SELF-ASSEMBLY, INTEGRATION, CHARACTERIZATIONS AND APPLICATIONS OF PLASMONIC AND EXCITONIC NANOMATERIALS

Bijesh kafle

Follow this and additional works at: https://digitalrepository.unm.edu/chem_etds

Part of the Physical Chemistry Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the Electronic Theses and Dissertations at UNM Digital Repository. It has been accepted for inclusion in Chemistry ETDs by an authorized administrator of UNM Digital Repository. For more information, please contact amywinter@unm.edu.
Bijesh Kafle
Candidate

Chemistry & Chemical Biology
Department

This thesis is approved, and it is acceptable in quality and form for publication:

Approved by the Thesis Committee:

Prof. Terefe Habteyes, Chairperson

Prof. Yang Qin

Prof. John Grey

Prof. Alejandro Manjavacas
SELF-ASSEMBLY, INTEGRATION, CHARACTERIZATIONS AND APPLICATIONS OF PLASMONIC AND EXCITONIC NANOMATERIALS

by

Bijesh Kafle
B.Sc. Chemistry, Tribhuvan University, 2008
M.Sc. Chemistry, Tribhuvan University, 2010

DISSERTATION
Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy
Chemistry

The University of New Mexico
Albuquerque, New Mexico

July 2019
Acknowledgement

I would like to express my sincere gratitude towards my advisor prof. Terefe Habteyes for mentoring and guiding me throughout this long academic research. His guidance and mentorship helped me to grow better every day. He always kept my enthusiasm high for dealing with the problems faced with continuous support. Thank you for letting me work under your guidance.

I would also like to thank my committee member prof. Yang Qin and prof. John Grey, for being in my committee and providing continuous feedback and support whenever is needed. I would like to thank prof. Alejandro Manjavacas for feedback, supports to continuous make progress and solve problems.

I would like to thank my colleagues Tefera Entele Tesema, Sharmin Haq, Hamed Kookhaee, Chih-Feng Wang, Bisweswar Patra, and Isadora Nizalowski for their continuous support throughout these years.

I would like to thank my parents for continuous support throughout this journey. They have always been supportive during my journey, whether I am at good or bad condition.

Finally, I would like to thank my wife Suprabha Sharma, for eternal love and support throughout the years. You always motivated me, supported me and have been my strength through this crazy journey. Thanks for being in my life.
Dedication

To my family and wife
Plasmon on metal nanoparticles can efficiently confine, amplify light at the nanoscale. This property is beneficial for different applications such as harvesting energy of the broad solar spectrum, highly sensitive spectroscopy, photocatalysis, and many other optoelectronic applications. For plasmonic applications, it is necessary to understand the fundamental physical properties of the individual, coupled plasmonic nanomaterials, and their interaction with the surrounding environment, which is not fully understood yet. In this dissertation, the chemical and optical interaction in plasmonic interfaces has been investigated. Plasmon-enhanced photochemistry of \( p \)-aminothiophenol as a model molecule is investigated using highly sensitive surface-enhanced Raman spectroscopy (SERS). The result shows the effect of different surface ligands of gold nanorods can change in hot-electron dynamics and catalyze the reaction selectively with varying the pathways of reaction. The optical response of colloidal gold nanorods (AuNR) with gold film (AuF) is studied by measuring the single-particle scattering of plasmonic
nanoparticles using dark-field optical microscopy. The experiment reveals that the charge transfer plasmon mode dictates the scattering cross-section of colloidal gold nanorods directly placed on gold film and this mode is independent of the shape and size of the nanoparticle. Distance-dependent interaction of gold nanorods (AuNR) with gold film (AuF) is studied by using the layer-by-layer assembly of polyelectrolytes as well as transparent colloidal quantum dots film as a spacer layer. The photoluminescence and scattering property are measured alternatively of individual gold nanorods coupled to gold film. We experimentally demonstrated that light from a dielectric nanocavity couple out to far-field via both elastic and inelastic scattering processes. The later part of the dissertation focuses on the assembly of plasmonic and excitonic nanoparticles on surfaces. Droplet evaporation at a temperature higher than room temperature is shown as a simple and reproducible method for creating a monolayer of AuNR on different substrates. The assembly of AuNR is characterized using SEM and dark field optical microscopy. Finally, the self-assembly (using the Langmuir-Blodgett, LB technique) and stability study of near infrared emitting colloidal CdSeTe/ZnS alloyed quantum dots are presented. Photoluminescence and elemental analysis indicate that interatomic diffusion leads to crystal transformation upon exposure of the nanocrystals to ambient conditions.
Table of Contents

Acknowledgement ........................................................................................................................................... iii

Abstract ............................................................................................................................................................... v

List of Figures ...................................................................................................................................................... xi

List of Abbreviations ............................................................................................................................................ xviii

Chapter 1: Introduction ........................................................................................................................................ 1

1.1: Plasmonic nanoparticles: .............................................................................................................................. 1

1.2: Plasmonic hot electron generation: ............................................................................................................. 3

1.3: Surface Enhanced Raman Spectroscopy (SERS): ......................................................................................... 4

1.4: Outline of Dissertation: ............................................................................................................................ 6

1.5: References: .................................................................................................................................................... 8

Chapter 2: Experimental Methods: ................................................................................................................... 9

2.1: Dark field optical microscopy: .................................................................................................................. 9

2.2: Apertureless scattering near field optical microscopy (ANSOM): ......................................................... 10

2.3: Langmuir Blodgett (LB) technique: .......................................................................................................... 12

2.4: Layer by layer assembly of polyelectrolyte film: ....................................................................................... 14

Chapter 3: Surface Ligand-Mediated Plasmon-Driven Photochemical Reactions ....................................... 16

3.1: Introduction: ................................................................................................................................................ 16

3.2: Experimental Methods: ............................................................................................................................ 18
Chapter 3: Surface Functionalization and Plasmonic Properties

3.3: AuF-PATP-CTAB-AuNR sample: ................................................................. 18
  3.3.1: AuF-PATP-CIT-AuNR sample: ........................................................ 19
  3.3.2: AuNR-PATP sample: Replacing CTAB surface ligand with PATP: .......... 19
3.4: Results and Discussion: ........................................................................ 19
3.5 Optical and Structural Characterizations: .............................................. 29
  3.5.1: Atomic force microscope (AFM) and Raman scattering measurement: ....... 29
  3.5.2: Dark-field scattering and Raman scattering measurements: ................. 30
3.6: Conclusion: .............................................................................................. 34
3.7: References: ............................................................................................. 36

Chapter 4: Charge Transfer Plasmons ......................................................... 38

4.1: Introduction: ............................................................................................ 38
4.2: Experimental Methods: .......................................................................... 40
  4.2.1: Sample preparation: .......................................................................... 41
  4.2.2: Dark field Measurement: .................................................................... 41
4.3: Results and Discussion: .......................................................................... 41
4.4: Conclusion: .............................................................................................. 54
4.5: References: ............................................................................................. 56

Chapter 5: Light Emission from Dielectric Nanocavity ................................ 59

5.1: Introduction: ............................................................................................ 59
5.2: Experimental Methods: .......................................................................... 61
  5.2.1: Layer by Layer assembly of polyelectrolytes layer: .............................. 61
  5.2.2: AuF-QD-Film Formation: .................................................................. 61
5.3: Results and Discussion: .......................................................................... 61
Chapter 6: Temperature Mediated Assembly of Gold Nanorods on Gold Film and its Near-field Optical Characterization

6.1: Introduction: .................................................................................................................. 71

6.2: Experimental Methods: .............................................................................................. 73

   6.2.1: Assembly of AuNR at room temperature: ............................................................. 73
   6.2.2: Assembly of AuNR by spreading ethanol: ............................................................ 73
   6.2.3: Assembly of AuNR at different temperature: ...................................................... 73
   6.2.4: Assembly of AuNR by immobilization of polyvinyl pyridine polymer: .............. 73

6.3: Results and Discussion: .............................................................................................. 74

   6.3.1: Droplet evaporation methods .............................................................................. 74
   6.3.2: Evaporative self-assembly of AuNR using ethanol as solvent........................... 78
   6.3.3: Assembly of AuNR using polymer modified AuF ............................................... 81

6.4: Conclusion: .................................................................................................................. 85

6.5: References: .................................................................................................................. 87

Chapter 7: Stripping and Transforming Alloyed Semiconductor Quantum Dots via Atomic Interdiffusion

7.1: Introduction: .................................................................................................................. 88

7.2: Experimental Methods: .............................................................................................. 92

7.3: Structural and Optical Characterization: .................................................................... 92

7.4: Results and Discussion: .............................................................................................. 94

7.5: Conclusion: .................................................................................................................. 111
8.3.1: Layer by layer assembly of monolayer QDs thin film and AuNR using polyelectrolytes layer as spacer ................................................................. 120

8.4: References................................................................. 122
List of Figures

Figure 1-1: Schematic of how light interacts with metal nanoparticles and gives rise to surface plasmon resonance. ................................................................. 1

Figure 1-2: Schematics of hot electron generation in plasmonic metal nanoparticles ........ 4

Figure 2-1: Schematic showing the dark-field scattering microscopy and spectroscopy experimental setup. Representative dark field image is shown. ........................................ 10

Figure 2-2: Schematic showing excitation and detection layout for elastic (Rayleigh) and inelastic (Raman) scattering measurement using near field optical microscopy .......... 12

Figure 2-3: Photograph of the Langmuir Blodgett trough. ........................................ 13

Figure 2-4: Monolayer film formed using Langmuir Blodgett film. AFM topography of CdSeS/ZnS monolayer film. ................................................................. 13

Figure 2-5: Structural drawing of PDDA (left) and PSS (right) ................................. 14

Figure 2-6: AFM topography of polyelectrolyte film formed by layer by layer assembly of oppositely charged polyelectrolytes .............................................. 15

Figure 3-1: Calculated near-field enhancement and localization for the excitation field oriented (a) 30° from the surface normal (significant projection along the vertical axis, vertical polarization, VP), and (b) parallel to the sample plane (horizontal polarization, HP). Image size: 80 nm × 120 nm. (c) SERS signal intensity obtained with VP (red curve) and HP (black curve). Each curve represents the average of 10 spectra obtained from different locations on the sample. The theoretical and experimental results are obtained at 633 nm excitation wavelength.................................................. 20

Figure 3-2: SERS spectra of (a) AuF-PATP-CIT-AuNR, (c) AuF-PATP-CTAB-AuNR (average of 20 spectra acquired from different locations on the same sample), and (e) SiO2-PATP-AuNR samples. The corresponding molecular structures of the reactant (self-assembled PATP) and surface ligands in the AuF-AuNR gaps are shown in the schematics on the right side of each spectrum in (b), (d) and (f). A strong peak is observed at 1328 cm⁻¹ in (c) but not in (a) and (e), indicating a photochemical reaction pathway induced by the CTAB surface ligand. The spectra are obtained at λ = 633 nm excitation wavelength at normal incidence (see Figure 2-1). ........................................ 21

Figure 3-3: Correlation of CTAB content on the AuNR surface with the 1328 cm⁻¹ band intensity. (a) Strong relative Au-Br vibration band intensity at 180 cm⁻¹ and strong
relative intensity of N-O vibration band at 1328 cm\(^{-1}\). (b) Moderate relative intensity of Au-Br and N-O vibration bands. (c) Au-Br and N-O vibration bands are absent. (d) Raman spectrum of solid PATP. (e) Raman spectrum of solid PNTP. The bands at 409 cm\(^{-1}\) (due to Au-S stretching vibration) indicate that the PATP molecules are chemically bonded to the AuF (a & b) and to the AuNR (c) surfaces. All the results are obtained at \(\lambda = 633\) nm with grazing incidence (see Figure 2-1)................................. 24

Figure 3-4: Comparison of the SERS intensity of CTAB coated AuNRs on gold film (black curve) and PATP molecules sandwiched between the gold film and CTAB coated AuNRs (red curve). Clearly, in the analysis of the PATP, PNTP and DMAB SERS spectra, the contribution of the CTAB surface ligand can be ignored............................ 25

Figure 3-5: SERS spectra of PNTP (a,b) sandwiched between AuF and CTAB-coated AuNRs and (c,d) adsorbed directly on AuNRs replacing CTAB. The intensity maps in (a) and (c) represent series of spectra recorded with acquisition times of 200 ms (a) and 100 ms (b) at 1.0 mW incident laser power. The higher intensity in (c) than that in (a) as seen in the color scale is due to the effective aggregation of the AuNR during incubation in the PNTP solution. This aggregation creates highly intense hot spots. The spectra are obtained at a \(\lambda = 633\) nm excitation wavelength using the setup in Figure 2-1................... 27

Figure 3-6: Excitation field polarization dependence of the near-field amplitude and localization. The labels \(\mathbf{k}\) and \(\mathbf{E}\) represent the propagation direction and electric field vectors of the excitation source (\(\lambda = 633\) nm). The AuNR has diameter 40 nm and length 80 nm. The AuF-AuNR gap is 2 nm. (a) The excitation field is oriented 30\(^{\circ}\) from the surface normal, and the field has projections along the vertical (AuF-AuNR axis) and horizontal (long axis of the AuNR). (b) The excitation field is oriented as in (a) but the AuNR is rotated 90\(^{\circ}\) in the sample plane so that there is no projection of excitation field along the long axis of the AuNR. (c) The excitation field is oriented in the sample plane parallel to the long axis of the AuNR. (d) The excitation field is oriented in the sample plane perpendicular to the long axis of the AuNR. Notice that the near-field is more enhanced and strongly localized in (a) and (b), where the excitation field has projection along the vertical axis that induces strong coupling between the AuNR plasmonic nanoantenna and the polarizable gold substrate. In terms of maximum local field amplitudes in the AuF-AuNR gap (a) > (b) > (c) > (d) (see scale bar) ......................... 30

Figure 3-7: Top panel: intensity map of 200 spectra acquired sequentially with 0.1 s acquisition time and laser intensity of 1.0 kW/cm\(^2\). Bottom panel: the spectrum obtained by taking the average of the 200 spectra................................................................. 32

Figure 3-8: SERS spectra acquired at different laser powers (see labels) show the same signatures of the PNTP and DMAB. The spectra are acquired from different locations on the same sample. The SERS spectra are obtained using AuNRs of nominal diameter 40
nm and length 92 nm (the sample scheme is AuF-PATP-CTAB-AuNR). CTAB is removed through one round of centrifugation and removal of the supernatant solution. 33

Figure 3-9: (a) Atomic force microscope (AFM) topography of gold nanorods on PATP functionalized gold film. Notice that the gold film is deposited using electron-beam evaporation that produces rough granular structure. The AFM topography is obtained using the setup shown in Figure 2-2. (b) Representative scattering spectra of AuNRs on AuF and silica substrates. All the spectra are similarly broad due to the large number of single and aggregated AuNRs in the focal volume................................................... 34

Figure 4-1: Optical response of gold nanorods placed on different substrates. (a,b) Schematics of the system under study consisting of a gold nanorod of length L and width w, placed directly on a silica substrate (a), or on a 50 nm-thick gold film deposited on silica (b). (c,d) Experimental single-particle scattering spectra for nanorods of width w = 40 nm and different aspect ratios A = L/w, as indicated by the labels, placed on either the silica (c) or gold (d) substrates. (e,f) Numerical simulations of the scattering spectrum of the nanorods of panels (c) and (d) performed by using a finite element method (FEM) approach. In all cases, the scattering spectra are normalized to their maximum value .... 42

Figure 4-2: Characterization of the scattering spectra. (a,b) Measured single-particle scattering spectra for a large collection of different nanorods placed on the silica (a) and gold (b) substrates. The background color and labels indicate the nanorod dimensions. (c,d) Linewidths of the different spectra of panels (a) and (b) plotted as a function of the energy of the plasmon resonance. Again, the nanorod dimensions are indicated by the color of the symbol. ................................................................. 45

Figure 4-3: Charge transfer plasmon mode. (a) Calculated scattering spectra for a nanorod of width w = 40 nm and aspect ratio A = 3.7 placed on the silica (green curve) and gold (red curve) substrates. (b) Induced surface charge maps (upper panels) and radiation pattern (lower panels) calculated at the resonance peaks of panel (a). The left and right columns display the results for silica and gold substrates, respectively. The insets in the lower panels show the experimental dark-field images. ......................... 47

Figure 4-4: Effect of surface ligands. (a) Normalized scattering spectra of a nanorod of w = 40 nm and A = 1.7 placed on the gold substrate. The solid curves show the theoretical predictions assuming the nanorod is in direct contact with the substrate (red curve), or is separated from it by a 1.5 nm-thick dielectric spacer with dielectric function ε = 2 (green curve), while the black dots correspond to the experimental single-particle measurements. (b) Comparison of the scattering spectra of the nanorod of panel (a) for different values of conductivity of the dielectric spacer, as indicated by the legend. (c,d) Same as (a,b), but for a nanorod of w = 40 nm and A = 3.7. ................................................................. 50
Figure 4-5: Effect of particle shape on the charge transfer plasmon resonance. Energy of the plasmon resonance as a function of the “squareness” of the nanorods, calculated for multiple nanorods of varied width \( w \) and aspect ratio \( A \), as indicated by dot color and the legend. Squareness is defined as the ratio between the width of the facet \( w_f \) and width of the nanorod \( w \), as depicted in the inset. ................................................................. 53

Figure 5-1: Assembly of quantum dots layer on metal film (a) Schematic of system for study the dark field scattering: quantum dots layer is formed on gold film and gold nanorods are dispersed on top of sample (b) AFM topography of the QD film formed on AuF. The height profile from the AFM scan (right panel). ...................................................... 62

Figure 5-2: Optical response of gold nanorods of width \( w = 40 \text{nm} \) (aspect ratio \( A: 2.3 \)) in water. (a) Single particle dark field scattering for gold nanorods (AuNR) deposited with different distance on gold film (b) Single particle photoluminescence measurement for gold nanorods (AuNR) deposited with different distance on gold film (AuF) using laser \( \lambda = 633 \text{nm} \). ....................................................................................................................... 63

Figure 5-3: Correlated single particle dark field scattering and emission spectra at 1.5 nm nanocavity (a) Dark field spectra and Luminescence spectra (b) Dark field spectra and Raman spectra................................................................................................................................. 65

Figure 5-4: Correlation of Dark Field scattering of gold nanorods (A: 2.2) and corresponding its emission (red spectrum) deposited directly on AuF.......................... 67

Figure 5-5: Photoluminescence spectra from just from AuF film. ........................................... 67

Figure 5-6: Optical characterization of sample (a) bright field image of quantum dots film on gold film (b) Dark field image of gold nanorods on top of quantum dots and gold film. ................................................................................................................................. 68

Figure 6-1: Evaporative self-assembly of gold nanorods on gold film (a) Dark field scattering of gold nanorods assembly. The nanorods are deposited at the coffee ring (b) Dark field scattering of gold nanorods assembly inside the ring (scale bar 5 \( \mu \text{m} \)) (c) Bright field image of gold nanorods showing the coffee ring (scale bar 20 \( \mu \text{m} \)).............. 75

Figure 6-2: Droplet evaporative assembly AuNR on AuF film (a) Topography of AuNR-AuF in ethanol recorded simultaneously. (b) height profile of topography of AuNR-AuF (c) Near field optical amplitude (O3) (d) Line profile of third harmonic near field amplitude (e) Near field phase (S3) (f) Line profile of optical phase................................. 77

