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in

Materials Science and Engineering

by

Su-Wen Hsu

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2014
The Dissertation of Su-Wen Hsu is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

Chair

University of California, San Diego

2014
DEDICATION

This dissertation is dedicated to my parents, my sister, and my brother, without whom I could never have finished this ordeal. Their support kept me going through the darkest times, and I will be eternally grateful.
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**Major Field:** Materials Science and Engineering / NanoEngineering

Studies in Optical Property of Bimetallic Alloy Nanocrystals  
Professor: Andrea R. Tao

Studies in Optical Property of Copper Chalcogenide Nanocrystals  
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ABSTRACT OF THE DISSERTATION

Synthesis, Characterization, and Applications of Plasmonic Semiconductor Nanocrystals

by

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Semiconductor nanostructures are ideal candidates for non-metallic plasmonic materials that operate in the near- to mid-infrared range. In contrast to metal nanostructures, semiconductor nanomaterials have the advantage of possessing tunable carrier concentrations. However, unlike metal nanoparticles which are already widely exploited in plasmonics, little is known about the shape-dependent localized surface plasmon resonances (LSPRs) and near-field electromagnetic behavior of semiconductor nanocrystals. Moreover, a major challenge in the fabrication of plasmonic semiconductor nanomaterials is the ability to control LSPRs by independently varying the size, shape, and carrier density of the nanocrystal.
In this dissertation, I describe colloidal synthetic methods for fabricating shaped Cu$_{2-x}$S nanocrystals in which the morphology and stoichiometry of Cu$_{2-x}$S can be modulated. These shaped Cu$_{2-x}$S nanocrystals are used to observe the plasmon response for specific LSPR modes. Specifically, I discuss the plasmon response of Cu$_{2-x}$S nanodisks as a model nanocrystal system.

I demonstrate that LSPR wavelength can be tuned by independently varying the aspect-ratio of the disk and the overall carrier density of the nanocrystal. Increased carrier density in Cu$_{2-x}$S occurs with oxidation and the formation of copper vacancies, an effect which can be suppressed by carrying out synthesis under an inert atmosphere. Using post-synthetic oxidation, Cu$_{2-x}$S nanodisks achieve a critical carrier density beyond which the nanocrystals undergo an irreversible phase change, which limits tuning capability. To circumvent this, I use a solvothermal process to generate nanodisks with different crystal phases that enable carrier densities beyond this critical limit.

This dissertation also explores the differences in near-field coupling between Cu$_{2-x}$S nanodisks. These experiments were carried out on self-assembled two-dimensional nanodisk arrays. Varying nanodisk orientation produces a dramatic change in the magnitude and polarization direction of the local field generated by LSPR excitation. Moreover, plasmonic coupling is only observed for Cu$_{2-x}$S phases that possess carrier densities above a critical value.

Overall, this dissertation provides new methods for tuning the plasmonic response of semiconductor nanocrystals by controlling size, shape, and carrier density. It also
demonstrates new strategies for designing electromagnetic junctions or coupled plasmonic architectures that operate in the infrared using nanocrystals as building blocks.
CHAPTER 1
LOCALIZED SURFACE PLASMON RESONANCES OF NANOMATERIALS

1.1 Metal Nanocrystals

Materials that possess a dielectric constant with a negative, real component and a small positive, imaginary component (such as silver and gold) are capable of supporting surface plasmon resonances (SPRs).\(^1\)\(^2\) These resonances are excited by incident electromagnetic radiation which causes coherent oscillations with the conduction electrons.

For surface plasmon polaritons (SPP), plasmons propagate in the x- and y-directions along the metal-dielectric interfaces and perpendicular field \(E_z\) decays exponentially with a characteristic length \(\delta_d\) (the order of the optical wavelength) in the dielectric and a characteristic length of \(\delta_m\) (the skin depth) in the meta as depicted in scheme 1-1. When light interacts with particles much smaller than the incident wavelength, the conduction electrons of the particle oscillate within the bound volume of the nanoparticle (NP) with a frequency characterized by the excitation of a localized surface plasmon resonance (LSPR),\(^1\)\(^3\) as depicted in scheme 1-2. LSPR wavelength is determined by the NP size, shape, material, and its local dielectric environment.\(^4\)\(^8\) For example, as the diameter of a gold NP increases, the NPs exhibit an absorbance peak that continuously red-shifts to longer wavelengths.
Scheme 1-1 Surface plasmon polariton (or propagating plasmon) on metal-dielectric interface. The plasmon propagates in the x- and y-directions and the decays in z-direction. Adapted from ref. 1.

Scheme 1-2 Localized surface plasmon resonance (LSPR) on metal nanoparticles. The requirement of formation LSPR in particle is the size of particles much small than the incident light wavelength ($\lambda$). Adapted from ref. 1.

The shape-dependent LSPRs of metal NPs can be observed in anisotropic morphology nanocrystals. The spherical NPs typically show a single dipolar LSPR mode whereas anisotropic NPs exhibit multiple higher-order LSPR modes. These higher-order LSPRs modes arise from uneven charge distribution within the nonspherical particle
volume and often result in large electromagnetic field enhancements localized near the corners and edges of the NPs. For example Ag nanocubes with edge about 80 nm, the extinction spectrum curve (Figure 1-1) shows four strong LSPR modes. The highest wavelength mode (~540nm) is the dipolar LSPR mode. The second highest wavelength mode (~480nm) is quadrupolar LSPR mode which corresponds to light oscillation at the eight corners of the cube. And the plasmon modes at wavelength 390nm/360nm correspond to light oscillation at the edges of the cube. Because of this field enhancement, anisotropic NPs composed of Ag and Au are currently being pursued as platforms for subwavelength focusing and imaging, surface-enhanced Raman spectroscopy, and photovoltaics.  

\[1, 9, 10\]

![Figure 1-1](image.png)

**Figure 1-1** The extinction spectrum of Ag nanocube colloidal aqueous with edge side about 80nm. The largest wavelength of extinction peak at \(\lambda \sim 540\text{nm}\) is the dipole LSPR mode. The second largest wavelength at \(\lambda \sim 480\text{nm}\) corresponds the quadrupolar LSPR mode. And the third and fourth peaks at \(\lambda < 400\text{nm}\) are higher order LSPR mode.
Moreover, the compounds of metal NPs also play an important role for tuning the plasmonic response. Bimetallic NPs have exceptional LSPRs that differ from metal NPs composed of a single metal. These hierarchical nanostructures have been reported to be excellent catalysts due to the synergistic effect of the two metals in promoting molecular adsorption and activation.\textsuperscript{11-19} For Au-Ag bimetallic NP, the synergistic surface chemistry of two metal surfaces enhancement of the CO oxidization process as Figure 1-2.\textsuperscript{11}

![Figure 1-2](image1.jpg)

Figure 1-2 Structure model for CO and O\textsubscript{2} adsorption on surface of Au-Ag alloy. The yellow balls and the blue balls represent Au and Ag in Au\textsubscript{25}Ag\textsubscript{30} alloy nanoparticle, respectively. The red balls represent the oxygen atoms, and the gray ball is for the carbon atom. Adapted from ref. 11.

Ag-Au bimetallic NPs have been demonstrated that possess unique LSPR properties attributed to NP morphologies, such as core-shell,\textsuperscript{20} hollow,\textsuperscript{21} porous,\textsuperscript{22} and cage-like NPs.\textsuperscript{23} Bimetallic NPs are typically achieved by chemical reactivity at the NP template-solvent interface. In galvanic deposition reactions, a redox couple is established between metal ions in solution (be deposited) and the metal NP template (be etched).\textsuperscript{22, 24}
1.1-1 Plasmonic Response of Bimetallic Nanoparticles: Polyelectrolyte-Templated Synthesis

Colloidal nanoparticles (NPs) are versatile templates for solid-state transformations in the synthesis of bimetallic or hybrid nanostructures. Metal NPs can serve as substrates for materials deposition or displacement reactions that lead to the formation of core-shell,20, 25-29 porous,22 hollow,21, 30-32 and cage-like23, 33 morphologies. The advantages of these hierarchical nanostructures have been demonstrated by the fabrication of porous and hollow Au-Ag nanostructures that possess unique surface plasmon resonance properties22. The optical properties of these metal nanostructures are tailored by controlling their overall morphology, and such nanostructures have been utilized for applications such as biomedical phototherapies23 and surface-enhanced Raman spectroscopy.34 Bimetallic NPs have also been demonstrated to be excellent catalysts due to the synergistic effect of the two metals in promoting molecular adsorption and activation.11, 15-19, 29, 33 By utilizing a NP template, these catalysts can be engineered to possess a beneficial “atom economy” where an active metal (typically costly transition metals such as Pt, Pd, and Rh) is predominantly located in an enriched surface layer. This chemical synthesis is particularly advantageous for the current generation of catalytic materials because it is a scalable, solution-based approach.

Material control in these and other bimetallic nanostructures is typically achieved by chemical reactivity on the NP template-solvent interface. For example, in galvanic displacement reactions, a redox couple is established between the metal ions in solution (to be deposited) and the metal NP template (to be etched)22, 24, 26 as scheme 1-3.
Scheme 1-3 Illustration summarizing the morphological and structural changes involved in the galvanic replacement reaction between a silver nanocube and an aqueous HAuCl₄ solution. Adapted from ref. 24.

By exploiting materials with favorable electrochemical redox potentials, spontaneous deposition occurs as metal ions are reduced while the exposed NP surface is concurrently oxidized. However, the role of molecules bound at the NP surface is largely unexplored in these transformation reactions. NP templates are typically synthesized by utilizing polymers, surfactants, or molecular ligands to passivate the NP surface. Because galvanic deposition is largely a surface-driven charge transfer reaction, these chemical species are expected to significantly alter deposition rate, mechanism, and subsequent alloy formation.

Here, I demonstrate that adsorbed polyelectrolytes on the NP surface can play a key role in the galvanic deposition mechanism by i) dictating the NP surface charge density and ii) presenting a hydrodynamic barrier for reactant diffusion. These parameters allow for a new chemical strategy to control the transformation of the NP solids via
surface modification, and also provide a unified growth mechanism for the widely varying NP morphologies that have been achieved through galvanic displacement reactions. The resulting nanostructures can be engineered to possess tailored, hierarchical morphologies with compositions that present new opportunities for systematically studying the optical catalytic properties of bimetallic NPs.

Bimetallic Au-Ag NPs were prepared by galvanic deposition of Au onto colloidal Ag NP templates. Colloidal Ag NP templates were prepared by reducing an aqueous solution of AgNO$_3$ in the presence of sodium citrate, according to literature methods.$^{35}$ An aqueous solution of silver nitrate (0.0127g , 7.5 mM, Sigma) was refluxed for 5 minutes at T= 100°C. An aqueous solution of citric acid trisodium salt (2 wt%, Sigma) was quickly injected into the hot solution. Different sizes of citrate-coated Ag NPs were prepared by adding different injection volumes, ranging from 1.5 to 6 mL. The as-prepared NPs are polycrystalline and roughly spherical in shape, with an average diameter of 62.6 ± 8.6 nm (Figure 1-3, inset). The bulk extinction spectrum for the colloidal dispersion was measured by UV-Vis spectroscopy and shows a sharp peak at 425 nm attributed to the dipolar surface plasmon resonance (SPR) mode for spherical Ag NPs.

In order to study the effect of surface chemistry NP on galvanic deposition reaction, the layer-by-layer (LBL) technique was used to coat different polyelectrolyte on NP surface. To modify the NPs with a positively-charged polyelectrolyte layer, the citrate-coated Ag NPs were dispersed in 6 mL of an aqueous poly(allylamine hydrochloride) (PAH) solution (0.56 wt%, Mw=15k, Sigma) and incubated for 20 h at room temperature with stirring. The dispersion was then precipitated by centrifugation and redispersed in DI
water (repeated three times) to remove excess PAH as shown schematically in Figure 1-3A. I denote this template as PAH-1.

To modify the NPs with a negatively-charged polyelectrolyte layer, PAH-1 NPs were dispersed in 6 mL of an aqueous poly (sodium 4-styrene sulfonate) (PSS) solution (0.56 wt%, Mw=70k, Sigma) and incubated for 20 h at room temperature while being stirred. The NPs were then centrifuged and redispersed in DI water to remove excess PSS (repeated three times), forming a PAH/PSS coating which I denote as PSS-1. Sequential LBL deposition was achieved by repeating these polyelectrolyte incubation steps until the desired NP coating was achieved.

Zeta-potential measurements performed by dynamic light scattering indicate that the as-made NPs are negatively charged ($\zeta=-43.8$ mV), confirming the presence of a weakly adsorbed layer of citrate ions at the Ag surface. Prior to carrying out deposition, Ag NPs were chemically modified using a layer-by-layer (LBL) approach to adsorb shells of charged polyelectrolytes at the NP surface.$^{30}$ Advantageously, this surface modification strategy is a general method that can be extended to a variety of NP systems. Figure 1-3B shows zeta-potential measurements for PAH-1 ($\zeta=+61.3$ mV) and PSS-1 NPs ($\zeta=-27.0$ mV), confirming that successive LBL polyelectrolyte adsorption has occurred. Figure 1-4, TEM image analysis indicates that the PAH-1 layer is ~0.95 nm thick and the PSS-1 layer is correspondingly ~1.5 nm thick.

This incubation procedure can be carried out for multiple cycles to produce multiple polyelectrolyte shells with alternating charge. LBL deposition is also confirmed by a red-shift in the SPR peak, which indicating an increase in the dielectric constant of NP environment due to polyelectrolyte adsorption and the appearance of the PSS
absorbance peak at 225nm, which is known to increase linearly with LBL adsorption (Table 1-1).

**Figure 1-3** Synthesis and surface modification of Ag NP templates prior to carrying out galvanic displacement. (A) Schematic of the LBL assembly of differently charged polyelectrolyte layers (above) and (B) the corresponding zeta-potential measurements indicating changes in NP surface charge with each successive layer deposition. Inset: SEM of as-made citrate-capped Ag NPs.

**Figure 1-4** TEM image of citrate coated, first PAH coated, and PSS-PAH coated Ag nanoparticle templates. Scale bar is 20nm.
Table 1-1 UV-Vis measurements after LBL adsorption of differently charged polyelectrolytes on NP templates. The maximum SPR peak red-shifts with increased adsorption of polyelectrolytes (due to a change in the dielectric environment of the NP) and the increasing absorbance intensity at 225 nm indicates the adsorption of PSS.

<table>
<thead>
<tr>
<th>NP coating</th>
<th>Max. extinction peak (nm)</th>
<th>FWHM of max. peak (nm)</th>
<th>Intensity, $\lambda=225\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate (as-made)</td>
<td>425</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Layer 1: PAH</td>
<td>423</td>
<td>113</td>
<td>--</td>
</tr>
<tr>
<td>Layer 2: PSS</td>
<td>426</td>
<td>141</td>
<td>0.1381</td>
</tr>
<tr>
<td>Layer 3: PAH</td>
<td>428</td>
<td>148</td>
<td>0.1007</td>
</tr>
<tr>
<td>Layer 4: PSS</td>
<td>430</td>
<td>155</td>
<td>0.2701</td>
</tr>
<tr>
<td>Layer 5: PAH</td>
<td>439</td>
<td>160</td>
<td>0.2077</td>
</tr>
<tr>
<td>Layer 6: PSS</td>
<td>444</td>
<td>182</td>
<td>0.5643</td>
</tr>
</tbody>
</table>

Longer polyelectrolyte incubation times and higher concentrations of polyelectrolyte do not result in significantly different zeta-potentials or shell thicknesses, suggesting that polyelectrolyte adsorption is self-limiting once full surface coverage is achieved. LBL deposition can be used to tune the overall surface charge exhibited by the Ag NPs, as demonstrated by the deposition of multiple polyelectrolyte layers.

I then carried out galvanic displacement reactions utilizing LBL-modified Ag NPs with different surface charges as the sacrificial templates for Au deposition, as shown in Figure 1-5. Polyelectrolyte-coated Ag NPs were incubated in aqueous solutions of gold chloride hydrate (HAuCl₄) at various reaction times and concentrations. Figure 1-5B shows scanning and transmission electron microscope (SEM and TEM) images of PAH-1 after performing galvanic deposition of Au yield bimetallic NP compositions with an Au-Ag atomic ratio of approximately 2:3.

Reaction of the NPs with HAuCl₄ results in the formation of hollow nanostructures with an outer diameter of $71.3 \pm 12.3$ nm and an inner diameter of $54.2 \pm$
4.3 nm. Au is deposited in a uniform layer over the template surface, leading to the formation of a uniform Ag-Au alloyed shell. Ag consumption occurs by diffusion of Ag atoms from the NP core to the reaction interface.

**Figure 1-5** Galvanic displacement with AuCl₄⁻ onto a positively charged NP template. (A) Schematic of first pathway for galvanic displacement, where Au deposition onto a PAH-coated Ag NP results in a hollow nanostructure. (B) TEM and SEM images for the bimetallic NPs resulting from the galvanic displacement reactions. Scale bars are 20 nm and 100 nm, respectively. (C) UV-Vis extinction measurements during the galvanic displacement reaction. The as-made Ag NP templates display a characteristic surface plasmon peak at 425 nm prior to the galvanic reaction. The steady red-shift of this peak during the displacement reaction indicates that Au deposition results in the formation of a bimetallic NP with a larger overall radius.

This is confirmed by UV-Vis extinction measurements, which show that the SPR peak gradually red-shifts as the deposition reaction is continued (Figure 1-5C). This red-shift is attributed to:
(i) An increase in diameter of nanoparticle due to the deposition of Au on the NP surface,
(ii) The changing dielectric function of the alloy as the atomic percent of Au is increased
(iii) An increase in the void size of the hollow structure and a reduction in the thickness of alloy wall.\textsuperscript{24}

As the Au displacement continues, the reaction becomes diffusion-limited and Ag atoms are either diffused into the bimetallic alloy or are consumed at the AuCl\textsubscript{4}\textsuperscript{-} reduction front. Analysis by energy-dispersive X-ray spectroscopy (EDS) confirms that the resulting hollow nanostructure is uniformly composed of both metals and that dealloying does not occur at this composition ratio (Figure 1-6 and 1-7). Interestingly, the resulting hollow Au-Ag NPs are faceted at their outer surface, which is likely due to the strong chemical interaction between PAH and the NP surface.

\textbf{Figure 1-6} Representative SEM images of PAH- and PSS-coated Ag NPs at different reaction concentrations of AuCl\textsubscript{4}\textsuperscript{-} during galvanic deposition. As the [AuCl\textsubscript{4}\textsuperscript{-}] atomic % approaches 50\% in the resulting bimetallic NP, dealloying of the Au-Ag NP is evidenced by the large holes in the nanostructure.
Elemental analysis shows the formation of uniform Au-Ag alloy composition of approximately 40 atomic % Au and 60 atomic % Ag over the entire particle. Cu is present due to the presence of the support grid. The corresponding STEM image shows that the Au-Ag NP has hollow structure with faceted outer surface.

Using PSS-coated Ag NPs as the reaction template, galvanic displacement with Au results in the formation of aggregated, porous nanostructures rather than the hollow shells templated by PAH-coated NPs. Figure 1-8 shows SEM and TEM images of PSS-1 after the displacement reaction, where the resulting nanostructure appears to be composed of a number of smaller metal NPs (d<20 nm) that are interconnected to form a porous volume with an average outer diameter of 89.7 ± 5.2 nm.

The UV-Vis extinction measurements in Figure 1-8C show that the SPR gradually decreases in intensity, indicating the dilution of Ag NP composition with Au atoms without a corresponding increase in NP size. UV-Vis measurements indicates that Au deposition does not occur uniformly at the surface of the Ag NP template since no SPR red-shift is apparent and no new SPR peaks can be attributed to conformal Au coating.
The porous aggregate structure of the bimetallic NP suggests that Ag is consumed directly from the exposed template surface rather than from the interior core of the NP template.

Figure 1-8 Galvanic displacement with AuCl\textsubscript{4}\textsuperscript{-} onto a negatively charged NP template. (A) Schematic of second pathway for galvanic displacement, where Au deposition onto a PSS-coated Ag NP results in a porous, aggregate bimetallic NP. (B) TEM and SEM images for the bimetallic NPs. Scale bars are 20 nm and 100 nm, respectively. (C) UV-Vis extinction measurements during the galvanic displacement reaction. The decrease in the plasmon peak intensity without a corresponding wavelength shift indicates that Au deposition does not occur conformally at the Ag NP surface.

To determine the manner in which Au is deposited (and Ag is consumed) during the galvanic displacement reaction, I observed the evolving nanostructure morphology at
early stages of Ag NP reaction with HAuCl₄. The formation of porous, aggregate nanostructures appear to be driven by localized Au deposition that is promoted by the negatively-charged PSS adsorbed at the NP surface, as seen in Figure 1-9.

