficiency and the detector typically measures close to 1% of the total signal. Lakowicz and his co-workers presented a new approach to the collection of fluorescence that can provide 50% light collection efficiency using simple optics.^[1,2] They demonstrated that the emission arising from fluorophores in the proximity of thin metal surfaces (thin films), couple with the surface plasmon modes of the metal surface, leading to directional and wavelength resolved emission. This phenomenon based on the novel fluorophore-metal surface interactions is known as Surface Plasmon Coupled Emission (SPCE). SPCE is characterized by three important aspects namely: angularity, enhancements and polarization. Surface plasmons in metals are excited only at certain angles of incidence at which maximum absorbance of incident energy occurs leading to a corresponding minimum reflectivity on the metal surface; this angle is the SPR angle. It is important to note that, SPR occurs when the incident light is p-polarized (transverse magnetic) where the electric vector is parallel to the plane of incidence. SPCE is characterized by a predominantly p-polarized emission.^[2,3] The angularity, polarization and the directional emission which occurs through a prism on which the metal+fluorophore substrate is mounted leads to enhancement in the detected signal. A directional emission occurs at the SPR angle in a symmetric manner enabling >50% of the signal to be detected with an optical fiber.

In SPCE, the thin metallic films are usually coated with around 5 nm SiO₂, to prevent oxidation and any self quenching of fluorescence which may occur at the surface of the metal. This protective coating is termed as a spacer layer which otherwise has no role in the generation of the SPCE. We chose graphene as a spacer layer for our work which has already been proven to be a passivating coating on the surface of silver for SPR experiments. However, graphene has very interesting electronic and optical properties which have been previously exploited for developing sensing platforms based on Fluorescence Resonance Energy Transfer (FRET).^[4] Graphene on silver has also been reported to support surface plasmons.^[5,6,7] We have fabricated graphene-silver substrates and subsequently performed the angularity, polarization and enhancement studies. Further, surface plasmon resonance (SPR) theory is often used to predict the angular distribution associated with SPCE and forms the basis of several commercially available software packages. The SPR angle-dependent reflectivity curves presented in this work are calculated using with TFCalc. 3.5 software (Software Spectra, Portland, OR, USA).

Experimental:

The SPCE substrate was fabricated by coating 50 nm Ag on a glass slide by thermal evaporation. The thickness was monitored by a profilometer and verified using AFM. Graphene prepared by chemical exfoliation was spin coated onto the 50 nm Ag. FT-Raman and AFM were performed to verify an overcoat of slg/blg (single layer/bi layer) on the silver. 10 μ M rhodamine b in 1% (wt.) PVA was spin coated at 3000 rpm to give a final coating profile of (50 nm Ag+ slg/blg+ 30 nm PVA-RhB). The fabricated SPCE substrate was affixed to a hemi cylindrical prism which was mounted on a sample stage. The source used is a p-polarized, 532 nm c.w. laser (5-50 mW). The detector used

is an Ocean Optics USB-4000 fiber optic spectrometer. The beam was directed onto the SPCE substrate and the angularity, polarization and enhancement studies were conducted.

To supplement the angularity data from the experiments conducted, the angle of minimum reflectivity can be modeled using the TFCalc software by feeding the input parameters such as: coating thickness, refractive index and source wavelength ($\lambda = 532$ nm). In our work, we have used the TFCalc software to model a 50 nm silver substrate which is further coated by slg-blg (single (d) / bilayer (2d) graphene, $d = 0.34$ nm), with a 30 nm PVA+ rhodamine b overcoat. The minimum reflectivity curve was generated on feeding the refractive index of graphene ($d = 0.34$ nm) as $n_z = 2.0 - 1.0i$. The emission of rhodamine b occurs around $\lambda = 580$ nm.

Results and Discussion:

The SPCE analyses for the 50 nm Ag+ slg/blg+ 30 nm PVA-RhB yielded the following results: The angularity was measured by moving the detector about the central axis of the prism until maximum signal intensity was recorded corresponding to the minimum reflectivity of the silver substrate. This angle was recorded on either sides of the prism. The angle of minimum reflectivity was predicted to be 49.8° using TFCalc Fig.1 and the experimental observation was 50° , in coherence with the simulated value. The polarization studies were performed by incorporating the polarizer in both the p and s configurations at the detector side, and the output signal was recorded. The output signal was 97% p-polarized in accordance with the SPCE theory, Fig.2. The enhancements were recorded as the ratio between the directional SPCE signal, and the free space signal which is isotropic. 10 fold signal enhancements were observed Fig.3.

