

Ultrasensitive Detection of D-glucose and TNT molecules using Vertically Aligned Self-assembled Gold Nanorods



A thesis submitted towards partial fulfillment of the BS-MS Dual
Degree Program

by

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under the guidance of

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Certificate

This is to certify that this thesis entitled “*Ultrasensitive Detection of D-glucose and TNT molecules using Vertically Aligned Gold Nanorods*” submitted towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research (IISER), Pune represents original research carried out by **Amey Anant Apte** at IISER, Pune under the supervision of **Prof. Dr. Sulabha K. Kulkarni** during the academic year 2013-2014.

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Dedicated to my family

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Abstract

Nanoscience is a rapidly growing discipline related with Materials Science which deals with the study of structures and materials on the scale of nanometers. Devising ingenious methods of working with nanomaterials for real-world applications is known as Nanotechnology. The properties of materials change remarkably as one transitions from the bulk to the nanoscale. This happens mainly due to the increasing spatial confinement of electrons (which determine many material properties) and the increasing surface area to volume ratio. Nanomaterials occupy a somewhat special position on the size-scale, situated between the atoms (ruled completely by quantum effects) and bulk objects. Also, unlike their bulk counterparts, the properties of nanomaterials are a function of their sizes. Thus, development of experimental methods of obtaining any given nanomaterial of a precise size enables control over their properties. It is this versatility which makes nanomaterials specially suited for a variety of applications.

Nanoparticles of the noble metals such as gold, silver, and copper have the ability to confine and resonantly enhance incident electromagnetic fields due to *localized surface plasmon resonances*. These are collective oscillations of the conduction electrons of metals in response to external electromagnetic fields. Nanomaterials supporting LSPRs are referred to as plasmonic nanomaterials. Noble metal nanostructures can exhibit these optical resonances from the visible to the near-infrared region of the electromagnetic spectrum, which makes them viable candidates for the possibility of controlling the interaction, confinement and flow of light at the nanoscale. Since this is much faster than controlling electric current, Plasmonics can spread its metaphorical technological wings and leap off like electronics did, in the 1960's. In short, plasmonic nanomaterials offer excellent potential for applications that might very well constitute the next technological revolution.

This work focuses on nanoparticles of gold - specifically, gold nanorods. Anisotropic nanoparticles such as rods offer more interesting properties than isotropic ones - in this case, plasmonic properties. The synthesis of colloidal gold nanorods via wet chemical methods and their characterization by absorption spectroscopy and scanning electron microscopy was carried out. Further, gold nanorods were self-assembled on clean silicon substrates into a variety of novel superstructures using a simple, solvent evaporation strategy, on large (few tens of μm^2) scales. The most exquisite self-assembly of all, in the form of hexagonally close-packed large arrays of vertically aligned gold nanorods was studied. Finally, it was shown that self-assembled vertically aligned gold nanorods (VA-GNRs) can serve as probes or substrates for ultra-high sensitive detection of molecules such as D-glucose and TNT (2,4,6-trinitrotoluene) via Raman spectroscopy. These molecules were chosen as model systems due to their very low Raman cross sections as well as to show that the vertical assemblies of gold nanorods can offer even as low as yoctomole sensitivity. The advantage of these vertical assemblies is their extremely high reproducible morphology accompanied by ultrahigh sensitivity which would be useful in general in many fields where very small amount of analyte is available. Moreover the assembly can be reused number of times after removing the already present molecules. The method of obtaining VA-GNRs is simple, inexpensive and reproducible., and hence has the potential to be designed and developed for technological applications requiring ultra-sensitive detection.

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Chapter 1

Introduction

Nanoscience is the study of structures and materials on the scale of nanometers ($1\text{ nm} = 10^9\text{ m}$). Nanomaterials, defined as objects having at least one dimension in the range 1 nm to 100 nm, occupy a special position between the atoms and macroscopic objects. As bulk materials approach the nanoscale, the reduction in size increases their surface area to volume ratio. This causes increased electron confinement which begets unexpected electrical, mechanical, and optical properties differing considerably from that in bulk. The manipulation of matter at this scale for harnessing these interesting effects toward practical applications is termed as nanotechnology. The idea was conceived in 1959 by the eminent physicist Dr. Richard Feynman in his now famous talk *There's Plenty of Room at the Bottom*.

The emergence of nanotechnology occurred in the 1980s due to K. Eric Drexler's extensive efforts for public awareness of the concepts and advantages of nanotechnology. Practical efforts were considerably aided by IBM's research center in Zurich with the advent of technologies like the scanning tunneling microscope in 1981 and later in that decade, the atomic force microscope, for the precise manipulation of atoms and molecules. Further pioneering work on carbon, metallic and semiconducting nanomaterials helped open new areas of nanoelectronics and nanophotonics. At the turn of the millennium, intense scientific attention and global efforts started focusing on nanotechnology with the aid of project roadmaps, far-reaching collaborations and substantial research grants, targeted towards studies, goals, and applications of nanotechnology.

This work focuses on a particular class of nanomaterials – gold nanomaterials, more specifically anisotropic gold nanorods. Gold nanorods have excellent plasmonic properties which form potential applications in the areas of ultra-high sensitive detection using a technique called Surface-enhanced Raman Scattering (SERS), even up to the single-molecule level. Herein, as well as in the subsequent chapters, the work done on the synthesis, properties and potential applications of gold nanorods as substrates for the ultra-sensitive optical detection of various organic molecules is discussed.

1.1 Gold

Gold has been regarded as the most precious and valuable metal by mankind, since it was first extracted in the 5th century BC.^[1] It is a noble, malleable and ductile metal with atomic number 79, placed in the 11th group of the periodic table. Denoted by the chemical symbol 'Au' following from the Latin word *aurum* which means 'the glow of

Property	Value
Atomic number	79
Atomic weight	196.9
Electron configuration	$[Xe]4f^{14}5d^{10}6s^1$
Density	19.3 g cm^{-3}
MP/ BP	$1064^\circ\text{C}/ 2970^\circ\text{C}$
Electrical resistivity	$22.14 \text{ n}\Omega \text{ m}$
Atomic radius	144 pm
Lattice parameter	408 pm (fcc)

Table 1.1: *Key properties of bulk gold.*

sunrise’, bulk gold is highly dense, has a characteristic yellow sheen, a very low electrical resistivity value, and is chemically inert towards many reactions. It crystallizes in an fcc lattice. The key properties of gold are summarized in Table 1.1.

However, the properties of gold become even more spectacular when its size falls in the nanometer range (100 nm and less). As with other nanomaterials, these properties stem from the dielectric confinement and localization of electrons as well as the growing surface area to volume ratio. The larger ratio of surface area to volume in nanomaterials imply greater chemical reactivity, whereas spatial electron confinement gives rise to unique optical absorption and photoluminescence properties, as well as electromagnetic enhancement.^[2] Metallic nanoparticles have the interesting ability to confine resonant photons via collective oscillations of their free aka conduction electrons, at the nanoscale. These oscillations are termed as localized surface plasmon resonances (LSPRs), and they are electromagnetic modes associated with the collective motion of the electrons.

1.2 Plasmons

A plasmon is a quasiparticle used to denote the collective oscillations of free electrons, and is described theoretically by the Drude model (ideal case, no damping) and further improvised with the Drude-Lorentz model to include damping effects. An important parameter from these models is the plasma frequency ω_p which is expressed as

$$\omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m_e}}$$

Here, n is the number of electrons per unit volume, ϵ_0 is the permittivity of free space and e , m_e are the electronic charge and mass, respectively. The plasma frequency indicates the coherency of oscillations of the electrons with incident electromagnetic waves; this in turn explains the reflectivity of metals for visible light and their transparency for ultraviolet light. Plasmons can be excited by electrons as well as free space photons i.e. electromagnetic waves. At the nanoscale, surface effects assume importance and hence, the major contributions to the electronic and optical properties of metallic nanoparticles come from *surface plasmons*.

1.3 Mie and Gans theories - preludes to surface plasmon resonances

Gustav Mie formulated the theory for optical properties of spherical metal nanoparticles (specifically, gold) in his seminal paper.^[3] He applied Maxwell's equations with appropriate boundary conditions in spherical coordinates to solve the diffraction problem of a single sphere of arbitrary material within the framework of classical electrodynamics. The target sphere had a given radius and a phenomenological dispersive dielectric function $\varepsilon(\omega)$. The theory described briefly herein, is sourced from the 2nd chapter of the book *Optical Properties of Metal Clusters* by Uwe Kreibig and Michael Vollmer.^[4] The optical properties are represented by absorption and scattering cross sections, σ_{abs} and σ_{sca} respectively. These can be expressed in terms of intensity loss of incident light using Beer-Lambert's law (N being the number density):

$$\Delta I_{abs}(z) = I_0(1 - e^{-N\sigma_{abs}z})$$

and

$$\Delta I_{sca}(z) = I_0(1 - e^{-N\sigma_{sca}z})$$

Usually, both processes contribute, and one defines the extinction cross section σ_{ext} as

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$$

Mie's theory calculates the extinction cross section for a metal nanosphere as

$$\sigma_{ext} = \frac{2\pi}{k^2} \sum_{L=1}^{\infty} (2L+1) \text{Re} \{a_L + b_L\}$$

Here, k is the wavevector, a_L and b_L are expressed in terms of cylindrical Ricatti-Bessel functions and L is the order of the partial wave described by the corresponding vector spherical harmonics. The *quasistatic approximation* holds when the size of the nanosphere is very small as compared to the incident wavelength ($R \ll \lambda$). In this case, the electromagnetic field is treated to be the same throughout the entire particle, and is determined solely by the scalar potential. This simplifies the expression for the extinction cross section as

$$\sigma_{ext} = 9 \frac{\omega}{c} \varepsilon_m^{3/2} V_0 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2}$$

Here, V_0 denotes the volume of the nanosphere, and ε_m is the dielectric function of the surrounding medium. This formula is valid only for dipolar contributions ($L = 1$), and shows a resonance at

$$\varepsilon_1(\omega) = -2\varepsilon_m$$

However, one assumes that $\varepsilon_2(\omega)$ is either very small, or does not vary much near the resonance. This resonance condition cannot be satisfied by ordinary dielectric materials since it requires the real part of the dielectric function to be negative; but it can be satisfied by metals. One more important observation is the dependence of this resonance on the refractive index (or the dielectric function) of the surrounding medium. Noble metals such as silver, gold and copper satisfy the above resonance condition for ω lying in the visible region of the electromagnetic spectrum, if the surrounding medium is free space (or air), whereas that for aluminum lies in the ultraviolet region. It was interpreted almost 60 years after Mie's paper that the collective oscillations of different multipole orders such as dipole, quadrupole etc. are nothing but *plasmon polaritons* i.e. plasmon oscillations excited by external electromagnetic fields.

Mie's theory was extended by Richard Gans to calculate the optical properties of ellipsoidal clusters.^[5] Assuming an ellipsoid with half-axes a , b , and c , he solved Laplace's equation in an ellipsoidal coordinate system and obtained the following expressions for the different cross sections:^[1]

$$\sigma_{sca,i} = \frac{k^4}{6\pi} |\alpha_i|^4$$

$$\sigma_{abs,i} = k \text{Im}(\alpha_i)$$

$$\alpha_i = 4\pi abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_i(\varepsilon_1 - \varepsilon_m)}$$

Here, k is the wavevector and α_i is the polarizability of the metal cluster. L_i is the depolarization factor, expressed as

$$L_a = \frac{abc}{2} \int_0^\infty \frac{dq}{(a^2 + q)f(q)}$$

$$L_b = \frac{abc}{2} \int_0^\infty \frac{dq}{(b^2 + q)f(q)}$$

$$L_c = 1 - L_a - L_b$$

$$f(q) = \sqrt{(q + a^2)(q + b^2)(q + c^2)}$$

Here, q is an integration variable. Gans theory shows that the cross section values depend upon the size and shape of the ellipsoid. Moreover, for prolate ellipsoids ($a > b = c$), there exist two distinct plasmon modes; a transverse mode associated with electron motion along b and c axes, and a longitudinal mode associated with a (longer) motion along the a axis.

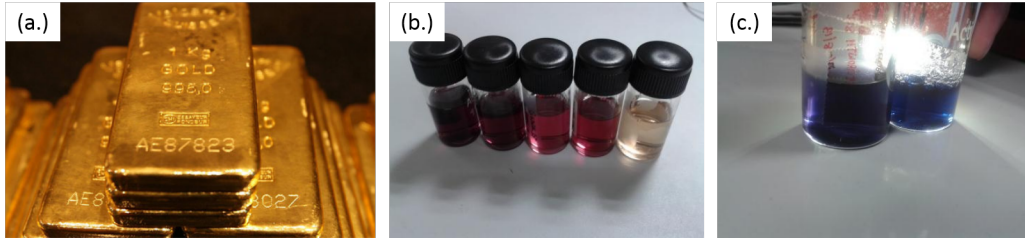


Figure 1.1: *Striking difference in the optical properties of (a.) bulk gold, (b.) gold nanorod solutions and (c.) gold nanostar solutions. (Sources: (a.) Wikimedia Commons. (b.), (c.) SKK NanoLab, IISER Pune.)*

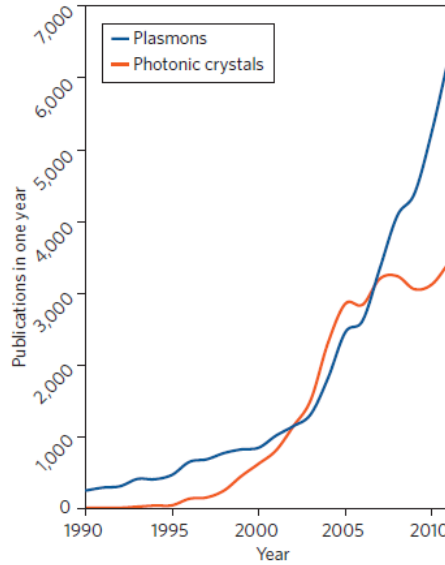


Figure 1.2: *Explosive growth in the number of publications related to plasmonics and photonics in the past decade.*^[6]

1.4 Plasmonics

The interaction between light and matter on the nanometer-size scale is the realm of nanophotonics. Plasmonics is a specialty of nanophotonics that explores the interaction of light with nanoscale metallic structures, in essence materials that support surface plasmon resonances. SPRs have been studied since Ritchie in 1957, predicted theoretically the plasma losses in thin metallic slabs due to the motion of fast electrons.^[6] However, the emergence of sophisticated techniques of synthesis, fabrication and analysis have helped make remarkable strides in this discipline. A few notable examples include the discovery and applications of Surface-enhanced Raman Scattering (SERS), development of scanning electron and atomic force microscopies, the advent of precisely controllable nanofabrication (electron-beam and ion-beam lithography) and the nanoscale imaging of light using near-field scanning optical microscopy (NSOM).^[7] One can see the almost exponential nature of increase in the publications related to plasmonics in Fig. 1.2.