TEM analysis indicates that Au deposition and Ag etching processes both occur at the surface of the colloidal Ag template. At the onset of the galvanic reaction, Au deposits at discrete nucleation sites on the template surface. This is confirmed by EDS mapping and analysis (Figure 1-9 C-E), which indicates highly concentrated regions of Au at the surface of the NP template. The location of these Au nucleates are likely to be correlated with the morphology of the underlying polycrystalline Ag NP, and I observe that Au is preferentially deposited at high surface-energy defect sites such as the twin plane defect shown in Figure 1-9 C. As the reaction proceeded, I observed the growth of these Au nucleates in addition to the formation of shallow pits in the Ag NP localized near the Au.

These pits indicate the consumption of Ag from the template surface and are reminiscent of morphologies reported for galvanic deposition of metals onto semiconductor surfaces, where metal nucleation sites are embedded in the center of etched holes at the surface of crystalline Si and Ge. As the Ag NP is continuously etched and fresh Ag surfaces are exposed, simultaneous Au deposition and Ag etching continue until the entire core of the NP template is penetrated. These nucleation sites eventually develop into the larger bimetallic lobes that are observed in the final NP after continuous reaction with HAuCl₄. This progressive reaction accounts for the presence of (i) larger alloy nucleates at the surface and (ii) enriched Au concentrations at the resulting NP’s surface.
Figure 1-9 Galvanic displacement with AuCl₄⁻ onto a negatively charged NP template. (A) Schematic of second pathway for galvanic displacement, where Au deposition onto a PSS-coated Ag NP results in a porous, aggregate bimetallic NP. (B) TEM and SEM images for the bimetallic NPs. Scale bars are 20 nm and 100 nm, respectively. (C) UV-Vis extinction measurements during the galvanic displacement reaction. The decrease in the plasmon peak intensity without a corresponding wavelength shift indicates that Au deposition does not occur conformally at the Ag NP surface.

I explored the effect of polyelectrolyte layer thickness on the galvanic displacement reaction. Figure 1-10 depicts the difference in reaction rates for galvanic Au deposition onto Ag NPs with sequential, oppositely charged polyelectrolyte layers and the corresponding bimetallic NP morphologies. Reaction rate was determined by monitoring
the exponential decay of the intensity of the Ag SPR peak, which is indicative of Ag consumption. I coated Ag NPs with up to six polyelectrolyte layers. Overall, I observe a decrease in the galvanic reaction rate with an increase in the total number of layers. I attribute this effect to an increase in the hydrodynamic barrier for AuCl$_4^-$ ion diffusion. Ionic transport to the deposition front is severely hindered as the polyelectrolyte coating increases in thickness.

![Figure 1-10](image)

**Figure 1-10** The effect of multiple polyelectrolyte layers. Dependence of reaction rate on polyelectrolyte layer number, as measured by the decay rate of the Ag SPR peak intensity. The blue symbols denote PAH-terminated NPs and the red symbols denote PSS-terminated NPs.

For Ag templates coated with only a few layers of polyelectrolyte, NPs terminated with a positively-charged PAH layer undergo faster displacement relative to NPs terminated with a negatively-charged PSS layer. This is also consistent with the morphology observed for all PAH-terminated templates shown in Figure 1-11, where fast
nucleation of Au results in conformal shell growth over the surface of the entire NP template. Regardless of reaction rate or total number of polyelectrolyte layers, galvanic deposition onto PAH-terminated NPs consistently results in a hollow bimetallic shell structure. This underscores the importance of surface charge in these surface-directed NP transformations, which is dictated by the terminal polyelectrolyte layer. I attribute this to the strong electrostatic attraction between PAH and AuCl$_4^-$, which promotes faster Au deposition at the onset of the displacement reaction.

I obtained drastically different bimetallic NP morphologies using PSS-terminated NPs to template the galvanic reaction. As seen in Figure 1-11, the terminal PSS layer promotes island-like nucleation of Au on at the template surface. As the number of polyelectrolyte layers increases, however, I observe the resulting bimetallic NP structure more clearly as smaller Au-enriched nucleates that are supported by a cage-type structure. The cage structure appears to be initial Au nucleation sites on the original template. For the polycrystalline Ag NPs used in these experiments, these are likely to be boundaries of the multiple twin planes that extend to the surface of the NPs. These initial sites for Au deposition can then support the further growth of specific nucleates, as seen for PSS-1.

However, as the number of polyelectrolyte layers increase, diffusion of Ag and AuCl$_4^-$ towards the deposition interface is hindered by the increased hydrodynamic barrier. For the PSS-terminated templates, this encourages the growth of fewer nucleates that possess larger diameters. For PSS-1, which is coated with two polyelectrolyte layers, the cage structure is almost entirely covered by bimetallic nucleates that are 10-20 nm in size; for PSS-2, the number of nucleates decreases and they range from 35-45 nm in diameter. For PSS-3, which is coated with six polyelectrolyte layers, the final
morphology of the bimetallic NP is the cage structure attached to a single nucleate with the largest observed nucleate possessing a diameter of 70 nm. Thus, the overall polyelectrolyte layer thickness dictates the number and of nucleation sites that are allowed to grow. This ability to dictate diffusion in and out of the cage structure is expected to have important consequences for designing hierarchical structures utilizing galvanic displacement.

![Figure 1-11 TEM images of the final bimetallic NP morphologies of the reacted templates in Figure 1-10. Numbers correspond to the total number of polyelectrolyte layers coating each template. The scale bar is 20 nm.]

This charge-controlled mechanism for galvanic displacement is not specific to the PAH-PSS system. To confirm that surface charge dictates the pathway for Au nucleation rather than the specific chemical composition of the polyelectrolyte coating, I observe that similar results can be achieved with various polyelectrolyte pairs, including combinations of PAH, PSS, the poly(acrylic acid) PAA, poly(diallyldimethylammonium chloride) PDDA, and the mixed polymer poly(3,4-ethylenedioxythiophene):poly(styrene
In each case, positively charged NP templates give rise to hollow bimetallic nanoparticles and negatively charged templates result in porous or aggregated structures. In Figure 1-12, the zeta-potential measurements of indicating changes in NP surface charge with PDDA as positively charged NP templates and PSS as negatively charged NP templates. The TEM images in Figure 1-13 gave the evidence of the morphology of bimetallic nanoparticles after galvanic deposition reaction is surface charge dependent. I observed this reaction tendency in a variety of different polyelectrolye pairs, indicating the importance of surface charge over the exact chemical makeup of the template surface coating in Figure 1-14.

![Zeta-potential measurements](image)

**Figure 1-12** Zeta-potential measurements of the LBL assembly of differently charged polyelectrolyte layers indicating changes in NP surface charge with each successive layer deposition Inset: SEM of as-made citrate-capped Ag NPs.
Figure 1-13 Galvanic displacement results for PDDA/PSS-coated AgNPs as templates. The TEM and SEM images for PDDA-terminated NPs after displacement show in top row. Scale bars are 20 nm and 100 nm, respectively. The TEM and SEM images for PSS-terminated NPs after displacement show in bottom row. Scale bars are 20 nm and 100 nm, respectively.

Figure 1-14 The effect of multiple polyelectrolyte layers. Dependence of reaction rate on polyelectrolyte layer number, as measured by the decay rate of the Ag SPR peak intensity. The green symbols denote PAH-terminated NPs and the red symbols denote PSS-terminated NPs.
This tendency is similar with PAH-PSS system which shows that the positively charged terminated NP templates undergo faster displacement relative to NPs terminated with negatively charged terminated NP templates. This due to the strong electrostatic attraction between positively charged polyelectrolyte layer and AuCl$_4^-$, which promotes faster Au deposition at the onset of the displacement reaction.

I also observed the morphology of the bimetallic NP after galvanic deposition reaction is dependent on the surface charged of anisotropic nanoparticles, such as nanocubes (Figure 1-15) and nanorods.

![Figure 1-15](https://example.com/figure1-15.png)

Figure 1-15 Galvanic displacement results for PAH/PSS-coated Ag nanocubes as templates. (a) The TEM and SEM images for PAH-terminated NPs after displacement. (b) The TEM and SEM images for PSS-terminated NPs after displacement.
Here, I have demonstrated a simple technique for controlling the morphology and surface composition of bimetallic NPs using a surface-controlled galvanic deposition reaction. Colloidal Ag NPs are utilized as sacrificial templates for the electroless deposition of AuCl$_4^-$ from aqueous solution. The surface charge of these NPs can be readily modified through the LBL assembly of polyelectrolytes with alternating positive and negative charge. Upon reaction with AuCl$_4^-$ ions, the Ag NP templates are converted to Au-Ag alloy NPs through two different displacement pathways: if the NP surface is terminated with a positive polyelectrolyte layer, Ag is consumed from the interior of the NP; if the NP surface is terminated with a negative polyelectrolyte layer, Ag is consumed from the exposed surfaces of the NP as shown in Figure 1-16. The final bimetallic NP morphology is controlled by the terminal polyelectrolyte layer, which dictates initial Au deposition, and the total thickness of the polyelectrolyte coating, which dictates the hydrodynamic barrier for reactant diffusion.

![Figure 1-16 TEM image and schematic](image)

**Figure 1-16** TEM image and schematic shows the morphology of negatively charged nanoparticle templates after galvanic deposition.

I propose that these charged surface layers control galvanic charge transfer by
controlling nucleation and diffusion at the deposition front. This surface-directed synthetic strategy can be advantageously used to tailor both overall NP morphology and Au surface concentrations.

Overall, the LBL strategy for controlling galvanic deposition is particularly advantageous because the charge and thickness of the polyelectrolyte shell can be readily tuned through sequential electrostatic deposition. This ability to tailor NP morphology and surface composition should allow systematic studies of the cooperative metal effect and the evaluation of these bimetallic as potential nanocatalysts for reactions such as low-temperature CO oxidation.

1.2 Semiconductor Nanocrystals

More recently, LSPRs have been reported for nonmetallic nanocrystals composed of doped semiconductor materials such as Cu$_{2-x}$S, Cu$_{2-x}$Se, and Sb-doped SnO$_2$. Plasmonic nanocrystals composed of these materials are advantageous because LSPR wavelength can be dynamically tuned by controlling free carrier density through chemical and electrochemical doping processes. In Figure 1-17, the LSPR frequency ($\omega_{sp}$) of doped semiconductor can be estimated by

$$\omega_{sp} = \frac{1}{2\pi} \sqrt{\frac{Ne^2}{\varepsilon_0 m_e (\varepsilon_\infty + 2\varepsilon_m)}}$$

Here N is free carrier concentration, $\varepsilon_0$ is permittivity of free space, $m_e$ is effective mass of the free carrier, $\varepsilon_\infty$ is high frequency dielectric constant, and $\varepsilon_m$ medium dielectric constant.
Localized surface plasmon resonance (LSPR) frequency dependence on free carrier density and doping constraints. Metal nanomaterials possess the carrier density about $10^{23}$ cm$^{-3}$ and their plasmonic responses locate in Ultraviolet to Visible range. For degenerately doped semiconductor, the carrier density can be tuned in $10^{19}$-$10^{22}$ cm$^{-3}$ which corresponds the LSPR in entire infrared range. Adapted from ref. 38.

For the semiconductor NPs sizes ranging from 2 to 12nm with doping carrier concentration of $10^{19}$-$10^{22}$ cm$^{-3}$, their LSPRs lie in infrared range. Below $10^{19}$ cm$^{-3}$, the number of carriers (for a 10nm nanocrystal) may be too low (<10) to support an LSPR mode.

In the traditional extrinsically doped semiconductors and metal oxides, the extra carriers of nanocrystals are generally increased by increasing the dopant atoms. For example, tin doped indium oxide (ITO) is classic transparent conductive oxides which the wavelength of plasmonic resonance can be varied from 1600nm to 2200nm by electrochemically applying a bias voltage or controlling the concentration of Sn dopants as depicted in Figure 1-18 and 1-19, respectively. However, the number of free carriers in extrinsically doped nanocrystals is lower than the number of impurities/defects due to a portion of the extra carriers can be trapped.
Another type of plasmonic semiconductor is self-doped semiconductor which includes copper deficient copper chalcogenides and oxygen deficient metal oxides. For self-doped semiconductor, free carriers arise from the tuning in the oxidation state of one of their elements into sub-stoichiometric phases.

Figure 1-18 Tuning of LSPRs of ITO nanoparticles by application of an electrical potential. By applying a voltage bias, the LSPR of the NPs blue-shift by 1200 nm in the NIR region. A film of such NPs can be served as a voltage-tunable filter for selective transmission of IR light (i.e., heat). Adapted from ref. 42.

Figure 1-19 Extinction spectra of tin doped indium oxide (ITO) shows that the LSPR wavelength blue-shift with increasing dopant concentration (%Sn) at range 0-10% of Sn. The LSPR wavelength red-shifts with increasing dopant concentration at Sn >15%. Adapted from ref. 43.
In order to compensate for the sub-stoichiometry of one of the components, this results in extra electrons in the conduction band, or in holes in the filled valence band. For example, Cu$_{2-x}$S has different stoichiometric structures that can be obtained by tuning the number of copper deficiencies during the synthetic process or post-synthetic treatment. Cu$_{2-x}$S is a particularly interesting material for plasmonics due to the carrier density can be tuned in the range of 10$^{20}$~10$^{22}$ cm$^{-3}$ by controlling the stoichiometric of copper sulfide which corresponds the plasmonic response in near-infrared (NIR) to infrared (IR) range. In addition, it is composed of highly earth abundant elements and possesses an environmentally benign composition. These cause copper sulfide nanocrystals be a candidate material for low-cost, active, and tunable building blocks for NIR-IR plasmonics materials.

Previously, it has been shown that spherical Cu$_{2-x}$S nanocrystals possess an LSPR mode in NIR range and the absorption wavelength of LSPRs can be tuned by introducing copper vacancies into the Cu$_{2-x}$S lattice. Hole carriers of spherical Cu$_{2-x}$S NPs are generated by these vacancies are produced upon exposure of the nanocrystals to oxygen, which caused the LSPR band to blue-shift as the dopant concentration is increased. However, the plasmonic response of semiconductor nanocrystals affected by their shape, carrier density is not fully understood. And no study to-date has investigated the plasmonic coupling between semiconductor nanostructures.

1.3 Plasmonic Coupling

When two metal NPs are brought in proximity to each other, the near-field on one NP can interact with that on the other particle. Thus, the electric field $E$ felt by each
particle is the sum of the incident light field $E_0$ and the near-field $E_{nf}$ of the neighboring particle. As a result of this near-field interaction, plasmon oscillations of the two nanoparticles become coupled. The plasmonic response sensitivity (shift of plasmonic response) shows that almost increase near-exponentially with a decrease in the inter-particle gap (normalized with particle size) as depicted in Figure 1-20. Under the theoretical prediction, this plasmon oscillation coupling phenomenon also can be observed at the semiconductor nanocrystals with appropriated carrier density.

![Graph showing exponential decay of sensitivity with increased S/D](image)

**Figure 1-20** Near-field plasmonic coupling between Au NPs. The plasmonic response sensitivity is exponential decay with increased the S/D (interspace gap normalized with particle size). Adapted from ref. 44.

In order to study the plasmonic coupling between NPs, two-dimensional arrays with tunable the space between NPs is required. Self-assembly of NPs has been identified as an important process where the building blocks spontaneously organize into ordered structures by thermodynamic and other constraints. This strategy can be directed,
enhanced, or controlled by changing the energy or entropy landscapes, using templates or applying external fields, or controlling the surface chemistry of NPs.

Self-assembly refers to the process which nanoparticles or other discrete components spontaneously organize due to thermodynamic equilibrium, the organized structures being characterized by a minimum in the system’s free energy. Essential in Self-assembly is that the building blocks organize into ordered, macroscopic structures, either through direct interactions (e.g. by interparticle forces), or indirectly using a template or an external field. The thermodynamic forces which drive self-assembly need to be modulated, either by chemistry, templating, or external fields for large scale orderly superlattice structure. In Figure 1-21 shows the assembly of particles by external fields, such as alternating current (AC) electric fields in (a) and flow-field in (b).

Langmuir Blodgett (LB) assembly method is used to fabricate molecular monolayer at the air-water interface. In a typical process for preparing LB monolayers, amphiphilic molecules are first dissolved in a volatile organic solvent and then spread onto the water surface. As the solvent evaporates, the molecules are trapped on the water surface, forming a monolayer. A moving barrier is then used to change the area of the monolayer, thus effectively tuning the intermolecular distance. As the film is compressed, it can undergo phase transitions from gas to liquid to solid phases as depicted in scheme 1-4. The film can be transferred to a solid substrate (e.g., by dip-coating), forming a monolayer coating over a large area. The LB technique is not limited by small molecules; monolayers of polymers and nanomaterials have been prepared in similar manner. The nanomaterials monolayer with various interspaces between nanomaterials can be controlled by tuning the surface pressure of LB monolayer. And the interactions forces
between nanoparticle-nanoparticle and nanoparticle-water interface can be used to design the orientation of 2D arrays.52-55

**Figure 1-21** Directed assembly of particles in external fields (a), including the growth of microwires from gold nanoparticles, assembly of micrometer-diameter colloidal particles into hexagonally close-packed arrays in AC electric fields, assembly of metallo-dielectric janus particles, and ellipsoidal particles. (b) Flow-field induced self-assembly. Adapted from ref. 46.

**Scheme 1-4** The phase transfer diagram of Langmuir Blodgett (LB) film with changing surface pressure of film. Adapted from ref. 51.
The electron beam lithography technique is another method to fabricate two-dimensional NP arrays with tunable dimensions and spacing. For example, Su et al. used the lithographically produced Au NP array to demonstrate plasmon coupling in nanomaterials and observe that the plasmon shift shows an exponentially decays with increased interparticle separation.\textsuperscript{56} Gunnarsson et al. also proved this near-exponential decay coupling behavior in Ag nanodisks arrays.\textsuperscript{57} Jain et al. studied the plasmon coupling between Au nanodisks arrays with different interparticle separations which fabricated by lithographically. They observed polarization dependence of the plasmon coupling and exponential-like decay of the plasmonic shift with interparticle gap for polarization along the interparticle axis as depicted in Figure 1-22.\textsuperscript{58}

**Figure 1-22** a) Gold nanodisk (88-nm in diameter) pairs array with tunable interparticle separation was fabricated by lithography technical. The SEM image shows the inter-particle is 12nm. Extinction spectra show that the LSPR of the NP pair array (b) Red-shifts with decreasing gap for polarization along the inter-particle axis. (c) Blue-shifts very slightly with decreasing gap for polarization perpendicular to the inter-particle axis. Adapted from ref. 58.
In this dissertation, I will describe the synthesis methods for fabrication of different copper sulfide nanocrystals. And the systematic study of plasmonic responds in copper sulfide nanocrystals by independently tuning size, shape, and carrier density of copper sulfide nanocrystals. Then I also fabricated copper sulfide NPs into the two dimensional (2D) arrays by Langmuir Blodgett (LB) technique and study the plasmonic response of these 2D arrays. I also describe the carrier density dependent plasmonic coupling between copper sulfide nanocrystals.

Chapter 1, in part, is a reprint of the content as it appears in Langmuir.

