ABSTRACT

MODELING THE BEHAVIOR OF GOLD NANOPARTICLES AND SEMICONDUCTOR NANOWIRES FOR UTILIZATION IN NANODEVICE APPLICATIONS

by Andrew Makepeace

Gold nanoparticles and semiconductor nanowires are widely studied for novel optical and electrical properties, and for possible application in nano-chemical sensors and high efficiency photovoltaic arrays. Herein, we pursue a finite difference time domain analysis of several varieties of gold nanoparticles and semiconductor nanostructures. We present the optical absorption of single particles which compares well to the optical extinction of particle colloids and photocurrent measurements of single nanostructures. We also present local electric fields generated by excited metallic and semiconductor particles.
MODELING THE BEHAVIOR OF GOLD NANOPARTICLES AND SEMICONDUCTOR NANOWIRES FOR UTILIZATION IN NANODEVICE APPLICATIONS

A Thesis

Submitted to the Faculty
of Miami University
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Physics
by
Andrew Makepeace
Miami University
Oxford, Ohio
2013

Advisor
Jan Yarrison-Rice

Reader
Herbert Jaeger

Reader
James Clemens
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Theory</td>
<td>9</td>
</tr>
<tr>
<td>2.1 Spherical Nanoparticles</td>
<td>10</td>
</tr>
<tr>
<td>2.2 Infinite and Very Long Cylinders</td>
<td>14</td>
</tr>
<tr>
<td>2.3 Short Cylinders and Arbitrary Shapes</td>
<td>21</td>
</tr>
<tr>
<td>3. Au Nanoparticles</td>
<td>30</td>
</tr>
<tr>
<td>3.1 Measurement of Extinction</td>
<td>31</td>
</tr>
<tr>
<td>3.2 Au Nanospheres</td>
<td>34</td>
</tr>
<tr>
<td>3.3 Au Nanorods</td>
<td>37</td>
</tr>
<tr>
<td>3.4 Au Bipyramids</td>
<td>41</td>
</tr>
<tr>
<td>3.5 Particles on Surfaces</td>
<td>44</td>
</tr>
<tr>
<td>4. Semiconductor nanowires</td>
<td>48</td>
</tr>
<tr>
<td>4.1 Bare Round InP Nanowires</td>
<td>51</td>
</tr>
<tr>
<td>4.2 Bare Hexagonal InP Nanowires</td>
<td>57</td>
</tr>
<tr>
<td>4.3 Bare Tapered Hexagonal InP Nanowires</td>
<td>58</td>
</tr>
<tr>
<td>4.4 Tapered Hexagonal InP Nanowires on an SiO₂/Si Surface</td>
<td>60</td>
</tr>
<tr>
<td>4.5 Tapered hexagonal InP Nanowires on an SiO₂/Si Surface With Metal Contacts</td>
<td>62</td>
</tr>
<tr>
<td>5. Conclusions</td>
<td>67</td>
</tr>
<tr>
<td>6. Bibliography</td>
<td>69</td>
</tr>
</tbody>
</table>
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nano-chemical sensor strategy</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>Nanowire based photovoltaic array strategy</td>
<td>3</td>
</tr>
<tr>
<td>3.</td>
<td>Plasmon resonance</td>
<td>4</td>
</tr>
<tr>
<td>4.</td>
<td>Nanoparticle activation strategy</td>
<td>5</td>
</tr>
<tr>
<td>5.</td>
<td>Semiconductor nanowire heterostructures</td>
<td>6</td>
</tr>
<tr>
<td>6.</td>
<td>Photocurrent due to one and two photon absorption</td>
<td>7</td>
</tr>
<tr>
<td>7.</td>
<td>Spherical Nanoparticle</td>
<td>11</td>
</tr>
<tr>
<td>8.</td>
<td>Theoretical extinction of a spherical nanoparticle</td>
<td>14</td>
</tr>
<tr>
<td>9.</td>
<td>Cylindrical nanoparticle</td>
<td>15</td>
</tr>
<tr>
<td>10.</td>
<td>Theoretical polarization index of an infinite cylinder as a function of particle diameter</td>
<td>20</td>
</tr>
<tr>
<td>11.</td>
<td>Theoretical polarization index of an infinite cylinder as a function of excitation energy</td>
<td>20</td>
</tr>
<tr>
<td>12.</td>
<td>Lumerical GUI</td>
<td>22</td>
</tr>
<tr>
<td>13.</td>
<td>Real and imaginary index of refraction fit</td>
<td>23</td>
</tr>
<tr>
<td>14.</td>
<td>FDTD Yee cells and spatial mesh</td>
<td>24</td>
</tr>
<tr>
<td>15.</td>
<td>Perfectly Matched Layer (PML) reflection</td>
<td>26</td>
</tr>
<tr>
<td>16.</td>
<td>FDTD light sources</td>
<td>28</td>
</tr>
<tr>
<td>17.</td>
<td>Absorption spectrometer setup</td>
<td>31</td>
</tr>
<tr>
<td>18.</td>
<td>Raw spectrometer data</td>
<td>32</td>
</tr>
<tr>
<td>19.</td>
<td>Measured 25nm x 59nm nanorod extinction</td>
<td>32</td>
</tr>
<tr>
<td>20.</td>
<td>The measured extinction of various sizes of Au nanospheres</td>
<td>34</td>
</tr>
<tr>
<td>21.</td>
<td>FDTD setup for a spherical particle</td>
<td>35</td>
</tr>
<tr>
<td>22.</td>
<td>FDTD absorption, scattering, and extinction for 29nm and 90nm nanospheres</td>
<td>36</td>
</tr>
<tr>
<td>23.</td>
<td>TEM micrograph of 13nm Au nanospheres</td>
<td>36</td>
</tr>
<tr>
<td>24.</td>
<td>The measured extinction of various sizes of Au nanorods</td>
<td>37</td>
</tr>
<tr>
<td>25.</td>
<td>FDTD setup for an Au nanorod</td>
<td>38</td>
</tr>
<tr>
<td>26.</td>
<td>Comparison of experimental and FDTD extinction for a 25nm x 59nm Au nanorod</td>
<td>38</td>
</tr>
<tr>
<td>27.</td>
<td>TEM micrograph of Au nanorods</td>
<td>39</td>
</tr>
<tr>
<td>28.</td>
<td>The measured extinction of 10nm x 36nm Au NRs and FDTD predictions for various similar lengths of particles</td>
<td>40</td>
</tr>
<tr>
<td>29.</td>
<td>Measured Au bipyramid extinction</td>
<td>41</td>
</tr>
<tr>
<td>30.</td>
<td>FDTD setup for Au bipyramids</td>
<td>42</td>
</tr>
<tr>
<td>31.</td>
<td>TEM micrograph of Au bipyramids</td>
<td>42</td>
</tr>
<tr>
<td>32.</td>
<td>Comparison of measured and FDTD Au bipyramid extinction</td>
<td>43</td>
</tr>
<tr>
<td>33.</td>
<td>Local electric fields for an Au bipyramid</td>
<td>43</td>
</tr>
</tbody>
</table>
34. FDTD setup for an Au bipyramid on a CdS surface ..................................................45
35. Local electric fields for an Au bipyramid on a CdS surface .....................................45
36. Transmission caused by an Au bipyramid .................................................................46
37. The Vapor Liquid Solid (VLS) technique for semiconductor nanostructure growth ...49
38. VLS grown GaAs nanowires .....................................................................................50
39. VLS grown CdS nanosheets .....................................................................................50
40. SEM micrograph of a single nanowire photocurrent device .....................................51
41. FDTD setup for a round InP nanowire ...................................................................52
42. Comparison of Van de Hulst theory and FDTD predictions for polarization index as a function of diameter .................................................................53
43. Polarization index for a 26nm NW ..........................................................................54
44. Polarization index for various round nanowires .......................................................55
45. Local electric field of a round InP nanowire under 800nm excitation .......................56
46. FDTD setup for a bare hexagonal InP nanowire .......................................................57
47. FDTD predictions for a hexagonal InP nanowire with experimental photocurrent data .................................................................58
48. FDTD setup for a tapered hexagonal InP nanowire ...................................................59
49. FDTD predictions for a tapered hexagonal InP nanowire with experimental photocurrent data .................................................................60
50. FDTD setup for a tapered hexagonal InP NW on an SiO$_2$/Si substrate ..................61
51. FDTD predictions for a tapered hexagonal InP NW on an SiO$_2$/Si substrate with experimental photocurrent data ..................................................62
52. FDTD setup for a tapered hexagonal InP NW on an SiO$_2$/Si substrate with metal contacts .........................................................................................63
53. FDTD predictions for a tapered hexagonal InP NW on an SiO$_2$/Si substrate with metal contacts with experimental photocurrent data ..................................................63
54. Local electric fields for a tapered hexagonal InP NW on an SiO$_2$/Si substrate with metal contacts .................................................................65
Acknowledgements

I would like to acknowledge the valuable input of the faculty at Miami’s Center for Advanced Microscopy and Imaging (CAMI), our collaboration at the University of Cincinnati, and my advisor, Jan Yarrison-Rice.