Figure 6-3: Elevated temperature evaporative self-assembly of gold nanorods on gold film (inside the ring). (a) Dark field scattering of gold nanorods films deposited at \( \sim 35\)-degree (b) SEM image of gold nanorods on gold film (c) Dark field scattering of gold
nanorods deposited at ~55 degree (d) representative SEM image for sample (c) (scale bar 1 µm).........................................................................................................................................78

Figure 6-4: Assembly of gold nanorods by spreading ethanol solution. (a) Dark field image of gold nanorods (b) SEM image of the gold nanorods (scale bar 1 µm).............. 79

Figure 6-5: Evaporative assembly AuNR on AuF film in presence of solvent (a) Topography of AuNR-AuF in ethanol recorded simultaneously. (b) Height profile of topography of AuNR-AuF in ethanol (c) Near field optical amplitude (O3) (d) Line profile of third harmonic near field amplitude (e) Near field phase (S3) (f) Line profile of optical phase............................................................................................................................................... 81

Figure 6-6: Images of gold nanorods immobilized on gold film modified using polyvinyl pyridine (a) Dark field image (b) SEM image of gold nanorods (AuNR) on gold film (AuF) (scale bar 1 µm)............................................................................................................................................... 83

Figure 6-7: (a) Topography of Polyvinyl pyridine film (PVP) recorded simultaneously. (b) Line profile of topography of PVP film (c) Near field optical amplitude (O3) (d) Height profile of third harmonic near field amplitude (e) Near field phase (S3) (f) Line profile of optical phase............................................................................................................................................... 84

Figure 6-8: Self assembled AuNR on polyvinyl pyridine functionalized AuF (a) Topography of AuNR-PVP-AuF recorded simultaneously. (b)Height profile of topography of AuNR-PVP-AuF (c) Near field optical amplitude (O3) (d) Line profile of third harmonic near field amplitude (e) Near field phase (S3) (f) Line profile of optical phase .............................................................................................................................................. 85

Figure 7-1: (a) TEM image of the NIR CdSeTe/ZnS QDs used in this study. (b) Size distribution of the QDs. (c) Absorption and PL spectra of the QDs suspended in toluene (blue line), suspended in chloroform (green line), and assembled on water (red line)..... 96

Figure 7-2: AFM height (a) and phase (b) images of the LB film of QDs, where coverage with surfactant (S) molecules is minimal. (c) AFM image of the QD film coated with thin layer of surfactant layer. (d) AFM image of the QD film coated with stack of surfactant layer (representative of large portion of the film). (e) Line profile across the dashed line in (d) shows the thickness of the surfactant layers. .......................................................................................................................... 97

Figure 7-3: Results on the QD film exposed to water for ~7 min. (a) AFM and (b) PL scan images of the same area (90 × 90 µm2) of the QD film coated with excess surfactant. (c) Representative PL spectra obtained at different locations on the film. The variation of the PL at different locations is due to the non-uniformity of the film, which can also be seen in the PL intensity image in (b). Enlarging the intensity scale by a factor
of 20, two weak peaks are observed at \(~630\) and \(~660\) nm with different relative intensity at different locations as seen in the inset of (c).............................. 98

Figure 7-4: Results on the QD film exposed to water for \(~20\) min. (a) AFM and (b) PL scan images of the same area (90 × 90 \(\mu\)m\(^2\)). (c) Representative PL spectra obtained by centering selected regions [marked 1, 2, and 5 in (b)] in the laser focus......................... 100

Figure 7-5: Spatiospectral analysis of the sample region imaged in Figure 5.5. (a) Application of short-pass and long-pass filters to selectively map the different spectral regions. The PL scan obtained with short-pass (b) and long-pass (c) reveals different spatial localization of the red-emitting and NIR-emitting quantum dots (compare the areas marked 1, 2, and 4 in the two PL intensity images). (d) PL spectra obtained by centering the region marked 3 (b, c) in the laser focus and monitoring the PL spectra as a function of time. (e) Peak PL intensity extracted from (d) plotted as a function of time 102

Figure 7-6: Representative PL spectra (normalized to the same maximum) obtained on QD films prepared by LB (red line) and drop-casting (DC) (blue line) procedures compared to the spectra of the QDs as they are assembled on the water surface (black line). The DC film is prepared by applying the solution (QDs in chloroform) directly onto the substrate, avoiding the exposure to water......................................................... 104

Figure 7-7: (a–c) Comparison of X-ray photoelectron spectra of QD films prepared through drop-casting DC (black curves) and LB (red curves) procedures. (d) Ratio of composition of LB to DC for Cd 3d, Se 3d, Te 3d, Zn 2p, and S 2p electrons .......... 106

Figure 7-8: PL intensity of image of 96 × 96 \(\mu\)m\(^2\) area of a Langmuir-Blodgett film of CdSeTe/ZnS quantum dots exposed to water for 25 minutes. PL intensity image of (a) full spectrum, (b) shorter wavelength (\(\lambda\) < 694 nm) photons, and (c) longer wavelength (\(\lambda\) > 750 nm) photons ................................................................. 110

Figure 7-9: Photographic view (bright field image) and spectral property of CdSeTe/ZnS QD film prepared by drop-casting. (a) Thin films of QD-surfactant mixture are formed at the frontier of the solution expansion as the solvent (chloroform) quickly evaporates. (b) Going toward the center, where the drop is applied, the film becomes thicker. (c) Representative PL spectrum recorded close to the frontier of the film. The inset spectrum (intensity scale enlarged by a factor of about 25) shows signatures of the 630 nm and 660 nm peaks, which become negligibly small when the PL spectra are recorded close to the center of the film................................................................. 111

Figure 8-1: Schematics of configuration of excitonic (QDs) and plasmonic materials with respect to the AFM tip. For simplicity, only a single metal nanostructure, which is much larger than the quantum dots, is shown................................................................. 120
Figure 8-2: (a) Polyelectrolytes (PE) layer on top of CdSeS/ZnS. The height profile from AFM topography is ~10 nm (b) AuNR assembled on top PE-QD layer.
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSPR</td>
<td>Localized Surface Plasmon</td>
</tr>
<tr>
<td>AuNR</td>
<td>Gold Nanorods</td>
</tr>
<tr>
<td>AuF</td>
<td>Gold Film</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>PATP</td>
<td>Para-aminothiophenol</td>
</tr>
<tr>
<td>PNTP</td>
<td>Para-nitrothiophenol</td>
</tr>
<tr>
<td>DMAB</td>
<td>Dimercaptoazobenzene</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir Blodgett</td>
</tr>
<tr>
<td>PE</td>
<td>Polyelectrolytes</td>
</tr>
<tr>
<td>QDs</td>
<td>Quantum dots</td>
</tr>
<tr>
<td>CTAB</td>
<td>Hexadecyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per Minute</td>
</tr>
<tr>
<td>DF</td>
<td>Dark Field</td>
</tr>
<tr>
<td>PDDA</td>
<td>Poly (diallyldimethylammonium chloride)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly (sodium 4-styrenesulfonate)</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

This chapter provides brief introduction to key concept and techniques used in this dissertation.

1.1: Plasmonic nanoparticles:

Plasmonic nanoparticles have widely been studied in recent years. Upon the irradiation of light on metal nanostructures, the incident electromagnetic field interacts with the free conduction electrons of nanostructures. The oscillation of conduction electrons with the incident electromagnetic field is called surface plasmon resonance Figure 1-1. At the resonant condition, the metal nanoparticles absorb the photons of light while some absorbed photons may be reradiated to the surrounding, and this process is called scattering. On the other hand, the absorbed photon may be converted to phonons or lattice vibrations called the absorption.

Figure 1-1: Schematic of how light interacts with metal nanoparticles and gives rise to surface plasmon resonance.

Gustav Mie in 1908\textsuperscript{1} discussed the interaction of metal nanoparticles (spherical particles) with light forming the surface plasmon. Later on this kind of interaction have been
studied on different shapes and sizes of nanoparticles\(^2\). The plasmonic response for spherical nanoparticles at quasistatic approximation is given by polarizability (\(\alpha\))

\[
\alpha = 3\varepsilon_0 v \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right) \quad \text{----------------------------------------------- (1)}
\]

Where \(v\) is particle volume, \(\varepsilon_0\) is vacuum permittivity, \(\varepsilon = \varepsilon_r + i\varepsilon_i\) is complex dielectric function of metallic nanoparticles while \(\varepsilon_m\) is dielectric properties of the surrounding environment. The resonance condition is made when \(\varepsilon_r = -2\varepsilon_m\). Surface plasmon was first experimentally demonstrated by Otto in 1968\(^3\),\(^4\).

Gold (Au), Silver (Ag) and Copper (Cu) have their resonances at visible region of the spectrum. When the size of nanoparticle is smaller than the incident wavelength of light (\(\lambda >> R\)) the electric field gets localized at its surface called localized surface plasmon (LSPR). The LSPR's properties depend on the shape, size, orientation of the nanoparticles and on the dielectrics of surrounding medium\(^2\).

By tuning the optical properties of plasmonic nanoparticles, extensive research is done in the field of biological sensing, catalysis, photovoltaics, single-molecule spectroscopy, and surface enhanced Raman spectroscopy. Also, when coupled with the other nanomaterials such as semiconductor quantum dots (QDs), polymers, give new optical properties. The coupling could be either weak or strong. Thus, it is necessary to understand the type of interaction, interface chemistry and mechanism. The hybrid structure has been widely studied in plasmon enhanced fluorescence coupling, enhancing the vibrational signal of molecules, photothermal therapy, and many more potential applications.
1.2: Plasmonic hot electron generation:

Plasmon on metal nanoparticle decays by two different pathways one is radiative decay i.e. the transformation of plasmon into photons and another one is non-radiative decay due to the creation of electrons and holes\textsuperscript{5}. Upon photoexcitation, on plasmonic metal nanoparticles, the hot electrons are created instantaneously. Generally, the decay of plasmon through surface scattering produces energetic electrons and this phenomenon sometimes called as landau damping\textsuperscript{6}(non-radiative decay). The hot electron has non-thermal energy distribution and rapidly relaxes to Fermi-Dirac (thermal distribution) through electron-electron scattering processes\textsuperscript{7,8}. The overall process is shown in Figure 1-2. The generation of hot electron is dependent on the size and shape of nanoparticles, resonance energy and properties of metal nanoparticles.

One of the applications of plasmon generated hot electrons is study of photochemistry of adsorbate molecule at the surface. The mechanism involved the transfer of hot electrons to the unoccupied orbitals of the adsorbate molecule. Hot electron driven photochemistry has been studied in many studies like dissociation of H\textsubscript{2} molecules\textsuperscript{9}, photoelectrocatalysis\textsuperscript{10}, CO\textsubscript{2} reduction\textsuperscript{5,11}, esterification of aldehydes\textsuperscript{12}, conversion of para-aminothiophenol (PATP) to para-nitrothiophenol (PNTP)\textsuperscript{13} and vice versa\textsuperscript{14}. 
1.3: Surface Enhanced Raman Spectroscopy (SERS):

Surface-enhanced Raman Spectroscopy is a vibrational technique that enhances the Raman signal of the molecule due to enhanced electromagnetic field called localized...
surface plasmon. The first enhancement of the Raman signal is reported in 1974 where the pyridine is used as an analyte molecule adsorbed on silver electrode\textsuperscript{15}. In 1977 Van Duyne group reported the enhancement of Raman signal of adsorbed species at the metal nanostructures and explained the process is due to electromagnetic field mechanism\textsuperscript{16}. SERS have been widely used for the study of plasmon enhanced photochemistry, sensing, and different other processes.

The enhanced SERS signal is mainly due to two mechanisms: electromagnetic enhancement(EM) and the chemical enhancement\textsuperscript{17,18}. Excitation of surface plasmon on the metal nanoparticle amplifies the electromagnetic field near the surface. The amplification of the electric field causes the enhancement of the Raman signal. This mechanism is called EM of SERS signal and contributes to the largest Raman signal enhancement. The enhancement of the signal is proportional to the magnitude of the electromagnetic field to fourth power\textsuperscript{16}.

The chemical enhancement process involves charge transfer mechanism, where the excitation electromagnetic wave is in resonance with the plasmon resonance and the adsorbate. Similarly, the process involves where the excitation source is in resonance with the molecular excitation of adsorbate\textsuperscript{17}.

The total Raman signal is the product of both chemical and electromagnetic enhancement mechanism. The intensity of Raman scattering is directly proportional to the square of induced dipole moment, \( \mu_{\text{ind}} \) which is the product of electromagnetic field and Raman polarizability of molecule \( \alpha \)\textsuperscript{18}. 
SERS signal depends on distance between the metal nanoparticles and the adsorbate molecule. The largest signal enhancement occurs when the molecules are adsorbed near the surface while the signal decreases with distant between the nanoparticles and adsorbate molecule. Similarly, SERs signal depends on the excitation wavelength of laser, if the excitation wavelength is in resonance with the plasmon resonance, there is highest SERs signal and also depends on the resonance of the adsorbate molecule.

1.4: Outline of Dissertation:

Chapter 2 shows the experimental setup and methods used for the acquisition of data in this dissertation.

Chapter 3 shows the experimental results on selectively catalyzed plasmon driven photochemical reaction using para-aminothiophenol (PATP) as a model reaction molecule. Besides, we demonstrated the remarkable effects of surface ligands by comparing the photochemistry using citrate and hexadecyltrimethylammonium bromide (CTAB) as ligands on gold nanorods (AuNR).

Chapter 4 shows the single particle dark-field scattering of gold nanorods (AuNR) on gold film and the oxide-coated silicon substrate. We studied both experimentally and theoretically, the optical response of colloidal AuNR interaction with AuF. We remarkably found the scattering cross-section of these films is dominated by charge transfer plasmon mode and is independent of the shape and size of AuNR.

Chapter 5 shows the study of distant dependent single particle scattering and photoluminescence of gold nanorods controlled by using polyelectrolytes (PE) and QDs.
as a spacer layer. Here, we demonstrated the light emission from a dielectric nanocavity via both elastic and inelastic scattering processes.

Chapter 6 involves the simple ways of assembly of colloidal AuNR into two-dimensional films by using different methods. We have demonstrated the droplet evaporated assembly of AuNR at a higher temperature than the room temperature; reduces the conventional “coffee ring” and deposits the thin uniform monolayer of AuNR.

The next chapter 7 will focus on the assembly of colloidal quantum dots (QDs) using the technique called Langmuir-Blodgett. The optical property of monolayer of near-infrared CdSeTe/ZnS is studied. Photoluminescence and structural analysis shows the interatomic diffusion that leads to crystal transformation.

In chapter 8, the results from this dissertation work are summarized, and discussion towards future direction is presented.
1.5: References:

Chapter 2: Experimental Methods:

This chapter provides brief introduction of experimental techniques used for data acquisition in this dissertation.

2.1: Dark field optical microscopy:

The dark-field scattering measurement was performed using the GX51 Olympus microscope. The optical layout is shown in the schematic in Figure 2-1. The sample is excited with 100 W halogen lamp white light source. Dark-field scattering images of the individual nanoparticles were obtained by directing about 10% of the signal to the camera (Olympus UC30) that is attached to the microscope. The corresponding scattering spectra were then recorded by centering the particle of interest to the focus of the objective and directing about 90% of the light collected from the sample to the spectrometer (IsoPlane Spectrograph of Princeton Instruments), which uses a thermoelectrically cooled (−75 °C) and back-illuminated deep depletion CCD camera.
Figure 2-1: Schematic showing the dark-field scattering microscopy and spectroscopy experimental setup. Representative dark field image is shown.

2.2: Apertureless scattering near field optical microscopy (ANSOM):

The experimental set up for ANSOM is shown in schematic in Figure 2-2. The ANSOM is commercial setup from Neaspec GmbH which consists the tapping mode atomic force microscope (AFM) as base instrument. This is customized using pseudo-heterodyne interferomartic detection of the scattered light. A collimated laser passes through bunch of optics like half wave plate (HWP), polarizer (P) and splits into 50:50 using beam splitter (BS) into excitation source and reference beam. The excitation source is focused at AFM tip using parabolic mirror (NA 0.46). The scattered signal from the tip comes back through same path and mixed with previously splitted reference beam. The reflected beam mixed with reference beam is detected using different detector. The output of the optical signal can be demodulated at nΩ. We can modify the polarization of signal by
changing the polarization of reference beam ("path a" in Figure 2-2). This consist the elastic detection and we can perform imaging of plasmon scattering, infrared absorption and dielectric contrast.

Similarly, the scattered signal from tip sample area can be taken through channel “path b” and the incident laser is cut by using long pass filter. Only the inelastic signal is collected using spectrometer or photodiode. This channel can be used to perform different spectroscopy like Raman scattering, fluorescence and imaging inelastic scattering processes using single photon counter photodiode. Different wavelength of laser 633 nm, 532 nm, and 6μm is used, similarly different detectors like silicon, CdHgTe.
2.3: Langmuir Blodgett (LB) technique:

The Langmuir–Blodgett is usually used to deposit the monolayer of film on solid surface at usually-air interface precisely in controlled environment.

The schematic (Picture) of the Langmuir-Blodgett trough is shown in Figure 2-3. The trough consist the barriers which are controlled by computer program, and the Wihelmy plate is dipped in water subphase that measures the surface pressure of the monolayer film.

For the preparation of monolayer film using LB trough, water is held in Teflon trough. The desired substrate (oxide coated silicon, gold) is held on the arm and dipped into water subphase. Usually, 10-15 µl of an amphiphilic solution of quantum dots (QDs) or desired molecules are dropped on top of water subphase using Hamilton microsyringe. The solution is made usually using highly volatile solvents like chloroform or hexane.

When the solution is dropped on water subphase layer the solution covers the area of trough. As the solvent evaporates (usually wait time 5 minutes) the monolayer of film is formed. Then, the computer-controlled barriers are used to compress the monolayer film to get high packing density film. The packing density of the film is measured by monitoring surface pressure-isotherm provided by the Wihlmey sensor. Wait for 10 minutes for rearranging the film before transferring the film in solid substrate by pulling vertically up at certain speed. The monolayer film of CdSeS/ZnS QDs formed using Langmuir Blodgett film is shown in Figure 2-4.
Figure 2-3: Photograph of the Langmuir Blodgett trough.

Figure 2-4: Monolayer film formed using Langmuir Blodgett film. AFM topography of CdSeS/ZnS monolayer film.
2.4: Layer by layer assembly of polyelectrolyte film:

Oppositely charged poly (sodium 4-styrenesulfonate) (PSS) negative polyelectrolye and Poly (diallyldimethylammonium chloride) solution as positive polyelectrolytes (PDDA) was purchased from sigma Aldrich. The structural drawing is shown in Figure 2-5. Working solution for PSS and PDDA was made in 0.1m NaCl solution of final concentration 2mg/ml. The substrate (either oxide coated silicon or AuF) was dipped first on PDDA solution for 5 minutes and rinsed with distilled water for 1 minute then dipped again in PSS solution for 5 minutes and washed again for 1 minute. We can form the desired height of polyelectrolytes layer just adsorbing different cycles of polymers. AFM topography of 14 cycles of polyelectrolytes is shown in Figure 2-6.