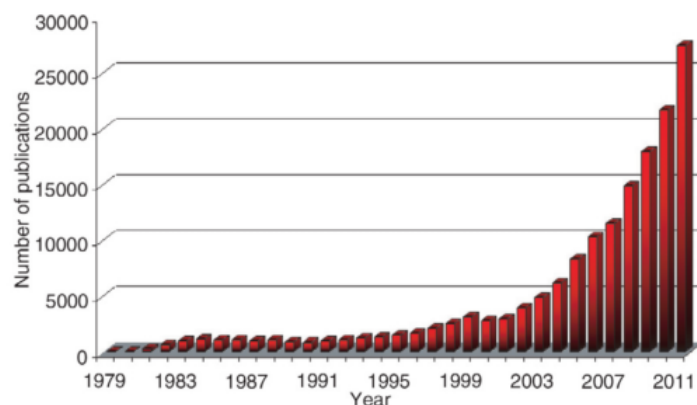


Figure 1.3: *Growing popularity of SERS, as referred from Web of Science-Thomson Reuters.*^[8]

1.5 Surface-enhanced Raman Spectroscopy - a boon of plasmonics

Raman spectroscopy (after Nobel laureate Sir C. V. Raman) is a spectroscopic technique used to observe and analyze vibrational and rotational levels or modes in molecules. It is based on Raman scattering, an inelastic form of light scattering which is explained in Chapter 2. Raman scattering is very much weaker than elastic Rayleigh scattering (which carries little valuable information¹) and is hence daunted by signal detection issues. Surface-enhanced Raman Spectroscopy (SERS) enhances the Raman signals of molecules adsorbed onto metallic plasmonic surfaces by many orders of magnitude.^[8]

SERS was first reported in 1974 regarding the Raman spectrum of pyridine adsorbed onto electrochemically roughened silver substrate.^[9] Further investigations agreed that signal enhancement in SERS was possible due to LSPRs on plasmonic nanomaterials such as silver, gold, copper etc. LSPRs cause confinement and resonant amplification of incident electromagnetic fields near sharp features such as gaps and crevices of plasmonic nanomaterials, otherwise known as *hotspots*. Enhancement factors of up to 10^{11} or even more have been reported.^[10,11] A smaller factor is the enhancement due to chemisorption between the adsorbed molecule and the metal substrate. These unique advantages allow potential applications of SERS in the fields of biosensing, chemical warfare vigilance, spectroelectrochemistry, catalysis and even single molecule detection.

1.6 Gold nanorods - plasmonic nanomaterials

Gold nanorods with cylindrical symmetry possess two distinct surface plasmon resonances – transverse and longitudinal. Gans theory gives very good experimentally verifiable results for calculating the optical properties of cylindrically-symmetric gold nanorods. It is experimentally observed that the longitudinal plasmon mode of gold nanorods exhibits higher sensitivity to its size and shape, than the transverse mode. Anisotropic gold nanorods (which are a central topic of this thesis) show remarkably different and intriguing optical properties from bulk gold (see Figure 1.1) such as vividly intense colors. Figure 1.1 (b.) and (c.) show how typical solutions of gold nanorods and nanostars look like.

¹Here, 'valuable' means spectroscopic information.

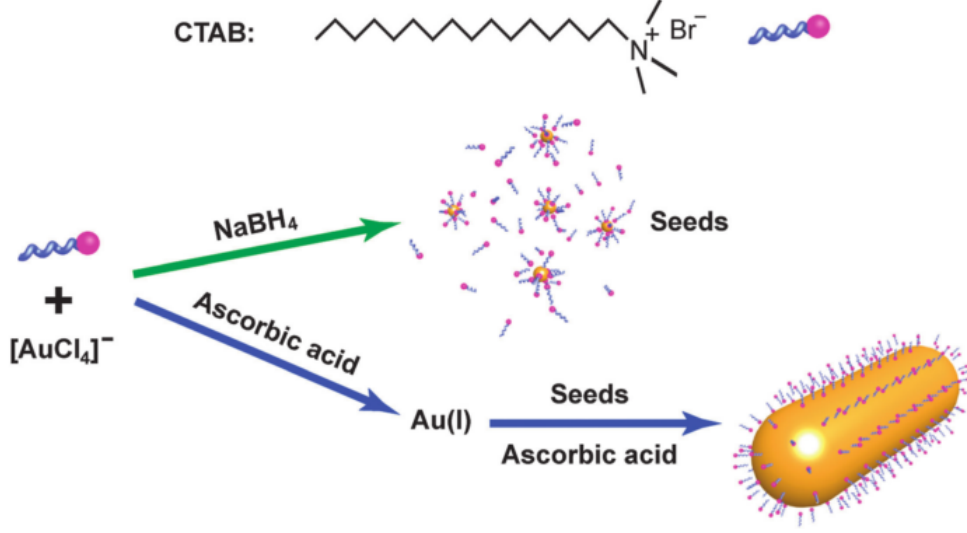


Figure 1.4: *Schematic for the synthesis of Au nanorods using the method developed by Nikoobakht and El-Sayed.*^[1]

The characteristically deep magenta and bluish-purple colors of such gold nanostructures result due to increased absorption of incident visible light, triggered by localized surface plasmon resonances.

Gold nanorods can be prepared by both top-down methods (direct fabrication) and bottom-up ones (wet-chemical,^[12] electro-chemical,^[13] solvothermal,^[14] photo-reduction, etc.). Amongst them, the most facile method for synthesizing high quality gold nanorods was pioneered by Nikoobakht and El-Sayed,^[12] and it relies on the wet-chemical route. Gold nanorods grow by the reduction of Au^{3+} ions in an aqueous solution onto nanometer-sized seeds via a surfactant-based (CTAB) soft template, which promotes anisotropy. A small amount of Ag^+ ions added to the solution deposit on the relatively high-energy $\{110\}$ Au facets and hinder further growth along this direction. As a result, the Au^{3+} ions are reduced mostly onto the $\{100\}$ facets and the longitudinal growth proceeds along this direction.^[15] A schematic is shown in Figure 1.4. Due to its simplicity and good yield, this method was extensively adopted for the synthesis of gold nanorod solutions, and the detailed experimental procedure is outlined in Chapter 2.

From Gans theory, it has been calculated that the longitudinal surface plasmon wavelength of an individual nanorod is given as^[1]

$$\lambda_{plasmon} = \lambda_p \sqrt{\varepsilon_\infty + \left(\frac{1}{L} - L\right) \varepsilon_m}$$

$$\lambda_p = \sqrt{\frac{2\pi^2 c^2 m^* \varepsilon_\infty}{N e^2}}$$

Here, ε_∞ is the high frequency dielectric constant of gold, m^* is the effective electron mass in gold and N is the number density of the conduction electrons. It shows that the

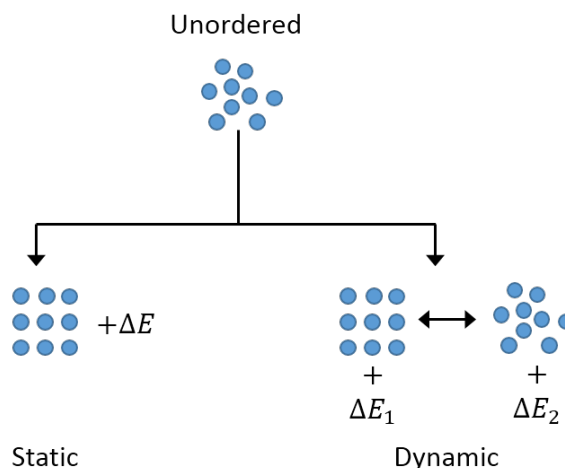


Figure 1.5: *Types of self-assemblies.*^[19]

longitudinal SPR is sensitive to the changes in the refractive index of the surrounding medium. In fact, redshifts of up to 120 nm are reported for longitudinal SPRs of Au nanorods when the surrounding refractive index changes by 0.4.^[1] A linear dependence between these redshifts as a function of the surrounding refractive index has also been observed.^[16,17] This enables applications in areas such as precise surface plasmon-based sensing. All in all, gold nanorods show spectacular sub-diffraction limit concentration of electromagnetic fields leading to large enhancements, increased absorption and scattering due to surface plasmon resonances (leading to vividly intense colors) and photothermal conversion abilities.^[1]

1.7 Self-assembly

The term ‘self-assembly’ applies only for spontaneously formed reversible, locally-ordered, thermodynamically stable assemblies. Weak reversible interactions (energies less than 0.5 eV) between molecules can give rise to large, well-defined, ordered and stable structures. Self-assembly thus results in a configuration that achieves equilibrium. Self-assembly has important applications since the close-packed arrangement of nanomaterials can be used for producing photonic band gap materials, Bragg mirrors, lasers, electroluminescent devices, sensors, photovoltaic solar cells and so on. Such applications are used in the fields of nanophotonics and nanoelectronics. For instance, ‘Supramolecular chemistry’ pioneered by Nobel laureate Dr. Jean Marie-Lehn, is fundamentally based upon the concept of self-assembly.^[18]

Self-assembly can be either static or dynamic.^[19] In static self-assembly, the ordered state is formed as the system reduces its free energy, approaching equilibrium. Unless any external force is present, the system shall remain at equilibrium. This contrasts with dynamic self-assembly in the sense that a constant influence from one or more external forces is necessary to maintain equilibrium. As soon as this input stops, the system ceases to be organized and de-assembles. An example of static self-assembly include crystallization from melts, whereas living beings are examples of dynamic self-assembly. Figure 1.5 illustrates the difference between the two types of self-assemblies.

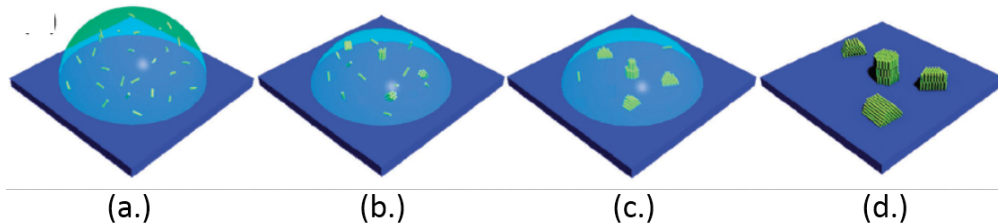


Figure 1.6: *Solvent-evaporation induced self-assembly of Au nanorods. (a.) drop placed on a substrate. (b.) increased interactions among individual nanorods leading to (c.) formation of super-structures as (d.) the solvent evaporates completely.*^[27]

1.7.1 Self-assembly of gold nanorods

Self-assembly of gold nanorods can result in many attractive properties. The individual LSPRs can be coupled to obtain large collective enhancement of optical properties. This can give rise to new collective plasmon modes,^[20] which can be distinct from the SPRs on the individual nanorods. As a result, the enhanced plasmonic response of the self-assembled nanorods can be potentially utilized for many optoelectronic and biomedical applications.^[1] There are three main ways to achieve self-assembly: solvent-induced evaporation, assembly through thiol molecules, and assembly through biomolecules and polymers.

Solvent-induced evaporation remains by far, the most widely adopted strategy to achieve self-assembly of gold nanorods. It takes advantage of the fact that liquid-crystalline phases of gold nanorods form as the solvent medium (i.e. a drop) evaporates slowly. The mechanism is schematically represented in Figure 1.6. Solution-based gold nanorods are usually capped with cationic surfactant CTAB bilayers for preventing agglomeration. These bilayers induce electrostatic repulsions and inter-chain attractions as two nanorods approach each other. When a drop of solution containing gold nanorods is placed on a flat substrate, the progressive evaporation causes the nanorods to be carried on to the edge of the drop, due to solvent flow. As a result, the local density of the nanorods increases at the edge, where it can counterbalance the inter-rod repulsive Van der Waals' interactions to produce ordered, liquid-crystalline phases. This is colloquially termed as the *coffee-ring effect*.

El-Sayed obtained ordered assemblies of gold nanorods which are stacked in horizontal layers in a side-by-side fashion.^[21] This might have resulted due to a larger probable capillary force along the length of the nanorods as compared to their width. It was also shown that these assemblies are sensitive to the aspect ratio of the nanorods.^[22] Ming et al successfully obtained 3D superstructures of self-assembled gold nanorods extending over an area $0.1\text{-}0.8\text{ m}^2$ and a depth of $1.7\text{-}2.2\text{ }\mu\text{m}$.^[23] Figure 1.7 shows scanning electron microscopy (SEM) images of self-assembled gold nanorod superstructures published in the literature.

1.7.2 Vertically aligned self-assembled gold nanorods

The anisotropic nature of gold nanorods can give rise to exotic vertically aligned self-assembled arrays. Such arrays are best obtained using the evaporation-induced route and have been reported by quite a few groups in the past couple of years, around the

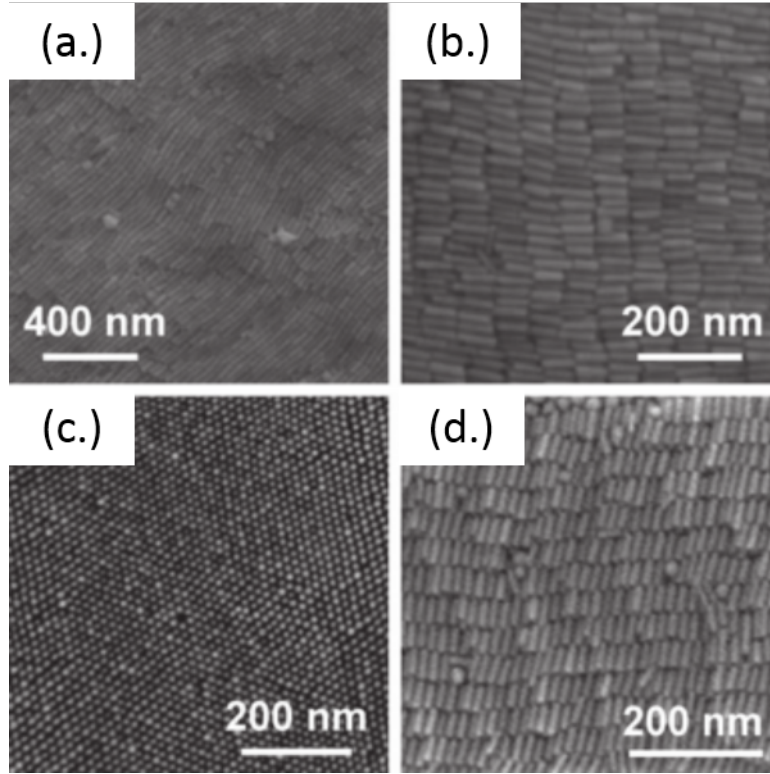


Figure 1.7: *SEM images of ordered self-assemblies of gold nanorods. (a.) Nematic and (b.) smectic-A phases.*^[20] (c.) *Top and (d.) side views of smectic-A phases achieved using gemini surfactants in place of CTAB.*^[21]

world.^[24–26] Peng et al achieved vertical self-assembly of CTAB-capped gold nanorods over various substrates such as silicon, GaN, ITO-coated glass, etc.^[25] Prof. Liz-Márzan’s group used gemini surfactant instead of CTAB for synthesis and resulting self-assembly of gold nanorods.^[24] They demonstrated nanorod islands up to fifteen monolayers deep. The nanorods in each layer were all vertically aligned and hexagonally close-packed (see Figure 1.7 (c.) and (d.)). Xie et al adopted a similar route of replacing CTAB with hexa (ethylene glycol) alkanethiol to obtain vertically aligned gold nanorods.^[27] Thai et al used thiol PEG-carboxyl modification of gold nanorods to induced vertically aligned multilayer self-assembly into prefabricated micro-patterned rings.^[26] Typically, these arrays extend over an area of few square microns. The inter-rod distances are measured to be $\sim 3\text{-}7$ nm.