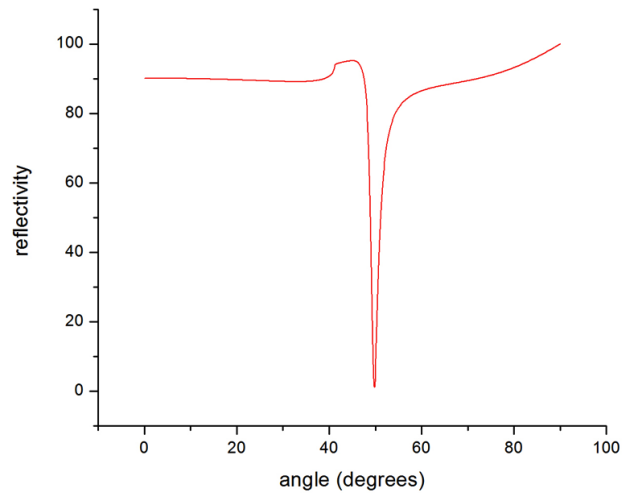


Fig. 1 Minimum reflectivity curve for (50 nm Ag+slg-blg+30 nm PVA-RhB) system at 49.8° , observed angle @ 50°

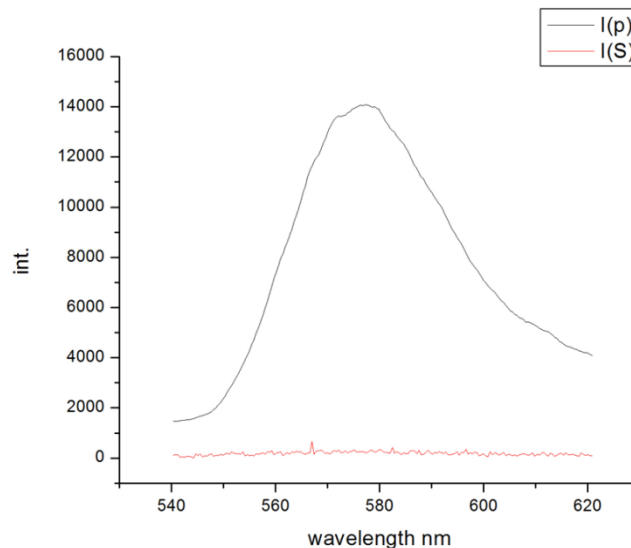


Fig.2 Polarization plot for (50 nm Ag+slg-blg+30 nm PVA-RhB) slide showing 97% p-polarization

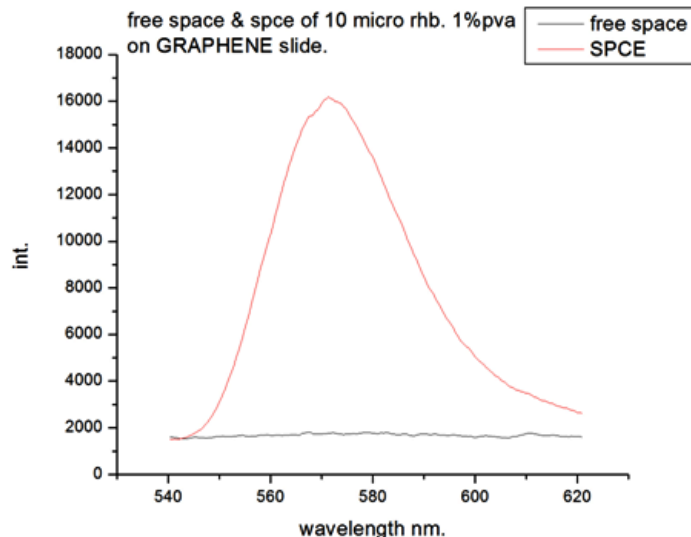


Fig.3 Graph showing 10 fold enhancements in SPCE vs. free space signal for (50 nm Ag+slg-blg+30 nm PVA-RhB) slide (RhB concentration=10 μ M)

Conclusions:

Preliminary results from our experiments show that graphene as a spacer layer leads to amplification in the SPCE signal by an order of over 2 fold in comparison to a 50 nm Ag+ 30 nm RhB-PVA system without a spacer layer, for which we have already performed the SPCE studies. The angularity and polarization studies yielded results in coherence with the SPCE theory. A 10 fold enhancement was observed which proves that, graphene is able to support the surface plasmons generated as a result of the transfer of energy, from the fluorescence of the dye to the plasmons on graphene. The propagating plasmons on the graphene sheet in turn generate SPR in the silver substrate. Further studies are being performed to understand the exact mechanism of energy transfer. We also intend to engineer graphene silver SPCE substrates with different thickness of graphene to understand the role of graphene as a function of its thickness. Such substrates can be applied to bio-sensing where low cost and high degree of sensitivity are important.

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