Figure 2-5: Structural drawing of PDDA (left) and PSS (right)
Figure 2-6: AFM topography of polyelectrolyte film formed by layer by layer assembly of oppositely charged polyelectrolytes
Chapter 3: Surface Ligand-Mediated Plasmon-Driven Photochemical Reactions

Contrary to the general expectation that surface ligands reduce the reactivity of surfaces by blocking the active sites, we present experimental evidence that surface ligands can in fact increase reactivity and induce important reaction pathways in plasmon-driven surface photochemistry. The remarkable effect of surface ligands is demonstrated by comparing the photochemistry of p-aminothiophenol (PATP) on resonant plasmonic gold nanorods (AuNRs) in the presence of citrate, hexadecyltrimethylammonium bromide (CTAB), and no surface ligands under visible light irradiation. The use of AuNRs with citrate and no surface ligand results in the usual azo-coupling reaction. In contrast, CTAB-coated AuNRs oxidize PATP primarily to p-nitrothiophenol (PNTP). Strong correlation has been observed between the N–O and Au–Br vibration band intensities, suggesting that CTAB influences the reaction pathway through the Br– counterions that can minimize the electron–hole recombination rate by reacting with the hole and hence increasing the concentration of hot electrons that drive the oxidation reaction.

3.1: Introduction:

Resonant excitation of plasmonic nanoparticles creates an intense local electromagnetic field that can be utilized for driving photochemical reactions under irradiation of low photon flux of visible light. \(^1\) Examples of plasmon-driven photochemical reactions include decomposition of organic molecules, oxidative coupling of self-assembled p-aminothiophenol (PATP) to produce p,p′-dimercaptoazobenzene (DMAB), \(^7\)

dissociation of hydrogen molecules,\textsuperscript{1,2,4} and conversion of aldehydes to esters,\textsuperscript{13} all at room temperature. In most studies, plasmon-driven photochemical reactions take place on the surfaces of chemically synthesized quasi-single crystalline colloidal nanostructures that show significantly less plasmon damping than lithographically fabricated polycrystalline nanostructures.\textsuperscript{14} However, the synthesis and survival of colloidal nanocrystals require stabilizing surface-bound ligands. In traditional heterogeneous catalysis, surface ligands are believed to reduce the catalytic activity of the nanocrystals by blocking the active surface sites.\textsuperscript{12,15-18} In plasmon-driven photochemistry, these inherent surface-bound ligands may play very different but pivotal roles that can be utilized for manipulating reaction selectivity. The mechanism of plasmon-driven photochemical reactions is believed to involve hot electron transfer from the nanocrystal to the adsorbed species (atoms, molecules, and ions),\textsuperscript{1,8,19,20-22} creating a hole (positive charge) in the nanocrystal. Hence, surface ligands that interact with the charge carriers (hot electrons and holes) are expected to drastically affect the reaction selectivity.

Here, we present the experimental evidence that surface ligands can indeed change the selectivity of plasmon-driven surface photochemical reactions in an unprecedented manner. To this end, using the plasmon-driven photochemistry of PATP as a model reaction, we have studied the effect of surface ligands on reaction selectivity by comparing the results obtained in the presence of citrate (CIT), hexadecyltrimethylammonium bromide (CTAB), and no surface ligands. Colloidal gold nanorods (AuNRs) are used as resonant plasmonic optical nanoantennas at 633 nm excitation wavelength. The results show that the same plasmonic nanocrystals can lead to different photochemical reaction pathways depending on the surface ligands.
3.2: Experimental Methods

3.3: AuF-PATP-CTAB-AuNR sample:

Sandwiching p-aminothiophenol (PATP) molecules between gold film (AuF) and CTAB coated gold nanorods (AuNRs). About 50 nm thick AuF was deposited on a silicon wafer using electron beam evaporation. PATP was purchased from Sigma Aldrich. The PATP molecules were self-assembled on the AuF by keeping the AuF in 1.0 mM PATP/ethanol solution overnight. The PATP functionalized AuF was washed with ethanol and ultrapure water thoroughly and dried by blowing nitrogen gas. Gold nanorods with hexadecyltrimethylammonium bromide (CTAB) surface ligand were obtained from Nanopartz, Inc. Gold nanorods with nominal diameter 40 nm and length 80 nm and 92 nm were used. For the shorter AuNRs, the excess stabilizing CTAB surfactant was removed through two rounds of centrifugation and re-suspension. One time centrifugation is sufficient for the longer AuNRs as solid-liquid separation is very effective due to the larger mass. 300 µL of original solution was taken and diluted with ultrapure water up to 1.5 mL in a small centrifuging tube. The diluted AuNR was centrifuged at 5000 RPM for 5 minutes. The supernatant solution was discarded and the residue was dissolved with ultrapure water and centrifuged at 4000 RPM for 4 minutes. The solid residue is then re-suspended by adding ultrapure water up to 250 µL. About 50 µL of the colloidal solution was dropped on PATP functionalized AuF and dried at ambient condition.
3.3.1: AuF-PATP-CIT-AuNR sample:

Sandwiching PATP molecules between AuF and citrate (CIT) coated AuNRs. The same procedure as above was followed except that citrate coated gold nanorods were used. The gold nanorods were obtained from Nanopartz, Inc.

3.3.2: AuNR-PATP sample: Replacing CTAB surface ligand with PATP:

First, the stabilizing excess CTAB was removed through one round of centrifugation and discarding the supernatant solution. The AuNRs were then re-suspended in 1.0 mM PATP/ethanol solution and kept overnight. The PATP molecules that were not chemically attached to the AuNR surface were removed by centrifuging (for 4 minutes at 4000 RPM) the resulting solution and discarding the supernatant solution. The solid residue was then dissolved in ethanol to a total volume of 250 µL. The PATP functionalized AuNRs (mostly aggregates) were then dispersed on silica or gold substrates for spectroscopic characterizations.

3.4: Results and Discussion:

The ligand effect has been studied by analyzing the surface enhanced Raman scattering (SERS) spectra of the following samples: (a) PATP molecules self-assembled on a gold film on which CIT-capped AuNRs are deposited (AuF−PATP−CIT− AuNR), (b) same as (a) but CTAB-coated AuNRs are used (AuF−PATP−CTAB−AuNR), and (c) PATP-functionalized AuNRs deposited on a silica substrate (SiO$_2$−AuNR−PATP). The details of the sample preparation and optical measurements are provided in Figure 2-1, Figure 2-2, Figure 3-8. The SERS experiments have been carried out using two different setups:
at grazing incidence for confirming the field localization (as described below) via polarization dependent measurements and at normal incidence using a high numerical aperture objective Figure 2-1. Representative scattering spectra of the AuNRs on different substrates Figure 3-9b show that the 633 nm excitation wavelength overlaps with the plasmon resonances.

Figure 3-1: Calculated near-field enhancement and localization for the excitation field oriented (a) 30° from the surface normal (significant projection along the vertical axis, vertical polarization, VP), and (b) parallel to the sample plane (horizontal polarization, HP). Image size: 80 nm × 120 nm. (c) SERS signal intensity obtained with VP (red curve) and HP (black curve). Each curve represents the average of 10 spectra obtained from different locations on the sample. The theoretical and experimental results are obtained at 633 nm excitation wavelength.

The results of finite-difference time domain (FDTD) electromagnetic simulations (Figure 3-1a, b) show that the nearfield is localized in the AuF-AuNR gap, where the PATP molecules are located (see Figure 3-6 for detailed calculation). The excitation field with a significant projection along the vertical axis (vertical polarization, VP) creates a more enhanced and localized near-field than horizontal polarization (HP), as can be seen comparing the results displayed in panels a and b of Figure 3-1. Consistent with this theoretical prediction, the SERS signal intensity obtained with the excitation electric field oriented 30° from the surface normal is significantly stronger than the intensity obtained
with HP, as shown in Figure 3-1c, confirming that the electric field is indeed localized in the AuF-AuNR gap region. We note that for excitation light focused with high numerical objective the electric field has projections along the vertical and horizontal axes (as in Figure 2-1). The SERS spectra of the three samples mentioned above are compared in Figure 3-2 along with the schematics that show the corresponding molecular structures of the reactant and surface ligands in the AuF−AuNR gaps.

Figure 3-2: SERS spectra of (a) AuF-PATP-CIT-AuNR, (c) AuF-PATP-CTAB-AuNR (average of 20 spectra acquired from different locations on the same sample), and (e) SiO2-PATP-AuNR samples. The corresponding molecular structures of the reactant (self-assembled PATP) and surface ligands in the AuF-AuNR gaps are shown in the schematics on the right side of each spectrum in (b), (d) and (f). A strong peak is observed at 1328 cm⁻¹ in (c) but not in (a) and (e), indicating a photochemical reaction pathway induced by the CTAB surface ligand. The spectra are obtained at λ = 633 nm excitation wavelength at normal incidence (see Figure 2-1).
In the spectrum shown in Figure 3-2 a (using citrate-coated AuNRs of diameter 40 nm and length 80 nm), the same vibrational bands are observed as in the reported spectra obtained on roughened silver surfaces\(^7\) and on citrate-coated silver and gold nanoparticles. \(^8,10,19-22\) The vibrational bands at 1143, 1392, and 1437 cm\(^{-1}\) are characteristic of the DMAB product\(^7,8,23\) formed via an oxidative coupling reaction of self-assembled PATP molecules,\(^9,10\) while the peaks at 1080 and 1580 cm\(^{-1}\) can be due to both PATP and DMAB.\(^7,8,23\) When the surface ligand is changed to CTAB for nominally the same size of AuNRs (AuF–PATP–CTAB–AuNR sample), a new prominent peak is observed at 1328 cm\(^{-1}\) in addition to the vibrational signatures of DMAB, as shown in Figure 3-2c. The peak at 1328 cm\(^{-1}\) can be assigned to N–O vibration, which may indicate that the PATP is oxidized to p-nitrothiophenol (PNTP). When the PATP molecules are directly adsorbed on the AuNRs replacing the CTAB surface ligands, the N–O vibrational band has completely disappeared, as shown in Figure 3-2e, regardless of the substrate (silica or gold). The results presented in Figure 3-2 have been reproduced on multiple samples with different aspect ratios of gold nanorods and ligand contents. It is also shown that the intensity of the 1328 cm\(^{-1}\) peak decreases rapidly with repeated removal of CTAB (compare the spectra in Figure 3-8). Clearly, the results presented in Figure 3-2 indicate that the appearance of the new prominent vibrational band is due to a product species that is formed via a reaction pathway induced by the CTAB surface ligands.

For the same sample, the relative intensity of the 1328 cm\(^{-1}\) peak varies slightly at different sites, which is advantageous for correlating the CTAB content with the product signals. Although the Raman signal of CTAB is very weak in the spectral region where
the analyte molecules have a much higher Raman signal (Figure 3-4), the low-frequency Au–Br vibration band is relatively strong. Therefore, the relative amount of CTAB on the AuNRs can be estimated based on the Raman scattering intensity of the Au–Br vibrational band. As shown in Figure 3-3a-c, strong correlation has been observed between the relative intensity of the Au-Br vibration band at 180 cm\(^{-1}\) and the relative intensity of the N-O vibration band at 1328 cm\(^{-1}\). Comparing the spectra in Figure 3-3a, b, it can be seen that the relative intensity of the N-O vibrational band decreases with decreasing relative intensity of the Au–Br band at 180 cm\(^{-1}\). For AuNRs incubated in PATP solution and dispersed on the silica surface (Figure 3-3c), the Au–Br band is completely absent and a Au–S vibrational band is observed at 409 cm\(^{-1}\), indicating that the CTAB ligand is successfully replaced by the PATP analyte molecules.
Figure 3-3: Correlation of CTAB content on the AuNR surface with the 1328 cm$^{-1}$ band intensity. (a) Strong relative Au-Br vibration band intensity at 180 cm$^{-1}$ and strong relative intensity of N-O vibration band at 1328 cm$^{-1}$. (b) Moderate relative intensity of Au-Br and N-O vibration bands. (c) Au-Br and N-O vibration bands are absent. (d) Raman spectrum of solid PATP. (e) Raman spectrum of solid PNTP. The bands at 409 cm$^{-1}$ (due to Au-S stretching vibration) indicate that the PATP molecules are chemically bonded to the AuF (a & b) and to the AuNR (c) surfaces. All the results are obtained at $\lambda=633$ nm with grazing incidence (see Figure 2-1)

The complete absence of the Au–Br band at 180 cm$^{-1}$ is correlated with the complete absence of the N–O band, as seen by comparing the blue and black spectra in Figure 3-3c. The Raman spectrum of the solid PATP shown in Figure 3-3d confirms that the PATP reactant molecule has no vibrational band around 1328 cm$^{-1}$ that can be enhanced by chemical and electromagnetic surface effects. On the other hand, the 1328 cm$^{-1}$ peak
frequency is in very good agreement with the NO vibrational frequency of solid PNTP, as shown in Figure 3-3e. Therefore, we propose that PNTP is the product of the competing reaction pathway that is induced by the CTAB surface ligand.

![Graph showing SERS intensity comparison](image)

Figure 3-4: Comparison of the SERS intensity of CTAB coated AuNRs on gold film (black curve) and PATP molecules sandwiched between the gold film and CTAB coated AuNRs (red curve). Clearly, in the analysis of the PATP, PNTP and DMAB SERS spectra, the contribution of the CTAB surface ligand can be ignored.

It is well established that plasmon-driven oxidation of PATP requires activation of adsorbed oxygen molecules by hot plasmon electrons, and the formation of PNTP is related to a higher concentration of activated oxygen. The mechanism of PATP oxidation to PNTP in the AuF–AuNR nanocavity in the presence of CTAB (see Figure 3-2d) may be similar to the mechanism of PNTP reduction to PATP on silver nanoparticles in acidic solution in the presence of halide counter ions (Cl\(^-\), Br\(^-\), and I\(^-\)) recently reported by Xie and Schlücker. In both cases, the photochemical reactions are believed to be initiated by hot electron transfer to chemisorbed species (electron transfer to O\(_2\) in the case of PATP oxidation, and electron transfer to H\(^+\) in the case of PNTP.
reduction). After the electron is transferred to the adsorbed species, the halide anions are believed to react with the hole on the metal surface, thereby minimizing the rate of electron–hole recombination processes and increasing the number of hot electrons that activate oxygen molecules. Electron transfer to molecular oxygen produces $O_2^-$ superoxide that is strongly adsorbed to the surface of the nanoparticles. The conversion of PATP to DMAB and PNTP possibly involves the same initial step, that is, reaction of the superoxide with the NH$_2$ group of PATP. In the photocatalytic oxidation of aniline on Pt nanoparticles supported on TiO$_2$, Shiraishi et al. detected nitrosobenzene and azobenzene. According to the mechanism proposed by Konaka et al., the formation of the azobenzene should involve a reaction between the nitrosobenzene product and unreacted aniline that may be at a very low number density depending on the concentration of charge carriers. The mechanism of plasmon-driven oxidation of PATP should be similar, and a high concentration of hot electrons preferentially leads to the formation of PNTP as opposed to DMAB. In principle, a high concentration of hot electrons should also lead to reduction of PNTP to PATP and DMAB, although the presence of oxygen in the ambient atmosphere favors the reverse reaction (the oxidation of PATP). To get insight into the surface ligand effect on the reductive reaction, the temporal evolutions of the SERS spectra of AuF–PNTP–CTAB–AuNR and SiO$_2$–AuNR–PNTP are compared, as shown in Figure 3-5.
Figure 3-5: SERS spectra of PNTP (a,b) sandwiched between AuF and CTAB-coated AuNRs and (c,d) adsorbed directly on AuNRs replacing CTAB. The intensity maps in (a) and (c) represent series of spectra recorded with acquisition times of 200 ms (a) and 100 ms (b) at 1.0 mW incident laser power. The higher intensity in (c) than that in (a) as seen in the color scale is due to the effective aggregation of the AuNR during incubation in the PNTP solution. This aggregation creates highly intense hot spots. The spectra are obtained at a $\lambda = 633$ nm excitation wavelength using the setup in Figure 2-1.

For the PNTP molecules sandwiched between AuF and CTAB coated AuNRs (AuF–PNTP–CTAB–AuNR sample), the intensity of the N–O stretching vibration at $\sim 1330$ cm$^{-1}$ decreases slowly and new weak peaks appear at 1136, 1176, 1386, and 1434 cm$^{-1}$ (indicated by the arrows in Figure 3-5 a,b) as a function of time. Most of these new frequencies are in good agreement with the vibrational signatures of DMAB bands mentioned above. The 1176 cm$^{-1}$ peak frequency is in agreement with the 1171 cm$^{-1}$ peak observed in the normal Raman spectrum of solid PATP in Figure 3-3 d. The bands at $\sim 1078$ cm$^{-1}$ (C–S stretch) and $\sim 1563$ cm$^{-1}$ (ring stretch), where the vibrational
frequencies of PNTP, PATP, and DMAB overlap, broaden with time, as seen in the intensity map in Figure 3-5a. The DMAB vibrational bands have also appeared upon irradiation of the PNTP molecules directly adsorbed on the AuNRs replacing CTAB (SiO2–AuNR–PNTP sample), but no significant spectral broadening has been observed as a function of time, as can be observed in Figure 3-5 c,d. In addition, in the absence of the CTAB ligand, the relative intensity of the 1176 cm\(^{-1}\) peak has decreased significantly, as can be seen comparing the spectra in panels b and d of Figure 3-5. The results of this comparative study clearly indicate that the presence of CTAB enables the reduction of PNTP to PATP at ambient conditions, which supports the mechanism that CTAB increases the number of hot electrons. Oxidation of PATP to PNTP has been observed on TiO\(_2\)–Au nanostructures under simultaneous excitations of the valence to conduction band transition of TiO\(_2\) using a UV source and the plasmon resonance of the gold using visible light\(^{22}\). Activation of oxygen molecules by the large number of conduction electrons available due to the excitation of the TiO\(_2\) component has been proposed as a possible mechanism for the conversion of PATP to PNTP\(^{22}\). The requirement of a high concentration of activated oxygen was also demonstrated in a flow cell experiment by Xu et al., where the vibrational signature of PNTP product was observed when oxygen was expanded to the interaction region and the excitation photon flux was increased from about 1500 W/cm\(^2\) (no PNTP formation) to 6400 W/cm\(^2\) (PNTP was formed)\(^9\). In our experiment, the ambient air is the source of oxygen and the PNTP product has been observed instantly upon irradiation of the sample at very low photon flux (as low as 300 W/cm\(^2\)) with acquisition times as short as 0.1 s (see Figure 3-7 and Figure 3-8). The relative intensities of the vibrational bands of the PNTP and DMAB products are
significantly more intense than those observed on TiO$_2$-Au composite structures with simultaneous excitation of the valence to conduction band electronic transitions and plasmon resonances, requiring UV and visible light sources.$^{22}$ These comparisons of our experimental observations with published data indicate that the surface ligand-induced oxidation of PATP is extremely efficient, which can be attributed to the fact that the ligands are naturally bound to the surface to efficiently interact with the charge carriers, which results in an increased concentration of activated oxygen molecules.