The mechanism behind this exotic self-assembly has not been exhaustively reviewed in the literature. However, Peng et al have proposed that the gold nanorods in the aqueous drop form the initial hexagonal nucleus in a side-side manner.^[25] Free nanorods then assemble around such nuclei ultimately leading to the formation of the arrays. Finally, these arrays stand up due to a balance between gravity and van der Waals’ interaction with the substrate. The larger contact area with the substrate minimizes the surface energy in the vertical alignment. This process is schematically shown in Figure 1.9.

Apart from their exquisite appearance and partially unclear mechanism of formation, vertically aligned arrays of gold nanorods have a number of interesting applications – excellent substrates for SERS, obtaining field emission, as well as enhanced light harvesting in photovoltaic solar cells. The small inter-rod separation enables intense plasmonic hotspots, which coupled with the long-range hcp ordering promises excellent use in SERS

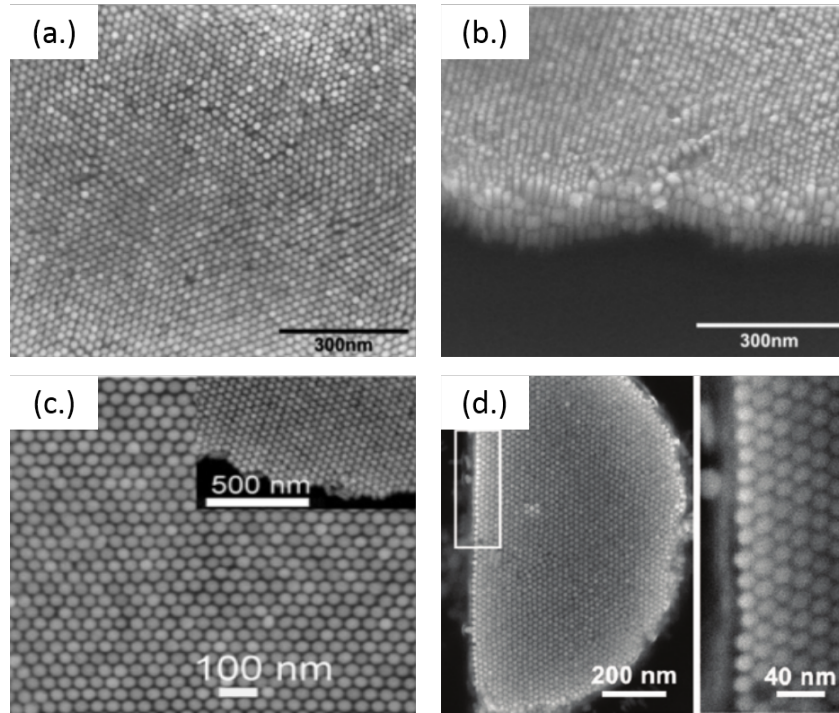


Figure 1.8: *FESEM images of self-assembled vertically aligned gold nanorods. (a.) Top and (b.) side views of thiol PEG-carboxyl modified nanorods.^[23] (c.) CTAB-capped nanorods.^[22] (d.) hexa (ethylene glycol) alkanethiol functionalized nanorods.^[24]*

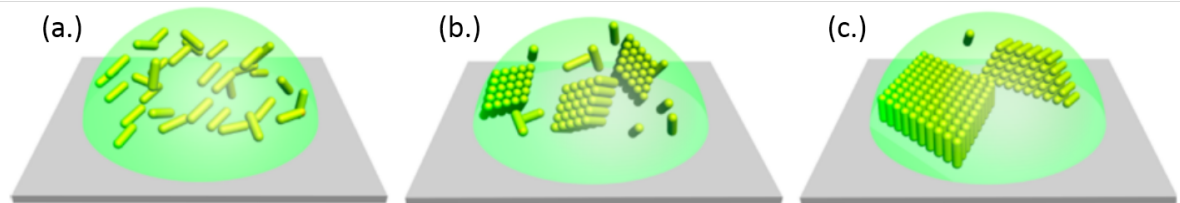


Figure 1.9: *Mechanism of vertical alignment in self-assembly.^[22] (a.) Initial dispersion of nanorods in solution. (b.) nucleation and growth processes of self-assemblies. (c.) final formation of vertically aligned arrays.*

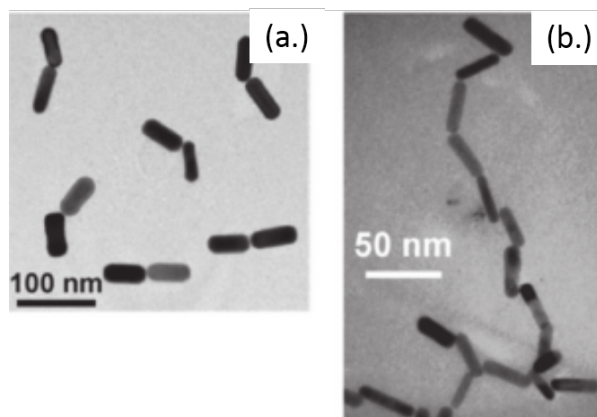


Figure 1.10: Assembly of gold nanorods into dimers and oligomers using thiol molecules.
[1]

sensing. The gaps between the rods can also trap adsorbed molecules via capillary forces. Using SERS, it is shown in Chapter 3 that vertically aligned nanorod arrays have the capability to detect few tens of adsorbed molecules.

In addition, self-assembly of gold nanorods can also be induced by the functionalization of gold nanorods using thiol molecules, biomolecules and certain polymers. Thiol molecules are mostly used to assemble nanorods into long chains (see Figure 1.10), which occurs via the formation of a strong semi-covalent Au-S bond.^[28] Selective binding of thiol molecules onto the ends or side-faces of gold nanorods can give rise to end-end or side-side assemblies. Assembly induced due to bifunctional thiol molecules such as cysteine, glutathione, 11-mercaptoundecanoic acid, 3-mercaptopropionic acid etc. is electrostatic in nature and dependent upon the pH of the solution. This makes it reversible, and hence dynamic.^[29] Polymers can also induce self-assembly of gold nanorods. It can be tuned by controlling the size and weight of the polymer, its solubility, etc.^[30] Even DNA has been used as a template for directing the self-assembly of gold nanorods to form close-packed lattices.^[31]

1.8 Summary

Nanoscience and nanotechnology are important areas of interdisciplinary, applied research of the 21st century. Metal nanoparticles support surface plasmon resonances which are collective oscillations of conduction electrons in response to external electromagnetic fields. Plasmonics, a sub-discipline of nanophotonics deals with the interaction of light with metallic nanostructures. Surface-enhanced Raman Spectroscopy (SERS) improves the inherently weak nature of Raman scattering to enable ultra-sensitive detection of various molecules. Plasmonic nanomaterials such as gold nanorods offer excellent sensitivities for SERS experiments.

Colloidal gold nanorods can be self-assembled into a variety of interesting 2D and 3D superstructures. The most exotic and slightly mysterious amongst all is the self-assembly of nanorods in a vertically aligned fashion. Finally, micron-sized arrays of vertically aligned gold nanorods can serve as excellent substrates for Surface-enhanced Raman Scattering of a variety of molecules due to their ability to generate uniform, intense plasmonic hotspots. This can be harnessed into applications for devices capable of ultra-sensitive

detection.

1.9 Bibliography

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Chapter 2

Experimental techniques

This chapter discusses the method of synthesizing seed-mediated, surfactant-stabilized colloidal gold nanorods, as well as the protocol to achieve evaporation-induced self-assembly. It also discusses the characterization and analysis techniques employed for all the experiments, as well as the methods of sample preparation for each of them. The fundamental principles underlying the operation of these techniques are also described herein.

2.1 Synthesis of gold nanorods

There exist two approaches to prepare gold nanorods, bottom-up and top-down.^[1] In the bottom-up method, the principal factor is the nucleation of gold seeds in aqueous solutions, followed by subsequent anisotropic growth due to reduction of Au^{3+} ions from the solution, onto the growing nuclei. Shape-directing agents and surface-stabilizing chemicals are often used for producing monodispersed and uniform nanorods. In the second approach namely top-down, Au nanorods are obtained through a combination of physical deposition and lithography processes. This work is based upon the wet chemical method of synthesizing gold nanorods, more specifically, the soft-template based seed-mediated growth method pioneered by Babak Nikoobakht and Mostafa El-Sayed.^[2] The key advantages of this facile method lie in the high yield, monodispersity and uniformity of the nanorods synthesized at room temperature. No special apparatus such as flasks, hot-plates, mantles, etc. is required.

2.1.1 Materials

Gold chloride hydrate ($HAuCl_4 \cdot xH_2O$), cetyl trimethyl ammonium bromide (*CTAB*), benzyl dimethyl hexadecyl ammonium chloride (*BDAC*), ascorbic acid, and D-glucose were purchased from Sigma Aldrich. Silver nitrate ($AgNO_3$) was purchased from Merck. Sodium borohydride ($NaBH_4$) was purchased from SRL Chem Pvt. Ltd, Andheri, India. All the chemicals were used without further purification. For all the experiments, Millipore Milli-Q water was used.

2.1.2 Procedure

In a typical reaction, a ‘seed solution’ was prepared by mixing *CTAB* (0.2 M, 5 ml) and $HAuCl_4$ (5×10^{-4} M, 5 ml). After gentle stirring, freshly prepared ice-cold $NaBH_4$ (0.01 M, 0.6 ml) was added, followed by vigorous stirring for two minutes. This caused

the colour of the solution to turn brownish-yellow. The ‘growth solution’ consisted of a binary surfactant solution of *CTAB* (0.2 M, 2.5 ml) and *BDAC* (0.15 M, 2.5 ml). To this, $AgNO_3$ (0.004 M, 0.2 ml) was added, followed by addition of a solution of $HAuCl_4$ (0.001 M, 5 ml) with gentle mixing. This caused the solution to turn golden yellow. Ascorbic acid (0.0788 M, 0.07 ml) was then added with shaking, which caused the resulting solution to turn colorless. Finally, 20 μl of the seed solution was added into the growth solution and the latter was kept to grow for twelve hours at room temperature. A dark magenta color of the growth solution indicated successful formation of the gold nanorods.

A minor disadvantage of this method is the simultaneous production of some spherical nanoparticles. However, the nanorods can be sequestered through simple centrifugation. Typically, 1 mL of the as-synthesized solution was centrifuged thrice at 9600 RPM for 20 minute periods, with intermediate re-dispersion of the precipitate in water to remove the excess surfactants and spherical nanoparticles (which occur in the supernatant fluid). After the third round, the precipitate was re-dispersed in 1 μl water to obtain the purified nanorod solution.

2.2 Self-assembly of gold nanorods

There are three principal strategies of obtaining self-assembly of gold nanorods – solvent evaporation induced assembly, assembly due to small thiol molecules, and assembly due to biological molecules and/or polymers. For the purpose of this work, the solvent evaporation-induced self-assembly was employed, mainly due to its ease of use and high reproducibility.

1 ml solution of the prepared gold nanorods was centrifuged according to the procedure mentioned above. However, after the third round, the precipitate was dispersed in 50 μl water, to prepare a more concentrated solution. 5 μl of this solution was drop-casted on a clean silicon wafer kept in a glass petri-dish sealed with parafilm at 21° C to achieve the self-assembly induced by slow evaporation.

2.3 Analysis techniques

2.3.1 UV-Vis absorption spectroscopy

Absorption spectroscopy measures the absorption of incident light by a sample as a function of its wavelength. A number of molecules undergo electronic transitions for incident energies in the ultraviolet and visible regions of the electromagnetic spectrum. Noble metal nanoparticles, however, support longitudinal surface plasmon resonances, i.e. surface electromagnetic modes which arise due to confined oscillations of the conduction electrons. Such resonances are usually dipolar in nature and can be excited by plane-polarized electromagnetic waves.^[1]

If a beam of light with incident intensity I_0 passes through a sample solution to a detector with final intensity I , the transmittance (T) of the sample is defined as

$$T = \frac{I}{I_0}$$

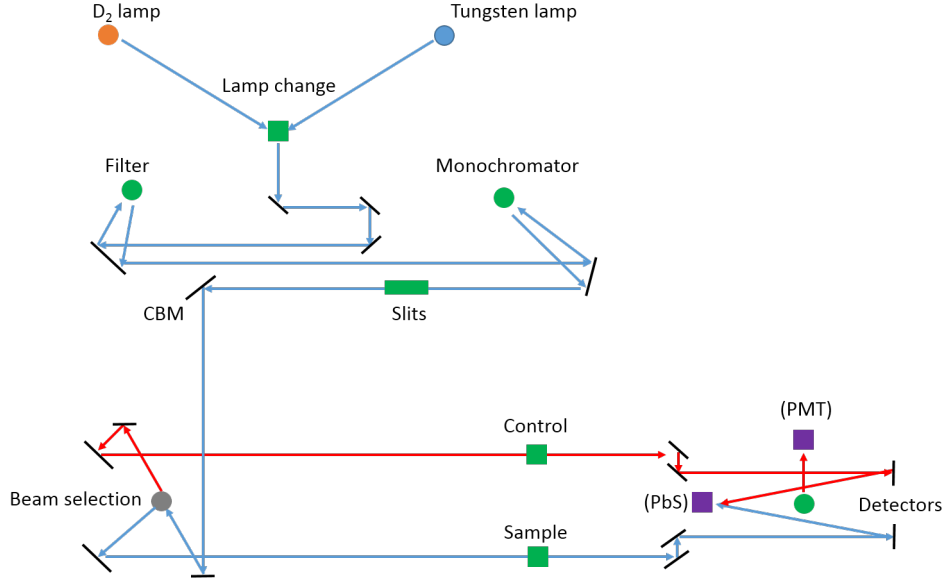


Figure 2.1: *Working schematic of the Perkin Elmer Lambda 950 UV-VIS spectrophotometer.*

The extinction (E) is defined as

$$E = 1 - T$$

Also,

$$E = A + S$$

where (A) is the absorbance and (S) is the scattering. UV-Vis absorption spectroscopy usually measures the total extinction of the sample solution. Figure 2.1 illustrates the schematic diagram of the Perkin Elmer Lambda 950 UV-VIS spectrophotometer setup used for this purpose.

The instrument uses a D_2 lamp as the UV source ($\lambda < 320$ nm) and a tungsten lamp for the visible-NIR regions. A monochromator is in-charge of selecting tunable wavelengths for the incident beam, which passes on to the sample stage through mirror optics. The transmitted beam (from the samples) is collected by a lead sulphide plate ($\lambda > 860$ nm) or a photomultiplier tube sensor, which is then analyzed and displayed by the software on a computer.

Liquid samples are conveniently analyzed by filling them in transparent glass containers called cuvettes, of calibrated spatial dimensions and optical parameters, whereas solid samples are affixed onto glass slides (transmission mode) or opaque substrates (reflection mode) for spectrum acquisition. Figure 2.2 illustrates how a liquid sample is contained in a typical upright transparent glass cuvette for measurement of the extinction spectrum.

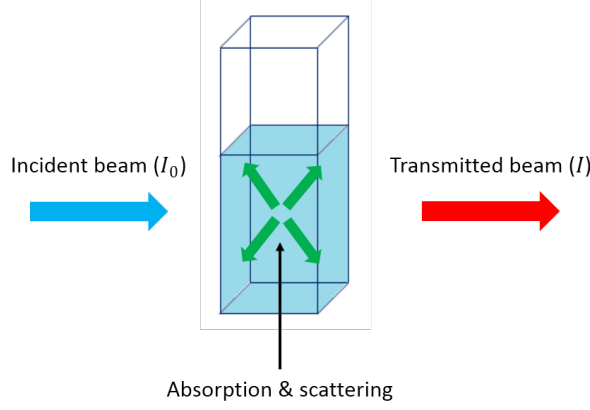


Figure 2.2: *Illustration of a liquid sample in a transparent glass cuvette.*

2.3.2 Field-emission scanning electron microscopy

Ernst Ruska developed the first electron microscope in 1933. Just as conventional optical microscopes use light of a suitable wavelength to image samples, electron microscopes use a sharply focused beam of electrons for imaging. Wave-particle duality states that the de Broglie wavelength λ of an electron having kinetic energy E is

$$\lambda = \frac{h}{\sqrt{2mE}}$$

where h is the Planck's constant and m is the electron rest mass. The Rayleigh criterion states the diffraction-imposed lower limit on the spatial resolution achievable in optical microscopes as ~ 200 nm. However, for an electron beam with $E = 5$ keV, the de Broglie wavelength is around 0.017 nm, which can be taken as the measure of the smallest resolvable feature in a sample.^[3] This shows that electron microscopes can achieve a significantly higher spatial resolution when compared with conventional optical microscopes. There are two types of electron microscopy techniques namely, scanning and transmission. A scanning electron microscope (SEM) uses backscattered electrons from a sample for imaging, whereas a transmission electron microscope (TEM) uses a beam of high energy electrons (~ 200 keV) transmitted through the sample for building the image.

The interaction of the incident electrons and the sample are quite complex, resulting in backscattered electrons, Auger electrons, visible light, X-rays, etc. which cause defocusing of the incident beam.^[3] This is the reason why typical SEMs do not reach the theoretical de Broglie resolution. However, the incident electron beam can be focused to a very small spot size using electrostatic lenses. Typical SEMs can reach practical resolutions anywhere between 1 to 20 nm.

Samples are prepared by drop-casting ($\sim 10 \mu\text{l}$) upon a clean silicon wafer. Non-conducting samples are sputtered with a ~ 5 nm gold coating so that high-resolution images are possible. Figure 2.3 shows the schematic diagram of the ZeissTM Ultra Plus FESEM used for recording the electron micrographs. The tungsten-zirconium oxide hybrid cathode acts as a thermal field emission source at operating voltages 3 to 30 kV. The two anodes and the field lenses ensure that the electron beam reaches the sample stage without any crossover. Precise focusing is possible with the electrostatic lenses.

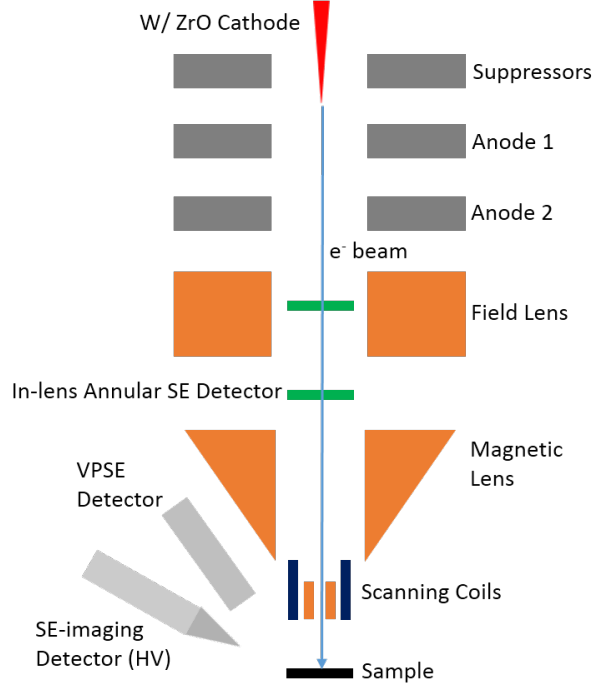


Figure 2.3: *Working schematic of the Zeiss Ultra Plus FESEM.*

The in-lens annular secondary electron detector is used to image samples at high vacuum ($\sim 10^{-7}$ torr). Non-conducting samples can be imaged without any conductive coating with the help of the variable pressure detector (VPSE). Standard conditions allow spatial resolutions up to 10 nm.

2.3.3 Raman spectroscopy

This technique is based on the eponymous effect discovered by Sir C. V. Raman in 1928. The scattering of incident photons from electrons in atoms/ molecules can be either elastic or inelastic. In elastic or Rayleigh scattering, the outgoing photon has the same frequency (and hence, energy) as the incident one. This is the dominant mode of scattering.

$$\nu_0 + a_0 \rightarrow \nu_1 + a_1$$

$$\nu_0 = \nu_1(\text{photon}),$$

$$a_0 = a_1(\text{scatterer})$$

However, inelastic scattering also occurs, i.e. when the incident photon loses (or gains) energy to the scatterer atom/ molecule, mediated by one phonon (first-order process).

$$\nu_0 + a_0 \rightarrow \nu_1 + a_1 + \gamma$$

$$\nu_0 \neq \nu_1(\text{photon})$$

$$a_0 \neq a_1(\text{scatterer})$$

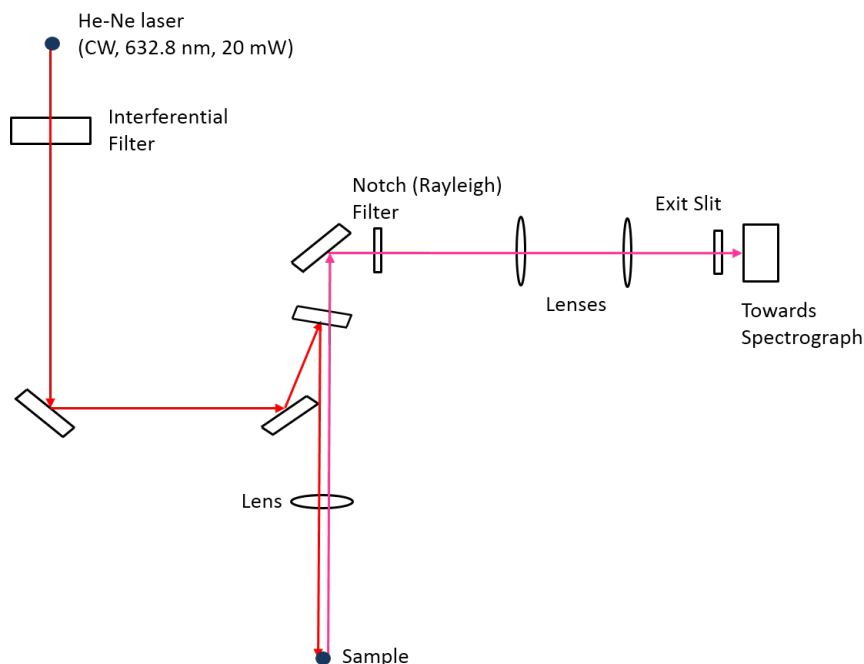


Figure 2.4: Working schematic of the Horiba Jobin Yvon LabRAM HR800 micro-Raman spectrometer.

$$\gamma \neq 0$$

This is termed as Raman scattering, and can be of two types; Stokes' scattering is when the outgoing photon has lower energy than the incident one ($\nu_0 > \nu_1$), whereas Anti-Stokes' scattering is when the reverse is true ($\nu_0 < \nu_1$). Raman scattering signals are inherently weak ($\sim 10^{-5}$ of the incident beam). The molecule is excited to a virtual state (lower in energy than a real electronic transition), along with a relaxation to the original state and a change in its vibrational energy. The shift in the photon frequency ($\nu_0 - \nu_1$) is taken as the vibrational frequency. Raman scattering differs from absorption/fluorescence in the sense that the excitation occurs to a virtual state rather than a real one.

Figure 2.4 shows the schematic of the Horiba Jobin Yvon LabRAM HR800 micro-Raman spectrometer used for recording Raman spectra of the samples. A Helium-Neon continuous wave laser emitting at 632.8 nm and 20 mW incident power is focused on the sample stage through mirror-based optics. The signal from the sample is collected in the backscattered configuration. A notch filter is responsible for masking the Rayleigh scattering line from the backscattered beam, which is then passed through a lens system towards the spectrograph for analysis. Both solid as well as liquid samples can be analyzed, by placing ($\sim$ few mg) or drop-casting them ($\sim 10 \mu\text{l}$) on a glass slide or an opaque substrate such as a silicon wafer. Opaque substrates are allowed since the spectra are acquired in the reflection mode.

2.4 Bibliography

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Chapter 3

Results and discussions

This chapter presents the results obtained from the characterization of gold nanorods, their self-assembly, and the experiments on Surface-enhanced Raman Spectroscopy. A discussion on various simulations used to illustrate the plasmonic properties of gold nanorods is also included.

3.1 Colloidal gold nanorods

Gold nanorods were synthesized using the two-step seed mediated growth method pioneered by Nikoobakht and El-Sayed^[1], which is described in Chapter 2. The synthesized solutions were characterized by UV-Vis absorption spectroscopy, and field emission scanning electron microscopy. As discussed in Chapter 1, gold nanorods with cylindrical symmetry show two distinct absorption peaks in the visible and/or near-infrared region of the electromagnetic spectrum due to the presence of localized surface plasmon resonances. The positions of these resonance peaks is sensitive to the size of the nanorods (refer Figure 3.1).

Usually, the seed solution shows a single absorption peak which appears to be quite blue-shifted from the otherwise interband transition-limited minimum wavelength absorption peak of gold nanoparticles at ~ 510 nm (see Figure 3.2). F. Vallée explains this effect as follows:^[2] Since the seed particles are usually 2-3 nm in diameter, the dielectric confinement is very high and the number density of conduction electrons is less than that in the

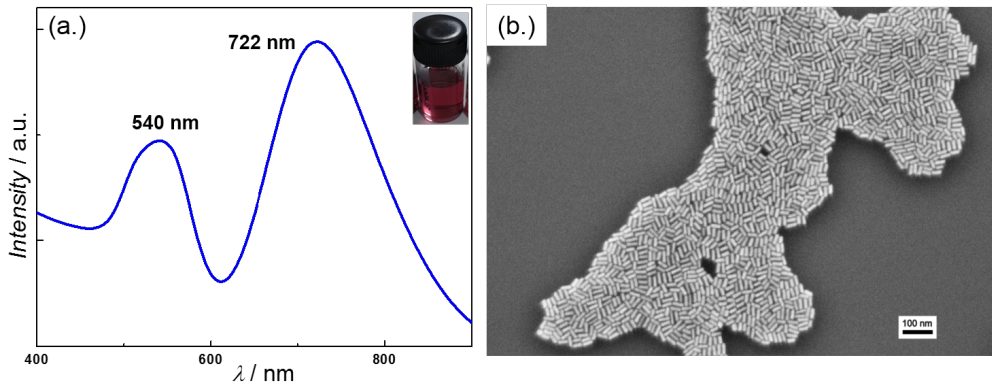


Figure 3.1: (a.) Absorption spectrum, and (b.) FESEM image of the synthesized gold nanorod solution.

bulk metal. This causes a slight red-shift in the plasma frequency of the seed particles. However, for noble metals such as gold, the d-electrons (bound) which are localized within the inner region of the particles are also affected by the size reduction, which causes a reduction in their polarizability, close to the surface. This decreases their contribution to the interband transitions, and induces a blue-shift in the surface plasmon resonance.

Figure 3.1 (a) shows the absorption spectra of a gold nanorod solution with its photograph in the inset, and Figure 3.1 (b) shows the corresponding FESEM image. The absorption peaks at 540 nm and 722 nm are attributed to the transverse and longitudinal SPRs respectively. The synthesized nanorods in Figure 3.1 (b) have an average length 34.2 nm and average width 8.9 nm.¹ The dimensions of the synthesized nanorods are dependent on the amount of seed particles added to the growth solution. The effected changes can be observed from the absorption spectra since the position of the longitudinal SPR peak is controlled by the aspect ratio of the nanorods.

3.1.1 Dependence on the amount of seed solution

In order to study the size dependence of the nanorods on the amount of seed solution used to begin with, four independent growth solutions were prepared, as part of a collaborative experiment. The amount of seed solution added was varied as 20 μ l, 30 μ l, 40 μ l and 50 μ l respectively. Figure 3.2 (a.) shows the UV-Vis absorption spectra of the seed solution. It can be seen that the seed particles show a single, small SPR at 470 nm, whereas the grown nanorod solutions exhibit two SPR peaks in Figure 3.2 (b.); the transverse one located at $\sim$ 500 nm, and the longitudinal one increasingly red-shifted from 676 nm to 750 nm. Tiwari et al have reported similar observations on the effect of seed amount on the growth of nanorods.^[3] It is believed that the increased amount of seed solution increases the overall aspect ratio of the nanorods. The longitudinal SPR peak thus red-shifts with an increasing aspect ratio. Figure 3.3 shows a photograph of the seed solution and the four different growth solutions.

3.2 Self-assembly

Gold nanorods described above were employed for self-assembly on clean silicon substrates. The strategy was to use solvent evaporation at a slow pace and ambient temperature and pressure conditions, as described in Chapter 2. Various types of assemblies were observed using FESEM, namely end-end, side-side, and the more important vertically aligned close-packed assemblies.

The driving force behind the self-assemblies is mainly based upon the transfer of nanorods from the bulk solvent to the thin film due to evaporation (which is convective in nature) and the subsequent interactions between the nanorods in the thin film, which give rise to the myriad superstructures.^[4] The evaporation of water from the surface of the film edge results in an influx of both water and the nanorods which causes their accumulation. As the nanorods are carried from the bulk of the drop towards its leading edge, the above influx forms dense assemblies. The space between the substrate and the evaporating solvent is filled successively by more nanorods, and can thus give rise to bilayers, and even multilayers.

¹Length measurements in all FESEM images were carried out using ImageJ, a public-domain image processing program.

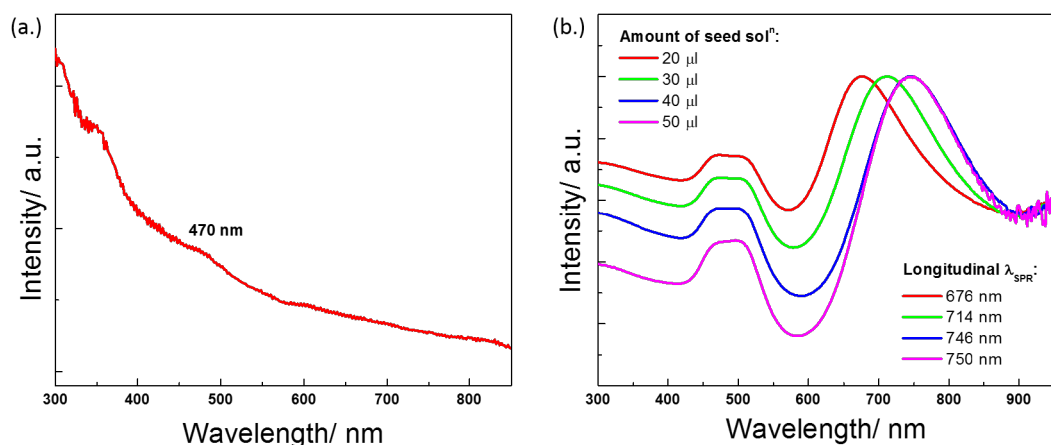


Figure 3.2: Absorption spectrum of (a.) seed solution, and (b.) overlaid spectra of the four grown nanorod solutions.

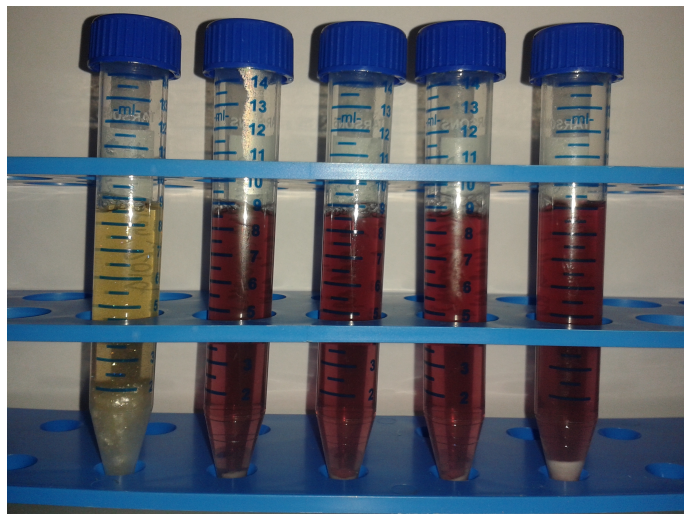


Figure 3.3: (L to R) Photograph of the seed solution and the four growth solutions in increasing order of amount of added seed.

3.2.1 Side-side assemblies

Figure 3.4 shows the FESEM images of the smectic/ side-side assemblies of gold nanorods obtained using the evaporation-induced strategy. The nanorods have an average length 29.8 nm and width 10.3 nm, equating to an aspect ratio ~ 2.89 . The assembly extends over approximately $2.5 \mu\text{m}$, shows possible presence of multilayers and has good translational and orientational ordering. The average lateral inter-rod separation was measured to be 3.0 nm. The length of the CTA^+ ion from the surfactant on the nanorods is $\sim 2.2 \text{ nm}$.^[5] Thus, the separation between two adjacent parallel nanorods should be around twice this length i.e. $\sim 4.4 \text{ nm}$. Since the measured average separation is less than this value, the alkyl chains of the CTAB surfactant must probably have been inter-digitated. This fact was also reported by Murphy et al.^[6] El-Sayed's group had reported such side-side assemblies for the first time with the possible explanation that the nanorods align parallel to each other due to higher lateral capillary forces along their lengths, as compared to

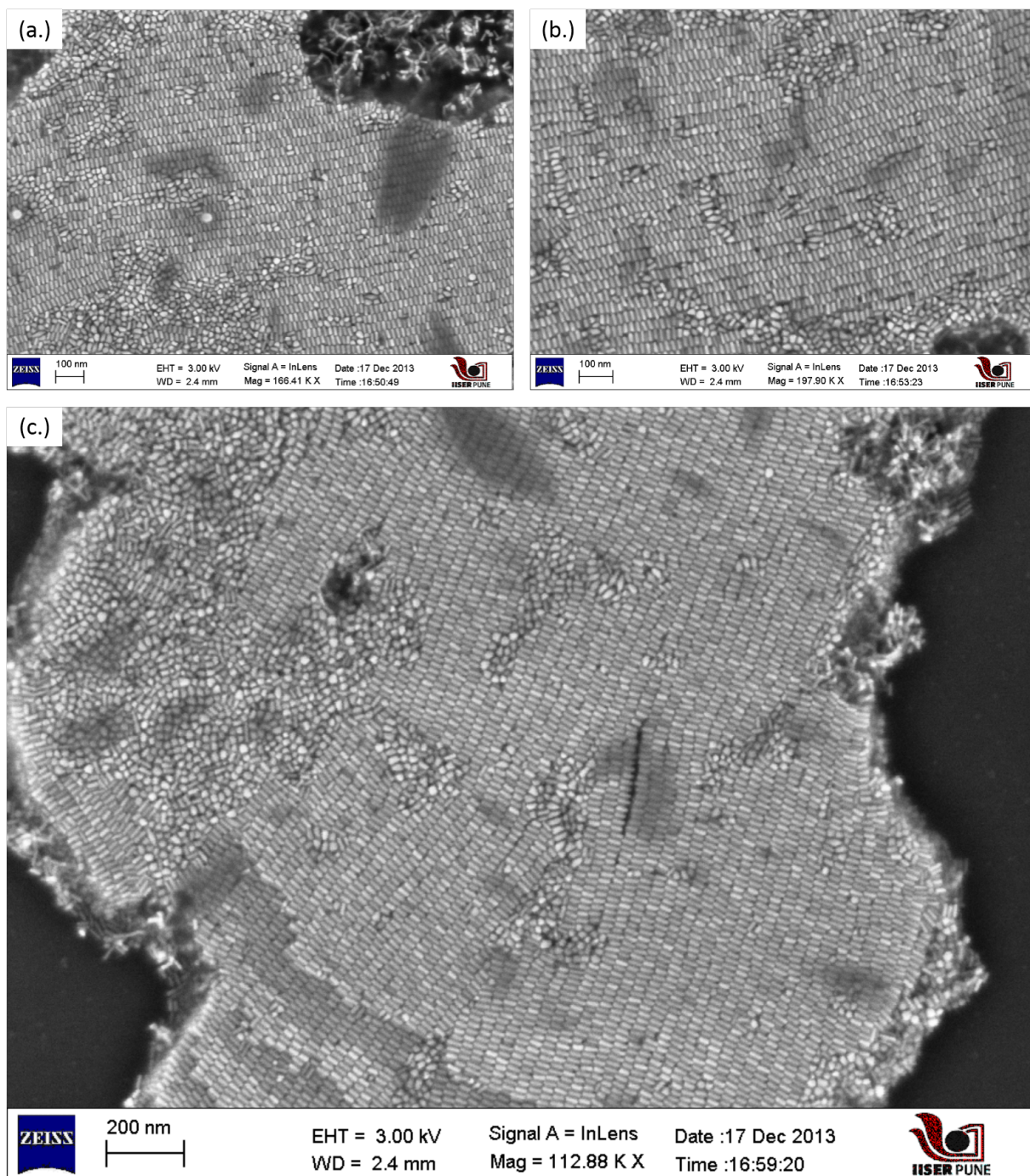


Figure 3.4: *FESEM images of gold nanorods forming side-side self-assemblies.*

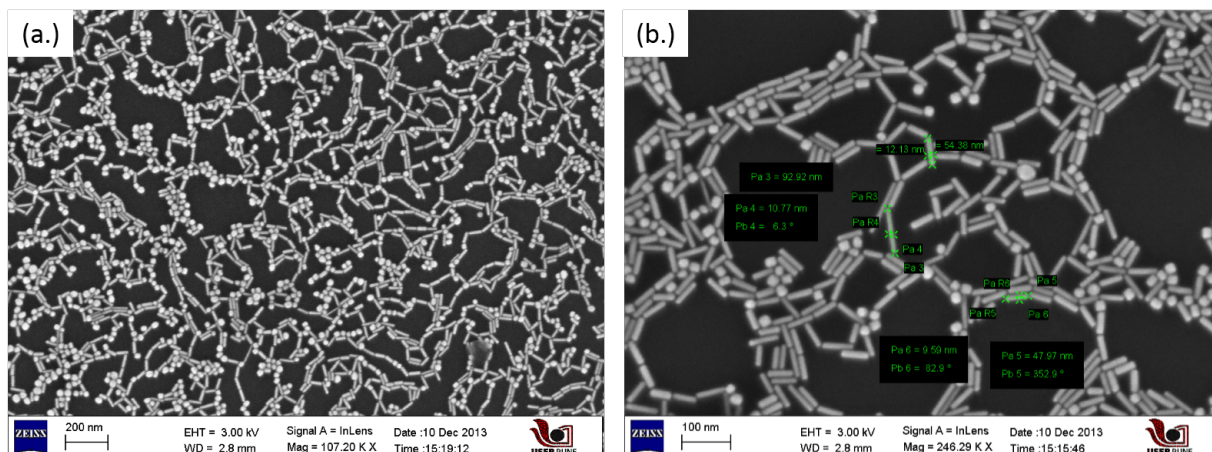


Figure 3.5: *FESEM images of gold nanorods forming end-end self-assemblies.*

their ends.^[4]

The nanorods are capped by CTAB, whose head group is a quaternary amine (N^+), and a bromide anion (Br^-), which acts as a solvated counter-ion. The Br^- ions can be in close proximity to the N^+ ions, or away from the surface of the nanorods. Hence it is conjectured that in case of such assemblies, the Br^- counter-ions present between two aligned nanorods (with the N^+ ions from CTAB) help in producing an electrostatically stable structure with close-packed ordering.^[7,8] The presence of other partially formed, non-uniform gold nanoparticles disrupts the translational ordering of the self-assembled nanorods as seen in Figure 3.4. These are typically by-products from the chemical synthesis of the nanorods, and can be eliminated with extensive centrifugation.

3.2.2 End-end assemblies

Figure 3.5 shows the FESEM images of end-end assembled gold nanorods. In this case, the nanorods were measured to have an average length of 45.2 nm and width, 10.3 nm. The nanorods in the chains are separated on average, by a distance of 3.6 nm. The principal observational difference between the end-end and side-side assemblies is the concentration of the nanorods, which affects their close-packing. Murphy et al. reported that nanorods with aspect ratio ~ 5 or greater have a tendency to align parallel to each other, and form smectic, side-side assemblies.^[6] However, it was observed in this work that the nanorods mentioned above, with an aspect ratio ~ 4.39 do form end-end assemblies.

End-end assemblies for nanorods with functional group modifications, such as biotin-streptavidin were initially reported by Murphy et al.^[9] Chang et al. used thioacetic acid for functionalizing the ends of gold nanorods.^[10] Using Immunoglobulin G, they achieved bio-induced end-end linked chains of gold nanorods. However, un-functionalized nanorods have also been reported to show such assemblies. The CTAB capping is less dense on the ends of the nanorods, as compared to their lengths. As a result, at low enough concentrations, the ends of the nanorods are more prone towards oriented attachment which gives rise to such assemblies. Also, intuitively, end-end assemblies forming one-dimensional chains is possible for anisotropic nanostructures such as gold nanorods. Murphy et al. also find that chain-like assemblies of nanospheres can be formed if local inhomogeneities in the surfactant capping groups are present.^[6]

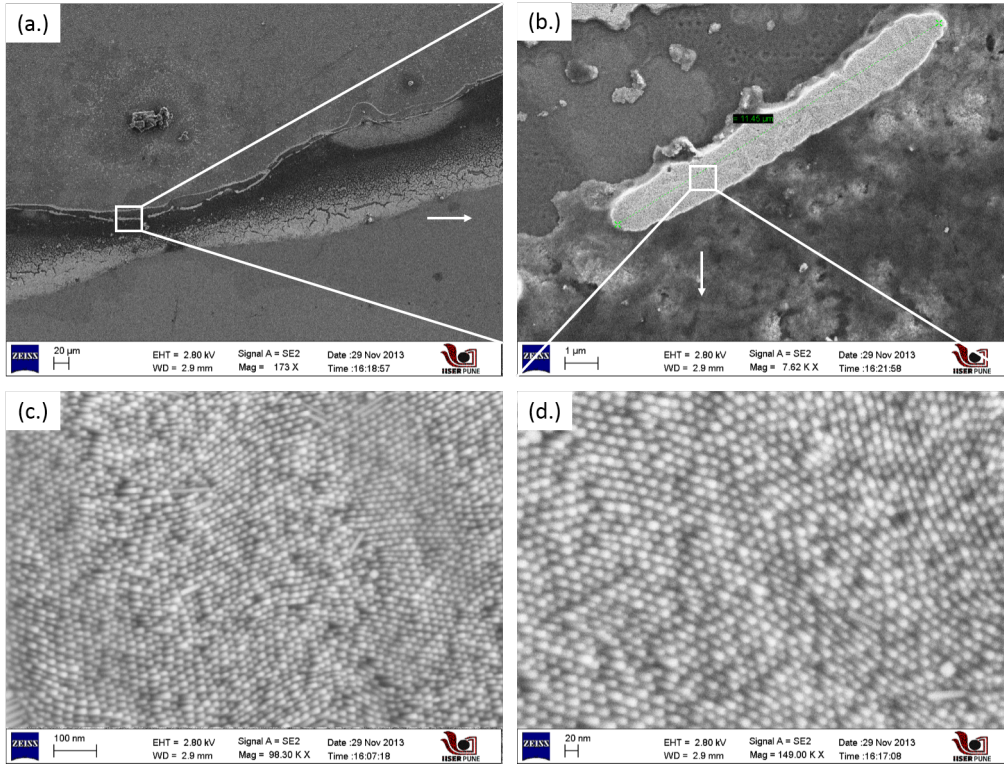


Figure 3.6: *FESEM images of self-assembled vertically aligned gold nanorod arrays.*

3.2.3 Vertically aligned assemblies

The most exotic assemblies of gold nanorods are the vertically aligned ones, and they form predominantly at the edges of the evaporated drop, due to the so-called *coffee-ring effect*. Typical assemblies extended over a range of a few μm , with the largest achieved range (in this work) of approximately $82 \mu\text{m}$. As discussed in Chapter 1, the nanorods are believed to come together in the aqueous medium of the drop to form close-packed nuclei, mostly in a side-side manner. More and more nanorods then assemble around such nuclei, which leads to the formation of the arrays in the solution. These arrays finally stand up due to a balance between the interacting van der Waals' forces, and gravity. It is also believed that in case of vertical alignment, the larger contact area with the substrate helps to minimize the surface energy.^[11,12]

Figure 3.6 shows successively zoomed FESEM images of one sample of vertically aligned arrays of gold nanorods, from the southeast edge of the 'coffee-ring'. Figure 3.6 (c.) and (d.) show that the vertically aligned nanorods have some defects such as interstitials and rifts. The average separation was measured to be 4.1 nm , which roughly corresponds to the average length of two CTAB molecules. However the occasional occurrence of defects help to observe the elongated nature of the standing nanostructures which are indeed nanorods, and not spherical nanoparticles that are also formed in small quantities as a by-product.^[13]

Figure 3.8 shows more regions of vertically aligned gold nanorod arrays. In these cases, the nanorods are almost perfectly vertically aligned, uniformly spaced, and extend over comparatively larger areas. A 2D Fast Fourier Transform (FFT) of Figure 3.8 (d.) shows hexagonal spots, which indicate that the nanorods are arranged in a hexagonally close-packed array. The presence of the second-order spots signifies the presence of long-range

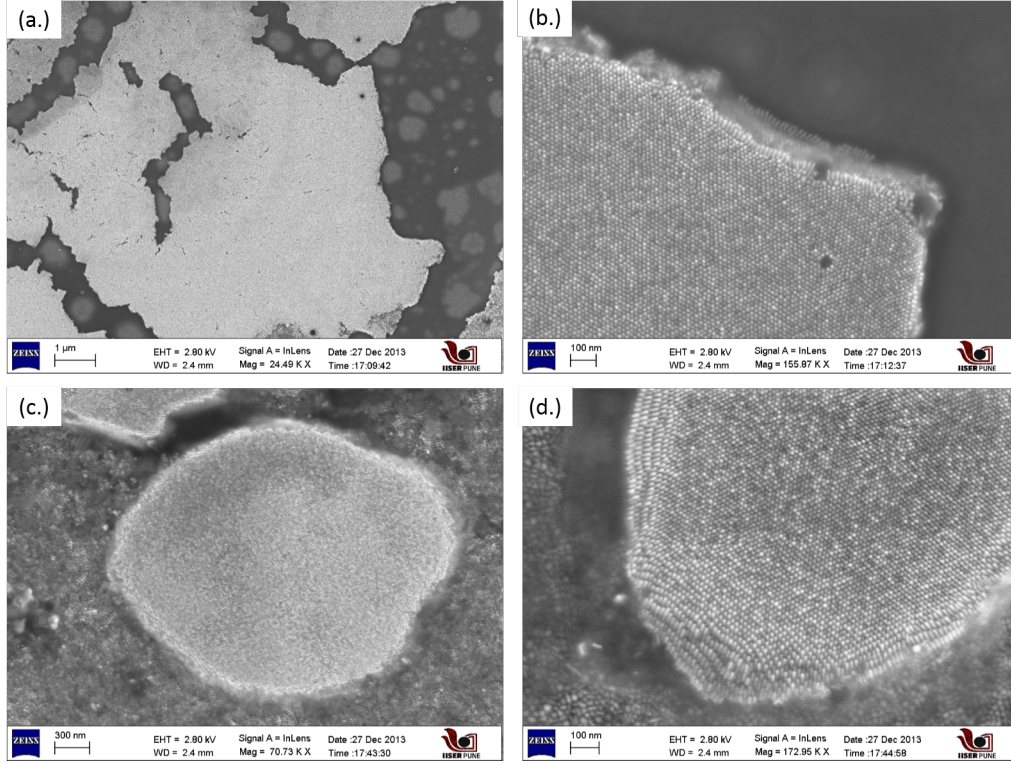


Figure 3.7: *FESEM images of vertically aligned gold nanorod arrays showing multilayer assembly.*

order. The inter-rod separation is measured to be 4.7 nm. The nanorods in Figure 3.8 (e.) are all vertically aligned, and extend over a distance of $\sim 41 \mu\text{m}$, which is believed to be very rare. An interesting effect observed (only) in the case of vertically aligned arrays of gold nanorods is the presence of various Moiré patterns. A Moiré pattern is formed when two distinct periodicities are superimposed, with slight misalignment. The result is the appearance of a third ‘spoof’ periodicity, which is dubbed as the Moiré pattern. Figure 3.9 shows a couple of FESEM images of vertically aligned gold nanorod arrays which show such Moiré patterns. The patterns can be seen in many regions as alternating ‘zebra’ like stripes of bright and dark contrast on the gold nanorod islands.

The concept of the Moiré is illustrated in Figure 3.9 (d.). Suppose the two superimposed periodic lattices have vectors $\vec{k}_1$ and $\vec{k}_2$. The Moiré periodicity is then given by as

$$\vec{k}_{\text{Moiré}} = \vec{k}_1 - \vec{k}_2$$

In the case of this work, the reason behind the appearance of Moiré patterns is explained as follows: the vertically aligned nanorod arrays show exceptionally close-packed long range periodic order. This forms one of the two periodicity components. The second component comes from the FESEM instrument itself. The electron beam from the FESEM is scanned in a rasterized fashion with a definite frequency. Read et al. have reported such electron beam Moiré patterns from periodic lithographically patterned substrates.^[14] They describe the spatial dependence of the image scanning pattern and that of the sample using Fourier series. The vector difference of these two frequencies gives rise to the Moiré pattern.

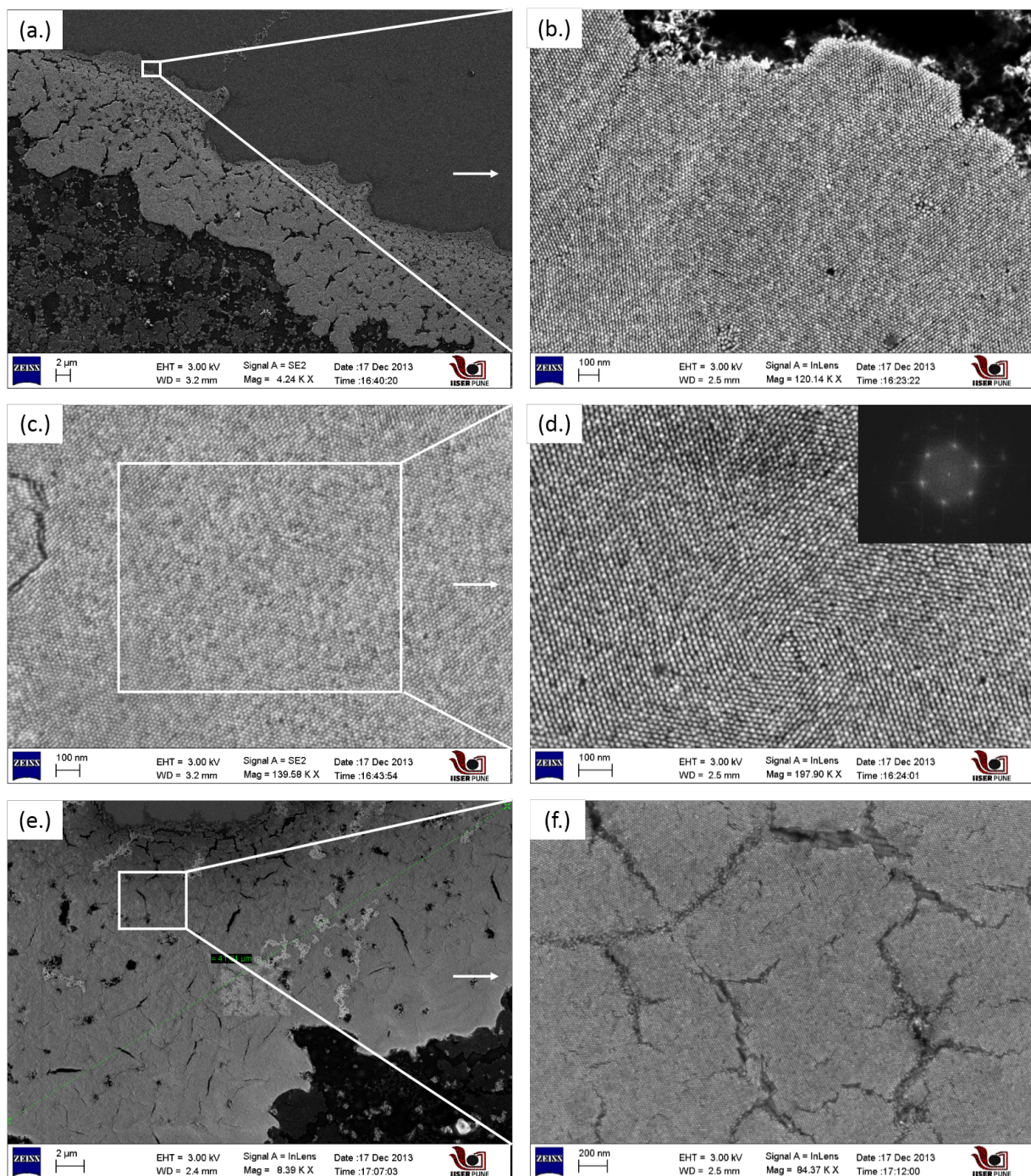


Figure 3.8: FESEM images of vertically gold nanorod arrays showing hexagonally close-packed, long range order.

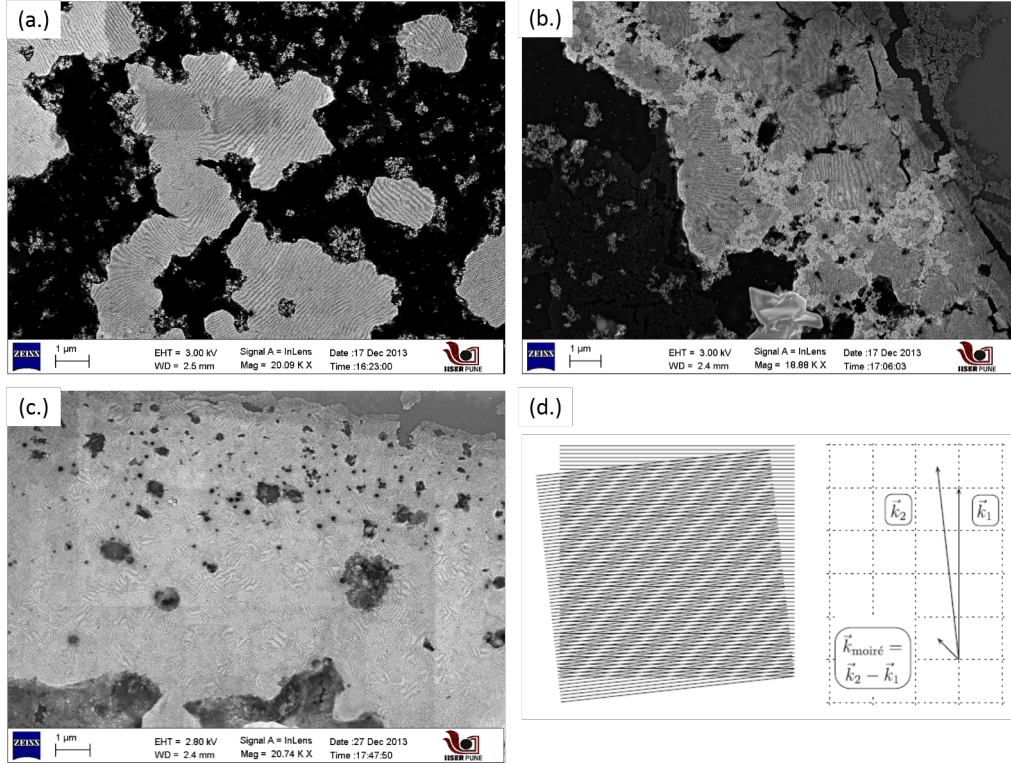


Figure 3.9: (a.), (b.), (c.) FESEM images of vertically aligned gold nanorod arrays exhibiting Moiré patterns. (d.) The concept of a Moiré pattern.^[34]

It was also observed that the Moiré patterns shift/ change as the images are zoomed in/ out during live acquisition. This can also be intuitively explained as follows: The scanning frequency of the electron beam rasterizer is fixed. But the apparent periodicity of the vertical arrays change with the zoom level. For a fixed image viewfinder size, the number of rods that fit in the image at lower zoom is more than that at higher zoom level. Thus, the periodicity of the sample in the viewfinder dimensions is subject to change with the level of zoom. This consequently changes the frequency of the Moiré, and as a result the whole pattern shifts with the zoom level.

Prof. Liz-Márzan's group has reported up to 15 layers of standing arrays of gold nanorods using the evaporation induced method.^[15] The inter-rod separation was observed to be ~ 3 nm. Recently, Peng et al. demonstrated monolayers of vertically aligned gold nanorod arrays with nominal inter-rod separations ~ 0.8 nm.^[11] The nanorod array was exposed to UV-Ozone treatment for 20 minutes, which destroyed the CTAB molecules acting as buffers between adjacent nanorods. Consequently, the gaps between the nanorods decreased from the usual value of ~ 3 nm. Both the groups successfully employed the standing arrays as efficient substrates for SERS sensing of biological prions and food contaminants respectively.

3.3 Electrodynamic simulations

The plasmonic responses and properties of metallic nanostructures can be studied using electrodynamic computer simulations. Various software packages (based on differing algorithms) are available. In this work, two different packages were used: DDSCAT 7.3 and

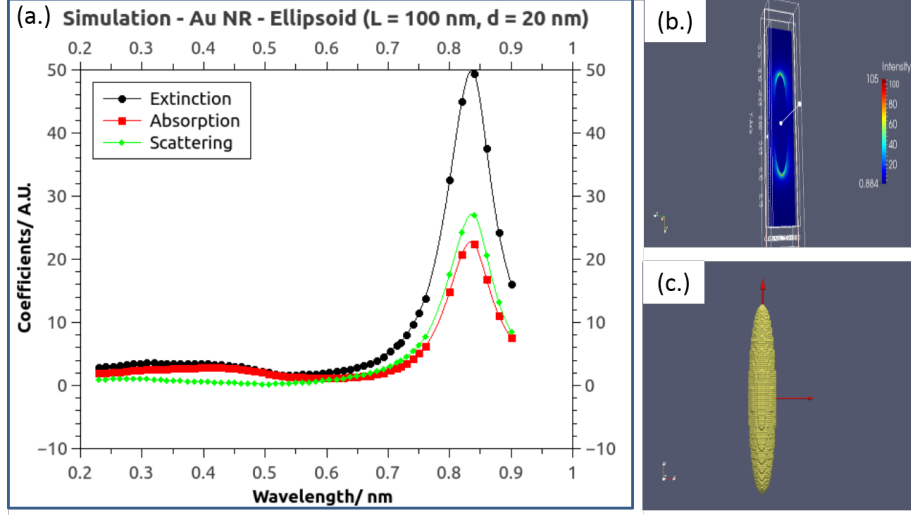


Figure 3.10: (a.) Absorption, scattering and extinction spectra of a single Au ellipsoid in longitudinal polarization. (b.) The near-field enhancement map. (c.) Visualization of the ellipsoid as a 3D array of polarizable, point dipoles.

COMSOL Multiphysics 4.2.

3.3.1 DDSCAT 7.3

DDSCAT, developed by Draine and Flatau in 1993, calculates scattering and absorption of incident electromagnetic waves on targets with arbitrary geometries using the Discrete Dipole Approximation (DDA).^[16] The target is replaced by an array of polarizable point dipoles, and the scattering problem for an incident wave interacting with these dipoles is solved numerically. The primary utility of the DDA is to simulate the behavior of dielectric targets with sizes comparable to the incident wavelength, or smaller. DDSCAT 7.3 is based on an implementation of FORTRAN-90.

The DDSCAT algorithm is flexible with respect to the target shape in the sense that if the target has a volume V , it is considered as a sphere of N point dipoles with point wise separation d and spherical radius a_{eff} . Thus,

$$V = Nd^3$$

and

$$a_{eff} = \sqrt{\frac{3V}{4\pi^3}}$$

Total cross-sections calculated in this manner are accurate to a few percent, if N is sufficiently large (10^4 or greater). In this work, DDSCAT 7.3 was used to simulate the plasmonic behavior of gold nanorods as a function of their size.

Figure 3.10 (c.) shows how the nanorod is approximated by a prolate ellipsoid of point dipoles while (b.) shows the near-field electric map with enhancement near the tips (for incident polarization along the nanorod length). Figure 3.11 shows the evolution of the

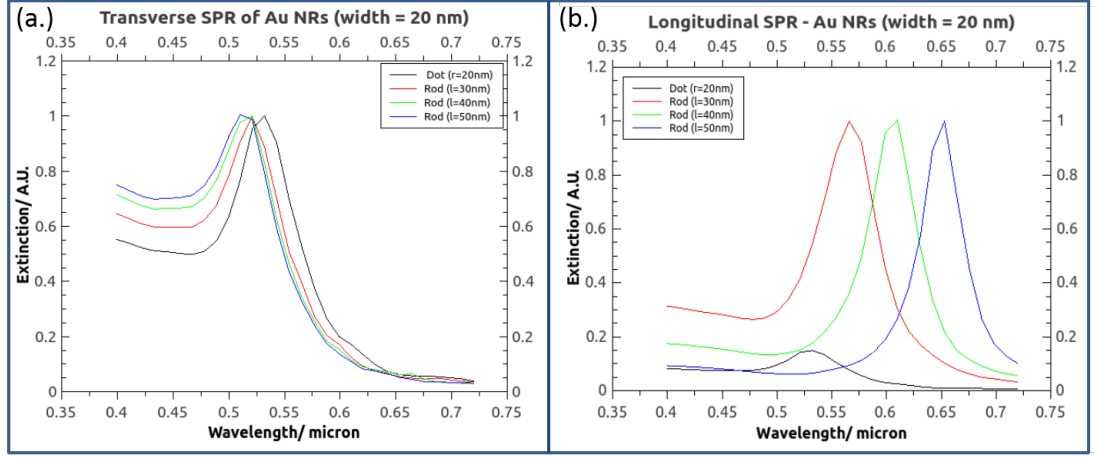


Figure 3.11: *Evolution of the extinction spectra from an Au nanodot into a nanorod.*

extinction spectrum from a gold nanosphere ($d = 20$ nm) to a nanorod (approximated as a prolate ellipsoid of successively increasing lengths). The incident electromagnetic wave is polarized along the width of the nanorod in Figure 3.11 (a.), whereas for Figure 3.11 (b.), it is polarized along the length of the nanorod. As a result, Figure 3.11 (a.) depicts the transverse SPR mode and (b.), the longitudinal SPR mode. While the transverse mode shows small change as the dot elongates, the longitudinal SPR is red-shifted by around 100 nm, consistent with practical observations.

3.3.2 COMSOL Multiphysics 4.2

Comsol Multiphysics is a full-fledged finite element method simulation environment. More specifically, the RF Module is used to solve Maxwell's equations using the finite element method with numerically stable edge 'vector' elements. In this work, the RF Module was used for simulating the plasmonic properties of vertically aligned gold nanorod arrays. The nanorods were modelled in a unit bilayered hexagonal cell, as cylinders with hemispherical end-caps of final lengths 40 nm and widths 10 nm. The two layers were mutually rotated about the vertical (z) axis by 30° . The inter-rod spacing was kept at 2 nm. The material properties of gold were assigned through a complex-valued dispersive dielectric constant modelled from Johnson and Christy's work.^[17] The electromagnetic wave at $\lambda = 524$ nm was polarized in the y -direction and incident on the vertical nanorods from the top. The substrate was modelled as silicon dioxide with a constant refractive index of 1.5. The surrounding medium was assigned a refractive index of 1 (air/ vacuum).

Figure 3.12 shows the results of these simulations. The small 2 nm gaps between adjacent standing nanorods serve as very good plasmonic hotspots, confining and amplifying the incident electromagnetic field. The enhancement factors between the hotspot were found to be as high as 10^9 . Considering the central nanorod in the hexagonal cell located at the origin, four vertical lines parallel to the z -axis (and along the rod lengths) were drawn in the gap between the nanorods in the first xy -quadrant, located at azimuthal angles (ϕ) 0° , 30° , 60° , and 90° respectively. For simplicity, these lines are shown as black dots in Figure 3.12 (a).

To elucidate the plasmonic enhancement in the hotspots, normalized electric field intensities were extracted along these lines and plotted as a function of the z -height above

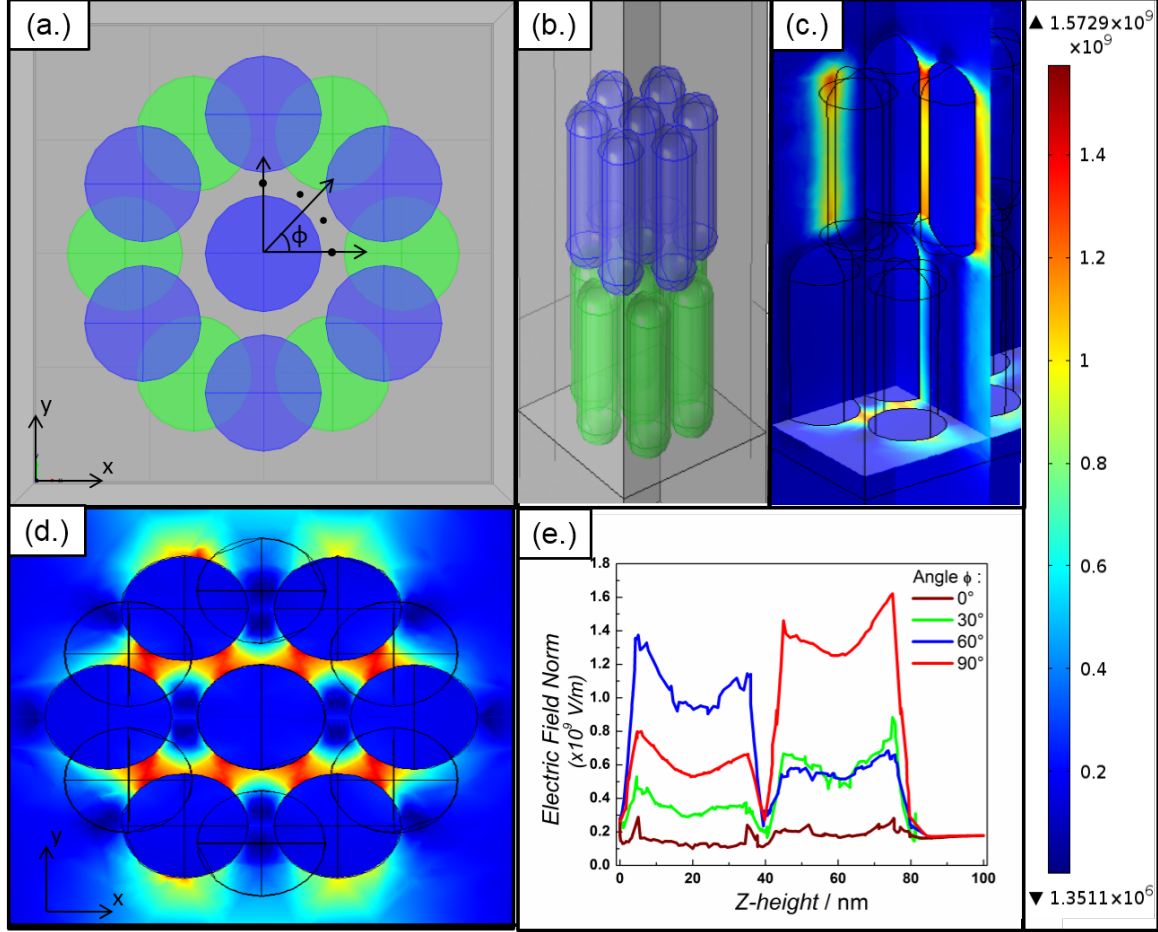


Figure 3.12: (a.) Top view of the hexagonally arranged GNR bilayer unit cell rotated by a relative azimuthal angle $\phi = 30^\circ$, on a silica substrate; the lower layer is shaded green and the upper one blue, for the sake of clarity. The distance between two adjacent rods is 2 nm. (b.) 3D view of the construction; the bilayer is in the xy -plane with the rods pointing in the z -direction. (c.) Normalized electric field color map with enhancement within the gaps in 3D view, and xy -plane and (d.) at a height 5 nm above the substrate. (e.) Values extracted along lines (depicted as black dots) parallel to the z -axis and located in the first xy -quadrant at azimuthal angles $\phi = 0^\circ, 30^\circ, 60^\circ$, and 90° respectively.

the substrate in Figure 3.12 (e). For better understanding, we can divide the abscissa into two regions, from $z = 0$ to 40 nm, and from $z = 41$ to 80 nm; these regions correspond to the two monolayers, since the height of each rod is taken to be 40 nm. For region 1, the highest enhancement can be seen for the vertical line at $\phi = 60^\circ$ (blue curve). This is explained by the fact that the line lies between adjacent vertical nanorods in the lower monolayer. The line at $\phi = 90^\circ$ (red curve) experiences more enhancement than the line at $\phi = 30^\circ$ (yellow curve) since the former one is located in the y-axis and is therefore closer to the sense of direction of incident polarization.

For region 2, the enhancement is maximum for the vertical line at $\phi = 90^\circ$, followed by the one at $\phi = 30^\circ$. Since the former line lies between adjacent vertical nanorods in the upper monolayer and is now in full sense of direction of the incident polarization, the electric field gets enhanced the most. This is followed by the line at $\phi = 30^\circ$, which although not in full sense of direction of the incident polarization, is nevertheless between two vertical nanorods of the upper monolayer. The line at $\phi = 0^\circ$ (green curve) experiences the least enhancement of all, simply because it is located on the x-axis and hence furthest in sense of direction of incident polarization, for all cases. Apart from all the detailed analysis, it is clearly demonstrated that a uniform hexagonal close-packed self-assembly of VA-GNRs indeed supports field enhancement and hence can be used as excellent substrates for Surface-enhanced Raman Spectroscopy (SERS) detection experiments.

3.4 Surface-enhanced Raman Spectroscopy experiments

Ultrasensitive, selective detection of molecules is necessary in various fields like medicine, forensics, pollution analysis, and security applications. Raman scattering spectroscopy has been a very well-established molecular finger-printing technique due to its high selectivity and accurate measurement capability of molecular vibration frequencies and their changes in different chemical surroundings. However, Raman scattering cross-section is inherently very small.^[18,19] Therefore, laser beams of appropriate wavelength and high power need to be used. It has been found about four decades back that it is possible to enhance the Raman signal using rough silver or gold substrates.^[20] Since then the search for more and more sensitive (reaching single molecule detection level), easy to prepare and cost-effective substrates for Raman spectroscopy continued.

The use of gold or silver nanostructures with different shapes, speckled silica-gold core-shell particles as well as shell isolated nanoparticles showed large enhancement factors for the Raman signals.^[21,22] The Raman signal enhancement or SERS can be chemical, or electromagnetic or a contribution of both the effects. In chemical effect the charge transfer complex is formed between the molecules and the substrate, whereas electromagnetic enhancement originates due to localized surface plasmon resonance (SPR). While the chemical enhancement would be molecule specific, electromagnetic enhancement by creation of ‘hot spots’ can take place for any molecule and mostly dominates.

In this work, self-assembled VA-GNRs were used to show that D-glucose and TNT can be detected with ultra-high sensitivity. The scheme of the experiment is illustrated in Figure 3.13. Although such self-assemblies have proven to be excellent in the detection of prions and orange juice contamination, further experiments on detection of other organic molecules are quite important because the sensitivity for different molecules may differ as Raman cross-sections differ for different molecules.^[11,15] For normal Raman scattering (NRS), the cross-section values for D-glucose and TNT are $5.6 \times 10^{-30} \text{ cm}^2 \text{ molecule}^{-1} \text{ sr}^{-1}$

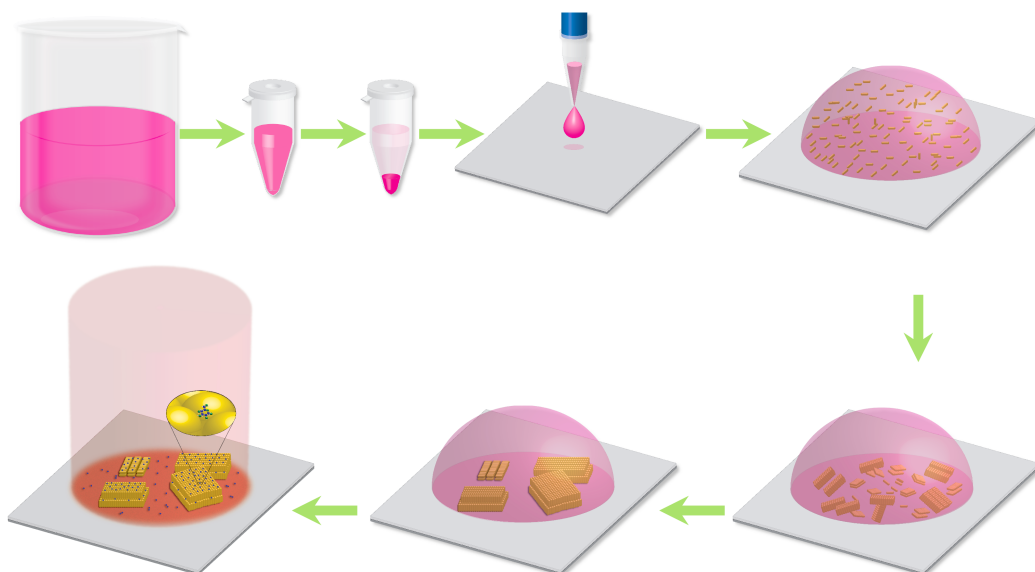


Figure 3.13: *Schematic of the Surface-enhanced Raman Spectroscopy (SERS) experiments.*

and $4.9 \times 10^{-31} \text{cm}^2 \text{molecule}^{-1} \text{sr}^{-1}$ respectively.^[23–25] According to the 2013 report of World Health Organization, there are 347 million people worldwide who are victims of diabetes mellitus. This number would almost double by 2035. It is known that uncontrolled diabetes increases the glucose level in blood circulation, affecting the nervous system and is a major cause of organ failure such as eyes, kidneys, heart etc. Although, it is not possible at present to cure diabetes, a regular monitoring of glucose level in the body and administration of appropriate dose of insulin or medication can keep diabetes under control, increasing the longevity of the patients as well as keeping normal health. Therefore, glucose-level monitoring amongst diabetic patients as well as early checks for diabetes among healthy persons is very important. The common glucose-level monitoring methods involve taking out the blood sample and analyzing it chemically, enzymatically (electrochemical or amperometric means), colorimetrically or spectroscopically.^[26] Detection of glucose by electrochemical method, in which, glucose is oxidized on a glucose oxidase (GO_x) covered substrate to obtain hydrogen peroxide, which in turn produces electric current using various nanomaterials has been discussed by Claussen et al.^[27] It is reported that glucose sensitivity up to $0.3 \mu\text{M}$ concentration can be achieved. Yang et al. developed a photonic crystal fiber to sense small concentrations of glucose using Raman spectroscopy.^[28]

In recent years, attempts have been made to improve and devise new SERS substrates to achieve high accuracy and sensitivity for glucose detection. However, the cross-sections are inherently very low and long data acquisition time along with the high laser power becomes mandatory. Therefore, it is important to enhance the Raman signal for accurate and quick or even continuous monitoring of body glucose levels. In this work, it is demon-

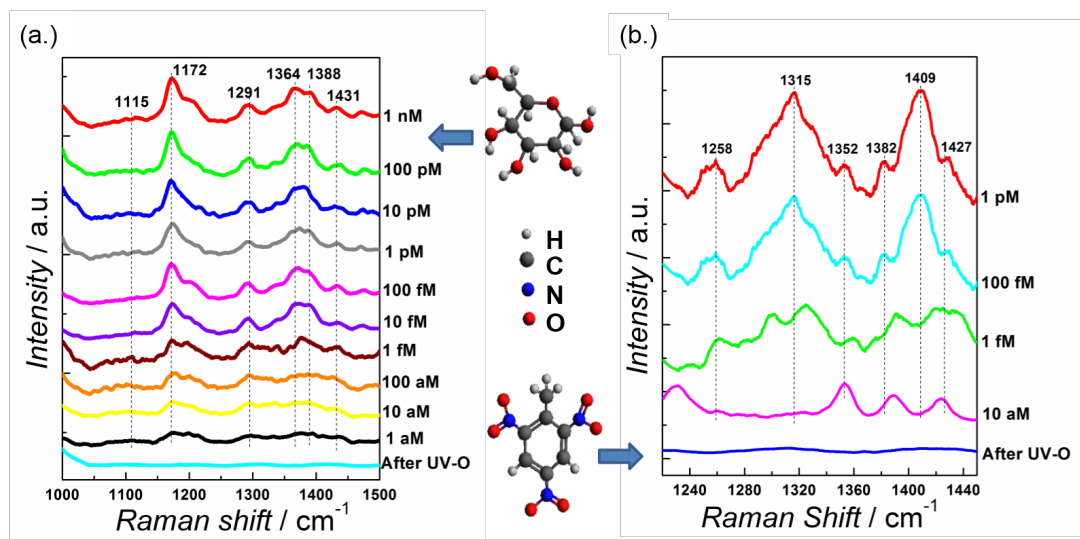


Figure 3.14: *SERS spectra of 4 μl glucose solution dropcasts of concentration 1 nM to 1 aM, and (b.) 8 μl TNT solution dropcasts of concentration 10 aM to 1 pM, on the self-assembled, vertically aligned gold nanorod arrays.*

strated that SERS investigations could be used to detect D-glucose with yoctomole-level accuracy. This would be helpful for glucose detection even in saliva or tears where glucose levels are much less than that in blood. This could be done with ultra-high sensitivity requiring minimal amount of body fluids.

In Figure 3.14 (a.), SERS spectra at various molar concentrations of D-glucose are shown. The spectra are normalized with respect to the peak at $\sim 1172\text{ cm}^{-1}$. The spectra were taken after removing CTAB layer by UV-Ozone treatment which altered neither the self-assembly of VA-GNRs nor the inter-GNR separation, as checked from FESEM images (not shown here). The spectra do not show any peak corresponding to CTAB after the UV-Ozone treatment. For D-glucose, peaks observed at 1115 cm^{-1} and 1172 cm^{-1} are attributed to stretching of (C-OH), (C-C) and bending of (C-O-H) modes, whereas those at 1291 cm^{-1} , 1364 cm^{-1} and 1388 cm^{-1} arise due to bending modes of (O-C-H), (C-O-H), and (C-C-H) and the peak at 1431 cm^{-1} was attributed to the pure CH_2 -vibration mode.^[29,30] However, Söderholm et al have observed the Raman peaks at 1098 cm^{-1} , 1125 cm^{-1} , 1264 cm^{-1} , 1340 cm^{-1} , and 1373 cm^{-1} .^[29] The differences in the peak positions can arise due to different proximities between the adsorbate molecules and the substrate. As the concentration was reduced from 1 nM to 1 aM, the intensity of all peaks reduced but signatures of the glucose molecules were clearly visible even for 1 aM concentration. Molarity calculations show that 4 μl volume of 1 aM D-glucose solution equates to 4 yoctomoles, which is equivalent to $\sim$ three D-glucose molecules. Thus, extremely high molecular sensitivity was achieved. SERS spectra checked after the cleaning showed that there were no signatures of glucose. Thus it is indeed possible to reuse the substrates.

In order to show that the assembly of VA-GNRs is a generic SERS probe, they were also tested with a molecule of still lower Raman scattering cross-section, namely TNT. The procedure used for Raman scattering data acquisition for TNT solutions remains exactly the same as for D-glucose solutions described above. The Raman spectrum of TNT is rich in vibrational modes due to presence of the aromatic ring, and the nitro and methyl groups, as reported earlier.^[31,32] Figure 3.14 (b.) depicts the SERS spectra

recorded for TNT solutions. The modes observed at 1258 cm^{-1} , 1409 cm^{-1} and 1427 cm^{-1} are attributed to ring stretching and CH_3 deformation. The peaks at 1315 cm^{-1} , 1352 cm^{-1} and 1382 cm^{-1} are characteristic modes of TNT which could be attributed to 4- NO_2 , 2,6- NO_2 and 2,4,6- NO_2 symmetric, C-N stretch respectively.^[31] Sun et al. have reported the SERS spectra of TNT gas on $Ag - SiO_2 - CNT$ substrates.^[32] They have identified modes at 1270 cm^{-1} , 1358 cm^{-1} , and 1434 cm^{-1} besides the modes at 817 cm^{-1} and 1538 cm^{-1} . We have recorded the SERS spectra in the range $1220\text{--}1450\text{ cm}^{-1}$ in which there is resemblance of all three vibrational modes observed as Raman shifts.^[33] Calculations show that $8\text{ }\mu\text{l}$ volume of 10 aM TNT solution corresponds to 80 yoctomoles, equivalent to ~ 48 molecules.

Ultra-high sensitivity obtained for D-glucose and TNT molecules using VA-GNR assemblies for SERS could be understood as follows: plasmonic hotspots are created in the gaps between gold/silver nanoparticles which enhance the local electric field. Attempts are often made to create large number of such hotspots in order to increase the optical signal. However in some cases, the use of randomly distributed nanoparticles can increase the separation and hence attenuate the electric field in such hotspots. This adversely affects the optical signal. On the other hand, VA-GNRs offer extensive and uniformly distributed hotspots in gaps as small as $\sim 3\text{ nm}$, thus greatly enhancing the local electric fields. In addition, the gaps between two VA-GNRs exert capillary force on analyte molecules in solution that increase their local concentration at such hot-spots. It is believed that the SERS spectra result from a pure electromagnetic enhancement as there is no chemical bonding between the analyte molecules and the VA-GNR surfaces. This makes it a universal and ultra-high sensitive SERS substrate.

3.5 Concluding remarks

Gold nanorods synthesized by the two step seed-mediated wet chemical method showed highly defined anisotropic shapes and aspect ratios, as observed from the FESEM images. These were further found to be easily tuned by varying the amount of the seed solution. The nanorod solutions exhibited distinct, well defined SPR absorption peaks in the visible and NIR region, as confirmed from absorption spectroscopy.

Solvent evaporation based strategy was successfully employed to achieve different self-assemblies on silicon substrates. The ones observed and studied were the side-side, end-end and more importantly, the vertically aligned assemblies. The latter were obtained on large areas ($\sim$ tens of microns) and displayed interesting Moiré patterns. Further, vertically aligned gold nanorod arrays were put to use as efficient substrates for Surface-enhanced Raman Scattering (SERS). D-Glucose and TNT solutions could be successfully detected up to the yoctomole level. These arrays are robust and reproducible, and have the potential to be employed for practical applications.

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Chapter 4

Summary and future directions

4.1 What was achieved

Nanoscience and nanotechnology are important areas of interdisciplinary, applied research of the 21st century. The properties of materials change remarkably from the bulk to the nanoscale. This happens mainly due to the increasing spatial confinement of electrons (which determine many material properties) and the increasing surface area to volume ratio. Unlike their bulk counterparts, the properties of nanomaterials are a function of their size. Thus, development of experimental methods of obtaining any given nanomaterial of a precise size enables control over their properties. As a result of this versatility, nanomaterials are specially suited for a variety of applications.

Noble metal nanoparticles have the ability to confine and resonantly enhance incident electromagnetic fields due to localized surface plasmon resonances. These are collective oscillations of the conduction electrons of metals in response to external electromagnetic fields. The size of metal nanoparticles determines the position of such resonant absorption in the electromagnetic spectrum. For example, silver, gold and copper exhibit plasmon resonances in the visible region, whereas aluminum, in the ultraviolet. Unlike isotropic nanomaterials, anisotropic gold nanorods support two distinct and rich surface plasmon resonances. This makes them viable candidates for the possibility of controlling the interaction, confinement and flow of light at the nanoscale. This is the realm of Plasmonics, a sub-discipline of nanophotonics, which deals with the interaction of light with metallic nanostructures. Surface-enhanced Raman Spectroscopy (SERS) is a technique that improves the inherently weak nature of Raman scattering to enable ultra-sensitive detection of various molecules. Plasmonic nanomaterials such as gold nanorods offer excellent sensitivities for SERS experiments, by virtue of their surface plasmon resonances.

In this work, gold nanorods were synthesized via the seed-mediated wet-chemical method that enables very high yield and purity at the cost of minimum experimental detail. They were subsequently characterized by experimental analysis techniques such as UV-Vis absorption spectroscopy, Field-emission scanning electron microscopy (FESEM), and Raman spectroscopy. The plasmonic properties of gold nanorods were studied in detail using computer simulation software like DDSCAT and COMSOL Multiphysics. Further, self-assembly of colloidal gold nanorods via the solvent-evaporation route was used to achieve a variety of interesting 2D and 3D superstructures such as side-side, end-end, and the most exotic and slightly mysterious amongst all, the a vertically aligned assembly. Finally, micron-sized arrays of vertically aligned gold nanorods were successfully employed as excellent substrates for Surface-enhanced Raman Scattering (SERS)

detection of a D-glucose and TNT solutions, with demonstrated sensitivity up to the yoctomole level.

4.2 What lies ahead

Vertically aligned arrays of gold-nanorods can also be self-assembled on to lithographically patterned substrates. The definite spacings between the patterns can enable interesting plasmonic coupling between the nanorods, which can lead to exotic effects such as Fano resonances, and increased electromagnetic enhancement. Unlike conventional (Lorentzian) resonances, Fano resonances have asymmetrical line shapes and occur due to a coupling between background and another resonant scattering process. Thus, self-assembly of vertically aligned gold nanorods on a transparent substrate followed by a check of the resulting transmission spectrum can spread light on this matter.

Another interesting application of self-assembled vertically aligned gold nanorods could be in field-emission devices. The potential to amplify electromagnetic fields and the presence of well-spaced, large area anisotropic rod-shaped structures could very well be suited for field-emitters, which can constitute a complete experiment in itself. Thus, the interesting plasmonic properties of gold nanorods enable the possibility of such experiments as well as the potential for device fabrication towards future technological applications.