CHAPTER 2

SYNTHESIS OF SHAPED Cu$_{2-x}$S NANOCRYSTALS

Solution-phase synthetic approaches have been used to fabricate a variety of different nanocrystal materials with controllable size and size distributions.$^{59-61}$ For synthesis compound semiconductor nanocrystals, metal-organic precursors are rapid injected into a vigorously stirred flask containing a hot coordinating solvent which subsequent nucleation can be triggered by supersaturation of precursor in reaction solution as depicted in Figure 2-1.$^{61}$

Figure 2-1 (A) Schematic figure explains the stages of nucleation and growth of monodisperse NCs by the framework of the La Mer model. (B) Representation of the simple synthetic equipments employed in the fabrication of monodisperse NCs. Adapted from ref.61
Due to the properties of nanoscale materials strong dependent on their dimensionality, there are several colloidal synthetic methods which were reported to control shape of nanocrystals. In these methods, inorganic particles are precipitated from molecular precursors in the presence of organic ligands. The ligands were adsorbed to the nanocrystal surface which plays a significant role for controlling nanocrystal growth by providing steric stabilization and preventing aggregation. The adsorbed ligands can change the growth kinetics and surface energies of different crystal faces, which result in anisotropic growth of low symmetry nanostructures, such as nanorods, nanodisks, and nanowires.\textsuperscript{62,63}

For synthesizing colloidal Cu\textsubscript{2}S nanocrystals, Hyeon’s group used the thermal decomposition of pre-synthesized copper oleate complexes in alkanethiol which acts as a solvent and sulfur source to fabricate copper sulfide nanoparticles.\textsuperscript{64} In order to simplify the synthesis process, Li’s group developed a solvothermal method to eliminate the steps for preparing the special copper precursors by directly using the copper salts and dodecanethiol to fabricate Cu\textsubscript{2}S nanocrystals.\textsuperscript{65} In solvothermal process, the shape and size of Cu\textsubscript{2}S NCs can be controlled by introducing additional salts and acid. Alivisatos’s group also fabricated Cu\textsubscript{2}S NPs with hexagonal-faceted morphology by injecting a cool copper salt solution into a hot solution which mixed with dodecanethiol, oleic acid, and ammonium diethyldithiocarbamate.\textsuperscript{66}

Another common method for synthesizing colloidal Cu\textsubscript{2}S NPs is solventless thermolysis of copper thiolates, which behave as a single-source molecular precursor. This method was first reported by Korgel’s group\textsuperscript{67}, they synthesized Cu\textsubscript{2}S nanodisks from the thermal treatment of copper dodecanethiolate (CuSC\textsubscript{12}H\textsubscript{25}). In their study, the
anisotropic disk-like morphology formation was attributed to faster deposition at the disk edges than at the basal plane of disk. The anisotropic growth of disk is due to the high surface energy facets in disk edge. In a later work, Chen’s group also carried out solventless thermolysis of CuSC\textsubscript{12}H\textsubscript{25} precursor at 200–220°C.\textsuperscript{68} Their precursor was shown to have a lamellar structure at room temperature, and the formation of nanodisks was attributed to the aggregation of small Cu\textsubscript{2}S nucleates constrained within this lamellar structure as XRD spectrum in Figure 2-2.

![Figure 2-2](image_url) Figure 2-2 Powder X-ray diffraction (PXRD) pattern of copper dodecanthiolate (CuSC\textsubscript{12}H\textsubscript{25}) precursor which shows the lamellar structure at room temperature. Adapted from ref. 69.

The decomposition of CuSC\textsubscript{12}H\textsubscript{25} was also investigated by Wang et al. using the hot injection method, where copper sulfide is obtained by using a solvent-based synthesis at temperatures between 160 and 220°C. In their study, lamellar CuSC\textsubscript{12}H\textsubscript{25} was identified as the precursor to copper sulfide formation.\textsuperscript{69} Recently, my group reported the possible mechanism for disk-shape Cu\textsubscript{2}S formation under thermolysis process is that molecular assembly of Cu alkanethiolates into an ordered liquid crystalline mesophase
plays an essential role in templating the disk morphology of the solid-state product (Figure 2-3).\(^\text{70}\)

![Figure 2-3](image)

**Figure 2-3** Schematic of mesophase copper alkanethiolate and the TEM image of copper sulfide nanoparticle after solventless thermolysis. Adapted from ref. 70.

Here, I used a solventless synthesis modified from Larsen's published protocols. In Larsen’s protocols,\(^\text{67, 71}\) sodium octanoate (NaOOC(CH\(_2\)\(_6\)CH\(_3\)) was used as a surfactant to facilitate transfer of the copper (Cu\(^{2+}\)) ions from the aqueous phase to the organic phase. 1-dodecanethiol was added as a sulfur source to form the waxy copper alkanethiolate precursor after solvent evaporation. In our method, copper thiolate-derived precursor (CuSCH\(_{12}\)H\(_{25}\)) is prepared by mixing solutions of 1-dodecanethiol in ethanol with aqueous copper nitrate. The resulting yellow-white precursor is separated and purified by centrifugation in ethanol and deionized water, and then placed under vacuum to remove solvent and obtain a powder. This powder was heated to form a dark-brown solid comprised of the nanodisks. When thermolysis is carried out in the presence of oxygen, the formation of Cu vacancies is promoted. This results in copper sulfide phases with varying stoichiometry of the form Cu\(_{2-x}\)S. However, carrier densities of nanodisks
are limited to a critical value for this synthetic method. The nanodisks possessing Cu deficiencies greater than the Cu$_{1.94}$S phase become unstable, undergoing catastrophic particle agglomeration and fusion (more details in chapter 3).

In order to synthesize colloidal nanodisks composed of different stoichiometries and carrier densities, such as Cu$_{7.2}$S$_4$ and CuS, a different method than the solventless thermolysis was necessary. I carried out a solvent-based method for obtaining copper sulfide nanodisks that employs Cu salt and S powder as a reactant and oleylamine as a nanocrystal capping agent. Oleylamine activates the S powder by forming oleylammonium hydrosulfide, which can then react with Cu$^{2+}$ ions to precipitate Cu sulfide.

![Scheme 2-1](image.png)

**Scheme 2-1** Synthetic methods for Cu sulfide nanodisks with varying Cu content. a) Chacocite nanodisks composed of Cu$_{2-x}$S (where x=0-0.06) were synthesized by the solventless thermolysis of Cu alkanethiolate. b) Cu$_{7.2}$S$_4$ and CuS were synthesized using a solvent-based method where Cu salt and S powder are heated in the presence of oleylamine. Cu content is tailored by phase varying the precursor ratio of S:Cu$^{2+}$ in the reaction bath.
The size of these copper sulfide nanodisks can be tuned by varying reaction conditions such as temperature and time. In order to compare the extinction spectra of nanodisks with varying Cu content, I aimed to synthesize nanodisk dispersions that possess similar disk aspect-ratios and size distributions such that spectral analysis can be carried out without an intensive consideration of size and shape discrepancies.

I also carry out a method for synthesizing facetted CuS nanoprisms that exhibit highly size-dependent (aspect ratio) LSPR modes. I observed that the halide anions (Cl\(^-\), Br\(^-\), I\(^-\)) exert a significant role on the morphology of copper sulfides. Halide anions mediating the growth of anisotropic nanostructure were also observed in Ag and Au nanostructures, demonstrating that the halide anions cooperatively stabilize the low-index Ag/Au surfaces and preferentially enhance the growth in a specific crystallographic direction.\(^{72-76}\) The copper sulfide nanocrystals undergo a ripening process which cause shape-focusing but size-defocusing. I attribute this ripening process to halide ion binding of facetted triangle prism particles more stable than the oleylamine binding of unfacetted disk-like particles. The unstable particles dissolved to small precursor particles and then re-precipitated as facetted particles. This causes the facetted prism nanoparticles to enlarge and the unfactted disk-like nanoparticles to shrink. In order to fabricate CuS nanoprisms with a uniform size distribution (size-focusing), I used seed-mediated synthesis to suppress the ripening effect.

2.1 Solventless Thermolysis for Cu\(_{2-x}\)S Nanodisks

The formation of copper sulfide nanocrystals through the solventless thermolysis process includes two steps. The first step is synthesis of copper-alkanethiolate precursor.
A 2.0 M solution of 1-dodecanethiol (C_{12}H_{25}SH, >98%, Sigma-Aldrich) in ethanol was prepared by mixing 4.83 mL of 1-dodecanethiol (20 mM) with 10 mL ethanol in a glass vial. An aqueous 1.0 M copper nitrate (Cu(NO_3)_2 \cdot 2.5H_2O, Fisher) solution was prepared by dissolving 1.16 g copper nitrate (5 mM) in 5 mL DI water in a glass vial. The 1-dodecanethiol solution was added to the copper nitrate solution and stirred vigorously until the solution became colorless and a yellow-white precipitate formed. The yellow-white suspension was collected by centrifugation, washed two times with DI-water and ethanol (volume ratio of 1:2) to remove the excess reagents, and then dried in a vacuum desiccator overnight to remove residual solvent and to obtain a yellow-white powder.

The second step is solventless thermolysis of copper-alkanethiolate precursor. The precursor was placed in a glass vial and heated in an oil bath at a temperature between 200°C to 220°C. The precursor turned into a dark-brown liquid which was then cooled to room temperature, dispersed in chloroform, and centrifuged at 7500 rpm for 7.5 min. to remove any by-products. This purification process was repeated three times. The purified product was dried under vacuum to obtain a brown powder for characterization.

For the solventless thermolysis process, the morphology and crystal structure of copper sulfide nanocrystals is sensitive to the reaction conditions. This is because copper sulfide is a self-doped p-type semiconductor which has different stoichiometric structures that can be obtained by tuning the number of copper vacancies. The morphology and crystal structure of copper sulfide nanoparticles synthesized under 200°C-220 °C is shown in Figure 2-4. The TEM images (Figure 2-4 b-d) of copper sulfide nanocrystals synthesized at three different temperatures shows that the size distribution of nanodisks increased with increasing synthesis temperature.
Figure 2-4 The crystal structure and morphology of copper sulfide nanoparticle synthesized at different temperature at 30min. a) XRD spectra of copper sulfide nanocrystals synthesized under 200°C (black curve), 210°C (red curve), and 220°C (blue curve). The relative morphology of copper sulfide nanocrystals shows in TEM image b) 200°C, c) 210°C, and d) 220°C.

The increasing nanoparticle polydispersity with increasing synthetic temperature is due to greater copper vacancies at the nanocrystal surfaces causing the increased growth rate. The XRD spectra in Figure 2-4 a) indicated that the nanodisks possess the chalcocite (Cu$_2$S) crystal structure. At higher synthetic temperatures, a mixture of chalcocite (Cu$_2$S) and yarrowite (C$_9$S$_8$) (the relative peak of yarrowite marked with * in
figure 2-4 a) is obtained. This provides evidence that the copper vacancies increased at higher synthetic temperatures. In order to synthesize the nanodisks with uniform size and crystal structure, I synthesize the copper sulfide nanodisks at temperatures \( \leq 200^\circ C \).

The morphology of copper sulfide nanocrystals formed under extended thermolysis reactions of copper alkanethiolate precursor was studied. After short synthetic times, the morphology of copper sulfide nanocrystals is spherical with average sizes about 4.0±0.5nm (as observed in the TEM image in Figure 2-5a). The particle size distribution of nanodisks was obtained by counting between 150-200 nanoparticles in TEM images.

The spherical nanoparticles undergo anisotropic growth to form the disk-like nanoparticle with average particle size about 10.7±1.9 nm in diameter and 3.9±1.0 nm in thickness (as the TEM image in Figure 2-2c shows). These disk-like nanoparticles prefer growth in the direction parallel to the basal plane which increases the diameter of disk-like nanoparticles while the thickness remains constant (Figure 2-5d-g).

The XRD in Figure 2-6 indicates that the nanodisks possess a crystal symmetry that is closely related to the hexagonal lattice of chalcocite (Cu\(_2\)S) and the crystal structure remains during the extended thermolysis reaction. The XRD spectra shows that the intensity of the (110) peak increases with increasing aspect ratio of nanodisks (ratio of diameter to thickness of disks). This result indicates that nanodisk growth occurs orthogonal to the c-axis in \(<110>\) direction which is consistent with the crystal structure of nanodisks reported by Larsen with (002) as the basal plane and the \(<110>\) direction parallel to basal plane.\(^{67}\)
The morphology of copper sulfide nanocrystals changes with extended reaction time. The TEM images correspond with different reactions shown in a-g and the size distribution are listed under the TEM images. The schematic image h shows that the morphology of nanoparticles changes from spherical-like nanoparticles to disk-like nanoparticles and the disk-like nanoparticle increase in aspect ratio with increasing reaction time.

The 1-dodecanethiol plays roles as ligand and sulfur source in copper sulfide nanodisk formation. During precursor formation, the thiol reacts with copper ions to form copper alkanethiolate in aqueous solution and the carbon chain length may affect the formation mechanism of copper sulfide nanocrystals. Figure 2-7 shows that the TEM image of copper sulfide nanocrystals made from different carbon chain length of thiols.
The morphology of nanocrystals remains the disk-like shape structure but the size of nanocrystals varies with the carbon chain length of the copper alkanethiolate precursor.

Figure 2-6 XRD spectra for powder samples of Cu$_2$S nanodisks that possess different aspect-ratios. The corresponding TEM image shows in Figure 2-6d)-g). As aspect ratio increases, the relative intensity of the diffraction peak corresponding to the (110) plane increases.

Figure 2-7 The morphology of copper sulfide nanocrystal from different carbon chain length of precursor a) eight carbon chain (octanethiol) with average size 10.6nm in diameter 3.1nm in thickness. b) twelve carbon chain (dodecanethiol) with average size 21.8nm in diameter 4.3nm in thickness. b) sixteen carbon chain (hexadecanethiol) with average size 32.2nm in diameter 5.8nm in thickness.
I attribute the similar disk-like nanocrystal formation in different carbon-chain lengths to the fact that the sulfur-copper bond remains relatively unchanged while the carbon chains lead to preferential growth direction of copper sulfide nanocrystals in the \langle 110 \rangle\ direction. But the different sizes of as-made Cu sulfide nanodisks synthesized by using different carbon chain lengths may be due to the precursor thermal stability which changes the thermolysis rate.

2.2 Solvothermal Synthesis for Cu$_{2-x}$S Nanodisks

Copper sulfide nanodisks were obtained by a solvent-based method that employs Cu salt and S powder as reactants and oleylamine as a nanodisk capping agent. Oleylamine activates the S powder by forming oleylammonium hydrosulfide, which can then react with Cu$^{2+}$ ions to precipitate copper sulfide. The stoichiometry of the copper sulfide phase can be tuned by varying the precursor ratio of S:Cu$^{2+}$ in the reaction bath. For S:Cu$^{2+} > 1.5$, an excess of S powder favors the formation of the covellite (CuS) crystal phase. For S:Cu$^{2+} < 0.75$, an excess of Cu ions favors the formation of the digenite (Cu$_{7.2}$S$_4$) crystal phase.

A 0.4 M copper nitrate solution was prepared by dissolving 0.0928 g copper nitrate (0.4 mmol) in 4 mL of a solvent mixture (oleylamine/1-octadecene, volume ratio of 1:3) in a glass vial. 0.0096g (0.3 mmol) sulfur powder was added to the dark blue copper nitrate solution and stirred for 5min. The glass vial was then placed in an oil bath and stirred at 180 °C. The dark-blue solution tuned into a dark green-blue solution. At the end of the reaction, the vial was cooled to room temperature and quenched by adding in 4 mL ethanol. The solution was then centrifuged at 3000 rpm for 5 min. to remove free
oleylamine and 1-octadecene. The precipitate was re-dispersed in chloroform and centrifuged at 7500 rpm for 7.5 min. to remove any by-products. A brown-green colloidal solution with crystal structure Cu$_{7.2}$S$_4$ was obtained. In order to synthesize the CuS nanocrystals, the amount of sulfur powder was increased to 0.0192g (0.6 mmol). All the synthesis and purification processes were kept the same.

The corresponding XRD spectra for nanodisks synthesized under different S:Cu$^{2+}$ ratios at 180 °C for 45min are given in the Figure 2-8. TEM images in Figure 2-9 show that all copper sulfide nanocrystals possess the disk-like morphology. The EDX spectra for these nanodisks which synthesize under different S:Cu$^{2+}$ are given the further evidence for the crystal structure in Figure 2-10.

![XRD spectra](image)

**Figure 2-8** XRD spectra for powder samples of copper sulfide nanodisks that possess different crystal structures. The corresponding TEM image shows in Figure 2-9.
Figure 2-9 The morphology of copper sulfide nanocrystal from solvent based synthesis with different Cu:S ratio as precursor a) Cu:S=1:1.5. b) Cu:S=1:1.25. c) Cu:S=1:1. d) Cu:S=1:0.75. All the synthesis processes are 180°C 45min.

Figure 2-10 EDX spectra of three copper sulfide crystal phases. a) CuS nanodisks, and b) Cu₇.₅S₄ nanodisks which were synthesized using the solvent based synthetic method with Cu+2:S=1:1.5 and 1:0.75, respectively. c) Cu₁₉₆S synthesized using the solventless thermolysis method. The experimental data is compares well with predicted Cu:S ratios.

Table 2-1 Cu and S ratio in three different crystal structures based on EDX analysis and theoretical prediction.

<table>
<thead>
<tr>
<th>Cu:S ratio</th>
<th>CuS</th>
<th>Cu₇.₅S₄</th>
<th>Cu₁₉₆S</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDX</td>
<td>51.6/48.4=1.07</td>
<td>64.8/35.2=1.84</td>
<td>66.9/33.1=2.02</td>
</tr>
<tr>
<td>Ideal</td>
<td>1</td>
<td>1.80</td>
<td>1.96</td>
</tr>
</tbody>
</table>
2.3 Shape- and Size-Focusing of CuS Nanoprisms

I observed that the halide anions (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\)) exert a significant effect on the morphology of copper sulfide nanocrystals synthesized in our solvent-based method. Facetted copper sulfide triangular nanoprisms were obtained with halide ions, rather than the un-facetted copper sulfide nanodisks obtained in the absence of halide ions. These halide anions mediating the growth of anisotropic nanostructures was also observed in Ag and Au nanostructures, which shows that the halide anions cooperatively stabilize the low-index Ag/Au surfaces and preferentially enhance the growth in specific crystallographic directions.\(^{72-76}\) Figure 2-11 shows the growth mechanism of the CuS triangular prisms, which are grown by a two-phase colloidal synthesis.

\[\text{Figure 2-11} \text{ Halide ions enhance triangle nanoparticle formation. a) Schematic shows that triangle nanoparticle formation in a two-phase synthetic method using 1-octadecene (top layer) and pentanediol (bottom layer).}\]

The top layer of the biphasic reaction mixture is made by dissolving sulfur powder in a 4 mL mixture of oleylamine and 1-octadecene (volume ratio of oleylamine to 1-octandence = 1:3) in a glass vial. The solution took on an orange color after 5 min
ultra-sonication. The bottom layer is comprised of a 0.1 M copper nitrate solution which was prepared by dissolving 0.0928g copper nitrate (0.4 mmol) and 0.1 mmol NaCl in a 4 mL mixture of water/1,5-pentanediol (volume ratio of 1:6). This two-phase solution was heated to 180 °C in an oil bath and the reaction prolonged to 30min. The precipitation reaction between copper ions and sulfur occurs at the interface between these two layers. Small CuS seeds capped with oleylamine are formed and transfer into the organic layer due to the hydrophobic capping ligand. In the organic layer, these CuS seeds grow into larger triangle nanoprisms under extended reaction time. Triangular nanoprisms are only observed when a halide ion such as Cl⁻, Br⁻, or I⁻ is present in pentanediol, as suggested by the TEM image in Figure 2-12.

![TEM images](image)

**Figure 2-12** TEM images show that the morphology of nanoparticles synthesized without halides (a), with chloride ions (b), bromide ions (c), and iodide ions (d), respectively. All the synthetic processes are 180 °C 45min.
TEM images show larger nanocrystals and a larger size distribution for nanoprisms synthesized with Cl\(^-\) (Figure 2-9b). The particle size distribution analysis based on the TEM images show that triangular prisms with edge lengths of 42.8 ± 22.3 nm, 31.3 ± 12.3 nm, and 14.3 ± 7.2 nm resulted from the addition of Cl\(^-\), Br\(^-\), and I\(^-\) ions, respectively. The size distribution of NPs changes with different halide ions due to the stronger binding of iodide ions on the NP surface compared to chloride and bromide ions. The stabilization at the NP surface slows the growth process. Similar control of the growth rate of anisotropic Au nanoparticles has been caused by the binding strength of halide ions on the metal surface.\(^{77,78}\)

Figure 2-13 shows the X-ray diffraction spectrum of CuS triangular nanoprisms synthesized with different halide ions, indicating that each reaction produces nanocrystals that possess the covellite crystal structure.

**Figure 2-13** XRD spectra for powder samples of copper sulfide nanodisks synthesized with various halide ions. The corresponding TEM images are shown in Figure 2-9.
To achieve better size and shape uniformity, I translated the two-phase colloidal synthesis described above to a single-phase synthetic method by using CuCl$_2$ as the Cu source. In the single-phase synthesis, both CuCl$_2$ and sulfur powder are dissolved into a mixed solvent system of 1-octadecene and oleylamine prior to reacting. The resulting nanocrystals are a mixture of facetted triangular nanoprisms and more rounded nanodisks after 30 min. of reacting as Figure 2-14c demonstrates. But the size is more uniform than the copper sulfide nanocrystals synthesized in the two-phase synthesis as observed Figure 2-14 b. The crystal structure of copper sulfide nanoparticles synthesized under both the two-phase and single phase synthetic methods is covellite CuS.