3.5 Optical and Structural Characterizations:

The characterizations of the samples have been carried out using two types of setups shown by the schematics in Figure 2-2 and Figure 2-1. The setup in Figure is developed for correlating dark field scattering of the plasmonic nanostructures with the surface enhanced Raman spectroscopy (SERS). The setup in Figure 2-2a allow us to correlate the atomic force microscope topographic images with the SERS as well as for polarization dependence studies of SERS. We note that most SERS experiments are carried out at normal incidence (Figure 2-2). In this type of normal incidence, effective orientation of the excitation electric field perpendicular to the sample plane is not possible.

3.5.1: Atomic force microscope (AFM) and Raman scattering measurement:

Detailed on setup is discussed in (chapter 2) Figure 2-2. The representative AFM image in Figure 3-9, single and aggregates of gold nanorods can be seen. No aggregation of CTAB surfactant molecules are observed, indicating that the excess stabilizing CTAB is successfully removed by the two rounds of centrifugation.
3.5.2: Dark-field scattering and Raman scattering measurements:

The experimental setup for measuring dark field and Raman scattering is discussed in detail in (chapter 2) Figure 2-1.

![Diagram](image1)

Figure 3-6: Excitation field polarization dependence of the near-field amplitude and localization. The labels $\mathbf{k}$ and $\mathbf{E}$ represent the propagation direction and electric field vectors of the excitation source ($\lambda = 633$ nm). The AuNR has diameter 40 nm and length 80 nm. The AuF-AuNR gap is 2 nm. (a) The excitation field is oriented $30^\circ$ from the surface normal, and the field has projections along the vertical (AuF-AuNR axis) and horizontal (long axis of the AuNR). (b) The excitation field is oriented as in (a) but the AuNR is rotated $90^\circ$ in the sample plane so that there is no projection of excitation field.
along the long axis of the AuNR. (c) The excitation field is oriented in the sample plane parallel to the long axis of the AuNR. (d) The excitation field is oriented in the sample plane perpendicular to the long axis of the AuNR. Notice that the near-field is more enhanced and strongly localized in (a) and (b), where the excitation field has projection along the vertical axis that induces strong coupling between the AuNR plasmonic nanoantenna and the polarizable gold substrate. In terms of maximum local field amplitudes in the AuF-AuNR gap (a) > (b) > (c) > (d) (see scale bar)

3.5: SERS Signal Intensity of AuF-PATP-CTAB-AuNR Sample with Time:

The SERS signals of the photochemical reaction products p-nitrothiophenol (PNTP) and p,p'-dimercaptoazobenzene (DMAB) have similar time dependence as shown in Figure 3-7, indicating that no conversion of one PNTP to DMAB or vice versa.
3.6: Dependence of the PATP Photochemical Reaction on Incident Laser Power:

The SERS spectra of the AuF-PATP-CTAB-AuNR samples have been recorded at different laser power ranging from 18 µW to 1.75 mW, which corresponds to intensity of ~30 W/cm$^2$ to 3500 W/cm$^2$. In all cases, the vibrational signatures of the products p-nitrothiophenol (PNTP) and p,p'-dimercaptoazobenzene (DMAB) have been observed as shown in Figure 3-7.
Figure 3-8: SERS spectra acquired at different laser powers (see labels) show the same signatures of the PNTP and DMAB. The spectra are acquired from different locations on the same sample. The SERS spectra are obtained using AuNRs of nominal diameter 40 nm and length 92 nm (the sample scheme is AuF-PATP-CTAB-AuNR). CTAB is removed through one round of centrifugation and removal of the supernatant solution.
Figure 3-9: (a) Atomic force microscope (AFM) topography of gold nanorods on PATP functionalized gold film. Notice that the gold film is deposited using electron-beam evaporation that produces rough granular structure. The AFM topography is obtained using the setup shown in Figure 2-2. (b) Representative scattering spectra of AuNRs on AuF and silica substrates. All the spectra are similarly broad due to the large number of single and aggregated AuNRs in the focal volume.

3.6: Conclusion:

In conclusion, contrary to the expectation that surface ligands reduce the reactivity of catalytic surfaces by blocking the active sites, the results presented here demonstrate that
surface ligands can indeed enhance the reactivity of surfaces and induce important reaction pathways in plasmon-driven photochemical reactions. This possibility may offer a new paradigm to control the efficiency and selectivity of plasmon-driven photochemical reactions simply by manipulating the surface ligands. The remarkable effect of CTAB on the photochemistry of PATP suggests that manipulation of the chemical and electronic properties of the surface-bound ligands is a simple and efficient approach for maximizing reactive intermediates that drive the overall reaction. The observation of PNTP product when using CTAB-coated AuNRs is an indication of increased concentration of activated oxygen. The strong correlation of the PNTP product signal with the CTAB content on the AuNR surface (Au−Br vibrational band intensity) is direct evidence that the surface ligand is responsible for the increased concentration of activated oxygen molecules.
3.7: References:

(1) Sun, M.; Xu, H. Small 2012, 8, 2777.
(3) Zhang, Z.; Xu, P.; Yang, X.; Liang, W.; Sun, M. Journal of Photochemistry and Photobiology C: Photochemistry Reviews 2016, 100, 100.
(27) Xie, W.; Schlücker, S. Nature Communications 2015, 6, 7570.
Chapter 4: Charge Transfer Plasmons

Understanding how the plasmonic response of a metallic nanoparticle is modified by its coupling with a metallic film is a fundamental research problem relevant for many applications including sensing, solar energy harvesting, spectroscopy, and photochemistry. Despite significant research effort on this topic, the nature of the interaction between colloidal nanoparticles and metallic films is not fully understood. Here, we investigate, both experimentally and theoretically, the optical response of surface ligand-coated gold nanorods interacting with gold films. We find that the scattering cross section of these systems is dominated by a charge transfer plasmon mode, for which charge flows between the particle and the film. The properties of this mode are dictated by the characteristics of the particle–film junction, which makes the frequency of this charge transfer plasmon far less sensitive to the nanoparticle size and geometry than a typical dipolar plasmon mode excited in similar nanorods placed directly on a purely dielectric substrate. The results of this work serve to advance our understanding of the interaction between metallic nanoparticles and metallic films, as well as provide a method for creating more robust plasmonic platforms that are less affected by changes in the size of individual nanoparticles.

4.1: Introduction:

When illuminated, metallic nanostructures are capable of sustaining collective excitations of their conduction electrons, commonly known as surface plasmons.\(^1\) These excitations couple strongly to light, resulting in large cross sections, and producing significantly

---

enhanced electric fields around the nanostructure.\textsuperscript{2,3} Thanks to these extraordinary properties, metallic nanostructures are being used to improve solar energy harvesting devices,\textsuperscript{4} drive chemical reactions using light,\textsuperscript{5-7} and increase the sensitivity of biosensors,\textsuperscript{8-11} to cite some relevant applications. The characteristics of a plasmon resonance are determined by the shape, size, and material properties of the metallic nanostructure that supports it, as well as by the dielectric environment in which the nanostructure is located.\textsuperscript{12} A paradigmatic example of such dependence is the red shift experienced by the plasmon resonance of a metallic nanostructure when placed near a dielectric substrate.\textsuperscript{13} The changes of the plasmonic response of the nanostructure become particularly strong if the substrate is metallic, due to the coupling with the conduction electrons of the latter,\textsuperscript{14-18} which results in an extraordinary electric field concentrated in the gap separating the two systems.\textsuperscript{19-23} This field enhancement is particularly large when molecular spacers on the nanometer scale are used.\textsuperscript{24} Due to this effect, coupled metallic particle-film structures have been the subject of extensive research in recent years\textsuperscript{24-30} as a promising platform for achieving ultrasensitive molecule detection,\textsuperscript{31-33} single molecule optomechanics,\textsuperscript{34} strong coupling,\textsuperscript{35} enhanced emission,\textsuperscript{36-38} and color printing.\textsuperscript{39} Despite the significant research effort and widespread applications of particle–film plasmonic systems, the interaction between a colloidal nanoparticle and metal film is not fully understood. Chemically synthesized metal nanoparticles are inherently coated with surface ligands (organic molecules) that provide a natural spacer of a thickness on the order of a few nanometers.\textsuperscript{40-44} The properties of this layer determine the nature of the interaction, and hence the plasmonic response of the coupled system. In particular, the existence of a conductive junction between the particle and the film enables a distinct
type of plasmonic resonances, commonly referred to as charge transfer plasmons,\textsuperscript{45} in which the charge oscillates between the two systems.\textsuperscript{46} These modes have been extensively investigated in particle dimers due to their potential for sensing applications,\textsuperscript{45,47-49} as well as for being a robust platform to observe quantum plasmonic effects\textsuperscript{50-53}.

Here, we investigate how the optical response of colloidal metallic nanoparticles is modified as a result of the interaction with metallic substrates. To that end, we analyze the scattering spectra of individual gold nanorods of different sizes deposited on both silica and gold substrates. We find that, when they are placed on the metallic substrate, the scattering response of the nanorods is dominated by a charge transfer plasmon mode, in which charges oscillate between the substrate and the nanorod. Surprisingly, the resonance frequency of this mode is only weakly dependent on the size and width of the nanorods, which is in sharp contrast with the behavior shown by nanorods with similar sizes when they are placed on the purely dielectric substrate, in which case the scattering spectrum is dominated by a dipolar mode whose spectral position varies strongly with the length and width of the nanorod. Using a combination of rigorous solutions of Maxwell’s equations and a simple analytical model, we show that the properties of the charge transfer mode are solely determined by the local characteristics of the particle–film junction and, therefore, are weakly sensitive to the dimensions of the particle. These results contribute to the advancement of the fundamental understanding of nanoparticle–film interactions, as well as to provide a basis for the development of plasmonic systems that are robust against differences in nanoparticle size.

4.2: Experimental Methods
4.2.1: Sample preparation:

All of the aqueous solutions of gold nanorods with cetyl-trimethylammonium bromide (CTAB) stabilizing surfactant were obtained from Nanopartz Inc. The gold film of ~ 50 nm thickness was deposited on an oxide-coated silicon wafer using electron beam evaporation. Prior to drop-casting on the different substrates, small amounts of the gold nanorod solutions were diluted about ten times by adding ultrapure water, and then 20 – 30 µL of solution was spread on the substrates. The solution was then blown off with dry nitrogen gas before it dried completely to avoid particle aggregation and accumulation of excess surfactant molecules.

4.2.2: Dark field Measurement:

The dark-field scattering measurement was performed using the GX51 Olympus microscope. The optical layout is shown in the schematic in Figure 2-1(Chapter 2).

4.3: Results and Discussion:

The system under study is depicted in Figure 4.1a and b. It consists of chemically synthesized gold nanorods of width w and length L, which are placed either directly on a silica substrate or on a 50 nm-thick gold film deposited on silica (see the section 4.2.1 for details of the sample preparation). The nanorods are excited by focusing a ring of white light using dark-field objective of numerical aperture of 0.9 (see Figure 2-1(Chapter 2) more details on the experimental setup).

The normalized spectra measured for gold nanorods placed on the silica and gold substrates are shown in panels (c) and (d) of Figure 4-1, respectively. In each case, we
analyze the scattering spectra of three different nanorods, all of them with the same width \( w = 40 \, \text{nm} \), but different aspect ratios \( A = L/w \), as indicated by the labels in the plot. When deposited on the silica substrate, the scattering spectra of the gold nanorods display a single peak in the analyzed spectral region, whose location significantly depends on the aspect ratio of the nanorods, shifting to lower energies as the length of the rod increases. This is exactly the expected behavior for the longitudinal dipolar plasmon of the nanorod, whose energy is inversely proportional to the nanorod length.\(^{12}\) Interestingly, when nominally the same nanorods are, instead, placed on the gold film, we find that their corresponding scattering spectra converge to essentially the same resonance energy near 1.8 eV, regardless of the aspect ratio of the nanorods.

**Figure 4-1:** Optical response of gold nanorods placed on different substrates. (a,b) Schematics of the system under study consisting of a gold nanorod of length \( L \) and width \( w \).
w, placed directly on a silica substrate (a), or on a 50 nm-thick gold film deposited on silica (b). (c,d) Experimental single-particle scattering spectra for nanorods of width $w = 40$ nm and different aspect ratios $A = L/w$, as indicated by the labels, placed on either the silica (c) or gold (d) substrates. (e,f) Numerical simulations of the scattering spectrum of the nanorods of panels (c) and (d) performed by using a finite element method (FEM) approach. In all cases, the scattering spectra are normalized to their maximum value.

For the purpose of understanding this behavior, we calculate the scattering spectra for nanorods of the same dimensions by rigorously solving Maxwell’s equations using a finite element method (FEM) approach. To reproduce the single crystalline nature of the nanorods, we model them as being faceted on four sides, with a facet width $w_f = 0.875w$. In all cases, the nanorods are assumed to be in conductive contact with the substrate at one of their facets. The choice of this configuration is based on the assumption that the surface ligands, which are initially coating the nanorods in solution, spread across the surface of the substrate during the deposition of the nanorods, which, together with the roughness of the substrate, enable a direct contact between them and the substrate. The validity of this assumption is confirmed later in the manuscript through experimental and theoretical evidences. The results of these calculations are shown in panels (e) and (f) of Figure 4-1. Comparing them with the measurements, we observe a very good agreement on the spectral position and line shape of the resonances. Importantly, the theoretical results reproduce the behavior observed in the experiment, namely the change from a size-dependent response when the nanorods are placed on silica to a largely size-independent response when placed on the gold film. Incidentally, the theoretical predictions display slightly broader resonances than those observed in the measurements. This difference could be attributed to the larger material losses in the structures used to tabulate the dielectric function that we employ in the calculations,$^{54}$ as compared to the expectedly more crystalline nanorods used in this experiment.
In order to verify that the behavior observed in Figure 4-1 is not particular to the analyzed nanorods, we measure single particle scattering spectra for over 200 gold nanorods on each substrate (silica and gold film), with different widths and aspect ratios. The results are displayed in Figure 4-2. In particular, panels (a) and (b) show the scattering spectra of the individual nanorods placed on the silica and gold substrates, respectively. The results are organized based on the dimensions of the nanorods, as indicated by the labels and the background color. We measure nanorods with \( w = 40 \text{ nm} \) and \( A = 1.7, 2.2, 3.7 \) (which correspond to \( L = 68, 88, 148 \text{ nm} \)) as well as \( w = 25 \text{ nm} \) and \( A = 2.3, 2.8, 3.6 \) (which correspond to \( L = 58, 70, 90 \text{ nm} \)), according to the specification for the colloidal solution. Examining the results of Figure 4-2a, we observe a clear jump on the average peak energy when the nominal size of the gold nanorods is changed. The small fluctuation within the same type of nanorods is a consequence of the size distribution in the colloidal solution.\(^{55}\) In contrast, as shown in Figure 4-2b, when the nanorods are placed on the gold film, their resonance energy is only weakly dependent on the size and aspect ratio of the nanoparticles. Notice that all of them fall approximately within a 0.3 eV window around the same energy. Furthermore, in this case, the scattering intensity does not scale with particle size; there instead appears to be an optimal particle size that couples light into and out of the system more efficiently. Even though the average resonance energy does not change appreciably with the significant change in the aspect ratio (from 1.7 to 3.7) of the gold nanorods, there is an appreciable fluctuation from particle to particle. This effect can be attributed to the sensitivity of the response to variations in the geometry of the particle–film interface, as well as changes in the distribution of surface ligands and the chemical composition of the environment.
Figure 4-2: Characterization of the scattering spectra. (a,b) Measured single-particle scattering spectra for a large collection of different nanorods placed on the silica (a) and gold (b) substrates. The background color and labels indicate the nanorod dimensions. (c,d) Linewidths of the different spectra of panels (a) and (b) plotted as a function of the energy of the plasmon resonance. Again, the nanorod dimensions are indicated by the color of the symbol.

We further analyze the scattering behavior of the nanorods by extracting the resonance energy and linewidths from the measured data, through the fitting of a Lorentzian function to the different experimental spectra. The corresponding results are summarized in Figure 4-2 c and d. Clearly, for nanorods on the silica substrate, the linewidth increases with resonance energy. We attribute this behavior to the larger overlap of the plasmon resonance with the interband transitions of gold, which is expected to increase the non-radiative losses, thus resulting in a broader lineshape.\textsuperscript{1,56,57} However, nanorods placed on gold show a weak relationship between linewidth and aspect ratio, with larger sizes...
resulting in a slightly larger linewidth, as shown in Figure 4-2. It is worth noting that this relationship is the opposite of what we observe for the same nanorods placed on silica. For example, considering the nominal width of 40 nm, gold nanorods with an aspect ratio of 3.7 display the narrowest linewidths when placed on silica, but the broadest linewidth when sitting on the gold film, as can be seen by comparing the data plotted in Figure 4-2c and d. This is consistent with the fact that the radiative losses increase with nanorod volume,\textsuperscript{17} while the non-radiative ones, which are associated with the material losses of the system, and therefore dependent on the dielectric function, stay constant due to the fixed plasmon energy.

In order to understand the origin of the difference in the response of the nanorods when placed on the silica and gold substrates, we calculate the induced charge and the radiation pattern associated with their plasmon resonance. In particular, we focus on a nanorod with $w = 40$ nm and $A = 3.7$, due to the large resonance energy shift when changing from silica to gold substrates, as shown in Figure 4-3a by the green and red curves, respectively. The corresponding induced surface charge maps are plotted in the upper panels of Figure 4-3b. The results for the nanorod placed on silica (left panel) confirm the longitudinal dipole nature of the resonance and, therefore, explain the observed correlation between aspect ratio and resonance position. The associated radiation pattern confirms this result. It corresponds to a dipole oscillating parallel to the substrate with a secondary lobe structure caused by the actual shape of the nanorod facet, which breaks the symmetry of the emission pattern. As expected, the majority of the radiation is emitted into the silica substrate.\textsuperscript{58}
Figure 4-3: Charge transfer plasmon mode. (a) Calculated scattering spectra for a nanorod of width $w = 40$ nm and aspect ratio $A = 3.7$ placed on the silica (green curve) and gold (red curve) substrates. (b) Induced surface charge maps (upper panels) and radiation pattern (lower panels) calculated at the resonance peaks of panel (a). The left and right columns display the results for silica and gold substrates, respectively. The insets in the lower panels show the experimental dark-field images.

On the other hand, for the nanorod placed on gold (right panel), we observe a completely different charge map. In this case, we find that the plasmon response is associated with a transfer of charge between the nanorod and the film, in which the entire nanorod is positively or negatively charged, with the film having the exact opposite charge. This
means that the scattering response of the nanorods placed on the gold film is dominated by a charge transfer mode. The radiation pattern corresponding to this mode is shown in the lower right panel of Figure 4-3b. In this case, based on the induced charge map, we expect a dipole oscillating perpendicular to the substrate, which consequently produces a doughnut-shaped radiation pattern. This is confirmed by the calculations, which also show a secondary lobe structure caused, again, by the faceting of the nanorod. Both radiation patterns are in good agreement with the experimental dark-field images shown as insets in the lower panels. It is worth noting that these results discard the possibility of the observed behavior being caused by the transversal mode of the nanorods.

