

**Confocal Raman Microscopy Study on Interactions and Transport of
Polymers with Nanomaterials**

by

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ABSTRACT

The overall goal of this thesis is to understand the interaction of polymers with carbon-based nanomaterials, specially graphene, and the polymer dynamics for the adsorption and diffusion of polymer chains into nanoporous particles in solution. In particular, we have taken advantage of the *in-situ* and high resolution image capability of confocal Raman microscopy (CRM) to characterize the water wettability and oxidative stability of graphene, the interactions between polymers and graphene, and the polymer diffusivity thorough nanopores.

The first chapter is an overview to introduce how the CRM technique can serve as an important characterization tool to study polymer-based nanomaterials. This chapter also summarizes how the following chapters are interrelated to advance our knowledge on the interactions and transport of polymers with nanomaterials. This chapter briefly presents how CRM can be useful in graphene research to understand (i) the water wettability and oxidative stability of graphene and (ii) polymer/graphene interactions. Using nanoporous silica, this chapter also introduces how the time-resolved image capability of CRM is used to study the polymer dynamics in solution under the confined geometry of nanoporous channels.

The second chapter describes the theoretical prediction and experimental verification of the spatial image resolution in CRM. For the first time, a single layer graphene on SiO₂ (300 nm)/Si substrate was used as an image resolution calibration standard to quantitatively and simultaneously measure the lateral resolution (LR_x) and depth resolution (DR_z). Our enhanced ability to quantitatively measure the image resolutions of CRM had eventually leaded us to elucidate the wettability of graphene immersed in water. Upon comparing the values of DR_z using different types of water for the same immersive objective lens, an evidence of forming an “air pocket” on top of graphene surface is identified. Specifically, I found DR_z values of 1.61 μm, 1.95 μm, and 2.81 μm when degassed water, “normal water” (i.e. un-degassed H₂O), and heavy water (i.e. un-degassed D₂O), respectively. Interestingly, the evidence of enhanced water wettability was not observed, in terms of CRM depth broadening of oxidized graphene immersed in water. When oxidized graphene is used with un-degassed water, we found that the value of DR_z is 1.94 μm. Those results show that dissolved gas and

hydrogen bonding in water play a critical role in controlling the water wettability of graphene particularly when the graphene layer is immersed in water.

The third chapter presents our original investigations on the oxidative stability of graphene in air upon the irradiation of light. Two different kinds of light sources have been employed; (i) “focused” laser by objective lens using monochromatic visible light (wavelength, $\lambda = 532$ nm) and (ii) ultra-violet/ozone using a mercury arc lamp. When an incident laser power (I_0) over 2 mW is used, graphene could be locally oxidized to form an oxidized graphene spot with radius of 0.3 μm upon focusing the light by an objective lens with 100x magnification. UV/ozone (power density = 27mW/cm²) shows evidence of graphene oxidation from CRM D band images after 5mins of irradiation. In the case of ozone-free UV light irradiation (33mW/cm²), graphene remains stable in air. We found that CRM images based on G and D bands from graphene are complementary. While G-band imaging is useful for pristine graphene sample with a different number of layers, D-band imaging provides more sensitive morphological evidence of oxidation in graphene. Oxidation of graphene under UV/Ozone is prone to occur on the edge regions of graphene. Our study on the oxidation of graphene will eventually provide us with opportunities to functionalize and pattern graphene.

The fourth chapter, *high image resolution* capability has been applied to extensively study Raman phonon vibration of graphene at various locations in a graphene “patch” on different substrates. Using various organic substrates of self-assembled monolayers (SAM) and polymers, the surface interactions between graphene and underlying substrates have been studied by monitoring the Raman G band shifts of the graphene. Understanding of such interactions between graphene and organic substrates is critical to controlling the properties of graphene-based electronic devices and polymer nanocomposites. When a graphene patch is deposited via the mechanical exfoliation of graphite on SiO₂ (300 nm)/Si substrates, a large graphene patch could be obtained. To study the edge effects on phonon vibration and interaction between graphene and polymer substrates, we have used statistical Raman data to investigate G band peak position and band width. The peak position and band width are correlated with materials properties of substrates. This allowed us to study the edge effects on the Raman phonon vibrations in a graphene patch. We found that the G band peak position

shifts from $1589.0 \pm 1.1 \text{ cm}^{-1}$ to $1593.2 \pm 1.3 \text{ cm}^{-1}$, where investigating graphene locations are from “Center” to “Edge”, respectively. The graphene phonon vibration should be affected whether the vibration occurs at the edge or center of a graphene patch. When organic and polymer substrates are used to study the surface interaction between graphene and substrates, G bands from graphene on varied substrates are shifted by the substrate’s properties. In the case of glassy polymers (PS, PMMA) and a rubbery polymer (SIS), their G band positions are similar to G-bands position of “Center” of graphene on bare SiO_2/Si wafer. When the substrate is FTS coated on SiO_2/Si substrate, the G-band position follows the “Edge” location of graphene on SiO_2/Si substrate. It is noted that the graphene phonon vibrations are related with surface properties, particularly adhesion with graphene. Our study elucidates that Raman spectra enable to study effect of substrate with graphene. Specifically, CRM could be powerfully applied to acquire images of graphene on substrate to analyze interphase interaction.

The fifth chapter, the *in-situ* image capability has been applied to quantitatively estimate the polymer chain diffusivity in nanopores based on the time-dependent concentration profiles of polymers within nanoporous particles. In particular, we have focused on how the size interplay between the polymer chains (R_g) and nanopores (R_p) affects the polymer adsorption and diffusion in the confined geometry of a nanoporous channel. We have chosen monodisperse polystyrene (PS) of three different molecular weights, 1,800 g/mol, 18,000 g/mol, and 102,000 g/mol in cyclohexane solution with NucleosilTM nanoporous silica particles with an average particle diameter of 6.88 μm and $R_p = 7.1 \text{ nm}$. This experimental choice, thus, allow us to study the size interplay between R_g and R_p for the polymer nanopore adsorption in the range of $R_g/R_p = 0.2, 0.6$ and 1.4 for the polymer adsorption and diffusion in solution into nanopores. When the R_g of PS in cyclohexane is smaller than R_p of the nanoporous silica (i.e. $R_g/R_p = 0.2$ and 0.6), the PS chains adsorb and eventually diffuse into the core from the nanopore openings in the micron-sized nanoporous silica particles. Based on the computational modeling of solute diffusion in spherical coordinate, we found that the chain diffusivity in a nanoporous channel ($D_{\text{pore}} = 3.5 \times 10^{-11} \text{ cm}^2/\text{s}$) in this case of $R_g/R_p = 0.6$. This corresponds to approximately four orders of magnitude in slowing down the polymer diffusion upon the confinement of nanopores, because the free chain diffusivity for PS

(18,000 g/mol) is estimated to be 8.38×10^{-7} cm²/s in cyclohexane based on the Stokes-Einstein equation.