Figure 2-14 a) XRD spectra of triangle nanoparticles synthesized under two-phase and one-phase methods respectively. In the two-phase method (black), Cu(NO$_3$)$_2$ and halide ions were dissolved in pentanediol and S powder was dissolved in the oleylamine/octadecene phase. In the one phase method, CuCl$_2$ has replaced Cu(NO$_3$)$_2$ and is dissolved in oleylamine/octadecene. The TEM images show the size distribution and morphology of nanoparticle synthesized under the two-phase and one phase methods in b)-c), respectively.
To promote the formation of triangular nanoprisms as the majority product, the dispersion is kept at the reaction temperature for 120 min. During this time, the nanocrystals are observed to undergo a ripening process where facetted nanocrystals grow at the expense of unfacetted, disk-like nanocrystals (schematic in Figure 2-15 a). I attribute this ripening process to halide ion binding of facetted triangle prism particles, stabilizing them relative to the oleylamine binding to the unfacetted disk-like particles. The unstable particles dissolved to small precursor particles and then re-precipitated as facetted particles. This causes the facetted triangle prism nanoparticles to enlarge and the unfacetted disk-like nanoparticles to shrink.

Figure 2-15 Triangular nanoparticle ripening with extended reaction time. a) Schematic shows that the triangle nanoparticles undergo ripening under by extending the reaction duration, where small particles dissolve and redeposit onto larger particles. Also, the small particles become truncated. The TEM images show triangle nanoparticle ripening under three different reaction times: 15 min, 30 min, and 120 min in b)-c), respectively.
After 15 min of the reaction, the nanocrystals possess a narrow size distribution with edge lengths of 21.2 ± 4.2 nm as the TEM image in Figure 2-12 b) demonstrates. After 30 min of reacting, the nanocrystals possess average edge lengths of 28.9 ± 10.2 nm as the TEM image in Figure 2-15c) demonstrates. After 120 min of reacting, the TEM image analysis of the resulting products clearly shows a nanocrystal dispersion that possesses a bimodal size distribution, with larger particles possessing edge lengths of 125 ± 70.2 nm and smaller particles with edge lengths of 16.7 ± 9.8 nm, as observed in the TEM images in Figure 2-15d). The large particles possess a highly facetted triangle prismatic shape and the small particles possess an unfacetted disk-like shape. The XRD spectra in Figure 2-16 indicate that the CuS nanocrystals retain the covellite (CuS) crystal structure during this ripening process.

![Figure 2-16](image.png)  
**Figure 2-16** XRD spectra of three triangle nanoparticle synthesized under 15 min (black), 30 min (red), and 120 min (blue). The crystal structure remains covellite (CuS) during the extended reaction time.
The triangle CuS nanocrystals undergo anisotropic growth which enlarges the triangle edge length about 6 times during extended reaction time, but the increase in triangle thickness is negligible as observed in the AFM result in Figure 2-17.

**Figure 2-17** Thickness of nano triangles changes during the time dependent experiment: a) the triangle particle with thickness = 6.30 nm at 30 min, b) triangle particle with thickness = 6.52 nm at 120 min.

This change in size distribution is further indicated by the visible and IR extinction spectra for the colloidal dispersions. In Figure 2-18, the extinction spectra of the colloidal dispersions indicate a time-dependent ripening process. After 15 min, the extinction spectrum shows one peak at 1080 nm corresponding to the in-plane dipolar LSPR mode (black curve). After 30 min, this single peak begins to split into two separate peaks centered at 1135 nm and small bump at 835 nm (red curve). After 120 min, the extinction spectrum shows a broad absorption response (cyan curve) that I attribute to overlapping LSPR modes associated with nanocrystals of two different sizes. To
distinguish the LSPR response for the larger and smaller nanocrystals, I carried out size separation by centrifugation to obtain two distinct nanocrystal populations.

![Graph showing absorption spectra of CuS triangle nanoparticles under different reaction times](image)

Figure 2-18 Absorption spectra of different CuS triangle nanoparticles under different reaction times, 15 min (black), 30 min (red), 60 min (blue) and 120 min (cyan).

The smaller unfacetted nanocrystals are 18.2 ± 8.6 nm in edge length as shown in the TEM image in Figure 2-19 d) and give rise to a single LSPR peak centered at 1100 nm (Figure 2-19 a) red curve). The larger triangular nanoprisms are 142 ± 80.5 nm in edge length as observed in the TEM image in Figure 2-19 c) and give rise to an LSPR peak centered at 1850 nm with a broad FWHM (blue curve in Figure 2-19 a)). A small feature in the extinction spectrum is also apparent at around 900 nm, which I attribute to a multi-polar in-plane LSPR mode associated with the triangular nanoprism geometry.
Figure 2-19 Size separation of triangle nanoparticles during ripening. a) Absorption spectra of CuS triangle nanoparticles before and after size separation: before size separation (black), and the size-separated small particles (red) and size-separated large particles (blue). The TEM images show the size distribution and morphology of nanoparticle before and after size separation in b)-d), respectively.

The TEM image and electron diffraction pattern of nanoprism in Figure 2-20 a) show that the basal plane of triangles is the (001) plane which is consistent with the basal plane of disk-like particles reported by Xie et al. And the powder XRD spectra of side-by-side packing orientation thin film in Figure 2-20 d) shows that only the (00n), where n is an even integer, peaks dominate, which is consistent with the basal plane of triangle being perpendicular to the c-axis. The corresponding TEM image of a side-by-side packed thin film is shown in Figure 2-20 c). These results indicated that the triangle are generated from the naondisks but grow sharp, faceted edges.
Figure 2-20 a) HRTEM image of triangle CuS nanoparticles with the basal plane parallel to the substrate, the <001> zone axis. b) The angle of each corner of the nanoprisms shows that the nanoprism is close to an equilateral triangle. c) TEM image of particles oriented in a side-by-side packed thin film d) the XRD spectrum of a thin film with the basal plane parallel to the substrate (red line) compared to the powder sample (black) which shows that only the (00n) face, with n = even, was occurrence in orderly packing thin film.

I attribute this ripening process to interactions between the oleylamine capping ligand and the Cl⁻ ion present in the reaction mixture. In the absence of halide ions, oleylamine forms a stable ligand shell on the CuS surface. In the presence of halide ions, the strong metal-halide interactions between Cu atoms and the ions are likely to promote the binding of halide ions to the CuS surface and to disrupt the binding between oleylyamine and CuS. This is further supported by the knowledge that oleylamine forms stable complexes with metal halide salts such as AuCl. Our observations support the hypothesis that the formation of metal-halide bonds at the CuS surface allow oleylamine to dynamically come on and off the CuS surface. This is supported by the observed temperature-dependence of the ripening process. When as-made triangular nanoprisms are heated for 30 minutes at temperatures below 160 °C, no change in the size or size distribution of the CuS nanocrystals is observed as shown by the TEM image in Figure 2-
The ripening process only occurs at temperatures of 160 °C and above, as indicated by the TEM images in Figure 2-21 showing the bimodal size distributions that develop at these temperatures.

**Figure 2-21** Triangle nanoparticles ripening by elevated reaction temperature. The TEM images show the size distribution and morphology of nanoparticles synthesized under different reaction temperature 140 °C, 150 °C, 160 °C, 170 °C, and 180 °C in a)-e), respectively.

In order to synthesize CuS nanoprisms with uniform size, I use a seed mediated method which separates the nucleation and growth processes into two different reaction batches. The CuS nanocrystals synthesized by the one-phase synthetic method at 140 °C for 45 min. were used as seeds for growing the uniform nanoprisms with edge lengths between 25-60 nm. The nanocrystal growth solution was prepared by dissolving 0.05 mmol copper (II) chloride and 0.75 mmol S powder in a mixed solvent of oleyamine (0.25 ml) and 1-octadecene (3.75 ml) in a glass vial. Next, the seed solution was dispersed in 1-octadecene and was added to the growth solution. The glass vial was placed in an oil bath.
at 120 °C for 75 min. The bright-blue solution tuned into a dark green-blue solution then was cooled to room temperature. Next, 4 mL ethanol was added, and the solution was centrifuged at 3000 rpm for 5 min. to remove free oleylamine and 1-octadecene. The precipitation was re-dispersed in chloroform, and further centrifuged at 7500 rpm for 7.5 min to remove any by-products. This serial seeding process can be continued until a desired copper sulfide nanoprinism size is obtained.

Figure 2-22 a) shows a TEM image of CuS nanocrystal seeds with particle size around 23.2 ± 2.8 nm. The CuS nanocrystal morphology and size varies with growth cycles as shown in figure 2-22 b)-d); with more growth cycles, the shape of the nanoprisms becomes sharper at the corners and the size increases from 23.2 ± 2.8 nm (seed solution) to 56.2 ± 10.3 nm (third growth cycle).

**Figure 2-22** Nanoprisms synthesized using the seed-mediated process. a) TEM image of seeds: CuS nanocrystals with size = 23.2 ± 2.8 nm. b) TEM image of the first growth: size = 31.3 ± 4.2 nm. c) TEM image of the second growth: size = 43.1 ± 7.7 nm. d) TEM image of the third growth: size = 56.2 ± 10.3 nm.
This increase in size corresponds to a spectral red-shift from 1050 nm to 1480 nm in the Vis-IR extinction spectrum of the colloidal dispersions (Figure 2-23). The size distribution increases slightly with each growth cycle, as evidenced by an increase in the FWHM from 620 nm to 780 nm after three growth cycles.

The morphology of copper sulfide nanocrystals synthesized from the thermolysis of copper alkanethiolate precursor is disk-like nanoparticles. The nanoparticles prefer growth in the <110> direction which is parallel to the basal plane and increases the aspect-ratio (diameter/thickness) of nanoparticles with increasing reaction time. In order to fabricate the copper sulfide nanocrystals with lower copper content (higher carrier density), I carried out solvent based synthesis to obtain Cu$_{7.2}$S$_4$ and CuS nanodisks. The stoichiometry of the copper sulfide phase can be tuned by varying the precursor ratio of S:Cu$^{2+}$ in the reaction bath. The size of the nanodisks synthesized under solventless
thermolysis and the solvent based synthesis can be tuned by varying the reaction time. These different copper sulfide nanocrystals with controllable size can be used to study the shape-dependent, size-dependent, and carrier density-dependent plasmon resonance.

I also observed that the halide anions (Cl\(^-\), Br\(^-\), I\(^-\)) exert a significant role on the morphology of copper sulfide nanoparticles. The triangle shape nanoprism were obtained by introducing halide anions into the reaction solution. The growth rate of nanoprism is controlled by the binding strength of the halide ion on the metal surface. These nanoparticles undergo a ripening process where facetted nanoprism grow at the expense of unfacetted disk-like nanocrystals due to the passivation of specific crystal facets by halide ions, enhancing the surface stability of the prisms relative to the unfacetted disk-like particles passivated only by oleylamine. The unstable particles dissolved to small precursor particles and then re-precipitated to form facetted particles. The uniform size distribution of CuS nanoprism can be arrived by using a seed-mediated method and the desired CuS nanoprism size can be obtained by continuous the seeding processes.

Chapter 2, in part, is a reprint of the content as it appears in *Journal of the American Chemical Society* and *Nano Letters*


CHAPTER 3

THE TUNABLE PLASMONIC RESPONSE OF SEMICONDUCTOR NANODISKS

Materials that possess a dielectric constant with a negative, real component and a small positive, imaginary component (such as noble metals) are capable of supporting surface plasmon resonances (SPRs). When the size of material scales down to nanoscale, where the size of the particle is much smaller than incident light wavelength, the electrons oscillate within the bound volume of the nanoscale particle, with a frequency characterized by the excitation of a localized surface plasmon response (LSPR). At the resonant LSPR wavelength, these metal nanoparticles (NPs) are characterized by intense light absorption and scattering that result from electromagnetic field localization at the metal surface. This unique ability to confine and manipulate light at sub-wavelength scales makes these nanostructures excellent materials for photoconduction, enhanced light absorbance and scattering, light coupling into nanoscale volumes, and negative-index optical response.

The NP size, shape, material composition, and its local dielectric environment can be used to tune the LSPR wavelengths of metal NPs.\textsuperscript{4, 7, 8, 80, 81} For shape-dependent LSPR, spherical NPs typically show a single dipolar LSPR mode, whereas anisotropic
NPs exhibit multiple higher-order LSPR modes (as shown in Figure 3-1). These higher-order LSPR modes arise from uneven charge distribution within the non-spherical particle volume and often result in large electromagnetic field enhancements localized near the corners and edges of the NPs, as seen in the case of Ag nanoprisms (Figure 3-2).

**Figure 3-1** LSPRs of different shapes of metal nanoparticles. Anisotropic nanoparticles exhibit multiple higher-order LSPR modes.

**Figure 3-2** Two-dimensional (2D) plots of E-field enhancement for an Ag nanoprism excited at the dipolar LSPR wavelength.
More recently, LSPRs have been reported for nonmetallic nanocrystals, including Si nanowires grown by gas-phase chemical vapor deposition and colloidal nanoparticles composed of Cu$_{2-x}$S$^{38,40,79,82,83}$, Cu$_{2-x}$Se$^{39}$, Cu$_{2-x}$Te$^{84}$, Cu$_3$P$^{85}$, In-doped and Sb-doped SnO$_2$$^{41,42}$, and Al-doped ZnO$^{86}$. Plasmonic nanocrystals composed of these materials are advantageous because LSPR wavelengths can be dynamically tuned by controlling free carrier density through chemical and electrochemical doping processes.$^{39,41}$ Cu$_{2-x}$S is a self-doped semiconductor with different stoichiometric structures that can be obtained by tuning the number of copper deficiencies during the synthetic process or by post-synthetic treatment.$^{39}$ Cu$_{2-x}$S is a particularly interesting material for plasmonics because stoichiometric Cu$_2$S is an indirect bandgap semiconductor with a bulk bandgap of 1.21 eV.$^{87}$ In addition, it is composed of highly earth abundant elements and possesses an environmentally benign composition.

Previously, it has been shown that spherical Cu$_{2-x}$S nanocrystals possess an LSPR mode in the NIR range and that the absorption wavelength of LSPRs can be tuned by introducing copper vacancies into the Cu$_{2-x}$S lattice.$^{38,39}$ Hole carriers of spherical Cu$_{2-x}$S NPs generated by these vacancies were produced upon exposure of the nanocrystals to oxygen, which caused the LSPR band to blue-shift as the dopant concentration was increased. In theory, the LSPRs of anisotropic semiconductor NPs are expected to exhibit the same shape-dependence as metal NPs due to the uneven charge distribution within the non-spherical particle volume.

In this chapter, I observe of shape-dependent LSPRs for Cu$_{2-x}$S nanodisks that possess in-plane and out-of-plane dipoles associated with the ultrathin disk geometry. I can demonstrate that anisotropic semiconductor nanocrystals display localized surface
plasmon resonances that are dependent on nanocrystal shape and that cover a broad spectral region in the near-infrared wavelengths. In-plane and out-of-plane dipolar resonances are observed for colloidal dispersions of Cu$_{2-x}$S nanodisks, and the wavelengths of these resonances are in good agreement with calculations carried out in the electrostatic limit. The wavelength, line shape, and relative intensities of these plasmon bands can be tuned during the synthetic process by controlling the geometric aspect ratio of the disk.

3.1 The Effect of Shape

In order to measure the plasmon resonance of colloidal Cu$_{2-x}$S nanocrystals, the as-made Cu$_{2-x}$S powder product was dispersed in chloroform. I used UV-Vis-NIR spectroscopy to characterize the LSPR peaks of the Cu$_{2-x}$S colloidal solution in the range of 800 nm to 3200 nm.

Figure 3-3 shows the NIR extinction spectra for colloidal dispersions of spherical Cu$_{2-x}$S nanocrystals with a diameter of 4.0 ± 0.5 nm (black dot is the experiment data and black curve is the fit curve), as well as for flat Cu$_{2-x}$S nanodisks with a basal plane diameter of 24.5 ± 8.6 nm and a height of 4.4 ± 1.3 nm (red dot is the experiment data and red curve is the fit curve). The spherical nanocrystals and nanodisks are synthesized by a solventless thermolysis process at different reaction time and then dispersed in chloroform to minimize the spectral background resulting from solvent absorption.
Figure 3-3 Shape-dependent LSPRs of Cu$_{2-x}$S nanocrystals. (a) Near-IR extinction spectra (dots) for colloidal dispersions of spherical nanocrystals (black) and nanodisks (red). The solid lines correspond to best fits of the extinction peaks used to calculate the free carrier concentrations. (b) TEM image of spherical nanocrystals. (c) TEM image of nanodisks. (d) Schematic of LSPR polarization for spherical and disk-shaped nanocrystals.

To prepare samples for transmission electron microscopy (TEM, FEI Tecnai Sphera), the nanodisks undergo solvent-transfer followed by sample deposition. Initially,
the nanodisks are dispersed in chloroform, which is known to dissolve the carbon support film on commercial TEM grids. To avoid this, I drop-cast the colloidal solution onto an air-water interface and allow the chloroform solvent to evaporate prior to nanodisk transfer to a TEM grid. Because the as-made nanodisks are highly hydrophobic, ordered stacks of nanodisks are generated by this dispersion at the air-water interface (Figure 3-3c)).

The NIR spectra of the nanodisks are characterized by two extinction bands near 1800 nm and 3100 nm. The presence of multiple extinction peaks is attributed to the excitation of shape-dependent dipolar LSPR modes, where excitation occurs for incident radiation polarized in two directions: parallel and perpendicular to the basal plane of the disk. In contrast, the dispersion of spherical nanocrystals gives rise to a single dipolar LSPR band near 1600 nm, which is consistent with previous reports that characterize Cu$_{2-x}$S nanocrystals in a similar diameter range$^{38}$. The onset of excitonic absorption for Cu$_{2-x}$S nanocrystal occurs near 900 nm, and does not show significant overlap with the spectral range shown here.

LSPR wavelength is dependent on the complex dielectric function of Cu$_{2-x}$S ($\varepsilon$) and the dielectric function of the surrounding medium ($\varepsilon_m$), as well as nanodisk size and shape. In the electrostatic limit where $d \ll \lambda$, the dipole polarizability ($\alpha$) of a nanodisk can be approximated using basic scattering theory for an oblate spheroid with semiaxes $a < b = c$. The following expression is obtained:

$$\alpha_j = 3\varepsilon_0 V \frac{(\varepsilon - \varepsilon_m)}{3\varepsilon_m + 3\varepsilon_j(\varepsilon - \varepsilon_m)}$$ (1)
where \( j = 1, 2, \) or 3, \( V \) is spheroid volume, \( \varepsilon_o \) is free space permittivity, and \( L_j \) is a shape-dependent constant calculated from the spheroid axis lengths. For the disk-like spheroid with an aspect ratio (diameter-to-height) of 5, \( L_1 = 0.588 \) for the electric field perpendicular to the basal plane and \( L_2 = L_3 = 0.206 \) for the in-plane electric field. For the resonance, the denominator term in equation (1) must be zero:

\[
3\varepsilon_m + 3L_j (\varepsilon_{r,j} - \varepsilon_m) = 0
\]

\[
\varepsilon_{r,j} = -\frac{(1-L_j)}{L_j} \varepsilon_m \quad (2)
\]

where \( \varepsilon_{r,j} \) is the real part of \( \varepsilon_j \). \( \varepsilon_r \) can be expressed according to the Drude theory:

\[
\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (3)
\]

where \( \omega \) is the incident radiation frequency, \( \gamma \) is the loss-associated collision frequency term, and \( \omega_p \) is the bulk plasma frequency. The collision frequency \( \gamma \) can be calculated from the extinction spectrum according to:

\[
\gamma = c \frac{\lambda_{1/2}}{\lambda_{max}^2} \quad (4)
\]

where \( c \) is speed of light, \( \lambda_{1/2} \) is the full-width wavelength at half-maximum (FWHM) of the absorption peak, and \( \lambda_{max} \) is the absorption maximum wavelength.

To calculate the free carrier density of a copper sulfide nanodisk, I use the relationship between bulk plasma frequency \( (\omega_p) \) and carrier density \( (N_h) \). The relationship can be expressed as:

\[
\omega_p = \sqrt{\frac{N_h e^2}{\varepsilon_o m_h}} \quad (5)
\]
where $m_h$ is the hole effective mass, approximated as $0.8m_0$ (where $m_0$ is free electron mass), and $e$ is the electron charge.

Using the information from the Fig. 3-3, I can calculate the free carrier density for in-plane and out-of-plane polarization:

**a. Out-of-plane:**

\[ \lambda_{max} \approx 1800 \text{nm} , \omega_{sp} = 0.69 \text{ eV}, \lambda_{1/2} \approx 1100 \text{nm} \]

\[ \gamma = c \frac{\lambda_{1/2}}{\lambda_{max}^2} = 0.42 \text{ eV} \]

Using $L_1 = 0.588$ and equation (2):

\[ \varepsilon_{r,1} = -1.57 \]

Using equation (3):

\[ \omega_p = \sqrt{(1 - \varepsilon_{r,1})(\omega_{sp}^2 + \gamma^2)} = 1.29 \text{ eV} = 1.96 \times 10^{15} \text{ s}^{-1} \]

Using equation (5):

\[ N_h = \frac{\omega_p^2 \varepsilon_0 m_h}{e^2} = 9.69 \times 10^{20} \text{ cm}^{-3} \]

To calculate % copper deficiency:

Volume of nanodisk

\[ V = \pi r^2 a = 2.07 \times 10^{-18} \text{ cm}^3 \]

The number of copper atoms in the nanodisk

\[ = N_A \times V \times \frac{P_{Cu^{2S}}}{M_{Cu^{2S}}} \times 2 = 87778 \]

The number of vacancies in the nanodisk

\[ = V \times N_h = 2006 \]
% of deficiencies in the nanodisk

\[
\frac{\text{number of deficiencies in nanodisk}}{\text{number of copper atoms in nanodisk}} \times 100\% = 2.29\%
\]

b. In-plane:

\[
\lambda_{max} \approx 3100\text{nm}, \omega_{sp} = 0.40\text{eV}, \lambda_{1/2} \approx 500\text{nm}
\]

\[
\gamma = c \frac{\lambda_{1/2}}{\lambda_{max}} = 1.56 \times 10^{13}\text{ s}^{-1} = 0.06\text{eV}
\]

Using \(L_2 = 0.206\) and equation (2):

\[
\varepsilon_{r,2} = -8.63
\]

Using equation (3):

\[
\omega_p = \sqrt{(1 - \varepsilon_{r,1})(\omega_{sp}^2 + \gamma^2)} = 1.26\text{eV} = 1.91 \times 10^{15}\text{ s}^{-1}
\]

Using equation (5):

\[
N_h = \frac{\omega_p^2 \varepsilon_0 m_h}{e^2} = 9.20 \times 10^{20}\text{ cm}^{-3}
\]

To calculate % of copper deficiencies:

Volume of nanodisk

\[
V = \pi r^2 a = 2.07 \times 10^{-18}\text{ cm}^3
\]

The number of copper atoms in the nanodisk

\[
= N_A \times V \times \frac{\rho_{Cu2S}}{M_{Cu2S}} \times 2 = 87778
\]

The number of vacancies in the nanodisk

\[
= V \times N_h = 1904
\]
% of deficiencies in the nanodisk

\[
\text{number of deficiencies in nanodisk} \times 100\% = 2.17\%
\]

Based on the calculation results, I find that the short-wavelength LSPR band at \( \lambda \approx 1800 \) nm corresponds to the out-of-plane dipole and the long-wavelength LSPR band at \( \lambda \approx 3100 \) nm corresponds to the in-plane dipole. The value for \( \omega_p \) is calculated to be in the range of 1.25-1.29 eV, with free carrier density estimated between \( 0.92 \times 10^{21} \) - \( 0.97 \times 10^{21} \) cm\(^{-3}\). This is consistent with previously reported carrier densities for doped copper chalcogenides.\(^{38, 40}\)

Figure 3-4a displays the NIR extinction spectra for nanodisks with various aspect ratios (diameter/ thickness). Nanodisks were grown by changing the reaction time for the thermal decomposition process, with the longest decomposition time of 60 min. yielding an aspect ratio of 6.78 (Figure 3-3b). As the dimensions of the nanodisk are increased, I observe that the LSPR wavelength for both absorbance peaks blue-shift to shorter wavelengths.

These results differ from the behavior of shape-dependent LSPRs for anisotropic nanoparticles composed of noble metals such as Au or Ag. For example, Ag disks synthesized using colloidal methods are known to exhibit multiple intense scattering peaks in the optical range, also due to the excitation of in-plane and out-of-plane dipolar LSPRs.\(^{8, 88, 89}\) However, in studies where the aspect ratio of these metal nanodisks is systematically varied, the in-plane LSPR wavelength is expected to red-shift as disk diameter increases, while the out-of-plane LSPR is expected to blue-shift (as show in
Figure 3-5). In contrast, both the in-plane and out-of-plane LSPR bands associated with the Cu$_{2-x}$S nanodisks blue-shift despite almost a two-fold increase in aspect ratio.

![Figure 3-4 Change in LSPR properties with varying disk aspect ratio. (a) Near-IR extinction spectra of colloidal Cu$_{2-x}$S nanodisk dispersions with aspect ratios as shown. (b) Corresponding TEM images for the nanodisk samples in (a).](image)
An exact electrodynamic calculation of the extinction spectra of oblate spheroid silver nanoparticles with different aspect ratios. The in-plane LSPR wavelength is expected to red-shift as disk diameter increases, while the out-of-plane LSPR is expected to blue-shift. Adapted from ref. 8

For the Cu$_{2-x}$S nanodisks, the observed blue-shifts in the LSPR wavelengths can be attributed to the sum of two effects:

1) An increase in nanodisk size

2) An increase in the carrier density due to thermal oxidation (theoretical calculation of carrier density is listed in Table 3-1)

These have been suggested to form Cu vacancies in the chalcogenide lattice due to outward diffusion of Cu ions. Figure 3-6 shows the calculated shift in the in-plane LSPR wavelength for each of these effects in comparison to the experimental data. Increasing thermal decomposition time is expected to introduce a greater number of Cu vacancies into the lattice and to increase $\omega_{sp}$, effectively counteracting the expected change in $\omega_{sp}$ from the increase in nanodisk aspect ratio.
Table 3-1 The carrier density of nanodisks with different aspect ratios based on the extinction spectra in Figure 3-3. The calculation method is shown in section 3-3.

<table>
<thead>
<tr>
<th>Aspect ratio</th>
<th>Wavelength</th>
<th>Carrier density(cm⁻³)</th>
<th>Deviation of carrier density</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.87</td>
<td>Out-of-plane</td>
<td>1997nm</td>
<td>0.802×10²¹</td>
</tr>
<tr>
<td></td>
<td>in-plane</td>
<td>3085nm</td>
<td>0.785×10²¹</td>
</tr>
<tr>
<td>5.09</td>
<td>Out-of-plane</td>
<td>1806nm</td>
<td>0.959×10²¹</td>
</tr>
<tr>
<td></td>
<td>in-plane</td>
<td>3066nm</td>
<td>0.935×10²¹</td>
</tr>
<tr>
<td>5.65</td>
<td>Out-of-plane</td>
<td>1713nm</td>
<td>1.036×10²¹</td>
</tr>
<tr>
<td></td>
<td>in-plane</td>
<td>3031nm</td>
<td>1.073×10²¹</td>
</tr>
<tr>
<td>6.78</td>
<td>Out-of-plane</td>
<td>1596nm</td>
<td>1.206×10²¹</td>
</tr>
<tr>
<td></td>
<td>in-plane</td>
<td>2995nm</td>
<td>1.237×10²¹</td>
</tr>
</tbody>
</table>

Figure 3-6 The calculated change in LSPR wavelength for the in-plane mode for nanodisks with independently increasing aspect ratios (solid) and carrier densities (dashed), compared to the experimental data (dot-dash) obtained from the spectra in Figure 3-4.
Figure 3-7 The calculated change in LSPR wavelength for the out-of-plane mode for nanodisks with independently increasing aspect ratios (solid) and carrier densities (dashed), compared to the experimental data (dot-dash) obtained from the spectra in Figure 3-3.

This additive effect is consistent with the shift in LSPR wavelength of the out-of-plane mode, where the changes in shape and carrier concentration both contribute to a blue shift in the wavelength in Figure 3-7. I also observe that the relative intensities of the two LSPR bands change significantly. A rapid rise in the peak intensity associated with the out-of-plane LSPR mode is attributed to the increase in total surface area of the basal plane per nanodisk. For plasmonic semiconductor nanocrystals, these results suggest that both shape effects and the effects of free carrier concentration must be carefully considered in tailoring LSPR properties.
The fabrication of an active or tailored plasmonic material could capitalize on the ability to tune both of these parameters independently. In Figure 3-8, the predication of LSPRs responds of nanodisks with different carrier density based on the Drude mode. For doped semiconductor nanodisks, their in-plane and out-of-plane LSPRs modes lie in the NIR region (1000-4000nm).

Figure 3-8 Nanodisk LSPRs. a,b) Electric field strength for in-plane and out-of-plane LSPR modes of a metal nanodisk with aspect-ratio = 4 (80 nm in diameter, 20nm in thickness). Simulations were carried out for a perfect metallic conductor with a) incident light propagation in the z-direction and polarized along y, and b) incident light propagation in the x-direction and polarization along z. c) Schematic showing regions of LSPR excitation associated with materials of varying carrier densities. Theoretical LSPR wavelengths of nanodisks are plotted with respect to aspect-ratio for carrier densities of $N = 3.0 \times 10^{22}$ cm$^{-3}$ (green line) and $N = 7.5 \times 10^{20}$ cm$^{-3}$ (red line), calculated using the Drude model.
A major difficulty in the synthesis of these doped semiconductor nanoparticles (Cu$_{2-x}$S and Cu$_{2-x}$Se in particular) is the ability to predictably change nanoparticle size or shape without modulating dopant concentration. These nanoparticles are typically fabricated using colloidal synthesis, where nanoparticle size or aspect-ratio (in the case of nanodisks) is readily increased by prolonging the reaction time.\textsuperscript{71, 90} For example, the Korgel group previously synthesized Cu$_{2-x}$S nanodisks with high aspect-ratios by controlling the synthetic temperature and duration, whereby longer reactions at higher temperature tend to produce higher aspect-ratios.\textsuperscript{71} Other examples of anisotropic Cu$_2$S nanostructures with large aspect-ratios include bicones\textsuperscript{91} and nanorods.\textsuperscript{92} However, in each of these earlier studies, the observed absorption peaks in the infrared were attributed to excitonic absorption instead of LSPR excitation. Thus, the relationships between nanostructure aspect-ratio, LSPR wavelength, and carrier density have remained largely unresolved.

The aspect-ratio and carrier density are positively correlated, which I attribute to a surface oxidation mechanism: a longer reaction time leads to larger nanodisks with greater aspect-ratios, but the increase in nanodisk surface area promotes the formation of copper vacancies at the Cu$_{2-x}$S surface. Thus, longer reaction times yielding high aspect-ratio nanodisks inevitably lead to higher charge carrier densities. This correlates with the observed LSPR properties of spherical semiconductor nanoparticles,\textsuperscript{40, 71, 93} where the carrier density of Cu$_{2-x}$S quantum dots was found to correlate with the quantum dot radius and quantum dot size was increased by prolonging the synthetic reaction time in Figure 3-9.
Figure 3-9 Size-dependent LSPRs of spherical copper sulfide nanoparticles. TEM images show average particle size: (a) 2.4±0.5 nm (b) 3.6±0.5 nm, and (c) 5.8±0.8 nm. Scale bar represents 50 nm in all images. Adapted from ref. 38.

A major challenge encountered in chapter III was the ability to independently address carrier density and nanodisk aspect-ratio which make the plasmon resonance cannot be expected by scattering theory and the Drude approximation. Scheme 4-1 depicts the effects of each property on the in-plane and out-of-plane LSPR wavelengths for Cu$_{2-x}$S nanodisks.

Based on Mie scattering theory, $\lambda_{\text{out}}$ (wavelength of out-of-plane mode) is expected to blue-shift and $\lambda_{\text{in}}$ (wavelength of in-plane mode) is expected to red-shift when only disk diameter is increased as seen in scheme 3-1(a). When only the hole carrier density ($N_h$) is increased, the Drude theory can be used to predict that both $\lambda_{\text{out}}$ and $\lambda_{\text{in}}$ are expected to blue-shift as in scheme 3-1 (b).
Scheme 3-1 How LSPRs are expected to change with respect to changes in a) aspect-ratio and b) carrier density.

However, the effects of carrier density were difficult to characterize due to the variability of the chemical synthesis, which was performed under a redox atmosphere.
Controlled oxidation of the Cu$_{2-x}$S nanodisks is further complicated by the polymorphic nature of copper sulfide compounds, whose crystallographic structures are typically determined by compound stoichiometry. The ability to independently modulate the oxidation of Cu$_{2-x}$S would further the plasmonic characterization of these self-doped semiconductor nanocrystals and would also provide new strategies for tuning LSPR wavelengths of high aspect-ratio structures.

Here, I demonstrate that the wavelengths of these LSPR modes can be modulated by independently varying the aspect-ratio of the Cu$_{2-x}$S disk. These variables can be controlled during nanocrystal growth by carrying out thermolysis of a copper-thiolate precursor under a specific gas environment. Our results show that during thermolysis, the presence of oxygen enhances the growth rate of crystalline Cu$_{2-x}$S nanodisks and the formation of Cu vacancies that contribute to free carrier concentration. By carrying out thermolysis under a nitrogen environment, I am able to tune the aspect-ratio of nanodisks independent of Cu vacancy formation.

3.2 The Effect of Aspect Ratio

In order to tune nanodisk aspect-ratio (the diameter (D) / thickness (T)) without simultaneously increasing carrier density, I synthesized Cu$_{2-x}$S nanocrystals by carrying out the thermolysis of copper-alkanethiolate under an N$_2$ purged environment where oxidation was suppressed under N$_2$. The powder precursor was placed in a round bottom flask capped with a rubber stopper. The flask volume was purged with N$_2$ a total of four times before carrying out thermolysis. For thermolysis, the glass vial or flask containing the powder precursor was placed into an oil bath while stirring at a temperature between
190°C and 200°C. The powder transformed into a dark-brown liquid which was then cooled to room temperature, dispersed in chloroform, and centrifuged at 7500 rpm for 7.5 min to remove any unwanted by-products. This purification process was repeated three times. The purified product was dried under vacuum to obtain a brown powder for characterization.

Figure 3-10 compares the XRD spectra and representative transmission electron microscope (TEM) images obtained for nanodisks synthesized under N₂ and air. Both methods produce colloidal nanodisks dispersions composed of a solid-state Cu₂₋ₓS phase that possesses a crystal structure closely related to the hexagonal lattice of chalcocite (Cu₂S). The nanodisks are oriented with a (002) basal plane and undergo radial growth in the direction parallel to this plane. The TEM image in Figure 3-10 b) and c) correspond to nanodisks with aspect-ratios of 3.87 ± 0.25 (D = 14.7 ± 4.3 nm, T = 3.80 ± 1.31 nm) and 4.65 ± 0.29 (D = 18.9 ± 3.6 nm, T = 3.94 ± 1.01 nm), synthesized under air and N₂ environments, respectively. The particle size distribution of nanodisks synthesized under air and N₂ was obtained by counting between 150-200 nanoparticles in TEM images.

While the two different gas environments do not prohibit nanodisk growth and can both form nanodisks with varying aspect-ratios, comparison of the relative rates of nanodisk growth show a significant difference and indicate two different modes of nanodisk growth. The thermolysis reaction that leads to the growth of anisotropic Cu₂₋ₓS nanodisks is characterized by two steps:

i) Decomposition of the copper-alkanethiolate precursor

ii) Solution-phase precipitation of Cu₂S.
These two steps favor a faster growth rate along <100> direction (parallel to the basal plane) of the hexagonal disk than along <001> direction, resulting in the formation of the anisotropic disk structure, as scheme 3-2.  

![Figure 3-10 XRD spectra and TEM images of nanodisks synthesized under air and N_2. a) XRD spectra show that both nanocrystal powders possess a crystal structure closely resembling the hexagonal lattice of stoichiometric chalcocite (Cu_2S). b) The morphology obtained for both samples are disk-shaped nanocrystals, seen here in stacked pancake-like structures that occur upon drying of the colloidal dispersion on the TEM grid.](image_url)
Scheme 3-2 a) Two steps of thermolysis copper precursor: i) decomposition of the copper-alkanethiolate precursor, and ii) solution-phase precipitation of Cu₂S. b) nanocrystal prefer growth in <100> direction, resulting in the formation of the anisotropic disk structure. Adapted from ref.100.

The shape of nanocrystals synthesized by thermolysis under air and N₂ both are the disk-like chalcocite (Cu₂S) nanoparticle. However, the growth rate of nanodisk under nitrogen is much slower than under the air. Figure 3-11 shows a graph of nanodisk aspect-ratio as a function of thermolysis time for two different temperatures (190 ºC and 200 ºC) and for air and N₂ gas environments.

At lower temperatures, I observe that thermal decomposition of the copper-alkanethiolate precursor does not occur. This is consistent with thermogravimetric analysis (TGA) measurements indicating that decomposition of the copper-dodecanethiol complex occurs at T = 178ºC (Figure 3-12), which I attribute to cleavage of the C-S bond.
Figure 3-11 Nanocrystal growth rates obtained air and N$_2$. A comparison of nanocrystal aspect-ratio (measured by TEM image analysis) and thermolysis time shows that the kinetics of nanocrystal growth are drastically different when thermolysis is carried out under different gas environments.

Figure 3-12 TGA of the copper-alkanethiol precursor indicates that decomposition of the precursor begins to occur at 178°C.
Higher reaction temperatures (> 210 °C) proceed quickly under air and make it difficult to observe the time-dependent nanodisk growth by removing aliquots for TEM imaging. Both air and N₂ reactions are sensitive to the reaction temperature, and carrying out the thermolysis reaction at a temperature of 200 °C results in a significantly faster growth rate than a slightly lower reaction temperature of 190°C.

I observe that the nucleation and growth of Cu₂ₓS nanodisks under air occurs much faster than when the reaction is carried out under N₂. Under air, high aspect-ratio (~7) nanodisks can be attained within one hour of the thermolysis reaction. In contrast, carrying out the thermolysis reaction under N₂ requires upwards of 6 h to achieve the same aspect-ratios.

Figure 3-13 shows TEM images of the nanodisks synthesized under N₂ at different thermolysis time, which possess an aspect-ratio of 3.25 ± 0.25 after 3h of thermolysis. The aspect-ratio of nanodisks can be increased to 4.65 ± 0.29, 6.60 ± 0.35, 7.10 ± 0.53 by extending the thermolysis reaction time to 4h, 6h, and 7h, respectively (for exact dimensions, see Table 3-2). The different growth rate of nanodisks synthesized under N₂ versus air is due to oxygen, which plays an important role in nanodisk nucleation and growth. Oxygen is known to promote the formation of copper vacancies in Cu₂ₓS, and others have hypothesized that this is largely a surface effect where small copper oxide particles are formed at the particle-liquid interface. Based on our data, I propose that copper vacancies formed near the nanodisk surface encourage precipitation of the copper alkanethiolate precursor onto the growing nucleation site. The slower growth rate of nanodisks observed under N₂ can thus be attributed to a lower occurrence
of these nucleation sites by suppressing the copper vacancies formation that facilitates Cu$_2$S precipitation on the nanodisk edges.

![TEM images of Cu$_{2-x}$S nanodisks](image)

**Figure 3-13** TEM images of Cu$_{2-x}$S synthesized under N$_2$, aspect-ratio (AR) nanodisks can controlled in the range of 3.0 – 7.0 by tuning thermolysis time. AR=3.25 ± 0.25 for 180min, AR=4.65 ± 0.29 for 240min, AR=6.60 ± 0.35 for 360min, and AR=7.10 ± 0.53 for 420min.

To measure the effect of nanodisk shape (independent of carrier density) on LSPR wavelength, I synthesized Cu$_{2-x}$S nanodisks under N$_2$ to obtain dispersions composed of nanodisks with varying aspect-ratios. Figure 3-14 shows the extinction spectra of these nanodisks with different average aspect ratios: 4.65 ± 0.29, 5.50 ± 0.43, 6.60 ± 0.35, 7.10 ± 0.53 in the NIR range as measured by UV-Vis-NIR transmission spectroscopy. The spectra for the colloidal dispersions (in chloroform) show a peak wavelength near 1800 nm corresponding to the out-of-plane LSPR mode, as previously assigned by Mie scattering calculations in chapter III.
Table 3-2 Average nanodisks dimensions which synthesize under different thermolysis temperature, time, and gas environments are obtained by TEM image analysis. Each value was obtained by counting between 150-200 nanodisks.

<table>
<thead>
<tr>
<th>Synthesis condition</th>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$, 190°C, 180min</td>
<td>7.05±1.2</td>
<td>2.82±1.01</td>
<td>2.50±0.27</td>
</tr>
<tr>
<td>N$_2$, 190°C, 300min</td>
<td>18.6±4.4</td>
<td>5.05±1.13</td>
<td>3.68±0.31</td>
</tr>
<tr>
<td>N$_2$, 190°C, 420min</td>
<td>21.7±2.6</td>
<td>5.49±0.74</td>
<td>3.96±0.39</td>
</tr>
<tr>
<td>N$_2$, 200°C, 180min</td>
<td>13.6±2.8</td>
<td>3.90±0.92</td>
<td>3.25±0.25</td>
</tr>
<tr>
<td>N$_2$, 200°C, 240min</td>
<td>18.9±3.6</td>
<td>3.94±1.01</td>
<td>4.65±0.29</td>
</tr>
<tr>
<td>N$_2$, 200°C, 300min</td>
<td>21.6±3.4</td>
<td>3.94±1.01</td>
<td>5.50±0.43</td>
</tr>
<tr>
<td>N$_2$, 200°C, 360min</td>
<td>36.5±6.4</td>
<td>5.53±1.30</td>
<td>6.60±0.35</td>
</tr>
<tr>
<td>N$_2$, 200°C, 420min</td>
<td>47.5±10.2</td>
<td>6.69±1.32</td>
<td>7.10±0.53</td>
</tr>
<tr>
<td>Air, 190°C, 40min</td>
<td>15.2±3.8</td>
<td>3.25±0.74</td>
<td>4.62±0.28</td>
</tr>
<tr>
<td>Air, 190°C, 50min</td>
<td>19.1±2.6</td>
<td>3.96±0.74</td>
<td>4.80±0.32</td>
</tr>
<tr>
<td>Air, 190°C, 60min</td>
<td>21.8±2.6</td>
<td>4.25±0.74</td>
<td>5.14±0.30</td>
</tr>
<tr>
<td>Air, 190°C, 70min</td>
<td>23.6±2.6</td>
<td>4.31±0.74</td>
<td>5.47±0.41</td>
</tr>
<tr>
<td>Air, 200°C, 15min</td>
<td>14.7±4.3</td>
<td>3.80±1.31</td>
<td>3.87±0.25</td>
</tr>
<tr>
<td>Air, 200°C, 30min</td>
<td>21.8±5.6</td>
<td>4.30±1.21</td>
<td>5.09±0.37</td>
</tr>
<tr>
<td>Air, 200°C, 45min</td>
<td>24.5±8.6</td>
<td>4.36±1.02</td>
<td>5.65±0.45</td>
</tr>
<tr>
<td>Air, 200°C, 60min</td>
<td>29.1±9.1</td>
<td>4.30±1.20</td>
<td>6.78±0.52</td>
</tr>
</tbody>
</table>

Nanodisks with an average aspect-ratio of 4.65 ± 0.29, $\lambda_{out} = 1860$ nm undergo a blue shift as the nanodisks grow larger and overall aspect-ratio is increased. This result is consistent with Mie scattering theory and with previously observed shifts in LSPR wavelengths for metal nanodisks. The in-plane LSPR mode (which appears at $\lambda_{in} = 3100$ nm for nanodisks synthesized under air) of the N$_2$-synthesized nanodisks undergoes a red-shift beyond the measurable wavelength range of the spectrometer due to the low carrier densities of these samples.
Figure 3-14 LSPR spectra and carrier density with varying nanodisk aspect-ratio.
a) IR extinction spectra for colloidal $\text{Cu}_{2-x}\text{S}$ nanodisks synthesized under $\text{N}_2$ with different aspect-ratios. The out-of-plane LSPR mode is observed to blue-shift while the in-plane LSPR mode lies beyond the measured wavelength range (> 3200 nm).

Carrier density can be calculated by using the Mie scattering theory and the Drude relationship between the bulk plasmon frequency ($\omega_p$) and hole carrier density ($N_h$). This relationship can be expressed as:

$$\omega_p = \sqrt{\frac{N_h e^2}{\varepsilon_0 m_h}}$$

where $m_h$ is the effective hole mass (approximated as 0.8$m_o$ where $m_o$ is electron mass), and $e$ is electron charge. A more detailed explanation of these calculations can be found in chapter 3-1.
Figure 3-15 shows that the calculated carrier densities for nanodisks varying with different aspect ratio synthesized under air and N₂. Based on our calculations, the carrier density of air-synthesized nanodisks increased from \( N_h = 8.9 \times 10^{20} \text{ cm}^{-3} \) to \( N_h = 12.3 \times 10^{20} \text{ cm}^{-3} \) as the nanodisks grew in aspect-ratio from \( 3.87 \pm 0.25 \) to \( 6.78 \pm 0.52 \), respectively (See Table 3-2 for exact nanodisk dimensions).

In comparison, I calculate that the carrier density of the N₂-synthesized nanodisks is approximately \( N_h = 7.7 \times 10^{20} \text{ cm}^{-3} \) for all of the observed aspect-ratios, remaining nearly constant as nanodisks grow in size. This indicates that carrying out thermolysis of the copper-alkanethiolate precursor under N₂ can suppress Cu oxidation during nanodisk formation (which increased the copper vacancies in copper sulfide crystals), enabling nanodisk growth without increasing the carrier density during an extended reaction time. The lower carrier density for the N₂-synthesized nanodisks also explains the absence of the extinction peaks associated with the in-plane LSPR mode. Given a carrier density of \( N_h = 7.7 \times 10^{20} \text{ cm}^{-3} \), I expect \( \lambda_{\text{in}} > 3200 \text{ nm} \) (see Table 3-3) based the Mie scattering and the Drude theory calculation which is beyond the detectable wavelength range of our instrumentation.

**Table 3-3** Theoretical expectation the in-plane mode of copper sulfide nanodisks synthesized under the N₂.

<table>
<thead>
<tr>
<th>aspect-ratio</th>
<th>4.65</th>
<th>5.50</th>
<th>6.60</th>
<th>7.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{out}} ) (nm)</td>
<td>1861</td>
<td>1762</td>
<td>1679</td>
<td>1650</td>
</tr>
<tr>
<td>( \lambda_{\text{in}} ) (nm)</td>
<td>3285</td>
<td>3500</td>
<td>3760</td>
<td>3860</td>
</tr>
<tr>
<td>carrier density( (x 10^{20} \text{ cm}^{-3}) )</td>
<td>7.72</td>
<td>7.75</td>
<td>7.70</td>
<td>7.75</td>
</tr>
</tbody>
</table>
Figure 3-15 The calculated carrier densities of nanodisks synthesized under air and N₂.

3.3 Post-Synthetic Oxidation

Unlike metal nanoparticles, nanoparticles composed of doped semiconductors possess LSPRs whose wavelengths can be tuned by controlling free carrier density. Dorfs et al. synthesized Cu₂₋ₓSe nanocrystals and observed reversible tuning of the LSPR through redox processes: Cu₂Se nanocrystals were oxidized to Cu₁.₆Se by exposing to oxygen or Ce(IV) ions, and reduced to Cu₂Se by adding an excess of Cu⁺ ions. They observed that the crystal structure did not change during the oxidation–reduction processes, despite the creation and annihilation of numerous copper vacancies (Figure 3-16). The number of vacancies limits the tuning the carrier density, and therefore the LSPR of Cu₂₋ₓSe.
Kriegel et al. examines copper chalcogenide ($\text{Cu}_{2-x}\text{S}$, $\text{Cu}_{2-x}\text{Se}$, and $\text{Cu}_{2-x}\text{Te}$) spherical nanoparticles and used diisobutylaluminium hydride (instead of $\text{Cu}^+$ ions) as a reducing agent to tune the LSPR by changing the crystal structure (Figure 3-17). By comparing the XRD and absorption spectra during the oxidation of the nanocrystals, they confirmed that the increasing of the LSPR intensity was correlated with the formation of copper vacancies in the spherical nanoparticles.

$\text{Cu}_{2-x}\text{S}$ spherical nanoparticles possess an LSPR mode in the near-infrared (NIR) range. Introducing $\text{Cu}$ vacancies into the $\text{Cu}_{2-x}\text{S}$ lattice generates hole carriers which cause the nanoparticle LSPR band to blue-shift as dopant concentration is increased. These self-doped semiconductor nanoparticles have the potential as actively tunable plasmonic materials capable of response to chemical or electrical stimuli. Further, these semiconductor materials have the potential to exhibit new optical or electronic properties that stem from coupled plasmonic and excitonic bands.

![Figure 3-16](image)

*Figure 3-16* Reversible tuning the LSPR in $\text{Cu}_{2-x}\text{Se}$ nanocrystals by redox reactions. Adapted from ref. 39.
Here, I observed that the carrier density of copper sulfide nanodisks can be independently increased by post-oxidized the as-made nanodisks in air environment. I demonstrate that independent of changes in nanocrystal size or shape, a maximum carrier density can be accommodated by the Cu$_{2-x}$S nanodisks before the nanocrystals undergo a catastrophic phase change. The nanodisks achieve a critical carrier density beyond which the nanocrystals undergo an irreversible phase change. This places a limit on how far an LSPR can be tuned in these doped semiconductor nanocrystals.
In order to study the effect of carrier density on the LSPR properties of the Cu$_{2-x}$S nanodisks, I carried out thermal oxidation to tune the carrier density of the nanodisks, independent of nanodisk shape. As-made nanodisks with an aspect-ratio of 4.65 ± 0.29 were heated in an ambient environment for various times ranging between 0-160 h and at three different temperatures of 80, 100, and 120 ºC.

Figures 3-18 shows that the change in the NIR extinction spectra for nanodisks with different thermal treatment times at 80ºC. For nanodisks oxidized at 80 ºC, two peaks are observed corresponding to the incident light polarizing long two different directions: in-plane ($\lambda_{in} \approx 3100$ nm which incident light polarizing parallel to basal plane) and out-of-plane ($\lambda_{out} \approx 1700$ nm which incident light polarizing perpendicular to basal plane) LSPR modes. With longer heat treatment, I observe that both peaks blue-shift.

![Figure 3-18](image.png)

**Figure 3-18** Tuning nanodisk carrier densities by thermal oxidation. a) IR extinction spectra of Cu$_{2-x}$S nanodisks oxidized at 80 ºC under air. Both in- and out-of-plane LSPRs are observed to blue-shift with increasing thermal oxidation time.
The TEM image in Figure 3-19 shows that the average size and shape of the nanodisks remain unchanged up to 135 h of thermal treatment at 80°C.

![TEM images](image)

**Figure 3-19** TEM images corresponding to nanodisk samples a) before oxidation, as-made nanodisks, b) after oxidation for 135 h at 80 °C.

A change in the polydispersity of the colloidal dispersion also has the potential to result in a broadening of the LSPR peak, even if the average particle size remains the same. To confirm that a change in the size or shape polydispersity does not occur during the annealing process, I carried out dynamic light scattering measurements on nanodisk samples dispersed in chloroform. The results are shown in Figure 3-20 and Table 3-4. These measurements indicate that the average hydrodynamic radius of the nanodisks (approximately 28 nm) and the size dispersity (given by the full-width half-maximum) remain unchanged after 135 h thermal treatment. This data indicates that the observed shift in LSPR wavelength is not due to a change in nanodisk geometry, and must result from a change in the carrier density of the Cu$_{2-x}$S.
Figure 3-20 Dynamic light scattering measurements show the size distribution of nanodisks a) Before thermal oxidation b) After thermal oxidation under air for 135 h at 80°C.

Table 3-4 Mean hydrodynamic diameter and full-width half-max values obtained by Dynamic light scattering for nanodisks before and after thermal treatment at 80°C.

<table>
<thead>
<tr>
<th>Anneal time</th>
<th>0 h</th>
<th>45 h</th>
<th>90 h</th>
<th>135 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Diameter (nm)</td>
<td>28.8</td>
<td>28.6</td>
<td>27.9</td>
<td>28.6</td>
</tr>
<tr>
<td>Half width (nm)</td>
<td>6.8</td>
<td>6.7</td>
<td>7.0</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Similarly, nanodisks treated at 100 °C display similar LSPR behavior. The extinction spectra of nanodisks thermally oxidized at 100 °C are shown in Figure 3-21.
Figure 3-21 Tuning nanodisk carrier densities by thermal oxidation. a) IR extinction spectra of Cu$_{2-x}$S nanodisks oxidized at 100 °C under air.

Figure 3-22 Tuning nanodisk carrier densities by thermal oxidation. IR extinction spectra of Cu$_{2-x}$S nanodisks oxidized at 120 °C under air.
At 120 °C, nanodisks show a blue-shift of the LSPR wavelengths $\lambda_{in}$ and $\lambda_{out}$ from 0-20 hours, but a large change is observed at longer times (Figure 3-22).

Using Mie scattering theory (see chapter III), I used values for $\lambda_{out}$ (wavelength of out-of-plane LSPR mode) obtained by UV-Vis-NIR measurements to calculate the carrier density for each nanodisk sample. Figure 3-23 shows a plot of carrier density as a function of thermal oxidation time for nanodisks heated at three different temperatures.

![Figure 3-23](image)

**Figure 3-23** Change in the carrier densities with thermal oxidation at different temperatures. The maximum carrier density obtained for the nanodisks is approximately $1.36 \times 10^{21}$ cm$^{-3}$, corresponding to a stoichiometry of Cu$_{1.94}$S.

As temperature is increased, the rate of formation of Cu vacancies (increasing carrier density) follows an Arrhenius rate law (Figure 3-24), as expected for a thermally
activated process. The rate constant, $k$ for each oxidation temperature was calculated by fitting the data in Figure 3-23 to the exponential rate law for an Arrhenius reaction. Based on this fit, the activation energy for Cu vacancy formation in the nanodisks by thermal oxidation is calculated to be $E_a = 14.6$ kJ/mol. For comparison, the activation energy for Cu vacancy formation in a CuGaS$_2$ single crystal which has an ordered packing arrangement with alternating layers of I-VI(Cu$_2$S) and III-VI (Ga$_2$S$_3$) is $E_a = 55.5$ kJ/mol. The low activation energy for vacancy formation in our nanodisks is attributed to the high surface energy associated with the nanoscale surfaces, particularly along the disk edges and other regions of high curvature where step edges and defects are expected to be prominent.

![Figure 3-24](image.png) **Figure 3-24** Rate of formation of Cu vacancies as predicted by an Arrhenius rate law fit.
I also observe that the carrier density within the Cu$_{2-x}$S nanodisks does not increase beyond a critical value of $N_h = 1.36 \times 10^{21} \text{cm}^{-3}$ regardless of thermal oxidation temperature or oxidation time. This critical carrier density corresponds to a stoichiometry of Cu$_{1.94}$S. For samples oxidized beyond this point, I observe that the Cu$_{2-x}$S nanodisks undergo an irreversible phase transformation that is characterized by a loss of nanodisk shape (as evidenced by TEM in Figure 5-10) and a change in the nanocrystal structure (as evidenced by UV-Vis-NIR and XRD in Figures 3-22 and 3-27 respectively).

Figure 3-19 (b) and 3-25 (b) show TEM images of nanodisk powders that have been heat treated at 80 °C and 120 °C, respectively, until reaching this critical carrier density. In Figure 3-19 (b), it is apparent that the nanodisks begin to experience re-shaping. In Figure 3-25 (b), the phase transformation is characterized by agglomeration and fusion of the nanodisks. I believe that heavy oxidation at the nanodisk surface disrupts the passivating dodecanethiol layer and promotes nanodisk sintering.

![Figure 3-25](image)

**Figure 3-25** TEM images corresponding to nanodisk samples a) before oxidation, as-made nanodisks, b) after oxidation for 60 h at 120 °C.
Figure 3-26 XRD spectra of nanodisks before and after thermal oxidation at 80 °C for 135h indicating crystal structure remain the chalcocite (hexagonal, Cu₂S) structure.

Figure 3-27 XRD spectra of nanodisks before and after deformation from thermal oxidation at 120 °C for 60h indicating a change in crystal structure from chalcocite (hexagonal,Cu₂S) to digenite (rhombohedral,Cu₉S₅).
Figures 3-26 and Figure 3-27 show the XRD spectra obtained for the heat-treated Cu$_{2-x}$S nanodisk powder at 80°C for 135h and 120 °C for 60 h, respectively. Compared to the unheated nanodisk powder, the XRD spectrum indicates that the nanodisks undergo a change in crystal structure from chalcocite (hexagonal unit cell, Cu$_2$S) to a mixed crystal structure of chalcocite and a lower copper-to-sulfur ratio, such as digenite (rhombohedral unit cell, Cu$_9$S$_5$).

To confirm that this structural change results from the formation of Cu vacancies and does not result from the extended heating time alone, I carried out thermal annealing of a powder nanodisk sample under N$_2$ at 120°C for 60 h. Based on TEM images (Figure 3-28), I observe that the nanodisks do not change size or shape after thermal treatment under N$_2$.

![Figure 3-28 TEM images corresponding to nanodisk samples a) before thermal oxidation, as-made nanodisks, b) after thermal oxidation for 60 h at 120 °C under N$_2$.](image)

This irreversible morphological and structural change observed for the Cu$_{2-x}$S nanodisks at high carrier densities contrasts with other studies indicating that the carrier densities of semiconductor quantum dots can be fully reversible when subjected to
oxidizing or reducing environments.\textsuperscript{41} For example, previous reports for Cu\textsubscript{2-x}Se quantum dots observe that spherical quantum dots with a carrier density corresponding to a stoichiometry of Cu\textsubscript{1.81}Se retain their \( \beta \)-phase Cu\textsubscript{2}Se crystal structure and do not undergo transformation to \( \alpha \)-phase Cu\textsubscript{1.78}Se.\textsuperscript{97} This suggests that utilizing carrier density as a tunable parameter for adjusting LSPR properties is limited by the structural stability of the semiconductor.

3.3 \textit{in situ} Oxidation

In order to study the plasmonic respond of copper sulfide naodisks beyond the critical carrier density under the post-oxidation process and to compare the extinction spectra of nanodisks with varying Cu content, I aimed to synthesize nanodisk dispersions that possess similar disk aspect-ratios and size distributions such that spectral analysis can be carried out without intensive consideration of size and shape discrepancies. I synthesized colloidal nanodisks composed of different stoichiometric copper sulfide phases, including: Cu\textsubscript{1.96}S (high Cu content, low carrier density), Cu\textsubscript{7.2}S\textsubscript{4} (high Cu content, moderate carrier density), and CuS (low Cu content, high carrier density). I used two different methods to achieve colloidal nanodisks composed of high Cu-content and low Cu-content copper sulfide phases.

Thermolysis of the single-source precursor results in the stoichiometric formation of chalcocite (Cu\textsubscript{2}S). However, nanodisk carrier densities are limited to a critical value for this synthetic method. I observed that nanodisks possessing Cu deficiencies greater than the Cu\textsubscript{1.94}S phase become unstable, undergoing catastrophic particle agglomeration and fusion\textsuperscript{83} in section 3.2.
To synthesize nanodisks with lower Cu content (higher carrier density, CuS), I carried out a solvent-based method (more detail in chapter II). The corresponding XRD spectra for these different nanodisks are given in the Figure 3-29. The nanodisks exhibit excitonic absorption that is characteristic of their quantum size, giving rise to the resulting colors of the colloidal dispersions (Figure 3-29 insert).

**Figure 3-29** XRD spectra of copper sulfide nanodisks synthesized by two different methods. In the solventless method, thermolysis of a single-source precursor results in formation of chalcocite (Cu$_2$S). In the solvent-based method, two different copper sulfide phases: covellite (CuS) and digenite (Cu$_{7.2}$S$_4$), can be formed by controlling the ratio of sulfur to copper precursors. These three copper sulfide crystal phases have the same nanodisk morphology with similar aspect ratios. Insert image of the as-made colloidal dispersions of nanodisks with varying Cu content. The color of each dispersion is attributed to strong excitonic absorption in the visible range.
Figure 3-30 shows TEM images and extinction spectra for colloidal nanodisks with high Cu content. Using the solventless thermolysis method, I obtained Cu$_{1.96}$S nanodisks with an average diameter of 26.72 ± 2.26 nm and an average aspect-ratio (AR) of 5.24 ± 1.32. The extinction spectra for these nanodisks (red line) show peaks resulting from LSPR excitation at wavelengths >1000 nm, while the broad feature in the 500-700 nm wavelength range is attributed to excitonic absorption. For these nanodisks I observe two broad spectral peaks attributed to LSPR excitation at $\lambda_{\text{max}}$= 1877 nm with a full-width half-max (FWHM) of 1287 nm and at $\lambda_{\text{max}}$= 3085 nm with a FWHM=465 nm. Peak height and width were determined with a Lorentzian curve fit. Also shown are the extinction spectra for two additional Cu$_{1.96}$S nanodisk dispersions that possess similar ARs of 4.11 ± 1.36 (black line) and 5.87 ± 1.29 (blue line).

**Figure 3-30** Extinction spectra and TEM images of Cu$_{1.96}$S nanodisks. The extinction spectra are shown for nanodisks with varying aspect-ratios (AR).
Using the solvent-based synthesis method, I obtained Cu_{7.2}S_{4} nanodisks with an average diameter of 25.92 ± 2.31 nm and average aspect-ratios of 5.31 ± 1.02 (Figure 3-31). The extinction spectrum for these nanodisks (red line) shows two spectral peaks at $\lambda_{\text{max}}= 1532$ nm with a FWHM=1024 nm and at $\lambda_{\text{max}}= 2893$ nm with a FWHM=343 nm. Also shown are the extinction spectra for two additional Cu_{7.2}S_{4} nanodisk dispersions that possess similar ARs of 4.21 ± 1.42 (black line) and 5.92 ± 1.52 (blue line).

![Image](image.png)

**Figure 3-31** Extinction spectra and TEM images of Cu_{7.2}S_{4} nanodisks. The extinction spectra are shown for nanodisks with varying aspect-ratios (AR).

Using the solvent-based synthesis method, I was also able to obtain CuS nanodisks with an average diameter of 23.72 ± 2.42 nm with AR=3.87 ± 0.95. For CuS
nanodisks, I only observe one spectral peak at $\lambda_{\text{max}} = 1070$ nm with a FWHM of 345 nm (Figure 3-32, black line). Also shown are the extinction spectra for two additional CuS nanodisk dispersions with similar ARs of $4.98 \pm 1.18$ (red line) and $5.71 \pm 0.79$ (blue line). A summary of all nanodisk morphologies is given in Table 3-5.

Figure 3-32 Extinction spectra and TEM images of CuS nanodisks. The extinction spectra are shown for nanodisks with varying aspect-ratios (AR).

To assign the different spectral features as either in-plane or out-of-plane LSPR modes, I used the Drude model and Mie-Gans scattering theory to calculate the expected carrier density associated with each peak. In chapter III, I used this method to demonstrate that Cu$_{2-x}$S nanodisks exhibit two spectral peaks that correspond to an out-of-plane dipolar LSPR mode near 1800 nm and in-plane LSPR mode near 3000 nm.$^{82,83}$ Table 3-6 shows the results of our calculations for nanodisks composed of
the various Cu content phases, and compares them with literature values for the carrier density of the corresponding bulk material.\textsuperscript{98-101}

**Table 3-5** The morphology of nanodisks composed of the three different copper sulfide phases, as analyzed from TEM images. Averages and deviations are obtained from analysis of >200 nanoparticles. Volume and surface area of the nanodisk is calculated by assuming a perfect disk shape, where volume = $\pi D^2 L/4$, surface area = $\pi D^2 + \pi DL$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Nanodisk Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (nm)</td>
</tr>
<tr>
<td>Cu$_{1.96}$S(black)</td>
<td>23.24±8.52</td>
</tr>
<tr>
<td>Cu$_{1.96}$S(red)</td>
<td>26.72±2.26</td>
</tr>
<tr>
<td>Cu$_{1.96}$S(blue)</td>
<td>27.85±1.62</td>
</tr>
<tr>
<td>Cu$_{1.72}$S$_4$(black)</td>
<td>24.21±5.22</td>
</tr>
<tr>
<td>Cu$_{1.72}$S$_4$(red)</td>
<td>25.92±2.31</td>
</tr>
<tr>
<td>Cu$_{1.72}$S$_4$(blue)</td>
<td>30.28±3.21</td>
</tr>
<tr>
<td>CuS(black)</td>
<td>23.72±2.42</td>
</tr>
<tr>
<td>CuS(red)</td>
<td>25.73±3.17</td>
</tr>
<tr>
<td>CuS(blue)</td>
<td>29.87±1.83</td>
</tr>
</tbody>
</table>

**Table 3-6** Calculated carrier densities for copper sulfide nanodisks based on measured LSPRs. Values for the effective hole mass and for bulk carrier densities are obtained from literature reports.\textsuperscript{38, 99-101}

<table>
<thead>
<tr>
<th>Composition</th>
<th>Calculated carrier density (cm$^{-3}$)</th>
<th>Effective hole mass</th>
<th>Bulk carrier density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in-plane</td>
<td>out-of-plane</td>
<td></td>
</tr>
<tr>
<td>Cu$_{1.96}$S</td>
<td>7.40x10$^{20}$</td>
<td>7.39x10$^{20}$</td>
<td>0.8m$_e$</td>
</tr>
<tr>
<td>Cu$_{1.72}$S$_4$</td>
<td>1.22x10$^{21}$</td>
<td>1.32x10$^{21}$</td>
<td>0.78m$_e$</td>
</tr>
<tr>
<td>CuS</td>
<td>1.01x10$^{22}$</td>
<td>---</td>
<td>0.55m$_e$</td>
</tr>
</tbody>
</table>
Our comparison indicates that while Cu$_{1.96}$S and Cu$_{7.2}$S$_4$ nanodisks exhibit in-plane and out-of-plane dipolar LSPR modes with similar resonant wavelengths to our previous study, CuS nanodisks exhibit only one peak that corresponds to the in-plane dipolar LSPR mode. Our spectral data is consistent with previous experimental and theoretical observations by Xie and colleagues, who observe that the in-plane and out-of-plane LSPR modes for CuS nanodisks overlap and are difficult to distinguish experimentally. Although the CuS nanodisks they study are significantly smaller in both diameter (~15 nm) and AR (~2), their results indicate that this spectral peak is dominated by the in-plane LSPR contribution. The observed difference in $\lambda_{\text{max}}$ for the in-plane dipolar LSPR modes between CuS nanodisks and the high Cu content nanodisks is $>$1800 nm. However, this large difference in $\lambda_{\text{max}}$ is both attributed to the large difference in effective hole mass between CuS (0.55\textit{m}_e) and the high Cu content phases (0.8\textit{m}_e and 0.78\textit{m}_e, respectively), to the increase in carrier density. A smaller effective hole mass is expected to significantly increase the frequency of plasmon oscillations, resulting in a blue-shift of the spectral peak.

I carried out electrodynamic simulations to confirm our LSPR peak assignments using finite-difference time-domain (FDTD) methods to model the far-field scattering coefficients of single CuS and Cu$_{1.96}$S nanodisks with diameters of 25 nm and thicknesses of 5 nm (in Figure 3-33 and 3-34). The optical constants for CuS and Cu$_{1.96}$S were obtained from reflectance and transmittance measurements of electrochemically deposited thin-films of the corresponding material.\textsuperscript{102, 103} It should be noted that our simulation results are limited to IR wavelengths below 2400 nm, which is the maximum
wavelength for which published optical data for Cu$_{1.96}$S exists. The simulation results obtained for a single CuS nanodisk are consistent with our experimental results and the results of Xie and colleagues, showing the large in-plane LSPR contribution in the near-IR wavelength range and a small overlapping contribution from the out-of-plane LSPR at a slightly shorter wavelength. The scattering coefficient for the in-plane LSPR peak at 1050 nm is approximately $Q_{sca}=18$ nm$^2$. However, the simulation results obtained for a single Cu$_{1.96}$S nanodisk deviates significantly from our experimental results, showing only a broad spectral feature resulting from an in-plane LSPR.

**Figure 3-33** (a) Extrapolated refractive index values function for bulk CuS. The extrapolated n and k curves were obtained from experimental optical transmittance and reflectance spectra reported by Nair and colleagues. b) Finite-difference time-domain simulation results for nanodisks composed of CuS, modeled with diameters of 25 nm and thicknesses of 5 nm. The two curves show the extinction cross-sections for an illuminating plane wave with in-plane and out-of-plane polarization. c-d) The color maps for field intensities at the observed peak maxima.
I believe that this large discrepancy stems from the derivation of optical constants for Cu$_{1.96}$S using polycrystalline electrochemically deposited thin-films having different electron and hole mobilities than single-crystalline nanoparticle. In compound semiconductors such as Cu$_{1.96}$S, carrier mobility is highly dependent on crystallographic direction. Polycrystalline materials are not expected to give rise to same far-field scattering response as single-crystalline materials, such as our nanodisks. This is less critical for CuS, which exhibits metal-like behavior and possesses free carriers that are “less localized.” The large discrepancy between our simulation and experimental results for Cu$_{1.96}$S nanodisks also highlights one of the major advantages in using colloidal
nanodisks for fabricating semiconductor plasmonics: crystallinity and carrier concentrations are more readily controlled during nanoparticle synthesis.

In this chapter, I used these disk-like copper sulfide nanocrystals to demonstrate commonality between the optical LSPR bands observed for anisotropic metallic nanoparticles and the NIR LSPR bands observed for semiconductor nanocrystals, as well as that tuning the shapes of semiconductor nanocrystals can access a large spectral range for LSPR excitation. These colloidal copper sulfide nanodisks possess two LSPR modes between 1000-3100nm in which excitation occurs for incident radiation polarized in two directions: parallel and perpendicular to the basal plane of the disk. I also used the theoretical calculation in the electrostatic limit to show that the extinction band at ~1800nm corresponded to the out-of-plane mode (polarization direction is perpendicular to the basal plane) and that the extinction band at ~3000nm corresponded to the in-plane mode (polarization direction is parallel to the basal plane) as shown in Scheme 3-3.

Scheme 3-3 The two extinction bands correspond to incident radiation polarized in two directions. The extinction band at the shorter wavelength is the out-of-plane mode in which the incident light is polarized perpendicular to the basal plane, and the extinction band at the longer wavelength is the in-plane mode in which the incident light is polarized parallel to base plane.
I also observed that the LSPR modes of copper sulfide nanocrystals could be tuned by varying the aspect ratio of the nanocrystals. However, the elongated aspect ratio of nanodisks accompanies the increase in nanocrystal carrier density, which results from the formation of copper vacancies during the thermolysis process. The aspect-ratio of \( \text{Cu}_{2-x}\text{S} \) nanodisks can be independently tuned by carrying out thermolysis of a copper-alkanethiolate precursor under a \( \text{N}_2 \) gas environment which suppresses the formation of Cu vacancies.

The carrier-density of \( \text{Cu}_{2-x}\text{S} \) nanodisks can be tuned independently of other properties via thermal oxidation of the as-made nanodisks. Nanodisks subjected to post-synthetic thermal oxidation in air exhibit changes in carrier densities that are independent of nanodisk shape. I observe that beyond a critical carrier density of \( N_h = 1.36 \times 10^{21} \text{ cm}^{-3} \), the nanodisks undergo an irreversible phase transformation that promotes particle agglomeration and fusion. Carrier density is thus limited to a specific range, placing an upper limit on LSPR wavelength tuning from the infrared wavelength range. In order to fabricate the carrier density beyond the critical carrier density barrier of post-oxidation, I synthesized higher carrier density copper sulfide (\( \text{Cu}_{7.2}\text{S}_4 \) and \( \text{CuS} \)) nanodisks with similar shape (aspect ratio) and size distributions by a solvothermal synthesis.

Using electrodynamic simulation to confirm the plasmonic response with different \( \text{Cu}_{2-x}\text{S} \) nanocrystals, the experimental plasmonic response from lower carrier density \( \text{Cu}_{1.96}\text{S} \) nanodisks is do not agree with the electrodymanic simulation result. I attribute the discrepancy to the plasmonic response of semiconductors to being strongly dependent on the crystallinity and carrier mobility in nanocrystals.
Shape-, size-, and carrier density-tuning plasmon response of Cu$_{2-x}$S nanocrystals may also provide a convenient strategy for sub-wavelength manipulation of electromagnetic radiation in the IR spectral region, with potential applications in thermal imaging and spectroscopy, IR-responsive coatings, and telecommunications.

Chapter 3, in part, is a reprint of the content as it appears in *Journal of the American Chemical Society*.


CHAPTER 4
PLASMONIC COUPLING BETWEEN SEMICONDUCTOR NANOCRYSTALS

Localized surface plasmon resonances (LSPRs) are excited when free carriers in metallic nanostructures oscillate in resonance with an incident light wave to produce intense electromagnetic fields localized at the metal surface. For nanoparticles with optimized sizes, shapes, and geometrical arrangements, this localization can lead to field enhancements nearing $10^7$ times the incident field intensity.\textsuperscript{8,104} For this reason, metal nanoparticles supporting LSPRs in the visible wavelengths have impacted research in a broad range of applications where light localization or focusing is critical, including optical platforms for surface-enhanced Raman spectroscopy,\textsuperscript{105,106} photovoltaics,\textsuperscript{107} and sub-wavelength optics.\textsuperscript{108}

Semiconductor nanostructures have emerged as a new family of plasmonic materials that are also capable of supporting LSPR excitation. In contrast to metal nanostructures, these semiconductor nanomaterials possess carrier concentrations that are tunable by designating dopant type and level, or by charge injection.\textsuperscript{39,83} For example, nanoparticles composed of degenerately-doped semiconductors such as Cu$_{2-x}$S and Cu$_{2-x}$Se exhibit increased carrier concentrations upon the generation of Cu vacancies.
As a result, the wavelength of LSPR excitation can be tuned within the infrared range by varying the Cu content of the nanoparticles. Highly anisotropic semiconductor nanostructures are also capable of supporting shape-dependent LSPRs, where the direction of polarization for a particular LSPR mode is governed by nanostructure shape.

However, no studies to-date have investigated the plasmonic coupling between semiconductor nanostructures and how these near-field interactions are affected by materials properties such as carrier density or mobility. In this chapter, I report on the near-field interactions between semiconductor nanodisks composed of degenerately-doped Cu$_{2-x}$S. These nanodisks exhibit pronounced dipolar LSPRs that occur for plane-wave illumination with polarization parallel to the basal plane of disk (in-plane LSPR) or normal to the basal plane of disk (out-of-plane LSPR), which allow us to tailor the direction of near-field coupling based on disk orientation (Figure 4-1). I synthesize nanodisks that possess varying Cu content using two different colloidal methods in chapter V. Next, I demonstrate that these nanodisks can be assembled into close-packed superlattices with different disk orientations as scheme in Figure 4-1 c). This is carried out by nanodisk surface modification with either hydrophobic or hydrophilic ligands, followed by assembly at an air-water interface. LSPR coupling occurs due to Coulomb interactions between nearest-neighbor nanodisks within the assembled thin-films, and I observe that the strength of coupling is highly dependent on both nanodisk orientation and carrier density. Given the observed tunable coupling and polarization response, these efforts towards engineering nanodisk plasmonic assemblies have the potential be extended towards sophisticated metamaterials or directly integrated into optical device structures that operate in the near- to mid-IR range.
Colloidal semiconductor nanodisks and assemblies. a) Nanodisks are expected to display two dipolar LSPR modes corresponding to in-plane excitation and out-of-plane excitation. b) Image of the as-made colloidal dispersions of nanodisks with varying Cu content. The color of each dispersion is attributed to strong excitonic absorption in the visible range. c) Schematic of different packing orientations for nanodisks. Orientation is dictated by surface modification of the nanodisks with hydrophobic or hydrophilic capping ligands.

4.1 Fabrication of Two-Dimensional Nanocrystal Arrays

One-, two- or three-dimensional regular arrays of nanoparticles exhibit unique electrical and optical properties compared to the colloidal nanoparticles that might be advantageously exploited in the design of future nanodevices. In the past few years, many studies have investigated the control of nanoparticle self-assembly or self-organization into two-dimensional (2D) and three-dimensional (3D) structures. For example, two- or three-dimensional superlattices of gold nanocrystals were spontaneously formed upon evaporation-induced self-assembly. There are different assembly procedures can be used to fabricate the 2D and 3D gold nanoparticles nanostructures, such as the cross-
linked or bridged method, layer-by-layer adsorption techniques, patterning by using inorganic or organic templates, electrophoretic deposition, and the Langmuir–Blodgett technique.

Here, I fabricated two-dimensional arrays of closely-spaced nanodisks using Langmuir-Blodgett assembly. The Langmuir-Blodgett (LB) technique is a room-temperature deposition process for deposing monolayer and multilayer films of organic materials at an air-water interface. This method allows the manipulation of organic molecules on the nanometer scale, thereby fabricating intriguing superlattice architectures of nanoparticles.

Thin-films of nanodisks are organized via compression at an air-water interface (Fig. 4-1c). The nanodisks adopt two different interparticle orientations:

(i) arranged vertically in stacks with their basal planes orthogonal to the air-water interface (pancake-like packing), or

(ii) arranged laterally with their basal planes parallel to the air-water interface (side-by-side packing).

I controlled nanodisk orientation by chemically modifying the surface of the nanodisks with hydrophobic or hydrophilic capping ligands. For hydrophobic ligand modified nanodisks preparation, a 4mL of as-made nanodisks colloidal solution (in chloroform) was mixed with 120 μL 1-dodecanethiol and incubated in room temperature 8 hours. The modified nanodisks was collected by the centrifugation at 9000 rpm for 7.5min, washed two times with chloroform to remove the free 1-dodecanethiol, and then re-dispersed in chloroform for self-assembly by Langmuir-Blodgett method. Nanodisks functionalized with end-grafted molecules of 1-dodecanethiol are rendered hydrophobic
and tend to minimize surface tension at the air-water interface forming stacked, pancake-like structures (Fig. 4-2 a).

**Figure 4-2** Oriented nanodisk thin-films. From left to right: TEM images of representative monolayers and multilayers, and SEM images of multilayers. a) Nanodisks capped with 1-dodecanethiol are hydrophobic and form stacked, pancake-like structures. b) Nanodisks capped with poly(ethylene glycol) methyl ether thiol are hydrophilic and assemble side-by-side at the air-water interface.

For hydrophilic ligand modified nanodisks preparation, a 4mL of as-made nanodisks colloidal solution (in chloroform) was mixed with a 0.1mM, 1mL poly(ethylene glycol) methyl ether thiol (PEG-thiol, Mw=5000) methanol solution and incubated in room temperature 24 hours. The modified nanodisks was collected by the centrifugation at 9000 rpm for 7.5min, and washed two times with methanol to remove the free PEG-thiol and then re-dispersed in chloroform for self-assembly.
functionalized by thiol-terminated poly(ethylene glycol) chains (Mw=5000) are rendered hydrophilic and tend to maximize their contact area with water by assembling side-by-side (Fig. 4-2b). The corresponding FTIR spectra of hydrophobic (1-dodecanethiol coated, black curve) and hydrophilic (PEG-thiol coated, red curve) copper sulfide colloids solution in Figure 4-3 indicate that the different surface chemistry of copper sulfide nanodisks was obtained.

![FTIR spectra of different surface chemistry coated nanodisk. The black curve corresponds nanodisks capped with 1-dodecanethiol which are hydrophobic. And the red curve corresponds the nanodisks capped with poly(ethylene glycol) methyl ether thiol are hydrophilic.](image)

**Figure 4-3** FTIR spectra of different surface chemistry coated nanodisk. The black curve corresponds nanodisks capped with 1-dodecanethiol which are hydrophobic. And the red curve corresponds the nanodisks capped with poly(ethylene glycol) methyl ether thiol are hydrophilic.

Close-packed films are generated by mechanically compressing the floating nanodisks until a desired surface pressure is achieved. The films can then be transferred from the air-water interface to a solid support by dip-coating. Dip-coating can be repeated several times to obtain arbitrarily thick multilayers of the nanodisk assemblies. It should be noted that these ligands do modulate the dielectric environment of the nanodisk,
resulting in a slight increase of the refractive index of the surrounding nanodisk medium. However, these ligands produce low-dielectric molecular shells that are unlikely to contribute to any Coulombic interactions that occur between neighboring nanodisks.

4.2 Orientation-Dependent Optical Response

The extinction spectra of Cu$_{1.96}$S, Cu$_{7.2}$S$_4$, and CuS nanodisks that are assembled into monolayers with stacked (red lines) and side-by-side (blue lines) orientations show in Figure 4-4, 4-5 and, 4-7, respectively. The extinction spectra for randomly oriented colloidal dispersions (black lines) are also shown for comparison.

![Figure 4-4](image)

**Figure 4-4** Orientation-dependent optical response. Extinction spectra of Cu$_{1.96}$S nanodisk films supported on a quartz substrate, with nanodisks oriented in the stacked orientation (red) and the side-by-side orientation (blue). For comparison, the extinction spectrum of the corresponding nanodisk dispersion in chloroform is also shown (black).

For both Cu$_{1.96}$S and Cu$_{7.2}$S$_4$ nanodisks, the most significant change that I observe is broadening of the out-of-plane dipolar LSPR for the side-by-side orientation. For
Cu$_{1.96}$S nanodisks, the FWHM of the out-of-plane LSPR increases to 1438 nm. For Cu$_{7.2}$S$_4$ nanodisks, the FWHM of the out-of-plane LSPR increases to 1520 nm. I believe that this broadening indicates weak electromagnetic coupling between the nanodisks.

![Figure 4-5](image)

**Figure 4-5** Orientation-dependent optical response. Extinction spectra of Cu$_{7.2}$S$_4$ nanodisk films supported on a quartz substrate, with nanodisks oriented in the stacked orientation (red) and the side-by-side orientation (blue). For comparison, the extinction spectrum of the corresponding nanodisk dispersion in chloroform is also shown (black).

To rule out broadening due to any radiative damping caused by the large interfacial contact between the nanodisks and the underlying quartz substrate, I carried out similar experiments for nanodisks assemblies sandwiched within polystyrene layers to provide a more homogeneous dielectric environment. The sample with and without the homogenous dielectric environment gave similar experimental results in Figure 4-6.
Figure 4-6 The Cu$_{7.2}$S$_4$ side-by-side assembled thin film with different dielectric environment. a) Schematic of assembled thin film deposits on quartz substrate by dip coating. b) Schematic of homogenous dielectric environment around the assembled thin film by forming the sandwiched within polystyrene layers. The polystyrene was deposited on quartz by spin-coating, and then the copper sulfide nanodisk assembled thin film on air-water interface was deposited on top of polystyrene layer by dip-coating. Finally, the second polystyrene layer was deposited on the top of copper sulfide assembled thin film by spin-coating. c) The extinction spectra of copper sulfide assembled thin film in different dielectric environment. The black line is the assembled thin film on quartz substrate and the red line is the assembled thin film around with polystyrene layers.

In contrast, the extinction spectra for close-packed films of CuS nanodisks show a drastic change in the infrared response depending on nanodisk orientation. For nanodisks arranged into stacks, I observe that the intensity of the spectral peak decreases significantly. The appearance of a broad spectral feature near 1000 nm may be indicative of excitation of the out-of-plane LSPR, which is expected to exhibit significant overlap with the near-IR band corresponding to the in-plane LSPR mode. Lack of significant a wavelength shift indicates that strong electromagnetic coupling between stacked nanodisks is not observed; peak broadening may indicate the presence of weak
electromagnetic coupling, as observed in the high Cu content nanodisks. For CuS nanodisks arranged into the side-by-side orientation, the in-plane LSPR exhibits a significant redshift to \( \lambda_{\text{max}} = 1411 \) nm. This redshift, in conjunction with peak broadening to a FWHM = 702 nm, can be attributed to strong inter-disk plasmonic coupling.

![Figure 4-7](image)

**Figure 4-7** Orientation-dependent optical response. Extinction spectra of CuS nanodisk films supported on a quartz substrate, with nanodisks oriented in the stacked orientation (red) and the side-by-side orientation (blue). For comparison, the extinction spectrum of the corresponding nanodisk dispersion in chloroform is also shown (black).

Angle-dependent IR extinction measurements were carried for nanodisk monolayers oriented in the side-by-side arrangement. The nanodisk films were rotated by varying the angle of incidence (\( \theta \)) between an unpolarized light source and the plane of the supported thin-film, where \( \theta = 0^\circ \) corresponds to normal incidence. The extinction spectra were fit to multiple Lorentzian peaks, which I used to obtain the relative changes in the intensity of the out-of-plane and in-plane LSPRs. The changes in intensity of
plasmon response in $\text{Cu}_{1.96}\text{S}$ side-by-side packing thin film with respect to $\theta$ for the various spectral peaks was presented in Figure 4-8, and the best-fit of these data points a sine-squared function is given by the dashed lines.

**Figure 4-8** Angle-dependent LSPR extinction measurements of $\text{Cu}_{1.96}\text{S}$ nanodisks with side-by-side packing orientation. The nanodisk films were rotated by varying the angle of incidence ($\theta$) between an unpolarized light source and the plane of the film, where $\theta=0$ corresponds to normal incidence, as shown in the schematic. The polar plot shows angle-dependent intensities of LSPR peaks for $\text{Cu}_{1.96}\text{S}$ side-by-side oriented nanodisk thin-films. Maximum LSPR intensities are normalized to 1 and fit with a sine-squared function (dashed lines).

For the side-by-side $\text{Cu}_{1.96}\text{S}$ nanodisks, the intensity of the spectral peak at $\lambda_{\text{max}}=1877$ (black squares) is a maximum at $\theta = 90^\circ$ whereas the intensity of the peak at $\lambda_{\text{max}}=3085$ (blue circles) is a maximum at $\theta = 0^\circ$. A similar polar plot is shown for the stacks oriented $\text{Cu}_{1.96}\text{S}$ nanodisks (Figure 4-9), showing the two LSPR peak intensities as the assembled thin-films are rotated. At $\theta = 90$, the intensity of the LSPR peak at $\lambda_{\text{out}}$ (black squares) is a maximum whereas the intensity of the LSPR peak at $\lambda_{\text{in}}$ (blue circles) is at a minimum.
Figure 4-9 Angle-dependent LSPR extinction measurements of Cu$_{1.96}$S nanodisks with stack packing orientation. The nanodisk films were rotated by varying the angle of incidence ($\theta$) between an unpolarized light source and the plane of the film.

For the side-by-side Cu$_{7.2}$S$_4$ nanodisks, the intensity of the peak at $\lambda_{\text{max}}=1532$ (black squares) is a maximum at $\theta = 90^\circ$ whereas the intensity of the peak at $\lambda_{\text{max}}=2895$ (blue circles) is a maximum at $\theta = 0^\circ$ in Figure 4-10. By comparing the relative peak amplitudes of the angle-dependent extinction, these measurements also indicate that the in-plane dipolar LSPR mode possesses the higher polarizability of the two LSPR modes. For CuS nanodisks oriented side-by-side, the intensity of the peak at $\lambda_{\text{max}}=1070$ (blue circles) is a maximum at $\theta = 0^\circ$ and confirms that this spectral feature is dominated by excitation of the in-plane LSPR in Figure 4-11.

I repeated our orientation-dependent plasmon response measurements by using p-polarized light and results shows in Figure 4-12, 4-13, and 4-14. The results show a similar polarization direction as unpolarized light observed, but with more pronounced angle dependence.
Figure 4-10 Angle-dependent LSPR extinction measurements of Cu$_{7.2}$S$_4$ nanodisks with side-by-side packing orientation. The nanodisk films were rotated by varying the angle of incidence ($\theta$) between an unpolarized light source and the plane of the film, where $\theta=0$ corresponds to normal incidence, as shown in the schematic. The polar plot shows angle-dependent intensities of LSPR peaks for Cu$_{7.2}$S$_4$ side-by-side oriented nanodisk thin-films. Maximum LSPR intensities are normalized to 1 and fit with a sine-squared function (dashed lines).

Figure 4-11 Angle-dependent LSPR extinction measurements of CuS nanodisks with side-by-side packing orientation. The nanodisk films were rotated by varying the angle of incidence ($\theta$) between an unpolarized light source and the plane of the film.
Figure 4-12 Angle-dependent LSPR extinction measurements of Cu$_{1.96}$S nanodisks with side-by-side packing orientation. The nanodisk films were rotated by varying the angle of incidence ($\theta$) between a p-polarized light source and the plane of the film.

Figure 4-13 Angle-dependent LSPR extinction measurements of Cu$_{7.2}$S$_4$ nanodisks with side-by-side packing orientation. The nanodisk films were rotated by varying the angle of incidence ($\theta$) between a p-polarized light source and the plane of the film.
4.3 The Effect of Carrier Density

To further compare the strength of plasmon coupling for copper sulfide nanodisks with varying Cu content, I examined shifts in $\lambda_{\text{max}}$ for the in-plane dipolar LSPR with respect to inter-disk spacing. This was carried out by collecting monolayers of side-by-side oriented nanodisks at different surface pressures during the assembly process. Figure 4-15 shows TEM images of the resulting CuS nanodisk monolayers, which I fabricated to possess varying fill factors in the range of 30-90%. Fill factor was calculated as the total percent coverage of a given surface area by the nanodisks as determined by TEM image analysis. As nanodisk fill factor is increased, the distance between neighboring nanodisks is decreased and the strength of near-field coupling interactions is expected to increase. The individual extinction spectra for nanodisk thin-films are given in the in Figure 4-16, 4-17, and 4-18.
Figure 4-15 TEM images show representative thin-film densities of Cu$_{2+x}$S nanodisks in the side-by-side orientation, obtained by varying the surface pressure of the film during the assembly process.

Figure 4-16 LSPR extinction measurements of coupling between nanodisks by varying the Cu$_{1.96}$S nanodisks content in side-by-side packing thin films with different fill factor in the range of 30-90%.
Figure 4-17 LSPR extinction measurements of coupling between nanodisks by varying the Cu$_{7.2}$S$_{4}$ nanodisks content in side-by-side packing thin films with different fill factor in the range of 30-90%.

Figure 4-18 LSPR extinction measurements of coupling between nanodisks by varying the CuS nanodisks content in side-by-side packing thin films with different fill factor in the range of 30-90%.
A plot of the wavelength shift ($\Delta\lambda/\lambda_0$) as a function of the disk separation distance-to-diameter ratio ($S/D$), a dimensionless parameter. The dashed lines shows least-squares fit to an exponential decay. For interlayer coupling between nanodisks, I increased the thickness of thin film by multiple deposition side-by-side packing on substrate.

Figure 4-19 shows the percent change in LSPR wavelength which is calculated as $\Delta\lambda/\lambda_0$, where $\Delta\lambda$ is the absolute shift in the $\lambda_{max}$ for the in-plane dipolar LSPR and $\lambda_0$ is the initial $\lambda_{max}$ measure for unassembled colloidal nanodisks. The percent change in LSPR wavelength is plotted as a function of the ratio of interdisk spacing to the nanodisk diameter ($S/D$). For CuS nanodisks, an exponential decay is observed for $\Delta\lambda/\lambda_0$ and I measured a maximum LSPR shift of $\Delta\lambda=419\pm8.2$ nm for the closest-packed monolayer. This is consistent with previous studies of metallic nanoparticles, which found that a near-field coupling decay distance of $0.2D$ is universal, regardless of particle shape or medium.\textsuperscript{44} In contrast, little-to-no change is observed in the $\Delta\lambda/\lambda_0$ for either Cu$_{1.96}$S or
Cu$_{7.2}$S$_4$ nanodisks, indicating that dipole-dipole coupling for nanodisks with high Cu content is quite weak.

Our results suggest two effects related to plasmonic coupling between semiconductor nanodisks. First, near-field coupling is highly dependent on carrier density. While there is evidence of weak near-field coupling in assemblies of copper sulfide nanodisks with moderate carrier densities (Cu$_{1.96}$S and Cu$_{7.2}$S$_4$), strong near-field coupling is only observed in CuS nanodisks which are known to exhibit metal-like behavior at room temperature. Second, I observe that near-field coupling also highly dependent on inter-disk orientation. Extinction spectra of copper sulfide nanodisks oriented side-by-side into close-packed monolayers show evidence of electromagnetic coupling. This is attributed to dipole-dipole coupling between neighboring nanodisks. However, I did not observe any evidence of electromagnetic coupling for nanodisks arranged into stacks. This is result somewhat surprising given the small spacing between the nanodisks in the stacked orientation. From TEM image analysis, the stacked nanodisks are spaced approximately 2.35±0.8 nm apart, well within the interparticle separation distance for strong coupling. Our observation of very weak Coulomb interaction between stacked copper sulfide nanodisks also deviates from observation for similarly Ag nanodisks$^{110}$ as well as graphene nanodisks, both of which exhibit strong near-field coupling in stacked configuration$^{111}$. Even for CuS nanodisks that exhibit metal-like electronic behavior, there is no evidence for dipole-dipole coupling for the out-of-plane LSPR mode and no significant change in the IR response is observed for stacked disks. This suggests that the out-of-plane dipolar LSPR possesses an extremely short decay length that does not permit strong plasmonic coupling even at short interparticle
distances, which is expected to be significant for semiconductors that experience some degree of electron/hole localization such as Cu$_{2-x}$Te nanorods.\textsuperscript{84}

To further confirm this orientation dependence, I investigated coupling for multilayers of the side-by-side oriented nanodisk films. I deposited up to nine nanodisk layers corresponding to a total film thickness of approximately 40 nm. The extinction spectra for these multilayer films are given in the Figure 4-20, 4-22, and 4-23.

![LSPR extinction spectra for multilayered films composed of nanodisks assembled in the side-by-side configuration for Cu$_{1.96}$S nanodisks.](image)

**Figure 4-20** LSPR extinction spectra for multilayered films composed of nanodisks assembled in the side-by-side configuration for Cu$_{1.96}$S nanodisks. To compare the relative intensities and $\lambda_{\text{max}}$ of each spectral peak, a baseline was obtained for each spectrum. Spectra with multiple, overlapping peaks were analyzed using a nonlinear least squares curve fit using commercial software (Origin Pro8). All peaks were fit to a Lorentzian function with R-square values $> 0.985$.

The intensity of LSPRs enhanced with increased the number of arrays layers due to increase the amount of nanodisks on substrate. In order to compare the intensity of out-of-plane mode and in-plane mode change with number of layers, I use the multiple peaks fitting function in origin to obtain the intensity of out-of-plane and in-plane modes and
then normalized spectra with the in-plane mode. Relative intensity of in-plane mode increase with increased the number of arrays on the substrate. The enhancement of in-plane mode in multiple-layers side-by-side packing arrays structure due to in-plane face dominates the surface of side-by-side packing arrays and the increased the number of arrays can enhance the incident light polarized along in-plane face.

![Figure 4-21](image)

**Figure 4-21** LSPR extinction spectra for multilayered films composed of nanodisks assembled in the stack packed configuration for Cu$_{1.96}$S nanodisks.

In the other hand, the LSPRs spectra of pancake-like stacks array change with increased the number of arrays layers, as figure 4-21. The intensity of both LSPRs modes increased with the number of arrays layers also due to the amount of nanodisks on substrate. However, the relative intensity of out-of-plane mode increased with increased the number of arrays layers. This is due to the out-of-plane face dominating of the surface of pancake-like stacks array and the increased the number of arrays can increasing the incident light polarized along the in-plane face.
Figure 4-22 LSPR extinction spectra for multilayered films composed of nanodisks assembled in the side-by-side configuration for Cu$_{7.2}$S$_{4}$ nanodisks.

Figure 4-23 LSPR extinction spectra for multilayered films composed of nanodisks assembled in the side-by-side configuration for CuS nanodisks.
For side-by-side packing, peak intensity increases significantly with the number of deposited nanodisk layers. If plasmon coupling is present between the nanodisk layers, I expect to observe a blue-shift for the in-plane LSPR and a red shift for the out-of-plane LSPR, consistent with what has been observed for other layered materials.\textsuperscript{111,112} Figure 4-24 shows the percent change in LSPR wavelength, $\Delta\lambda/\lambda_0$, for the in-plane LSPR mode that is characteristic of the nanodisk multilayers.

![Graph showing wavelength shift vs number of deposition](image)

**Figure 4-24** A plot of the wavelength shift ($\Delta\lambda/\lambda_0$) for the in-plane LSPR mode for Cu$_{1.96}$S (blue), Cu$_{7.2}$S$_4$ (red), and CuS (black) nanodisk multilayer thin-films as the number of layers is increased.

For the Cu$_{1.96}$S nanodisks, little to no shift in the LSPR wavelength is observed. For Cu$_{7.2}$S$_4$, a modest wavelength shift of $\Delta\lambda/\lambda_0 = 0.012$ ($\Delta\lambda = 20 \pm 4.5$ nm) is observed, indicating weak Coulombic interaction within the multilayer film. For CuS nanodisks, a
more significant redshift is observed for the multi-layer thin-film, with
$\Delta \lambda / \lambda_0 = 0.062$ ($\Delta \lambda = 92.1 \pm 7.2$ nm) for four nanodisk layers. However, no further
wavelength shift is observed upon the deposition of additional nanodisk layers. In all
cases, I observe a red-shift of the in-plane LSPR mode which is not characteristic of
interlayer plasmonic coupling. Rather, I attribute this to increased intralayer coupling that
results from an increased fill factor within the underlying side-by-side layers as an
additional nanodisk layer is deposited. This would also account for the lack of change in
the LSPR peak wavelength for multilayer films greater than five layers thick.

In summary, I show that copper sulfide (Cu$_{1.96}$S, Cu$_{7.2}$S$_4$, and CuS) nanodisks can
be assembled into superlattices that possess two different orientations, and that nanodisk
orientation plays a key role in dictating whether strong plasmonic coupling is permitted
within these assemblies. For nanostructures composed of semiconductors – and in
particular, compound semiconductors that possess significant crystal anisotropy – shape
and orientation are critical parameters in dictating near-field interactions. Strong
Coulombic interactions only occur when copper sulfide nanodisks are aligned in a side-
by-side arrangement such that dipole-dipole coupling is allowed between the in-plane
LSPR modes as scheme 4-1.

Moreover, these interactions are only observed for copper sulfide phases that
possess a critical carrier density value. For the copper sulfide phases examined here, a
decrease in Cu content is shown to significantly increase the charge polarizability of the
nanodisks. The poor plasmonic coupling observed for self-assembled stacks of nanodisks
and deposited nanodisk multilayers suggest that the LSPR decay length for copper sulfide
nanodisks is highly anisotropic with respect to the nanodisk geometry. This may result
from the inherent anisotropy of the copper sulfide crystal structures examined in this chapter. For example, bulk copper sulfide phases are known to exhibit hole mobilities that are highly dependent on crystallographic direction. Unlike for metals, future strategies for designing electromagnetic hot spots or coupled plasmonic architectures using semiconductor nanostructures may be required to take into account both the shape and crystallographic orientation of the nanostructure.

Scheme 4-1 Intralayer and interlayer coupling between nanodisks. For intralayer coupling between nanodisks, I tuned the nanodisks content in the side-by-side packing thin film. a-b) TEM images show representative thin-film densities of CuS nanodisks in the side-by-side orientation, obtained by varying the surface pressure of the film during the assembly process.

Chapter 4, in part, is a reprint of the content as it appears in Nano Letters

5.1 Plasmon Enhanced Infrared Spectroscopy

Semiconductor materials possess unique plasmonic response compared to metal materials which I observed the plasmonic response can be engineered in 1000-3000nm range by tuning the carrier density of nanocrystals. Light absorption in the NIR range due to LSPR excitation of lower carrier density copper, Cu$_{1.96}$S and Cu$_{7.2}$S$_4$, is expected to result in increased sensitivity of chemical detection by IR spectroscopy for molecules adsorbed at the surface of the NPs. The preliminary result of FTIR enhancement measurement shows in Figure 8-1. The FTIR spectra of analytes, PEG-SH and dodecanethiol, coated on the surface of copper sulfide nanodisks with the same concentration of analytic nanodisks solution shows that the low carrier density Cu$_{1.96}$S with plasmonic response in long wavelength (> 3000nm, <3300cm$^{-1}$) can enhance the aliphatic compounds (C-H stretch) around 2900cm$^{-1}$.

For heavily doped copper monosulfide (CuS) NPs are an ideal candidate for two photon excitation which is based on the idea that two photons of comparably lower energy than needed for one photon excitation can also excite a fluorophore in one quantum event, as the scheme 8-1. $^{113}$ This bases on of optical property of CuS that the
maximum plasmonic response of CuS nanodisks at ~ 1000nm (1.24eV) approach half energy of its excitation energy (~2.5eV, ~500nm) in Figure 8-2.

![Image](image1.png)

**Figure 5-1** IR enhancement measurement. FTIR spectra of analytes on copper sulfide nanodisk with different crystal structures a) PEG-thiol. b) Dodecanethiol.

5.2 Non-Linear Optics

Two-photon-induced luminescence of the CuS nanodisks was confirmed by measuring the dependence of the emission intensity on the excitation power. The CuS nanodisks with 5nm in thickness and 25nm in diameter were deposited on a glass cover slide, and single emission spots were measured. The emission intensity of CuS nanodisks show a close quadratic dependence of 2.37 on the incident power by observation for the increasing of excitation powers from 4 to 10 mW. The quadratic dependence behavior indicates that the excitation of CuS nanodisk is a two-photon process.\textsuperscript{114, 115}
Scheme 5-1 The concept of two-photon excitation vs the single photon excitation. Adapted from ref. 131.

Figure 5-2 The photoluminescence (PL) and extinction spectra of CuS nanodisks colloidal with average size 5nm in thickness and 25nm in diameter. a) PL spectrum shows that the maximum emission occurs at wavelength=489nm, and b) extinction spectrum shows that the maximum absorption is at wavelength=1030nm.
Figure 5-3 The emission of two photon photoluminescence (2PPL) of CuS nanodisks colloidal on varying the excitation power. a) the emission intensity of CuS nanodisk with excitation power at 800nm in 4-10mW range. b) the emission intensity dependence of CuS nanodisk on excitation power. c)-e) the two photon images of CuS nanodisk in 0,6,10mV extinction power, respectively.
REFERENCES


113. Two photon excitation. [http://www.ncl.ac.uk/bioimaging/assets/photos/2photon.jpg](http://www.ncl.ac.uk/bioimaging/assets/photos/2photon.jpg).