So far, we have assumed that, when placed on the gold film, the nanorods are in conductive contact with the metallic surface. However, we know that, due to the chemical synthesis process, the gold nanorods are partially covered by surface ligands (cetyltrimethylammonium bromide, CTAB) when they are suspended in solution, which, during the deposition process, are expected to spread across the substrate, leaving the nanorods in direct contact with it. In order to understand the role that the surface ligands can play in the optical response of the system, we repeat the calculations of the scattering response of a nanorod deposited on the gold substrate assuming, in this case, a dielectric spacer located between the nanorod and the substrate. The results of this calculation are shown in Figure 4-4. More specifically, in panels (a) and (c), we analyze the scattering spectra of nanorods with A = 1.7 and 3.7, respectively, and fixed w = 40 nm. The solid curves display the theoretical calculations performed assuming that the nanorods are either in direct contact with the substrate (red curve) or separated from it by a 1.5-nm-thick spacer with dielectric function ε = 2 (green curve), while the black dots represent
single-particle measurements for two nanorods of nominally the same dimensions as those modeled. Clearly, in the absence of conductive contact, the scattering spectrum displays several peaks that correspond to cavity plasmons confined to the dielectric spacer,\(^5^9\). The presence of these peaks and the broader lineshape of the spectrum when compared with the corresponding one for the direct contact configuration are in sharp contrast with the experimental results. It is important to remark that none of the hundreds of single-particle measurements we have performed display any extra peak. One may argue that, due to its cavity nature, these resonances may not be visible in the experiment due to the surface roughness of the metallic film. In order to discard that possibility, we have performed a careful analysis of the topography of our metallic film, together with simulations of the scattering spectra of the system considering different types of defects in the dielectric spacer. The several peaks are always present in the scattering spectrum when the nanorods are separated from the film by a dielectric spacer.
Figure 4-4: Effect of surface ligands. (a) Normalized scattering spectra of a nanorod of $w = 40$ nm and $A = 1.7$ placed on the gold substrate. The solid curves show the theoretical predictions assuming the nanorod is in direct contact with the substrate (red curve), or is separated from it by a 1.5 nm-thick dielectric spacer with dielectric function $\varepsilon = 2$ (green curve), while the black dots correspond to the experimental single-particle measurements. (b) Comparison of the scattering spectra of the nanorod of panel (a) for different values of conductivity of the dielectric spacer, as indicated by the legend. (c,d) Same as (a,b), but for a nanorod of $w = 40$ nm and $A = 3.7$.

Interestingly, by adding a finite conductivity $\sigma$ to the dielectric function of the spacer, which then becomes $\varepsilon = 2 + i\sigma/\varepsilon_0\omega$, it is possible to recover the results obtained for the case of the nanorods being in direct contact with the substrate. This is shown in panels (b) and (d), where we plot the scattering spectra of the nanorods calculated for different values of $\sigma$ in the range $10^3 \sim 10^7 \, \Omega^{-1}\, \text{m}^{-1}$, as indicated by the legend (for reference, the static conductivity of gold is $\sim 4 \times 10^7 \, \Omega^{-1}\, \text{m}^{-1}$). Examining these results, we observe that, as the conductivity increases, the multiple peaks in the spectrum disappear and a
single resonance, located at the frequency of the charge transfer plasmon, emerges. Interestingly, this transition seems to occur for values of the conductivity below $105 \, \Omega^{-1} m^{-1}$. Beyond that value, the increase of the conductivity does not alter the spectral position of the resonance, although it makes the resonance become stronger and narrower, which is consistent with the reduced dissipation associated with an increase of the conductivity.

It is worth noting that, when comparing the spectra obtained for the nanorods sitting on the dielectric substrate with those calculated for the nanorods separated from the metallic film by a 1.5-nm-thick dielectric spacer, we observe a red shift of the scattering spectrum for the nanorod with $A = 1.7$, and a blue shift for the one with $A = 3.7$. We attribute this behavior to the differences in the coupling between the longitudinal and transversal modes of the nanorods and the metallic film, which play an important role when the nanostructures have an aspect ratio different from 1.

The results analyzed in Figure 3.4 support the hypothesis that the behavior we observe in the experiment arises from the conductive coupling between the nanorod and the gold film. The experimental and theoretical results strongly suggest that the interface between the gold nanorods and the gold film is conductive, and the resonance can be described as a charge transfer plasmon. This is compatible with low CTAB coverage on the surface of the nanorods, which we have verified by repeating the measurements shown in Figure 4-2 for nanorods that are prepared using a procedure that is expected to remove a larger fraction of surface ligands. Indeed, a recent work has shown that the CTAB coverage on the surface of nanorods is not uniform. This, together with the surface roughness of the metallic film, can enable sufficient contact points between the nanorod and the film.
Furthermore, theoretical calculations have shown that, for gaps of \( \sim 0.4 \) nm, the conductivity arising from tunneling processes can be larger than \( 105 \ \Omega^{-1} \ \text{m}^{-1} \) for moderate electric fields.\(^{61}\)

The questions that are now posed are why there is a conductivity threshold for the charge transfer mode, and why its frequency is so weakly dependent on the dimensions of the nanorod. In order to answer these questions, we use a simple analytical model similar to that presented by Perez-González et al.\(^ {45}\) to explain the behavior of charge transfer plasmon in plasmonic nanoparticle dimers bridged by conductive junctions. We first assume that the combined nanorod and substrate system acts as a capacitor with a conductive junction connecting the two elements. When illuminated, the amount of charge flowing between the particle and the film, associated with the excitation of the charge transfer plasmon mode, must be such that it cancels out the field induced between the nanorod and the film. Therefore, in a first approximation, and ignoring any inhomogeneity of the field within the facet of the nanoparticles, this charge can be written as \( Q = CdE_{\text{ind}} \), where \( E_{\text{ind}} \) is the induced field, \( C \) is the capacitance of the system, and \( d \) the distance between the two elements. The product \( Cd \) defines an effective capacitance area \( A_c = Cd/\varepsilon_0 \), which depends exclusively on the geometry of the nanorod–film junction. For instance, if, instead of a nanorod, an extended planar surface is considered, \( A_c \) corresponds to the surface area. On the other hand, the current flowing between the nanorod and the film can be approximated as \( I = \sigma A_j E_{\text{ind}} \), where \( \sigma \) is the conductivity of the junction and \( A_j \) is the junction area, which, in our case, is equal to the facet area. Then, the frequency of the charge transfer plasmon, \( \omega_{\text{CTP}} \), can be obtained from the ratio \( I/Q \). By doing so, we can write \( \sigma \propto \omega_{\text{CTP}} A_c/A_j \). This equation states that, for
a given system, there is a minimum conductivity necessary to sustain the charge transfer plasmon, in accordance with the results of Figure 4-4b and d. Furthermore, in the limit of large conductivity (i.e., beyond the conductivity threshold), the frequency of the plasmon is expected to scale as $A_j/A_c$. Then, ignoring the effect of the hemispherical ends of the nanorods, $A_c$ is proportional to the surface area of the nanorod, and therefore to $w$. This makes the ratio between the junction and capacitance areas independent of the length of the nanorod (since both of them are proportional to it), thus depending only on the ratio between the facet and the nanorod widths, i.e., $A_j/A_c \approx w_f/w$. Accordingly, we expect the frequency of the charge transfer plasmon to scale with $w_f/w$, which can be understood as the “squareness” of the nanorod, as shown in the inset of Figure 4-5.

Figure 4-5: Effect of particle shape on the charge transfer plasmon resonance. Energy of the plasmon resonance as a function of the “squareness” of the nanorods, calculated for
multiple nanorods of varied width w and aspect ratio A, as indicated by dot color and the legend. Squareness is defined as the ratio between the width of the facet w_f and width of the nanorod w, as depicted in the inset.

To test the predictions of this model, we calculate the scattering spectra of nanorods placed in direct contact with a gold substrate, and with the same widths and aspect ratios as those analyzed in Figure 4-2, but varying their w_f /w ratio. We plot the energy of the resulting scattering peaks in Figure 4-5 as a function of w_f /w, using dots of different colors for the different nanorods, as indicated by the legend. Examining these results, we observe that, as w_f /w increases and approaches 1 (i.e., a square transversal cross section), the peak energies are blue shifted and tend to an asymptote, as predicted by our model. Furthermore, we find that, for each value of w_f /w, the resonance energies of all of the nanorods investigated fall within a \( \lesssim 0.3 \) eV window, in good agreement with the experiments (see Figure 4-2), for which we expect a uniform value of w_f /w determined by the synthesis of the nanorods. This confirms that the weak dependence of the scattering spectrum of the gold nanorods deposited on the gold film arises from the charge transfer nature of the resonance. We attribute the 0.3 eV variation to the effect played by the hemispherical ends of the nanorods, which is expected to change with their dimensions. Interestingly, the scattering spectra of nanorods placed on silica are almost independent of the value w_f /w, which is consistent with the dipolar character of the dominant resonance of the scattering spectra of these structures.

4.4: Conclusion:

In summary, we have presented a detailed experimental and theoretical study of the optical response of gold nanorods placed on both silica and gold substrates. We have found that, for nanorods placed on silica, the response is dominated by a dipolar surface
plasmon whose characteristics are very dependent on the size and aspect ratio of the nanorod. In contrast, when the same nanorods are placed on a gold substrate, the scattering spectrum displays a strong charge transfer plasmon resonance, for which charge flows between the particle and the substrate. This mode, in contrast to the typical dipolar resonance, is always located around the same energy, regardless of the width and aspect ratio of the nanorod. Using rigorous solutions of Maxwell’s equations, as well as a simple analytical model, we have shown that the properties of this mode are dictated by the characteristics of the particle-film junction. The results presented here provide new insights into the interaction of metallic nanoparticles with metallic substrates, which could be exploited to design plasmonic systems that are more robust against variations in the nanoparticle geometry.
4.5: References:


(13) Knight, M. W.; Wu, Y.; Lassiter, J. B.; Nordlander, P.; Halas, N. J. Nano Letters 2009, 9, 2188.


(17) Sobhani, A.; Manjavacas, A.; Cao, Y.; McClain, M. J.; García de Abajo, F. J.; Nordlander, P.; Halas, N. J. Nano Letters 2015, 15, 6946.


(22) Huang, S.; Ming, T.; Lin, Y.; Ling, X.; Ruan, Q.; Palacios, T.; Wang, J.; Dresselhaus, M.; Kong, J. Small 2016, 12, 5190.

(37) Hoang, T. B.; Akselrod, G. M.; Argyropoulos, C.; Huang, J.; Smith, D. R.; Mikkelsen, M. H. Nature Communications 2015, 6, 7788.
(38) Huang, J.; Akselrod, G. M.; Ming, T.; Kong, J.; Mikkelsen, M. H. ACS Photonics 2017, 5, 552.
(44) Hore, M. J.; Ye, X.; Ford, J.; Gao, Y.; Fei, J.; Wu, Q.; Rowan, S. J.; Composto, R. J.; Murray, C. B.; Hammouda, B. Nano Letters 2015, 15, 5730.
(50) Song, P.; Nordlander, P.; Gao, S. The Journal of Chemical Physics 2011, 134, 074701.
(52) Kulkarni, V.; Manjavacas, A. ACS Photonics 2015, 2, 987.
(54) Johnson, P. B.; Christy, R.-W. Physical Review B 1972, 6, 4370.
Chapter 5: Light Emission from Dielectric Nanocavity

Placing nanoparticles on metal film is a promising route to create the nanometer gaps with an enhanced electromagnetic field. To minimize the radiative loss and control gaps precisely a thin dielectric spacer layer is often used. The interaction between the dielectric nanocavity and gold nanorods (AuNR) gives rise to new hybridized plasmonic modes with a dramatic decrease in radiative damping. We experimentally studied the single particle dark field scattering and photoluminescence of AuNR on nanocavity alternatively. The DF spectra resemble with the emission spectra that signifies the plasmon mediated emission. Also, when the plasmon energy matches the vibrational modes of polymer, Raman mode is enhanced instead of photoluminescence from nanocavity. Here, we have reported the light can couple out from dielectric nanocavity via both elastic and inelastic scattering process.

5.1: Introduction:

The coherent oscillation of conduction electrons on metal nanoparticles is called localized surface plasmon (LSPR)\(^1\). This light-matter interaction creates a huge electromagnetic field and has tremendous technological applications, from biological sensing\(^2,3\), spectroscopy\(^4,5\), photocatalysis\(^6,7\), and solar energy harvesting\(^8,9\). The strongest field enhancement occurs when two nanoparticles come closer within nanometer gaps. Various techniques like self-assembly using molecular linker or modern lithographic techniques\(^10,11\) are used to form nanogaps. Using these methods, creating a smaller gap less than 10 nm is challenging, lacks precision and accuracy, where the maximum coupling occurs\(^12\). So, the promising method of creating nanogap is by depositing the
metal nanoparticles on metal film (NPOM), where the nanoparticle interacts with its mirror image on the metal film\textsuperscript{13,14}. These nanogaps are conductive which results in radiative loss and broadens the linewidth of plasmon modes forming low-quality factor nanocavity. A Thin dielectric layer is placed in between nanoparticles and metal film for efficient coupling of light\textsuperscript{15}. At resonant excitation, to gap modes plasmon, the electric field gets enhanced dramatically, which is useful for various light-matter interactions applications\textsuperscript{16,17}.

The emission from plasmonic nanometal is weak. The process takes place by the radiative recombination of electron and hole after the decay of surface plasmon\textsuperscript{18,19}. Many research groups have reported the emission from single gold nanoparticles matches its dark-field scattering suggesting plasmon modes acts as a radiating antenna to couple out light in far field\textsuperscript{20,21}. However, for nanoparticle on metal film (NPOM) the electric field is enhanced and scattering property is modified due to interaction with the metal surface\textsuperscript{22}. The light emission process from dielectric nanocavity (NPOM) is not fully understood. Therefore, we systematically studied the distant dependent scattering and luminescence property between AuNR and AuF nanocavity using oppositely charged polyelectrolytes by layer by layer and a transparent monolayer quantum dots (QDs) as a spacer layer. Upon light illumination, an image dipole is formed on the metal surface and the resulting dipole interacts with the image dipole. The strong electric field is confined strongly at a dielectric nanocavity. This bound electric field reduces the radiative damping and gives rise to enhanced luminescence. Here, we experimentally demonstrated the light coupling from a dielectric nanocavity via both elastic and inelastic scattering.
5.2: Experimental Methods:

5.2.1: Layer by Layer assembly of polyelectrolytes layer:

Oppositely charged poly (sodium 4-styrenesulfonate) (PSS) negative polyelectrolyte and Poly (diallyldimethylammonium chloride) solution as positive polyelectrolyte (PDDA) was purchased from sigma Aldrich. Working solution for PSS and PDDA was made in 0.1m NaCl solution of final concentration 2mg/ml. The AuF film was dipped first on PDDA solution for 5 minutes and followed by rinsing with distilled water for 1 minute then dipped again in PSS solution for 5 minutes and washed again for 1 minute. 1, 2, and 3 pairs of PDDA/PSS were formed to get the desired height.

5.2.2: AuF-QD-Film Formation:

50 nm of gold was evaporated on top of silicon wafer using titanium as an adhesion layers. CdS/ZnS quantum dots emission $\lambda=403$ nm was purchased from Ocean nanotech and formed monolayer of film on gold film using Langmuir-Blodgett (KSV NIMA). Gold nanorods (AuNR) with hexadecyltrimethylammonium bromide (CTAB) was purchased from Nanopartz Inc. 100µl of AuNR solution was taken and diluted 10 times to 1 ml using ultrapure water. Then, 50µl of AuNR solution is taken and dropped on top of QD-AuF film and blowout using nitrogen air.

5.3: Results and Discussion:

The different gap size of nanocavity is constructed by depositing (d=0-8.5 nm) spacer layer using layer by layer assembly of polyelectrolytes and a transparent monolayer of quantum dots. The monolayer film of QD is formed on gold film (AuF) using the
Langmuir-Blodgett method\textsuperscript{24}. The plasmon resonance of AuNR couple with the gap plasmon modes and radiates light (Figure 5-1a). The QD film form continuous film and thickness is 8.5 nm as confirmed by AFM Figure 5-2b. The AuF film is rough that may contribute some roughness in QD film (Figure 5-1b right panel). Solid bright spots appear when AuNRs are deposited on top of QD-AuF (Figure 5-6) but appear the doughnut shape when deposited directly on AuF. This distinctive scattering pattern has been discussed in previous reports\textsuperscript{22,25}.

![Figure 5-1: Assembly of quantum dots layer on metal film](image)

(a) Schematic of system for study the dark field scattering: quantum dots layer is formed on gold film and gold nanorods are dispersed on top of sample (b) AFM topography of the QD film formed on AuF. The height profile from the AFM scan (right panel).
The scattering property of AuNR on nanocavity is studied using dark-field spectroscopy (experimental set up chapter 2, Figure 2-1) and the PL is measured from the same particle using incident laser $\lambda=633$ nm alternatively. The scattering property of AuNR and cavity system is studied by dark field spectroscopy (chapter 2, Figure 2-1). More than 50 single particles optical property (both scattering and enhanced luminescence) are recorded.

Figure 5-2 represents the correlated intensity maps of single AuNR particle scattering (Figure 5-2b) and photoluminescence (PL) at different nanogaps (Figure 5-2a) (AuNR: diameter 40 nm A= 2.3). From Figure 5-2 a&b, it’s obvious the plasmon resonance of AuNR peak matches with the scattering peaks.

Figure 5-2: Optical response of gold nanorods of width $w = 40nm$ (aspect ratio A: 2.3) in water.(a)single particle dark field scattering for gold nanorods (AuNR) deposited with different distance on gold film (b) Single particle photoluminescence measurement for gold nanorods (AuNR) deposited with different distance on gold film (AuF) using laser $\lambda=633$ nm.

The stark difference between the dark-field scattering and PL is at 1.5 nm gap nanocavity (Figure 5-2 a) where multiple peak appear in PL spectra while we didn’t observe additional peak at DF spectrum (Figure 5-2 b). The additional peak at PL spectra (Figure 5-2a) may be higher order hybridized mode between AuNR and gap plasmon mode. The
presence of additional peak suggests PL measurement may be better in characterizing the plasmonic interaction. We have plotted the scattering and PL spectra for 3 nm gap nanocavity (Figure 5-3). The plasmon resonance peak AuNR is different (Figure 5-3 a&b) because discrepancy in size, shape and orientation of nanoparticles. In Figure 5.3 a, the DF spectra resembles with the emission from the nanocavity. But, in Figure 5.3 b, we measured the narrower scattering peak (red spectra) that matches the DF spectra. This peak corresponds to Raman vibrational peak for polyelectrolyte layer. Despite of observing luminescence for nanogaps, the enhanced Raman vibrational modes for polyelectrolyte layer is observed (Figure 5-3b), because the plasmon resonance overlaps with the vibrational frequency of polyelectrolyte spacer layer. This suggests the strong coupling in the nanocavity that couples out light via both elastic and inelastic scattering process i.e. photoluminescence\textsuperscript{31,32} and secondary light emission process as well\textsuperscript{27}. 
Figure 5-3: Correlated single particle dark field scattering and emission spectra at 1.5 nm nanocavity (a) Dark field spectra and Luminescence spectra (b) Dark field spectra and Raman spectra

We measured emission using low power (0.67 mw) cw 633 nm laser to avoid the photothermal damage and DF scattering of AuNR placed on different gap nanocavity alternatively. Most of the scattering spectrum matches to the luminescence spectra (Figure 5-2 a & b). On resonant excitation, for AuNR directly placed on AuF, we observed background scattering (weak emission) and often cutoff by the long pass filter used for filtering the excitation source (Figure 5-4). Similarly, there is no emission from AuF as shown in Figure 5.5. The enhanced PL from nanocavity (NPOM) suggests the gap plasmon mediated enhanced emission where AuNR couples light out of nanocavity.
NPOM geometry forms metal-insulator-metal cavity (MIM) with AuNR, spacer layer and AuF. Due to refractive index difference on dielectric gap than that of metal, the light is reflected back and forth within nanocavity and gets confined in smaller mode volume\cite{14,29,30}. The LSPR of AuNR hybridizes with nanocavity forming hybrid plasmon modes reducing the linewidth and increasing scattering intensity.

Photoluminescence from AuNR is due to formation of electron-hole after the decay of localized surface plasmon\cite{33,34}. These electron-hole pair may dissipate its energy interacting with phonons, molecules energy level may lead to secondary inelastic scattering process like Raman scattering which gives the broad background\cite{27} and small number of charge carriers recombine which emits photon\cite{35}. In other words, after the absorption of photon by metal nanoparticles, the electrons are excited from lower d band to sp band leaving behind the hot holes. This electron-hole can recombine radiatively giving emission through the interband transitions. Additionally, the electron can recombine with holes after dephasing of plasmon resonance and called as plasmon enhanced emission.

For NPOM system, we have lower radiative loss with enhanced electric field and increases the density of plasmon states significantly\cite{4,34}. The enhanced density of plasmonic states increases the radiative decay rate which enhances the emission, similar to enhancing spontaneous emission of emitting dipole\cite{4,36}. In simple words, the energy of electron and holes from AuNR matches the gap modes plasmon, thus couples strongly to gap plasmon modes that radiate PL strongly. Here, AuNR acts as an antenna which couple out light via inelastic light emission and photoluminescence out of nanocavity with significant enhancement due to surface plasmon\cite{37}. 
Figure 5-4: Correlation of Dark Field scattering of gold nanorods (A: 2.2) and corresponding its emission (red spectrum) deposited directly on AuF.

Figure 5-5: Photoluminescence spectra from just from AuF film.
Figure 5-6: Optical characterization of sample (a) bright field image of quantum dots film on gold film (b) Dark field image of gold nanorods on top of quantum dots and gold film.

5.4: Conclusion:

We experimentally measured the single particle DF and PL of AuNR on different gap modes using polyelectrolytes and QDs as spacer layer alternatively. From DF measurement, we observed reduced in linewidth and increased in scattering intensity compared to directly place on metal film. Similarly, on optical excitation, PL is measured from nanogaps while it quenches when directly placed on AuF. The DF and PL spectra matches which signify the plasmon mediated gap PL. In addition, we observed the enhanced Raman modes for polyelectrolyte layer when its vibrational band is in resonance with gap plasmon modes. This signifies the strong electric field in nanocavity which couples out via Raman scattering and PL process. The mechanism may be due to interaction between LSPR of AuNR and gap plasmon mode which results in reduced radiative loss and high-quality factor cavity which enhances the spontaneous emission.
5.5: References:


Chapter 6: Temperature Mediated Assembly of Gold Nanorods on Gold Film and its Near-field Optical Characterization

Assembly of colloidal anisotropic nanoparticles into 2-dimensional structure is widely research area for years because of its unique optical properties. Despite continuous research effort, the assembly of nanoparticles is still challenging. Here, we demonstrated simple, cost-effective and reproducible method of assembly of gold nanorods (AuNR) by droplet evaporation method. When the AuNR solution is evaporated at 35°C the so-called coffee ring is minimized and the AuNR nanoparticles are deposited into monolayer film without forming the ring. The SEM image of sample shows ordered film of AuNR over large area. It is believed increasing the temperature will induce the Marangoni effect that creates the surface tension gradient and moves AuNR away from the line of contact of solution. Thus, deposited AuNR optical property is studied using super resolution near field optical microscopy (ANSOM).

6.1: Introduction:

Assemblies of anisotropic plasmonic nanostructures into two-dimensional structures have been widely studied in recent years because we can tailor the unique optical properties of nanoparticles that can be used in various applications from catalysis, photovoltaics, optoelectronic devices, and spectroscopy\(^1-4\). However, assembly of nanoparticles into films and two dimensional (2 D) structures is still challenging. Different methods like Langmuir-Blodgett\(^5\), evaporative self-assembly\(^6,7\), assembly by immobilization using molecules and polymer\(^8\), DNA linkers have been widely used\(^9\). Out of these, droplet evaporative self-assembly methods have been widely used because it’s simple and cost
effectiveness\textsuperscript{1}. But, when dried the nanoparticles are generally assembled at the point of contact of solution forming the ring structure called “coffee ring”\textsuperscript{10}. Nanoparticles are usually assembled in the ring region while fewer nanoparticles are inside the ring with inhomogeneous particle distribution on the assembled surface that can be detrimental for the applications which require the uniform deposition of the particles. There is a continuous effort from many research groups to minimize these rings by changing the shape and size of nanoparticles\textsuperscript{11}, solvents\textsuperscript{12}, changing the substrate, particle concentration\textsuperscript{13} etc. But, still minimizing the coffee ring is challenging and it is desirable to have a homogenous assembly of nanoparticles forming the larger structures. Gold nanorods (AuNR) have been widely studied because their optical properties can be tuned just by changing their aspect ratio (width and length). Especially, AuNR assembly to two dimensional or superstructures is interesting because the optical properties (surface plasmon resonance) depend on the orientation of AuNR, the interparticle distance. Thus, the assembly of AuNR into 2 D structure is always beneficial for maximizing the electromagnetic field beneficial for different applications.

Here, we studied the different methods of deposition of gold nanorods (AuNR) on gold film (AuF) like droplet evaporation solution at room temperature, at higher temperature, spreading AuNR solution using ethanol solvent and also adsorption of AuNR on the surface of polyvinyl pyridine polymer (PVP) functionalized AuF. We have demonstrated the droplet evaporated assembly of AuNR at a higher temperature than the room temperature; reduces the conventional “coffee ring” and deposits the thin uniform AuNR layer at the center of the drop. The AuNR nanoparticles deposition methods, dark-field, SEM imaging and near field optical characterization will be discussed systematically.
6.2: Experimental Methods:

6.2.1: Assembly of AuNR at room temperature:

About 100 nm thick film AuF was deposited using electron beam evaporation. Gold nanorod (AuNR) with CTAB as capping ligands was obtained from Nanopartz Inc. AuNR with nominal size of diameter 40 nm and length of 80 nm was used. The excessive surface ligand was removed through one round of centrifugation. About 500 µl of AuNR solution was taken and diluted upto 1.8 ml in centrifuging tube. The diluted solution was centrifuged at 5000 RPM for 5 minutes. The supernatant solution was discarded, and the residue was re-suspended by adding about 200 µl of ultrapure DI water. About 50 ml of AuNR solution was dropped on AuF and dried at ambient temperature.

6.2.2: Assembly of AuNR by spreading ethanol:

Same procedure as above except ethanol solution was dispersed on AuF film before dropping AuNR solution. The ethanol solution helps the spread the AuNR solution and dried at room temperature.

6.2.3: Assembly of AuNR at different temperature:

Same procedure as above (section 6.2.1) except the AuF film was placed at 35°C on hot plate and about diluted 50 µl of AuNR solution was dropped and dried at 35°C. Similar procedure was used for forming assembly of AuNR at 55°C.

6.2.4: Assembly of AuNR by immobilization of polyvinyl pyridine polymer:

Poly 4-vinyl pyridine (PVP) was purchased from Sigma Aldrich and 1wt % solution was made by dissolving PVP in ethanol solution. The PVP polymer was self-assembled
by dissolving AuF substrate in 1wt % ethanol solution for 4 hours and washed gently using ethanol to remove loosely attached PVP. Gold nanorods solution was prepared using same procedure as above. For assembly of AuNR on PVP functionalized AuF. The diluted AuNR solution was heated at ~35°C on hot plate and PVP functionalized AuF is kept inside AuNR solution. The AuNR gets adsorbed at PVP functionalized AuF ~ 1 hour and we can monitor the adsorption process by monitoring the color change of solution.

6.3: Results and Discussion:

6.3.1: Droplet evaporation methods

Droplet evaporation method is widely used to form ordered structures over the years. During this evaporation method, most of the particles are dried at the periphery of the drop creating the ring called as the “coffee ring” region (Figure 6-1). Particles are randomly oriented at the coffee ring i.e. less likely to get ordered structures at the “coffee ring” region. While few particles assemble at the center of the ring (Figure 6-1b). Figure 6.1 c represents the bright field image of AuNR assembled at room temperature.
Figure 6-1: Evaporative self-assembly of gold nanorods on gold film (a) Dark field scattering of gold nanorods assembly. The nanorods are deposited at the coffee ring (b) Dark field scattering of gold nanorods assembly inside the ring (scale bar 5 µm) (c) Bright field image of gold nanorods showing the coffee ring (scale bar 20 µm)

In this context, we deposited the AuNR by drop evaporation at higher temperature than the room temperature. Figure 6-3 shows the droplet evaporation of AuNR solution and film formed at 35°C and 55°C. When AuNR are deposited at higher temperature the “coffee ring” region is minimized, and the nanoparticles are deposited inside the ring. The film formation is characterized using dark field imaging and by scanning electron microscopy (SEM).

Figure 6-3a shows the dark field image of AuNR deposited at 35°C. From the SEM image, Figure 6-3b taken inside the ring. Its clear AuNR formed monolayer film over the area inside the ring. Similarly, Figure 6-3c shows the dark-field image of AuNR deposited at 55°C. At 55°C, AuNR forms the monolayer film but size of the film formed is smaller than that of 35°C. It seems there may be a certain critical temperature where AuNR assembles into uniform film and covers the large area.
The mechanism of the coffee ring formation is explained in terms of capillary flow and pinned contact line process\textsuperscript{14}. During the evaporation of the solution, a line of contact is formed, and water evaporated from this line so there is a flow of solutes towards the contact line by capillary action and solutes dry at the ring forming the “coffee ring” structure. In contrast, increasing the temperature, a temperature difference is created between a contact point of liquid on the surface (substrate/solution interface) and in solution drop. Water evaporates faster at the center (Liquid drop) and creates the surface tension gradient between the point of contact and inside the liquid drop. This process is called Marangoni effect. The surface gradient causes AuNR deposit inside forming the AuNR 2D structure or film.

The optical near field characterization of AuNR deposited by droplet evaporation (at room temperature) is performed using ANSOM at wavelength 1597.5 cm\textsuperscript{-1} laser. Figure 6-2a. shows the topography of AuNR and Figure 6-2b shows the height profile of AuNR represented by dashed line (Figure 6-2a). The near field optical amplitude (Figure 6-2c) for AuNR shows the lower amplitude than the AuF (dash line). In addition, upper part on the nanoparticle red circle in Figure 6-2c amplitude is lower than bottom part. This is clearer in line profile of near field amplitude (Figure 6-2d). Similarly, near field phase profile of same particle upper part is positive while the lower end is negative (Figure 6-2f). It shows some ligands CTAB or any organics (red circle) is attached with AuNR and may have resonance with the excitation laser that gives the phase change between the AuNR and the surface ligands (Figure 6-2f). We demonstrated the material specific contrast of nanoparticles using ANSOM\textsuperscript{16-18}. 76
Similar results are obtained for the AuNR film formed at high temperature.

Figure 6-2: Droplet evaporative assembly AuNR on AuF film (a) Topography of AuNR-AuF in ethanol recorded simultaneously. (b) height profile of topography of AuNR-AuF (c) Near field optical amplitude (O3) (d) Line profile of third harmonic near field amplitude (e) Near field phase (S3) (f) Line profile of optical phase
6.3.2: Evaporative self-assembly of AuNR using ethanol as solvent

To minimize the coffee ring and form packed AuNR film, we spread ethanol solvent on AuF and deposited the AuNR drop on top. AuNR solution spreads on the gold surface and doesn’t form the coffee ring but nanoparticles are distributed randomly on the substrate. Figure 6-4a, b shows the AuNR are single and randomly distributed. When the ethanol covers the whole area of AuF the evaporation is faster and AuNR nanoparticles dry easily faster in some areas. Besides, ethanol dissolves the CTAB ligands of AuNR, the ligands may come apart from nanoparticles surface and forms CTAB film in some
part of the substrate and in some area, AuNR may be buried underneath the surface (Figure 6-5a).

Figure 6-4: Assembly of gold nanorods by spreading ethanol solution. (a) Dark field image of gold nanorods (b) SEM image of the gold nanorods (scale bar 1 µm)

The AuNR formed by evaporation using ethanol solvent is characterized using ANSOM. Figure 6-5a. represents the topography image of AuNR dispersed on AuF substrate. In topography, AuNR seems thinner and surrounded by surface ligands which are confirmed by AFM height profile (Figure 6-5b). Figure 6-5 c,d shows the near field optical amplitude and near field optical phase of AuNR on AuF substrate at laser wavelength of \(\lambda = 1597.5 \text{ cm}^{-1}\) recorded simultaneously. Near filed optical amplitude AuNR appears
brighter compared to AuF coated with CTAB surface ligands (with respect to droplet evaporative self-assembly Figure 6-2c, d). The amplitude signal is similar for two different nanoparticles in Figure 5d which suggests AuNR is surrounded by CTAB. Figure 6-5 e shows the near field phase for AuNR is lower while for AuF film is positive (maximum). i.e there is a phase difference between the nanoparticle and AuF substrate. The phase difference between substrate and AuNR particles may be the excitation source is in resonance with CTAB while AuNR doesn’t have the resonance. This suggests during solvent evaporation from AuNR solution, surface ligands (CTAB) comes off from AuNR and covered the AuF surface.
Figure 6-5: Evaporative assembly AuNR on AuF film in presence of solvent (a) Topography of AuNR-AuF in ethanol recorded simultaneously. (b) Height profile of topography of AuNR-AuF in ethanol (c) Near field optical amplitude (O3) (d) Line profile of third harmonic near field amplitude (e) Near field phase (S3) (f) Line profile of optical phase.

6.3.3: Assembly of AuNR using polymer modified AuF

Figure 6-6 shows the adsorption of AuNR nanoparticles on PVP functionalized AuF. AuNRs are adsorbed from solution to the surface of PVP modified AuF. As seen in
Figure 6-6a, b, AuNR nanoparticles are adsorbed on the PVP functionalized substrate and is mostly single particles without aggregation.

The PVP polymer adsorbs strongly on the substrate by pyridyl group\textsuperscript{19}. There are many unbound pyridyl group even after adsorption of PVP on the substrate which adsorbs AuNR particles on the PVP modified surface. The adsorption of AuNR is due to electrostatic interaction between AuNR with PVP functionalized AuF. The surface ligands of AuNR screen each other in solution and the repulsive interaction between the adsorbed AuNR and solution AuNR inhibits further adsorption.
Figure 6-6: Images of gold nanorods immobilized on gold film modified using polyvinyl pyridine (a) Dark field image (b) SEM image of gold nanorods (AuNR) on gold film (AuF) (scale bar 1 µm)

Figure 6-7 shows the topography and optical near field amplitude and phase of thin film of self-assembled PVP polymer. The excitation laser 1597.5 cm\(^{-1}\) has resonance with carbonyl stretch of PVP polymer\(^{20}\). The excitation laser 1597.5 cm\(^{-1}\) has resonance with carbonyl stretch of PVP polymer. To confirm the PVP is adsorbed on AuF substrate, the near field characterization is carried out. Figure 6-7a show the topography of PVP film on AuF. From height profile (Figure 6-7b) the height of self-assembled PVP film is ~3.5 nm. The near field amplitude of PVP film is lower than AuF (Figure 6-7c) because PVP polymer has resonance with excitation source. But there is no change is near field phase between PVP and AuF (Figure 6-7f) even after absorption with laser. Since the polymer film is thin, the near field interaction of tip is stronger for AuF than the PVP film because of strong plasmon enhanced coupling between probe and AuF\(^{21}\). This may be one of the drawbacks for the near field imaging system.
Similarly, we characterized self-assembled AuNR by PVP modified surface. Figure 8 shows the topography (Figure 6-8a) and near field amplitude and phase of AuNR. The near field amplitude of AuNR on PVP modified AuF (Figure 6-8c) shows the negative contrast than the PVP AuF (Figure 6-8d). AuNR doesn’t have any resonance with laser and gives the negative contrast. Similarly, there is phase change in near field phase between AuNR and PVP-AuF (Figure 6-8f).
6.4: Conclusion:

In conclusion, different methods for self-assembly AuNR in the AuF substrate are studied. We have demonstrated by drying the AuNR solution at 35°C, the “coffee ring” is minimized and homogenous deposition of AuNR into 2 D film is achieved. Similarly, when the nanoparticles solution drop is evaporated in the presence of ethanol as solvent, the surface ligand of AuNR is removed and surrounds the nanoparticles. We imaged the AuNR deposited by different methods in the mid-infrared region and reported the material-specific optical contrast using super resolution ANSOM. Most important, we
demonstrated a simple method of preparing the film of anisotropic AuNR into a monolayer film. Such methods of assembly of colloidal nanoparticles into 2 D structure can be excellent substrates from SERS to sensing applications.
6.5: References:

(20) Harnish, B.; Robinson, J. T.; Pei, Z.; Ramström, O.; Yan, M. Chemistry of materials 2005, 17, 4092.
Chapter 7: Stripping and Transforming Alloyed Semiconductor Quantum Dots via Atomic Interdiffusion

We report the transformation of near-infrared CdSeTe/ZnS quantum dots (QDs) that are exposed to water. When the colloidal QDs with 840 nm emission wavelength and 75 nm spectral line width are self-assembled on water surface and transferred to an oxide-coated silicon wafer using a Langmuir–Blodgett (LB) procedure, two prominent relatively sharp photoluminescence (PL) bands are observed at \( \sim 630 \) and \( \sim 660 \) nm peak wavelengths with line width of \( \sim 23 \) and \( \sim 39 \) nm, respectively. On the other hand, the PL spectrum of the QDs as they are assembled on the water surface is essentially the same as that of the solution phase. Structural analysis of the LB films shows that the QDs are stripped off the stabilizing excess surfactant molecules by the preferential interaction at the water–air interface. After the film is transferred, the QDs are interfaced with each other and with the substrate directly, while covered with the stack of surfactant molecules from the top. Based on analysis of the chemical composition using X-ray photoelectron spectroscopy of the LB film, the transformation of the CdSeTe/ ZnS nanocrystals is attributed to a diffusion of Te atoms from the core to the shell that can initiate inward diffusion of S atoms. This atomic interdiffusion minimizes lattice mismatch as the larger Te atoms are replaced by the smaller S atoms and can lead to formation of either CdSe/CdS or CdSeS nanocrystals that emit at 630 and 660 nm wavelengths, respectively.

7.1: Introduction:

\[3\] This chapter has been published previously as Kafle, B.; Tesema, T. E.; Kazemi, A.; Habteyes, T. G. *The Journal of Physical Chemistry C* 2016, 120, 12850.
As the synthesis of semiconductor nanocrystals is advancing, understanding their behavior under different environmental conditions is critically important for many applications including biological imaging,\textsuperscript{1} solar cells\textsuperscript{2-4}, and detection\textsuperscript{5-7}. To date, chemical, photochemical, and photophysical studies of semiconductor nanocrystals have been focused on binary nanocrystals such as CdSe,\textsuperscript{8-18} CdTe,\textsuperscript{19-23} PbS,\textsuperscript{23-28} and PbSe\textsuperscript{28-30} quantum dots (QDs). In general, for these binary QDs, the expected changes in optoelectronic properties are related to chemical modification of the crystal surfaces that can be passivated by growing higher band gap materials\textsuperscript{31-33} and surface chemical treatments.\textsuperscript{34-38} One of the attractive characteristic of semiconductor QDs is tunability of their band gap energy or emission wavelength simply by changing their size for a fixed material composition.\textsuperscript{39} However, the tunability afforded by size variation is limited and does not allow covering the NIR spectral region, for example, using the most common CdSe and CdTe nanocrystals. QDs that absorb and emit NIR photons are needed for both biological imaging (due to the deeper penetration of NIR radiation into tissues than visible wavelengths)\textsuperscript{40,41} and for solar cell applications as the NIR region covers a significant portion of the solar spectrum. Alloyed ternary nanocrystals such as CdSe\textsubscript{1-x}Te\textsubscript{x} provide broader band gap tunability to cover the 700–900 nm spectral region via variation of the composition x.\textsuperscript{42-44} This has been the motivation for the continual advancement of chemical synthesis of alloyed nanocrystals.\textsuperscript{43,45-49} However, the behavior and stability of alloyed nanocrystals can differ from the binary nanocrystals drastically because of the lattice mismatch between the binary components, and yet post growth studies of physical and chemical properties is lacking. Understanding their stability and
behavior under different environmental exposure is critically important for any technological application.\textsuperscript{50}

In this work, using CdSe\textsubscript{1−x}Te\textsubscript{x} QDs as model systems, we study the transformation of alloyed nanocrystals self-assembled on water surface. The formation free energy (\(\Delta A\)) of an alloyed CdSe\textsubscript{1−x}Te\textsubscript{x} nanocrystal at its equilibrium configuration \(\sigma\) can be written as

\[
\Delta A (\sigma) = A(x, \sigma) - [(1 - x)A_{\text{CdSe}}(a_{\text{CdSe}}) + x(A_{\text{CdTe}}) + E(x)]
\]

(1)

where \(A\), \(A_{\text{CdSe}}\), and \(A_{\text{CdTe}}\) are the Helmholtz free energies of the alloy, pure CdSe, and pure CdTe, respectively, containing the same number of Cd atoms; \(a_{\text{CdSe}}\) and \(a_{\text{CdTe}}\) are the equilibrium lattice constants of the binary compounds; and \(E(x)\) is the strain energy cost to maintain lattice coherence at the interface.\textsuperscript{51} For solids, where the volume change is negligible, the changes in the internal energy (\(\Delta U\)) and enthalpy (\(\Delta H\)) can be assumed equal, and the Gibbs free energy change (\(\Delta G = \Delta H - T\Delta S\)) can be used in place of \(\Delta A = \Delta U - T\Delta S\), where \(T\) is temperature and \(\Delta S\) is entropy change. Generally, \(\Delta H\) is positive that results in large miscibility gap in the \(x-T\) phase diagram, where the binary components phase separate and exist at their equilibrium lattice constants. Extensive theoretical studies by Zunger and co-workers show that the interfacial strain energy can lower \(\Delta H\) to an extent that it can be negative, resulting in growth conditions in which ordered alloyed and superlattice crystal structures can be formed even at room temperature.\textsuperscript{51,52} However, depending on the thermodynamic and kinetic conditions, atomic interdiffusion can transform the fabricated alloyed nanocrystals to different crystal forms and compositions. Atomic interdiffusion in epitaxially grown semiconductor heterostructures has been observed for various systems including GeSi/Si\textsuperscript{53,54} and
InGaAs/GaAs\textsuperscript{55,56} interfacial structures at much lower temperature than expected according to the activation energy required for atomic diffusion. Although the reason for the low temperature interdiffusion has been debated\textsuperscript{57} following the first report,\textsuperscript{53} it is likely that the lattice strain enhances crystal defect concentration that is known to facilitate atomic diffusion.\textsuperscript{55} Interfacial diffusion has also been observed in colloidal nanorods with CdTe/CdSe heterojunction, where the diffusion of Te and Se atoms across the junctions results in nanorods with reduced length-to-width aspect ratio and uniform composition across its length and width.\textsuperscript{58} This work is focused on providing experimental evidence for the transformation of NIR CdSeTe/ZnS core/shell QDs to red-emitting nanocrystals when the NIR QDs self-assembled on water surface and transferred to a solid substrate. The crystal transformation is studied by analyzing the photoluminescence (PL) spectral characteristics as it has been successfully applied in previous studies of interdiffusion in epitaxially grown semiconductor heterostuctures.\textsuperscript{56} The interpretation of the PL data is supported by analysis of the chemical composition using XPS as well as structural and size analysis using atomic force microscope (AFM) and transmission electron microscope (TEM). When the alloyed QDs that emit at 840 nm are assembled on water surface, transferred to an oxide coated silicon wafer, and photoexcited, two new emission peaks at ~630 and ~660 nm are observed, which are assigned to CdSe and CdSeS core nanocrystals, respectively. A plausible mechanism is suggested for the crystal transformation. The alloyed CdSeTe/ZnS core/shell QDs are likely to be in metastable state due to lattice mismatch and the strain energy cost as well as concentration of point defects. There is about 6\% lattice mismatch between CdSe and CdTe and 17\% between ZnS and CdTe.\textsuperscript{59} Lattice strain is believed to increase
concentration of point defects\textsuperscript{55} that reduces the resistance for diffusion compared to in a perfect crystal.\textsuperscript{60} On the other hand; the lattice mismatch is minimized if the relatively larger Te atoms are replaced by S atoms through the process of atomic interdiffusion.

\textbf{7.2: Experimental Methods:}

The CdSeTe/ZnS core/shell QDs suspended in toluene were obtained from the NanoOptical Materials Inc. To make the solution suitable for LB procedure (Figure 2-3), the toluene solvent was evaporated in vacuum, and the QDs were resuspended in chloroform to attain concentration of 10 mg/mL. The LB films were prepared on oxide coated silicon wafer that was cleaned by sonicating in acetone, isopropanol, and ultrapure water for 5 min each, followed by 5 min ultraviolet ozone treatment (Novascan Technologies, Inc.). After the substrate was rinsed with ultrapure water and blow dried with nitrogen, it was immersed in the ultrapure water subphase in the LB trough (KSV NIMA). The QD solution was gently applied to the water surface using Hamiltonian microliter syringe and was allowed to stabilize for different duration depending on the target exposure time of the QDs to the water surface. The film was then compressed at a typical speed of 10 mm/min until a target pressure of 20–35 mN/m was attained. The compressed film was stabilized for about 5 min and transferred to the substrate by pulling the substrate out at a speed of 5 mm/min at a constant compression surface pressure. The transfer was also carried out by scooping the compressed film manually holding the substrate at 5°–10° from the water surface and gently pulling out, which resulted in more continuous film.

\textbf{7.3: Structural and Optical Characterization:}
Schematic of the experimental setup used for the optical characterization of the QD films is shown in Figure 2-2 (Chapter 2). The excitation laser is focused at the AFM tip–sample junction using a parabolic mirror (numerical aperture, NA = 0.46). The AFM (Neaspec GmbH) is operated by scanning the sample, while the tip is stationary. The topography and PL intensity images can be obtained simultaneously but to avoid PL quenching by the tip, the images are obtained sequentially without losing the center of the scan. That is, during the PL scan, the tip is retracted up vertically, and intensity images are obtained detecting the emitted photons using a single photon counting module (Excelsitas Technologies Corp.). (path b Figure 2-2).

The PL spectra of an area of interest are acquired by directing the emitted light to the spectrometer (IsoPlane Spectrograph of Princeton Instruments) that uses thermoelectrically cooled (−75 °C) and back-illuminated deep depletion CCD camera. The results obtained at 532 nm excitation wavelength are used in our subsequent discussion. However, the results are also reproduced at 405 and 633 nm excitation wavelengths. In addition, the PL spectra of the QDs were recorded as the QDs were assembled on water surface. For this part of the experiment, a transparent 2 in. wafer holder was used to contain the water so that illumination and collection could be performed through the bottom of the container. The size of the QDs has been analyzed using a JEOL 2010 TEM operated at 200 kV acceleration voltages. A significant amount of the excess surfactant molecules (mixture of trioctylphosphine oxide and hexadecylamine) was removed to improve the image contrast. The chemical composition of the QD film was analyzed using X-ray photoelectron spectrometer (Kratos Ultra DLD spectrometer, Al Kα source at 225 mW). Three areas per sample were analyzed. Low and
high-resolution spectra were acquired at 80 and 20 eV pass energies, respectively. Charge neutralizer was utilized for charge compensation at bias voltage of 3.1 V, filament voltage of −1.0 V, and filament current of 2.1 A. Data analysis and quantification were performed using the CasaXPS software, and a Shirley background was used. All the spectra were charge referenced to the C 1s at 285.0 eV.

7.4: Results and Discussion:

A representative TEM image of the QDs is presented in Figure 7-1a, and the size distribution is plotted in Figure 7-1b. The average diameter is determined as 6.7 ± 0.8 nm, where the uncertainty represents one standard deviation. The PL spectra of the QDs in solution (Figure 7-1c) confirm that replacing the toluene solvent with chloroform as described in the Experimental Section has no effect on the emission property of the QDs as can be seen from the overlap of the blue and green curves with peak position at λ = 840 nm and full width at half-maximum (fwhm) of ~75 nm. The QDs have also similar spectral characteristics when they are assembled on the water surface as shown by the red curve. The AFM height (Figure 7-2a) and phase (Figure 7-2b) images show the packing of the QDs, where the thickness of the excess surfactant deposited on top of the QDs is minimal. In this region, the thickness of the QD film ranges from 10 to 25 nm compared to ~6.7 nm average diameter of the QDs determined from the TEM images. Assuming about 1.5 nm thickness of surface ligands, the smallest film thickness (~10 nm) determined from the AFM images agrees with the TEM data. However, the film thickness is much larger than 10 nm in the significant portion of the film, indicating aggregation of the QDs (while on the water surface during the LB procedure) that produces thicker than a monolayer film. In the overwhelmingly large portion of the film,
the QDs are covered with thick layer of excess surfactant as shown in Figure 7-2c-e. The stabilizing excess surfactant can be removed at a risk of introducing destabilizing effects, but it is not necessary for the present study. When the solution is spread over water, the QDs and the stabilizing excess surfactant form separate layers as a result of different favorable interaction at the water-air interface. In effect, the QDs are confined between the water surface and the excess surfactant for the duration of the LB procedure. After the transfer, the naked surfaces of QDs are interfaced with the substrate directly and covered by the blanket of surfactant layer from the top. In this regard, the presence of the excess surfactant is beneficial for the present study because it minimizes exposure of the QDs to air (oxygen) during and after the film preparation, prolonging their stability at ambient condition.
Figure 7-1: (a) TEM image of the NIR CdSeTe/ZnS QDs used in this study. (b) Size distribution of the QDs. (c) Absorption and PL spectra of the QDs suspended in toluene (blue line), suspended in chloroform (green line), and assembled on water (red line)
Figure 7-2: AFM height (a) and phase (b) images of the LB film of QDs, where coverage with surfactant (S) molecules is minimal. (c) AFM image of the QD film coated with thin layer of surfactant layer. (d) AFM image of the QD film coated with stack of surfactant layer (representative of large portion of the film). (e) Line profile across the dashed line in (d) shows the thickness of the surfactant layers.

The results obtained on the QD film that is exposed to water for about 7 min are presented in Figure 7-3. In the topographic AFM image displayed in Figure 7-3a, stacks of surfactant molecules are evident but the PL intensity image (Figure 7-3b) obtained at $\lambda = 532$ nm excitation wavelength reveals that the QDs are present underneath the thick surfactant layer. The variation of the PL intensity across the scan area ($90 \times 90 \mu m^2$) confirms that the QD film is not uniform throughout. The relatively high intensity in some areas is indicative of aggregation of the QDs. This type of non-uniformity of LB film has not been observed for CdSe/ZnS and CdSeS/ZnS core/shell QDs, where uniformly close-packed monolayer films are obtained, consistent with previous studies.\textsuperscript{61}
Figure 7-3: Results on the QD film exposed to water for ∼7 min. (a) AFM and (b) PL scan images of the same area (90 × 90 μm2) of the QD film coated with excess surfactant. (c) Representative PL spectra obtained at different locations on the film. The variation of the PL at different locations is due to the non-uniformity of the film, which can also be seen in the PL intensity image in (b). Enlarging the intensity scale by a factor of 20, two weak peaks are observed at ∼630 and ∼660 nm with different relative intensity at different locations as seen in the inset of (c).

Nevertheless, for the alloyed QDs exposed to water for 7 min, the PL spectra (Figure 7-3c) acquired from different areas are similar apart from the intensity variation that is also evident in the intensity image. The PL peak observed at 840 nm in solution is blue-shifted to ∼820 nm, and the line width is broadened from 75 to ∼83 nm, which may indicate significant changes in the surface chemical properties and introduction of defects.
when the film is transferred to the substrate. In contrast, for CdSe/ZnS and CdSeS/ZnS QD films, the spectral characteristics of the QDs in the solid film are the same as that of the QDs suspended in solution. This stability difference can be attributed to the reactivity of the CdSeTe QDs and the ZnS coating is less likely to be a continuous shell. The more striking effect of exposing the alloyed QDs to water and transferring to the solid surface is the observation of weak peaks at 630 and 660 nm that do not appear in the solution phase PL spectra (see Figure 7-1c) and in the spectra of the QDs as they are assembled on the water sub-phase before the film transfer. As can be seen in the inset figure in Figure 7-3c, the relative intensity of the two new peaks varies when the spectra are acquired at different locations, but the peak wavelengths are consistently within the ranges of 630–633 and 660–665 nm (for simplicity, these peaks will be referred as 630 and 660 nm peaks from now on). The results on the QD film exposed to water for ~20 min is presented in Figure 7-4.
Figure 7-4: Results on the QD film exposed to water for ∼20 min. (a) AFM and (b) PL scan images of the same area (90 × 90 μm2). (c) Representative PL spectra obtained by centering selected regions [marked 1, 2, and 5 in (b)] in the laser focus.

As discussed above, the QDs are covered with excess surfactant layer (Figure 7-4a), and the PL image (Figure 7-4b) shows intensity variation within the scan area. Five regions are numbered in the PL intensity image for further analysis. The representative PL spectra shown in Figure 7-4c are drastically different from that of the solution phase shown in Figure 7-1c. The weak intensity peaks at 630 and 660 nm observed in Figure 7-3 (∼7 min exposure time) are now dramatically enhanced to the extent that they are comparable to or stronger than the original peak at 820 nm. The new peaks have characteristically much narrower line widths (∼23 nm for the 630 nm and ∼39 nm for the 660 nm) than the peak at 820 nm that has a line width of ∼83 nm. Clearly, these short wavelength peaks with narrow line widths cannot be assigned to emissive deep trap
surface states, which usually have very broad spectral features and appear at longer wavelengths than the main core emission resonances.\textsuperscript{62,63} As mentioned above, the preferential interaction at the water-air interface pushes the surfactant molecules up and leaves QDs on the water surface. The fact that the relative intensity of the 630 and 660 nm peaks is higher for films exposed to water for longer time suggests that the origin of the new peaks is related to interfacial interaction on the substrate that is possible when the QDs are stripped off the stabilizing excess surfactant molecules, and complete stripping of the surface ligands by the preferential interaction at the water-air interface takes longer than 10 min. For understanding the origin of the new emission peaks, the spatial distribution of the emitters has been analyzed using spatio-spectral imaging as demonstrated in Figure 7-5a-c. That is, using short-pass and long-pass spectral filters, the emission peaks in the red and near-infrared spectral regions are selectively mapped as shown in Figure 7-5b and c. Comparing the short (\(\lambda < 695\) nm, Figure 7-4,Figure 7-5b) and long (\(\lambda > 750\) nm, Figure 7-5c) wavelength intensity images, significant differences can be observed in the spatial distribution of the emitters. For example, the regions labeled 2 and 4 are the brightest spots when shorter wavelength photons are detected as seen in Figure 7-5b. But when the longer wavelength photons are detected, these regions have about average PL intensity as seen in Figure 7-5c. On the other hand, region 1 has the highest intensity when the longer wavelength photons are detected but only average intensity for short wavelength photon detection (similar results obtained on a different sample are compared in Figure 7-8). The stark difference in the spatiospectral images clearly indicate that the emission peaks in the red (\(\lambda \sim 630\) and 660 nm) and near-infrared (\(\lambda \sim 820\) nm) spectral regions do not originate from the same nanocrystals and therefore
cannot be assigned to an interface or deep trap surface states within the alloyed CdSeTe/ZnS quantum dots. Hence, the 630 and 660 nm peaks must be due to new nanocrystals that are formed when the alloyed NIR QDs are exposed to water and transferred to a solid substrate. The relative photostability of the nanocrystals is studied by monitoring the PL intensity at 630, 660, and 820 nm wavelengths as a function of time, while keeping the laser focus at the region labeled 3 in Figure 7-5b and c, where the PL intensities in the two images are comparable.

Figure 7-5: Spatiospectral analysis of the sample region imaged in Figure 5.5. (a) Application of short-pass and long-pass filters to selectively map the different spectral regions. The PL scan obtained with short-pass (b) and long-pass (c) reveals different spatial localization of the red-emitting and NIR-emitting quantum dots (compare the areas marked 1, 2, and 4 in the two PL intensity images). (d) PL spectra obtained by centering the region marked 3 (b, c) in the laser focus and monitoring the PL spectra as a function of time. (e) Peak PL intensity extracted from (d) plotted as a function of time.
The photobleaching trend can be seen in the representative spectra (Figure 7-5d) acquired at different times. For more quantitative comparison, the peak intensities are plotted as a function of time in Figure 7-5e, after normalization of the intensities such that the initial value is unity for each peak. Rapid exponential decay is observed for the 820 nm peak intensity. In contrast, the 630 nm peak intensity first increases during the first ~50 s and decreases monotonically for the longer illumination time. The 660 nm peak intensity decays at a slower rate than the 820 nm peak but faster than that of the 630 nm. The peak intensity decays at different rates when monitored at different locations, but the relative order of the photostability remains the same. The relative photostability of the 630 and 660 nm peaks suggests that the new nanocrystals have more stable surface chemical properties than the original NIR QDs. This may suggest that the larger and more reactive Te atom has diffused out of the core of the nanocrystals. This process can lead to the formation of CdSe based nanocrystals that can emit at 630 nm. The outward diffusion of Te can also result in an inward diffusion of S atom from the ZnS shell, which can plausibly result in the formation of CdSeS alloyed nanocrystals that emit at 660 nm. This proposed mechanism is supported by analyzing the effect of water medium as follows. The role of water medium in facilitating the crystal transformation can be understood by comparing the spectra of the LB films to that of the films prepared by drop-casting (DC) the quantum dot solution directly on the substrate and to the spectra of the QDs as they are assembled on the water surface as demonstrated in Figure 7-6.
Figure 7-6: Representative PL spectra (normalized to the same maximum) obtained on QD films prepared by LB (red line) and drop-casting (DC) (blue line) procedures compared to the spectra of the QDs as they are assembled on the water surface (black line). The DC film is prepared by applying the solution (QDs in chloroform) directly onto the substrate, avoiding the exposure to water.

