Utilizing Hybrid Plasmon Modes to Probe Nanoparticle-Polymer Interfaces

By

Michael Bushell

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Department of Chemistry, acceptance of the thesis

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Dr. Anatoli Ianoou

Abstract

Nanoparticle-polymer composite materials have widespread applications in fields such as: sensing, electronics, and biology, due to their desirable physical properties. However, many fabrication techniques render little control over nanoparticle incorporation, and homogeneity of the resulting material. This thesis focuses on the thermally induced embedding of silver nanocubes (AgNCs) into polymer surfaces. The AgNCs were deposited onto polymer films, through a Langmuir approach, which allows fine control over nanoparticle density in the monolayer. The AgNC monolayer was then heated above the glass transition temperature of the polymer, which facilitates the irreversible incorporation of the AgNCs. Embedding of the AgNCs were monitored in real-time, through spatially separated hybrid plasmonic resonances supported by the AgNCs when deposited onto the polymer film, which allowed the determination of a surface layer on top of the bulk polymer with enhanced mobility as well as diffusion constants for the embedding process.

Preface

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Chapter 1:

Section 1.3

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Chapter 3:

Section 3.1

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Chapter 6:

Appendix B

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List of abbreviations

PVP: Polyvinylpyrrolidone

PS: Polystyrene

PVC: Polyvinylchloride

PMMA: Poly(methyl methacrylate)

P2VP: Poly(2-vinylpyridine)

LS: Langmuir-Schaefer

EG: Ethylene Glycol

THF: Tetrahydrofuran

UV-Vis: Ultraviolet-Visible

LSPR: Local Surface Plasmonic Resonance

SPR: Surface Plasmonic Resonance

AFM: Atomic Force Microscopy

RPM: Revolutions Per Minute

T_g: Glass Transition Temperature

λ : Wavelength

ϵ : Dielectric constant

E: Electric field

ω : Frequency

FCC: Face-Centered Cubic

SERS: Surface Enhanced Raman Scattering

MW: Molecular weight

K: Kelvin

°C: degrees Celsius

nm: nanometer

Da: Atomic mass unit or Dalton

W: Watt

TFSF: Total-field scattered-field

1 – Introduction

1.1 Motivation and outline

Polymer films have widespread application in many fields from biology to electronics, as they are cost-effective and have many useful properties including: conductivity,¹ biocompatibility,² rubberiness,³ and physical/chemical robustness.^{4,5} This makes polymer materials useful in a variety of applications: as protective, optical or dielectric coatings, lubricants, adhesives, and synthetic membranes, to name a few. A common approach to optimize these polymer materials is through the incorporation of inorganic substances, forming hybrid polymer materials. Specifically, the incorporation of inorganic nanoparticles into polymer films is of interest, as it can enhance polymer physical properties such as, film stability and organic solar cell efficiency.^{6–9} More importantly, a polymer coating can enhance nanoparticle properties such as: biocompatibility, facilitating targeted drug delivery,¹⁰ sensing,¹¹ and conductivity, allowing for flexible electronics¹² and specific interactions between polymers can even allow directed assembly of nanoparticles.¹³

Some of the more interesting applications involve incorporation of conductive^{8,9,14} or semi-conducting¹⁵ nanoparticles into a conductive polymer film: this can drastically change the sheet resistance of the film, which in tandem with the increased absorption of light, makes incorporating nanoparticles into these polymers of great interest for organic solar cells.^{8,15} However, fine control over nanoparticle embedding and concentration of

nanoparticles is necessary in order to minimize charge recombination at the metal sites, which can cause a decrease in external quantum efficiency of the solar cell.^{8,9}

A common technique to make these composite materials involves mixing of a polymer and nanoparticle solution, then subsequent casting, typically via spin coating.⁶ This technique renders little control over the embedment depth and interparticle distances. A more precise technique is the synthesis of nanoparticles in a polymer matrix or vice versa.¹⁶ However, it is challenging to control the size and concentration of particles and the polymer simultaneously.

This thesis focuses on the production and characterisation of silver nanocube (AgNC)-polymer nanocomposites and their use as a far-field nanoruler, capable of measuring polymer physical properties. The AgNCs can embed into the polymer film through an irreversible, thermally activated diffusion process. The embedding of the AgNCs can be monitored in real-time, through spatially separated hybrid plasmonic resonances supported by the AgNCs when deposited onto a dielectric substrate, such as a polymer film. Effectively making the nanocomposite a far-field nanoruler, using a spectrophotometer to measure the nanoscale position of the AgNCs in respect to the polymer. This nanoruler aspect of the nanocomposite allows for fine control over AgNC embedment, which can be monitored in real-time using a simple far-field spectrophotometer. The deposition of the AgNCs was done through a separate Langmuir process, which allows excellent control over interparticle distances within the nanocube monolayer. Overall, this forms a controllable novel technique to produce optimized nanocomposite materials.

The nanoruler aspect of the AgNCs was also used to determine the diffusion constants for the embedding process. Utilizing the embedding data, an Arrhenius relationship was used to determine the activation energy of the process for three different homopolymers. The extreme spatial sensitivity that the AgNCs have to their local refractive index allowed the confirmation of a surface layer on top of the bulk polymer, with enhanced segmental relaxation, signified as a lower embedding temperature than the bulk polymer. Applying the information obtained from the diffusion dynamics for homopolymer films, AgNCs were embedded into discrete polymer domains within immiscible polymer blends. The nanoruler aspect of the AgNCs allowed determination of enhanced surface confinement effects for some polymer blends, with the bulk polymers dynamics unchanged. This brings exciting insight into interfacial interactions within blended polymer-nanoparticle materials, as well as a tool to selectively embed metal nanoparticles into discrete polymer domains, which can be further generalized to other metal nanoparticles or segmented polymers, such as block copolymers. This work emphasizes a simple, controllable way to alter polymer properties using heat, which is of great interest in the production of useful functional materials.

The final project focuses on preliminary work revolving around using AgNC's strong plasmonic modes to catalyze chemical reactions. In this work, polystyrene was grown on AgNCs through the free-radical polymerization of styrene through plasmonic heating and hot carrier processes. The plasmonic heating process relied on photothermal heating of the AgNC's to produce the necessary energy to form benzoyl radicals, which initiates the polymerization reaction. The second method utilized hot carrier generation from AgNC's plasmon modes to initiate the styrene polymerization reaction. Both

methods featured similar trends, with high effective powers causing thermal decomposition of the polystyrene coating, and low powers having a circular coating, representative of the incident Gaussian laser beam. This preliminary study brings an interesting approach for multi-coloured printing and with optimization sub-diffraction-limited polymer patterning.

The following introduction sections give an in-depth overview on the necessary theory for the mechanism of the plasmonic based nanoruler. The first section focuses on the general theory of plasmons, plasmonic properties within metal nanoparticles, and their interaction with other nanoparticles and dielectric environments through the formation of hybrid plasmonic modes. This section is significant in order to understand the scope of plasmon based sensing platform used in this thesis. The next section focuses on polymers and their dynamics. It also introduces theory on surface confinement effects and justification for segregated domains within an immiscible polymer blend. Following this is a description of the thermally activated irreversible embedment of metal nanoparticles into polymer surfaces. This section goes into detail on the thermodynamics for the process, and the plasmonic shifts associated with the embedding of the AgNCs, which is vital to understand the kinetic data obtained from the UV-Vis measurements. The final section highlights classical approaches to measure surface dynamics of polymer films. This is important as it effectively compares the nanoruler technique used in this thesis and its applicability within polymer science.

Additional information (Appendices) on less pertinent topics can be found in Chapter 6, including information on nanoparticle synthesis (with an emphasis on the polyol approach for AgNCs) and deposition of AgNCs onto substrates (with emphasis on

the Langmuir technique). A brief overview of Maxwell's equations, and the Finite Difference Time Domain (FDTD) method is also in Chapter 6, due to the prevalence of FDTD simulations used in this thesis to model optical properties of materials.

Subsequent sections (Sections E and F) provide information on the free-radical polymerization of styrene and a simplistic description plasmonic heating. Specifically, the section on the free-radical polymerization of styrene gives necessary background on the process utilizing a free-radical initiator. This is vital to understand the affect of an initiator on the free radical process for styrene. The following section provides a basic mechanism for plasmonic heating (photothermal heating), and the desirable traits for the plasmonic material. This section is significant as it brings insight on the photothermal effect and the affect of absorption, and thermal conductivity on the local temperature increase. This is vital to describe the experimentally observed polymerization and thermal degradation of polystyrene.

1.2 Plasmonics

Plasmonics is the study of the interaction between delocalized electrons of a metal and the electromagnetic field associated with light. A plasmon can simply be defined using classical electromagnetics as free electrons in the conduction band of the metal excited by the electric field component of light.¹⁷ The electric field applies a force causing the electrons to collectively oscillate: this oscillation is strongest when the electric field is in resonance with the electrons.^{18,19} In general, these plasmons propagate along the surface

of the metal, and these surface plasmon resonances (SPR) are sensitive to the morphology of the metal particles and to their local environment.^{18–20}

1.2.1 Localized surface plasmonic resonance (LSPR)

Surface plasmon polaritons are propagating electromagnetic waves along the surface of a conducting material, which results from the interaction of incident light and the free electrons in the conductor. When a surface plasmon is confined to a particle size smaller than the wavelength of light, the particle's free electrons oscillate locally around the particle, which is called localized surface plasmon resonance (LSPR).¹⁷ The electric field associated with light applies a force on the electrons in the conduction band of the metal, causing the electrons to oscillate.^{17,21} As seen in Figure 1.1 the electrons' collective oscillation causes charge separation due to the oscillating electric field, and a restoring force is applied to the electrons in an attempt to return them to their original state.^{17,18,21} The perturbation due to the incident electric field and the natural restoring force of the electrons causes the coherent resonant oscillation of the electrons in the conduction band of the metal. The associated LSPR enhances electromagnetic fields close to the particles surface and the particle's extinction has a maximum at the plasmon resonance frequency.^{17,18} The extinction of a particle is defined as, the sum of its absorbed and scattered light, as a result it is considered unitless. The extinction of the LSPR is sensitive to the composition,²² size,²³ shape²⁴ and dielectric surroundings²⁵ of the material, which allows tuning of the LSPR energy.^{17,18}

Figure 1.1: Illustration of a localized surface plasmon resonance and the electric field associated to the surface of the nanoparticle

1.2.2 Simple plasmonic models

To model the interaction of light with matter, a cross-sectional approach is typically used, as it factors out the geometric shape of the particle. A particle's optical cross-section represents the loss of energy (by scattering or absorption) from an incident light source and has units of area. The extinction of light (σ_{ext}) by a plasmonic nanoparticle can be represented as a sum of the scattering (C_{sca}) and absorption (C_{abs}) cross-sections of an electromagnetic wave propagating towards a single particle, multiplied by the total concentration of the particles ($\mathcal{N}$) (Equation 1).¹⁹

$$\sigma_{ext} = \mathcal{N}(C_{abs} + C_{sca}) \quad (1)$$

The extinction of a material can be defined by its dielectric function (ϵ), which represents the interaction of the materials electrons with light. The dielectric function is complex, and the real part is related to the slowing of the propagation of light, as described by the refractive index, while the imaginary part is related to the loss of energy, by absorption or scattering of light. The optical response of a nanoparticle can be characterised by the materials dielectric function, which can be obtained by solving Maxwell's equations (Appendices, A.1). A German physicist, Gustav Mie in 1908, found an exact solution to Maxwell's equations associated with the optical response of a sphere

immersed in a homogeneous medium, excited by a monochromatic electromagnetic plane wave.²⁶ However, in the majority of applications, perfectly spherical nanoparticles equally dispersed into a uniform electromagnetic medium is unrealistic. Unfortunately, exact solutions to non-spherical particles are very challenging, and as a result Mie-scattering approach is often used as an approximation.²⁷

There exist many ways to model a materials interaction with light, such as: time dependant density functional theory,²⁸ discrete dipole approximation,²⁹ T-matrix,³⁰ and finite differential methods.^{31,32} In all methods, the material is simulated based on its permittivity. A metals absolute permittivity (ϵ_{abs}) describes the polarizability of the metals electrons influenced by an electric field, with a high permittivity representing a high resistance to the electric field. Relative permittivity, often called a dielectric constant (ϵ) is the quotient of the absolute permittivity and the permittivity in a vacuum, by definition, the dielectric constant of a material (ϵ_m) will always be greater than 1. An experimental bulk dielectric function has contributions from interband (inter) and intraband (intra) electronic transistions.¹⁹ The experimental dielectric function (ϵ_{exp}) is usually considered the sum of the inter and intra contributions (Equation 2).

$$\epsilon_{exp}(\omega) = \epsilon_{inter}(\omega) + \epsilon_{intra}(\omega) \quad (2)$$

Interband contributions are due to electron transitions from occupied to unoccupied electronic bands, which are separated by an energy gap. Excited interband electrons relax due to restoring forces, defined by the energy difference between the excited and ground state, typically thought of as electron-hole pair recombination. Intraband transitions are small, inherently forbidden electronic transitions at the Fermi level, typically generated by small energies (wavelength $\gg$ unit cell size) and allowed by phonon

vibrations. The excited electrons in an intraband transition are essentially free; thus, classical models can predict their energies.¹⁹ One such bulk model is the Drude model, which can be modified to approximate the extinction cross section (C_{ext}) of a dilute concentration of small spherical nanoparticles of radius (R), in a homogenous dielectric medium (ε_m) (Equation 3).³³ At the resonance condition, the extinction cross-section becomes very large; this condition is met when $\varepsilon_r + 2\varepsilon_m$ approaches 0, and ε_i^2 is very small.^{33,34}

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{\frac{3}{2}}}{\lambda} \left(\frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2} \right) \quad (3)$$

The Drude model makes many important assumptions, specifically that electron-electron collisions are linear, Coulombic interactions between electrons are negligible (independent electron approximation), and that there are no long-range ion-electron interactions. The last assumption is largely invalid, as electron collisions with the now charged metal atoms are probable and could lead to ionization or charge recombination. With these assumptions, electron collisions will only be with other electrons, and the probability of these collisions is independent of the electron's velocity and position, which is valid due to the large number of electrons in the system.

Since the Drude model pertains the free oscillation of electrons with respect to a charged metal particle, it can be used to model a dipolar plasmon. Equation 4 represents that approximation for a dipolar plasmon frequency, assuming a small spherical metal nanoparticle (diameter ≤ 10 nm). A material's dielectric function is complex, which equals the sum of the real (ε_r) and imaginary (ε_i) components. For intraband transitions, the real part of the dielectric function can be represented as Equation 4.¹⁹

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega \left(\omega + \frac{i}{\tau} \right)} \Rightarrow 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (4)$$

Where ε_r represents the real component of the dielectric function, ω_p is the bulk plasmonic frequency, ω is the frequency of incident radiation. Since a random electron's mean free path at room temperature is now of a comparable size to the particle, typically a few nanometers,¹⁹ a new dampening term (τ) needs to be introduced that takes into account the surface scattering of electrons. This term is a function of any characteristic that changes the mean free path of the free electrons (e.g. the size and shape of the nanoparticle).³⁵ For simplicity, a new term is often considered, γ , which represents the dampening force parameter ($\omega i/\tau$). Equation 4 can be re-arranged to find the bulk plasmonic frequency (Equation 5).

$$\omega_p = \sqrt{(1 - \varepsilon_r)(\omega^2 + \gamma^2)} \quad (5)$$

Since the incident radiation is typically in the visible-near IR range. $\gamma \ll \omega$; and the resonance condition by MIE theory, $\varepsilon_r = -2\varepsilon_m$, Equation 4 can be further simplified and solved in respect to the resonant excitation frequency (Equation 6).³⁶

$$\omega_{\max} = \frac{\omega_p}{(2\varepsilon_m + 1)^{\frac{1}{2}}} \quad (6)$$

1.2.3 Choice of metal nanostructure

As mentioned, plasmons are extremely sensitive to changes in their electric field: by changing the shape or permittivity of the material, its plasmon frequency can be tuned across a wide range of wavelengths.^{21,33,35} As the size of a nanoparticle increases there is a decrease in the restoring force, which dampens the oscillations, causing a lowering

in the resonant frequency. The effect can also be explained: as the nanoparticles' size increases the electron cloud experiences more delocalization, thus, increasing depolarization, which dampens the electron oscillations to lower energies.³⁷ Therefore, as particle size increases the LSPR red-shifts.

For small spherical nanoparticles there is a dipolar distribution of charge at the surface (Figure 1.1). However, as the size of the nanoparticle increases multipolar charge distributions arise, forming higher order resonances. Specifically, these higher order plasmons feature higher angular momenta, and because of this are at a higher energy. Aside from a dipolar mode (D), another important plasmonic mode for this work is the quadrupolar plasmonic mode (Q).

Aside from size, the shape of the metal nanoparticle plays a significant role in the extinction of the nanoparticles. Specifically, edges and vertexes help facilitate the multipolar charge distributions, needed for higher order resonances, even in small nanoparticles.¹⁹ Spectrophotometry can be used to measure the extinction of a plasmonic material, the corresponding width and shape of the extinction peaks in a UV-Vis spectrum can give an idea on how sharp or rounded the edges are, because the more rounded the edges, the broader and higher energy the resonances. This is due to less delocalization of the electron clouds, which causes a smaller restoring force.¹⁹ Charge accumulation at the vertexes and edges of cubic nanoparticles causes an extremely high electric field intensity, thus nanoparticles with many edges and vertexes such as polyhedrons, will be more sensitive to their local electric environment.¹⁷ The Quality factor (Q) is a numerical representation for the sharpness/narrowness of a plasmon, which is desirable because it leads to stronger local-field enhancement and refractive index sensitivity. Silver can

support a strong surface plasmon from 300 - 1200 nm. In fact, silver has the largest Quality factor over this range (Equation 7),²¹ making silver desirable for plasmonic sensors.

$$Q = \frac{\omega \left(\frac{d\varepsilon_r}{d\omega} \right)}{2(\varepsilon_i)^2} \quad (7)$$

Where ω , is the angular frequency of light and ε_i , is the imaginary dielectric function and ε_r , is the real dielectric function for the plasmonic material.

1.2.4 Coupling of plasmons

When plasmonic nanoparticles are close together their plasmonic modes can couple together, which generally results in a new red-shifted plasmonic mode. A simple description of this effect is illustrated in Figure 1.2. Two nearby oscillating dipoles can interact depending on the polarization of incident light in respect to the particles, forming parallel or perpendicular coupling modes. Only the oscillations parallel to the incident beam will interact with the light, exhibiting a “bright mode”. For a particle, the perpendicular modes are thought of as “dark modes” as it does not form a net electronic dipole, and thus, is not observed in the extinction spectra. The bright mode will be heavily

Figure 1.2: illustration of the parallel and perpendicular coupling modes in a nanoparticle dimer, with ω_p representing the frequency of incident light.

red-shifted as expressed in Figure 1.3, while the dark mode will be slightly blue-shifted (Figure 1.3).