I would also like to thank my family, without whose support this work would not have been possible.
1. Introduction

Semiconductor nanowires (NWs) are an active field of research with applications in chemical sensing, photovoltaics, and batteries [1,2,3,4]. Together with a collaborative group at the University of Cincinnati, it is our overarching goal to design and fabricate a hand held chemical sensor with high selectivity and high sensitivity (Fig. 1), and to investigate semiconductor NW based photovoltaics (Fig. 2). For this purpose, we are working toward an understanding of the nanodevices’ components which will provide a predictive strategy for component selection and optimum device performance. Focusing on the chemical sensor, we need to understand metal nanoparticle (NP) plasmon resonance and semiconductor nanowire photocurrent, both
experimentally and theoretically. The ability to mathematically model the interaction of Au NPs and semiconductor NWs provides a testing ground to utilize before actual devices are fabricated. First we will introduce plasmon resonance for the simple case of

**Figure 1:** Top: A nano-chemical sensor in the "off" state. Bottom: A nano-chemical sensor in the "on" state.
spheres and some properties of semiconductor NWs. We will then present some experimental measurements of plasmon resonance in Au NSs and nanorods (NRs). Finally, we will address computational work that has been done towards understanding these components, and present a timeline outlining past and future work.

The collective oscillation of conduction electrons known as a plasmon (Fig. 3) is central to the design of a semiconductor NW based chemical sensor. Metal NPs exhibit a strong plasmon resonance for certain frequencies of light, which depend on the size and shape of the NP, at which they can absorb and scatter strongly. Plasmon resonance has been widely studied [5], and for spheres, the extinction cross section ($C_{ext}$) can be derived explicitly:

$$C_{ext} = \frac{24\pi^2 R^3 \epsilon_m^3}{\lambda} \frac{\epsilon_i}{((\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2)}$$

(1)

**Figure 2:** A proposed semiconductor NW enhanced photovoltaic array
Where $R$ is the radius of the nanosphere (NS), $\varepsilon_m$ is the permittivity of the surrounding medium, $\varepsilon_r$ is the real part of the permittivity of the sphere, $\varepsilon_i$ is the imaginary part of the permittivity of the sphere, and $\lambda$ is the wavelength of the exciting light.

Because of the wavelength dependence of the permittivities, there exists a resonance where

$$Re[\varepsilon(\omega)] = -2\varepsilon_m$$  \hspace{1cm} (2)

which is commonly known as the Fröhlich condition. Here the plasmon becomes responsible for producing an additional component to the electric field, as Maxwell’s equations predict. This field is highly localized around the NP and polarization dependent. Plasmon resonance greatly amplifies the E field at pointed features. Since the resonance also depends on the index of the surrounding medium, a chemical sensor takes advantage of the fact that capturing target molecules shifts the resonant wavelength, allowing for an “on/off” type of signal readout.

**Figure 3:** An illustration of plasmon activity in Au Nanospheres in the presence of a passing light wave.
Semiconductor NWs naturally absorb near their band gap, where photons of correct energy create excitons which are then separated by either an external or intrinsic bias and used to conduct. An exciton is an electron hole pair, such as may be optically generated in a semiconductor. NWs and NSs are mostly single crystalline and exhibit high quantum efficiency [6, 7, 8, 9, 10]. In an NW-based device, Au NPs are chosen such that their plasmon resonances match the absorption of the NW. The photoabsorption of the NW is increased many fold as a result. It is our strategy to functionalize Au NPs so they bind only with target molecules (Fig. 4), and then deposit them onto semiconductor NWs or nanosheets [11, 12, 13]. The system is illuminated by light capable, through either a one or two photon process [11], of creating excitons, but at slightly different wavelength than the resonance of the NPs. When the target molecule is present, it will bind with the functional coating of the NPs and shifts the plasmon resonance of the system. This excites enhanced local field and stimulate greater absorption, and therefore photocurrent, in the semiconductor nanostructure. Similarly, Photovoltaic applications will depend on arrays of nanowire heterostructures (Fig. 5) [14, 15, 16, 17, 18, 19, 20] which provide a large, textured surface to maximize the absorption and resulting exciton generation. The natural bias of the semiconductor

**Figure 4**: An illustration of the "lock and key" model for the activation of plasmonically active nanoparticles in a nano-chemical sensor.
As stated above, for chemical sensing applications, it is essential to tune the resonance of NPs to a wavelength near to that of the exciting light. For this purpose, the plasmon resonances of a variety of sizes and shapes of Au NPs have been determined. NSs typically display one broad peak according to its plasmon resonance while NRs, because of their geometry, display two broad resonance peaks. The excitation delivered to the sample, $exc$, is determined by simply measuring the transmission through a cuvette of deionized water. Then, after measuring the transmission through a sample, $trans$, the extinction, $ext$, can be calculated as follows

$$ext = 1 - \frac{trans}{exc}$$  

We make use of the fact that the resonance peaks shift toward the red as the characteristic length increases. NSs are symmetric, and thus have no polarization dependence. NRs have two characteristic length scales, the radius and the length, each of which has a different resonance, making the NRs polarization dependent. Again, as characteristic length scales increase, so does absorption wavelength.

**Figure 5**: Semiconductor nanowire heterostructures. Left: an axial heterostructure. Right: A radial heterostructure.
For a chemical sensor, it is desirable to have as large a difference between the “on” state and the “off” state as possible. For this purpose, a two photon exciton generation process is being considered. Figure 6a shows photocurrent as a function of exciting photon energy. In this plot, it is clear that charge carriers only appear when photons above a specific energy are present. At 10K, the transitions from three different valence bands to the conduction band in CdS are apparent, labeled A, B, and C. At room temperature, the transitions still exist, but are obscured by thermal noise. In a two photon process, two lower energy photons are simultaneously absorbed in order to excite an electron from the valence band to the conduction band in a semiconductor. For a single photon process, photocurrent generated in a nanosheet by a pulsed laser goes as

\[
I_1 = \frac{A_1 e P}{h \nu} \alpha L
\]

(4)

where e is the elementary charge, P is the average laser power, \( h \nu \) is the laser energy, \( \alpha \) is the linear absorption coefficient, L is the NSh thickness, and \( A_1 \) is the carrier collection coefficient.

**Figure 6:** Photocurrent in a GaAs nanosheet as a function of exciting photon energy (left) and as a function of laser power (right).
For a 2 photon process,

\[ I_2 = \frac{A_2 e P^2}{2 h v} \beta L \frac{\tau_p}{f S} \]  

(5)

where \( A_2 \) is the carrier collection coefficient, \( \beta \) is the nonlinear two photon absorption coefficient, \( \tau_p \) is the laser pulse duration, \( f \) is the laser pulse repetition rate, and \( S \) is the laser cross section. For a one photon process, the photocurrent is directly proportional to laser power (Fig. 5). For a two-photon process, the photocurrent generated depends on the square of the laser power (Fig. 5). In the case of a chemical sensor, the concentration of local electric fields and increased optical coupling provided by the metal NPs resonating at either a one or two photon frequency should increase the power perceived by the semiconductor nanostructure, and generate a greater photocurrent. If a two photon process were to be used, a greater percent change between the “on” and “off” state compared to a one photon process would result, even though the current generated by a two photon process is much less than that generated by a one photon process (Fig. 5).

Analytic theoretical treatments are available for the analysis of some simple shapes of nanoparticles, including spheres [21], flat, thin sheets, infinite cylinders, and very long cylinders [22]. Beyond these shapes, however, numerical solutions must be employed [23]. A Finite Difference Time Domain (FDTD) approach was taken to both confirm known results and to investigate particles that have no analytic solution. In the case of Au NPs, spheres, rods and bipyramids were all investigated and found to be in good agreement with experimental extinction measurements. The local electric fields of some NPs was also recorded, and the local fields were found to be enhanced by resonating plasmons. Semiconductor NWs, including short cylinders, hexagonal prisms, tapered hexagonal prisms, NWs on surfaces, and full photocurrent devices were also simulated, and the results compared to photocurrent data gathered by our collaborators at the University of Cincinnati. Au NPs on semiconductor surfaces were also investigated, and found to increase optical coupling between the surrounding medium and the semiconductor in addition to enhancing local fields.
2. Theory

We address here the theoretical treatments of three different examples. We first consider metal nanospheres, then a long metal cylinder with a nanoscale diameter, and finally we describe the case where shorter semiconducting nanowires must be studied using a computational approach. Several solutions to Maxwell's equations are available for describing the optical behavior of near wavelength and sub wavelength sized particles. For particles with spherical symmetry, infinitely long cylinders, or flat sheets, the solution can be known exactly. Very long cylinders and a few other shapes have approximate solutions, whereas most shapes, including cylinders with a smaller aspect ratio, have no analytic solution and must be approximated computationally.
2.1 Spherical Nanoparticles

Many of the interesting optical properties of metallic nanoparticles are due to the surface plasmons that display resonances which are characteristic of the geometry and size of the particle. A plasmon is simply a collective oscillation of free electrons in the metal, driven by the electric fields of incident light.

Hence, the normally strongly reflecting Au can absorb strongly at the input wavelength where the plasmons resonate. Presented here is a description, originally presented by Jackson, of the response of a metallic sphere to an incident electromagnetic wave [21]. We begin with Laplace’s equation relating electric field, \( \vec{E} \), to electric potential, \( \Phi \).

\[
\vec{E} = -\nabla \Phi \quad (6)
\]

and

\[
\nabla^2 \Phi = 0 \quad (7)
\]

In this case, the solutions to the differential equations for \( \Phi \) are simply a superposition of Legendre polynomials.

\[
\Phi(r, \theta) = \sum [A_l r^{-l} + B_l r^{-(l+1)}] P_l(\cos(\theta)) \quad (8)
\]

Where \( r \) is the distance from the particle as shown in figure, \( l \) is an integer, \( A_l \) and \( B_l \) are constants to be determined, and \( P_l \) is the \( l^{th} \) Legendre polynomial. We will split the region into two regions, the volume inside the sphere, \( \Phi_i \) and the volume outside the sphere, \( \Phi_o \) (Fig. 7).
In this case, since the potential must be finite in all space, we have

\[ \Phi_I = \sum_{l=0}^{\infty} A_l r^l P_l(\cos(\theta)) \quad (9) \]

and similarly, for outside the sphere, we have

\[ \Phi_o = \sum_{l=0}^{\infty} [A_l r^l + B_l r^{-(l+1)}] P_l(\cos(\theta)) \quad (10) \]

Note that far from the sphere, the potential must change as

\[ \Phi_o = -E_0 z = -E_0 r \cos(\theta) \quad (11) \]

since in this limit, the particle behaves as a point rather than a sphere.

**Figure 7**: A round nanoparticle for theoretical consideration. \( E_0 \) is the amplitude of the incident field, \( \omega \) is the frequency of the exciting field, and \( \varepsilon, \varepsilon_m \) are the permittivities of the particle and the medium respectively.
Hence,

\[ B_1 = -E_0 \]  \hspace{1cm} (12)

\[ B_l = 0, \forall l \neq 1 \]  \hspace{1cm} (13)

We also have a continuity condition to consider. The potential just inside the sphere must be equal to the potential just outside the sphere, so

\[ \frac{-1}{a} \frac{\partial \Phi_i}{\partial \theta} |_{r=a} = \frac{-1}{a} \frac{\partial \Phi_o}{\partial \theta} |_{r=a} \]  \hspace{1cm} (14)

And

\[ -\epsilon_0 \epsilon \frac{\partial \Phi_i}{\partial r} |_{r=a} = -\epsilon_0 \epsilon_m \frac{\partial \Phi_o}{\partial r} |_{r=a} \]  \hspace{1cm} (15)

Applying these conditions, we have

\[ \Phi_i = \frac{-3\epsilon_m}{\epsilon + 2\epsilon_m} E_0 r \cos(\theta) \]  \hspace{1cm} (16)

With applied field \( E_0 \) as defined in figure 7. We also have

\[ \Phi_o = -E_0 r \cos(\theta) + \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} E_0 a^3 \frac{\cos(\theta)}{r^2} \]  \hspace{1cm} (17)

Now we can define a polarization for the nanosphere

\[ \vec{p} \equiv \epsilon_0 \epsilon_m \alpha \vec{E}_0 \]  \hspace{1cm} (18)

Where \( \alpha \) is the polarizability

\[ \alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \]  \hspace{1cm} (19)
We are now prepared to write the electric field inside and outside the sphere

\[
\overrightarrow{E}_i = \frac{2\varepsilon_m}{\varepsilon + 2\varepsilon_m} \overrightarrow{E}_0
\]  
\[ (20) \]

\[
\overrightarrow{E}_o = \overrightarrow{E}_0 + \frac{3n(n \cdot \hat{p}) - \hat{p}}{4\pi\varepsilon_0\varepsilon_m r^3}
\]  
\[ (21) \]

Since \( \varepsilon \) is wavelength dependent, there exists a resonance condition for both the polarizability and the interior electric field. This condition is commonly known as the Frölich condition

\[
Re[\varepsilon(\omega)] = -2\varepsilon_m
\]  
\[ (22) \]

By allowing the electric field to change in time with the form

\[
\overrightarrow{E}(r, t) = E_0 e^{-i\omega t} \hat{z}
\]  
\[ (23) \]

It is clear that the particle will interact with the electric field, absorbing or scattering the light. We can write absorption and scattering cross sections, describing how strongly the particle will absorb or scatter as follows

\[
C_{scattering} = \frac{k^4}{6\pi} |\alpha|^2
\]  
\[ (24) \]

And

\[
C_{abs} = k Im[\alpha]
\]  
\[ (25) \]

Where \( k \) is the wavenumber of the incident radiation. The total extinction is therefore

\[
C_{ext} = C_{scattering} + C_{abs}
\]  
\[ (26) \]

Or, allowing

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2
\]  
\[ (27) \]
We have

\[ C_{\text{ext}} = \frac{9 \omega}{c} \frac{e^{3/2} V}{[\epsilon_1 + 2\epsilon_m]^2 + \epsilon_2^2} \]  

(28)

Where \( V \) is the volume of the particle and \( c \) is the speed of light in a vacuum. This extinction is experimentally measurable for a colloid of such particles with a simple absorption spectrometer.

The extinction predicted by eq. 23 for a 50nm Au NS (Fig. 8) shows a clear resonance peak near 2.47eV, which is 502nm. This is roughly consistent with the observed resonance peak of spherical Au NPs, though experimentally, there is always polydispersion in NP size and shape. Another resonance peak is seen in the violet near 3.00eV, or 314nm.

2.2 Infinite and Very Long Cylinders

It is also useful to consider cylindrically shaped particles with a very large aspect ratio, that is particles the length of which is much larger than the diameter (Fig. 9). The treatment which follows was developed by Van de Hulst [22]. Again, considering a time
varying electric field as in equation 23, Maxwell's equations take the form

\[ \nabla \times \mathbf{H} = i k m^2 \mathbf{E} \]  \hspace{1cm} (29)

And

\[ \nabla \times \mathbf{E} = -i k \mathbf{H} \]  \hspace{1cm} (30)

Where the wavenumber, \( k \), is

\[ k = \frac{\omega}{c} \]  \hspace{1cm} (31)

With frequency \( \omega \). Also \( m^2 \) is defined as

\[ m^2 = \varepsilon - \frac{4 \pi i \sigma}{\omega} \]  \hspace{1cm} (32)

Where \( \sigma \) is the conductivity of the material. We will now consider the scalar wave equation

\[ \nabla^2 \psi + k^2 m^2 \psi = 0 \]  \hspace{1cm} (33)
And let

$$\overline{M_\psi} = \nabla \times (a_z \cdot \psi)$$

(34)

Where \(a_z\) is the unit vector in the z direction. Also let

$$mk\overline{N_\psi} = \nabla \times \overline{M_\psi}$$

(35)

With

$$mk\overline{M_\psi} = \nabla \times \overline{N_\psi}$$

(36)

Now let \(u, v\) be solutions to equation 29, such that

$$\vec{E} = \overline{M_v} + i\overline{N_u}$$
$$\vec{H} = m(-\overline{M_u} + i\overline{N_v})$$

(37)

Now the general solution in cylindrical coordinates is

$$\psi_n = e^{in\theta} Z_n \left[ r\sqrt{m^2k^2 - h^2} \right] e^{-ihz + i\omega z}$$

(38)

Where \(h\) is an arbitrary constant to be determined, \(n\) is an integer, and \(Z_n\) is a Bessel function of order \(n\). We now have

$$M_r = \frac{-in}{r} \psi$$

$$mkN_r = -ih \frac{\partial \psi}{\partial r}$$

$$M_\theta = \frac{-\partial \psi}{\partial r}$$

$$mkN_\theta = \frac{-nh}{r} \psi$$

$$M_z = 0$$

$$mkN_z = (m^2k^2 - h^2)\psi$$

(39)
With an incident plane wave

\[ \psi_0 = e^{i\omega t - ilx - ihz} \quad (40) \]

With

\[ h = k \sin \alpha \]
\[ l = k \cos \alpha \quad (41) \]

Where \( k \) is the amplitude. Now represent the spatial variation in terms of a sum of Bessel functions.

\[ e^{-ilx} = e^{-i r \cos \theta} = \sum_{n=-\infty}^{\infty} (-i)^n J_n(lr)e^{in\theta} \quad (42) \]

And substituting into eq. 40, we have

\[ \psi_0 = e^{i\omega t - ihz} \sum_{n=-\infty}^{\infty} (-i)^n J_n(lr)e^{in\theta} \quad (43) \]

Where \( J_n \) is the \( n \)th Bessel function. All relevant quantities must be continuous at the boundary of the particle and medium. Therefore, we have radial functions of the form

\[ H_n^{(2)} \left[ r \sqrt{k^2 - h^2} \right] \quad (44) \]

for the scattered wave, where \( H_n^{(2)} \) is the \( n \)th second Hankel function. Henceforth, the \( (2) \) will be suppressed and \( H_n \) will simply be written. For the internal wave, we have

\[ J_n \left[ r \sqrt{m^2 k^2 - h^2} \right] \quad (45) \]

Now let

\[ F_n = e^{in\theta + i\omega t} (-1)^n \quad (46) \]

We are now prepared to write the specific solutions to our wave equation. We are interested in two different situations. The first, where the incident electric field is parallel to the axis of the rod (the z axis) and the function \( v \) is 0, and the second, where the magnetic field is parallel to the axis and the function \( u \) is 0.
For the first
\[ r > a: \quad u = \sum_{n=-\infty}^{\infty} F_n [J_n(kr) - b_n H_n(kr)] \]  
\[ r < a: \quad u = \sum_{n=-\infty}^{\infty} F_n d_n J_n(mkr) \]  

(47)

For the second, we have
\[ r > a: \quad v = \sum_{n=-\infty}^{\infty} F_n [J_n(kr) - a_n H_n(kr)] \]  
\[ r < a: \quad v = \sum_{n=-\infty}^{\infty} F_n c_n J_n(mkr) \]  

(48)

The coefficients \(a_n, b_n, c_n, d_n\) determine the proportion of light scattered and internalized and are therefore central to the problem. These coefficients for the field outside the particle are

\[ a_n = \frac{J_n'(y) J_n(x) - m J_n(y) J_n'(x)}{J_n'(y) H_n(x) - m J_n(y) H_n'(x)} \]  
\[ b_n = \frac{m J_n'(y) J_n(x) - J_n(y) J_n'(x)}{m J_n'(y) H_n(x) - J_n(y) H_n'(x)} \]  

(49)

Where
\[ x = k a \]  
\[ y = m k a \]  

(50)

Now define
\[ T_1(\theta) = \sum_{n=-\infty}^{\infty} b_n e^{i n \theta} \]  

(51)

For the parallel case, and
\[ T_2(\theta) = \sum_{n=-\infty}^{\infty} a_n e^{i n \theta} \]  

(52)
For the perpendicular case. Note that for the case where \( kr >> 1 \), the functions \( u \) and \( v \) can be written

\[
u, v = \left( \frac{2}{\pi kr} \right)^{1/2} e^{-ikr + i\omega t - i3\pi/4} T_{1,2}(\theta) \tag{53}\]

Since \( u \) and \( v \) solve the wave equation, we know the fields outside the cylinder. We can therefore write the intensity of light scattered by the cylinder

\[
I = \frac{2}{\pi r k} |T(\theta)|^2 I_0 \tag{54}\]

Since the cylinder is infinite (or at least very long compared to its diameter), we have

\[
P_{\text{scat}} = l c_{\text{scat}} I_0 \tag{55}\]

Where \( l \) is the length considered, \( P_{\text{scat}} \) is the power scattered by the particle, \( c_{\text{scat}} \) is the scattering cross section, and \( I_0 \) is the incident plane wave's intensity. Hence,

\[
c_{\text{scat}} = \frac{3}{\pi k} \int_0^{2\pi} |T(\theta)|^2 d\theta \tag{56}\]

Similarly, the extinction cross section is given by

\[
c_{\text{ext}} = \frac{4}{k} \text{Re}[T(0)] \tag{57}\]

Which is the absorption of the particle normalized to the physical size of the particle, in this case, the length, since the particle is considered to be very long. Recall that by using the appropriate \( T \), one can consider light polarized with electric field in the direction of the axis of the particle, \( c_{\text{ext}} \parallel \), or polarized with the electric field perpendicular to the axis of the particle, \( c_{\text{ext}} \perp \). This result can be used to predict a polarization index, \( P_{\text{abs}} \), defined to be

\[
P_{\text{abs}} = \frac{c_{\text{ext}} \parallel - c_{\text{ext}} \perp}{c_{\text{ext}} \parallel + c_{\text{ext}} \perp} \tag{58}\]
The polarization index is a useful tool for evaluating the extinction response of a single particle as a function of wavelength. This result applies only when the diameter is much smaller than both length and exciting wavelength. Note (Fig. 10) that at a diameter of about 220nm, the polarization index begins to oscillate wildly. At 800nm excitation, the wavelength of the exciting light in InP is 242nm. Here, the diameter becomes very

**Figure 10:** Van de Hulst prediction for the polarization index of a round NW with a very large aspect ratio as a function of diameter

**Figure 11:** Van de Hulst prediction for the polarization index of a round NW with a very large aspect ratio as a function of excitation energy
close to the wavelength, and the approximation is no longer valid. As a function of energy (Fig. 11), Van de Hulst predicts $P_{\text{abs}}$ that is dominated by parallel absorption until 1.45eV, at which point perpendicularly polarized absorption becomes stronger. A very deep negative feature occurs at 1.7eV, indicating that the parallel absorption becomes negligible compared to the absorption of perpendicularly polarized light.

2.3 Short Cylinders and Arbitrary Shapes

Unfortunately, the response of cylinders with a diameter similar to the length, or which are interacting with light of a wavelength similar to the diameter have no analytic solution. In this case, it is necessary to discretize Maxwell’s equations [23]. We will assume for simplicity a problem with one spatial dimension. The argument can be expanded to three spatial dimensions. Again, considering a scalar wave equation of the form

\[
\frac{\partial^2 u}{\partial t^2} = c^2 \frac{\partial^2 u}{\partial x^2}
\]

(59)

With solutions

\[
u(x, t) = F(x + c\Delta t) + G(x - c\Delta t)
\]

(60)

Where $F$ and $G$ are propagating wave solutions.

We also have

\[
\frac{\partial^2 u}{\partial x^2} = F''(x + c\Delta t) + G''(x - c\Delta t)
\]

(61)

And

\[
u_{j}^{n+1} = F[(j + n + 1)\Delta x] + G[(j - n - 1)\Delta x]
\]

(62)

Where $n$ and $j$ are integers associated with the time and spatial step respectively. This is an exact discrete solution to the scalar wave equation.
The associated recursion relation is

\[ u_{j+1}^n = u_{j+1}^{n-1} + u_{j-1}^{n-1} \]

Since the solution is exact, and it applies to any scalar wave equation, it is possible to determine the behavior of arbitrarily shaped particles with suitably sized space and time steps. This solution is commonly known as the Finite Difference Time Domain (FDTD) solution to Maxwell’s equations, and it is widely employed. As long as the step size in both space and time is small enough, the solution is arbitrarily precise up to the onset of significant finite representation error. In our case, finite representation error is smaller than one part in one million over the entire simulation.

Figure 12: Lumerical FDTD Graphical User Interface (GUI)
A proprietary Maxwell solver known as Lumerical was employed to simulate particles of various shapes and compositions. The Graphical User Interface (GUI) (Fig. 12) contains many powerful tools for creating complicated objects, running multivariable parameter sweeps, and collecting and interpreting results. Objects are uniquely defined in the simulation space by their shape, position, index, and mesh order. Mesh order determines which object takes precedence when two objects overlap. This allows the construction of nearly any shape. Complex permittivity data (recall that the Frölich condition itself relies on a permittivity that varies with wavelength) for all objects is fit with a polynomial curve for continuity (Fig. 13), and then used to generate frequency domain results. Although it does not make use of Graphical Processing Unit (GPU) processing resources, Lumerical is designed to make full use of available system resources, including multiple central processing cores. In order for Lumerical to take advantage of this functionality, processor core binding must be enabled in the “resources” menu.

Figure 13: Left: Lumerical’s fit for the real part of the index of refraction for Silicon. Right: The fit for the imaginary part of the index of refraction for Si. Note that the points are not interpolated.
The simulation region itself consists of a collection of Yee cells (Fig. 14). Since there is no general requirement that Yee cells be uniformly spaced, they may be coarser in regions where less spatial resolution is needed. Mesh grading allows the mesh to become finer in materials that have a higher index of refraction (and hence shorter wavelengths at the same frequency). Conformal mesh algorithms improve accuracy further by averaging the index in mesh cells that contain two or more objects of different indices, or to completely ignore the electric field in the presence of a perfect electrical conductor. Mesh overrides (Fig. 14) allow custom meshes around objects of particular interest. Since computational resources are finite, and the simulation region

Figure 14: a.) A typical Yee cell, with the electric field components known at the cell corner and the magnetic field components known at the cell center. b.) A z-normal view of an InP NW on an SiO₂ surface with a mesh override. The mesh cells are shown in orange. Note that the cells are very coarse outside of the influence of the override. c.) A magnified view of one corner of the InP NW. The finer, overridden mesh is visible here.
must be at least as large as the largest wavelength present, it is necessary to employ these tools to refine the simulation.

The boundaries of the simulation may be perfectly reflecting, symmetrical (a mirror for electric fields, and an antimirror for magnetic fields), periodic \((E(x,y,p) = E(x,y,-p))\), where \(p\) is a point on the z boundary), or perfectly absorbing. It is not physical to simply stop tracking the fields or simply set them to 0 at the simulation boundary since the field values at the boundary must be known for the FDTD algorithm to function, and any such constraint would erroneously affect the results. Hence, in a simulation that is to occur in an approximation of empty space, an absorbing medium must attenuate all incident light before it reaches the simulation boundary. The most efficient known algorithm for this purpose is known as a Perfectly Matched Layer (PML) [24].

PMLs are extremely common, and in a purely analytical treatment, a single PML will eliminate all incident fields without reflection. However, in an FDTD implementation, each PML will allow a certain amount of light to pass through it, as well as reflecting a portion of the incident light back into the simulation region (Fig 15). This can be a significant source of error, even in simulations that have a proper spacing between scatterers and PML boundaries. For this reason, many PMLs are typically employed at the simulation boundary. Each PML minimizes reflection by allowing a larger portion of incident light through it. In most cases, this is sufficient to reduce reflection back into the simulation to negligible levels and attenuate the fields to near 0 by the boundary of the simulation. PML attenuation needs to be 0 at 90° incidence (a plane wave propagating along the surface, for example), so in order for the function to be continuous, the boundary reflectance depends on the angle of incidence. If no structures extend through the PML layer, reflectance typically drops to 6% at 89° incidence, and 0.000001% at 85°. If structures do extend through the PML boundary, the reflectance is somewhat higher. Typical total PML reflections averaged over all wavelengths and angles of incidence are usually constrained to a maximum of 0.01%.
Energy is injected into the system using a variety of sources (Fig. 16) including plane waves, Gaussian shaped waves, dipole emitters, point sources, and others. For most simulations, the Total Field Scattered Field (TFSF) source was employed. This source appears to objects contained within it to be a plane wave infinite in extent, however, at the source boundary, the field due solely to the source is eliminated. This is possible due to the fact that the electric and magnetic fields involved are linear and

Figure 15: Typical reflectance as a function of angle of incidence for a PML boundary layer. The x minimum is far lower due to the fact that no structures pass through it.
field from the source can be tracked separately from the field that has interacted with the particle.

In a simulation with a TFSF source, the computer sets aside two separate blocks of memory for the electric field inside the TFSF source box region, one for the injected field, called \( E_i \), and one for the scattered field, \( E_s \). At the beginning of the simulation, \( E_i \) contains whatever field is being injected, and \( E_s \) is empty. As electric field in \( E_i \) enters a scattering object, the field value for that position in the simulation space is transferred from \( E_i \) to the same spatial location in \( E_s \). Outside of the TFSF source box, only \( E_s \) is propagated. This allows an accurate picture of the scattering caused by a particle without having to run a reference simulation with no particle. This also allows absorption and scattering (the components of extinction) to be tracked independently. This algorithm also eliminates any erroneous interaction between a plane wave source and an absorbing boundary.

Monitors record electric and magnetic fields as a function of space and time. Though large monitors tend to be computationally expensive, they are necessary for the collection of data. More sophisticated groups of monitors are employed to measure things such as absorption or far field behavior. Absorption is measured by encompasing the particle with monitors and tracking the net Poynting flux, that is

\[
\Phi_s = \int_{\text{Surface}} \vec{E} \times \vec{H} \cdot d\vec{a}
\]  

(64)

into the particle at steady state. Since the flux measured is resolved by frequency, the absorption calculated is as a function of frequency. By placing a similar monitor outside of a TFSF source region, scattering as a function of wavelength may be measured. The sum of the absorption and scattering measured this way provides an extinction which can be compared to the absorption of colloids of nanoparticles of the same size and shape.
Figure 16: a.) A dipole type source with blue polarization vector. b.) A Gaussian type source with blue polarization vector and purple propagation vector. c.) A plane wave type source with blue polarization vector and purple propagation vector. d.) A plane wave TFSF source type with blue polarization vector and purple propagation vector. The direct influence of the source ends at the gray source boundary.
Lumerical also contains a sophisticated scripting language which allows the procedural generation of arbitrary shapes of objects, custom monitors, sources, experiment designs, and real time data analysis. The syntax is a specialized version of Wolfram’s Mathematica. The language retains a great many of the plotting and linear algebra functions while adding FDTD specific functionality. Of particular interest is the parameter sweep tool. This function allows the user to choose a parameter over which to scan, and data to be collected after each iteration. Lumerical then builds the series of simulations according to the user’s setup script, and runs them either sequentially or simultaneously, depending on the availability of system resources. An additional script is often useful to obtain the desired quantities, such as absorption, in real time, as opposed to saving a very large amount of superfluous data from iteration to iteration.
3. Au Nanoparticles

Au Nanoparticles are widely known and studied for their interesting optical properties. Au nanospheres are easily chemically precipitated and have historically been used as a dye for stained glass. Since the particles are so small, it is the properties of colloids that are normally measured. It is therefore important for any operating theory to predict colloidal behavior. Individual particles tend to concentrate electric fields and can be useful for chemical sensors, photovoltaics, Surface Enhanced Raman Scattering (SERS) [25], and various other strategies involving nanoscale optical antennas. Single nanoparticles also tend to increase optical coupling between the air and the surface on which they rest.
3.1 Measurement of Extinction

Au nanoparticle extinction of nanoparticle colloids was measured using an absorption spectrometer (Fig. 17). An incandescent light source was used to generate the probe light. Although the light is not consistent in brightness over the relevant spectrum (Fig. 18), the desired quantity is a ratio, and such a light source proves to be adequate. A neutral density filter with an optical density ranging from 0.5 to 2.0 was used to ensure that the spectrometer CCD did not saturate. A biconvex lens with a focal length of 8cm was used to focus the probe light in the sample. Data was collected by a fiber optic cable, and channeled to an Ocean Optics USB 4000 spectrometer.

**Figure 17:** Absorption spectrometer setup.
Noting that
\[ C_{\text{trans}} = C_{\text{tot}} - C_{\text{ext}} \]  

(64)

Where \( C_{\text{trans}} \) is the transmitted light, \( C_{\text{tot}} \) is the total light injected into the system, and \( C_{\text{ext}} \) is the extinction (Fig. 18, 19). In figure 18, it is clear that a great deal of light is scattered or absorbed by the colloidal NRs due to the lower number of CCD counts at

Figure 18: Spectrometer data for an incandescent light source shown through a cuvette of deionized water, and data for light shown through a cuvette of 25x59nm Au NR colloid.

Figure 19: The extinction of a colloid of 25x59nm NRs as calculated according to eq. 65 from the data presented in fig. 18.

Noting that
\[ C_{\text{trans}} = C_{\text{tot}} - C_{\text{ext}} \]  

(64)

Where \( C_{\text{trans}} \) is the transmitted light, \( C_{\text{tot}} \) is the total light injected into the system, and \( C_{\text{ext}} \) is the extinction (Fig. 18, 19). In figure 18, it is clear that a great deal of light is scattered or absorbed by the colloidal NRs due to the lower number of CCD counts at
every wavelength. There are two places in particular where the counts are very low with respect to the light source, indicating two places where the particles absorb or scatter preferentially. For the particle in figure 19, these occur at 513nm and 637nm. A peak occurs for each characteristic length scale in the particle’s geometry. In this case, two peaks indicate two characteristic lengths. In order to make these locations more evident, we define

\[
\sigma = \frac{C_{ext}}{C_{tot}} = 1 - \frac{C_{trans}}{C_{tot}} \tag{65}
\]

Since it is most useful when normalized to the total light available, \( \sigma \) is what will be referred to as “extinction” from now on. Particles of different shapes exhibit different extinction peaks according to where their plasmons resonate. Colloids of nanospheres typically display one broad extinction peak, since the spheres have only one characteristic length, and are invariant under rotational transforms, there exists only one valid plasmon, and one plasmon resonance. Rods, however, have two characteristic lengths: a diameter, and an axial length. Because of this, two distinct plasmons result. This yields two plasmon resonance peaks in the extinction curve. The two extinction peaks in figure 19 clearly indicate that the particles have two characteristic lengths. In this case, the particles are Nanopartz 25nm x 59nm Au NRs.
3.2 Au Nanospheres

Au nanospheres are commercially available and absorb/scatter light very strongly when as an aqueous colloid. The sphere’s simple shape and the availability of robust theory makes such particles a logical test case for testing our FDTD approach. As expected, their experimental extinction peak varies with nanoparticle size (Fig. 20). As the particles’ diameter increases, the plasmon resonance of the particles redshifts. A colloid of 29nm particles resonates at 513nm, whereas a colloid of 90nm particles resonates at 566nm.

![Figure 20: Experimental Au NS extinction for a variety of commercial aqueous Au NSs.](image)
Au nanospheres were simulated using Lumerical (Fig. 21). A TFSF source was used to inject broadband plane wave excitation. Cross section monitors encompassed the particle, both inside and outside the TFSF source box, in order to record scattering and absorption. x, y, and z normal 2D field monitors were employed to measure local electric fields, and a mesh override provided increased mesh resolution in the vicinity of the particle. Real and imaginary refractive index data was taken from the CRC handbook. The number of Yee cells in the cross section of a particle ranged from 1300 cells for a 29nm NS to 4400 cells for a larger 90nm NS. Convergence testing confirmed that these levels of resolution are sufficient to accurately represent the NSs being studied.

**Figure 21:** Lumerical setup for the simulation of an Au NS.
The FDTD simulation predicts extinction peaks according to resonating plasmons (Fig. 22). The peaks do not correspond well to observed extinction in colloids. It is not clear why this may be. In addition, the FDTD theory predicts that smaller particles, in this case 29nm NSs, will absorb very strongly at their plasmon resonance, with very little scattering. In contrast, a 90nm NS will scatter fairly strongly at its resonance. A simple extinction measurement will not resolve these two quantities independently.

Upon inspection, the nanospheres are not monodisperse with respect to size, nor

Figure 22: FDTD results for a 29nm NS (left) and a 90nm NS (right).

Figure 23: TEM micrograph of 13nm Au NSs on a carbon coated formvar "lacy" grid.
is the average size of the particles exactly what is quoted on the packaging (Fig 23). They are also not exactly spherical in shape. Many display roughly octagonal cross sections. These discrepancies help explain the small disagreement in peak position and width.

When illuminated by resonant light, strong plasmons develop. The local field developed by the oscillating plasmon dipole reinforces the exciting field, resulting in local fields 3.6 times stronger than the exciting field under broadband excitation. Excited just at resonance, the enhancement can be even greater. In the absence of other objects, the plasmon dipole moment lies along the polarization vector of the exciting light. Fields inside metals are also typically lower than those outside the particle.

We will now consider particles with other simple symmetries in order to gain an idea of how particle shape affects the resonance patterns.

### 3.3 Au Nanorods

Since cylindrical NPs, called nanorods, are available commercially, and cylindrically symmetric particles are important to our motivating devices, we will now consider Au NRs.

![Figure 24: Experimental extinction of a collection of commerically available aqueous Au NRs.](chart)
**Figure 25:** Lumerical FDTD setup for an Au NR.

**Figure 26:** Experimental extinction of 25nm X 59nm Au NRs (blue), FDTD calculated extinction for a simulated Au NR under illumination polarized parallel to the long axis of the NR (red), and simulated Au NR under illumination polarized perpendicular to the long axis of the particle (green).
Since each characteristic length in the geometry of the particle allows a unique plasmon resonance, we expect that cylinders will display two plasmon resonance peaks, one for the axial length, and one for the diameter. Indeed, commercially available Au NRs display a characteristic double peak (Fig. 24) in their extinction curve. Note that not all curves display a double peak. In the case of 25nm x 34nm NRs, the aspect ratio is so close to 1 that the peaks become convoluted, and only one, broad peak is apparent. In the case of 10nm x 44nm NRs, the peaks occur at the very edges of the wavelength range of the spectrometer. Particles of this shape are well suited to applications which require plasmonic nanostructures that resonate at visible wavelengths, as they can be engineered to resonate at any visible wavelength.

Au NRs were simulated using Lumerical (Fig. 25). Real and imaginary index data for Au was taken from the CRC handbook and fit for continuity. A broadband TFSF plane wave source was used in order to separate absorption and scattering. PML boundary conditions were used, and standard cross section monitors were employed to measure absorption and scattering. Results of simulations agree well with experimental

**Figure 27:** TEM micrograph of commercially available Au NRs. Note the large range of sizes and the presence of many defective particles.
measurement of extinction in an aqueous colloid (fig. 26), with the exception of peak width. For the long wavelength peak occurring at 638nm, the Full Width Half Maximum (FWHM) of the experimental longer wavelength peak is approximately 162nm. This represents a very broad resonance, with particles reacting to photons of a wide spectrum of energies. In contrast, the FWHM of the FDTD predicted peak is approximately 60nm. While still fairly broad, this peak represents a response to a far narrower spectrum of photon energies.

For instances where the exciting light is polarized along the long axis of the NR, resonant plasmons enhance local electric field strength much more strongly than in the case of spheres. Again, the NRs have a distribution of sizes and shapes (Fig. 27). Many of the particles are indeed rod shaped, but there is also a nontrivial inclusion of large, oddly shaped particles. The rods shown in figure 27 tend to have rounded ends, but the difference in FDTD extinction curves between particles with round ends and particles with square ends is minimal, and it was decided that those computational resources would be better spent in other simulations.

In order to understand the relationship between the length of a NR and its peak position, and how the distribution of sizes might affect the peak width, NRs with a diameter of 10 nm and various lengths were simulated with Lumerical (Fig. 28). As expected, increasing NR length redshifts the corresponding resonance peak of the particles.

**Figure 28**: Experimental data for an Au NR colloid quoted to be 10nm x 36nm as well as FDTD predictions for NRs with a diameter of 10 nm and various lengths.
particle. If one considers a mixture of particles with a distribution of sizes, and therefore resonance peaks, it becomes clear that significant uncertainty with respect to NR length can lead to broader resonance peaks for colloids.

3.4 Au Bipyramids

Au bipyramids [26] were examined for their ability to strongly concentrate electric fields in their vicinity due to sharp structures. The electron plasma is concentrated at these points and at resonance, extremely large fields can develop. These fields are useful to excite excitons in either our proposed nano chemical sensor or the nanowire based photovoltaic device. The extinction curve of colloidal BPs (Fig. 29) displays a complex resonance structure with two prominent features: one peak at 823nm for the log axis of the particle, and a shorter convolution of peaks around 550nm for shorter length scales.

The bipyramids were simulated using Lumerical (Fig. 30), with PML boundary conditions, a broadband TFSF plane wave source box, and refractive index data from the CRC handbook. The bipyramid shape was approximated by two square based Au pyramids. Extinction peaks of Au BPs synthesized by Nick Geitner match FDTD

![Figure 29](image)

**Figure 29**: Experimental extinction of 32.3nm X 97.9nm Au BPs prepared by Nick Geitner [26]
extinction well, except for a peak at 665nm, which appears to be far too strong compared to experimental extinction (Fig. 31).

Figure 30: Lumerical FDTD setup for a square Au BP.

Figure 31: Experimental (blue), perpendicularly polarized FDTD prediction (red), and parallel polarized FDTD prediction (green) extinction curves for 32.3nm X 97.9nm Au BPs.
Real BPs have the inherent size polydispersion and defective particles found in other bottom up processes (Fig. 32 a). Furthermore, these particles display a rounded particle shape.

Figure 32: TEM of 32.3nm X 97.9nm Au BPs synthesized by Nick Geitner. [26].
a.) Lower magnification showing particle polydispersion. b.) Higher magnification showing rounded particle shape.

Figure 33: 2D electric field map for an Au BP illuminated by light polarized parallel to the long axis of the particle. Linear color map values (left) and log base 10 color map values (right).

Real BPs have the inherent size polydispersion and defective particles found in other bottom up processes (Fig. 32 a). Furthermore, these particles display a rounded
shape (Fig. 32 b) that is difficult to replicate in Lumerical, and that may be responsible for the presence of the anomalous peak. It was decided that instead of investing further computational resources in order to more accurately model these particles, other nanostructures would be pursued. Local fields are found to be enhanced over 30x in a broadband simulation (Fig. 33). This is especially useful for devices relying on a two photon process, since intensity is proportional to the square of the field, and two photon photocurrent is proportional to the square of the intensity, local two photon photocurrent could potentially be enhanced 1.34 million times. The region in which the electric field is enhanced is focused around the pointed end of the nanostructure, and dissipates quickly as one moves away from the particle. A base 10 log scale electric field map of the same particle is provided to show that the enhancement does not end abruptly, but rather decreases quickly but steadily as distance from the pointed end increases.

3.5 Particles on surfaces

The plasmons generated in noble metal particles help to couple external fields to semiconductor or insulating substrates. This effect is particularly useful in sensing applications where local light intensity is important, and in the case of photovoltaics where total angle dependent optical coupling is a priority.

A 32nm x 98nm Au BP was placed on a CdS sheet (fig. 34). The total absorption of the particle as well as local electric field intensities were recorded (fig. 35). Large monitors directly above and below the particle, but outside the TFSF source were
**Figure 34:** Simulation setup for a square Au BP on a CdS NSh. The direction of propagation of the source plane wave has been rotated such that it is parallel to the long axis of the BP.

**Figure 35:** An Au BP on a 50nm thick CdS sheet under broadband illumination. The local fields projected by the plasmons penetrate into the substrate, increasing optical coupling.
used to measure total scattering and total transmission. Optical coupling, $T$, will be defined as

$$ T = \frac{P_{\text{particle}}}{P_{\text{no particle}}} $$  \hspace{1cm} (66)

Where $P$ is the power transmitted through the monitor at steady state. Not surprisingly, $T$ is found to be greatest where the particle’s surface plasmon resonates (fig. 36). This is fortunate for any device that depends on the generation of photocurrent by resonant photons. In the chemical sensor presented in the introduction chapter, both the optical coupling and the concentration of local fields should contribute to increased signal for the device. The effect is especially important since two-photon absorption depends on the square of the intensity of the light, meaning that both increased total transmission and higher local field intensity contribute to increased signal, yielding a larger difference between the “on” and “off” states than in a one-photon process.

It is now clear that noble metal particles have desirable and simulable properties for the applications of chemical sensors and perhaps photovoltaic arrays. We will now turn our focus to gaining an understanding of the semiconductor structures necessary to construct such devices.

![Figure 36: Net transmission through the CdS NSh surface caused by the Au BP.](image)
Au NPs are essential to the operation of a nano chemical sensor, and may be extremely useful for NW based photovoltaic arrays. The NP’s plasmons resonate at frequencies determined by their overall geometry, and a resonance exists for each characteristic length in the particle. NSs have only a diameter, and display only one resonance peak. NRs have an axial length and a diameter, and so they have two plasmon resonance peaks. As a characteristic length increases, the wavelength of resonant light red shifts in all cases. Au BPs have many more characteristic lengths, and therefore display a complicated extinction pattern, dominated by a resonance peak for the long axis, and another for the shorter axis. BPs are particularly interesting for their ability to strongly concentrate plasmonic electric fields, and therefore dramatically amplify exciting fields. Such enhancement has been shown to be up to 36 time stronger than the exciting field, which could translate to an enormous increase in local photocurrent generation. BPs have also been shown to increase optical coupling between a surface and a medium where their plasmons resonate.

In this chapter, we have shown that various Au NPs have been simulated. Although the effect is not as strong as is seen experimentally, the resonance of Au spheres has been shown to red shift with increasing size. The proportion of scattering to absorption was also shown to increase with increasing size. The position of resonance peaks for Au NRs have been predicted with good precision, and discrepancies in extinction curve FWHM are explained by experimental NP size polydispersion. Au BPs have also been simulated, with certain characteristic resonances appearing in correct locations. Total local field enhancement was found to be over 34 times the exciting field in a broad band simulation. The rounded geometry of the experimental BPs made further refinement too time consuming to pursue. When placed on a semiconductor surface, Au BPs are found to increase optical coupling where the plasmons resonate. This is another potential mechanism by which photocurrent may be enhanced.
4. Semiconductor Nanowires

Semiconductor nanowires (NWs) have been studied for a variety of reasons, including novel optical properties [27, 28, 29], electrical properties [30, 31, 32, 33], crystal lattices not seen in bulk [33], and application in advanced chemical sensors and photovoltaics [1, 2, 3, 4]. Semiconductor NWs considered here are grown using a Vapor Liquid Solid (VLS) technique (fig. 24) [34, 35, 36, 37, 38], in which Au NPs are arrayed on the intended substrate, usually a semiconductor wafer, and then exposed to precursor molecules under carefully controlled temperature, pressure, III/V precursor ratios, and time conditions.

The Au NPs melt and absorb gaseous precursor molecules which then
precipitate, forming a crystal under the NP. The result is a high aspect ratio semiconductor nanostructure which may be monocrystalline. By changing growth conditions, semiconductor NWs (Fig. 38) and nanosheets (Fig. 39) may be formed. By changing the availability of different precursor molecules, NW heterostructures, both axial and radial, may be formed. Tapering near the base of the structure often results from migration of wayward precursors from the substrate surface to the nanostructure. This appears as a pyramid shaped mound at the base of the finished NW (fig. 38 a). Far from the base, VLS grown NWs exhibit only mild tapering over several microns of length (Fig. 38 b). Other defects include twinning, or changing spontaneously from one crystal structure to another, usually Zincblende to or from Wurtzite. This appears as a striped pattern in a TEM micrograph (Fig. 38 c). VLS nanosheets can be 50nm thick and several microns wide and long (Fig 39 a). Such nanosheets are very smooth (Fig 39 b) and provide a great deal of surface area on which to place activated NPs for a chemical sensor device. VLS NWs may be made of a variety of semiconductors, including InP, GaAs, AlGaAs, InAs, CdS, and others.

Figure 37: An illustration of the VLS process for semiconductor nanostructure growth.
**Figure 38** VLS grown GaAs NWs. a.) SEM micrograph of NWs as grown on their original substrate. b.) A TEM micrograph of a single NW. c.) A high magnification image of a single NW showing the Au precursor and defects. [11]

**Figure 39** VLS grown GaAs nanosheets. a.) An SEM micrograph of many nanosheets, each roughly 5µm across. b.) An SEM micrograph of a single nanosheet, roughly 50nm thick. [11]
We will focus on a photocurrent device composed of a single InP NW on a substrate of 300nm of SiO$_2$ on a thick Si wafer (fig 40). The contacts are composed of a thin (~20nm) layer of Ti for lattice matching purposes covered with a thicker (~200nm) layer of Al. The gap between electrodes near the center of the micrograph is 4µm, and the NW itself is approximately 275nm in diameter. Experimental photocurrent data for this device was obtained by our collaborators at the University of Cincinnati. It is necessary to understand the behavior of such a device in order to predict the behavior of a semiconductor NW based chemical sensor or photovoltaic array. We will begin our model with the simplest case: a cylindrical InP NW in free space. For a NW of this size, there is no suitable analytic theory, so once again, we turn to an FDTD simulation.

4.1 Bare Round NWs

Since spherical quantum dots are well understood and not useful for our motivating devices, we will first consider semiconductor structures with cylindrical
symmetry. In order to understand the behavior of VLS grown NWs, our collaborators have made extensive photocurrent \([11]\) and time resolved photoluminescence \([8]\) measurements. It is expected that photocurrent excited in a NW is directly proportional to the total absorption of the NW at optical wavelengths. Therefore, Lumerical simulations were designed to simulate the structures and devices involved in the measurement of photocurrent from single InP NWs. Round NWs of very large aspect ratio have an analytic solution presented by Van de Hulst, so in order to test the accuracy of the simulation strategy, 4µm long round InP NWs were simulated using a narrow wavelength range TFSF source box, PML boundary conditions, and a cross section monitor to track the absorption cross section of the particle (Fig 41). The index data was obtained from the SOPRA N&K database. The absorption cross section was taken for both axial and transverse polarizations of \((800\pm0.01)\)nm exciting light. A

**Figure 41:** FDTD setup for a 275nm x 2µm InP NW.
polarization index ($P_{abs}$) was calculated and plotted against the particle’s diameter (Fig. 42). Such simulations were performed for round NWs ranging from 10nm to 300nm in diameter and compared to Van de Hulst theory. The two methods agree well below ~240nm. A photon that has a wavelength of 800nm in vacuum has a wavelength of 238nm in InP. Recall that the Van de Hulst theory requires the diameter to be much larger than both the length of the NW and the wavelength of exciting light. Hence, the simulations are in good agreement with existing theory.

The polarization index of round NWs of various sizes is shown in figures 43 and 44. For NWs with a small diameter (Fig. 43), FDTD theory is very successful in predicting experimental photocurrent, even though the actual device may be slightly tapered or hexagonal in shape. In this case, the structure is so much smaller than the wavelength of exciting light that these small discrepancies do not affect the polarization index much. For larger sizes of NW (Fig. 44), the polarization index oscillates, and is negative over several intervals. No one size of NW is negative over the entire range for

Figure 42: Van de Hulst theory (blue) and FDTD calculation (red) for the polarization index of a round, 275nm diameter InP NW excited at 800nm.
which the photocurrent device exhibits a negative polarization index, but it appears as though a combination of these curves may provide the appropriate response. A tapered NW may provide several widths over which to resonate, and therefore shift the polarization index towards the experimental data.

RMS electric fields in and around an InP NW under 800nm light were recorded (Fig. 44). Even for the semiconductor, which does not have the abundance of conduction electrons with which to form plasmons that metals do, local fields are seen to project strongly into the surrounding medium. A strong mode structure is also apparent for both polarizations of exciting light. For the case of parallel polarization, a strong mode with internal hotspots of electric field of over 3 times the exciting field is apparent. The field projects directly out of the bottom of the particle with a local field strength over 3 times the exciting field. The local fields also project out of the end of the particle with a strength over 4 times that of the exciting field. For the case of perpendicular polarization, a higher frequency internal mode with maximum field strength of over 3 times that of the exciting field develops. In this case, the field projects from the bottom of the wire in two distinct and symmetrical lobes with field strength.

**Figure 43:** Polarization index for a 26nm diameter InP NW (red) and FDTD prediction (blue)
about twice that of the exciting field. The local fields project strongly from the ends of the wire, with values up to 5 times that of the exciting field.

Although this simulation is better able to represent a NW of this size and shape than available analytic theory, it is not able to accurately represent the photocurrent device in question. We will proceed to iteratively improve the simulation such that the changes are as small as possible so that the effects of each change are as clear as possible. Our first step will be to change from a cylindrical particle to a hexagonal prism.

**Figure 44:** Various sizes of round InP NWs compared to experimental photocurrent data.
Figure 4: Electric field maps for various cross sections of a round, 275nm x 5um InP NW under both parallel and perpendicular polarization. The excitation wavelength is 800nm. Field profile for plane c, parallel polarization is a log base 10 plot.
4.2 Bare Hexagonal InP NWs

Due to the high degree of crystallinity exhibited by VLS NWs, most specimens are hexagonal prisms in shape. In order to more closely represent the photocurrent device being tested by our collaborators, a hexagonal NW with a diameter (Fig. 46) of 275nm and a length of 4µm was simulated. In this case, a broadband TFSF source with PML boundaries was employed. Index of refraction data was taken from the SOPRA N&K database for this and following simulations.

By measuring absorption with illumination by both axially and transverse polarized light, a polarization index was calculated and plotted against the excitation energy (fig. 47). Experimental data for the photocurrent of a single InP NW device is included for comparison. While the simulation yields results that do become negative at

Figure 46: Lumerical FDTD setup for a hexagonal prism shaped InP NW, and the size parameter considered.
1.32eV and again at 1.38eV, the experiment indicates that the $P_{\text{abs}}$ from photocurrent, and therefore absorption, of an actual NW device quickly becomes negative at 1.33eV and remains negative until data ends at 1.63eV. Though the predicted curve is negative for a significant portion of the wavelengths for which the experiment shows a negative $P_{\text{abs}}$, the simulation does not reflect experiment strongly enough to conclude that the system is being accurately modeled, and the simulation must be further refined.

### 4.3 Bare Tapered Hexagonal InP NW

According to SEM micrographs collected by our collaborators (Fig. 40), the NW used in the device being studied is tapered significantly in the region where photocurrent is being generated. A simulation similar to that described in section 4.3 with a NW tapered from 240-325nm over a 4$\mu$m length was designed (Fig. 48) in order to determine the effect of significant tapering on the polarization index (Fig. 49).
tapered NW was placed such that it has a flat side laying on an imaginary surface. The exciting light is incident to this surface. Hence, the light strikes the NW at an angle as similar as possible to that in the experimental photocurrent device. The tapering raised the value of the calculated polarization index everywhere across the spectrum considered. From 1.3eV to 1.4eV the shape of the curve remains roughly consistent, although higher. There is a sharp decrease in both curves near 1.33eV, although the FDTD curve only becomes negative for a span of 0.01eV. This outcome was unexpected, as it seemed reasonable that a greater number of available diameters would increase absorption of axially polarized light, and therefore decrease $P_{abs}$. After 1.4, a prominent valley seems to have disappeared entirely. Though this step is

**Figure 48:** Lumerical FDTD setup for a tapered hexagonal InP NW.
counterproductive with respect to matching the experimental \( P_{\text{abs}} \) curve, the simulated device does more accurately reflect the geometry of the physical device.

In addition the NW is being photographed through approximately 200nm of Al. The primary electrons may therefore scatter before generating signal in the NW. This may lead to an inflated image of the NW and anomalously high diameter measurements. Since the NW between the contacts was destroyed between photocurrent measurement and imaging, the exact amount of inflation is not known. We then decided to proceed with a tapered NW and further replicate the physical geometry of the experimental photocurrent device.

4.4 Tapered Hexagonal InP NW On an SiO\(_2\)/Si Surface

The actual photocurrent device rests on a 300nm thick SiO\(_2\) surface with a thick

Figure 49: FDTD predictions for the polarization index of a tapered, hexagonal InP NW (purple), and experimental photocurrent data (red).
Si wafer underneath. The simulation from 4.3 was altered to reflect this fact (fig. 50). The tapered NW was placed such that one flat side rests on the SiO$_2$ surface, as a physical NW would be expected to lay. Again, this creates a situation where the incident light strikes the NW at an angle. The TFSF source box was made to end at the boundary between the NW and the SiO$_2$ substrate so that the scattering effect of the NW could be observed.

A polarization index was determined by FDTD calculation (Fig. 51). In our region of interest, the Pabs dramatically decreases, bringing the FDTD predictions much closer to the experimental values. The polarization index values are now negative from 1.31eV to 1.55eV. The polarization index also increases to a peak value of 0.08 at larger energies. In this case the FDTD curve becomes negative 0.035eV before the

---

**Figure 50:** Lumerical FDTD setup for a tapered hexagonal InP NW on 300nm SiO$_2$ and a substrate of Si.
experimental curve. Again, the simulation does not yet match experiment closely enough to claim that the system is being accurately modeled, even allowing for a great deal of experimental uncertainty.

4.5 Tapered Hexagonal InP NW On an SiO$_2$/Si Surface With Metal Contacts

The photocurrent device fabricated by our collaborators at UC also includes metal contacts composed of a thin (~20nm) layer of Ti in order to bridge the crystal structure to a thicker (~200nm) layer of Al. The simulation from 4.4 was altered to reflect a more complete model, including a 20nm layer of Ti and a 200nm thick layer of Al at both ends (Fig. 52). The simulated NW extends 800nm into the metal contacts, and the metal extends another 500nm beyond the wire at both ends. The absorption cross section of the NW was only measured for the 4µm portion of the wire which lay outside of the contacts. The polarization index was plotted as a function of excitation.

Figure 51: FDTD predictions for a tapered, hexagonal InP NW on an SiO$_2$/Si substrate (orange) and experimental photocurrent data (red).
Metallic contacts strongly contribute to the negative $P_{\text{abs}}$ and remove early oscillations observed on each of the previous simulations. There now exists a strong negative feature at 1.36eV, and a positive peak at 1.66eV.

**Figure 52:** Lumerical FDTD setup for a tapered hexagonal InP NW on an SiO$_2$/Si substrate with Ti/Al contacts.

**Figure 53:** FDTD predictions for a tapered, hexagonal, InP NW on an SiO$_2$/Si substrate with metal contacts (beige), and experimental photocurrent data (red).

energy (Fig. 53). Metallic contacts strongly contribute to the negative $P_{\text{abs}}$ and remove early oscillations observed on each of the previous simulations. There now exists a strong negative feature at 1.36eV, and a positive peak at 1.66eV. The FDTD curve
does not exactly match the experiment. Overall, the FDTD curve becomes negative at 1.31eV and remains negative until 1.52eV. The experimental photocurrent curve does not become negative until 1.335eV, and remains negative through at least 1.60eV. Although local minima seem to coincide at 1.38eV, the experimental curve remains much more negative, coming to a minimum of -0.32, with the FDTD prediction at only -0.14. Recall that we have assumed that the photocurrent is always directly proportional to NW absorption, when in reality, there may be more complexities to consider. Local saturation could introduce a nonlinear element to the relationship between absorption and photocurrent. Electron and hole mobility will also affect exciton recombination rates, and therefore photocurrent.
Figure 54: Electric field plots for a tapered hexagonal InP NW on SiO2/Si with metal contacts. The top two plots are under excitation polarized parallel to the long axis of the particle, and the bottom two are under excitation polarized perpendicular to the long axis of the particle. Excitation propagation and polarization directions are indicated above the maps.
Local RMS electric fields were also recorded for the complete photocurrent device (fig. 54). In this plot, the exciting field has a value of 1. White lines have been added at index boundaries for visual clarity. The dashed line represents the SiO$_2$ substrate boundary. Due to the fact that the TFSF source subtracts source light at its boundary, all fields to the right of the dashed line are due entirely to scattering caused by the NW or metal contacts. A strong mode structure is apparent for both polarizations of incoming light. For the case of parallel polarization, internal fields reach twice the strength of the exciting field. For the perpendicular case, internal fields only reach about 1.6 times the strength of the exciting field, but local fields project from the sides of the NW with a strength up to 2.2 times the strength of the exciting field. This mode also projects into the SiO$_2$ substrate, but dissipates almost entirely before it reaches the Si. In the case of perpendicular polarization, a somewhat weaker mode is apparent in the SiO$_2$ substrate. For both polarizations the field in the mode is most intense inside the narrow end of the particle. Due to the fact that the contacts are metal and good conductors, and that the gap where the NW enters is less than $\frac{1}{2}$ of 1 wavelength, they act like Faraday cages, and prevent strong fields from forming in the portion of the wire that is covered by the contacts.

The FDTD strategy has been shown to agree well with both experiment and existing theory for NWs with very small diameters. FDTD electric field predictions show internal mode structures semiconductor NWs of various shapes, which may allow for local saturation of photocurrent generation and therefore a complicated relationship between predicted absorption and observed photocurrent. FDTD NW geometry was systematically altered to reflect an experimental NW device, moving from round NWs to tapered hexagons, adding an SiO$_2$/Si substrate, and finally adding metal contacts. The SiO$_2$ surface is shown to dramatically decrease the P$_{abs}$ curve for lower energies. For the final simulation with a tapered InP NW on an SiO$_2$/Si surface with metal contacts, local minima for FDTD absorption and experimental photocurrent measurements coincide at 1.38eV, although the experimental photocurrent P$_{abs}$ is much more negative than the FDTD prediction. Metal contacts also damp out small oscillations at lower energies.
5. Conclusions

Our objective was to understand the behavior of and processes relevant to essential components of semiconductor nanodevices. Specifically, we studied metallic spheres, rods, and pentatwinned bipyramids, as well as semiconductor nanowires of various morphologies. Toward this end, we examined existing theory describing the optics of subwavelength particles, and decided on a computational approach. A high performance computer was selected in order to make possible the large, highly detailed simulations required. The proprietary FDTD software Lumerical was selected for its versatility and powerful analytical capabilities.

Chapter 3 details the treatment of several varieties of Au NPs. Au NSs, NRs, and BPs were modeled and compared to experimental measurements of aqueous colloidal optical extinction. FDTD simulation successfully predicted plasmon resonances at 591nm and 638nm for a 25nm x 59nm Au NR. Simulations concerning Au NPs on a CdS surface were also conducted, and predictions made about the
plasmonically caused optical coupling between the CdS and the surrounding medium. In particular, there should be greater transmission of optical power at the frequencies at which the plasmons of the NP resonate. The calculated electric fields in the vicinity of the NPs were also presented. NPs with a pointed structure or high aspect ratio concentrate fields up to 34 times the exciting field in a broadband simulation.

Chapter 4 describes a series of simulations used to better understand a photocurrent device used by our collaborators at the University of Cincinnati. We begin with a proof of concept which shows that our simulations agree with accepted theory when the NW is round and its diameter is small. We then build progressively more intricate simulations moving from round NWs to hexagonal NWs to tapered hexagonal NWs. We then simulated a tapered hexagonal NW on an SiO$_2$/Si surface. Finally, metal contacts were added in order to simulate a physical device as closely as possible. Results roughly correlate to experimental device photocurrent measurements. Local minima for FDTD absorption and experimental photocurrent measurements coincide at 1.38eV, although the experimental photocurrent polarization index is about a factor of 2 more negative. Local fields were recorded and analyzed, with local fields exceeding twice that of the exciting field, and clear mode structures for both particles in empty space, and those on surfaces. It will be necessary to understand more fully the relationship between absorption and photocurrent before further progress can be made.

Further work should include an FDTD study of semiconductor NW heterostructures, both axial and radial. Work should also include a study of the effect of the presence of Au NPs of different shapes on the absorption of a semiconductor NW. A complete photovoltaic array of NWs could also be simulated using an FDTD technique with periodic boundary conditions.
6. Bibliography


