In this chapter, a detailed account of the methods/techniques used as part of this thesis work has been presented:

1. Spin-coating:
In the preparation of thin films, spin coating is a common technique used widely in both industries and academia. Other techniques such as dip coating, drop-casting exist for forming a thin film, however spin-coating has its advantage of being a swift and a concise procedure. Spin coating is capable of producing uniform thin films with thickness ranging from few nanometers to microns.

Spin coating has been used for application in thin film electronics, semiconductor research and nanotechnology. The typical process involves mounting of the substrate (often glass slide or silicon wafer) on to a rotating disc which has vacuum provision to hold the substrate in place. The desired material of interest like polymer or colloidal solution was dropped on the center of the substrate. The speed and duration of coating was then set to a value of interest. As the substrate began to spin, the centripetal force ensured the uniform spread of the material over the substrate. The excess material was thrown off the edges of the substrate. Simultaneously the evaporation of the volatile solvent present in the material resulted in giving a uniform dry thin film. Apart from the rotation speed and duration, the thickness of the film depends on various factors like viscosity, surface tension, suspended particles, evaporation rate, to name a few.

In this research work, Spektrospin - 10k - a digitally controlled spin coater unit manufactured by Spektron Instruments Inc., India, was used (Figure 2.1). A single step programming was utilized with an acceleration time of 10 sec to reach the desired speed and it was maintained there for the required time period. After this the spinning was allowed to decelerate and stop in 10 sec.

![Figure 2.1. Spin coater.](image)
2. **SPCE instrumentation:**
The SPCE platform was home built based on the original set up as described by Smith D et al. and Gryczynski et al. The set up consisted of 2 rotating stages (Figure 2.2a). One used for mounting the sample (prism with silver substrate) and the other for housing the optic fiber that collects the angular emission. The sample holder was made of rubber material upon which the sample could be placed. A hemi-cylindrical prism was used for all the studies. Excitation in all of the SPCE experiments was accomplished with a continuous wave laser (532 nm of power 5-50mW with TE cooled module was used, until mentioned otherwise) that was fixed in position as all the experiments were performed in reverse Krectshmann (RK) configuration. The excitation spot size was controlled with an aperture. The emission was collected by the optic fiber after passing through a filter to screen the excitation beam. A sheet polarizer was manually placed between the prism and the filter to observe the polarization of SPCE. The rotating stage was used to move the collecting optic fiber to observe the SPCE angular emission. The fiber was coupled to an Ocean Optics 2000+ Spectrometer. In case of mobile phone based SPCE, the mobile phone was mounted on the rotating stage in the place of the optic fiber (Figure 2.2b). The filter and polarizer were attached to the front side of the mobile camera with a tape. Further processing of the image was done using an Android application available from the Google play store.

![Figure 2.2. a) SPCE setup with detector a) spectrometer and b) mobile phone.](image)

3. **Time-correlated Single Photon counting (TCSPC):**
TCSPC is a technique used to determine the lifetime of a fluorophore. Typically a short laser pulse was used to excite the sample of interest. The emission profile was plotted with respect to time it took to arrive at the detector. This allows one to determine the decay profile and the resolve the multi-exponential decays. The excitation pulse was split into reference pulse and the sample pulse which was compared to extract the actual lifetime. TCSPC in this work was carried out to determine the time resolved fluorescence decay profile of Rhodamine dyes in different spacer and cavity
environment. The excitation source used was 490 nm pulsed LED. The emission intensities were counted by Horiba Jobin Yvon TCSPC system (Figure 2.3) and the fluorescence decay was analyzed using IBH- DAS V6.2. The TCSPC facility present at National Center for Ultra-fast Processes, Taramani Campus, University of Madras, Chennai was utilized for all of the experiments.

4. Electron Microscopy:
The constraints of magnification and resolution of light microscopes has led to the development of electron microscopes. In an electron microscope, electron beams of high energy are used to image the material of interest. This provides information regarding the morphology and topography of the material. The two main types of electron microscopes used widely are Transmission electron microscope (TEM) and Scanning electron microscope (SEM).

In SEM, the surface of the material of interest is scanned with the electron beam i.e. the electrons reflected/scattered off the surface of the material is captured. Hence the imaging provides us with the information regarding the surface related details such as topography and composition. On the other hand, TEM as the name suggests “tunnels” or beams the electron beams into the object. Thus giving a view of the material inside its surface and is capable of viewing upto individual atoms. In terms of resolution and magnification, TEM has upper hand and in terms of depth of the image captured than SEM. With respect to sample preparation, SEM is advantageous as TEM requires ultra-thin samples and preparation of which generally takes longer time. In this thesis work, SEM and TEM have been used to characterize the metal loaded carbon nanomaterials.

5. Simulation methods:
5.1. SPR angle simulations:
Angular reflectivity curves for optical thin film coatings can be computationally determined using TF,Calc., by Software Spectra Inc. As the SPR reflectivity minimum angle is the expected angle of plasmon-coupled emission for a given thin film stack, this simulation helps to validate the observed SPCE. This software can also be used to compute changes in the electric field intensity of an incident beam when passed through different thin film coatings. In this thesis work, the refractive index of various thin films was used to determine the theoretical angle of SPCE emission and also to optimize the DNA bio-spacer for enriched output.
5.2. Finite-Difference Time-Domain Simulations (FDTD):
FDTD or Yee’s method is a versatile tool for computational electrodynamics. This technique has wide range of applications including plasmonics. This grid-based differential method solves Maxwell’s equations to arrive at the steady state electromagnetic field behavior. We have used Lumerical’s ‘FDTD Solutions’ for determining the coupling of radiating dipoles with graphene plasmons, intensity of the electromagnetic field at the hot-spots between various spacer materials and silver thin film.