Figure 1.3: Plasmon hybridization scheme of two dipolar modes in a nanoparticle dimer. The two modes will mix to form an asymmetrically coupled anti-bonding mode and symmetrically coupled bonding mode.

Coupling of plasmons can be represented by hybridization arguments. Analogous to molecular orbital overlap, plasmons can mix in an electromagnetic analogue forming new hybridized modes as seen in Figure 1.3.^{31,38} Figure 1.3 shows the hybridization scheme between two dipolar plasmonic modes, these modes mix to form a low energy 'bonding' mode and a higher energy 'anti-bonding' mode. The anti-bonding mode has no net dipole moment upon illumination with planar light, and therefore, is not easily excited by incident light, this type of plasmon is commonly called a dark plasmon resonance or a dark mode.¹⁸ The bonding mode however, is a bright plasmon and will result in a strong LSPR mode, red-shifted to the original dipole. The difference in energy of these new hybridized modes increases as the interaction between the two original plasmons increases, assuming no quantum tunnelling.^{39,40} Thus, as the particles come closer together the energy splitting becomes larger. Interestingly, the splitting between the bonding and anti-bonding modes is asymmetric, since the anti-bonding mode undergoes

a small blue shift when compared to the larger red shift in the bonding resonance. A fascinating consequence of the hybridization model is the ability for higher order modes (higher angular momenta) in plasmonic particles to couple together. This can form new bright hybrid plasmon modes from inherently dark plasmons,^{31,41} which will be further explored in the next section.

1.2.5 Plasmon-dielectric substrate interactions

As previously discussed, the surface plasmon of a nanoparticle is very sensitive to its local environment. For a nanoparticle on a dielectric substrate, the substrate breaks the symmetry of the nanoparticle's dielectric environment, which can cause a large change in the plasmon modes present.¹⁸ The plasmon induced charge density of the nanoparticle is screened by induced surface charges on the substrate, effectively causing a superimposed electromagnetic image of the nanoparticles electric field on the substrate (Figure 1.4, Left).^{19,32}

Figure 1.4: (Left) Demonstrating the substrate distance dependence for the coupling of a plasmonic nanoparticle. (Right) FDTD simulated UV-Vis spectrum for a nanoparticle 100 nm above the dielectric substrate (Solid line), and on the substrate (Dashed line), with normal (to the substrate) (D_h , Red) and parallel (D_v , Blue) polarized light.

The image of the particle can be described using a semi-classical Lagrangian approach,⁴² although, the common description is a generalized hybridization argument, similar to coupling dipolar resonances. This interaction is very distance dependant, and breaks the dipolar symmetry, which can result in the formation of new higher order plasmonic modes, as seen with D_h in Figure 1.4 (Red dashed).

When a plasmonic particle approaches the surface of a dielectric substrate, the dielectric substrate's charge separation causes a disruption in symmetry. This asymmetry breaks the degeneracy of the plasmon modes, such that the plasmon modes with charge densities closer to the substrate will couple more than modes with charge densities located farther away, as can be observed in Figure 1.4. In Figure 1.4, it is seen that as the particle moves to being on the substrate, the interaction found in the D_h mode is much stronger than that of the D_v mode, which leads to the D_h mode being more red-shifted.⁴³ The symmetry breaking induced by the dielectric also allows hybridization between higher order modes, due to the formation of multipoles.

As previously mentioned, nanoparticle shape plays a significant role in the corresponding LSPR. Many of the models discussed involve small spherical nanoparticles, which is primarily due to simplicity, since, in small spherical nanoparticles, the electron displacement is balanced. This results in dipolar plasmon resonances,¹⁹ while for non-spherical nanoparticles, the LSPRs can have an uneven charge distribution, resulting in unique absorption and scattering properties.³⁴ In particular, sharp features such as corners and edges, lead to an uneven distribution of charge, causing electric field enhancement around the sharp features, enabling smaller particles to support higher order modes.^{21,44} Nanostructures with structural anisotropy can support additional

plasmon modes: for example, plasmonic nanorods and wires support longitudinal and transverse plasmonic modes.^{45,46}

LSPRs are sensitive to their local electric environment. Thus, changes in the electric permittivity of the environment causes a subsequent shift in the LSPR of the material. Recall from Equation 6, which used a Drude approach to represent the maximum plasmonic frequency, by converting frequency to wavelength and expressing the dielectric constant to the refractive index ($\epsilon_m = n_m^2$).¹⁷ A simplistic relationship between the refractive index of the environment and the maximum resonance wavelength (λ_{max}) can be made (Equation 8).

$$\lambda_{max} = \lambda_p \sqrt{2n_m^2 + 1} \quad (8)$$

Equation 8 shows that with increasing refractive index of the medium, the plasmon shift wavelength will also increase (red-shift). Under small ranges the relationship between λ_{max} and n_m is considered linear.^{47,48}

In this work silver nanocubes (AgNCs) are used since these particles have increased charge accumulation at edges and vertexes, which generate high-intensity electric fields.⁴⁹ This subsequently leads to high refractive index sensitivity.^{17,25,50,51} When AgNCs are placed on a dielectric substrate, hybridization of the dipolar mode, D^0 and quadrupolar mode Q^0 into hybrid dipolar (D) and quadrupolar (Q) modes occurs (Figure 1.5),¹⁸ where the D mode is concentrated to the area of greatest refractive index (typically the substrate), while the Q mode is confined to the surroundings (Figure 1.6). Consequently, the D mode is more sensitive to the refractive index of the substrate, while the Q mode is more sensitive to changes above the substrate.

When a cube is used instead of a spherical nanoparticle the charges that are induced by the substrate occupy a larger area, due to the greater contact area with the substrate, resulting in greater hybridization. As well, the fact that cubes have higher order plasmonic modes allows for more interactions to occur. The dipolar mode in cubes and the quadrupolar mode can hybridize due to similar surface charge distributions and energies allowing for a large degree of hybridization as shown in Figure 1.5.

Figure 1.5: UV-Vis spectrum of an AgNC on a dielectric substrate, with corresponding charge maps emphasizing the spatial separation of the hybrid plasmonic modes. Panel 1: Extinction (black), scattering (blue-dashed) and absorption (red-dashed) cross sections of an AgNC on a dielectric substrate. Panel 2: cartoon representing the hybridization of the dipolar (D^0) and quadrupolar (Q^0) modes forming new hybrid dipolar (D) and quadrupolar Q modes, with a cartoon representing their cross-sectional charge maps. (made in Paraview) Panel 3: Cartoon representation of a dipolar plasmon in a cubic nanoparticle excited by the same polarized light used in panel 1 and 2.

Figure 1.5 illustrates the mixing of the dipolar D^0 and quadrupolar Q^0 modes. The bonding mode (D^0+Q^0) is primarily from the D^0 and is a hybridized dipolar mode (D). The antibonding (D^0-Q^0) mode is primarily Q^0 in character and is a hybridized quadrupolar mode (Q). The coupling between the inherently dark Q^0 mode and the bright D^0 allows the resulting hybridized quadrupolar mode to be excited by incident radiation. Another important consequence is that the D mode has its E-field closer to the substrate which makes it sensitive to the substrate's refractive index (Figure 1.6), while the Q mode is farther away, making it more sensitive to changes in the local environment (Figure 1.6).¹⁸ This aspect will be further explored in section 1.4.2.

Figure 1.6: UV-Vis spectrums of AgNCs in solution and on a dielectric substrate, with corresponding cross-sectional electric field maps of the hybrid dipolar (D) and quadrupolar resonances (Q).

1.3 Polymer Properties

A polymer is a molecule which has repeating molecular subunits. The chemical structures of polymers used in this work, namely polyvinylpyrrolidone, polystyrene, polyvinyl chloride, poly(methyl methacrylate) and poly(2-vinylpyridine), can be seen in Figure 1.7. Polyvinylpyrrolidone was the capping agent of the AgNCs, while polystyrene, polyvinyl chloride, poly(2-vinylpyridine), poly(2-vinylpyridine) and poly(methyl methacrylate) were used as polymer substrates that the AgNCs were deposited onto. The structures of the polymers are important as they dictate interpolymer interactions, which can drastically impact polymer properties.

Figure 1.7: Chemical structures of the polymers used. The repeating subunit is in the brackets, and n represents the number of monomeric units.

Two properties that are of specific interest in this work are the glass transition temperature of the polymer and the diffusion of nanoparticles into the polymer. Three factors that can affect these properties are:

- 1) Length of the polymer chain
- 2) Functionality of the pendant groups
- 3) Tacticity of the polymer chain

Commonly, chain length is expressed by the degree of polymerization, which quantifies the number of monomers incorporated into the chain. Synthetic polymers are typically

produced to have a range of molecular weights (Section E, Appendices). As such, molecular weights are typically expressed with some statistical significance. Two common ways to express molecular weights are mass average molecular weight (M_w or commonly MW) and number average molecular weight (M_n). M_n represents the mean of masses in a sample of n polymer subunits (Equation 9), while M_w represents a different approach, which aims to emphasize molecular size more (Equation 10). In general, the distribution of chain sizes in a polymer sample is defined using the dispersity ($\mathcal{D}$) (Equation 11), where 1 is perfectly uniform (monodisperse).

$$M_n = \frac{\sum_i (N_i M_i)}{\sum_i (N_i)} \quad (9)$$

$$M_w = \frac{\sum_i (N_i M_i^2)}{\sum_i (N_i M_i)} \quad (10)$$

$$\mathcal{D} = \frac{M_w}{M_n} \quad (11)$$

Polymer chain length greatly influences the polymer's physical properties. As chain length increases, so do the Van der Waals attractive forces. These attractive forces cause an increase in melting and boiling temperatures as more energy is needed to disrupt the added stabilization forces. The increase in stabilization forces also acts to reduce the free movement of the polymer chains, effectively increasing the viscosity of the polymer.^{52,53} The viscosity of the polymer increases until it reaches a specific threshold, called the entanglement threshold, where the long polymer chains re-arrange and intertwine with one another.

In polymer science, the functional groups that come off the carbon backbone are called pendant groups. Similar to molecules, the functionality of these pendant groups

greatly influences the polymers physical properties. A polymer with different functional groups may have stronger or weaker inter-molecular interactions, which drastically changes properties such as melting point, melt viscosity and glass transition temperature.^{52,54–56} The arrangement of these pendant groups can also play a role in the final properties of the polymer. The tacticity of the polymer describes the relative stereochemistry of the chiral centers on the polymer backbone. There are three types of tacticity as represented in Figure 1.8.

- 1) Isotactic, where all substituents are on the same side of the polymer chain.
- 2) Syndiotactic, where there is an alternating arrangement of substituents on the polymer chain.
- 3) Atactic, where there is a random placement of substituents on the polymer chain.

Figure 1.8: Showing chemical structures for the three tacticities of PMMA.

Although the polymers used in this work were all atactic and well above the entanglement threshold, polymers like PMMA and PS can have tacticity. In theory, a syndiotactic conformation would lead to the least steric hindrance, allowing for tighter packing of the polymer chains. This in effect allows more stabilizing interactions, which decreases the

ability for the polymer chains to re-arrange. For example, isotactic PMMA and PS have increased mobility over their syndiotactic and atactic analogues.^{57–59}

The concept of an entanglement threshold has been around since 1948.⁶⁰ Although, the first semi-generalized form dates back to 1951.⁵³ Through studying the molecular weight dependence of polyisobutylene on its liquid viscosity, Fox and Flory found an asymptotical relationship between molecular weight and viscosity. This signifies a threshold molecular weight, where the polymers intermolecular forces do not drastically change. This is now referred to as the entanglement threshold, sometimes called critical entanglement length, where at a certain chain length, the polymer chains wrap and re-organize around each other (Figure 1.9). At this point the polymer mobility is not of single chains but rather of conformational changes of the polymer chains in the large macrostructure. This is called segmental mobility; the idea of segmental mobility was first formally introduced by Bueche⁶¹ in 1953 and later elaborated by Gibbs and Adam⁶² in 1965. The later sections aim to focus more on the mobility of the polymer and its specific surface properties.

Figure 1.9: Cartoons representing polymer entanglement. (Left) 3 polymer chains entangled together. (Right) Cartoon representing the enhanced free movement (grey circle) at the end of two entangled polymer chains.

1.3.1 Glass transition temperature

The glass-liquid transition, commonly referred to as the “glass transition” is the reversible transition from a polymers glassy state into a rubbery-like state. The specific volume of the polymer represents the free space of the polymer chains, and because of this, it is highly dependant on the kinetic properties of the polymer chains. For amorphous glassy polymers the glass transition represents the sudden increase in specific volume, which represents a greater degree of freedom for the polymer chains.⁶³ The glass transition temperature (T_g) is the range of temperatures for which this transition can occur.⁶³ The glass transition is not a phase change, and is intrinsic only to amorphous polymers. In contrast, the melting temperature is characteristic of crystalline polymers, where the polymer chains become a disordered liquid. Interestingly, almost all polymers have some amorphous character, thus, it is possible for a polymer to have both a glass transition temperature and a melting temperature.

When a polymer is above its glass transition temperature, it possesses decreased polymer relaxation times. This can be represented as an increase in the degrees of freedom for a polymer chain. For unentangled polymer chains this is represented as a increase in chain mobility, allowing the chains to flow around each other more easily, whereas for entangled polymers this is represented as faster segmental relaxation.⁶⁴ In either case, a polymer with a high T_g has more restriction on the polymer chain motion and relaxation than a polymer with a lower T_g . Thus, the glass transition temperature is affected by anything that affects the degrees of freedom of the polymer chains, such as:

- 1) Chain stiffness.
- 2) Intermolecular forces.

- 3) Side groups on the backbone.
- 4) Cross linking.
- 5) Film thickness.

Stiffening groups on the chain can reduce the flexibility of the chain which raises the T_g . An example of a stiffening group is a carbonyl group, due to the double bond restricting free rotation of the polymer. Intermolecular forces in polymers tend to be much larger than for molecules, due to the large nature of the polymer chains and their tendency to wrap around each other. Thus, compounds such as PVC which have a large dipole due to the Cl-C bond will have a higher than expected T_g due to the stronger interactions reducing free movement. PVC has a bulk glass transition reported between 80-90 °C,^{65,66} whereas, polyethylene has a T_g reported between -125 to 35 C,⁶⁷ with the variability being due to the challenges in controlling crystallinity. Side groups, or more often called pendant groups, raise the bulkiness of the polymer which reduces the free movement and increases the T_g . An example of this is the phenyl group on polystyrene, which raises the bulk T_g to ~100 °C.^{55,56,68} Another effect is the tacticity of the pendant groups if all the polymer chains are syndiotactic or isotactic the T_g will change depending on the nature of the pendant group.^{69,70} Cross linking polymer chains also reduces the free rotation in a molecule which in effect reduces the free mobility of the polymer chains, increasing the T_g .

Another property that effects the glass transition temperature is the thickness of the polymer films. As the film become thinner the surface contribution to the overall energy of the system increases. Some argue that this can result in an increase in the density of the polymer for ultra thin films (< 50 nm), causing a slight increase in glass transition

temperature.⁷¹ Although, the generally accepted surface effect is due to polymer chain confinement, which essentially reduces the stabilizing interactions of the polymer at the surface of the film.

1.3.2 Polymer chain confinement and surface effects

Polymer films with thicknesses on the order of nanometers have been studied extensively, due to their unique properties in respect to their bulk counterparts. These properties result due to confining the polymer chains to a similar length scale of its molecular building blocks. This chain confinement can cause polymer chain movement to be drastically different than the bulk analogue and have a drastic effect on the properties of the polymers that require chain reorganization and relaxation.⁷² Specifically, the surface polymer chain mobility in thin films (thickness < 200 nm) is similar to the bulk analogue; however, the segmental relaxation is very sensitive to the film thickness.^{72–74} Two such properties that are affected by this surface effect are the glass transition of the polymer and diffusion through the polymer. These properties are affected by anything that alters the free mobility of the polymer chains.⁶⁴ It is possible for a polymer to possess a surface layer on top of the bulk polymer, each with different segmental relaxation rates (Figure 1.10).^{75,76} Figure 1.10 represents the glass transition curve for a bulk amorphous polymer (Black) and for a polymer with two intrinsic dynamic regions (Red).

Figure 1.10: Specific volume relationship to the glass transition. (A) (Blue) Representing the solid-liquid phase change, (Black) the bulk glass transition, and (Red) two glass transitions attributed to the surface and bulk relaxations. (B) Cartoon representing the surface and bulk layers of a polymer film.

In order to probe these surface properties, extreme surface sensitivity is required, which can be challenging by traditional methods such as differential scanning calorimetry. In this work, a new method is proposed: by monitoring the embedding of silver nanocubes into polymer surfaces, physical constants can be determined. This concept will be explored in more detail in sections 1.4.2.

1.3.3 Polymer blends and unique morphologies

Immiscible polymer blends are commonly used, as they form well defined reproducible 3-D structures, driven by self-association of the polymer chains.^{77–79} The popularity of polymer blends is due to the ability to enhance polymer properties in a simple cost-

effective way.^{80,81} The morphology of the immiscible ternary polymer blend can be rationalized by surface energy arguments (Equation 12).

$$\lambda_{bc} = \gamma_{ab} - (\gamma_{ac} + \gamma_{cb}) \quad (12)$$

Where λ_{bc} is the spreading coefficient, which represents the possibility of a two-phase interface between phases b and c inside of a larger phase a, and γ represents the interfacial surface energy between two phases. In order for phase c to encapsulate phase b, the spreading coefficient λ_{cb} must be positive. However, if λ_{cb} and λ_{bc} are both negative then phase b and c will segregate. Four major phase segregations can form as represented in Figure 1.11. The spreading coefficients can also be represented using the free energy of the system. (Equation 13).⁸²

$$G = \sum_i n_i \mu_i + \sum_{i \neq j} A_{ij} \gamma_{ij} \quad (13)$$

Figure 1.11: Cartoon representing four common polymer segregations in immiscible ternary polymer blends, with the corresponding spreading coefficients.

Where G represents a modified Gibb's free energy, γ_i is the chemical potential of phase i , n_i is the number of moles of phase i . This first term is the same for all morphologies shown in Figure 1.11, although by changing the weight fraction of the ternary blend this first term can be altered. The second term varies for each morphology specified in Figure 1.11, where A_{ij} represents the interfacial surface area between phases i and j , γ_{ij} is the interfacial surface tension between phases i and j .⁸³ The thermodynamically favorable morphology will have the smallest Gibb's free energy, which allows a way to hypothesize the morphology. It should be noted that this model assumes that the kinetic properties are negligible. Therefore, large deviations are expected for viscous polymer blends.

Although the size of the domains for blends are generally large (> 100 nm), in comparison to block co-polymers, the ability to tune the morphology of the polymer by changing the solution composition, reproducibility of the blends and the large domains, allow for the AgNCs to be deposited onto discrete polymer domains. Due to the size of the AgNCs used in this work, block copolymers are incompatible, as large domains are necessary to ensure the AgNCs are placed onto defined sections, with different physical properties, and not on polymer interfaces, which can enable the selective embedment of the AgNCs into individual polymers within the blend.

In this work a ternary polymer blend of PS/P2VP/PMMA was used due to its ability to form large well-defined segmented morphologies (Figure 1.12).⁷⁹ As a result of the different intermolecular forces between the polymers, well-defined structures are formed, and can be identified by using the difference in solubilities of the polymer. Figure 1.12 shows AFM images of a PS/PMMA/P2VP solution as cast (a) and after dissolution in different solvents. In (b), ethanol was used to dissolve only the P2VP, while in (c),

cyclohexane was used to dissolve PS. This simple analysis can help confirm the spatial orientation of the three polymers, and if cross sections from images (a-c) were superimposed the composition of the film can be obtained (d). Images (e-f) represent AFM images of a (1/1/1 w/w/w, 3% in THF) solution, the morphological changes from (a) to (e) are apparent. A similar analysis was done to determine the morphology of the individual polymers (e-g). Although this approach for determining polymer composition is imperfect, largely due to polymer swelling, or partial wetting due to the solvent, it still provides adequate support that there are three chemically different polymer components present.

Figure 1.12: (a,b,c,d) AFM images of PS/PMMA/P2VP (1:1:1 w/w/w) dissolved in THF solution spin cast onto a coated glass slide. (a) as cast, (b) immersion in ethanol, immersion in cyclohexane, (d) cross sectional analysis (PS = blue, PMMA = green, P2VP = Red). (e,f,g) AFM images of PS/PMMA/P2VP (3:1:1 w/w/w) cast from THF onto a coated glass slide. (e) as cast, (f) after immersion in ethanol, (c) after immersion in cyclohexane. Adapted with permission from ⁽⁷⁹⁾ © 1999 American Chemical Society

1.4 Nanoparticle Embedding into Polymer Surfaces

Ultra-thin polymer films are interesting due to their unique properties with respect to their bulk counterparts.^{74,76,84} Ultra-thin polymer films can have drastically different physical properties, such as glass transition temperature and diffusion through the polymer, due to the change in surface mobility of the polymer film.⁶⁴ A more advantageous approach to alter the polymer's properties is the incorporation of nanoparticles into the polymer, as nanoparticle concentration, size and depth of embedding can be used to control the polymer properties. Addition of nanoparticles can increase polymer solar cell efficiency,¹⁵ sensing,⁸⁵ thin-film stability,^{6,7} and allow fabrication of unique particle assemblies.¹³ Incorporation of nanoparticles into a robust polymer shell or film, can enhance nanoparticle properties, by making the nanoparticles more biocompatible and even more stable; thus facilitating targeted drug delivery.^{10,86,87} Therefore, exploring interfacial interactions between nanoparticles and thin polymer films is of significance for the development of unique functional nanocomposite materials.

This section will cover the irreversible thermally activated embedment of particles into polymer films. There are differing theories on the mechanism for the embedment. One theory is that the particles embed due to the presence of a wetting layer (surface layer) close to the interface of the particle and the polymer substrate. The wetting layer can draw up the particle due to a difference in pressure, which causes the net capillary pressure to drive the particle below the surface of the polymer.^{88,89} The presence of a wetting surface has been well documented (Section 1.3.2), however, this process anticipates full embedding of the particle into the polymer, which doesn't always happen.

Thus, a different model must be used, one that considers the thermodynamics of the system.

For simplicity, this model makes many assumptions: (1) the surface wetting layer on top the bulk polymer doesn't exist, (2) the model revolves around a rigid sphere embedding into a perfectly flat polymer infinite surface. The two main forces are assumed to be Van der Waals attraction between the spherical particle and the polymer surface, and the entropic force forcing the particle out of the polymer.⁹⁰ Considering both interactions, a minimum point can be determined where the particle is at a particular position in the polymer. The next section will go into detail on the thermodynamics of the model. Additional theory for: silver nanocubes synthesis (Appendix B), and subsequent deposition via a Langmuir approach (Appendix C) can be found in Chapter 6.

1.4.1 General Physical Model

The thermodynamics for nanoparticle embedment can be modeled using Helmholtz free energy.⁹⁰ Where Helmholtz free energy (Equation 14) represents the maximum amount of work that can be done on a system spontaneously at constant temperature (T) and volume.

$$\Delta A = \Delta U - T\Delta S \quad (14)$$

Where, U signifies the internal energy of the system, S represents Entropy and, A Helmholtz free energy, the process is spontaneous if $\Delta A < 0$. For a free particle on top of a non-interacting surface the surface free energy can be represented as Equation (15).⁹⁰ Where α represents area, and γ_p is the surface free energy of the particle.

$$A_{surface} = \alpha\gamma_p \quad (15)$$

Equation 16 shows the surface free energy for a fully embedded particle.

$$A_{surface} = a\gamma_{ps} \quad (16)$$

Where γ_{ps} is the interfacial free energy of the interface between the polymer and the particle. The difference between the final (Equation 16) and initial states (Equation 15) is Equation (17).

$$\Delta A_{surface} = a(\gamma_{ps} - \gamma_p) \quad (17)$$

Thus, for the embedding to be spontaneous, $\gamma_p > \gamma_{ps}$. Alternatively, free energy can be represented as the work needed to go from the particle on the polymer surface to embedded into the surface. To embed the particle, an initial void in the polymer surface must be created, which requires work equal to $a\gamma_s$, where γ_s is the surface free energy of the polymer surface. Upon the particle filling the void, free energy is regained (aW_{ps}) where W , represents the work of adhesion between the particle and the polymer.⁹⁰ The free energy change can therefore be represented as:

$$\Delta A_{surface} = a(\gamma_s - W_{ps}) \quad (18)$$

Thus, if $W_{ps} > \gamma_s$ the process will be spontaneous.

Holding the equality of Equation 17 and Equation 18, W_{ps} can be expressed as Equation 19.

$$W_{ps} = \gamma_s + \gamma_p - \gamma_{ps} \quad (19)$$

Thus, for complete embedment $\gamma_p > \gamma_s + \gamma_{ps}$.

However, as the particle embeds into the polymer, the surface area of the polymer increases due to the polymer reforming around the particle. Therefore, it is possible that this work (W_{ps}) will cause the incomplete submersion of the particle, because the two forces work in opposition to each other the system will find a local minimum in energy which may lead to the particle reaching a maximum distance embedded (h^*).

Figure 1.13: Cartoon representation showing the different surface energies for the AgNC-polymer nanocomposite.

In this work AgNCs capped with PVP are used, thus, Equation 19 needs to be altered slightly. Assuming AgNCs and PVP interaction is approximately the same for each polymer and the main effect upon changing the polymer substrate is the different interaction with the PVP the inequality now becomes Equation 20, with a cartoon representation seen in Figure 1.13.

$$\gamma_{capping\ agent} > \gamma_{Polymer\ Substrate} + \gamma_{PolymerCap} \quad (20)$$

1.4.2 Spectral shifts due to AgNC embedding and kinetics of the process

Metal particles such as gold and silver are capable of embedding into polymer films when heated above the polymer's glass transition temperature.^{91–93} Two major constraints must be satisfied for the embedding to occur. The first is a kinetic requirement, which states

that the polymer must be above its glass transition temperature. This allows the polymer chains to flow, permitting the necessary polymer re-arrangements for nanoparticle embedding. With higher temperatures providing greater mobility of the polymer; thus, faster embedding of the particle. The second requirement is a surface energy argument (Equation 20), which is always satisfied for bare metal nanoparticles⁹⁰ and polyvinylpyrrolidone (PVP) capped silver nanoparticles embedding into PS, PVC and PMMA films.⁴⁸

AgNC's when supported on a dielectric substrate exhibit strong hybrid plasmon resonances (Section 1.2.5, Figure 1.6) that are spatially separated; thus, sensitive to different environments simultaneously.^{50,91} The hybrid dipolar plasmon (D) is focused towards the area of highest refractive index and the hybrid quadrupolar plasmon (Q) is situated towards the area of lower refractive index.¹⁸ This anisotropy allows real-time sensing of the polymer-nanoparticle interface as the particle embeds into the polymer.

As the nanocubes embed into the polymer the effective refractive index of the nanocube's environment increases, which causes a subsequent red-shift in the D mode (Figure 1.14).²⁵ The Q mode begins red-shifting when the AgNC is about halfway embedded into the polymer (Figure 1.14, $t_1 - t_2$). Near full embedding of the AgNCs is seen at t_3 , with the Q mode overlapping onto the D mode, representing a near-isotropic local environment. The high sensitivity that the AgNCs have to their local refractive index enables, very accurate monitoring of the embedding of the particle into the polymer thin film. The spatial sensitivity of the AgNC also enables probing of a thin-surface layer above the bulk polymer, which has a lower glass transition than the bulk. This surface layer is in accordance with many other studies for ultra-thin polymer films.^{75,76}

Figure 1.14: Typical UV-vis spectra of AgNCs embedding into a polymer substrate at three stages of embedment denoted t_1 (bottom spectrum), t_2 (middle), t_3 (top) with cartoon of the AgNC at each stage.

As the AgNCs embed into the polymer, the peak positions of the corresponding hybrid plasmonic mode shifts, this shift can be modeled by the electric fields spatial sensitivity of the AgNCs (Equation 21).

$$E(x) = E_0 e^{-\frac{x}{l_d}} \Rightarrow E_0 e^{-kx} \quad (21)$$

Where E_0 , is the maximum electromagnetic field, and l_d , is the electric field decay length, x , is the position of the nanoparticle relative to the interface, and k , is a new constant ($k = 1/l_d$). Assuming the velocity of the cube is approximately constant at an intermediate time of embedding, allows the formulation of a velocity dependent expression (Equation 22).

$$E(t) = E_0 e^{-k(x_0 + vt)} \quad (22)$$

Where x_0 , is the initial position of a nanocube and v , is its average embedding velocity, which is further simplified by grouping together constants (C) (Equation 23).

$$E = Ce^{-kvt} \quad (23)$$

Equation 23, can then be related to the LSPR maximum wavelength (Equation 24).⁹⁴

$$\Delta\lambda_{max} = m\Delta n[1 - e^{-2kvt}] \quad (24)$$

Where m , is the refractive index sensitivity of the AgNCs and Δn , is the refractive index change between the surroundings (air) and the polymer substrate. Equation 24 gives a basic model for the time evolution for the LSPR peak maximum shift as the embedment occurs. All D mode shifts were successfully fit using this exponential decay relationship (Equation 24), which suggests that the velocity v of the nanocube embedding was essentially constant, validating the assumption made for Equation 22. From this fitting only the product kv can be obtained, since k is unknown, in order to determine v , a new approach must be used. To determine the velocity of the nanocube embedding another method was used, using the far-field nanoruler aspect of the AgNCs.⁹¹ Utilizing the spatial sensitivity of the Q mode, the initial average velocity can be calculated as (Equation 25):

$$v = \frac{x_{1/2}}{t_{1/2}} \quad (25)$$

Here $x_{1/2}$ and $t_{1/2}$ are the depth and time of halfway nanocube embedding (Figure 1.15, B). Since, the initial red-shift in the Q mode signifies approximately halfway embedment, $t_{1/2}$ can be determined as shown in Figure 1.15, A. Since the size of the AgNCs is measured before heating, the half-edge length $x_{1/2}$ can be determined independently by TEM measurements of the particles, or AFM measurements of the monolayer before

heating. This gives a way to determine the average velocity of the AgNC embedment (Equation 25).

Figure 1.15: Physical model used to calculate the diffusion constant. (A) Normalized D mode shift (open circles), normalized Q mode shift (filled circles) and temperature of the sample (green squares). The fitting of the sample temperature data was used to determine the time at which the sample temperature is approximately constant (t_{iso}) and when the nanocrystals are embedded halfway ($t_{1/2}$). (B) Cartoon representing embedment of the AgNCs at t_{iso} and $t_{1/2}$.

In this work, the temperature initially is rapidly increasing, before reaching a constant set value (Figure 1.15, A), this will cause drastic changes in the dynamics of the film leading to errors for the calculated physical constants. To minimize these errors, only data from the isothermal regions were used in the calculations. The time when the system reaches the isothermal regime was determined (t_{iso} , Figure 1.15, A) and further calculated the embedding depth x_{iso} (Figure 1.15, B). Since the velocity is constant, x_{iso} can be determined using Equation 26. The isothermal time (t_{iso}) is determine based on the intersection of two lines, which are artificially elongated in Figure 1.15, A to emphasize

the intersection point. The first line was determined by a linear fit (with a 100 second time interval) centered on where the slope is approximately half its maximum. This was to minimize the variance associated with the initial heating. The second line was a linear fit of the horizontal, isothermal regime (Figure 1.15, A).

$$x_{iso} = x_0 + vt_{iso} = \left(\frac{x_{1/2}}{t_{1/2}} \right) t_{iso} \quad (26)$$

The diffusion constant (k_D) can then be calculated using Equation 27.

$$k_D = \frac{(x_{1/2} - vt_{iso})^2}{t_{1/2} - t_{iso}} \quad (27)$$

The isothermal time t_{iso} , is strongly dependent on the final set temperature, due to higher temperatures taking longer to reach thermal equilibrium. With few exceptions, the isothermal regime was reached before any major spectral changes were observed.

1.5 Nanorulers

Nanorulers are molecules or materials that can measure nanoscale distances and are of particular interest as they allow determination of the thickness, displacements, and morphology of nanoscale features. This information is vital for fields like biology as knowing the specific folding and spatial orientation of active sites is important in effectively designing many biological systems.⁹⁵ Many nanorulers rely on specific fluorophore interactions such as fluorescence based energy transfer with the bio-molecule of interest,⁹⁶ and due to strict orientations required, these fluorophore based nanorulers aren't very useful outside of the specific application. However, plasmon based nanorulers also allow for extreme surface sensitivity,^{97–100} and potentially large dynamic ranges.¹⁰¹

In general, plasmon based nanorulers rely on the spatial sensitive interaction between a plasmonic particle and a metal surface or emitter,¹⁰² whether through coupling interactions with another particle,¹⁰⁰ metal film¹⁰³ or Fano resonances resulting from this coupling interaction.¹⁰⁴ Because of this, they require very specific particle-surface distances and; thus, are extremely sensitive to shape of the individual components, making these nanorulers, challenging to produce. These plasmon coupling based nanorulers are also very sensitive to changes in the system and require calibration when the system is altered.

Alternatively, refractive index based plasmonic nanorulers are of interest as they are simply based on changes in the refractive index of the surroundings, and thus, do not require any specific interparticle distances. In this work AgNCs are used due to their hybrid plasmonic modes, which allow spatial sensing of the local refractive index.²⁵ These AgNCs have proven to be excellent nanorulers for polymer surfaces^{48,91} as their spatially sensitive hybrid plasmonic modes allow the tracking of the AgNCs as they embed into the polymer.

1.5.1 Measuring surface mobility of polymers

Nanoscale polymer films have been of interest due to their unique physical properties, namely polymer dynamics.^{76,84} Due to restricting degrees of freedom of the polymer chains to a similar length scale of its molecular building blocks, which leads to polymer chain confinement (Section 1.3.2).^{64,74,84} It is important to note classical techniques used

to measure the surface dynamics of polymers, in order to compare with the AgNC nanoruler approach used in this thesis.

The concept of a polymer surface layer goes back many years,¹⁰⁵ however, accurately measuring the surface layer is very challenging. The first conclusive study was done by Meyers *etal.* in 1992.¹⁰⁵ This work attempted to measure the surface of polystyrene (PS) using atomic force microscopy (AFM). They used relatively large PS (high MW), with a molecular weight from 13-1000 kDa, this is important as the surface dynamics was expected to be dominated by the entanglement of these large polymer chains. Interestingly, they found at the entanglement threshold (19 kDa) the surface of the polymer becomes more ordered, this transformation was thought to be due to increased surface mobility of the polymer. This work alone doesn't confirm the presence of a mobile layer, as factors like specific interactions with the AFM tip, and the tip radius make the results questionable.

A common approach to measuring the glass transition temperature of polymer films is through differential scanning calorimetry (DSC). DSC effectively measures heat transfer in a material. The effective heat capacity of the polymer changes from its glassy to rubbery state (Figure 1.16), due to a drastic increase in heat flow, as the energy barrier associated with the glass transition (T_g) is overcome. For polymers with some crystallinity, a negative peak is seen (T_c) representing the exothermic heat release due to the polymer chains forming ordered crystals, and of course there would be a positive peak representing the melting point (T_m) for the semi-crystalline polymer.

Figure 1.16: Representing the effective heat capacity changes in a polymer.

DSC techniques work well in determining the bulk glass transition of a material, however, it is very challenging to obtain any surface information. This is due to small signal to noise for thin films, as the surface layer is very thin in respect to the bulk. For thicker films, the dynamics are dominated by the bulk layer, as the surface layer is typically less than 10 nm thick. Although, this engineering challenge has been overcome, Ediger *et al.*¹⁰⁶ used DSC measurements to determine the T_g of PS nanospheres. A jump in specific heat associated with the glass transition was found to decrease with size of the particles. The authors attributed this to a central core with bulk dynamics and an outer surface with enhanced dynamics. This approach allowed for a greater surface to bulk ratio, and with a sufficient amount of PS nanospheres suspended into solution, gives a large enough signal. The use of nanospheres in solution likely changes the surface dynamics in respect to a film. Although the nanospheres were suspended in water, effectively forming a free-standing film in solution, the corresponding surface T_g only differed by 1-2 °C in comparison to bulk. One of the earliest studies by McKenna and

Jackson¹⁰⁷ utilized DSC measurements of polymers confined to small pores of Vycor glass. Interestingly, they discovered terphenyl confined to a 4 nm pore showed the biggest effect, with a decrease of 18 °C in respect to the bulk T_g . Although, both of these cases involved a great degree of ingenuity, the result is arguable, due to the perturbation to the polymer system.

Due to the limitations of DSC as a surface technique, new approaches have been developed and adopted to determine the surface T_g of a polymer. What might be the most interesting technique is the use of mass spectrometry and contact angle measurements to determine the surface T_g of PMMA.⁵⁴ Although, this technique is very polymer dependant and not universal. A more universal technique is monitoring the embedding of a tracer into polymer films. This has been shown with metal nanoparticles embedding into polymer films.^{108,109} In general, Au nanoparticles are used and the embedding of the particles are monitored by use of AFM topology measurements. This technique is very precise and near-universal, as the metal nanoparticles should embed into almost any polymer film.^{90,91} However, this technique is very time consuming, and at high embedding rates the AFM measurements will not give accurate topology, as the particles are embedding as the tip is scanned. In, this work, AgNCs are used as nanorulers due to their spatially sensitive plasmonic modes. This allows monitoring of the embedding process in real-time through use of a far-field spectrophotometer. Enabling the determination for the diffusion constants, activation energy, and glass transition temperatures for homopolymer and immiscible polymer blended films.

2 - Method

2.1 Materials

Silver nitrate (99%+), polyvinylpyrrolidone (PVP, $M_w \sim 55\,000$), polystyrene (PS, $M_w \sim 192\,000$) polymethylmethacrylate (PMMA, $M_w \sim 120\,000$), polyvinylchloride (PVC, $M_w \sim 48\,000$), anhydrous ethylene glycol (EG, 99.8%), sodium chloride (99%+), sodium sulfide (98%+), styrene (99.9% with 4-tert-butylcatechol as stabilizer), benzoyl peroxide (>98%) and mineral oil (Heavy) were purchased from Sigma-Aldrich and used as obtained. Ethanol (95%) was obtained from Commercial Alcohols and used without further purification. Toluene (99.5%) and Tetrahydrofuran (THF, 99.0%) were purchased through Caledon. Chloroform (99.5%+) was purchased through Alfa Aesar, Acetone (99.5%+) and Methanol (99.8%+) were purchased from VWR International. Poly(2-vinylpyridine) (P2VP, $M_w 200\,000 - 400\,000$) was purchased from Polysciences Inc. 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC, powder) was purchased from Avanti Polar Lipids.

2.1.1 Synthesis of Silver Nanocubes

All glassware was soaked in a solution of aqua regia (3 parts hydrochloric acid and 1 part nitric acid) for 30 minutes. Glassware was then rinsed; 52 times with tap water, 32 times with distilled (reverse osmosis) water, and 16 times with deionized water ($18.2\text{ M}\Omega\cdot\text{cm}$) and dried in an oven. Silver nanocubes were synthesized according to a procedure described in literature¹¹⁰ and specified below. The reaction was quenched via an ice bath once the desired spectrum was observed, dipolar resonance at $\approx 480\text{ nm}$. Once cooled the solution was purified by centrifugation (Thermo, Legend Micro 21) 3 times in ethanol at 12 000 RPM, the first for 30 min, second for 10 min and third for 10 min intervals,

decanting off the supernatant and replacing with fresh EtOH each round. The resulting centrifuge tubes were then stored in a refrigerator at 4 °C until use.

Specifically, the synthesis started by dissolving 0.4g of PVP in 15 mL of EG in a round bottom flask with a polytetrafluoroethylene coated magnetic stir bar. The solution was then heated in a mineral oil bath at 150 °C at stirred at 300 RPM for at least 1 hour to ensure oxidation of EG to glycolaldehyde. During this period a NaCl solution was prepared by dissolving 0.2808g of NaCl in 10 mL of EG. A Na₂S solution was quickly produced by dissolving 0.0023 g of Na₂S in 10 mL of EG. Na₂S can react with water in the air to produce hydrogen sulphide, thus, N₂ gas was used to fill the headspace of the vial to minimize exposure with air. This solution was mixed on a vortex to aid the dissolution of Na₂S. The resulting solution was not sonicated due to the potential formation of NaS, which won't react as quickly with Ag⁺.

A solution of AgNO₃ was prepared by dissolving 0.24 g of AgNO₃ in 5 mL of EG in an opaque vial. The resulting mixture was then mixed on a vortex and sonicator to ensure complete dissolution of the AgNO₃ crystals. Coloured tape was used to cover the vial in an attempt to reduce photodegradation of AgNO₃, and N₂ gas was used to fill the head space of the vial, to minimize sulfuration of Ag.

The NaCl solution was added to the reaction flask by pipetting 25 µL via a micropipette to the reaction flask. The Na₂S solution was then added to the reaction flask, by quickly injecting 175 µL of the Na₂S solution by use of a micropipette. The solution was then allowed to stir for 5 minutes, after which 1.5 mL of the AgNO₃ solution was injected by use of a syringe pump (0.5 mL/min). The reaction was monitored constantly using a UV-Vis spectrometer (Shimadzu, UV-2450). Typically, a peak at 400 nm appears

soon after injection, representing the bright dipolar mode of small silver nanospheres. After approximately 20 minutes the dipolar mode starts broadening and red-shifting, representing larger silver nanospheres. When a multipolar peak at 350 nm was observed a second injection of the silver nitrate solution was added by injecting 1.5 mL at a rate of 1.5 mL/min, this step is vital to ensure a seed-mediated growth process. Once the dipolar peak had reached the desired wavelength (typically 475-485 nm) the reaction vessel was placed in an ice bath to quench the reaction, until the reaction vessel was cool to the touch. Approximately 1 mL aliquots of the resulting solution was added to 2 mL centrifuge tubes (Eppendorf) and diluted in ethanol. The resulting reaction tubes were centrifuged for 30 minutes at 12,000 RPM. The supernatant was removed via a Pasteur pipette and the pellet was re-dispersed in ethanol. The resulting centrifuge tubes were centrifuged for 10 minutes at 12,000 RPM, the above step was repeated 2-3 more times. The resulting solution has an opaque pale brown colour and was stored at 4 °C until use.

2.1.2 Preparation of polymer thin films

PS, PMMA, and PVC thin films were produced by spin coating polymer solutions on glass slides. Glass slides (Globe, soda lime) were cleaned by sonication in methanol, rinsing with acetone and with deionized (18.2 MΩ·cm), the slides were dried under rough vacuum at 110 °C ($\approx$ 3 inHg, or about 0.1 Bar). PS (3% w/w in toluene), PMMA (4% w/w in toluene) and PVC (3% w/w in THF) solutions were filtered using a 0.22 μ m polytetrafluoroethylene syringe filter and were spun at $\sim$ 4000 RPM for 1 minute using a homemade spin coater to obtain $\sim$ 150 nm thick films. The spun films were allowed to rest at room temperature for 1.5 hours to let the majority of the solvent evaporate and were annealed overnight

above the polymers glass transition temperature, 135 °C for PMMA and PS, and 115 °C for PVC.

For the polymer blends, all solutions were 3% w/w (total mass of polymer/mass of THF solvent). The resulting solutions were not filtered to minimize removal of large polymer domains due to filtration. The polymer solutions were spun at ~ 4000 RPM for 45 seconds, and were allowed to rest at room temperature for 2 hours, after which they were annealed overnight at 140 °C.

All cast polymer films were stored at room temperature and pressurized under nitrogen until use.

2.1.3 Langmuir-Schaefer deposition

AgNC's were deposited onto the polymer films by Langmuir-Schaefer deposition, similar to literature.⁹¹ Except no 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC) was used for the homopolymer work, this was to minimize the effect of lipid interactions to the AgNC-polymer interface, which can potentially influence surface polymer dynamics.

Specifically, a UV-Vis spectrum of the AgNCs suspended in ethanol was obtained and the extinction of the dipolar resonance was compared to a standard sample, to determine the optimal aliquot of the AgNC solution to use for Langmuir deposition. The resulting AgNC aliquot was diluted to 2 mL (in ethanol) in a centrifuge tube and centrifuged at 12000 RPM for 30 mins. After the supernatant was decanted chloroform was added, this sample was then centrifuged at 13000 RPM for 5 minutes, twice, in attempt to substitute the original solvent (ethanol) with the more volatile chloroform. After the supernatant was removed, the solution was allowed to evaporate at room temperature

under a constant flow of N_2 , to evaporate the chloroform, the remaining solid was then re-dispersed into 250 μL of chloroform with 10 μL of ethanol, to ensure a known concentration of AgNCs. When using DOPC, 10 μL of a 1 g/mL solution (DOPC in ethanol) would be added at the same time as the chloroform instead. In either case the resulting solution would be sonicated and vortexed until homogeneity (a small amount of silver coating on the inside of the vial was acceptable).

The Nima 311D Langmuir-Blodgett trough was previously cleaned using chloroform and filled with deionized water. An isotherm was obtained with a bar speed of 35 mm^2/min if the isotherm produced a non-flat curve with a final pressure of 0.3 mN/metre or greater the surface was removed using an aspirator and re-cleaned using chloroform. This process was continued until the trough was deemed clean. The silver nanocube solution was slowly deposited onto the surface of the water using a micro syringe, the monolayer was left to settle for 25-30 minutes. In the case of using DOPC the trough was opened and closed (annealing) to get the desired uniform layer of silver nanocubes which appear as a yellow film, without the DOPC spacer, the AgNCs are likely to irreversible aggregate and as such, the maximum compression pressure of 0.7 mN/m was used. An isotherm was obtained to determine the desired pressure for deposition, generally at the liquid-gas phase at about 0.3 - 0.7 mN/metre. The polymer slides were then gently placed on the surface of the trough and immediately dried under N_2 gas. The resulting silver nanocube monolayers optical properties were analyzed by UV-Vis spectrophotometry (Shimadzu, UV-2450), to ensure no large coupling peak (600-900 nm), which represents particle aggregation, and satisfactory density of the monolayer, represented by the extinction. Utilizing the UV-Vis measurements, allows changes to the

set pressure for deposition for subsequent samples. The resulting AgNC monolayers were characterized by topological measurements using atomic force microscopy (AFM) and were stored under nitrogen until use.

2.1.4 Silver Nanocube-Polymer Thin Film Heating Experiments

Nanocube-polymer nanocomposites were heated using a homemade heating set up, designed to measure the temperature and UV-Vis spectra automated, in real-time. The heating setup was comprised of a heating pump (Thermo Fisher Scientific, RTE 7) pumping 95% EG into an aluminum heating block (Ocean Optics, CUV-ALL-UV cuvette holder). A xenon light source (Ocean Optics, PX-2) and detector (Ocean Optics, USB2000-UV-vis) were coupled to the heating block by use of optical fibers. A thermocouple (Vernier, TCA-BTA) was used to measure the temperature of the slide by direct attachment of the k-type thermocouple wire to the top of the sample. For all but PMMA heating experiments, time interval between spectral measurements was 3.1-3.8 seconds. However, for PMMA the time interval was increased to 30 seconds, to reduce UV light exposure.

2.1.5 Spectra processing

All spectra were processed and analyzed using OriginLab analysis software. For PS and PVC experiments, peak maxima were determined by batch peak processing using a first derivative fitting with a Savitzky-Golay (polynomial order 3, window size 25 points) smoothing to reduce baseline noise; this result was then compared to 100 - 200 randomly picked times to test validity. For the PMMA experiments, the lamp needed to be turned off in between accumulations causing more noticeable baseline shifts. Due to the

challenges of this baseline shift, only manual peak picking was used. The resulting Arrhenius plots were fit using a direct weighted linear fit in Origin Pro 2016, to better account for the increasing error on the temperature.

2.1.6 Topological measurements

Topography measurements were done using atomic force microscopy (AFM, Ntegra NTMDT, Russia, 100×100 μm scanner) in semi-contact mode with (512×512) or (1024×1024) points per image, with silicon (135 μm long, 0.3–6 $\text{N}\cdot\text{m}^{-1}$ spring constant (NSG03), resonance frequency 90 kHz, NT-MDT). AFM images were processed with Nova image processing software.

2.1.7 Finite-Difference Time-Domain Simulations

Finite difference time domain (FDTD) simulations were performed using Lumerical solutions Inc. (FDTD solutions version 8.17.1102). The simulated objects consisted of a 64 nm silver nanocube with a corner radius of 12.5 nm and a 2 nm layer of PVP, supported onto a 150 nm PS film. All of which is supported onto a SiO_2 substrate extended to the boundaries of the simulation (800 nm). The materials for Ag,^{111,112} PVP,¹¹³ and PS¹¹⁴ were described by fitted analytical permittivity data. A total-field scattered field (TFSF) light source was used, with a perfect matched layer (PML) boundary condition. The mesh extended at least 10 nm past the AgNC with a mesh size of 0.5 nm. The simulation was done from 300-800 nm with 251 total points.

2.1.8 Thermal polymerization of PS

1 mL of styrene filtered by gravity through a Al_2O_3 and glass wool packed column was added to 56 mg of benzoyl peroxide dissolved in 10 mL of toluene. This solution was

heated on a sand bath at 90 °C, to reduce the chance of fire. Three boiling sticks were added, and the solution was stirred at 400 RPM. The solution was gently heated to 130 °C over the span of 56 minutes. The reaction was deemed complete by increase in viscosity, and inability for the viscous liquid to be dissolved in methanol.

2.1.9 Optically induced polymerization of PS

Plasmonic heating driven reactions: 1 mL of styrene was filtered by gravity through a Al_2O_3 and glass wool packed column, to remove the 4-tert-butylcatechol stabilizer. This resulting solution was then added to 50 mg of benzoyl peroxide dissolved in 10 mL of toluene. This solution was added to a large cuvette with a stirring bar, and the AgNC monolayer was submerged in the solution and clamped. Excitation was done using an Ar/Kr ion laser (Coherent) focused onto the AgNC sample at 458 nm for 1 minute.

Plasmonically induced radicalization of styrene: 1 mL of styrene was filtered by gravity through an Al_2O_3 and glass wool packed column. From the filtered solution, one drop was added to the AgNC monolayer, which was deposited onto a Al_2O_3 coated glass slide through Langmuir-Blodgett deposition. This was to better align the D mode with the 488 nm laser line, to get more efficient absorption of light, thus, generating more localized heat. A coverslip was then placed on top to sandwich the filtered styrene to effectively coat the sample. The laser beam (488 nm) was focused through the AFM stage using a 60x objective, this enabled AFM imaging of the illuminated spot after heating. Laser power, and illumination time were altered to determine the effect on the degree of heating and radicalization of the polymer.

3 - Results and Discussion

3.1 Interfacial Diffusion of Silver Nanocrystals into Polymer Surfaces Monitored by Hybrid Plasmon Modes

Thin polymer films are of interest due to polymer chain confinement effects, which alters the physical properties, especially at the surface of the polymer.^{74,76,84} For example, the glass transition temperature and diffusion through the polymer.⁶⁴ Polymer properties can also be altered by incorporating nanoparticles into the polymer film.^{6,7,13,15,85} Incorporation of nanoparticles into a robust polymer shell or film can, in turn, enhance nanoparticle properties.^{10,86,87} Therefore, investigating interfacial interactions within nanoparticle-polymer composites is of significance for the development of functional nanocomposite materials.

This work utilizes the irreversible incorporation of AgNCs into polymer thin films when heated above the polymer's T_g . This provides a simple, controllable way to embed nanoparticles into polymer films. When the AgNCs are deposited onto a dielectric substrate they possess spatially separated hybrid plasmonic modes, a hybrid dipolar mode (D) that is concentrated to the area of greatest refractive index (typically substrate) and a hybrid quadrupolar mode (Q), which is focused to the surroundings (Section 1.4.2). As the AgNCs embed, the effective refractive index increases, causing an exponential⁹⁴ red-shift in the corresponding plasmonic mode (Section 1.4.2). Due to the spatial separation of these hybrid modes, the embedment of the nanocubes can be monitored in real-time through use of a far-field spectrophotometer. This enables determination of the

kinetics for the diffusion process, for polystyrene (PS), poly(methyl methacrylate) (PMMA), and polyvinyl chloride (PVC) films.

3.1.1 AgNC Homopolymer monolayers and FDTD simulations

TEM images of the AgNCs used, can be seen in Figure 3.1 (A,B). The corresponding histogram of the AgNC size can be seen in panel C, showing a normal distribution, with an average size of 64 with a standard deviation of 12 nm.

Figure 3.1: (A and B) Transmission Electron Microscopy (TEM) images of AgNC, with corresponding scale bar. (C) Corresponding histogram of several TEM images.

AFM images of the polymers before deposition were used to ensure a smooth and thick film (Figure 3.2). The desired thickness of the film was between 120 - 160 nm, ensuring the film is sufficiently thicker than the length of the cubes, which is necessary for full embedment. The desired roughness of the film was less than 2 % of the film thickness (root mean square roughness), typically ~3 nm. This was to ensure a uniform refractive index and surface dynamics across the film. AFM images for PMMA, PS and

PVC can be seen in Figure 3.2. Each polymer has characteristic surface morphology, with PS having long chain-like domains, PMMA having smaller segmented chains, and PVC having small circular indents, with tall cylindrical morphology at the edge. Due to the larger inherent roughness in the PVC films, a roughness of less than 8 nm was accepted,

Figure 3.2: Example of AFM images for each homopolymer used in this work.

and previous work has shown these large domains do not drastically effect the refractive index the AgNCs sense.⁴⁸

Figure 3.3: (Left) AFM image of AgNCs deposited on a PMMA film. (Right) Corresponding histogram of the Atomic Force Microscopy (AFM) image, with Bi-Gaussian peak fitting to determine the average size of the AgNCs.

Figure 3.3 displays an AFM image for AgNCs deposited onto a PMMA film (Left) and histogram of the AgNC height (Right). The sizes of the AgNCs after deposition may not be representative of the original AgNC sample (Figure 3.1), since the increased error associated with the AFM topological measurements likely overestimates the AgNCs sizes. To determine the average size of the AgNCs, many AFM measurements were performed before embedding (for each heating experiment), this was judged to give the most representative results for each sample. A histogram was plotted for the AFM images (Figure 3.3, Right), and a Bi-Gaussian distribution was used to determine the size. The left fit peak (Red) represents the height distribution of the polymer film, while the right peak represents the size distribution of AgNCs on top of the polymer (Green). Thus, the average size of the AgNCs is the difference in the peaks maxima, which was determined to be 68.4 nm, about 5 nm greater than the TEM images suggest (Figure 3.1).

Figure 3.4: FDTD simulated extinction cross section for a 64 nm AgNC coated with 2 nm of PVP, embedding into a 150 nm PS film. Refer to Section 2.1.7 for full FDTD protocol.

The Finite Difference Time Domain (FDTD) simulated spectra for AgNC embedding into a PS film can be seen in Figure 3.4, which shows a 3-D representation of the UV-Vis spectrum, illustrating the peak shifts as the AgNC embed into the polymer, with the characteristic initial D mode (~ 450 nm) shift and subsequent Q mode (~ 400 nm) shift observed. Figure 3.5 shows the Q mode shift in respect to distance embedded from this FDTD simulation (Left) and experimental results with the Q mode evolution in respect to time (Right). In both cases the Q mode is initially insensitive to the AgNC embedment, but at some distance embedded, the Q mode starts to shift. Further analysis of the Q mode data from the simulated 64 nm AgNC, shows that the Q mode starts shifting at about halfway embedded (31.3 nm embedded). Utilizing this information, it becomes possible to determine the time at which the AgNCs embed halfway (Figure 3.5, Right).

Using the average height of the AgNCs from AFM images taken before embedding, diffusion constants can be determined through Equation 26 and 27 (Section 1.4.2).

Figure 3.5. (Left) Finite-Difference Time-Domain (FDTD) simulated results representing the Q mode change as the AgNCs embed into a PS film. The intersection of the two lines represents the half the edge length of the AgNCs. ($x_{1/2}$). (Right) Experimental data representing the Q mode evolution in time for AgNCs embedding into a PS film.

As illustrated in Figure 3.6, the measured temperature of the sample is initially increasing, the temperature stabilization time was dependent on the desired set temperature of the heating block, ranging from 100 s to 300 s. Therefore, the temperature of the sample is continuously changing initially during the embedding of the AgNCs. Which allowed the determination of surface and bulk embedding temperatures (T_e) for each polymer; however, this also leads to relatively large variance in the measured physical constants. Due to this, the median temperature during each transition step was used as T_e . For example, the surface T_e for Figure 3.5 was calculated to be 80.6°C with the bulk being 103.8°C . The final reported surface and bulk T_e values were calculated as an average from each trial, with the standard deviation reported as the error. Since the thermocouple was not attached to the part of the sample making direct contact with the

heating block, the onset temperature drastically underestimates the actual temperature of the measured sample. The error associated with this was emphasized more with the lower temperature samples, due to the sample taking longer to heat up to the polymers T_e . This effect was taken into account by only using the times at which the sample's temperature was constant (t_{iso}) as represented in Figure 1.15 and Equation 27 (Section 1.4.2).

Figure 3.6: Temperature measurement of the sample (green), and dipolar resonance evolution (black) for PVC, with the surface (red) and bulk (blue) transitions and corresponding regression statistics.

3.1.2 Polystyrene-AgNC film

Extinction spectral map for a PS-AgNC heating experiment with a final temperature of 105.3 °C can be seen in Figure 3.7 (Left). There is the expected red-shift of the D mode at 462 nm and subsequent shift of the Q mode at 398 nm. The Q mode shifts at 165

seconds, and after 530 seconds the Q mode begins to converge with the D mode. This is characteristic of the embedding process, due to an isotropic local electric environment around the AgNCs. The right panel (Figure 3.7) shows the temperature of the sample during UV-Vis measurements and the D mode wavelength evolution in respect to time. Two kinetic steps are seen, attributed to initial embedding into the surface layer of PS, followed by embedding into the bulk polymer.

By analyzing the temperature of the sample for these two regimes (Figure 3.7), the two embedding temperatures (T_e s) can be determined. The first transition (Figure 3.7, Right) depicted in red, had a T_e of 93 ± 1 °C, while the second transition depicted in blue had a T_e at 101 ± 2 °C, which is within error of the bulk T_g for PS.¹¹⁵ This result suggests the presence of a surface layer with enhanced segmental mobility on top of the bulk polymer, allowing the particle to embed a small amount, below the bulk T_g of the polymer.

Figure 3.7: (Left) UV-vis spectra for the heating of AgNCs on PS to an equilibrium temperature of 105.3 °C. (Right) Temperature of the sample and D mode evolution in time, with the two steps representing the surface (red) and bulk (blue) transitions.

Using the nanoruler aspect of the AgNCs (Section 1.4.2), the diffusion (embedding) constant (k_D) for AgNCs embedding into PS films was determined, and ranged from 0.7-2.9 nm² s⁻¹ for heating experiments performed between 95 °C and 102 °C. Using this, an Arrhenius relationship was plotted (Figure 3.8), with a linearity coefficient of 0.79. The activation energy of diffusion (E_D) was calculated to be 220 ± 51 kJ mol⁻¹ for AgNC's embedding into the PS film. This value is about an order of magnitude larger than a previously reported result of 19.9 kJ/mol for a PMMA/PS binary film, and 14.4 kJ/mol for 16.5 nm Au nanoparticles in water.¹¹⁶ This is expected because the diffusion constant depends greatly on the size of the diffusing material.^{117,118}

Figure 3.8: Arrhenius plot for the PS-AgNC heating experiments. With a Pearson's correlation constant of -0.91 and a R-square correlation constant of 0.82.

3.1.3 Poly(methyl methacrylate)-AgNC film

An extinction spectral map for a PMMA-AgNC heating experiment, with an equilibrium temperature of 118 °C, can be seen in Figure 3.9 (Left). The baseline noise in the spectrum is a symptom of a shorter integration time, which is aimed to eliminate UV

damage of the PMMA film. Two discrete transition states can also be seen for PMMA (Figure 3.9, right), the corresponding T_e 's are found to be, 111 ± 2 °C and 115 ± 1 °C for the surface and bulk transition respectively.

Figure 3.9: (Left) UV-vis spectra for the heating of silver nanocubes on PMMA to an equilibrium temperature of 118.07 °C. (Right) Temperature of the sample and dipolar mode evolution in time, with the two steps representing the surface (red) and bulk (blue) transitions.

The T_g of similarly sized PMMA is generally reported between 118-130 °C.^{54,119} This variance is due to the relatively large temperature range for the glass transition, as well as the strong relationship with tacticity and film thickness.¹¹⁹ This effect is likely the reason for the small temperature deviation of the two transitions.

Figure 3.10: Arrhenius plot for the PMMA-AgNC heating experiments. With a Pearson's correlation constant of -0.90 and a R-square correlation constant of 0.81.

The diffusion constants for AgNCs embedding into PMMA thin films ranged from 0.3 – 2.8 $\text{nm}^2 \text{s}^{-1}$ at 109.2 -114.1 °C, the corresponding Arrhenius plot can be seen in Figure 3.10, with a linearity coefficient of 0.81. The activation energy for the diffusion process was determined to be $84 \pm 18 \text{ kJ mol}^{-1}$ (Figure 3.10). The large x-axis error bars are due to the high temperature set-point required to heat the sample above PMMA's bulk T_g .

3.1.4 Polyvinyl chloride-AgNC film

Extinction spectral map for a PVC heating experiment heated to an equilibrium temperature of 101.6 °C can be seen in Figure 3.11 (Left). The high mobility of the polymer at this temperature is suggested by the almost immediate shift in the D mode (Right). Two discrete transitions can be seen in Figure 3.11 (Right). The T_g s were determined to be: 77 ± 5 °C and 96 ± 5 °C, for the surface and bulk, respectively. The effect of MW on the T_g for PVC has not been well studied, although for similar weighted PVC, a T_g of 80-90 °C has been reported.^{65,66}

Figure 3.11: (Left) UV-vis spectra for the heating of silver nanocubes on PVC heated to an equilibrium temperature of 101.6 °C. (Right) Temperature of the sample and dipolar mode evolution in time, with the two steps representing the surface (red) and bulk (blue) transitions.

Figure 3.12. Arrhenius plot for the PVC-AgNC heating experiments. With a Pearson's correlation constant of -0.98 and a R-square correlation constant of 0.95.

The calculated diffusion constants ranged from 0.0-2.2 nm² s⁻¹ for a temperature range of 86.6-101.1 °C. The Arrhenius plot for the PVC sample (Figure 3.12) ($R^2 = 0.94$), with a corresponding activation energy of 239 ± 31 kJ mol⁻¹.

3.1.5 Conclusion

The method developed in this work enables considerable control in nanoparticle concentration and embedment depth, which is of great interest in the fabrication of nanoparticle- polymer nanocomposites. The concentration of nanocubes in the composite is defined in a separate process to the embedding. Due to the hybrid plasmon modes intrinsic to supported silver nanocubes (size >40 nm), it is possible to monitor in real-time, with excellent spatial resolution, the nanocubes embedding into the polymer film. This method was used to form nanocomposites of silver nanocubes with three different polymers: polystyrene, poly(methyl methacrylate) and polyvinyl chloride. In addition to the formation of the tuneable nanocomposite, the method also allows characterization of physical properties of the polymer substrate. Namely, it allowed the confirmation of two polymer dynamics within the polymer film, featuring a thin surface layer on top of the bulk polymer with enhanced segmental mobility. The temperature at which nanoparticle embedding occurs differed by 5 - 20 °C for the two layers and was specific to the polymer. Lastly, constants for nanocube diffusion into the polymer films were determined, with the activation energy for the process based on an Arrhenius relationship. This study demonstrates the potential use of plasmonic based nanorulers in studying interfacial dynamics in polymer-nanoparticle nanocomposites. Which is of use for the fabrication of functional nanocomposite materials, in which fine control over nanoparticle-polymer interactions is required.

3.2 Selective embedment into immiscible polymer domains

Polymer blends are of particular interest as they are a cost-effective means to optimize polymer material properties, such as: conductivity,¹ bio-compatibility,² rubberiness,³ and physical/chemical robustness.^{4,5} Incorporation of nanoparticles into polymer blends can even further enhance the useful properties of these polymer blends, such as domain solubility and stability,¹²⁰ and can lead to nanoparticle induced morphological changes.¹²¹ Interestingly, the optical properties of the nanoparticles can be tuned by changing the percentage of polymers within the blend.¹²² Generally metal or metal oxide nanoparticles are used due to their advantageous electrical and optical properties.

Immiscible ternary polymer blends are of interest as they possess segregated polymer domains with different physical properties, such as polymer dynamics.^{123,124} In this work a blend of polystyrene (PS), poly(2-vinylpyridine) (P2VP) and poly(methyl methacrylate) (PMMA) was used due to its ability to form tuneable well defined domains, with different glass transition temperatures: 100 °C, 105 °C, and 118 °C for PS,¹¹⁵ P2VP¹²³ and PMMA,⁵⁴ respectively. AgNCs were deposited onto the polymer blends using a Langmuir technique and were then embedded through the thermally induced irreversible embedment previously explored (Section 1.4.2).¹²⁵ This allows for fine control over AgNC embedment depth while simultaneously monitoring the embedding in real-time. The temperature specificity of the embedding process allows the selective embedment of AgNCs into the individual polymer domains within the blended polymer film (Figure 3.13).

The morphology in immiscible polymer blends can be altered by simply changing the composition of the polymer solution and the large size of the domains allow for the AgNCs to be adequately spaced on discrete polymer segments, making polymer blends

advantageous over block-copolymers, in this case. Although polymer blends were used, this general concept can be further applied to any polymer with segregated domains, such as block copolymers, and various types of metal particles such as gold nanoparticles can be used instead of AgNCs. This work is significant for the production and characterization useful hybrid nanoparticle-blended polymer materials.

Figure 3.13: Cartoon representing selective embedment of silver nanocubes into an immiscible ternary polymer blend. Where red, blue and green represent different polymers forming defined domains. Each polymer has a different glass transition temperature (T_g).

3.2.1 PS/PMMA/P2VP blend (34.5%/31.0%/34.5%)

Figure 3.14 shows the AFM images for a 34.5%/31.0%/34.5% (PS/PMMA/P2VP) polymer blend. Row (Inset) 1 represents the film as cast, the left image is 40x40 μm in size and right is 20x20 μm in size. Two major domains can be seen, with one spatially taller than the other, which forms ring like structures throughout the film. When AgNCs are deposited on top of the polymer film (Figure 3.14, 2) the two domains become more apparent, likely due to the added contrast from adding the ≈ 70 nm nanocubes. These two morphologies are defined as a 'Hill' and a 'Valley', and as expected, the height of the cubes is the same for both domains: 77 ± 14 nm and 77 ± 13 nm for the Hill and Valley domains, respectively. There also appears to be aggregation of the AgNCs in small sections of the film.

As the sample is heated above the T_g of PS and P2VP, but below the T_g of PMMA (Figure 3.14, 3), a drastic decrease in height in the Hill domain is seen (10 ± 7 nm), signifying almost full embedding into that polymer domain. A small amount of embedding into the Valley domain is also seen (48 ± 14 nm), and there is visible aggregation of the AgNCs on this domain. Interestingly, a new well defined circular domain (Circle domain) is seen, with different topology than the previous domain. The AgNCs on this Circle domain are 55 ± 18 nm tall. Due to PS having the lowest T_g , it is hypothesized that it would have the largest degree of embedding, suggesting PS was the Hill domain. Since P2VP has a T_g around 105°C , it is expected that it is the Valley domain, which is further supported by the aggregation seen, as no significant aggregation was seen for PS or PMMA homopolymers. From this it is deduced that the Circle domain was PMMA.

When the sample is heated above the T_g of PMMA as well (Figure 3.14, 4), full embedment into the Hill domain is seen, represented by the height of 10 ± 8 nm. Approximately halfway embedding into the Circle domain was seen (34 ± 15 nm), supporting the idea of it being PMMA. Interestingly, no further embedding into the Valley domain is seen, as the height of the AgNCs was 42 ± 14 nm, this is due to aggregated particles having a lower overall surface energy, which effectively breaks the surface energy requirement for embedding (Section 1.4.1). This makes the embedding process thermodynamically unfavorable, and as such the particles are not expected to embed. Due to the unfavorable interaction between the predominately non-polar PVP capping agent and the polar P2VP surface, self association of the nanocubes occurs to minimize this interaction, observed as aggregation in the AFM images.

Figure 3.14: AFM images for a 34.5%/31.0%/34.5% (PS/PMMA/P2VP) blend. (1) as cast, (2) with AgNCs deposited, (3) subsequent heating at $109.7 \pm 0.3 \text{ }^{\circ}\text{C}$, (4) heating at $122.6 \pm 0.5 \text{ }^{\circ}\text{C}$.

3.2.2 PS/PMMA/P2VP blend (48.7%/23.1%/28.2%)

Figure 3.15 shows the AFM images for a 48.7%/23.1%/28.2% (PS/PMMA/P2VP) polymer blend. Row 1 represents the film as cast, with 40 x 40 μm (Left), 20 x 20 μm (Middle) and 10 x 10 μm (Right) AFM images. By simply increasing the relative amount of PS by a factor of two, in comparison with the 34.5%/31.0%/34.5% blend, a drastic change in polymer morphology is seen (Figure 3.15, 1). The film goes from large ring like chains (Figure 3.14, 1), to smaller circular hill domains. This is a testament for the sensitivity that polymer blends have to the inter-molecular forces within the blend. The two domains referred to as Hill and Valley can still be seen once the AgNCs are deposited on top (Figure 3.5, 2). As expected, the topology on both domain segments are the same: 73 ± 19 nm and 68 ± 21 nm, for the Hill and Valley domains, respectively.

As the sample is heated just below the bulk T_g of PS (Figure 3.15, 3), a small decrease in height for the AgNCs on the Valley domains is observed (44 ± 17 nm), while the Hill topology stays the same (67 ± 17 nm). This is attributed to the previously observed surface layer for PS homopolymers (Section 3.1.2). This surface layer has increased mobility, effectively having a lower T_g , allowing for a small amount of embedding below the Bulk T_g of the polymer. Interestingly, small sections of AgNC aggregates can be seen (Section D.1, Figure 6.6 for larger AFM images), which signifies the presence of the P2VP domain.

When the sample is heated well above the T_g of all three polymers (Figure 3.15, 4), essentially full embedment is observed, with an average height of 8 ± 7 nm and 14 ± 10 nm for the Valley and Hill domains, respectively. Interestingly, the aggregated sections

are largely undisturbed, with an average height of 65 nm. Thus, even at 120 °C the embedding of aggregated particles is still thermodynamically unfavorable.

Figure 3.15: AFM images for a 48.7%/23.1%/28.2% (PS/PMMA/P2VP) blend. (1) as cast, (2) with AgNCs deposited, (3) subsequent heating at 97.3 ± 0.3 °C, (4) heating at 120.6 ± 0.5 °C.

3.2.3 PS/PMMA/P2VP blend (30.3%/33.3%/36.4%)

Figure 3.16 shows the AFM images for a 30.3%/33.3%/36.4% (PS/PMMA/P2VP) blend, row 1 shows the film as cast. The topology shares similarities to the 34.5%/31.0%/34.5% blend, with two major domains forming a semi-circular chain like structure. However, there seems to be a decrease in degree of separation of the domains (Figure 3.16, 2). Unlike, the 34.5%/31.0%/34.5% blend (Figure 3.14, 2), the circular ring like structures assumed to be from PMMA are initially present. The height of the cubes on the two domains were: 78 ± 15 nm and 79 ± 14 nm for the Hill and Valley domains respectively.

When the sample is heated at just below the bulk T_g of PS (Figure 3.16, 3), a small degree of embedding is seen, with the average height of the cubes, 46 ± 15 nm for the Valley and 59 ± 18 nm for the Hill domain. Since no visible aggregation is seen, it is hypothesized that the P2VP domain is not exposed at the surface of the film, suggesting it is the major component of the film, similar to what was seen for a 1/1/1 blend spin casted on a SiO_x substrate.⁷⁹ Interestingly, the cubes on the circular domains have the same height as the Hill domain, which supports the concept that they are both composed of PMMA. Consequently, the valley domain is hypothesized to be PS. Which suggests inversion of the domain when PS is changed from the major (Figure 3.15, PS = 48.7%) to minor (Figure 3.16, PS = 30.3%) component of the solution.

As the sample is further heated above the T_g of PMMA (Figure 3.16, 4), near full embedding into the Valley domain is seen, supporting the PS hypothesis, with an average height of 19 ± 11 nm. A small amount of embedding was also found for the Hill domain with an average height of 40 ± 14 nm, suggesting the Hill domain is PMMA. Interestingly, the degree of embedding is much lower than the 48.7%/23.1%/28.2% sample (Figure

3.15, 4). Which had an average height of 8 ± 7 nm and 14 ± 10 nm for the Valley and Hill domains, respectively, at 120.6 ± 0.5 °C, which is about 2 degrees Celsius lower. This result suggests either a reduction in the embedding rate, or that the system had reached a new thermodynamic minimum state (Section 1.4.1). Another fascinating observation is the relative placement of the PS and PMMA domains in the blend. Recall from Figure 3.14 (34.5%/31.0%/34.5%), the PS domain was determined to be the Hills, and P2VP was the Valley. This suggests inversion of the polymer morphologies, due to a subtle increase in the P2VP and PMMA, while reducing the PS composition.

Figure 3.16: AFM images for a 30.3%/33.3%/36.4% (PS/PMMA/P2VP) blend. (1) as cast, (2) with AgNCs deposited, (3) subsequent heating at $99.7 \pm 0.3^\circ\text{C}$, (4) heating at $122.3 \pm 0.4^\circ\text{C}$.

3.2.4 PS/PMMA/P2VP blend (60.0%/20.0%/20.0%)

Figure 3.17 shows the AFM images for a 60.0%/20.0%/20.0% (PS/PMMA/P2V2) blend (larger version of these AFM images can be found in Section D.2), row 1 shows the film as cast. It shares similarities to the 48.7%/23.1%/28.2% blend (Figure 3.15, 1), with well defined circular domains, except in this case the domains are considerably smaller. Once AgNCs are deposited on top (Figure 3.17, 2), the two domains can be easily discerned. However, these domains seem to be more chain-like than the circular domains seen in Figure 3.15. The height of the cubes on these domains were: 76 ± 18 nm and 70 ± 17 nm for the Hill and Valley domains, respectively. Some sections of aggregation can also be seen, suggesting the presence of P2VP at the surface.

When the sample is heated just below the bulk T_g of PS (Figure 3.17, 3), a small amount of embedment is seen in the Valley domain, with a decrease in average height to 54 ± 19 nm. However, the height of the AgNCs on the Hill domain is unaffected at 70 ± 18 . Supporting the idea that the Valley domain is PS and the Hill domain is PMMA.

When the sample was further heated to just below the bulk T_g of PMMA, full embedment into the Valley domain is represented with an average height of 8 ± 8 nm, supporting the hypothesis that it is PS. Interestingly, near full embedment into the PMMA domain is seen as well, with a height of 25 ± 19 nm. This suggests drastically different kinetics for this blend in comparison to 30.3%/33.3%/36.4% (Figure 3.16), which further suggests possible surface confinement effects, causing a reduction in embedding rate.

Figure 3.17: AFM images for a 60.0%/20.0%/20.0% (PS/PMMA/P2VP) blend. (1) as cast, (2) with AgNCs deposited, (3) subsequent heating at 98.4 ± 0.3 °C, (4) heating at 112.5 ± 0.6 °C.

3.2.5 Embedding Summary

The glass transition dependence on AgNC embedment (Section 1.4.1) enabled the identification of discrete polymer domains within the PS/PMMA/P2VP ternary polymer

blends from, the relative heights of the AgNCs at various temperatures; since AgNCs will only embed when the polymer is above its glass transition temperature (T_g). This allows the selective embedment of the AgNCs into the polymer domains and can act as a tool to identify the polymer since the embedding temperatures were previously determined (Section 3.1.2 and Section 3.1.4). A summary of the temperature dependence of the embedding of the nanocubes into each polymer domain can be found in Table 3.1. Below is a brief overview on the selective embedment into the immiscible ternary polymer blends (Sections 3.2.1-3.2.4).

For a 34.5%/31.0%/34.5% (PS/PMMA/P2VP) blend (Section 3.2.1), it was determined that the Hill domain was PS, the Valley domain was P2VP and the Circle domain was PMMA (Figure 3.14). The aggregation on the Valley domain supported that the polymer was P2VP as AgNC aggregation is uncharacteristic for PMMA and PS homopolymers. Essentially full embedment of the AgNCs into the Hill domain was observed at 109.7 ± 0.3 °C, representing it as PS. The AgNCs on the PMMA domain embedded about halfway at 122.6 ± 0.5 °C, while the AgNCs only embedded slightly into the P2VP domain at the same temperature. The PMMA domain was only apparent after heating of the sample at 109.7 ± 0.3 °C, suggesting the AgNCs changed the interfacial energy at the surface of the film, which caused polymer re-arrangements to obtain a new thermodynamic minimum state. Interestingly, the PMMA domains become less apparent when the sample is heated to 122.6 ± 0.5 °C, potentially due to additional polymer re-arrangements.

For a 48.7%/23.1%/28.2% blend (Section 3.2.2), it was determined that the Hill domain was PMMA and the Valley domain was PS (Figure 3.15). Unlike the

34.5%/31.0%/34.5% sample (Figure 3.14) essentially full embedment was observed for AgNCs on both the PS and PMMA domains heated to 120.6 ± 0.5 °C (Figure 3.15). A small amount of particle aggregation was observed indicating the presence of P2VP at the surface, suggesting the majority of the polymer was below the surface, predominately interacting with the polar glass surface. The topology of the sample is very different from the 34.5%/31.0%/34.5% blend, with small circular domains instead of the larger chain-like domains (Figure 3.14), which is a testament to the tunability of the ternary blend.

For a 30.3%/33.3%/36.4% blend (Section 3.2.3), it was determined that the Hill domain was PMMA and the Valley domain was PS (Figure 3.16), suggesting phase inversion of the PS domains in respect to the 34.5%/31.0%/34.5% sample (Figure 3.14). Near complete embedment was observed for AgNCs on the PS domain and less than half for the PMMA domain heated to 122.3 ± 0.4 °C. The reduction of embedding into the PS and PMMA domains in respect to the 34.5%/31.0%/34.5% blend (Figure 3.14) was due to a change in the interfacial surface energy caused by altering the composition of the solution or a reduction in the embedding kinetics. The topology of the sample appears similar to the 34.5%/31.0%/34.5% blend (Figure 3.14) except the PMMA and P2VP domains have inverted.

For a 60.0%/20.0%/20.0% blend (Section 3.2.4), it was determined that the Hill domain was PMMA and the Valley domain was PS (Figure 3.17). Full incorporation of the AgNCs was observed for the PS domain and near full embedment was determined for the PMMA domain heated at 112.5 ± 0.6 °C, which is comparable to the 48.7/23.1/28.2 blend (Figure 3.15) and more than the 30.3/33.3/36.4 (Figure 3.16) blend which are heated to ≈ 120 °C, which further signifies a blend dependant reduction in embedding

rate. The topology of the sample (Figure 3.17) lends characteristics from the 48.7/23.1/28.2 and 30.3/33.3/36.4 blends; since it possesses similar circular domains as found in sample 48.7/23.1/28.2 (Figure 3.15), with chain like domains similar to the 30.3/33.3/36.4 (Figure 3.16) blend.

Table 3.1: Summary of the AgNCs height on each discrete polymer domain for all polymer blends, with the corresponding temperature (T_r is room temperature).

Blend (PS%/PMMA%/P2VP%)	Temperature (°C)	H_{Hill} (nm)	H_{Valley} (nm)	H_{Circle} (nm)
34.5/31.0/34.5	T_r	77 ± 14	77 ± 13	
	109.7 ± 0.3	10 ± 7	48 ± 14	55 ± 18
	122.6 ± 0.5	10 ± 8	42 ± 14	34 ± 15
48.7/23.1/28.2	T_r	73 ± 19	63 ± 21	
	97.3 ± 0.3	67 ± 17	44 ± 17	
	120.6 ± 0.5	14 ± 10	8 ± 7	
30.3/33.3/36.4	T_r	78 ± 15	79 ± 14	
	97.7 ± 0.3	59 ± 18	46 ± 15	
	122.3 ± 0.4	40 ± 14	19 ± 11	
60.0/20.0/20.0	T_r	76 ± 18	70 ± 17	
	98.4 ± 0.3	70 ± 18	54 ± 19	
	112.5 ± 0.6	25 ± 19	8 ± 8	

3.2.6 Surface confinement effects

Figure 3.18 shows a comparison between the UV-Vis spectra of a homopolymer and a blend. Initially, the peak widths for the D and Q are bigger for the 60.0%/20.0%/20.0% blend (Figure 3.18, A). This is consistent with the expected result of having a broader plasmon peak, since to a certain degree, the AgNCs are deposited onto all three polymers, each of which has a different refractive index. Specifically, PMMA has the lowest refractive index ($n = 1.497$ at 486.1 nm),¹¹⁴ and PS having the largest ($n = 1.599$ at 486.1 nm),¹¹⁴ the refractive index of P2VP hasn't been thoroughly studied, but is believed to be around 1.5 over the visible range.^{126,127} Since the UV-Vis measurement is from the ensemble of all the cubes on each polymer, the resulting D and Q peaks are the superpositions, leading to broader peaks than nanocubes deposited on a single polymer (Figure 3.18, A).

The final UV-Vis spectra for the PS homopolymer and the PS/PMMA/P2VP blend are different (Figure 3.18, A), this is partially due to the differences in temperatures between the two samples (Figure 3.18, B) and possible kinetic differences in the embedding. The PS homopolymer supported sample shows near full embedment of the AgNCs, with the D and Q overlapping, while for the blend almost no shift in the Q mode is seen, and about a 25 nm shift in the D mode is observed. Comparing the heat maps between these samples (Figure 3.5, C and D) it is clear that the rate of embedding is drastically different, however, this could simply be due to the temperature difference. With the AgNC-PS nanocomposite showing essentially full embedment at 2000 s. This is in

stark contrast to the 60.0%/20.0%/20.0% (PS/PMMA/P2VP) blend, where the D mode continues to slowly shift even at 10000 s, and Q mode only shifts 4 nm in total (Figure 3.18, A).

Figure 3.18: A) UV-Vis spectra from the heating experiments for AgNC-polymer nanocomposites, (Blue) a 3.0/1.0/1.0 (PS/PMMA/P2VP) polymer blend and a homopolymer PS (Red) initially at $t=0$ (Solid), and the final spectrum (Dashed). B) The corresponding temperature measurements for the PS homopolymer and the 3.0/1.0/1.0 blend. C) UV-Vis spectral Heatmap for the 3.0/1.0/1.0 blend-AgNC heating experiment. D) UV-Vis spectral Heatmap for the PS homopolymer-AgNC heating experiment

Due to the temperature differences in these two samples, no definite conclusion can be made. Thus, a new approach was used, namely, comparing the Arrhenius plot for

the PS homopolymer and the blends which were specifically heated such that only AgNCs on PS would embed (Figure 3.19). Samples 30.3%/33.3%/36.4% and 60.0%/20.0%/20.0%, which were heated below the bulk T_g of PS, were outliers, from the PS homopolymer Arrhenius relationship (Figure 3.19). Interestingly, their bulk transitions do follow the trend (points left of the dotted line, Figure 3.19). This suggests that only the surface layer of the polymer is affected by the change in molecular interface. This is in agreement with literature results using spherical polymer particles.¹⁰⁶ These results showed that varying the size of the particle does not change the bulk T_g of the polymer, but it does drastically increase the specific heat capacity, which is represented as a thin layer on top of the bulk polymer.¹⁰⁶ Another study looked at the reduction in T_g for polymer spheres capped with silica, and found that the confinement effect seen for spheres is not due to the shape of the polymer, but rather the interfacial surface energy difference from the free surface and the bulk polymer.¹²⁸ By modifying the composition of the polymer blend, the surface free energy is changing,^{77,83} which likely is the cause for the enhancement of the surface confinement effects.

Figure 3.19: Arrhenius plot for homopolymer PS films, with the PS kinetic data from the ternary polymer overlaid. The bulk T_g of PS is outlined as the maroon dashed line.

3.2.7 Conclusion

This work develops a technique to fabricate and controllably optimize nanoparticle-blended polymer nanocomposite functional materials, based on the thermally activated irreversible embedment of AgNCs into polymer surfaces. Immiscible polymer blended films were produced through a simple spin coating approach, forming defined polymer domains, driven through self-association of the polymers. Utilizing the temperature selectivity of the embedding process AgNCs were selectively embedded into individual polymer domains, within immiscible ternary polymer blends. This allowed the determination for the specific positions of the polymers within the blends. As the AgNCs

embed into a polymer, the effective refractive index increases, causing a shift in the peak positions observed in a UV-Vis spectrum. This gives a sensitive way to monitor the embedding of the AgNCs in real-time, allowing the determination of the dynamics for the embedding process. Based on these UV-Vis measurements, surface confinement of PS was concluded for some polymer blends; however, the bulk dynamics were not affected. This work emphasizes a controllable technique to produce, characterize and optimize nanoparticle-polymer nanocomposite materials, while monitoring the embedding process in real time. This is of interest in fields that require fine control over nanoparticle incorporation within segregated polymer domains, such as polymer blends and copolymers; this work also brings interesting insight into polymer dynamics within polymer blends.

4 - Future Direction and Preliminary Results

4.1 Photo induced growth of polystyrene

The ability to precisely pattern polymer films has a significant role in electronics and optics due to its ability to form well ordered nanoscale templates. Typical cost-effective patterning techniques are: photolithography, imprint lithography or polymer mold processes, however, these approaches are unable to produce well defined nanoscale features, making them invalid for some applications.¹²⁹ Higher resolution processes such as electron-beam lithography¹³⁰ and block-copolymer templates¹³¹ can produce well-defined high-resolution structures, although, at much higher costs.¹³² In this section a new technique is proposed, which utilizes the photocatalytic properties of plasmons to pattern polystyrene onto AgNC monolayers. Two methods are explored, a photothermal and a hot carrier (electron) approach. The photothermal approach utilizes the heat generated from the AgNCs to cause the radicalization of benzoyl peroxide, which allows the free-radical polymerization of styrene (Section E, Appendices). In contrast, the second approach relies on hot-electrons generated from the AgNCs to start the polymerization of styrene. This work acts as fundamental groundwork for plasmon-activated chemistry and brings a new polymer patterning technique, which can be further optimized, potentially allowing colour-nanoscale printing.

4.1.1 Growth of polystyrene using a radical initiator and plasmon induced heating

The classical polymerization approach was first used (Section 2.1.8), to ensure adequate removal of the stabilizing agent (4-tert-butylcatechol), which acts to inhibit the free radical

process.¹³³ This approach utilizes conventional heating to form the radical species necessary for the subsequent polymerization of styrene (Section E, Appendices). Experimental procedure can be found in Section 2.1.8. Specifically, the reaction flask contained 1 mL of filtered styrene and 56 mg of the initiator (benzoyl peroxide) dissolved in 10 mL of toluene and was first heated at 90 °C, increasing the temperature every 10 minutes until a viscous liquid formed. The viscous liquid formed after 56 minutes at 130 °C and was found to be insoluble in methanol. Although this is a very simple test, it does signify a hydrophobic viscous compound, which in this case is likely polystyrene. From this first experiment, it is recognized the necessary temperature for the polymerization reaction of styrene is approximately 130 °C, which was higher than the expected 80 °C.¹³⁴ This is likely due to the sub-optimal Al₃O₃ filtration, leading to the presence of some 4-tert-butylcatechol stabilizing agent in the solution, which drastically reduces the reaction rate.¹³³

The second experiment was aimed to test the extent of classical styrene polymerization using the photothermal heating of the AgNCs (Section F, Appendices) to overcome the 130 °C thermal barrier. An AgNC monolayer on glass was chosen to have a high extinction and strong particle coupling, allowing for efficient collective heating of the particles. The resulting AFM images can be seen in Figure 4.1. Fascinatingly, there seems to be a relationship with the resulting AFM images and the power (Figure 4.1).

Figure 4.1: AFM images of photothermal PS growth using benzoyl peroxide as the free radical source at different powers.

For 10 mW, there appears to be larger particles where the laser beam was focused, hinting at polystyrene coating the AgNCs. There seems to be no bare AgNCs in the center of the beam, which is likely due to the Gaussian nature of the focused laser beam, with the highest effective power at the center of the beam. Bare AgNCs are seen about 12 μm from the center of the beam, suggesting that the particles were not hot enough, due to the lower effective power those AgNCs experienced. A similar trend is

seen at 19.0 mW, except a small hole is visible in the centre. This hole is believed to be due to decomposition of the polymer, which suggests a local temperature of about 230-280 °C.¹³⁵ However, in this case the particles appear taller than the AgNCs, suggesting some polymer still remains, or possible AgNC melting. The same observation is seen with 30.0 mW, except, spatially the growth appears to better represent the Gaussian beam, appearing in a more circular pattern. At 40.7 mW there appears to be more decomposition of PS in the center of the circle, to the point where the AgNCs in the center appear the same height as the rest of the film. Interestingly, there appears to be an accumulation of polymer at the ridge of the circle, representing the lowest effective power of the beam. This suggests the local temperature is not high enough to allow thermal decomposition of the polystyrene. At 74.1 mW and 99.0 mW similar topology is observed, except there appears to be large chainlike structures protruding from the polystyrene circle. These chains are attributed to the free radical polymer species that can further react with excess styrene as outlined in Section E (Appendices). Although the local heat at these points is likely lower than the 80-130 °C necessary for the benzoyl peroxide to react, these free radical polymer species can continue the growth to a small degree, forming large vine like domains. At 125.7 mW there appears to be a large degree of decomposition of PS, and possible re-arrangement AgNCs to the ridges, which can be seen in the image as the large concentration of particles at the edges of the circle, and relatively disperse AgNCs in the center of the beam.

The UV-Vis spectrum shows a loss in hybridization of the AgNCs and although this is expected for PS growth onto the AgNCs, the section of the growth is very small (Figure 4.2) with respect to the beam size of the spectrometer. Thus, the cause for the shift in the

UV-Vis spectrum is likely adsorption of reagents, such as unreacted benzoyl peroxide, an unwanted bi-product that is challenging to wash off without removing the AgNCs or the resulting PS coating. Because of this, the reaction was tried using only styrene, relying on the generated hot-electrons from the AgNCs to jump start the free radical process, as described in the next section.

Figure 4.2: UV-Vis spectrum of AgNCs deposited on a glass substrate before and after the styrene polymerisation reaction.

4.1.2 AgNCs as a free electron source

It has been reported that along with plasmonic heating, it is possible to generate high energy electron-hole pairs, typically called hot carriers.^{136,137} These high energy electrons have short lifetimes (femtoseconds), and low probabilities. The generation of these electrons is directly proportional to the absorption cross section of the material. Some work has been done studying the probability of hot electron generation, and found that silver promotes longer lifetime hot-electrons, due to a lower electron mean free path, effectively minimizing electron scattering events.¹³⁷ Also, the capping agent on the

AgNCs, PVP, has also been shown to effectively increase hot electron lifetimes.¹³⁸ This makes AgNCs a great candidate for the polymerization of styrene in the absence of a free radical source.

Preliminary attempts to grow a polystyrene coating using the hot-electrons approach were performed using AgNCs deposited on Al_2O_3 , illuminated with 100 mW laser at 488 nm for 10 mins. Al_2O_3 was used to better align the D mode of the AgNCs with the laser line, to maximize the absorption of light. However, only a small amount of growth was observed by AFM, Figure 4.3 (Left). An array of other powers and times were also attempted, although no dots were visible in the optical microscope or AFM. The fact that growth is only seen at the highest power was attributed to the low extinction of the AgNC sample (Figure 4.3, Right). In order to test this hypothesis a new sample with higher extinction was used (Figure 4.4).

Figure 4.3: (Left) AFM image of a AgNC monolayer on Al_2O_3 , after the styrene radicalization reaction, with illumination at 100 mW for 10 minutes. (Right) UV-Vis spectrum before styrene reaction.

Aside from the higher extinction, this sample is preferred due to the aggregation of the particles, which is observed as a large coupling peak from 600 nm to 900 nm in the UV-Vis spectrum (Figure 4.4). Particles being closer together can collectively heat the surroundings, effectively increasing the local temperature around the particle, speeding up the styrene polymerization reaction and polystyrene decomposition.

Figure 4.4: UV-Vis spectrum of the AgNC monolayer deposited on Al₂O₃ used in Figure 4.5

The same reaction conditions as the previous sample (Figure 4.3) were used for this newer sample, using hot-electrons generated from the AgNCs (Figure 4.4). Three powers were used: 100 mW, 75 mW and 50 mW. The AFM image for the 100 mW with 10 mins illumination (Figure 4.5) shows a clear enhancement in growth compared to the previous sample (Figure 4.3). The growth looks similar to the higher power results seen when benzoyl peroxide was present (Figure 4.1), although, it is important to note the time of illumination is much higher in this case. From this information we can conclude that styrene polymerizes in large chain-like morphology and decomposes at the center of the laser beam. The radius of the visible polymerization area is much larger (diameter > 35

μm) than the expected beam width (diameter $\approx 15\ \mu\text{m}$) and even still much larger than Figure 4.1. In the thermally activated reaction, which occurs in the presence of benzoyl peroxide as a source of initial radicals, polymerization occurs if the temperature exceeds a determined threshold of $\sim 130\ ^\circ\text{C}$ (Section 4.1.1). These conditions can only occur at the laser beam (spot); thus, defining the spatial boundary for the polymerization. If benzoyl peroxide is absent, polymerization is not thermally activated and will continue even at $30\ ^\circ\text{C}$.¹³⁹ Due to the nature of this free radical process (producing a radical polymer upon each addition of monomer), it is likely that the polymerization reaction radiated from the center of the beam, forming a polymer ring that is not limited by the beam size and consequently, can be much larger.

Reducing the time of illumination to 5 minutes (Figure 4.5), drastically reduced polymer decomposition, appearing similar to the 30 mW trial in Figure 4.1, except with

Figure 4.5: AFM images for heat electron assisted polymerisation of styrene using AgNCs deposited on Al_2O_3 , with the spectrum in Figure 4.4.

larger polymer chains radiating from the circular ridge. By further shortening the time to 2.5 minutes (Figure 4.5) only a small amount of growth can be seen, although the exposed section is still clearly visible from the background. For 1 minute illumination (Figure 4.5), the exposed section can barely be discerned from the background, although large chain-like domains can be seen extending from the center ring. For 10 second illumination, no ring structure is seen, and instead chain-like domains seem to extend from a center point semi-randomly. This is likely because only the center of the beam applied enough power to generate the necessary high-energy free-electrons, and so the free-radical process continued from a small section in the middle of the beam, forming semi-randomly orientated arrays of polymer.

Reducing the power to 75 mW for 1 minute illumination resulted in a very small amount of growth similar to what was achieved for the 100 mW, 10 second trial (Figure 4.5). This is expected, since the power is lower, the probability of generating the hot-

Figure 4.6: Transmission optical microscopy images of the AgNC sample exposed to the laser, 10x magnification.

electrons also decreases.¹³⁷ As well, 50 mW was attempted, although nothing visible could be seen in the AFM images, and only a small discolouration was observed in the optical microscope (Figure 4.6).

Interestingly, the dots are all visible in the optical image (Figure 4.6). The 100 mW 10 minute dot has a large hole in the center of it, which has a similar optical signature to the background (AgNCs on Al_2O_3). A similar hole is seen with the 5, and 2.5 minute dots as well, although progressively smaller. This hole is attributed to PS decomposition at the center of the laser beam, as seen with the AFM images (Figure 4.5). The high contrast of the hole is due to the change in refractive index from the AgNC sections coated with PS, and the sections with bare AgNCs, which are likely re-arranged or rounded. It is also interesting to note, that the 10 second illumination dot for the optical image is more noticeable than the AFM image (Figure 4.7), and the 50 mW dot is slightly visible as well, with this being attributed to AgNCs extreme refractive index sensitivity. This allows for very sensitive contrast between the PS coated areas and the bare AgNCs.

The next attempt was to draw polymer on top of the AgNCs by raster scanning the laser beam. The resulting lines can be seen in Figure 4.6. Two attempts were made: the first rastered up and down about 5 times and the second rastered left to right once. As expected longer exposure caused more PS polymerization and thus, greater contrast in the optical microscope. This result shows that polymer printing on AgNCs can be achieved, and can easily be optimized by using a sample with a better absorption cross section at the laser line, and smaller volume.¹³⁷

Figure 4.7: AFM image for the 100 mW reference point without styrene.

It is important to account for plasmonic heating in hot electron experiments. To discern such contribution an experiment was performed, where the AgNC monolayer was exposed to the laser beam at 100 mW for about 1 minute (Figure 4.6), without styrene. This dot appears to be much smaller than others obtained previously and appears white. Since there is no styrene present, no polymerization was expected, suggesting the white dot is re-arrangement or melting of AgNCs.

The AFM image of this reference dot can be seen in Figure 4.7. The height of the AgNCs increases and density of the monolayer decreases drastically in the center laser beam suggesting some melting, agglomeration and re-arrangement of the AgNCs, which

is expected at very high temperatures. In previous experiments with styrene present, heat generated by the AgNCs was likely transferred by the liquid, effectively lowering the temperature of the AgNCs potentially preventing agglomeration and melting. This is supported by the fact that after about 30 minutes all of the styrene had evaporated (for Figure 4.6), even though it was sandwiched between the sample and a coverslip. This heat transfer reduces the rate of temperature increase for the AgNCs as described in Equation 18 (Section F.1), causing less thermal degradation of PS. In order to test this hypothesis, a new set of experiments were done, using the same experimental set up as before (Figure 1.25), except no styrene was used. In the “dry” control (Figure 4.8) no liquid was added to the slide. The second control used a different liquid, toluene instead of styrene. Toluene also a high-boiling point liquid, however, it should not undergo any polymerization reaction. Finally, we repeated the last experiment with longer exposure time. The relative size and opacity of these control dots give some information on the effect of heat transfer within a liquid vs air.

The resulting optical images can be seen in Figure 4.8, which shows the styrene polymerization dots in Figure 4.6 and the new control dots in the same frame (Top). The major features to note are the much smaller size of these control dots, and similar to Figure 4.6, these reference dots seem to be hollow in the middle. Upon further magnification it can be seen that the 2.5 minute toluene sample has no apparent hole in the center of the beam, likely due to heat transfer to the toluene liquid. This was also represented as a rapid evaporation of the Toluene, within about 15 minutes. Looking at the 10 minute illumination dots, the impact that this heat transfer has is apparent, as the air sample appears to be bigger and have a larger void in the center. The final control

was to monitor the effect of illumination for a poorly focused beam. As expected a poorly focused beam delivery less power, which causes less heating overall. This was observed as slight discolouration of the AgNC monolayer (Figure 4.8), likely due to slight rounding of the AgNCs.

Figure 4.8: Transmission optical microscopy images of the AgNC sample with sample dots and new control exposures. (Top) 4x magnification including the sample dots from Figure 4.6 and new control dots outlined in the white box. (Bottom) 10x magnification on the control dots.

4.1.3 Conclusion

This work showcases two photochemical methods for the polymerization of styrene. The first method utilizes the heat generated from AgNCs under illumination to overcome the thermal barrier associated with a free-radical initiated process. Growth was observed by AFM measurements on spots illuminated with power as low as 10 mW. A three-stage process was found, which showed growth on the AgNC monolayer at low powers, decomposition of the polymer layer in the center of the laser beam for intermediate powers. At high powers a large degree of AgNC re-arrangement was observed, with no polymer coating in the center of the beam and a circular ridge of polymer around the edges. The second method used high energy free-electrons from the AgNCs upon illumination, to produce the necessary free radicals for the polymerization of styrene. Due to the short lifetime and low probability of generation, growth was only observed above 75 mW. A similar pattern of growth and decomposition relative to the first method was observed. Interestingly, the optical microscopy images provided greater contrast compared to the AFM images, even though they possess $\approx 100\times$ lower spatial resolution. This work provides a straightforward way to pattern polystyrene onto plasmonic structures, which provides a useful tool in the micro and nano patterning techniques.

5 – Concluding Remarks

This work emphasizes the production of AgNC-polymer nanocomposites and their use as a far-field nanoruler. When deposited onto a dielectric substrate, such as a polymer film these AgNCs possess spatially separated hybrid plasmon resonances, which allows sensing two local environments simultaneously, forming a refractive index based nanoruler. The first project used the nanoruler aspect of supported AgNCs to monitor, in real-time, the thermally activated embedment of the AgNCs into homopolymer thin-films, based on far-field UV-Vis extinction measurements. This enabled the determination for diffusion constants, and activation energies of the embedding process for each, polystyrene (PS), poly(methyl methacrylate) (PMMA), and polyvinyl chloride (PVC) thin films. The hybrid plasmon modes also probed a thin layer on top of the bulk polymer, in accordance with literature for a surface layer on top of the bulk polymer with enhanced polymer mobility. This study demonstrates the potential for plasmonic based nanorulers as well a controllable technique to incorporate metal nanoparticles into polymer surfaces. This is of great importance for the fabrication of functional nanocomposite materials, where fine control over nanoparticle-polymer interactions is required.

The second project utilized the temperature specificity of the embedding process to selectively embed AgNCs into discrete polymer domains within an immiscible polymer blend. The ternary film was made from blended solutions of PS, PMMA, and poly(2-vinylpyridine) (P2VP) of varying compositions. Differences in dynamics of the polymers within the blend enabled the identification of the segmented domains. Utilizing the nanoruler aspect of the AgNCs, kinetics for the AgNCs embedding into PS domains were

determined and compared to previous work for PS homopolymers. Interestingly, at temperatures below the bulk glass transition temperature (T_g) of PS, there was deviation from the previous Arrhenius relationship, however, strong agreement was determined when the temperature was above the bulk T_g of PS. This effect is tentatively explained by surface confinement effects, likely enhanced from the presence of the other polymers. Although polymer blends were used, this work should apply to any segmented polymer domain, such as ordered block copolymers. This work brings interesting insight into polymer-nanoparticle interactions within segmented polymer domains, which is of importance in producing optimized nanocomposite materials. Future work on the controllable incorporation of metal nanoparticles like, AgNCs into existing polymer materials like organic solar cells is of potential interest, as it can enhance its quantum efficiency.

The final project emphasized the use of plasmons in photochemistry through two approaches: plasmonic heating, and hot electron process, both through the thermally activated free-radical polymerization of styrene. The first approach used benzoyl peroxide as the initial free-radical source, utilizing the heat generated from the photothermal relaxation of the AgNCs' plasmons. A three-stage process was observed, which showed polymer growth on the AgNC monolayer at low powers, decomposition of the polymer layer in the center of the laser beam for intermediate powers and a large degree of AgNC re-arrangement and polymer decomposition at high powers. The second photocatalytic approach relied on hot-electrons generated from the AgNCs to initialize the free-radical polymerization reaction. Due to the short lifetime and low probability of hot-electrons, growth was only observed above 75 mW; however, the same pattern of growth and

decomposition was observed, supporting the hypothesis that the polymer is undergoing thermal decomposition. Interestingly, the optical microscopy images provided superior contrast in comparison to the AFM images, even though they intrinsically have much lower resolution. This emphasized AgNCs refractive index sensitivity, as the colour changes observed represented polymer growth and AgNCs re-arrange and agglomeration. This work provides a straightforward way to pattern polystyrene onto plasmonic structures, which provides a useful tool for micro and nano patterning and polymer printing applications. Future research will monitor the polymerization reaction through surface-enhanced Raman spectroscopy measurements, to give better support of the polymerization claims, and potentially understand the kinetics of the process. More work on optimizing the AgNCs sizes and monolayer density, and potentially changes in the dielectric substrate can facilitate raster-printing of polystyrene, which is exciting due to the potential of forming a multicolour printing technique. Future work emphasizing the potential nanoscale printing aspect is of particular interest. Two simple techniques can be implemented, namely, using of a pulsed laser source (instead of continuous wave), or through the use of a dilute AgNC monolayer.

6 – Appendices

This section includes information on the theory for FDTD simulations, silver nanocube synthesis, assembly of nanocubes onto substrates through a Langmuir approach, and selected larger AFM images for the selective embedding experiments. This section also contains basic theory on free-radical polymerization of styrene and a simplistic description of plasmonic heating. Although, these sections are important, they do not follow the general theme of the thesis and as such, are detailed as additional information for readers interest.

Appendix A: Finite Difference Time Domain Simulations

A non-classical approach to solving Maxwell's equations (Equations 1-4) is Finite Difference Time Domain (FDTD). James Clerk Maxwell took a set of known laws of physics, such as Faradays law and Amperes law, and combined them into a set of four coherent equations, called Maxwell's equations. These equations describe the propagation of electric and magnetic fields, and their interaction with matter.

A.1 Maxwell's Equations

The first Equation is Gauss' law (Equation 1), which describes how electric fields interact with electric charges. The electric flux density (D), is sensitive to a material's electric permittivity. In Gauss' law an arbitrary volume (V) is chosen with a contour boundary (S). Essentially, this Equation relates the total charge inside the volume (V) to the total amount of electric flux (D) exiting the surface (S) of the material. This can be simplified by stating that the divergence of the electric flux density is equal to the volume free electric charge density (ρ_V).

$$\oint_S \mathbf{D} \cdot d\mathbf{A} = \int_V \rho_V \cdot dV \quad \text{Or} \quad \nabla \cdot \mathbf{D} = \rho_V \quad (1)$$

The second law is Gauss' law for magnetic fields (Equation 2), which states that the divergence of the magnetic flux density (B) is zero. This Equation states the impossibility of a magnetic monopole.

$$\oint_S \mathbf{B} \cdot d\mathbf{A} = 0 \quad \text{Or} \quad \nabla \cdot \mathbf{B} = 0 \quad (2)$$

The third law is Faraday's law of induction (Equation 3), which states that a changing magnetic field within a loop causes an induced current and, that a circulating electric field (E) causes a time dependant magnetic field (B), and vice versa. Vectors I and A relative directions are ambiguous and are treated using the right-hand rule.

$$\oint_C \mathbf{E} \cdot d\mathbf{l} = -\frac{d}{dt} \int_S \mathbf{B} \cdot d\mathbf{A} \quad \text{Or} \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (3)$$

The fourth and final law, is Maxwell extended Ampere's law or more commonly, Ampere's law (Equation 4). It states that a flowing electric current (J) gives rise to a magnetic field (H) that circles the current. As well, it states that a time dependant electric flux density (D) gives rise to a magnetic field that circles the D-field. This law gives the main foundation of all electromagnetism, a time dependant D-field causes an H-field, which then gives rise

Figure 6.1: The propagation of the electric ($\vec{E}$) and magnetic ($\vec{H}$) fields associated with light. These fields are orthogonal and in phase with one another.

to an E-field, which fundamentally explains the propagation of electromagnetic waves (Figure 6.1).

$$\oint_C \mathbf{H} \cdot d\mathbf{l} = \int_S \mathbf{J} \cdot d\mathbf{A} + \frac{d}{dt} \int_S \mathbf{D} \cdot d\mathbf{A} \quad \text{Or} \quad \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \quad (4)$$

Maxwell's equations have a simple solution in a vacuum, assuming no current ($\mathbf{J} = 0$) and no charges ($\rho = 0$), with propagating sinusoidal waves. The electric (E) and magnetic (H) fields associated with light, are orthogonal to one another and in phase, travelling at the speed of light (c) (Figure 6.1). In linear optics, the D-field can be related to E ($\mathbf{D} = \epsilon \mathbf{E}$) and the B field can be related to H ($\mathbf{B} = \mu \mathbf{H}$).¹⁴⁰ Where, μ is the permeability of the material, which is the degree of magnetization a material will undergo under a magnetic field, and, ϵ is the electric permittivity of the material. Since the electric field is what is of interest, the permeability is considered the permeability of free space, μ_0 .

A.2 Finite Difference Time Domain Approach

The basic approach for Finite Difference is to determine the electric and magnetic fields associated in small time or distance intervals: this approach in respect to time can be represented as Equations 10 and 11. Specifically, the simulation time is factored into “n” time intervals, where n is an integer (Equation 5). The result of the zeroth order approximation for the electric field ($\vec{E}^0$) can then be fed into the solution for the magnetic field (Equation 5). The result for the magnetic field can be used to find the first order approximation of the electric field (Equation 6). This 1st order approximation of the electric

field can then be used to find the magnetic field (Equation 7). This iterative process continues until, convergence is reached.

$$\vec{E}(t) \rightarrow \vec{E}^{n\Delta t} \quad \text{and} \quad \vec{H}(t) \rightarrow \vec{H}^{(n+1/2)\Delta t} \quad (5)$$

$$\vec{E}^{n+1} = \vec{E}^n + \frac{\Delta t}{\varepsilon} \vec{\nabla} \times \vec{H}^{n+1/2} \quad (6)$$

$$\vec{H}^{n+3/2} = \vec{H}^{n+1/2} - \frac{\Delta t}{\mu} \vec{\nabla} \times \vec{E}^{n+1} \quad (7)$$

In order to solve these equations the simulation area (grid) is split up into 3-D cells, with E-field and H-field vector components in a Cartesian grid, called a Yee cell (Figure 6.2).¹⁴⁰ The electric and magnetic fields are calculated at the boundary of these rectangles, rendering first order approximations, which are then fed into Maxwell's Equation in an iterative manner, until convergence is obtained. The space grid size, or more commonly referred to as mesh size, can greatly impact the simulation accuracy and computational time. Specifically, it is important that the electric field does not drastically change over one increment, as this can cause discontinuities at material interfaces. In general, a mesh size of at least 1/10th of the lowest wavelength is used (Equation 8), which includes the highest refractive index (n_{max}). However, for curved shapes where the rectangular mesh does not match the curvature well, the mesh size is typically reduced to about 1/50th of the size of the smallest dimension. For example, for a simulation of a 50 nm gold sphere, it is recommended to use a mesh size of 1 nm or lower. Although, for spherical particles a special mesh, referred to as a conformal mesh is typically used. Which aims to minimize this “staircase” effect from the material boundaries by factoring the contour integrals into two, one which only includes the region where the electric field is constant or non-zero. This works well for simple geometries but increases computational time.

Since FDTD is intrinsically a time differential technique it relies on the time scale of the simulation. The maximum time step (Δt) can be determined using a modified Courant-Friedrichs-Lewy condition (Equation 9), where c/n_{max} , represents the maximum speed of light through the medium.¹⁴⁰

$$(\Delta x, \Delta y, \Delta z) \leq \frac{\lambda_{min}}{10n_{max}} \quad (8)$$

$$\Delta t \leq \frac{\sqrt{(\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2}}{\frac{c}{n_{max}}} \quad (9)$$

Figure 6.2: 3-D representation of a Yee cell. The Yee cell exists on a cartesian co-ordinate (x,y,z) with the electric components on the middle of the edges (E) and magnetic components on the middle of the faces (fields),

The idea behind FDTD is to solve Maxwell's equations in respect to time, as previously mentioned. The result of $E(t)$ can then be related to frequency ($E(\omega)$), through a Fourier transform (Equation 10), where t is the simulation time.

$$\vec{E}(\omega) = \int_0^t e^{i\omega t} \vec{E}(t) \quad (10)$$

Appendix B: Synthesis of Silver Nanocubes

Metallic nanoparticles can be synthesized in a variety of ways.^{141–146} Bottom-up approaches, in general, rely on the reduction of metal precursors and the subsequent nucleation of these zero-valent atoms. Due to the small size of these nanoparticles, they possess very high surface energies, and because of this capping agents and other stabilizing compounds need to be added. These capping agents can also act as structural guiding agents, effectively slowing the nucleation of metal precursors on certain facets of the nanoparticle.^{144,147,148} A common approach to synthesizing silver nanoparticles is the Lee-Meisel method. This method uses citrate as a reducing and a capping agent, which allows synthesis of quasi-spherical nanoparticles.¹⁴⁹ Another method is the Creighton method, which uses NaBH₄ as the reducing agent.¹⁵⁰ For this work, silver nanocubes (AgNCs) were synthesized with the use of the Polyol process. The Polyol process allows for greater control over the morphology, than the other methods. In this case the Polyol process is used to produce relatively monodisperse nanocubes, however, this synthesis can be modified to produce a wide range of sizes.¹⁵⁰

B.1 The Polyol process

The Polyol process is a seed mediated growth method, that has been used to produce silver nanostructures of various sizes and morphologies.^{151,152} Polyol synthesis involves the reduction of silver by a Polyol such as ethylene glycol (EG) at high temperatures (150

°C), with EG also acting as the solvent for the reaction.^{110,150} Ethylene glycol gets oxidized by dissolved O₂ producing glycolaldehyde as illustrated below.

The glycolaldehyde then reduces the silver ions to produce zero-valent silver.

The amount of glycolaldehyde produced is dependent on temperature; thus, one can control the nucleation and growth processes by changing the reaction temperature.¹⁴⁴ Although it is believed that glycolaldehyde is the reducing agent for silver, recent studies show the reduction of Ag⁺ using the Polyol method under vacuum or Argon gas.¹⁵³ This suggests a secondary reduction mechanism, specifically, that ethylene glycol itself can act as a reducing agent, although, this mechanism is not currently well understood.¹⁵⁴

To avoid agglomeration of the silver nanoparticles a capping agent, polyvinylpyrrolidone (PVP) is used. The oxygen and nitrogen atoms of PVP help to

promote adsorption of PVP onto silver atoms, due to their unpaired electrons.¹⁵⁵ PVP also acts as a structural guiding agent which allows the cubic morphology (Section B.3).

The reduction rate of Ag^+ can be increased by the addition of sodium sulphide (Na_2S). Na_2S dissociates, forming sulphide and in slightly acidic conditions HS^- , which interacts very strongly with silver, producing Ag_2S . Ag_2S nanoparticles can catalyze the reduction of Ag^+ by reducing the reduction potential allowing the rapid formation of seeds.¹⁵⁶

B.2 Nucleation of Silver Nanoparticles

Nucleation of silver nanoparticles begins with the continuous reduction of Ag^+ to Ag^0 . Due to the large concentration of Ag^+ in solution and the relatively fast rate of reduction, the solution becomes quickly saturated with Ag^0 particles. However, due to the energy costs associated with reducing the entropy of the system, solid nucleation does not occur until

Figure 6.3: Growth mechanism for nanoparticles in respect to reaction time and concentration of zero valent metal atoms. Adapted with permission (¹⁵⁷) © 2013 Royal Society of Chemistry.

a critical concentration (C_{crit}) is reached (Figure 6.3).¹⁵⁷ Once this concentration is reached the growth of silver nanoparticles starts, reducing the concentration of precursor atoms, as some have already reacted to form nuclei. Growth will continue as long as the concentration of precursor atoms is greater than the saturation concentration (C_s),¹⁵² since the continual growth on the formed nuclei is more energetically favorable. The thermodynamic driving force for the formation of these nuclei is to lower the Gibbs free energy associated with these solid nanocrystals, in comparison to solvated silver atoms.¹⁵⁷

The initial nuclei are small and can change morphologies. As the nuclei grow, the structural fluctuations dissipate, and at this point they are considered “seeds”. These crystalline seeds have defined structures. The three types of seeds are: single crystal, singly twinned crystal and multiply twinned crystal (Figure 6.4).¹⁵⁸

The structural defects in twinned seeds reduce the surface energy of the particle, making twinned morphologies the most abundant morphology.¹⁵⁸ The shape of the nanocrystals (Figure 6.4) is dependent on the initial morphology of the seeds. Therefore, controlling the morphology of the nuclei is required to ensure the desired final shape of the nanocrystal. The shape of the growing nuclei can be controlled by the reaction kinetics. Controlling the reaction kinetics can force a desired seed morphology, the morphology can also be controlled by using a selective etching agent, used to etch undesired growth. Using structure-directing agents can change some of the crystal facets surface energies, effectively increasing or decreasing the reaction rates at certain facets of the nanocrystal. As can be seen in Figure 6.4, single crystalline seeds are required to produce the desired

cubic structure. Therefore, the next sections describe the selection of single crystalline seeds, necessary for the synthesis of silver nanocubes.

Figure 6.4: Showing an assortment of Ag nanostructures. A) Showing the possible reaction paths of Ag nanostructures using the polyol process. B-I) showing experimental SEM results for each Ag morphology. Reproduced with permission (¹⁵⁸) © 2011 American Chemical Society

B.3 Controlling Morphology by use of a capping agent

In general, colloidal nanoparticles require a surfactant or capping agent to prevent the agglomeration of the nanoparticles. The driving force behind agglomeration is the resulting reduction in surface energy of particles. However, a capping agent can also be used to direct the shape of the nanoparticle.^{147,159} The capping agent can selectively bind to a certain crystal lattice facet, which under the right concentration, can passivate the

surface, effectively reducing the growth rate along that surface. Crystalline Ag has a face centered cubic (fcc) crystal lattice. For fcc metals the surface energy (γ) follows the order of $\{111\} < \{100\} < \{110\}$.¹⁶⁰ Thus, growth is dominant on the $\{100\}$ and $\{111\}$ facets of silver as it produces lower energy nanoparticles. When a facet is passivated, incoming metal atoms will preferentially add to the non-passivated facet as it has higher surface energy. It has been shown that at high concentrations, PVP will selectively bind to the $\{100\}$ facet of Ag, thus, the incoming metal atoms will preferentially bind to the non-passivated $\{111\}$ facet.^{147,161} These adatoms will migrate to the face edges, causing an elongation of the $\{110\}$ facet, which for single crystal seeds leads to the formation of silver nanocubes.^{144,158}

B.4 Controlling Morphology by use of oxidative etching

It is possible to oxidize the zero valent metal atoms back into ions. As such, selective etching can allow the dissolution of unwanted nucleation on the nanoparticle. It has been demonstrated that O_2 and Cl^- in solution can be used to etch twinned seeds.^{144,162} The chloride forms co-ordination bonds to silver, which facilitate the oxidation of the silver by dissolved O_2 .¹⁶² This etching is favoured for singly twinned and multiply twinned seeds as these geometries contain more surface defects which serve as sites for the initial chloride co-ordination. In order to make use of this, trace amounts of NaCl or HCl are added to the reaction vessel, forming the Cl^- ions necessary for this selective etching process. Since etching is preferred for singly twinned and multiply twinned seeds, the single crystalline morphology will dominate, which is necessary to form cubic seeds. The resulting shape of the nanostructure depends on the etchant. For example, Br causes

singly twinned seeds, due to bromine forming weaker bonds to the Ag. Resulting in the selective etching of multiply twinned seeds and not singly twinned seeds leading to predominately bipyramidal morphology.¹⁶³

B.5 Controlling morphology by use of reaction kinetics

It has been demonstrated that trace amounts of S^{2-} in the Polyol process increases the reaction rate significantly.¹⁶⁴ The S^{2-} reacts with Ag^+ ions in solution, rapidly forming Ag_2S nuclei. The Ag_2S nuclei then act as additional sites for the growth of silver precursors. As well, the Ag_2S nanoparticles have been shown to catalyze the reduction of Ag^+ by reducing the reduction potential.^{165,166} Interestingly, the addition of S^{2-} also forms singly crystalline seeds, since twinned seeds have added strain due to the twin defect, causing twinned seeds to not grow as fast as singly crystalline seeds. Typically, Na_2S is added to the reaction vessel, to form the S^{2-} . Thus, the use of Na_2S will cause a high yield of singly crystalline seeds even in the absence of oxidative etching.¹⁶⁷

B.6 Seed mediated growth

The Polyol process utilizes a seed mediated approach to growth, in this type of synthesis, nanoparticle seeds are injected into the reaction just prior to the addition of additional silver precursor. Thus, growth of these nanoparticles can occur without the need for the nucleation step. This can help render larger nanoparticles with better monodispersity (uniformity) due to Ostwald ripening.¹⁶⁸ Which makes controlling the seed morphology even more important in producing high quality AgNCs.

Appendix C: Assembly of Nanoparticles on a Substrate

Assembly of nanoparticles onto a substrate is important for many applications.^{169–172} Fine control over inter-particle distance is vital to obtain a useful nanoparticle-material. For example, in many sensing applications using plasmonic nanomaterials, unwanted aggregation can lead to a decrease in sensitivity of the material. Contrarily, other applications that rely on surface enhanced Raman scattering require strong coupling of plasmonic modes, making closely packed particle assemblies ideal. Common ways to deposit nanoparticles are: self assembly, spin coating and Langmuir type depositions. The use of self-assembly is ideal for scalability, however, it can lead to issues including low yield, multilayer coatings, and importantly little control over nanoparticle distances. Spin coating is simple; however, it offers no control over inter-particle distances. In particular, the ease of spin coating is dependant on the inter-molecular interactions between the solvent, solute and the substrate. Langmuir films however, allow fine control over inter-particle distances, and coating density for monolayers. Although this approach is not very scalable, the added control over the final nanocomposite is crucial in this work. Specifically, the ability to produce optically dense monolayers of AgNCs, while simultaneously controlling aggregation and coupling.

C.1 Langmuir deposition of AgNCs

Langmuir films involve the dispersion of organic molecules on a water/air interface, with the spacing between particles being adjusted by the manipulation of a movable barrier. This monolayer can then be deposited onto a solid support by vertical dipping (Langmuir-Blodgett) or horizontal stamping of the substrate (Langmuir-Schaefer). The control of

packing in the monolayer is due to the lateral surface pressure the molecules or particles exert on one another. Metal nanoparticles are often well suited for this technique as they feature organic stabilizing capping agent that are typically hydrophobic or feature hydrophobic tails pointing away from the metal nanostructure.¹⁷³ Silver nanocubes are a good example of this because the capping agent, PVP, features a polar pyrrolidone moiety pointing towards the metal and a hydrophobic chain directed away.¹⁷⁴

Langmuir monolayers are controlled by isothermal compression, where the surface pressure (P_{surf}) is monitored by a Wilhelmy plate, which is immersed at the air water interface.¹⁷⁰ The Wilhelmy plate is often a clean piece of paper with specific dimensions. The vertical force it experiences (F) is a product of surface tension (ST), buoyance and gravity. The surface tension term represents the water molecules that the plate is displacing. Since the plate is of a specific width (w), height (h) and mass, the gravity term and the buoyance term are negligible, rendering Equation (11).

$$F = 2(w + t)(ST)(\cos\theta) \quad (11)$$

Since the wetting angle (θ) is perpendicular to the water surface, Equation 11 can be further simplified (Equation 12) and related to the surface tension (ST). The surface pressure (P_{surf}) can then be related to ST using Equation 13, where C is a constant representing the absolute surface tension of the liquid.

$$ST = \frac{F}{2(w + t)} \quad (12)$$

$$C = ST + P_{surf} \quad (13)$$

By compressing the monolayer the surface tension will decrease, thus, increasing the surface pressure of the monolayer.

The LB isotherm can be described in phases analogues: liquid, solid and gas as seen in Figure 6.5. The gas phase is characterised by near zero pressure; the particles have large free volumes and do not interact much with each other. As the pressure increases the liquid phase is approached and the isotherm develops a gradual slope, due to increasing inter-molecular interactions.¹⁷³ The plateau in the isotherm before changing from the liquid to the solid phase is a “sub-phase transition” from liquid-expanded and liquid-condensed phases. This plateau is due to the reorganisation of the particles, because their free volumes are approaching their dimensional size. At high surface pressures the free volumes of the particles become very small signified by a near vertical line in the isotherm, which represents the solid phase.

Figure 6.5: Pressure-area isotherm of a LB monolayer showing the gas, liquid and solid phases.

Deposition of the resulting monolayer onto a solid substrate can be accomplished in two ways: Langmuir-Schaefer and Langmuir-Blodgett. Specifically, Langmuir-Blodgett

deposition involves the vertical dipping of the substrate into the monolayer, and after submersion the substrate is slowly lifted out of the meniscus. Langmuir-Schaefer deposition is the horizontal stamping of the substrate to the nanoparticle-water interface. Langmuir-Schaefer is employed when both the monolayer and the substrate are hydrophobic, whereas, Langmuir-Blodgett is typically employed when the substrate is hydrophilic, due to the requirement of the positive meniscus. Langmuir Blodgett can also be performed on a negative meniscus, with a slow downward dipping direction, although this is much more challenging.

Appendix D: Selective embedment into immiscible polymer domains: larger AFM images

D.1 PS/PMMA/P2VP blend (48.7%/23.1%/28.2%)

Figure 6.6: AFM images for a 48.7%/23.1%/28.2% (PS/PMMA/P2VP) blend with AgNCs deposited and subsequent heating at 97.3 ± 0.3 °C.

D.2 PS/PMMA/P2VP blend (60.0%/20.0%/20.0%)

Figure 6.7: AFM images for a 60.0%/20.0%/20.0% (PS/PMMA/P2VP) blend with AgNCs deposited.

Figure 6.8: AFM images for a 60.0%/20.0%/20.0% (PS/PMMA/P2VP) blend with AgNCs deposited and subsequent heating at 98.4 ± 0.3 °C.

Figure 6.9: AFM images for a 60.0%/20.0%/20.0% (PS/PMMA/P2VP) blend with AgNCs deposited and subsequent heating at 112.5 ± 0.6 °C.

Appendix E: Free-radical polymerization of styrene

PS is typically made through the free radical polymerization of its monomer, styrene.^{134,139}

The general reaction scheme is typically broken up into three major phases: initiation, propagation and termination, as can be seen below. The first step (Initiation), represents the free radical species ($R_1\cdot$) reaction with the monomer (M), which results in a radical polymer species. The second step (Propagation) is the subsequent reactions with the new radical polymer species and the monomers. Due to the nature of the reaction, in theory, only a small amount of initiator is needed, as the propagation step is self-sustaining as long as there exists unreacted monomer. At some point, the radical species can react with one another producing a stable compound, this is represented in termination (a, b), which effectively stops the polymerization reaction. In many cases, a free radical scavenger or a reactive non-radical molecule is added to stop or slow the polymerization, which can help generate a narrower size distribution.

In the case of PS, a common initiator is benzoyl peroxide, as it quickly forms radical species when heated above 80 °C, the major reactions can be seen below.¹³⁹

The ability for benzoyl peroxide to form different radical species is important in the efficient polymerization of styrene, although, due to the thermodynamically favorable formation of CO₂ gas, the phenyl radical is surprisingly prominent.¹³⁹ A basic polymerization scheme of styrene can be seen below (Figure 6.10), for simplicity only showing the phenyl radical reaction pathway. However, the benzoyl peroxide radical can also be represented by simply substitution.

Initiation: **Propagation:** **Termination:**

b)

c)

Figure 6.10: Reaction scheme for the polymerization of styrene. Showing each major step of the free radical process: Initiation by a phenyl radical produced from benzoyl peroxide, propagation of the subsequent polymer and termination of the polymer in three common routes.

Appendix F: Plasmonic Heating

Plasmonic metal nanoparticles can efficiently convert absorbed optical energy into heat.^{175,176} This brings an array of new interesting applications for plasmonic nanoparticles being used as nanoscale heat sources. This work, for example, utilizes the local heat to grow polystyrene on the AgNCs. This section will briefly describe the theory behind this interesting process.

F.1 Plasmonic heating mechanism

As mentioned in the section 1.2.3 the size and shape of a plasmonic nanoparticle greatly affects its optical properties. In general, as the size of the nanoparticle increases, a red-shift is seen in its extinction spectra and an increase is seen in its scattering cross-section.¹⁷⁷ Since only absorbed energy can be converted to heat, having a particle with a large absorption cross-section (σ_{abs}) is desirable. The power of heat generated (Q) in a nanostructure can be described using Equation 14. Assuming the size of the particle is constant and perfectly spherical, a simple expression for the absorption cross section can be formulated (Equation 15).¹⁷⁵

$$Q = \sigma_{abs} I = \sigma_{abs} \left(\frac{nc\varepsilon_0}{2} \right) |E_0|^2 \quad (14)$$

Where, I represents the irradiance of the incoming light, n , is the refractive index of the medium, E_0 , is the plane wave electric field amplitude for the incident light, $E(r)$, is the total electric field amplitude, ε_n , is the permittivity of the nanoparticle, and k , is the wave vector of propagating light, defined as $k = \frac{n\omega}{c}$, where c is the speed of light.

$$\sigma_{abs} = \frac{k}{\varepsilon_0 |E_0|^2} \int \text{Im}(\varepsilon_n) |E(r)|^2 dr \quad (15)$$

Substituting Equations 28 and 29 and factoring out constants from the integral generates a new representation (Equation 16).

$$Q = \frac{n\omega}{c\epsilon_0|E_0|^2} \left(\frac{nc\epsilon_0}{2} \right) \text{Im}(\epsilon_n)|E_0|^2 \int |E(r)|^2 dr = \frac{n^2\omega}{2} \text{Im}(\epsilon_n) \int |E(r)|^2 dr = q(r) dr \quad (16)$$

Where $q(r)$ represents the volumetric power density of heat generation.¹⁷⁵ This allows a formulation for the temperature variation in the system (Equation 17), where l , is the size of the nanoparticle, v_0 , is the volume of the nanoparticle $\left(\frac{4}{3}\pi r^3\right)$ and κ is the thermal conductivity of the nanoparticle.¹⁷⁵ For a spherical particle, the temperature increase inside the particle can be solved, assuming the thermal conductivity of the particle is much larger than that of the medium, and thus, the particle essentially, instantly transfers its heat (to its surroundings) (Equation 18), where κ_0 is the thermal conductivity of the surroundings.

$$\delta T \sim \frac{l^2}{\kappa} \frac{Q}{v_0} \quad (17)$$

$$T_0 = \frac{Q}{4\pi\kappa_0 r} \quad (18)$$

Figure 6.11: (Left) Cartoon representing the spatial separation of the hybrid Q mode in AgNCs (Right) and corresponding heat generated.

From Equation 18 it becomes important to choose a material that has a suitable permittivity while still having a small volume. In this work, AgNCs were used, primarily due to the Q modes strong absorbance cross-section,⁵⁰ and spatial confinement.¹⁸ This should allow for efficient absorption, over a smaller volume of area. In theory anisotropically heating the nanoparticle. However, due to the high thermal conductivity of silver, the heat will dissipate very quickly, heating the whole particle (Figure 6.11). However, if the AgNCs were selectively over-coated in a thermal insulator like SiO₂, it becomes possible to efficiently anisotropically heat the local environment.

The generally accepted theory for the heat generation, is through electron-phonon coupling into the crystal lattice of the material.¹⁷⁸ This increase in electronic and vibrational degrees of freedom, efficiently generates heat local to the particle. The temperature increase will then depend on the heat transfer to the surroundings and the flux of energy converted from light.

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