As it can be seen in Figure 7-6, the 630 and 660 nm peaks are completely absent for the QDs on the water surface (black line) and are hardly noticeable in the PL spectrum of the film prepared by the DC procedure (blue line). For the DC film, signatures of the two peaks become apparent when the intensity scale is enlarged by a factor of >20 (Figure 7-9), suggesting that spreading the QD-surfactant mixture on the substrate has similar but negligible effect as on the water surface in the LB procedure. Unlike on the water surface, when the solution is directly spread on the substrate, the QDs are not effectively separated from the surfactant molecules, and therefore they are dried as they are embedded in the stabilizing molecules. Exposing the DC film to air for extended time does not result in the growth of peaks at 630 and 660 nm. In contrast, when the QD solution is spread on water surface during the LB procedure, the QDs and stabilizing surfactant molecules are separated, forming water-QDs-surfactant-air interface as
discussed above. When the film is transferred, the naked side of the QDs is directly interfaced with the substrate, which may create a chemical potential gradient to facilitate outward diffusion of Te atom and minimize lattice mismatch in the crystal. The composition of the nanocrystals has been studied by analyzing the X-ray photoelectron spectra of the DC and LB QD films. Representative results are compared in Figure 7-7. The overall spectra are in good agreement with published results, and the discussion here primarily focuses on the comparison of the spectra for the DC and LB films. Analysis of the spectra indicates that the Te to Se composition ratio is 0.18 for the DC film, which corresponds to CdSe$_{0.85}$Te$_{0.15}$ approximate composition. The composition of Zn and S are determined as $\sim$8.5% each, which correspond to a slightly less than a monolayer thickness of ZnS shell and a 6.3 nm core diameter of CdSeTe. The experiment has been performed on two sets of samples, and reproducibly significant broadening of peaks has been observed for the LB films with respect to the corresponding transitions for the DC films as illustrated in Figure 7-7a-c for Cd, Se, and Te 3d bands. For example, the fwhm of the Cd$^{3/2}$ transition band is 0.97 eV for the DC film, which is in good agreement with the literature value of 0.98 eV for CdSe/ZnS QDs, and it increases to 1.28 eV for the LB film. Closely inspecting all the spectra presented in Figure 7-7, greater degree of asymmetry can be seen on the higher energy side for the LB film than for the DC film. This may be attributed to significant changes of surface properties and increased contribution of surface atoms.
Figure 7-7: (a–c) Comparison of X-ray photoelectron spectra of QD films prepared through drop-casting DC (black curves) and LB (red curves) procedures. (d) Ratio of composition of LB to DC for Cd 3d, Se 3d, Te 3d, Zn 2p, and S 2p electrons.

The weak peak at 406.6 eV in Figure 7-7a is reproducible, which may be indicative of Cd–S bond in the crystal.\(^{65}\) We note that the spectra in Figure 7-7 are for the case in which prominent oxidation peaks (e.g., TeO\(_2\) that we have observed at \(\sim576.0\) eV for samples exposed to air for longer times) are completely absent, and therefore none of the spectral features can be attributed to oxidation effects. The LB and DC films have also been compared by calculating the ratio of the respective compositions for each atom as plotted in Figure 7-7d. Ideally, the ratio should be 1.0 for all of the atoms as long as the crystals remain intact. The significant deviation for zinc (ratio of 0.24) from unity can be due to two possible reasons: (i) a loss of Zn from the ZnS shell during the LB procedure or (ii) a change in the overlayer (surfactant) thickness. The loss of zinc is expected to
introduce surface defects that should change the spectral characteristics of the QDs significantly. However, as shown in Figure 7-1c, the peak wavelength and fwhm of the PL spectra of the QDs assembled on water surface are essentially the same as that of the original solution. Therefore, we conclude that the ZnS shell remains intact while the QDs are on the water surface (until the film is transferred to the substrate). On the other hand, as shown in Figure 7-2 and discussed above, the interfacial interaction at the water-air interface creates a thick surfactant layer that covers the quantum dots. As a result, on average the QDs in the LB film are covered by a thicker surfactant layer than in the DC film, which results in weaker signal for all the atoms in the LB film because the electron signal is proportional to \( \exp(-t/L \cos \theta) \), where \( t \) is the thickness of the over layer, \( L \) is the inelastic mean free path of the electron at a given energy, and \( \theta \) is the signal collection angle (the angle of photoelectrons with respect to the surface normal).\(^{66}\) With a binding energy of 1022 eV, the Zn 2p\(_{3/2}\) electrons have the lowest kinetic energy (465 eV) and the shortest \( L \) (1.6 nm), compared to the kinetic energy of 1323 eV and \( L \approx 3.5 \) nm for S 2p electrons, for example.\(^{67}\) Therefore, the signal attenuation is expected to be most pronounced for zinc with increasing overlayer thickness, resulting in the observed deviation of composition ratio from an ideal value of 1.0. For Te, the LB to DC composition ratio is slightly higher than 1.0 despite the fact that for Te 3d electrons the effective attenuation length is shorter than that of the Cd 3d and Se 3d electrons.\(^{67}\) In addition, with respect to the composition of the DC film, there is significant increase of ratio of Te 3d signal to the other signals for the LB film: an increase of \( \sim 16\% \), \( \sim 20\% \), and \( \sim 17\% \) with respect to Cd 3d, Se 3d, and S 2p, respectively. This observation of relative increase of Te 3d signal indicates that the relative concentration of Te on the
surface of the nanocrystals has increased, which is a direct evidence of diffusion of Te from the core to the shell. This outward diffusion of Te can lead to an inward diffusion of S to fill the vacant sites. This process minimizes the lattice mismatch and the strain energy cost as the larger Te atoms are replaced by the smaller S atoms. This observation is in agreement with the appearance of CdS signature in the Cd 3d band (Figure 7-7a), and the atomic interdiffusion can result in the transformation of CdSeTe/ZnS either to CdSe/CdS nanocrystals that emit at 630 nm or to alloyed CdSeS nanocrystals that emit at 660 nm. At the same time, it is likely that the ZnS shell is transformed to ZnTe. LB films of CdSe/ZnS and CdSeS/ZnS core/shell QDs have been prepared and the spectral characteristics of the film are essentially the same as that of the solution phase. This observation further confirms that the transformation of CdSeTe/ZnS nanocrystals is due to the large lattice mismatch and strain energy that can be minimized when the bigger Te atoms in the crystal core are replaced by the smaller S atoms through the process of interdiffusion of atoms. Since the spectral changes (appearance of the 630 and 660 nm peaks) have been observed after the QDs are transferred from the water surface to the substrate, interfacial interactions and/or exposure to air (oxygen) can be proposed as possible factors that facilitate the atomic interdiffusion process. The 630 and 660 nm peaks have been observed in the PL spectra of freshly prepared LB films for which signatures of TeO₂ are absent in the XPS spectra. On the other hand, significant blue-shift and spectral broadening are observed for the fresh samples including those prepared by drop-casting. These significant spectral changes cannot be attributed to a difference of the refractive index of the solution and the film as this is not the case for the CdSe/ZnS and CdSeS/ZnS QDs. The spectral blue-shift and broadening can be indicative of subtle
changes (e.g., increased defect concentration) on the surface of the nanocrystals. Defect concentration is known to speed up atomic interdiffusion.\textsuperscript{60} In addition, the diffusion process can be facilitated by interfacial interactions (QD–QD and QD-substrate) that can create chemical potential gradient and may also lower the activation energy barrier of the diffusion process\textsuperscript{60}. Under this favorable condition, the strain energy cost that is specified in eq 1 can be enough to drive the atomic interdiffusion process. Depending on the favorability of the thermodynamic and kinetic conditions, the atomic interdiffusion can lead to the formation of CdSe/CdS core/shell or alloyed CdSeS nanocrystals coated with ZnTe as mentioned above. Considering all the samples we have prepared and analyzed, the relative intensity of the peak at 660 nm (due to CdSeS QDs) is higher than that of the 630 nm (due to CdSe/CdS QDs). In fact, in some areas, the emission peak at 660 nm is the only prominent peak observed in the visible region as demonstrated by the red line in Figure 7-6. This observation may suggest that the conditions are favorable to result in complete miscibility to form alloyed CdSeS QDs. It should also be noted that the fact that the emission peak at \(~820\) nm (resonance of the original alloyed nanocrystals on the substrate) is observed in almost all areas for all the samples may suggest that only some of the alloyed QDs (that are metastable) transform into more stable crystal composition. Consistent with the above-proposed mechanism, the 630 nm emission wavelength and 23 nm fwhm are in agreement with corresponding spectral characteristics of the CdSe/ZnS QDs with similar core diameter as confirmed in a separate measurement. On the other hand, if all the S atom of the ZnS shell diffuse into the crystal to fill in the lattice sites of Te, the resulting CdSeS nanocrystal is expected to emit around 660 nm which agrees with the longest emission wavelength of commercially available CdSeS/ZnS nanocrystals,
which we have characterized separately. The 660 nm wavelength is also within the range of CdTe QD emission wavelengths. However, for CdTe QDs to emit at 660 nm, the diameter has to be $\sim 4.5$ nm, which is significantly larger than the diameter ($\sim 3.4$ nm) that can be obtained from the transformation of individual CdSe$_{0.85}$Te$_{0.15}$ nanocrystals to the binary CdSe and CdTe nanocrystals. In addition, this crystal transformation requires drastic change of lattice structures that is not plausible. Transformation of individual alloyed nanocrystals into type II QDs may also be considered as an alternative mechanism, which is less likely for the following reasons. This mechanism will result either in CdSe/CdTe/ZnS or CdTe/CdSe/ZnS core/shell/shell type II QDs. The former does not emit because of the lower band gap energy of CdTe shell than the core. The latter is expected to emit at much longer wavelength than 660 nm, and the line width would be broader than that of the observed peak.

![Figure 7-8](image.png)

Figure 7-8: PL intensity of image of 96 $\times$ 96 $\mu$m$^2$ area of a Langmuir-Blodgett film of CdSeTe/ZnS quantum dots exposed to water for 25 minutes. PL intensity image of (a) full spectrum, (b) shorter wavelength ($\lambda < 694$ nm) photons, and (c) longer wavelength ($\lambda > 750$ nm) photons.
Figure 7-9: Photographic view (bright field image) and spectral property of CdSeTe/ZnS QD film prepared by drop-casting. (a) Thin films of QD-surfactant mixture are formed at the frontier of the solution expansion as the solvent (chloroform) quickly evaporates. (b) Going toward the center, where the drop is applied, the film becomes thicker. (c) Representative PL spectrum recorded close to the frontier of the film. The inset spectrum (intensity scale enlarged by a factor of about 25) shows signatures of the 630 nm and 660 nm peaks, which become negligibly small when the PL spectra are recorded close to the center of the film.

7.5: Conclusion:
In summary, using near-infrared CdSeTe/ZnS QDs as model systems, we have demonstrated the transformation of metastable alloyed nanocrystals to more stable forms. When the ZnS coated alloyed CdSeTe QDs with 840 nm emission wavelength and 75 nm spectral line width are self-assembled on water and transferred to a silica substrate using a Langmuir–Blodgett procedure, two new prominent sharp emission peaks are observed at $\sim 630$ and $\sim 660$ nm emission wavelengths that have $\sim 23$ and $\sim 39$ nm fwhm’s, respectively. On the basis of analysis of the crystal composition using X-ray photoelectron, we conclude that the relative concentration of Te atoms on the surface of the nanocrystals has increased significantly, which clearly indicates the diffusion of Te atoms from the core to the shell. This outward diffusion of Te atoms can then initiate inward diffusion of S, which can lead to the formation of either CdSe/CdS or CdSeS quantum dots. Based on size analysis, these new nanocrystals are expected to emit at 630 and 660 nm wavelengths, respectively. Since no spectral changes have been observed for the QDs as they are assembled on the water surface, surface defect concentration and interfacial interactions that create chemical potential gradient and lower the activation energy barrier of the diffusion process are suggested as possible mechanisms that facilitate the outward diffusion of Te atom to minimize the strain energy cost. This work emphasizes the importance of post-synthesis characterization of alloyed nanocrystals, which have potential applications in biological imaging and optoelectronic devices.
7.6: References:


(2) Luther, J. M.; Law, M.; Beard, M. C.; Song, Q.; Reese, M. O.; Ellingson, R. J.; Nozik, A. J. Nano Letters 2008, 8, 3488.


(41) Frangioni, J. V. Current opinion in chemical biology 2003, 7, 626.
(43) Bailey, R. E.; Nie, S. Journal of the American Chemical Society 2003, 125, 7100.
(45) Jang, E.; Jun, S.; Pu, L. Chemical Communications 2003, 2964.
(47) Allen, P. M.; Bawendi, M. G. Journal of the American Chemical Society 2008, 130, 9240.
Chapter 8: Summary and Future directions

8.1: Summary:

This thesis has described the understanding of fundamental areas in plasmonic; the influence of substrate in the optical properties of plasmonic nanoparticles, chemical reactivity at the plasmonic nanoparticle surface, the role of ligands in hot electron generation, methods of assembly of nanoparticle and a thin film of the semiconductor nanocrystal. The optical plasmonic response of metallic nanoparticle interaction with a metallic film is studied by using dark field optical microscopy. We demonstrated the scattering cross-section of gold nanorods is dictated by charge transfer plasmon mode and this mode is independent of shape and size. Plasmon-enhanced photochemistry of p-aminothiophenol molecule is studied using highly sensitive surface enhanced Raman spectroscopy (SERS). We experimentally demonstrated the effects of different surface ligands on AuNR in hot-electron dynamics that increase the reactivity and selectivity of the reaction pathways. The dramatic effects of surface ligands are demonstrated in the presence of CTAB and citrate as surface ligands and studied the photochemical transformation of PATP molecule. Similarly, we studied the distant dependent scattering of AuNR interaction with AuF by using polyelectrolytes and QDs film as a spacer layer. Distance dependent scattering and photoluminescence properties of single gold nanorods are studied alternatively. We observed the light emission from the dielectric nanocavity takes place via both elastic and inelastic process. Finally, we demonstrated a simple, cost-effective and reproducible method of assembly of gold nanorods (AuNR) by droplet evaporation method. When AuNR solution is evaporated at higher temperature than room temperature the so-called coffee ring is minimized and the AuNR particles are deposited
into monolayer film without forming the ring. Here, by increasing the temperature induces the Marangoni effect. Due to this effect, it creates the surface tension gradients between the point of contact and inside the drop. This surface gradient causes AuNR deposit inside forming the AuNR 2D structure or film.

In future direction, we have self-assembled near infrared colloidal QDs CdSeTe/ZnS film using the Langmuir-Blodgett methods. Here, we have reported the transformation of near-infrared CdSeTe/ZnS quantum dots (QDs) that are exposed to water. When the colloidal QDs with 840 nm emission wavelength and 75 nm spectral line width are self-assembled on water surface, two prominent relatively sharp photoluminescence (PL) bands are observed at ∼630 and ∼660 nm peak wavelengths with line width of ∼23 and ∼39 nm, respectively.

8.2: Future direction:

8.3: Plasmon exciton coupling:

Quantum dots are semiconductor nanocrystal having high bandgap tunability, high quantum yields. These nanocrystals can bridge the gap between the bulk metals and molecules and opens the new avenues. Additionally, they have high photostability. By tuning the composition of a particle, it can tune a broad range of spectrum.

The coupling of QDs and AuNR is widely studied since its application from photovoltaics, sensing, catalysis, optoelectronic devices, and detection\textsuperscript{1-3}. Coupling of AuNR near to QDs either quenches the emission of QDs or enhances the emission of QDs leading to the transfer of energy from donor to acceptor. Depending upon the size of
AuNR and the extent of spectral overlap between emission of donor and acceptor different theoretical model are explaining the energy transfer process. When the gold nanoparticles size is (<2 nm) there is no surface plasmon and the energy transfer process takes place by interacting dipole of QDs with the metal surface called nonmetallic energy transfer (NSET)\(^4\,\text{\textsuperscript{6}}\). While for the larger nanoparticles with spectral overlap between LSPR of AuNR and emission of fluorophore (QDs), the energy transfer process is due to dipole-dipole interaction leading to non-radiative energy transfer called Forster energy transfer (FRET)\(^7\,\text{\textsuperscript{8}}\). These processes are highly distance dependent. To have the effective energy transfer the tuning of distance as well as the size and optical properties of donor and acceptor are important.

Energy transfer process has been widely studied using conventional diffraction limited far-field techniques. As it is well known from the Forster formalism, the energy transfer efficiency depends on donor-acceptor separation distance sensitively. Unfortunately, there are other competing non-radiative excitation energy decay channels that show similar distance dependence as the energy transfer, and therefore it is very difficult, if not impossible, to separately study the energy transfer efficiency as a function of distance and other interface properties using conventional far-field measurement techniques. The focus of this research will be to study the energy transfer efficiency while controlling the coupling distance with nanometer accuracy. The close-packed monolayer of QDs will be coupled with AuNR varying the distance by optically transparent spacing material shown in Figure 8-1. Placing AuNR nanoparticles on top will help us to image the metal nanoparticles using ANSOM setup (Chapter 2). For effective coupling, we will use the QDs whose emission and the AuNR plasmon resonance spectrally overlap.
We can correlate initially the energy transfer efficiency using FRET model. The efficiency of FRET at distance is

\[ d_0 = 0.211[k^2\Phi_{QD}(n)^{-4}J(\lambda)]^{1/6} \]

Where \( k^2 \) = relative orientation of transition dipole of QDs and AuNR

\( J(\lambda) \) = overlap between the QDs and AuNR

\( \Phi_{QD} \) = Quantum yield of donor in absence of acceptor.

Thus, the efficiency of quenching,

\[ E = \frac{1}{1 + \left(\frac{d}{d_0}\right)^6} \]

Where \( d \) = distance between the donor and acceptor.

Here, we will study the PL properties of QDs in presence of AuNR as a function of distance between QDs-AuNR. From this study we will be able to understand the energy transfer efficiency with distance.
Figure 8-1: Schematics of configuration of excitonic (QDs) and plasmonic materials with respect to the AFM tip. For simplicity, only a single metal nanostructure, which is much larger than the quantum dots, is shown.

8.3.1: Layer by layer assembly of monolayer QDs thin film and AuNR using polyelectrolytes layer as spacer
Figure 8-2: (a) Polyelectrolytes (PE) layer on top of CdSeS/ZnS. The height profile from AFM topography is ~10 nm (b) AuNR assembled on top PE-QD layer.
8.4: References: