Chapter 7

Magnetic Nanospacers
1. Motivation:
2-dimensional electron systems have recently drawn great research interest.\(^1\) Graphene and its nanocomposites in particular have been extensively used in numerous photonics and electronic applications owing to their intrinsic 2D plasmons.\(^2,4\) Graphene’s intrinsic plasmons are unique and different from that of metallic nanoparticles.\(^5\) Grigorenko et. al explained that in order to trail the incident electric field, the π-electrons in graphene move outward and are dragged back due to disturbance of charge and overshoot again, leading to an oscillation of the electron cloud.\(^6\) In addition to this, it is also known that the plasmon losses in graphene are lesser than that in metallic nanoparticles.

Surface plasmons - electronic oscillations on metal thin films, have also been exploited extensively for plasmonic applications.\(^7\) In addition to the fluorophore-metal thin film interaction in SPCE, low-dimensional carbon materials with delocalized π-electron cloud have also shown to couple with the fluorescent molecules such as Rhodamine 6G.\(^8\) Graphene and fullerene have previously been reported as spacers in plasmon-coupled emission studies giving 40 and 30 fold enhancements respectively.\(^9,10\) Moreover, metal nanoparticles of gold and silver also exhibit substantial fluorescence enhancements. In chapter 3, we have presented the use of single layered graphene, carbon nanotubes and fullerenes (C60 and C70) as spacers that help in the coupling of fluorescence with the surface plasmons.

Recently Xie et al\(^{11}\) have reported the use of external magnetic field for modulation of surface plasmon-coupled emission. Along similar lines, current areas of research in plasmonics include the design of substrates influenced by external magnetic field, temperature, electric field, to name a few.\(^{12}\) In this context, we wanted to explore the effect of a nanomaterial’s magnetic property on the SPCE enhancements. In this chapter, we discuss the unique plasmonic properties of magnetic nanocomposites of doped graphene to achieve augmented fluorescence emission from a radiating dipole. So far a judicious combination of earth-abundant ceramic nanomaterials with cost-effective transition metals and π-conjugated materials as cavity materials and spacers in plasmon-coupled emission studies has not been reported. In this context, we have investigated the use of nanocomposites containing particles of iron carbides, oxides and nitrides on N-doped graphene (Fe-C) as hybrid spacer material for SPCE substrates.
2. Experimental methods:

2.1. Preparation of Fe-MF

Melamine formaldehyde prepolymer was prepared by heating 50 mL aqueous mixture of 2.6 g melamine and 3.7 g paraformaldehyde to obtain a transparent solution that was filtered. 10 mL of this filtered solution was taken and its pH was adjusted to 10 using 30% ammonia solution. An aqueous solution of iron salts containing 0.306g of FeSO₄·7H₂O and 0.540g of FeCl₃·6H₂O was added dropwise to the above solution under constant stirring. A light brown precipitate was obtained. To this mixture, 30mL of dil. HNO₃ (pH 3.5) was added and the entire solution was kept for aging for 80°C for 4 hrs. The resultant solid was filtered and washed several times with water and dried at 130°C for 24 hrs and labeled as Fe-MF.

2.2. Preparation of Fe-C-MF

Fe-MF was pyrolyzed in a tube furnace, in Argon atmosphere for 4 hrs at 800°C with the heating rate at 25°C/min and the cooling rate at 10°C/min to obtain Fe-C-MF.

2.3. Preparation of C-MF

To 10 mL pre-polymer solution, 30 mL of dil. HNO₃ was added and the entire solution was aged at 80°C for 4 hrs to obtain MF colloidal spheres that was filtered, washed and dried. The obtained white solid was calcined at 800°C for 4 hrs in argon atmosphere.

2.4. Preparation of α-Fe₂O₃

α-FeOOH was prepared using a known procedure. This was carbonized in Argon at 800°C to obtain hematite.

2.5. Preparation of Fe-C-PH

Fe(III) acetylacetonate 88 mg (0.25 mmol) and 1,10-phenanthroline 45 mg (0.25 mmol) were taken in a beaker containing 15 mL of ethanol and sonicated for 2 hrs. In another beaker, 280 mg of exfoliated graphene oxide in 35 mL of ethanol was taken and sonicated for 2 hrs. The suspension obtained after mixing GO suspension and Fe (III) acetylacetonate – phenonthrole complex in ethanol was sonicated for 2 hrs and then refluxed for 4 hrs. Ethanol was evaporated using rota-evaporator to give a black colored solid powder. This powder was carbonized under Argon flow of 30 mL/min at 800°C.
for 4 hrs with heating rate of 25 °C/min. Graphene oxide was synthesized using known Hummers’ method.13

2.6. Preparation of NGR

1,10-phenanthroline (45 mg) was pyrolyzed on graphene oxide (280 mg) in a tube furnace, in Argon atmosphere for 4h at 800°C with the heating rate at 25°C/min and the cooling rate at 30°C/min to obtain N-doped graphene (NGR).

2.7. Preparation of EGRO

Graphene oxide was reduced in Argon atmosphere for 4 hrs at 800°C with the heating rate at 25°C/min and the cooling rate at 30°C/min to obtain graphene (GR).

2.8. Preparation of Fe-C-PH –A

Fe-C-PH (50 mg) was treated with 30 mL HCl and washed several times with distilled water.

2.9. Plasmonic Studies:

Similar to that described in previous chapters two modes have been used namely - single layer (spacer mode) obtained when the nanomaterial / composite is admixed with Rh6G in PVA and spin coated on a silver thin film. While double layer (cavity mode) was obtained when nanomaterial / composite is dispersed in PVA and spin coated as a layer on top of a SPCE substrate. The radiating dipole was excited with a 532nm c.w. 5mW laser in reverse Kretschmann geometry. The emission was passed through a 550nm long pass filter before collecting through a fiber optic cable coupled to Ocean Optics 2000+ spectrometer. Time correlated single photon counting (TCSPC) studies were carried out with 490nm pulsed LED laser and Horiba JobinYvon TCSPC system. A Moto X mobile phone running Android Lollipop was used for SPCE imaging. An Android application named “Color Grab” was downloaded from Google Play store and was used to obtain values for CIE plot.

3. Results and discussion:

Fe-C-MF was prepared by pyrolyzing a hybrid organic-inorganic precursor nanocomposite of FeOOH and melamine formaldehyde resin (Figure 7.1), which was obtained by co-precipitating FeOOH from iron salts in the presence of melamine-Formaldehyde prepolymer14. In Figure 7.2a, the FESEM image of Fe-C-MF is shown.
with uniform distribution of nanoparticles on graphene. Microstructure of the nanoparticles were observed in the range of 100-200 nm with the use of TEM imaging, as seen in Figure 7.2b. Fe-C-PH was obtained by carbonizing Iron-1,10 phenanthroline (1:1) complex deposited on graphene. Morphology of Fe-C-PH as visualized by FESEM (Figure 7.3a) consisted of spherical iron-rich nanoparticles supported on graphene sheet. The TEM image of Fe-C-PH has been shown in Figure 7.3b. In the bright field image, dark spots are in the size range of 12-50 nm while graphene sheet was seen lighter in contrast with wrinkles appearing as dark lines. Fe-rich nanoparticles being rich in electrons must be concentrated in the darker regions.

Figure 7.1. Schematic depiction of the synthesis route adopted for the Fe-C-MF & Fe-C-PH.

Figure 7.2. Fe-C-MF sample characterization: (a) FESEM image, (b) TEM image.
The comparison of Fe-C-MF and Fe-C-PH as spacer and cavity materials in SPCE substrates has been presented in Figure 7.4. In this context, nanomaterials have been utilized in two ways to augment SPCE enhancements – (i) introducing a layer of nanomaterial between the fluorophore and the silver thin film and (ii) sandwiching the fluorophore between the nanomaterial and the silver thin film. In the former configuration, the graphene nanocomposites are sandwiched between the fluorophore and silver thin film. In the current study, the fluorescence emission from the dipole emitters present near the graphene surface couples with graphene’s π-plasmons that in turn is coupled with the silver surface plasmons resulting in a coupling cascade.

In the absence of graphene, only the fluorophores that are perpendicularly oriented to the silver surface couple with the surface plasmons. Hence graphene-free cavity shows...
less Purcell factor and enhancement. We have carried out TCSPC studies for fluorophores present on the silver thin film in the absence of graphene. The average decay time and Purcell factor for a fluorophore present in a graphene free cavity was found to be 3.272 ns and 1.131 respectively. Absence of graphene resulted in an increased decay time and lower Purcell factor in comparison with data presented in Table 7.1. This highlighted the need for graphene based cavity to achieve augmented enhancements in SPCE.

### Table 7.1. Correlation between Purcell factor and SPCE enhancements for Fe-C-PH/Ag and Fe-C-MF/Ag cavities.

<table>
<thead>
<tr>
<th>Cavity</th>
<th>$\tau_{\text{Avg}}$ (ns)</th>
<th>Purcell Factor</th>
<th>Fluorescence Enhancements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C-PH/Ag</td>
<td>0.4446</td>
<td>8.33</td>
<td>82</td>
</tr>
<tr>
<td>Fe-C-MF/Ag</td>
<td>0.4629</td>
<td>7.99</td>
<td>23</td>
</tr>
</tbody>
</table>

In chapter 3 we understood that graphene plasmons couple with dipole emitters at all angles, except for the perfectly parallel oriented emitters. This ensures that photons from additional dipole emitters are coupled into graphene plasmons. Graphene hence acts as an efficient spacer that funnels the electromagnetic radiation from the dipole emitters to couple with the silver surface plasmons resulting in augmented coupling efficiency and greater SPCE enhancements. The N-doping and loading of nanoparticles on graphene can influence this process by scattering or absorbance, perturbing the graphene plasmons. The latter configuration having the fluorophore entrapped in a nanocavity experiences the Purcell effect resulting in altered fluorescence emission and is referred to as the cavity mode. In the current thesis work, we combine the effect of nanoparticles and graphene, by fabricating a nanocomposite that could be employed as both a spacer and a cavity material. The nanoparticles on graphene aid in amplifying the coupling efficiency in the spacer mode and in significant electromagnetic field enhancement when used in the cavity mode. We have studied the efficiency of these composites as spacer material, by monitoring their coupling of the fluorescence emission from the radiating dipole with the silver surface plasmons.

The Fe-C-MF sample showed high enhancement due to effective fluorescence coupling, resulting in high emission intensity. To understand the origin of such an enhancement in the case of Fe-C-MF, three control samples were chosen. The
unpyrolyzed precursor to Fe-C-MF that contained a homogeneous distribution of
FeOOH needles in melamine-formaldehyde resin (Fe-MF) that showed just around 30-
fold enhancement. Carbonizing FeOOH in Ar atmosphere gave hematite ($\alpha$-Fe$_2$O$_3$) and
its plasmonic activity too was fairly low as compared to Fe-C-MF. The third control,
C-MF, an N-doped graphene sample obtained by pyrolyzing melamine formaldehyde
resin, also exhibited a similar trend as that of $\alpha$-Fe$_2$O$_3$. These results indicate that the
use of only Fe or N-doped graphene cannot result in >40 fold fluorescence
enhancement. In comparison with these results, Fe-C-PH sample showed a relatively
lower enhancement as a spacer. This could be on account of lower Fe concentration and
smaller size of Fe particles in the Fe-C-PH material as compared to that of Fe-C-MF,
as inferred from the microstructure analysis. The controls, NGR, ERGO and the sample
having no iron content (achieved by acid treatment), labeled Fe-C-PH-A once again
showed a similar trend in enhancement; lower than Fe-C-PH, indicating that both these
controls are similar in their structures and properties. In addition to this, the
fluorescence enhancements reported here are higher than that reported for pure
graphene. For Fe-deposition on graphene enhances the electric field intensity resulting
in augmented fluorescence coupling with the graphene plasmons.

We further studied the emission of Rh6G in a cavity environment present
between the nanocomposite and silver thin film (Figure 7.4). As both the nanomaterial
and the radiating dipole are present in an infinitesimal volume, the close range $\pi$-$\pi$
interaction between Rh6G and graphene alters the emission enhancement. N-doping
of graphene must be reducing the $\pi$-$\pi$ interactions with Rh6G manifesting as dissimilar
enhancements from graphene and N-doped graphene cavities. In essence, fluorescence
quenching on account of $\pi$-stacking of fluorophores is reduced in the case of N-doped
graphene. Apart from this, the electronic structure and optical properties of graphene
are also reported to be affected by doping. However the precise mechanism and the
innate ability to harness amplified fluorescence enhancements by tunable doping
remains to be explored.

We believe that the size effects of the nanoparticles loaded on to the N-doped
graphene dominate the N-doping effect, accounting for the difference in enhancements
in the case of Fe-C-MF and Fe-C-PH. It is intuitive that no plasmonic coupling occurs
when the fluorophore is oriented at 0° parallel to the graphene $\pi$-plasmons. Further, the
coupling efficiency tends to a maximum when the fluorophore’s orientation angle
approaches 90° perpendicular to the graphene plasmons. Hence, as more of the non-parallel radiating dipoles are encountered in the case of NGR, an overall increase in plasmon-coupled emission intensity is seen in this sample compared to undoped ERGO. In addition to this, Fe-decoration on N-doped graphene, enhances the electric field intensity, and in turn the dipole coupling\textsuperscript{17}, resulting in amplification of fluorescence enhancement in the case of Fe-C-PH based cavity.

Figure 7.5 depicts the decay time of Rh6G trapped in between two nanocavities: Fe-C-MF/Ag and Fe-C-PH/Ag, with a slight variation in the decay times. Table 1 presents the decay time and the corresponding Purcell factor for the two different cavities. The effect of a nanocavity environment on the spontaneous emission of a fluorophore under the weak coupling regime has been determined using the Purcell factor.\textsuperscript{18} It is clear that Fe-C-MF/Ag showed lesser Purcell factor than Fe-C-PH/Ag. It is interesting to note here that both α-Fe\textsubscript{2}O\textsubscript{3} and C-MF show similar, high enhancements both as spacer and cavity materials.

![Figure 7.5. TCSPC plot showing the decay of Rh6G trapped in Fe-C-PH/Ag and Fe-C-MF/Ag cavities](image)

In addition to the large fluorescence enhancements attained using these materials, the interesting aspect of this work lies in differentiating the properties of Fe-
C-MF and Fe-C-PH, synthesized via pyrolysis process. They mainly differ in the weight ratio of Fe/C and relative concentration of inorganic phases. It is intuitive that the active sites required for an efficient plasmonic coupling involves a combination of phases in an appropriate stoichiometry along with suitable interfaces. Pyrolysis of Fe salts/complexes (containing N) on graphene can generate doubly coordinated Fe to nitrogen on graphene (FeN₂/C) or tetra coordinated species (FeN₄/C). It is probable that the density and combination of FeN₂/C and FeN₄/C active sites formed during the pyrolysis for Fe-C-MF and Fe-C-PH are different. This difference will impact the electric field coupling with the graphene plasmons. Recently, the role of surface plasmons in the Casimir effect was investigated. Also, the effect of fundamental graphene-graphene Casimir interaction has an impact on the optical and plasmonic properties of graphene. We believe that the extent of Casimir effect between the graphene folds or stacks in Fe-C-MF and Fe-C-PH also influences the graphene plasmons directly, by affecting their efficiency in achieving augmented fluorescence enhancements. Interestingly the Casimir effect is also expected to be higher for magnetic materials. Since both Fe-C-MF and Fe-C-PH are magnetic, given their size difference, we postulate that the plasmonic enhancements could be further tuned by tapping their magnetic Casimir effect that influences the graphene plasmon intensity.

This thesis work has also extended our mobile phone based SPCE technology to observe the change in plasmon-coupled fluorescence emission based on both the Casimir effect and Purcell effect. A mobile camera was used as a detector and the directional emissions were captured as images (Figure 4a) and processed using an Android freeware to obtain the corresponding values based on Commission Internationale de leclairge (CIE) xY 1931 color space. The CIE plot or chromaticity plot clearly shows the influence of the two materials of interest: Fe-C-MF and Fe-C-PH on the emission profile of Rh6G (Figure 7.6).
4. Conclusion:
This chapter describes the first time use of Fe-C composites as spacers by attaining 116 fold SPCE signal enhancement. Augmented emission was the net result of coupling with the graphene plasmons and enhanced electric field, ‘hot-spot’ intensity, due to Fe-deposition on graphene. In case of nanocavities, we have presented the correlation between plasmon-coupled fluorescence enhancements, Purcell Factor and Casimir effect. Distinct performance of the composite as a SPCE spacer material was seen based on the synthetic route adopted and choice of graphene/N-doped graphene template. We believe that the ability to tune the performance of these hybrid composites as cavity material or spacers, in addition to altering its coupling with a radiating dipole, can pave way to interesting applications in future.

5. References:


