Title
Mercury Sensing with Optically Responsive Gold Nanoparticles

Permalink
https://escholarship.org/uc/item/0327r0g6

Author
James, Jay Zachary

Publication Date
2012

Peer reviewed|Thesis/dissertation
Mercury Sensing with Optically Responsive Gold Nanoparticles

By

Jay Zachary James III

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering – Mechanical Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:
Professor Catherine P. Koshland, Co-chair
Professor Carlos Fernandez-Pello, Co-chair
Professor Xiang Zhang
Professor Peidong Yang

Spring 2012
Abstract

Mercury Sensing with Optically Responsive Gold Nanoparticles

by

Jay Zachary James III

Doctor of Philosophy in Engineering-Mechanical Engineering

University of California, Berkeley

Professor Catherine P. Koshland, Co-chair

Professor Carlos Fernandez Pello, Co-chair

Mercury, a potent neurotoxin, is a global environmental problem. New mercury sensing technologies are needed to meet the expanding demands on the mercury observation network. We demonstrate the utility of gold nanoparticles as a stand-alone, inexpensive, and sensitive mercury monitor. Gold nanoparticles display a peak in the visible range of their UV-vis absorbance spectra due to localized surface plasmon resonance (LSPR). The energy of this resonance is affected by adsorption of mercury. Isolated individual gold nanorods with an average length and diameter of 60 and 20 nm saturate after adsorption of 4 attograms of elemental mercury, and produce a 3 nm blue shift in their LSPR, with the shift dependent on the surface-area-to-volume ratio and aspect ratio. A modified Gans theory model predicts the shift at saturation given the particle dimensions if saturation occurs with 45% monolayer coverage.

Nanoparticle films on a transparent substrate show potential as a practical and robust method for sensing low levels of mercury vapor. The adsorption of 15 atoms of Hg causes a 1 nm shift in the LSPR wavelength of 5 nm gold spheres. The rate of shift in the peak absorbance is linear with mercury concentrations from 1 to 825 μg Hg/m$^3$. The speed of the sensor response is limited by diffusive mass transfer and can be enhanced by optimizing the sample delivery characteristics. We modeled the diffusive mass transfer and optimized the sample delivery accordingly. Regeneration of the sensing films, done by heating to 160°C, allows for repeatable measurements on the same film.
I dedicate this dissertation to my parents, Jay and Beverly James.
Abstract .......................................................... 1
Dedication .......................................................... i
Table of contents ................................................... ii
Acknowledgements .................................................. ix
1. Introduction ...................................................... 1
   1.1 Mercury in the environment ................................. 1
      1.1.1 Sources of mercury ....................................... 1
      1.1.2 Biological and geochemical mercury cycle .......... 2
      1.1.3 Health impacts .......................................... 3
      1.1.4 Mercury regulation ..................................... 4
         1.1.4.1 Atmospheric mercury pollution regulations in the United States .. 4
         1.1.4.2 International regulation .......................... 5
      1.1.5 Mercury detection ..................................... 5
   1.2 Noble metal nanoparticles and light ....................... 7
      1.2.1 Sensing applications of noble metal nanoparticles ... 7
   1.3 Dissertation hypothesis .................................... 9
   1.4 Dissertation outline ....................................... 9
2. Materials and methods .......................................... 9
   2.1 Introduction ................................................ 9
   2.2 Materials .................................................... 9
   2.3 Instrumentation ............................................ 10
      2.3.1 Ultraviolet-visible spectrometer (UV-vis) .......... 10
      2.3.2 Transmission electron microscope (TEM) .......... 10
      2.3.3 Dark-field microscope/spectrometer ................. 11
      2.3.4 Langmuir-Blodgett trough .......................... 11
      2.3.5 Mercury vapor analyzer ................................ 11
      2.3.6 Additional instrumentation ........................... 12
   2.4 Experimental methods ....................................... 12
      2.4.1 Gold nanoparticle synthesis ........................... 12
         2.4.1.1 Spherical gold nanoparticle synthesis .......... 12
         2.4.1.2 Photochemical nanorod synthesis ............... 15
         2.4.1.3 Seed mediated growth method .................... 18
      2.4.2 Nanoparticle film formation ........................... 19
         2.4.2.1 Silanization ........................................ 19
         2.4.2.2 Immobilizing gold nanoparticles ................. 20
            2.4.2.2.1 Wet deposition .............................. 20
            2.4.2.2.2 Langmuir-Blodgett method ................. 20
      2.4.3 Single particle imaging and spectroscopy .......... 22
         2.4.3.1 Dark field microscopy ............................ 22
         2.4.3.2 Dark field spectroscopy .......................... 24
         2.4.3.3 TEM imaging ...................................... 26
         2.4.3.4 Convolution of TEM and optical data for single particles .... 26
      2.4.4 UV-Vis absorbance spectroscopy of nanoparticles .. 28
   2.4.5 Mercury exposure ......................................... 28
      2.4.5.1 Static exposure ...................................... 28
      2.4.5.2 Cross-flow exposure with TEM grid ............... 29
Acknowledgements

Self-sufficiency is unlikely and limiting. Accordingly, before beginning my dissertation I would like to acknowledge several people for their gracious advice and support.

I would like to thank my advisors Dr. Donald Lucas and Professor Catherine Koshland. As mentors, they pushed me to relentlessly improve my experimental techniques and my voice as a writer and presenter of our findings. I knew immediately that it would be a pleasure to work with them, but could not have anticipated the significance of their direction in my academic development. In addition to these two primary advisors, I would be remiss not to credit Professor Carlos Fernandez-Pello for his guidance. Carlos communicates his confidence in my abilities with an authority that can convince me even in my most diffident moments. For that, among an array of good reasons, I am forever indebted to him.

I would like to thank my labmates, Jeff Crosby and Dr. Amara Holder, for providing daily conversation and important feedback on my work. A postdoctoral fellow in Professor Peidong Yang’s lab, Dr. Joel Henzie, offered invaluable advice. Learning from his expertise in the field of inorganic nanoparticles greatly enriched my experience. Prior to Joel’s mentorship, Dr. Martin Mulvihill, then a PhD student in Professor Yang’s lab, introduced me to a variety of equipment and strategies for my research.

This work would not have been possible without the financial support of the National Institutes of Health Superfund Research Program.
1. Introduction

Gold and mercury are elemental neighbors with opposite desirability. Our gold fantasies are mirrored by mercury anxieties. Alchemists tried and failed to permute mercury to gold. Later, miners successfully used mercury to bare gold. Liquid mercury preferentially wets gold surfaces and will separate the traces of gold from sediments. Now, inversely, we demonstrate the separation of mercury from gaseous mixtures using gold nanoparticles. The subsequent effect on the localized surface plasmon resonance (LSPR) forms the basis of an elegant novel mercury sensing technique.

Our interest in this particular interaction between gold and mercury is both fundamental and practical in nature. In the former sense we hope to create a detailed understanding of the mercury adsorption by nanostructured gold surfaces. Changing composition during the exposure drives a shift in the localized surface plasmon resonance. We exploit this phenomenon in our novel mercury sensor to quantify ultra-low (μg/m³) concentration of elemental mercury vapor.

1.1 Mercury in the environment

Mercury is a known neurotoxin, and human activity has augmented its prevalence in our environment. Mitigating the health and ecological risks that accompany our industrial behavior means monitoring and limiting mercury emissions. The ultimate risk of impaired health depends on the mercury contamination in our food, primarily in large fish. The path of the emissions to the dinner plate is not fully characterized, but there is strong evidence that mercury pollution is impacting human health. Protecting the future of our environment will require corrective actions informed by a detailed understanding of the mercury cycle.

1.1.1 Sources of mercury

Mercury is a naturally occurring element and is emitted to the atmosphere from geological sources. Volcanoes and mercury-enriched lands release mercury at an estimated rate of 500 Mg per year.³ The natural sources of mercury are located along the global mercuriferous belt, areas along plate tectonic boundaries that are geologically enriched with mercury. These areas include western North America, central Europe, and southern China.

Elemental mercury is the most volatile species and at 25 °C has a vapor pressure of 0.26 Pa (21 mg/m³). Geothermal activity increases the flux of mercury to the atmosphere and has been estimated to account for 60 Mg of the total emissions per year.¹ The high temperatures associated with geothermal activity affect the vapor pressure and evaporation rate of the mercury. At 60 °C the vapor pressure is 3.5 Pa (254 mg/m³). Estimates of the emissions from volcanoes vary widely (75-700 Mg per year) due in part to the lack of mercury measurements in volcanic plumes.²–⁴

Anthropogenic sources contribute an estimated 2200-4000 Mg of mercury to the atmosphere per year, the major sources of which are combustion of fossil fuels (especially coal), metal production, caustic soda production, gold mining, and waste incineration. Stationary combustion sources account for 60% of the total anthropogenic emissions.⁵,⁶

Despite declining emissions in the United States and Europe the global emissions have remained nearly constant since 1990. In these countries reductions in mercury emissions were an unintended benefit of the SO₂ and particulate regulations of the 1980s. Flue gas desulfurization and electrostatic precipitators can reduce mercury emissions.⁵
Development in other regions, especially Asia, has countered these improvements. Asia now accounts for 50% of the global emissions, and it continues to grow. Coal fire power plants in China lack the exhaust gas treatments used in Europe and the United States and tend to burn coal that is enriched with mercury. The contribution from artisanal gold mining is expected to be 450 Mg per year, although there is a large degree of uncertainty around this number given the diverse and disperse nature of the small scale mining efforts.

1.1.2 Biological and geochemical mercury cycle

Mercury pollution travels long distances in the atmosphere and subsequently follows a complex biological and geochemical cycle. The chemical forms of mercury during the cycle behave differently both in transport and biologically. Elemental mercury is the most volatile form and is the primary component of the mercury entering the ecosphere. Methyl mercury is the most important form from a public health perspective and comes from biological activities in mercury-enriched waters. The final destination of the mercury cycling through the environment is believed to be deep sea sediments. The time scales of each process are important to project the concentrations in our environment and food.

Elemental mercury is the most commonly emitted species and is also the most widely transported species. Gaseous elemental mercury has a long atmospheric lifetime (>1 year) and will travel across the globe before being deposited. The long lifetimes allow for mixing of the mercury in the atmosphere. The result is a near homogenous distribution of mercury pollution in the atmosphere away from sources. The annual mean gaseous elemental mercury concentration is 1.4 ng/m$^3$ in the northern hemisphere and 0.9 ng/m$^3$ in the southern hemisphere.

Oxidation occurring in the atmosphere slowly converts the elemental mercury into the divalent form, and some mercury is adsorbed by particles. Both of these secondary forms are significantly more water-soluble and allow the wet deposition of mercury, the dominant form of mercury deposition. Dry and wet deposition of elemental mercury is not final, because much of it will return to the atmosphere. To generate a mass balance of the oceanic mercury we can compare the rates of deposition and evasion from the ocean surface, the two largest channels of mercury to and from the ocean as shown in Fig. 1.1. Much smaller than the fluxes at the surface of the ocean is the flux of mercury to the deep ocean sediments (600 Mg per year). This flux is important because the deep ocean sediments are believed to be the sink for environmental mercury. Before mercury enters the deep ocean sediment it presents a risk to the environment and human health.
Figure 1.1 Fluxes (Mg per year) of mercury in the global biogeochemical cycle. Anthropogenic contributions are shown in red and natural contributions in black. From Selin (2009).  

Sulfur- and iron-reducing bacteria methylate the divalent mercury found in their environment. These bacteria thrive in wetlands, lake sediments, and coastal sediments. Once methylated, the mercury accumulates in biological material magnifying in concentration up the predatory food chain. This results in predatory fish with a factor $\geq 10^6$ more methylmercury than the aqueous concentration in their environment. 

The historical deposition rates for mercury are important to understanding historical backgrounds and understanding the impacts of the elevated atmospheric mercury concentrations today. For the ratio between present day deposition rates and pre-industrial rates, researchers have examined glacial cores and sediment samples from remote lakes. The two sources different estimates of the augmentation factor; lake sediment data suggests factors of 2-2.7, but the glacial core data suggests factors of 15-20. 

1.1.3 Health impacts
Mercury is prevalent throughout our environment, and human exposures to this neurotoxin occur through many channels. The primary route for people not occupationally exposed to mercury is through the consumption of fish. Large fish tend to be highly contaminated with methylmercury. Methylmercury is lipophilic, so it readily bioaccumulates in the large fish we eat; being lipophilic also increases the human toxicity.

The toxicity of methylmercury is exemplified by two high profile epidemic exposures. In the 1950s, industrial methylmercury pollution killed and maimed residents of Minamata, Japan. In the 1970s, Iraqis in the middle of a famine ate bread made with methyl mercury tainted grain seed. In both these tragic events, the children exposed in utero experienced the most serious neurological effects, including mental retardation, blindness, cerebral palsy, and deafness.

While these catastrophic incidents emphasize the dangers of mercury pollution they involved anomalously high exposures. Three major epidemiological studies of the developmental effects of non-acute mercury exposure have helped generate a better understanding of the risks from exposures typical to our current environment. The studies were located in the Faroe Islands, New Zealand, and the Seychelles. They focused on prenatal and early life exposures to mercury, to develop a reference dose protective of the most vulnerable population. Axelrad et al. (2007) combined the results of these three studies to generate a dose-response prediction for prenatal mercury exposure and IQ. They found each ppm increase in the mercury concentration of a mother’s hair correlated with a reduction in a child’s IQ of 0.13-0.25 points.

Neurodevelopmental toxicity is the most sensitive endpoint but there is emerging evidence that cardiovascular effects are significant for low levels of exposure. A review of the literature of mercury’s toxic effects on the heart found associations for a broad range of heart diseases with that of myocardial infarction being most prominent.

1.1.4 Mercury regulation
Regulating mercury protects public health and the environment. Multipronged regulatory efforts attempt to address the wide variety of mercury sources and exposure pathways. The atmospheric emissions reach around the globe, but efforts for global emissions regulations are incomplete. Regional regulations are limited and the U.S. Environmental Protection Agency only recently (December 2011) moved to control the largest emitters. Here we will focus on the regulation of atmospheric mercury pollution.

1.1.4.1 Atmospheric mercury pollution regulations in the United States
The effectiveness of mercury regulation has been plagued by a bifurcation in standards and inattention to the largest emitters. The Environmental Protection Agency (EPA) has the authority to regulate mercury under the Clean Air Act (CAA) and Resource Conservation and Recovery Act (RCRA). Under section 112 of the CAA mercury is listed as a hazardous air pollutant (HAP) and can therefore be regulated under maximum achievable control technology (MACT) standards. The CAA, amended in 1977 and 1990, exempted old plants; this preferential treatment incentivizes extending the life of out dated plants to avoid the cost of meeting the mercury emission standards placed on new constructions. This same problem exists in the history of the RCRA; old hazardous waste facilities are “grandfathered in.” Another issue with the EPA’s regulation of mercury pollution has been their hesitation to regulate the largest emitters, coal-fire utility boilers. In 1992, the EPA did not include coal-fire utility burners in the source
category list, but included industrial boilers that are responsible for 5 times less mercury pollution.

For two decades the regulation of mercury pollution originating from utility coal fire boilers and other electricity generating units (EGUs) has been a contentious issue. It started with the omission of utility boilers from the source category list in 1992. In 2000 the EPA listed power plants for regulation under the CAA air toxics provisions. Before they could promulgate a mercury regulation, the EPA reversed their decision in 2005 and removed power plants once again. In 2008 the District of Columbia Circuit Court vacated EPA’s action of removing power plants from the section 112(c) source category list. On December 16, 2011 the United States Environmental Protection Agency (EPA) issued the Mercury Air Toxics Standards (MATS). They represent the first federal standards that require power plants, or EGUs, to limit their emissions of mercury. These standards are clearly long overdue. EGUs are the dominant national source of mercury pollution, but avoided the breadth of the 1990 Clean Air Act (CAA) Amendments for 21 years.

The emission standards of the MATS are established relative to the performance of the best available technology. Emission standards for existing sources are set to be equivalent to the performance of the top 12% best-controlled sources, and the existing sources will have 4 years to meet the ruling. Similar standards were previously established under the 1990 CAA Amendments for municipal waste combustors and medical waste incinerators and the emissions have dropped more than 95%. The overall cost of implementing the CAA has been outweighed by the benefits. The MATS ruling is expected to continue this tradition of cost effective environmental regulation.

1.1.4.2 International regulation

Mercury, a neurotoxic global pollutant, demands global regulation. The long lifetime of mercury in the atmosphere (>1 year) allows long-range transport, limiting local emission controls from protecting all environments. Policy makers are working towards a worldwide effort similar to the sulfur dioxide or CFC regulations of the 20th century.

In 2009, the governing council of the United Nations Environmental Programme (UNEP) began the development of a legally binding global instrument on mercury pollution. Their goal is to complete the negotiations by 2013. They have divided the scope of their efforts into categories including: mercury control from coal combustion, reducing mercury in artisanal mining, and increased the understanding of mercury fate and transport in the environment.

Anticipating a global policy, the European Commission began a five-year project in 2010 called the Global Mercury Observation System (GMOS, www.gmos.eu) to create a coordinated global network adequate for improving models and making policy recommendations. The new system expands on the regional efforts made in North America (i.e. the Mercury Deposit Network and North American Airborne Mercury Experiment) and the independent observations made around the world. A preliminary assessment by GMOS points to gaps in emissions monitoring and in the spatial coverage of environmental observations, mostly in the southern hemisphere. Lack of an inexpensive, stand-alone, low power, low maintenance sensor is a primary technical issue confronting the GMOS.

1.1.5 Mercury detection
Atomic absorption and atomic fluorescence are the most commonly used analytical techniques to determine the mercury concentration in a sample. These orthodox techniques rely on the intensity of light absorbed or emitted from mercury atoms at 253.65 nm. Sample pretreatment upstream of the spectroscope is often needed to convert mercury into its elemental form, reduce interferences from common compounds, and preconcentrate samples having low mercury. Running the sample through strong reductants (e.g., SnCl₂, NaBH₄) and evolving the elemental mercury in an inert gas is the typical method for measuring the total mercury concentration in the sample. Preconcentration uses materials with a high affinity for mercury to separate the mercury from the sample mixture. Typically traps are made of metal surfaces (e.g., gold, copper, silver) in form of thin coatings or high surface area wools and wires. Alternatively the technique can use a liquid trap of acidic KMnO₄. The subsequent evolution of the mercury in an inert gas has the benefit of both enhancing the concentration and removing the interferents (e.g., O₂, H₂O). The gains in sensitivity are joined by sacrifices in simplicity. Atomic absorption or fluorescence equipped with these pretreatments can detect mercury down to low nanogram masses.

Atomic absorption/fluorescence spectrosopes, long established techniques, have been employed as constant emissions monitors (CEMs) and are specified in a number of approved methods (e.g., NIOSH 6009, EPA IO-5.0). Currently, hazardous waste incinerators are required to measure the mercury levels in their exhaust. Without a CEM the lag time between periodic sample collection and measurement can take several weeks. The use of CEMs gives a much better sense of the environmental impact of such sources. The better time resolution also allows the direct diagnosis of issues in the control technology, improving their overall environmental behavior.

Chemical sensor alternatives to these spectroscopic methods have also been developed and, in some cases, are commercially available. They rely on the selective adsorption of mercury and a physical response corresponding to the amount of mercury collected. Gold is the premier material in these sensors because of its stability and affinity for mercury. Different properties of gold films (e.g., mass, resistivity, reflectivity) are vulnerable to amalgamation, and have been utilized in mercury sensing techniques.

The increase in mass of a gold film can be measured conventionally with a microbalance or by interpreting the resonant frequency of a cantilevered beam. Thundat et al. (1995) demonstrated the quantitative detection of adsorbed mercury with gold-coated microcantilevers. Picogram resolution was obtained by monitoring changes in the resonant frequency of the cantilever bending.

Resistivity changes in gold films are proportional to the adsorbed mercury mass, an effect utilized by commercially available mercury vapor analyzers with ~μgHg/m₃ resolution. A design reported by McNerney et al. (1972) bifurcates the sample stream and employs two thin gold films in parallel. In the reference side of the sensor mercury is removed from the sample before it arrives at the gold film. The other film sees the full mercury concentration. The comparison of the two films’ conductivities was used to detect mercury down to 0.05 ng with a linear response range over three orders of magnitude. Heating to 150 °C for ten minutes regenerates the sensor.

Adsorbed mercury also induces changes in the optical properties of gold films, measurable with surface plasmon resonance spectroscopy or reflectivity spectroscopy. Optically thin gold coatings on the ends of multimode optical fibers increase in
reflectivity upon adsorption of mercury. The technique is sensitive down to ppb mercury concentrations. Unfortunately the adsorption of $\text{SO}_2$, $\text{CO}_2$, $\text{CO}$, $\text{O}_2$, and $\text{H}_2\text{S}$ all interfere with the sensor’s performance. An alternative optical technique using surface plasmon resonance spectroscopy found that at a fixed angle the reflectivity of a gold film is linearly related to the mercury coverage of the metal surface.$^{28}$

1.2 Noble metal nanoparticles and light

Interest in the optical properties of metal nanoparticles dates back to Roman times. Artisans have used the vibrant colors of metal colloids in decorative glass; the most famous remaining example of which is the Lycurgus Cup from the 4$^{th}$ century AD. The recent boom in interest in metal nanoparticles coincides with the scientific fervor over nanomaterials. Collective attention on size dependent properties has bred rapid advances in syntheses, understanding of physical phenomena, and inventive applications.$^{30-32}$

Localized surface plasmon resonance (LSPR) is the mechanism behind the unique optical properties of metal nanoparticles. LSPR arises when conduction band electrons interact with incident light in a coherent oscillation. Localized surface plasmon resonances cause field enhancements, creating small volumes of high intensity electric fields. Another characteristic property of the LSPR is the scattering and absorbance of light. With control over nanoparticle shape, size, and composition we can modulate the location of the LSPR peak. The position of the LSPR peak also depends on the dielectric constant of the surrounding medium. The LSPR wavelength of spheroid gold nanoparticles in water is around 520 nm with the colloidal solution resembling red wine. Changing the nanoparticle shape to more complex anisotropic geometries greatly affects the optical properties. Baculiform gold nanoparticles can display two peaks of absorbance in the visible range whose relative position is a function of the particle aspect ratio.$^{31-33}$

Applications for metal nanoparticles have arrived in unison with the advancing understanding of their unique optical properties. Some applications that utilize the LSPR phenomenon include metamaterials$^{34,35}$, surface-enhanced Raman spectroscopy (SERS)$^{36-38}$, and colorimetric sensing techniques.$^{39-41}$ Standing at the interface between fundamental investigation and the needs of society, scientists and engineers continue to develop inventive applications of fresh discoveries.

1.2.1 Sensing applications of noble metal nanoparticles

The Raman signal of molecules near a nanostructured surface can be greatly enhanced. The Raman signal is non-linearly related to field intensity, and LSPR causes intense local amplification of the electric field. In 1997 Nie and Emory reported the detection of single rhodamine 6G molecules adsorbed onto silver nanoparticles.$^{42}$ The intrinsic Raman enhancement factors were on the order of $10^{14}$ to $10^{15}$. A similar technique using a film of octahedral silver nanoparticles was shown to detect arsenate down to 1 ppb.$^{36}$ This technique also provided speciation, with distinct signals between arsenite and ansenate.

Metal nanoparticles have also been used as chemical sensors based on shifts in LSPR. The LSPR wavelength depends on the size$^{41}$, shape$^{32}$, composition$^{43}$, local dielectric constant$^{44}$, and inter-particle spacing.$^{45}$ Changes in LSPR can be monitored using UV-vis spectroscopy. Adsorption of molecules or atoms onto the nanoparticle surface can change either the composition or local dielectric constant. This phenomenon is exploited in our mercury sensing technique and in an array of other studies.
Becker et al. (2010) combined a boundary element model with single particle spectrometry to explore the refractive index sensitivity of gold nanorods. They found the optimal aspect ratios to be between 3 and 4. Sun and Xia found that gold nanoshells had a higher sensitivity factor (i.e., shift in LSPR wavelength per unit change in medium dielectric refractive index) than equivalently sized solid nanoparticles. For a spherical nanoshell 50 nm in diameter and 4.5 nm thick the sensitivity factor was 408.8 while a solid nanoparticle 50 nm in diameter has a sensitivity factor of 60.0.

Plasmon coupling between neighboring particles has a dramatic effect on absorbance spectra. The plasmons of closely spaced metal nanoparticles interact similar to coupled mechanical oscillators. At close spacings, less than 2 particle diameters, the coupling is strong and recognizable by a red-shift in the peak absorbance. Storhoff et al. have utilized the characteristic LSPR red-shift of closely spaced gold nanospheres as the basis of a method for detecting unamplified DNA sequences. Sönnichsen et al. employed pairs of gold and silver nanoparticles in a molecular ruler. The nanoparticles are an unblinking and photobleaching resistant alternative to organic fluorophores, which allowed them to continuously monitor separations of up to 70 nm for more than 3,000 seconds. Woo et al. applied a finite-difference time-domain simulation of axially aligned gold nanorod dimers. They scrutinized the effects of gap distance, longitudinal plasmon energy, and nanorod end shape on the dimer coupling energy. They also describe the dependence of Fano interferences in hetero-dimers on the gap distance and plasmon energy of the nanorod monomers.

The complex dielectric function of the nanoparticle material depends on the composition. Changing the composition can therefore change the plasmon energies. Our work follows that of others who have advanced the understanding of bimetallic nanoparticles. Nanoalloys of gold and silver show a linear relationship between LSPR wavelength and alloying mass fraction. Bimetallic gold and mercury nanoparticles and the composition dependence of the LSPR are the topic of several previous published works. Henglein and Giersig (2000) performed a radiolytic reduction of Hg(II) in an aqueous solution containing colloidal gold nanoparticles. The LSPR wavelength of the amalgam particles was blue shifted from that of the pure gold particles. Previous work was not limited to spherical particles and supplies a variety of amalgamation techniques. Bubbling gaseous mixtures containing mercury vapor produces amalgam particles. Alternatively the amalgam particles can be produced by reducing divalent mercury in the presence of gold nanoparticles. Mertens et al. added beads of elemental mercury to aqueous 11 nm gold nanoparticles and stirred the solution to promote the amalgamation of the nanoparticles.

A gold nanoparticle’s size and shape affect their response to mercury. Morris et al. passed saturated mercury vapor in nitrogen (18 mg/m³) through 10 ml colloidal solutions of gold and silver nanoparticles at 3.6 LPM. Aliquots of the solution were removed at various times and their absorbance spectra were recorded. Both gold and silver nanoparticles experienced blue-shifts LSPR wavelengths during the exposure that eventually stopped shifting, suggesting saturation with mercury vapor. The found the shifts experienced by 5 nm gold particles to be greater than those for 15 nm gold particles, but did not report exact values of the shift magnitudes.

Later, Morris et al. reported a similar study using gold nanoparticle films. Gold nanoparticles (3, 5, 12, and 22 nm) were wet deposited onto silanized glass substrates.
The films were subsequently placed into a jar containing a bead of mercury at room temperature (20 ± 2 °C). At that temperature the vapor pressure of mercury supplies a concentration of 15 mg/m³. After 90 minutes in the sealed jar the 5 nm particles were 8% Hg and the 22 nm particles were 3% Hg as measured by EDS. This greater mass fraction of mercury for smaller particles helps explain the higher sensitivity suggested in the previous study.

1.3 Dissertation hypothesis

Gold nanoparticles are efficient collectors of mercury vapor. The LSPR wavelength of gold nanoparticles, being dependent on composition, will respond to the amalgamation process. The rate of LSPR shift can act as the basis for a highly sensitive, low cost, low power, and low maintenance mercury vapor monitor. Optimizing the sensor’s performance involves multiple channels: enhanced mass transfer, decreased mass limit of detection, and resistance to interferences.

1.4 Dissertation outline

The outline of this dissertation is as follows. First, the materials and experimental methods used in the subsequent two sections are described in detail (section 2). The intent of these descriptions is to provide protocols that allow reproduction of these experiments and to clarify the subsequent sections. Section 3 describes the interaction of individual gold nanorods with mercury vapor. A variety of particle shapes and sizes are probed (using TEM and dark field spectroscopy/microscopy) before and after exposure to μg/m³ concentrations of elemental mercury. Comparison of the shifts of the longitudinal LSPR at saturation gives insight into the mercury adsorption. Section 4 describes a more practical mercury sensor. Using the optimum particles suggested by the results in section 3, we were able to produce a sensor capable of reliably measuring mercury vapor concentrations lower than 1 μg/m³. The sensor is based on a film of 5 nm gold nanospheres on a transparent substrate. The regeneration and possible interferences of the sensor are also discussed. Section 5 introduces mass transfer concepts to the discussion of chemical sensing with the nanoparticle film sensor as the experimental basis for a model. The intent is to provide a model that directs the optimization of chemical sensing by enhancing mass transfer.

2. Materials and methods

2.1 Introduction

This section describes the materials, instrumentation, and methods that were used to complete all work included herein. The goal of this section is to provide a clear protocol for the reproduction and expansion of our work. The materials listed in section 2.2 are described in detail (chemical formula, grade, purity, and source). Section 2.3 logs the instrumentation in similar detail. In the final section, 2.4, we expound the protocols used in our experimental preparations and observations.

2.2 Materials

The following chemicals were procured and used as received: sodium citrate dehydrate (Na₃C₆H₅O₇•2H₂O, lab grade, Fisher Scientific), hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄•3H₂O, lab grade, ≥99.9% Across Organics), sodium borohydride (NaBH₄, reagent grade, 98.5%, Sigma-Aldrich), 4-dimethylaminopyridine (DMAP) (C₇H₁₀N₂, >98%, Fluka), tetraoctylammonium bromide ([CH₃(CH₂)₇]₄N(Br), >98%, Fluka), toluene (C₆H₅CH₃, ≥99%, Sigma-Aldrich), sodium sulfate (Na₂SO₄, anhydrous, ≥99%, Fluka), hydrogen peroxide (H₂O₂, 31%, Baker), concentrated sulfuric acid
(H₂SO₄, 95-98%), ammonia hydroxide (NH₄OH, 28% NH₃ in water, 99.99+%, Sigma-Aldrich), anhydrous ethanol (C₂H₅OH, 99.5% denatured, Sigma-Aldrich), anhydrous methanol (CH₃OH, 99.8%, Aldrich), isopropanol (IPA) (C₃H₇OH, Sigma-Aldrich), 3-aminopropyltriethoxysilane (APTES) (C₉H₂₃NO₃Si, 99%, Fluka), 3-mercaptopropyltriethoxysilane (MPTES) (C₉H₂₂O₃SSi, technical grade, ≥80%, Alfa Aesar), 3-aminopropyltrimethoxysilane (APTMS) (C₆H₁₆O₂SSi, 97%, Fluka), mercuric chloride, CTAB (98%, Alfa Aesar), silver nitrate (AgNO₃, 99.9995%, Premion), sodium hydroxide (NaOH, 98%, Baker), and dodecyltrimethylammonium bromide (DTAB) (99%, Fluka).

The following compressed gases were also procured and used as received: argon (Ar, pre-purified grade, AirGas), nitrogen (N₂, ultra high purity, AirGas), and air (zero grade, Airgas).

The following materials were procured and used as received: silicone nitride transmission electron microscopy grids (1mm x 1mm x 50 nm thick window, Ted Pella), quartz wafers (diced 1x1cm, University Wafer), hydrophobic nanorods (NSol, NanoPartz), and 5 nm gold nanoparticles (Ted Pella).

In all subsequent sections, the chemicals and gases are identified by either their acronym and/or molecular formula.

2.3 Instrumentation

2.3.1 Ultraviolet-visible spectrometer (UV-vis)

The spectrometer used was an HR4000 from Ocean Optics. The detector is a linear CCD array (TCD1304AP, Toshiba). The detector has 3648 pixels, each 8 x 200 µm and having a well depth of 1x10⁵ electrons. The detector is sensitive to light in the range of 200-1100 nm, but the grating (HC-1) provides a 200-1050 nm range and 0.239 nm optical resolution (FWHM). This spectrometer directs the light through a symmetrical crossed Czerny-Turner design. The light enters through a SMA 905 connector, passes through the entrance slit (25 µm), is reflected by a collimating mirror, is diffracted and reflected by the grating, and focused by a final mirror onto the detector. All the internal geometries are fixed. The SMA 905 connector is designed for optical fibers and is aligned with the entrance slit to ensure concentricity. The signal to noise ratio is 300:1 at full signal with a dark noise count of 12 RMS counts. Mirrors are designed for maximum reflectivity (>95%) and minimal stray light (<0.05% at 600 nm).

The HR4000 is controlled by Ocean Optics’ software package (SpectraSuite) installed on a desktop computer. The spectrometer and computer communicate through USB. SpectraSuite acts as a graphical display of data, controller of spectrometer settings, and performs data analysis. SpectraSuite is a modular software platform that is Java-based, so it can run on all operating systems. For data capture, SpectraSuite offers control of the episodic nature of the storage, whether it is every scan, once per fixed number of scans, or the first available scan after a set time period.

2.3.2 Transmission electron microscope (TEM)

The TEM used in these experiments was a H-7650 from Hitachi. It was operated at 120 keV. The stage has three axes of translation control and two axes of tilt control. Images are captured with an AMT digital camera. At 60kx there is 0.26 nm/pixel in the digital image. The TEM is also equipped with a energy-dispersive x-ray spectroscopy (EDX) from EDAX. The detector in the EDAX is cryogenically cooled by a 10 L liquid
nitrogen Dewar. The EDAX Gensis software was used to label and quantify the components in the sample.

2.3.3 Dark-field microscope/spectrometer

The microscope used for the dark field optical work is an Olympus IX71. It is an inverted microscope with a two-tiered V-shape design. The external power supply increases the frame stability by minimizing thermal expansion. The microscope has coaxial coarse and fine focusing knobs (minimum fine focus gradation of 1 µm). There are two image ports one for the color digital camera and another that connects to the spectrometer. The path of the light and its intensity are selected on the front panel. The condenser lens used is specific to the dry type dark field applications (U-DCD, Olympus). It has an adjustable numerical aperture (0.92-0.8) and a working distance of 4.52 mm. The focal length is 11.8 mm.

The spectrograph connected to the left side-port of the microscope is adjustable to both image and collect spectra using the same CCD (Acton 2300i, Princeton Instruments). The key is the adjustable grating with a mechanical range between 0-1400 nm. The gratings sit on a turret and can be selected for the desired effect. The focal length is 300 mm and the aperture ratio is 1/3.9. The wavelength accuracy is ± 0.2 nm with a repeatability of ± 0.05 nm.

Our spectrograph is equipped with a cryogenically cooled 1340x100 CCD array (SPEC-10, Princeton Instruments). Filling the reservoir with liquid nitrogen brings the detector temperature down to -120 ºC and the read noise down to 3 e rms. The dynamic range is greater than 16-bit with operation at either 100 kHz or 1 MHz. The data acquisition is run through the proprietary WinView/WinSpec software suite (Princeton Instruments). The software allows users to specify the read rate, binning parameters, and regions of interest. The region of interest selects an active section of the CCD for data collection.

2.3.4 Langmuir-Blodgett trough

A Nima 611 Langmuir-Blodgett trough was used for nanoparticle film fabrication. The design consists of a rectangular teflon trough with a well at the end. The trough is equipped with a pressure sensor. The sensor uses a Wilhelmy plate (a small length of chromatography paper) to measure the surface pressure. We leveled the trough by adjusting the four threaded legs supporting the trough. The motorized barrier and dipper are controlled through Nima’s software. Feedback from the pressure sensor controls the position of the barrier while the dipper draws the substrate through the film. The steady pressure guarantees a uniform film. The software also collects the surface pressure data. To clean the trough we used a Buchner funnel connected to a vacuum source. The funnel removes contaminants from the surface or drain the trough after use. We used Kimwipes soaked in chloroform or water to remove residues from the drained trough.

2.3.5 Mercury vapor analyzer

A commercial gold film conductometric elemental mercury vapor monitor (Jerome 431-X) was used to verify mercury vapor concentrations during certain calibrations. The monitor is based on the resistance changes in a gold film upon the adsorption of mercury vapor. Two thin gold films, a reference and a sensor, are configured in a Wheatstone bridge circuit. The Wheatstone bridge is designed to detect miniscule changes in electrical resistance. During operation, the sensor film is exposed to mercury while the reference film is sealed. The monitor’s microprocessor computes the concentration based
on the changes in resistance of the sensor film. The published range of the sensor is 0.003 mg/m$^3$ to 0.999 mg/m$^3$. In our experience the monitor was unreliable below .02 mg/m$^3$. The precision is 5% relative standard deviation (at 0.100 mg/m$^3$). The response time is 12 seconds with a flow rate of 0.75 LPM. Either 110 VAC or the internal nickel cadmium battery can power the monitor.

There are a number of potential interferences. The manufacturer claims that hydrocarbons, carbon monoxide, carbon dioxide, sulfur dioxide, and water vapor do not cause any interference. Investigations of the sensitivity of the resistance of gold films to water vapor have shown an interference$^{55}$, and there is no explicit discussion in the Jerome’s specifications as to how the film is protected from these effects. The specifications do mention that water condensation on the film can cause irreparable harm. Chlorine, nitrogen dioxide, hydrogen sulfide, and mercaptans are potential interferences, and the monitor attempts to remediate these effects through the use of an acidic gas filter.

2.3.6 Additional instrumentation

We used a peristaltic pump (Master Flex C/L, Cole Parmer), a USB thermocouple (National Instruments), and a humidity monitor (Thermohygrometer, Cole Parmer).

2.4 Experimental methods

2.4.1 Gold nanoparticle synthesis

Nano-dimensional features can be produced in a variety of ways. Our work has focused on non-lithographic techniques, specifically the wet chemical synthesis of gold nanoparticles. By growing the particles from dissolved gold salts we have the ability to make different shapes and sizes of nanoparticle with good monodispersity.

2.4.1.1 Spherical gold nanoparticle synthesis

DMAP (C$_7$H$_{10}$N$_2$) stabilized gold nanoparticles (AuNPs) were synthesized using the method of Gandubert and Lennox (2005)$^{56}$ We found the method to repeatably produce spheres 6 nm in diameter.

To begin, we synthesized a gold colloid in toluene following the Brust two-phase method.$^{30}$ An aqueous solution of hydrogen tetrachloroaurate (HAuCl$_4$•3H$_2$O, 500 mg in 50 mL) was mixed with tetraoctylammonium bromide in toluene (3.06 g in 100 mL). Vigorous stirring results in the complete transfer of the tetrachloroaurate to the organic phase, which assumes a deep orange color. We slowly added a fresh solution of sodium borohydride in water (525 mg in 30 mL). The organic phase responded by changing color to a dark ruby red. After 12 hours of stirring the organic phase was separated and washed with Millipore water. After washing, the toluene suspended nanoparticles were dried over anhydrous sodium sulfate and diluted to 250 mL. These particles will remain stable in the toluene solution but we continued with our protocol to conjugate with DMAP.

The transfer of the particles to water and conjugation with DMAP follows the method proposed by Gittins and Caruso.$^{57}$ We prepared a solution of DMAP in water (3.05 g in 250 ml) and added it to nanoparticles suspended in toluene. The gold particles transferred into the aqueous phase. We separated the red aqueous phase (Fig. 2.1) from the toluene. These DMAP stabilized particles were stable for months.
We characterized the gold nanoparticles with UV-Vis spectroscopy and TEM imaging. The absorbance displayed a peak in the visible range reaching its maximum at a wavelength of 525 nm (Fig. 2.2). We deposited a 20 μL droplet of the colloidal solution onto a carbon coated copper TEM grid and allowed the water to evaporate. Using ImageJ photo-analysis software we collected measurements of the particles images by the TEM. An example of one such TEM image appears in Fig. 2.3. The average diameter of the particles was 6 nm and the shape is consistently spherical.
Figure 2.2 UV Vis absorption spectrum of DMAP gold nanoparticles in water
2.4.1.2 Photochemical nanorod synthesis

We synthesized gold nanorods (AuNRs) using the photochemical method. Following Kim et al., we started with a 3 mL solution of hexadecyltrimethylammonium bromide (CTAB) in water (0.08 M) and 1.26 mg of tetradodecylammonium bromide. CTAB will stabilize the nanoparticles and aids their anisotropic growth. Different amounts of 0.01 M silver nitrate aqueous solutions were added depending on the desired aspect ratio. We added acetone and cyclohexane, 0.065 and 0.045 mL respectively, to the solution, which we then sonicated for 10 minutes. After sonication we added 0.25 mL of 0.024 M hydrogen tetrachloroaurate. The solution was then transferred to a quartz cuvette and irradiated by a mercury lamp (254 nm wavelength UV light) for 30 hours. During the irradiation the solution is stirred with a small magnetic stirrer to ensure good mixing and uniform irradiation. After the first hours the color will change to a blue-green. The final color depends on the volume of silver nitrate added, and a photo of an example colloid is
shown in Fig. 2.4. Increasing the illumination time, to beyond 30 hours, will result in spheroidization of the particles.

![Photo of nanorod solution showing the blue color of the final colloid.](image)

**Figure 2.4** Photo of nanorod solution showing the blue color of the final colloid.

To purify the AuNR solution and remove excess CTAB the particles went through a series of washing steps. The solution was centrifuged at 3000 rpm for 10 minutes and the supernatant was removed. The supernatant was centrifuged again at 10000 rpm for 10 minutes. The supernatant resulting from this centrifugation was removed and the particles were suspended in Millipore water.

We performed UV-Vis absorbance spectroscopy and TEM imaging to characterize the resulting AuNRs. The absorbance spectra exhibited the double peaks characteristic of gold nanorods with a transverse peak at 527 nm and a longitudinal peak >600 nm increasing in wavelength for greater aspect ratios. The sensitivity of the longitudinal peak to aspect ratio made the generation of two nanorod solutions with identical longitudinal resonances difficult. The spectrum shown in Fig. 5 has a longitudinal resonance of 635 nm.
Figure 2.5 UV-Vis absorbance of a photochemically generated nanorod solution

We prepared TEM grids by evaporating a 10 µL volume of dilute nanorod solution. Images of the particles revealed their shape to be somewhat unusual. Generally nanorods have a pyramidal tip, but our synthesis produces square ended nanorods. The nanorods synthesized with 31.5 µL of silver nitrate had an average aspect ratio of 2.2 and are shown in Fig. 2.6.
2.4.1.3 Seed mediated growth method

We followed the seed mediated growth method of Jana et al. to synthesize AuNRs. The first step is the preparation of the seed particles; we started with 20 mL of hydrogen tetrachloroaurate and tri-sodium citrate in water (both - 2.5×10^{-4} M). While stirring, we added 0.6 mL of a 0.1 M solution of 0°C sodium borohydride to the solution. The sodium borohydride reduces the dissolved gold and the seed particles are formed causing an abrupt change in color of the solution from yellow to pink. These citrate capped particles act as the seeds for the growth of the nanorods.

A 10 mL growth solution of hydrogen tetrachloroaurate (2.5×10^{-4} M) and cetyltrimethylammonium bromide (CTAB, 0.1 M) was prepared in Millipore water. We added 0.05 mL of 0.1 M ascorbic acid and 0.025 mL of the seed solution. With no stirring the solution changed color to a reddish brown over 15 minutes. This AuNR solution was stable at room temperature for 6 months. The two LSPR peaks are clearly shown in the absorbance spectrum (Fig. 2.7).
Figure 2.7 UV-vis absorbance spectrum of seed mediated synthesis of gold nanorods.

2.4.2 Nanoparticle film formation
2.4.2.1 Silanization

We silanized quartz substrates to provide an attractive surface for the wet deposition of gold nanoparticles. Silane molecules bound to functional groups are used to attract target molecules or, in our case, target nanoparticles. It was originally developed in conjunction with fiberglass composites, and has since found favor in micro- and nanolithography. We employed vapor and liquid phase silanizations, both with the intent to generate monolayer films.

Successful salinization begins with a clean substrate. First we wiped residue from the substrate surface with an ethanol soaked Kimwipe. Then the quartz surfaces were submerged in piranha solution (1:3 hydrogen peroxide in concentrated sulfuric acid) for 15 minutes (Caution! Piranha is a strong oxidizer and should not be stored in closed containers). We remove the substrates and rinsed them in water (Millipore, 18.2 MΩ) then ethanol. The substrates were dried in a jet of nitrogen. Finally the substrates were cleaned with a plasma cleaner (Harrick) on high RF-level using oxygen at 0.30 Torr for 5 minutes.

The vapor method relies on a vacuum chamber and a volatile precursor. The gas phase precursor molecules react with the surface in dry conditions. The process requires fewer steps and produces less solvent waste than aqueous methods. Another advantage is that vapor phase modification is generally agreed to give monolayer coverage.

After cleaning the vapor phase silanization protocol followed these steps.

1. 1 mL of silane solution in an open vial was placed inside the vacuum chamber.
2. Prepared substrates were placed onto a clean glass slide and set inside the vacuum chamber. We closed the vacuum chamber and connected it to the vacuum line.
3. After 2 hours the vacuum line was closed and the chamber was returned to ambient pressure. We turned the substrates over to silanize the opposite side. The chamber was once again opened to the vacuum line for another 2 hours.
4. We cured the substrates in a furnace for 3 hours at 110 °C. They were removed from the furnace, rinsed in water, and dried under a stream of nitrogen.
5. They substrates were stored in air at room temperature.

Solution based silanizations followed the method of Frederix et al. First we cleaned the quartz substrates by: rubbing them with ethanol soaked wipes, immersing them in 2 M sodium hydroxide (NaOH) for 1 hour, and a 7 minute treatment of 1:1:5 hydrogen peroxyde (30% v/v), NH4OH (25% v/v), and ultra pure water at 90 °C. This treatment should provide a fresh oxide layer on the quartz substrates. We then immersed the substrates in a silane solution (MPTES or APTES, 2% v/v) in a 95:5 water and methanol mixture. The substrates are left in the silane solution overnight (>12 hours) then removed and dried in air. The film is annealed at 115 °C in the furnace for 15 minutes.

2.4.2.2 Immobilizing gold nanoparticles
2.4.2.2.1 Wet deposition

Introducing an attractive surface to a colloidal solution of gold nanoparticles causes the gradual formation of a film. First, the quartz substrates were functionalized to target nanoparticles using the salinization processes described above. Then they were incubated in colloidal solutions overnight (14 hours). The nanoparticle concentration, pH and ionic strength of the solution, type of silane, and silane coverage influence the success of the deposition.

For our single nanoparticle spectroscopy experiments we needed a film of widely separated individual nanoparticles. If the spacing became less than 5 μm the particle spectra could not be completely isolated in our dark field spectrometer. The experiments also called for a substrate that was electron transparent, so we used TEM grids with 1 mm square, 50 nm thick window (Ted Pella). Incubating the grids in a diluted solution of AuNR (Nanosol, NanoPartz) in ethanol (1:100) for 15 seconds resulted in adequately disperse films.

2.4.2.2.2 Langmuir-Blodgett method

Our ability to control the assembly of nanoparticle films is essential to both the execution of our experiments and to the final design of a localized surface plasmon resonance based mercury sensor. The wet deposition methods above can produce nanoparticle films but we were unable to generate predictable particle densities. Our most successful film generation used the Langmuir Blodgett method.

The Langmuir Blodgett method was originally proposed to make molecular films, but has since become popular for nanoparticle assembly. The method takes advantage of a hydrophobic layer of particles on the surface of a trough of water. At least one moveable barrier stands as the boundary of the nanoparticle film. The barrier compresses or expands the floating nanoparticle film’s density. Much like the type in a printing press, the order of the particles is formed completely before being transferred to the solid substrate.
The first step in our Langmuir Blodgett protocol was the preparation of the substrates and nanoparticles. Quartz, diced in 9 mm squares, acts as the transparent substrate for the nanoparticle film. Before use, the quartz surfaces were cleaned in piranha solution for 15 minutes, **(Caution! Piranha is a strong oxidizer and should not be stored in closed containers)** rinsed in water (18.2 MΩ, Millipore) and ethanol, and dried in nitrogen. Non-polar soluble 5 nm gold nanoparticles (Ted Pella) were suspended in chloroform and deposited, drop-wise, onto the water surface held by a Teflon Langmuir-Blodgett trough (Nima). After 30 minutes, the film was compressed, using the motorized Teflon barrier. The particle monolayer forms while floating on the aqueous subphase, controlled by the uniaxial compression of the trough surface area. The substrate “dipper” then drew the submerged quartz chips and TEM grids (silicon nitride, Ted Pella) through the floating nanoparticle layer, fixing the particles to the substrate surfaces while the barrier holds the film at a uniform compression.

![Diagram](image)

**Figure 2.8** Langmuir-Blodgett trough diagram.
2.4.3 Single particle imaging and spectroscopy

2.4.3.1 Dark field microscopy

Dark field microscopy is a method of microscopy that excludes the unscattered beam from the image. The image is characteristically dark in background with bright areas describing the scattering bodies in the sample. Dark field microscopy relies on different mode of sample illumination. A hollow, rather than complete, cone of light is focused on the sample, and passes outside the bounds of the objective lens. Focusing the objective lens on the sample plane gives an image where the features of the sample appear as bright in contrast to the dark background. The diagram in Fig. 2.10 shows how a patch stop between the lamp and condenser lens removes the interior of the cone for dark field illumination.
Dark field illumination is a powerful tool for nanoparticle science. In bright field microscopy the contrast from individual nanoparticles tends to be too weak to be imaged, but the highly effective scattering behavior of individual noble metal nanoparticles makes them visible in the dark field mode. Dark field microscopy is not the only option. Recently, photothermal spectroscopy,\textsuperscript{9} total internal reflection microscopy,\textsuperscript{10} and near-field scanning optical microscopy\textsuperscript{11} have also demonstrated the direct observation of individual nanoparticle optical properties. The laser illumination used in photothermal spectroscopy causes thermal reshaping of the nanorods. The broadband light used in our dark field microscopy caused no reshaping, and non-destructive imaging/spectroscopy was required for our study. Using white light for illumination, a color micrograph depicts the variation in scattered color (Fig. 2.11).
2.4.3.2 Dark field spectroscopy

Dark field spectroscopy was performed on the same microscope and with the same CCD as the imaging described above. To take a spectrum, we rotated the grating and inserted a slit aperture. The image on the CCD becomes a geometric representation of the intensity of the different wavelengths of light. From left to right the wavelengths increase and are calibrated for a given grating angle.

To collect the scattered light spectrum of a single particle, we have to separate that signal from all the other light scattered from the sample. By positioning a bright spot at the center of the slit aperture and constricting the slit width to that of the spot we can isolate the probed area horizontally. In the vertical dimension, the CCD collects rows of spectra with respect to their vertical position in the image. If a bright spot appeared at height Y in the image, its spectrum will appear at height Y when the grating is rotated. Therefore to isolate the particle spectrum in the vertical direction, we had to select the vertical pixel range occupied by the particle in the slit.

We needed a white scattering signal to collect the lamp spectrum. The white sample consisted of a film of evaporated milk on a silicon nitride TEM grid. The microspheres left by the milk scatter the lamplight efficiently. The same white film was used as a standard for all the dark field spectroscopic measurements. The white signal is shown in Fig. 2.12.
Figure 2.12 Scattered light spectrum from the microsphere (milk) film.

We process the scattered spectra using a spectrum of the background and lamp. We subtract the background light (light not scattered by the particle). The background is taken in unison with the particle spectrum by selecting an area not containing a particle for collection. After removing the background intensity, all that remains is the scattered intensity from the particle. We divide this spectrum by the lamp spectrum. This ratio normalizes the scattered spectrum for the wavelength dependent intensity of the illumination. The final result is shown in Fig. 2.13 for the normalized scattered intensity of a single gold nanorod.
2.4.3.3 TEM imaging

We used transmission electron microscopy to image nanoparticles. Because we are working with particles as small as 5 nm in diameter the TEM is the best tool for resolving shape and size. For the purpose of recording nanoparticle shape, size, and inter-particle spacing we collected images with the TEM’s digital camera. Standard imaging mode was sufficient for this study.

2.4.3.4 Convolution of TEM and optical data for single particles

Combining the TEM images and optical characterization of individual nanoparticles required synchronization across two greatly different fields of view. In the optical microscope the magnification used is 60x when the lowest magnification capable of resolving individual particles in the TEM is 500 times more. There is added confusion from the rotation of the TEM grid with respect to the angle imaged in the optical microscope.

The position of each AuNR on the grid window acts as a map to relate data collected in the two instruments. Each instrument can generate such a map; the TEM provides the stage position of each image and the AuNR appear as bright spots in the dark field image. With the TEM we scan the grid window, in a 50 µm by 50 µm raster pattern, for isolated single AuNRs. A particle is considered isolated if its nearest neighbor is more than 5 µm away. We capture 30kx-images of all AuNR discovered during the raster scan, both isolated and bunched. Each TEM image taken includes the

Figure 2.13 Single particle scattered spectrum.
corresponding stage location. In Fig. 2.14, the recorded positions are plotted with respect to the adjacent grid-window corner and overlaid onto the dark field image, with the TEM stage positions shown as rings and the scattered light from the AuNR as the bright spots in the background dark field image.

Figure 2.14 Map overlaying the TEM image locations and the dark field image of disperse gold nanorods.

The TEM stage positions all coincide with bright spots in the dark field image, confirming that the same particle is observed by each method. For further verification, the measured aspect ratio from the TEM images was compared to the longitudinal LSPR wavelength in Fig. 2.15; the LSPR wavelength increases with aspect ratio as expected.32,33
2.4.4 UV-Vis absorbance spectroscopy of nanoparticles

We performed ultra-violet-visible absorbance spectroscopy of nanoparticles in solution and assembled in films. All arrangements used a deuterium/halogen light source connected by optical fiber to a collimating lens that illuminated the sample. The light passed through the sample where the excitation of the particles’ surface plasmons absorbed and scattered light. The transmitted beam was then collected by another collimating lens. The lens was coupled to an optical fiber that fed into the spectrometer (HR4000, Ocean Optics). The light source requires at least 15 minutes after being turned on to reach steady state.

We collected the spectrometer data using a desktop computer. The software package included with the spectrometer (SpectraSuite, Ocean Optics) offers control of the spectrometer settings and some analysis of the data collected. To take an absorbance measurement we first needed to set the integration time and desired number of spectra to average. Then we collected a bright spectrum with no sample in the path of the beam and a dark spectrum with the shutter closed. After returning the sample and opening the shutter we could begin collecting absorbance spectra.

2.4.5 Mercury exposure

2.4.5.1 Static exposure

The only static exposure method employed in our experiments used a tinted glass jar (1 liter) as the sample chamber. The jars were equipped with a septum lid. This allowed us to inject saturated mercury vapor using a gas-tight syringe. The saturated
mercury vapor was drawn from the vapor space of a sealed vial (75 ml) through a septum. The concentration in the vial’s vapor space was assumed to be equivalent to the partial pressure for mercury at the measured temperature.

After sealing the jar with a nanoparticle film chip inside and injecting the saturated vapor we left the chamber sealed for 24 hours. The chip was then removed and reanalyzed for changes in absorption.

This technique is an insufficient method characterize the mercury vapor interaction with gold nanoparticle films for a number of reasons:

• mixing of the saturated vapor in the jar is inconsistent
• sample is diluted by the air contained in the jar
• requires long collection times

2.4.5.2 Cross-flow exposure with TEM grid

We exposed disperse films of gold nanorods to a steady flowing stream with a constant concentration mercury. The requirements of the apparatus were:

• constant mercury concentration
• steady flow
• repeatability
• verifiable Hg concentration

First we prepared a mercury dilution in a Teflon sample bag (SKC). The bags have a three-liter capacity and were inflated using tank air (Zero Air, Airgas). Before each preparation the bag was inflated and deflated 5 times to purge any contamination. The mercury concentration was monitored during each purge using a Jerome mercury analyzer. After the purge, the bag was inflated to capacity and sealed. A septum capped vial containing a bead of mercury acted as a reservoir of saturated mercury vapor. We used a gas-tight syringe to remove milliliter volumes of the saturated mercury vapor from the vial and added them to the sample bag, which was equipped with a septum for injection. We allowed an hour for the mercury vapor to mix with the air in the bag. To check the concentration in the bag we used the Jerome mercury analyzer. The Jerome is equipped with a pump capable of drawing the air from and connects easily and securely to the outlet of the bag with a short piece of ¼” Teflon tubing. A routine of 3 sequential measurements was followed. If the concentrations measured were not consistent within the error of the Jerome (9%) more time was allowed for mixing. After recording the concentration of the mercury dilution the sample bag was ready for use.

Drawing sample air from the bag requires the use of a pump because the bag holds samples at ambient pressures only. Our apparatus employed a peristaltic pump (pump model, manufacturer) to draw a steady stream of air through our flow cell. Peristaltic pumps are positive displacement pumps. The pump moves fluid through a flexible tube through the pinching/rolling motion of rollers attached to the pump’s rotor. A Gilibrator connected to the outlet of the pump measured the volumetric flow rate through the pump. Before connecting the sample bag the pump was primed and allowed to reach a steady flow rate.

The exposure was ready to start once the sample bag dilution and pump are ready. The TEM grid was placed into the flow cell (¼” Teflon tubing) arranged with its face parallel to the tube axis. The flow cell connects the sample bag to the Masterflex tubing used in the peristaltic pump. A diagram of the flow cell is shown in Fig. 2.16.
The exposures were conducted for varying concentrations of mercury at a constant flow rate of 13 cc/min. After an hour of exposure the bag was disconnected from the Teflon tubing. The concentration in the bag was checked against the pre-exposure concentration using the Jerome. We carefully removed the TEM grid from the flow cell and placed it in a TEM grid holder. Different holders were used before and after exposure to ensure no contamination of unexposed grids.

The final step is a purge of the system. The pump is left on drawing room air through the flow cell for an hour. Room air is thought to be acceptable as a purging fluid because the concentration of mercury in the room is at least an order of magnitude below the range of concentrations tested in this apparatus.

2.4.5.3 Cross-flow exposure of quartz chips

Initial exposures of gold nanoparticle films on quartz chips were carried out using a quartz flow cell (Cell style 49, Starna Cells). The cell consists of a demountable window equipped with inlet and outlet ports to allow fluid flow. The butted quartz seal is not sufficient for high pressures so the flow rate were limited accordingly. A diagram of the flow cell arrangement is shown in Fig. 2.17. An adjustable collimating lens holder (Ocean Optics) served dual purposes as flow cell holder and for optical alignment. After inserting the quartz chip and aligning the chip with the collimating lenses the adjustable holder was clamped down onto the cell, holding it in place. The quartz cell has excellent transmittance and allowed in situ tracking of the quartz chip’s absorbance spectrum.
Figure 2.17 Quartz flow cell diagram.

This exposure technique was similar to that above for the TEM grid in cross flow. The differences are the use of a quartz flow cell in place of the Teflon tube flow cell and a slightly larger volumetric flow rate (15 cc/min). The diluted samples were prepared and pumped the same as before.

For higher flow rates and repeated exposures of the same chip we abandoned the quartz flow cell for a more robust flow cell made from a length of Pyrex tube. A diagram of the flow cell is shown in Fig. 2.18. The AuNP coated quartz chip was affixed with a silicone adhesive to a 1.25 cm inner-diameter Pyrex tube such that the film faced normal to the axis of the tube. The collimating lenses and tube were held in a fixed position with the beam perpendicular to sensor chip, ensuring observation of a consistent area of the chip during the absorbance measurements.
The heating tape was used during regeneration and was off during exposures. Following regeneration the chip and flow cell need time to cool down to a steady temperature. This cool-down was monitored using a k-type thermocouple in contact with the chip. During cool-down we would flow clean air over the chip to accelerate the cooling with forced convection. The cool-down takes over 1 hour in 5 LPM of flowing air.

A permeation tube (VICI Metronics) in a steady flow of air supplied a constant mercury concentration for the higher flow rates. The permeation tube consists of a bead of mercury inside a length of polymer tubing. Diffusion through the tube wall limits the mass transfer to a constant rate for a given temperature. The interior of the tube remains at the equilibrium concentration set by the vapor pressure of the mercury bead. The temperature of the carrier gas and the permeation tube sets the mass flow rate of mercury ($m$):

$$\log(m_1) = \log(m_0) + 0.03(T_1 - T_2)$$ \hspace{1cm} (2.1)

where $T$ is temperature ($K$). Each degree increase in temperature causes a 7% increase in the mass flow rate. The emission of mercury from the permeation tube does not change immediately with shifts in temperature. To ensure a steady concentration in the flow we allowed $>1$ hour for equilibration. During equilibration the flow rate, temperature, and pressure of the air were constant.

During all exposures using the Pyrex flow cell, the temperature of the air was monitored with a k-type thermocouple. At 295 K, the typical temperature, the permeation tube emits mercury at 60 ng/s. In a stream of 57 LPM of air at 295 K the permeation tube system provides $1.05 \mu g_{Hg}/m_{air}^3$. 

Figure 2.18 Depiction of the Pyrex flow cell used for high-flow exposures and regeneration.
The calibration gas manifold allows the equilibration of the permeation tube where the gas is vented and the ability to switch between clean and mercury containing air. It is shown in Fig. 2.19.

![Diagram of manifold used to generate mercury sample gas using a permeation tube.]

**Figure 2.19** Diagram of manifold used to generate mercury sample gas using a permeation tube.

The manifold is capable of tens of liters per minute of airflow and was used to expose the AuNP-coated chips to mercury concentrations ranging from 1.0-8.6 μgHg/m₃. During the exposure rotameter 1 was closed and all the air that passed the permeation tube subsequently flows over the chip. The reading from rotameter 2 measured the flow rate past the permeation tube. With a constant volumetric flow rate through rotameter 2, the concentration ($c_{Hg}$ - g/m³) seen at the chip becomes:

$$c_{Hg} = \frac{\dot{m}}{Q}$$

where Q is flow rate (m³/sec) and $\dot{m}$ is the mass flow rate (g/sec) calculated in equation 2.1.

### 2.4.5.4 Impinging flow exposure

The next sample exposure apparatus utilized the enhanced mass transfer of an impinging jet. The jet/sensor assembly is shown in Fig. 2.20.
We ran the jet exposures at a flow rate of 18 LPM. The mercury calibration gas is generated in the same manifold as the cross flow exposures (Fig. 2.19). At 295 K a 20 LPM flow entrains $3 \mu g_{Hg}/m_{air}^3$ while passing over the permeation tube.

The chip is mounted on a mirror-polished silver plate using silicone glue along two edges of the chip. The mirror plate was held in an three-axis adjustable lens mount secured to an optical bench. The beam and jet were aligned with the center of the chip during exposure. To collect a bright reference spectrum, the mirror was adjusted upwards until the beam was entirely off of the chip.

On the opposite face of the mirror we placed heating tape used for regeneration. The temperature of the chip was tracked throughout exposure and regeneration by a thermocouple in contact with the chip. Temperature measurements were used to track the regeneration step, and correct for temperature dependent shifts in the absorbance spectra.

2.4.6 Regeneration of nanoparticle film

The adsorption of mercury onto gold is reversible; heating of a gold/mercury amalgam drives off the mercury as vapor. Using this phenomenon we regenerated nanoparticle film sensors. During the regeneration, heat was supplied by a heating tape with the current (heating power) controlled by an autotransformer. The temperature of the film during regeneration was monitored and recorded with a USB thermocouple connected to a desktop computer. An example of the temperatures recorded during a regeneration cycle is shown in Fig. 2.21. Regenerations were tested at temperatures between 380 and 513 K. The regeneration of the substrates between 400 and 433 K was found to be repeatable and sufficient for restoring the sensitivity of the film to mercury vapor. Heating to 513 K cause irreversible changes to the particle film morphology.
3. Mercury vapor interaction with individual gold nanorods

3.1 Introduction

Gold nanoparticles are a powerful tool for mercury monitoring and collecting. A solid understanding of the role of the particle geometry is a major component in the development of a competitive gold nanoparticle-based mercury monitor. The shape and size of gold nanoparticles influence their response to mercury vapor. Detailed understand of these effects are needed to optimize gold nanoparticle based mercury sensing. Current techniques for nanoparticle synthesis are unable to provide monodispersity. Therefore studying size- and shape-effects in detail is difficult for ensembles of synthesized particles. Alternatively, observations of the interaction between individual gold nanoparticles and mercury provide explicit evidence of the shape and size effects needed for improved designs.

Studies have shown that the peak in the localized surface plasmon resonance (LSPR) of gold nanoparticles shifts when the particles are exposed to mercury. Gold nanoparticles in both colloidal solutions and films respond to mercury vapor with a blue-shift in LSPR wavelength. Rex et al. developed a method for sensing aqueous mercury concentration with colloidal gold nanorods (AuNRs). By adding known concentrations of HgCl$_2$ to a solution of gold nanorods and sodium borohydride, Hg(II) is completely reduced to elemental mercury and subsequently adsorbed by the AuNRs. They found the limit of detection to be 6.6 x 10$^{-13}$ g·L$^{-1}$ and LSPR wavelength shifts up to 70 nm, attributed to a combination of composition and shape change in the AuNR suspension.
Here we report the optical response and mercury collection capacity of isolated individual AuNRs exposed to low concentrations of mercury vapor. Using individual particles results in fewer variables than for particle films, where aggregation of particles and interactions of nearby particles occur. The LSPR of an individual nanorod depends on its size, shape, composition, and environment, while the LSPR of a film of particles also depends on the spatial distribution of particles.\textsuperscript{45,47} Films typically have particles with a range of sizes and shapes; following individual particles allows comparison of shape and size effects based on distinct measurements and not statistical characterization.

3.2 Individual AuNRs before exposure to mercury vapor

Size, shape, and dark field spectral measurements for specific AuNRs require a combination of optical microscopy with transmission electron microscopy (TEM) (Hitachi H-7650). The TEM is equipped with EDX to provide composition measurements of the nanoparticles. Disperse films of AuNRs on a silicon nitride TEM grid with a 1 mm square, 50 nm thick window (Ted Pella) are made by a 15 second incubation in diluted AuNR in ethanol (Nanosol, NanoPartz). The size distribution of these commercially sourced particles appears in Fig. 3.1 and 3.2. The size was determined using ImageJ analysis of TEM images.

![Graph showing variation in particle diameter and radius](image)

**Figure 3.1** Variation in particle diameter and radius in a solution of commercially available gold nanorods.
Figure 3.2 Histogram representing the dispersion in measured particle aspect ratio (N=59).

The position of each AuNR on the grid window acts as a map to relate data collected in the two instruments. Each instrument can generate such a map; the TEM provides the stage position of each image and the AuNR appear as bright spots in the dark field image. With the TEM we scan the grid window, in a 50 µm by 50 µm raster pattern, for isolated single AuNRs. A particle is considered isolated if its nearest neighbor is more than 5 µm away. If the particles are less than 5 µm apart the dark field spectroscope cannot observe their scattered spectra individually. We capture 30kx magnification images of all AuNR discovered during the raster scan, both isolated and bunched. Each TEM image taken includes the corresponding stage location. In Fig. 3 the recorded positions are plotted with respect to the adjacent grid-window corner and overlaid onto the dark field image, with the TEM stage positions shown as rings and the scattered light from the AuNR as the bright spots in the background dark field image. Bright spots without corresponding rings represent scattering sources that were not imaged in the TEM. In cases where multiple nanoparticles are less than 2 µm apart they will appear as overlapping rings but single bright spots in Fig. 3.3. This highlights the difference in resolution between the TEM and optical microscope.
The TEM stage positions all coincide with bright spots in the dark field image, confirming that the same particle is observed by each method. For further verification the measured aspect ratio from the TEM images was compared to the longitudinal LSPR wavelength in Fig. 3.4; the LSPR wavelength increases with aspect ratio as expected.\textsuperscript{32,33} After initial characterization, the gold particles are exposed to 13 cc/min of 14, 30, or 98 µg/m$^3$ concentrations of mercury vapor in air for one hour. The mercury vapor samples consist of a controlled dilution of saturated Hg-vapor in air held by a 3-liter Teflon sample bag. Using a gas-tight syringe, we draw mercury vapor from the vapor space of a sealed vial containing a bead of mercury. This saturated vapor is added to a sample bag that has been inflated with pure air (Zero Air, AirGas). Measurements of mercury concentration in the sample bag before and after exposure were collected using a mercury vapor analyzer (Jerome 431X). The amalgam nanorods were then reanalyzed with TEM, EDX, and dark field spectroscopy as described above.
3.3 AuNRs after exposure to mercury vapor

Figure 3.5a shows a single gold nanoparticle before and after exposure to mercury. There is no significant change in the shape or size of the particle. We expect some growth to occur during the adsorption of elemental mercury, but it appears to be less than the spatial resolution of the TEM image. For bulk gold, the adsorption process becomes saturated with 40% surface coverage. A similar submonolayer of mercury would change the diameter less than 1 nm, and such a change would not be observed. We were unable to measure any changes in geometry as well. We had originally thought that the suppression of melting temperature through amalgamation would make the particles vulnerable to spheroidization. For these particles the melting point suppression is apparently not enough to cause any melting at room temperature. The particles were stable over the course of multiple days at room temperature.

Adsorption of mercury was confirmed by composition measurements using an EDX spectroscpe. EDX analysis revealed the mercury mass to be 1.5±1.1% the mass of gold; before exposure to mercury no mercury was measured in the particle. The composition data corroborates the lack of growth in the particle dimensions.

While shape and size changes were not measurable, chromatic changes in the light scattered by the individual particles were significant. Spectra from a single AuNR before and after mercury exposure in Fig. 3.5b show a 2.9 nm blue shift.
Figure 3.5 TEM images (a) and dark field spectra (b) of an individual AuNR before and after exposure to mercury vapor.

The LSPR blue shifts an average of 3 nm upon amalgamation, and shows no dependence on the Hg vapor concentration in the tested range (14, 30 and 98 µ/m³), suggesting that the particles are saturated with Hg. The average shifts for the AuNR are
plotted against the mercury concentration during exposure in Fig. 3.6. The error bars represent the standard deviation of all the LSPR shifts measured in the run. We expect some spread in shift magnitudes caused by the varying shapes and sizes of the particles probed. The average shift magnitudes suggest that the saturation condition does not depend on the concentration of mercury during the exposure.

![Graph showing LSPR blue shift as a function of mercury concentration](image)

**Figure 3.6** LSPR blue shift as a function of mercury concentration. No significant trend is observed, suggesting that the particles are saturated with mercury.

The LSPR blue shift at saturation depends on individual AuNR dimensions. Gold nanospheres exhibit larger LSPR shift at saturation with decreasing diameter. Individual nanorods show a similar size effect. However, the rods have two dimensions - diameter and length - as opposed to the single dimension for spheres. This adds to the complexity of characterizing the size effect. Surface-area-to-volume ratio (SA:V) is a metric that includes differentiation of particle shapes as well as the size. AuNRs with a larger SA:V exhibit greater LSPR shifts between their pure-gold and saturated-mercury states, as shown in Fig. 3.7. The SA:V is calculated using a cylindrical model of each particle using the diameter and length measured from a 30kx TEM image of the AuNR.
A nanorod’s longitudinal LSPR wavelength has a strong dependence on the particle’s aspect ratio. The shift at saturation correlates positively with aspect ratio within the range of nanoparticles tested (Fig. 8); larger aspect ratios are capable of larger shifts before saturation. Other LSPR sensors have shown larger aspect ratio AuNRs to be more sensitive to changes in environmental dielectric constant. Aspect ratio and SA:V are difficult to decouple experimentally, given the random distribution of particle shapes and sizes. Of the particles tested those with the largest aspect ratios also have the largest SA:Vs. Because the aspect ratio and SA:V are closely related, many more particle shapes would need to be tested in order to separate their effects.
3.4 Model for the LSPR of amalgam nanorods

We modeled the wavelength dependence of the extinction coefficient for amalgam nanoparticles to better understand the blue shift upon mercury adsorption. Bimetallic nanoparticles have been found to have LSPR peak wavelengths with a linear dependence on alloy fraction.\(^3\) Given the initial LSPR peak (\(\lambda_{LSPR}^{Au}\)) and the predicted peak for a pure mercury nanorod (\(\lambda_{LSPR}^{Hg}\)) of the same dimensions and surrounding media, the mass fraction of mercury (\(w_{Hg}\)) can be calculated from the observed amalgam LSPR (\(\lambda_{LSPR}^{Au-Hg}\)):

\[
w_{Hg} = \frac{\lambda_{LSPR}^{Au} - \lambda_{LSPR}^{Hg}}{\lambda_{LSPR}^{Au} - \lambda_{LSPR}^{Hg}}
\]

To complete our model we need a prediction of the pure gold and pure mercury LSPRs. Link et al. (1999) presented a model for extinction from noble metal nanorods based on Gans theory:\(^3\)

\[
\gamma = \frac{2\pi\mathbf{N}V\varepsilon_m^{3/2}}{3\lambda} \sum_j \frac{(\frac{\varepsilon_2}{p_j^2})}{(\varepsilon_1 + (1-p_j)\varepsilon_m)^2 + \varepsilon_2}
\]

\(\gamma\) is the extinction coefficient, \(N\) the number of particles per unit volume, \(V\) the particle volume, \(\varepsilon_m\) the dielectric constant of the surrounding media, \(\lambda\) the wavelength of the interacting light, and \(\varepsilon_1\) and \(\varepsilon_2\) are the real and complex parts of the material dielectric function. Link et al. refer to \(P_j\) as the depolarization factors for the three axes A, B, and C of the rod. Because of the axial symmetry two of these are equal and A refers to the length of the rod. The depolarization factors are calculated using the following equations:
\[
P_A = \frac{1-e^2}{e^2} \left[ \frac{1}{2e} \ln \left( \frac{1+e}{1-e} \right) - 1 \right] \\
P_B = P_C = \frac{1-P_A}{2} \\
e = \sqrt{1 - (B/A)^2}
\]

where $A/B$ is the aspect ratio.

To calculate the LSPR of an average-sized particle (62 nm long, 20 nm diameter) we input the metal's known complex dielectric (Arakawa and Inagaki 1991) and the refractive index of the environment. The model does not provide for the heterogeneity of the particle's immediate surroundings (a particle with an attached ligand on a substrate in air). We use an average index of 2 to match the calculated pure gold peak with the experimentally observed peak. The predicted longitudinal LSPR peak wavelength of the 20x62 nm mercury nanorod (HgNR) is 480 nm, and 756 nm for the AuNR. The chromatic distribution of the extinction coefficient for a nanorod of each material is presented in Fig. 3.9.

![Figure 3.9](image-url)

**Figure 3.9** Calculated spectra for pure-Au and pure-Hg nanorods (62 nm long, 20 nm diameter)

We observed saturated particles of this size shift 3 nm, or 1% the difference between the LSPR wavelengths of AuNR and HgNR of those dimensions, suggesting that a saturated particle consists of 1% Hg and 99% Au. The EDX data, size measurements, and LSPR model are all in agreement that the mass of mercury in a saturated AuNR is on
the order of 1% the rod mass. Previous work by Levlin et al. found that single crystal gold surfaces exposed to mercury vapor saturate before formation of a complete monolayer, they estimate the coverage at saturation to be <50%. In the case of our particles a complete monolayer would result in a mass fraction of 2.5% Hg, so the observed 1% Hg suggests 45% monolayer coverage.

We generated a model that calculates the shift at saturation given a particle diameter and length. The model uses equation 3.1 to predict the LSPR shift, where the two bounding LSPR wavelengths (mercury and gold) are predicted by equation 3.2. The mass fraction calculation assumes 45% surface coverage, which takes into account the dimensions of the particle. We ran the model for a range of aspect ratios while holding the SA:V constant (SA:V=0.22, an average value from the experiments). The modeled dynamic range dependence on aspect ratio is non-linear and is plotted in Fig. 3.10. The dependence is limited to a portion of equation 3.1, namely the difference between the pure gold and pure mercury nanorod LSPR:

\[ (\lambda_{\text{LSPR}})_{Au} - (\lambda_{\text{LSPR}})_{Hg} = f(A/B) \]  
\[ \left( w_{Hg Sat} \right)_{SA:V=c} \neq f(A/B) \]  

where \( (w_{Hg Sat})_{SA:V=c} \) is the mass fraction of mercury at saturation for a fixed SA:V.

Figure 3.10 Aspect ratio dependence of shift at saturation predicted by the model (fixed diameter).

Alternatively, we fixed the aspect ratio to 3 and calculated the shifts for a range of SA:V ratios. The result shows that the shift is directly proportional to SA:V, which is apparent in Fig. 3.11. With the aspect ratio fixed there is no difference between the pure
gold and mercury nanorod LSPRs calculated in equation 3.2, but mass fraction at saturation is proportional to SA:V:

\[
\left( \lambda_{LSPR}^{Au} - \lambda_{LSPR}^{Hg} \right)_{A/B=C} = \text{Constant} \tag{3.8}
\]

\[
\left( w_{HgSat} \right)_{A/B=C} \propto SA:V \tag{3.9}
\]

![Figure 3.11](image)

**Figure 3.11** SA:V dependence of shift at saturation predicted by the model (fixed aspect ratio).

Using the model we can differentiate the modes of influence for SA:V and aspect ratio. It would be possible experimentally, but would require a different assortment of nanorods than used here. The particle dimensions in the model are independent variables while the dimensions of the physical particles are randomly distributed. The data we were able to collect experimentally was compared to the model by inputting each measured particle’s dimensions and plotting the predicted shift to the data in Fig. 3.7 and 3.8. The comparison is shown below in Fig. 3.12 and 3.13.
Figure 3.12 Overlay of the experimental results (circles) and model (squares) arranged by aspect ratio.

Figure 3.13 The same data as Fig. 3.12 but arranged by SA:V.
The model is accurate in predicting the LSPR of AuNRs before and after saturation with mercury. The modeled shift at saturation is essentially the same as the experimental results, and supports our assumption that gold nanoparticles saturate with less than submonolayer coverage of mercury. The model predicts shifts with less sensitivity to changes in aspect ratio in the range from particles tested. For these 12 particles, the average percent difference between the model and experimental results is 5%. An alternative core/shell model (Appendix I) shows similarly approximates the experimental results.

The observed behavior has significance for mercury collection as well; surfaces of nanoscale gold particles collect as well as those of bulk gold. This behavior allows us to predict the gains possible by replacing continuous gold films with particle films in mercury trapping applications. Nanoparticle surfaces saturate similarly to bulk gold surfaces but the huge SA:V reduces the required gold mass. The AuNRs used here collect 4.6 times more mercury per gram of gold than a 20 nm thick continuous gold film. The advantage over continuous films is increased through the use of small particles and larger SA:V geometries. For example, baculiform particles are preferable to spherical particles of the same volume for mercury collection and mercury vapor sensitivity.

Selective adsorption by gold nanoparticles makes LSPR based mercury sensing different than sensors that monitor index of refraction. AuNR based LSPR sensors that monitor the local index of refraction are not directly improved by increasing SA:V.\textsuperscript{41,46} Two nanorods of differing SA:V but similar aspect ratios experience the same shifts in extinction coefficient for equivalent changes of medium index of refraction (equation 3.2).

3.5 Comparison to Rex et al.

As described in the introduction, Rex et al. reported on the interaction of gold nanoparticles in solution to aqueous mercury.\textsuperscript{50} Their success prompted our shift in nanoparticle shape from spheres\textsuperscript{52} to nanorods. There are a few key differences between the response of nanorods in solution and the individual nanorods described in this paper:

- Rex et al. found the limit of LSPR-shift at saturation to be 70 nm while we found them to be less than 4 nm.
- The aqueous exposure method produced significant changes to the particle shape. We observed no shape change upon saturation with mercury.

The differences between the exposure conditions appear to cause the disparity in the resulting limit of LSPR-shift. The addition of sodium borohydride to the nanorod solution produces immediate shape change even in the absence of mercury. Sodium borohydride can be used as the reducing agent in gold nanoparticle synthesis, reducing gold salts and growing larger particles. The two differences listed above are linked because nanoparticle LSPR is sensitive to shape, composition, and size.

3.6 Conclusion

The saturation of AuNRs (~62x20 nm) with mercury results in a 3 nm blue shift of LSPR wavelength, where shifts depend on both SA:V and aspect ratio. Comparison of particle sizes and EDX measurements before and after exposure suggest particles saturate with a composition 99% Au and 1% Hg. The mass fraction of mercury at saturation is consistent with the collection process being limited to the adsorption a submonolayer of
mercury vapor. This result agrees with similar studies on gold films\textsuperscript{67} and gold nanospheres\textsuperscript{51,54}.

Using a modified Gans theory to predict the LSPR wavelength of the alloy particles we were able to explain the SA:V and aspect ratio dependence of the LSPR shift. The model can predict the shift at saturation of a particle with a specified diameter and length within 5\%. The SA:V determines the mass fraction of mercury at saturation which is linearly related to the LSPR shift of a particle of fixed aspect ratio. Increasing aspect ratio with a fixed SA:V causes an increase in LSPR shift at saturation as well. Whether the goal is mercury collection or mercury sensing increasing the SA:V ratio improves performance.

4. Mercury sensing with gold nanoparticle films

4.1 Introduction

Current air monitors are amply sensitive to detect the global background (1.2 ng/m\textsuperscript{3}), but are costly and high maintenance\textsuperscript{68}. Preconcentration of trace mercury vapor samples is required for ambient measurements and depends on gold surfaces to effectively trap and quickly release mercury in detectable amounts. Concentrations as low as 0.1 ng/m\textsuperscript{3} can be analyzed using a trap made of gold coated sand that feeds a cold vapor atomic fluorescence (CVAFS) or absorption spectroscopy (AAS)\textsuperscript{19,20}.

Beyond providing selective adsorption for sample collection, gold is used to detect mercury in various measurement techniques. Thundat et al. (1995) demonstrated the quantitative detection of adsorbed mercury with gold-coated microcantilevers\textsuperscript{26}. Picogram resolution was obtained by monitoring changes in the resonant frequency of the cantilever bending. Resistivity changes in gold films are proportional to the adsorbed mercury mass,\textsuperscript{27} an effect utilized by commercially available mercury vapor analyzers with ~\(\mu\text{g}_\text{Hg}/\text{m}_\text{air}^3\) resolution. Adsorbed mercury also induces changes in the optical properties of gold films, measurable with surface plasmon resonance spectroscopy\textsuperscript{28}. In nanoparticle form the optical property changes can be followed with simple and inexpensive visible light absorbance spectroscopy. Metal nanoparticles exhibit peaks in absorbance due to localized surface plasmon resonance (LSPR). The location of the peak depends on shape, size, composition, and local environment. Adsorption of mercury alters a gold nanoparticle’s complex dielectric function and causes a blue shift in the LSPR wavelength, seen in both colloidal solutions\textsuperscript{50-53} and films\textsuperscript{54,69}. Our recent work studying the LSPR response of individual gold nanorods achieved attogram (10\textsuperscript{-15} g) resolution and found the sensitivity to be proportional to the nanoparticle’s surface-area-to-volume ratio\textsuperscript{70}. Responding to the technical needs of an expanding mercury observation network we are developing a reliable, sensitive, and inexpensive method for LSPR-based mercury detection.

We compared the performance of various configurations of our mercury sensor by adjusting the particle type, particle spacing, and sample flow characteristics (geometry and flow rate). Nanoparticle films on a transparent substrate collect and respond optically to mercury vapor. Gold particle size and shape impacts the sensitivity and stability of the sensor; 5 nm spherical particles are more sensitive than larger particles (8 nm spheres) and more stable than baculiform nanoparticles under elevated temperatures (100 °C). Closely packed particles can cause plasmon coupling which results in a red-shift and broadening of the LSPR peak. The density of nanoparticles in the film also affects the mass limit of detection. The shifts in LSPR wavelength depend on the mercury mass.
adsorbed per particle and in this sense are directly proportional to the surface density of nanoparticles in the film. We also observed the collection of mercury by a nanoparticle films under different sample flow conditions. Increases in sample flow rate enhance the diffusive mass transfer. Impinging flow provided a greater enhancement than cross-flow for equivalent flow rates.

4.2 Response of nanoparticle films to mercury vapor

4.2.1 Calibrating UV-vis spectra to mercury concentration in a flowing sample

Gold nanoparticles respond to mercury vapor with a blue shift in their LSPR wavelength.\textsuperscript{50–54,70} We aim to quantify the mercury concentration in a sample through observations of the LSPR peak location of a nanoparticle film. Other techniques (CVAFS/AAS) measure mercury in the vapor phase. This volumetric measurement directly probes concentration. The LSPR shifts of nanoparticle based mercury measurements do not measure the vapor phase, but rather the mercury adsorbed onto the nanoparticle surface. The magnitude of the blue shift is proportional to the mass of mercury adsorbed.\textsuperscript{54,70} It follows that the LSPR shift as a function of time represents an integral of the adsorptive flux of mercury. The adsorptive flux of mercury onto a gold surface in a steady flowing system is proportional to the mercury vapor concentration. Therefore the time derivative of LSPR shift corresponds to a continuous measurement of concentration. In mathematical terms the above relationships are:

\begin{align}
\Delta LSPR(t) &= LSPR(t) - LSPR_0 \\
\Delta LSPR(t) &\propto (m_{HG})_{ads} = A_{AuNP} \int_0^t J_{HG} \, dt \\
for a steady flowing system, \quad J_{HG} &\propto c_{HG}
\end{align}

so,

\begin{equation}
\frac{dLSPR}{dt} \propto c_{HG}
\end{equation}

where \(\Delta LSPR\) is the shift in LSPR wavelength, \(LSPR_0\) is the initial LSPR wavelength, \((m_{HG})_{ads}\) is the mass of mercury adsorbed by the nanoparticles, \(A_{AuNP}\) is the surface area of the nanoparticles, \(J_{HG}\) is the adsorptive flux of mercury, and \(c_{HG}\) is the mercury concentration in the sample. The time derivative of the LSPR shift is also referred to as the \(v_{LSPR}\) herein, and will be used in the calibration of our nanoparticle based mercury sensors.

4.2.2 Nanorod film

4.2.2.1 Introduction

The optical properties of anisotropic nanoparticles are highly sensitive to changes of size, shape, and environment. Spherical gold nanoparticles have a single peak in their absorbance (\(\sim 520\) nm, loosely coupled to diameter), but gold nanorods have two peaks; a short wavelength peak (transverse band) corresponding to the absorption and scattering along the short axis of the nanorod and a long wavelength peak (longitudinal band) corresponding to the absorption and scattering along the long axis. The peak originating from the long axis scattering/absorption is tunable by controlling the nanoparticle’s aspect ratio (long axis divided by short axis).\textsuperscript{33} By tuning the longitudinal band to fall within the biological window (the wavelengths (650-950 nm) of visible light most readily transmitted through tissue) nanorods have an advantage over spheres for biological imaging,\textsuperscript{71} sensing,\textsuperscript{41} and photothermal therapy.\textsuperscript{72} Other advantages given by nanorods are the larger extinction cross-section and heightened sensitivity of the longitudinal band.
to changes in medium dielectric. Becker et al. found the optimal aspect ratio gold nanorod for dielectric sensing to be three. In this shape, the plasmonic sensitivity reaches a peak that no longer increases for increasing aspect ratio.\textsuperscript{46}

The interest in nanorod optical properties has led to the development of an array of sensing techniques. Some techniques rely on the optical changes due to coupling of neighboring nanorods in analyte-induced aggregation.\textsuperscript{40,45} Other sensors depend on selective adsorption of the analyte to the functional coating of the nanorod.\textsuperscript{73–75} The change in the local dielectric caused by this adsorption results in a measurable change in the LSPR peak. This technique closely resembles mercury sensing with gold nanorods discussed in the following section.

Rex et al. exposed gold nanorods to mercury in aqueous solutions. Elemental mercury has limited solubility in water (0.30 μMol kg\textsuperscript{-1} at 298 K). Water-soluble ionic mercury is the most prevalent form of aquatic mercury pollution and therefor the focus of study and regulation. Rex et al. elected to reduce the ionic mercury to elemental mercury using sodium borohydride, a strong reducing agent. The addition of the sodium borohydride causes the nanorods to change shape, and the shape change continues upon the addition of a mercuric chloride solution. Their characterization of the amalgam nanoparticles included TEM, EDX, and UV-vis spectroscopy. Recorded shifts in UV-vis absorbance spectra, 4 minutes after the addition of the mercuric chloride solution, were linearly related to the mercury concentration. Shape change is both an advantage and disadvantage. The LSPR wavelength shifts caused by spheroidization are much greater than those caused by changing composition.\textsuperscript{70} The main disadvantage to shape change enhanced mercury sensing with gold nanorods is the irreversibility of the exposure. Once a rod has changed shape its sensitivity to further mercury exposure is reduced and the particles must be discarded. The generation of a constant stream of identical nanorod solutions to run the measurements is a complicated problem. Nanorods age in solution with aggregation and shape change, so a larger reservoir of nanorods cannot be expected to remain in a steady condition. If fresh nanorod solutions are synthesized regularly they have to be thoroughly characterized for shape, size, and concentration. Any variation will change the sensitivity to mercury, requiring recalibration. Nanorods assembled into a film can be removed from their aqueous solution and kept in an inert environment to prevent aging, thus simplifying the calibration process.

4.2.2.2 Film characterization

We prepared nanorod films on quartz substrates and characterized them with UV-vis absorbance spectroscopy. Nanorods (Nsol, Nanopartz) suspended in ethanol, with an aspect ratio of 3.8 (10 nm x 38 nm), were spun down (5 min, 15 kRPM in centrifuge) and re-suspended in chloroform. We used the Langmuir-Blodgett technique with a surface pressure 18 mN/m for the film deposition. The resulting films had longitudinal peaks red shifted due to plasmon coupling. In solution the particles have a longitudinal LSPR wavelength of 780 nm but the films had an average of 850 nm (Fig. 4.1). Plasmon coupling between nanorods occurs when particles are closely spaced.\textsuperscript{48}
**4.2.2.3 Mercury exposure response**

Exposure to mercury vapor was followed by blue shifts in the LSPR wavelengths (longitudinal and transverse) of gold nanorod films. The shift direction was consistent with other studies of gold nanoparticle amalgams.\textsuperscript{50–52,54,70} Coincident with the blue shift there was a drop in absorbance magnitude at the peaks (Fig. 4.2). Both peaks, transverse and longitudinal, are recognizable in Fig. 4.2, but we will focus on the longitudinal LSPR because it demonstrated a higher sensitivity to mercury.
After extended exposure to mercury vapor, gold surfaces will saturate\textsuperscript{54,67,70}. A bare gold surface will initially adsorb mercury perfectly, with a sticking coefficient of 1.\textsuperscript{67} The growing surface coverage by mercury incrementally slows further adsorption of mercury. Data of the time dependent response of the LSPR to a steady flow of constant concentration mercury vapor in air shows signs of decaying adsorption efficiency. Figure 4.3 shows the displacement of the longitudinal LSPR from its original wavelength during an exposure to 0.4 µg/m\textsuperscript{3}. The shape of this curve is typical to all exposures; the LSPR-shift velocity decreases throughout the exposure.
Figure 4.3 Longitudinal LSPR wavelength displacement during an exposure to 0.4 µg/m³ mercury vapor in air.

Time resolved data of the peak position relate to the mercury concentration in the sample. A linear fit of the initial nanometer of shift in the LSPR with respect to time approximates the time derivative of the LSPR shift. This LSPR shift velocity should be proportional to the mercury concentration (see section 4.2.1 above). We ran a series of exposures under similar flow conditions (200 cc/min) but varying mercury concentration (0.4-9 µg/m³). The shift velocities show a positive correlation with mercury concentration (Fig. 4.4). The concentrations shown in Fig. 4.4 are either directly measured by a Jerome x-431 mercury analyzer or measured in a concentrated stream before a dilution. The error bars represent the published resolution of the analyzer.
A lack of control for interferences and a narrow range of tested concentrations limit the predictive strength of the calibration curve in Fig. 4.4. While not measured during these exposures we now know that temperature changes contribute to significant shifts in the LSPR wavelength. Lack of temperature data prevents the differentiation between the temperature driven shifts and those caused by mercury. Running at higher concentrations would mitigate the confounding temperature effect because the mercury-generated signal grows linearly with concentration. Another benefit of higher mercury concentrations would be a verification of the linear nature of the concentration dependent $v_{\text{LSPR}}$. A second batch of nanorod films were made using the Langmuir-Blodgett method but had much shorter wavelength longitudinal LSPR (750 nm). The lack of repeatability in the nanorod film generation prevented quantitative comparison of the data.

The exposure of nanorod films to mercury vapor is novel and the response is unlike previous aqueous exposures. The range of longitudinal LSPR peak shifts is significantly smaller for the nanorod film method. In the aqueous exposure technique employed by Rex et al. the longitudinal LSPR wavelength was shown to shift up to 60 nm.\textsuperscript{50} For higher mercury concentrations (1.57 Mol/L) they show the longitudinal and transverse peaks merging, which is caused by spheroidization of the nanorods. For nanorod films exposed to mercury vapor, the LSPR shift was much more limited; the particles appear to become saturated after a 2-4 nm shift. This saturation without shape change was shown explicitly in our study of the response of individual nanorods to mercury vapor.\textsuperscript{70} The chemical activity in the aqueous method partly explains the differences in the results. Sodium borohydride, a powerful reducing agent, is added to the aqueous solution to reduce the
ionic mercury to the elemental form adsorbed by the nanorods. The addition of sodium boroxydride in the absence of mercury causes shape change. In our reproduction of the Rex protocol we observed a greater shift of the LSPR from the sodium boroxydride alone and unsteady longitudinal LSPR peaks, even after the 15 minutes they suggest waiting before the mercury sample addition. In comparison our particle films are stable if they remain at room temperature in air.

A significant problem with nanorod based mercury vapor detection methods is the irreversibility of the mercury adsorption. Heating of the nanorods to temperatures as low as 100 °C will cause irreversible shape change. This prevents any regeneration of the type typically used in gold-based mercury collecting/detecting systems. To verify the shape instability we heated a mercury-saturated nanorod film in a furnace to 110 °C for 15 minutes. While being heated the nanorods in the film had changed shape. This was evident in the 20 nm blue shift of the longitudinal peak of the film’s absorbance. Particles having a smaller aspect ratio will have a shorter wavelength longitudinal peak. The shape change is irreversible and would affect the sensitivity to mercury vapor. A successfully regenerated chip would return to the original longitudinal LSPR wavelength. This would signify the evolution of the adsorbed mercury and a restoration of the film to its pre-exposure condition.

4.2.2.4 Conclusions

Nanorod films are sensitive to µg/m³ concentrations of mercury in air, with a linear relationship between concentration and LSPR shift rate amounting to 0.7 nm/hr per µg/m³. By using the Langmuir-Blodgett method we were able to generate batches of films in parallel. Quartz substrates and a quartz flow cell reduce the losses in the UV-vis spectrometry and allow in-situ tracking of the LSPR peaks. The shift of the LSPR peaks during exposure are in agreement with the saturation observed previously for gold nanorods, nanoparticles, and films.

The extrapolative and predictive power of these results is limited. Subsequent experiments should consider interferences (temperature changes) and increase the range of concentrations and number of experiments. Because of the lack of stability of the nanorods, we opted to explore more stable particle geometries capable of regeneration. Single use measurement tools have limited applications and would not compete directly with the state of the art mercury monitors. Regeneration is a key to our goal of generating a novel mercury sensing technology.

4.2.3 Nanosphere film

4.2.3.1 Design motivation of spheroid particle film

Optimizing LSPR based mercury sensing requires choosing the best material for selective adsorption and sensitive response. We used gold because it is a selective and stable mercury adsorbing material and can be grown in a variety of shapes and sizes of nanoparticles. We then determined the most sensitive and stable gold nanoparticle from available shapes and sizes. Morris et al. exposed films of gold nanospheres of varying size to saturated mercury vapor in room temperature air. They found that the shifts in LSPR at saturation were greater for smaller particles. Our previous work observing individual gold nanorods’ spectral response to µg/m³ concentrations of mercury in air found that the sensitivity was not dependent on size directly, but proportional to surface-area-to-volume ratio.
Beside sensitivity, functionality and stability are of concern when selecting the appropriate nanoparticles. Not all gold nanoparticles are equivalently stable. Nanorods and other complex geometries experience shape change with age and quickly change shape when heated. Unfortunately the high surface area geometries (which we desire for their sensitivity) are less stable than the smaller surface area shapes as a result of the thermodynamic advantage gained from reducing the surface energy.\textsuperscript{76,77}

We selected \(\sim 5\) nm spheres, because they have the largest surface-area-to-volume ratio while still having an observable peak in visible absorbance for an assembled film.\textsuperscript{65,64} Spheres are the minimum surface-area-to-volume ratio shape but they can be synthesized in much smaller sizes than the more complicated geometries. Being the minimum surface-area-to-volume geometry also serves as an advantage for the shape stability of spheroid particles.

Existing models and previous experiments can predict the response of a 5 nm AuNP’s LSPR to amalgamation. The LSPR wavelength of bimetallic nanoparticles shifts proportionally to alloying mass fraction.\textsuperscript{43} Due to differences in the complex dielectric, the LSPR wavelength of a 5 nm Hg particle would be 273 nm, 240 nm shorter than a AuNP of the same size. The Link et al. model predicts a shift of 2.4 nm for each percentage increase in the Hg mass fraction, which in the case of the 5 nm sphere is equivalent to 38 atoms of Hg. The model agrees with experimental observations comparing UV-Vis spectra with the measured mass fraction.\textsuperscript{51,53,70}

4.2.3.2 Film characterization for cross flow experiments

While we have observed the spectra of individual nanoparticles, both AuNP and amalgalm particles, with dark field spectroscopy, for a practical sensor we measure the spectral response of an array of particles using UV-Vis absorbance spectroscopy. There are a variety of assembly methods to generate such a particle film. We attempting wet-deposition and dry-casting with limited success compared to the Langmuir-Blodgett method. Dry-casting caused a “coffee ring” structure in the film with a lot of aggregation. The resulting films had strong heterogeneity and no distinct peak in absorbance. Wet-deposition created more homogenous films but did not have good repeatability for nanoparticle packing density. With the Langmuir-Blodgett method we were able to make up to 15 films in a single batch with homogenous packing density and absorbance spectra. The Langmuir-Blodgett method also offers better control over the film density.\textsuperscript{64}

TEM images show the AuNP-film to be near close-packed with particles having an average diameter of 4.8 nm. A typical TEM images is shown in Fig. 4.5a. There are roughly \(2 \times 10^{12}\) particles (18 \(\mu\)g) on each 1 cm\(^2\) chip. The close proximity of the particles allows coupling between neighboring plasmons, driving the resonance to longer wavelengths (isolated particles have an LSPR wavelength of \(\sim 520\) nm).\textsuperscript{45} The red shift in the LSPR is accompanied by a peak broadening shown in Fig. 4.5b. All films tested in cross-flow originate from the same Langmuir-Blodgett batch and have an average LSPR wavelength of 551 nm.
Figure 4.5 (a) TEM image of the Langmuir-Blodgett generated film showing the particle sizes and distribution in film. (b) A typical UV-Vis absorption of the nanoparticle film on quartz. The film’s LSPR wavelength is 550 nm.
4.2.3.3 Mercury exposure response

Initial exposures to mercury vapor employed a Teflon sample bag (3 L, SKC) with a controlled dilution of saturated mercury vapor in clean air (Zero Air, AirGas). A peristaltic pump drew the sample from the bag over the sensor chip at a constant flow of 15 cc/min. A quartz flow cell (Starna Cells) held the sensor chip for in situ recording of the absorbance spectra. Each spectrum saved is the average of 100 spectra with integration times of 80 msec. This technique was used for samples ranging from 25 to 825 μg Hg/m³. The concentration of each dilution was measured using a conductometric mercury analyzer with an accuracy of ±5% (Jerome J405 or Jerome x-431).

Films exposed to mercury vapor exhibit a blue shift in their LSPR wavelength. The shift rate slows as the chip saturates (Fig. 4.6). This response, and all those exposed using the bag method, is the first exposure to mercury for this film. The film has been kept in a mercury free environment and has not been through a regeneration cycle.

![Graph showing LSPR blue shift over time](image)

**Figure 4.6** Displacement in LSPR wavelength for the first exposure (15 cc/min, 825 μg Hg/m³) of a nanoparticle film.

Using a flow rate of 15 cc/min and mercury concentrations ranging from 25 to 825 μg Hg/m³, the films’ initial LSPR shift rates ($v_{LSPR}$) are proportional to the sample concentration. The shift rates for 6 films exposed to a range of concentrations show a correlation in Fig. 4.7. For each μg Hg/m³ increase in sample concentration the $v_{LSPR}$ increases by 0.023 nm/hr. The $v_{LSPR}$ is also proportional to the rate of mercury adsorption, which is controlled by the diffusive mass transfer of the trace mercury vapor.
The quartz flow cell apparatus did not include regeneration or a measurement of the chip temperature variation during the exposure. Temperature is known to affect the position of the LSPR wavelength, and is corrected for in all subsequent mercury exposures. However, these runs are less vulnerable to the temperature change interference. They were run at a low flow rate from a bag that was in thermal equilibrium with the room air. This limits the effects of convection seen in the later experiments using a compressed air source. Another mitigating factor against the thermal effect is the relatively high concentrations of mercury used in the exposures. The larger the mercury concentration the less likely temperature driven shifts will be significant. Regardless, temperature is a known interferent and was not monitored. This might have caused the spread seen in the calibration curve (Fig. 4.7).

4.2.3.4 Temperature dependence

Accuracy of the sensor can be improved by controlling for the confounding factors such as temperature. Observation of LSPR temperature dependence during the heating and cooling steps of regeneration prompted the use of a thermocouple to monitor the sensor temperature. The optical properties of all media change with temperature. The most notorious example is the mirage seen in hot weather where the gradients in the index of refraction of air near the ground create the illusion of pools of water. The thermal effects on our film LSPR are in part due to the changes of index of refraction of the air, but the changes to the complex dielectric function of the metal due to temperature change are the dominant effect.
Temperature data from a thermocouple in contact with the sensor chip can be used to correct for the thermal effects on the LSPR wavelength. A linear regression of the LSPR against temperature data from the hour before exposure allows normalization of the peak position; the LSPR peak temperature dependence was 1.7 nm/K (for the films described in section 4.2.3.7.2), but the temperature dependence changes with film morphology.

A method for temperature sensing based on the temperature-modulation of the LSPR was proposed by Srivastava and Gupta. They modeled the temperature dependent resonance of a nanoparticle film on an optical fiber probe. Our nanoparticle films are an experimental demonstration of this model, and agree with their prediction of red shifts with increased temperature in the range plotted in Fig. 4.8.

**Figure 4.8** Temperature modulation of the nanoparticle film LSPR with a linear fit used to normalize the LSPR wavelength during mercury exposure.

Additional confounding effects appear as a gradual red shifting of the LSPR for mercury free sample air. This shift is likely due to other adsorbates that increase the index of refraction surrounding the AuNPs causing the shift of the resonance to longer wavelengths. No efforts were made to correct for the red shifts, as they are slower (1x10^{-5} nm/sec) than the standard deviation (7%) of the sensor response to the tested mercury concentrations (1x10^{-4} nm/sec). Confounding effects will increase with respect to the mercury signal at lower concentrations, but have been mitigated through the use of protective monolayer films on similar gold film based sensors.\(^5\)

4.2.3.5 Regeneration
The need for continuous measurements and remote operation make a single-use sensor chip limited in appeal. Bulk gold releases mercury when heated to above 373 K, and the surface can be regenerated to collect gold in a repeatable fashion.\textsuperscript{21,27,67} We expected that gentle heating of the amalgam nanoparticle film evolves mercury as a vapor, but it was not clear that gold nanoparticles return to their original state, especially for non-spherical shapes.

Heating tape, wrapped about the tube and connected to an autotransformer, was used to heat (regenerate) the sensor. A low flow of tank air (6 LPM) during heating purged the system. A low temperature (433 K) for regeneration did not cause the nanoparticles to coalesce, allowing reuse of the film for further measurements. The sensor response to mercury exposure following an hour at 433 K was consistent, with no degradation observed for more than 30 regenerations.

We found minimizing the regeneration temperature to be protective of the film morphology that is irreversibly changed during high temperature heating. The bulk gold films used in conventional traps are more structurally stable and can survive the 1173 K temperatures they are commonly heated to during the evolution step. Preservation of the nanoparticle film morphology is key to a reproducible LSPR response; the melting point of the nanoparticles is size dependent, and melting point depression in nanoparticles makes the nanoparticle film vulnerable at lower temperatures than bulk gold. The depression is nonlinear with particle dimension, greatly impacting the melting temperature of our 4.8 nm particles.\textsuperscript{80} Heating to 513 K for one hour causes irreversible changes to the film wherein the particles coalesce, forming larger particles (d=8 nm). A TEM image of one such film is shown in Fig. 4.9. The larger diameter particles show a 50% reduction in sensitivity to mercury vapor, due in part to a reduction of the surface-area-to-volume ratio.
Figure 4.9 TEM image of nanoparticle film showing irreversible changes following heating to 513 K for 1 hour.

The 5 nm nanoparticle film, once melted and coalesced, becomes a film of larger nanoparticles with a significantly different absorbance spectrum. The new film has reduced packing density (Fig. 4.9). The effect on the absorbance can is shown in Fig. 4.10; lower packing density and larger particles have a narrower peak in absorbance blue shifted 22 nm from that of the original closer-packed 5 nm nanoparticle film. This is further verification that the density of the nanoparticle film determines the LSPR with close spacing causing red shifts due to plasmon coupling.
Figure 4.10 Absorbance of film before (red) and after (black) shape change from melting and agglomeration.

4.2.3.6 Fixed chip in cross flow

A single sensor chip was used in a series of exposures and regenerations to test the repeatability of the method and its agreement with flow rate trends of the mass transfer model. The peak traces show the characteristic decay throughout the exposure (Fig. 4.11), but the magnitude of the shift at saturation is significantly lower (3 nm) than the first exposures of the virgin films to mercury vapor (25 nm). For six runs done with a flow rate and concentration of 20 LPM and 3 μg/m$^3$ the $v_{LSPR}$ was 1.1 nm/hour on average with a standard deviation of 7%. Increasing the flow rate to 57 LPM with a sample of 1 μgHg/m$^3$ the $v_{LSPR}$ was 0.42 nm/hour.
Figure 4.11 Time trace of relative LSPR peak position during exposure to mercury vapor (3 \( \mu \text{g/m}^3 \) @ 20 LPM). A linear fit to the first nanometer of shift is used to determine \( v_{\text{LSPR}} \) for the run.

The sample delivery system supplies a mercury concentration proportional to the sample flow rate. To separate the flow rate effects from the concentration effects on the \( v_{\text{LSPR}} \) we must normalize the results to a single concentration. There is a linear relationship between concentration and \( v_{\text{LSPR}} \) for a steady flow rate, so to normalize the responses of the different exposures we multiply the \( v_{\text{LSPR}} \) by the ratio of the exposed concentration and a specified concentration. Figure 4.12 shows the experimental data normalized to a single concentration (1 ng\text{Hg/m}^3\text{air}, a typical ambient concentration\(^9\)). For flow rates below 40 LPM the flow in the Pyrex tube is laminar. The experimental results follow a square root dependence on flow rate for flows up to 40 LPM, but for 57 LPM flow (which is expected to be turbulent (Re = 3584)) the \( v_{\text{LSPR}} \) is three times faster than the laminar trend predicts. The curve showing the laminar prediction in Fig. 4.12 is a square root fit to the laminar experimental data. More detailed models will be discussed later in section 5.

The time resolution of LSPR sensing of ambient mercury needs to be competitive with the existing methods, some of which take 24 hours of collection. The time resolution is limited by the rate of adsorption, which increases with Reynolds number. At the greatest flow rate tested, 57 LPM, an ambient mercury measurement (1 ng\text{Hg/m}^3\text{air}) would take 410 hours to shift 1 nm. By accelerating the flow rate or implementing an impinging flow the time resolution can be reduced dramatically.
Figure 4.12 Normalization of all tests to a single concentration (1 ng/m$^3$) to demonstrate the effect of the sample flow rate. The experimental data (open circles) overlaid on the mass transfer models, laminar (solid line) and turbulent (dashed line).

4.2.3.7 Impinging flow

4.2.3.7.1 Introduction

Novel mercury sensing technologies would ideally provide equivalent concentration sensitivity and time resolution (minimum sampling time). For a given mass limit of detection the time resolution depends on how quickly that mass can be collected from the sample. The concentrations of interest for mercury sensing are quite low; ambient air measurements are in the ng/m$^3$ range. Models of convective mass transfer (section 5) predict that impinging flow (Fig. 4.13) will increases the collection efficiency of the trace mercury by the gold nanoparticle surfaces. This in turn reduces the time resolution improving the performance of the sensor. A full comparison of the mass transfer modes is given in chapter 5. Here we will limit the discussion to the experimental results of nanoparticle films exposed to impinging mercury flows.
4.2.3.7.2 Film characterization

For the impinging experiments we used a new film assembled with the same particles used in the cross-flow experiments. For the new film, we wanted to reduce the plasmon coupling effect that broadened the LSPR peak. To achieve this with the Langmuir-Blodgett method we used a lower surface pressure during deposition. This successfully provided a more disperse film (Fig. 4.14). Our analysis of the TEM image in Fig X with ImageJ software found the surface coverage to be 15% (less than half that of the film used in cross-flow (35%)). Plasmon coupling effects were less apparent with the LSPR wavelength at 527 nm (Fig. 4.15). The coupling effects are strongly related to inter-particle spacing and cause both red shifting and peak broadening in closely packed films. The absorbance in Fig. 4.15 is closer in shape to that of the coalesced film of larger particles (8 nm in diameter) in black in Fig. 4.10 than the densely pack film of equivalently sized particles shown in red in Fig. 4.10. Narrower peaks, smaller full-width-at-half-maximum, improve the resolving power of our LSPR wavelength determination. Narrower peaks should also result in a reduced mass limit of detection; better peak resolution means less shift is needed before an accurate slope can be attained.

Figure 4.13 Schematic of the impinging flow apparatus.
Figure 4.14 TEM image showing the packing density of the nanoparticle film used in the impinging flow experiments.
Figure 4.15 UV-vis absorbance of the nanoparticle film used in the impinging flow experiments.

The spectroscopic technique for the impinging flow is different than the transmission normal to the film used in the cross flow experiments. The reflected beam mode should theoretically yield a larger absorbance signal because the incident light passes through the nanoparticle film twice before being collected. Another benefit of the impinging flow apparatus was the fine control in the chip orientation. The mirror was mounted on a three axis adjustable optical stage.

4.2.3.7.3 Response to mercury exposure

Impinging flow tests were run at 20 LPM with 3 $\mu$g$_{\text{Hg}}$/m$_{\text{Air}}$. The first exposure to mercury vapor shifted 9 nm before the exposure ended (Fig 4.16). Saturation had not been reached after these 42 minutes. Accumulation of mercury on the gold particle had begun to impact the adsorption rate; the ninth nanometer of shift happened four times slower ($0.0015$ nm/sec) than the initial nanometers (first 5 nanometers linear at $0.006$ nm/sec).
After regeneration the response of the sensor slowed by a factor of 2, attributed to the incomplete evolution of mercury vapor. We run our regeneration routine at a reduced temperature (433 K) to protect the film morphology. Figures 4.16 and 4.17 show the differences in mercury response for a fresh nanoparticle film and a film that has been through 5 exposure/regeneration cycles. The shift after 42 minutes in the fresh film is 9.1 nm, but the used film has only shifted 5.8 nm in the same amount of time with the same conditions. The degradation in sensitivity occurs only after the first regeneration and the response thereafter is repeatable.
After the first regeneration, the response of the film to impinging samples was consistent and much faster than in cross flow. In response to repeated impinging exposures (20 LPM, 3 µg/m³), as described in the methods section, the nanoparticle film LSPR shifted 0.0030, 0.0033, and 0.0029 nm/sec for three consecutive runs. This $v_{LSPR}$ is ten times as fast that for cross flow exposures of the same concentration and flow rate; the collection efficiency in impinging flow is increased as expected (the mass transfer is modeled in chapter 5).

4.2.3.8 Interferences

LSPR shifts are not limited to the presence of mercury. The single variable signal (LSPR wavelength) is elegant but vulnerable to interference. Unchecked, interferences will affect the limit of detection of our nanoparticle based mercury sensor. Contaminants in the sample can cause changes in absorbance of the nanoparticle films, which would be superimposed with the mercury effects. We have shown how the LSPR wavelength of gold nanoparticles relates to mercury concentration and flow field for exposures to air containing mercury.

The risk posed by a contaminant depends on the strength of its impact on the absorbance of the film and the prevalence of the contaminant in the sampling environment. Previous work with mercury sensors based on resistivity of bare gold films show that selectivity restricts the limit of detection.\textsuperscript{24} Humidity, sulfuric acid vapor, volatile sulfides, volatile thiols, and halogens (iodine vapor) are all capable of producing resistivity changes equal in magnitude to 20 µg/m³ of mercury vapor.\textsuperscript{35} Rex et al. looked into the possibility of interferences from inorganic ions in their aqueous gold nanorod
based mercury detection scheme. They selected compounds as they appeared on the EPA list of potential contaminants commonly found in tap water. They chose to expose the nanorods to each contaminant at a concentration equivalent to the maximum allowable in drinking water. They found no statistically significant changes to the nanorod solution LSPR upon addition of the inorganic ions. Atomic absorption and atomic fluorescence methods for mercury measurements are also vulnerable to interference from contaminants such as water and oxygen.

Typically interfering species are removed through sample purification. The preconcentration step typical of cold vapor atomic fluorescence techniques removes the mercury from the sample stream with a gold trap. The traps are heated to vaporize the mercury which is then entrained in argon carrier gas. Other methods use traps to remove contaminants upstream of the sensor. The Jerome X-431 (see 2.3.5), a gold film resistivity based sensor, uses an acid gas filter to remove contaminants. A monolayer film on the gold surface can improve selectivity. For example, a self-assembled monolayer of hexadecanethiol blocks the effects of water and volatile sulfuric compounds.

While we hope to remove the interference from humidity in our LSPR-based sensor, other groups are attempting to exploit it for novel humidity sensing. Shinbo et al. found that the LSPR of a polyvinylalcohol (PVA) coated film of 20 nm AuNPs blue shifts ~3 nm after exposure to humidity. They attributed the blue shift to a swelling of the PVA film upon absorption of water, which reduced the local index of refraction (n). The initial peak of the nanoparticle film discussed is substantially red shifted (LSPR=543 nm) potentially due to the high index of refraction PVA coating.

We exposed a nanoparticle film to humid air in a method similar to that used for the impinging flow exposure to mercury. We generated humid air by flowing 5 LPM of dry air (Relative humidity (RH) of 1-2%) through a u-shaped silicone tube containing clean water (Millipore). The RH and temperature of the air were measured and allowed to equilibrate before the exposure began. The nanoparticle film was regenerated between exposures through gentle heating to 132 ºC for 30 minutes and cooling in a stream of dry air (5 LPM). The impinging flow was then switched to contain the humid air. The result was a near immediate increase in absorbance of the nanoparticle film and red shifts in the LSPR wavelength. After two hours of exposure to 70% RH air at 17.8 ºC the absorbance reached a new equilibrium shown in Fig. 4.18 and again across a narrower wavelength range in Fig. 4.19.
Figure 4.18 Nanoparticle film absorbance before (blue) and after (red) exposure to 70% RH air for 2 hours.
Figure 4.19 A closer look at the same data from Fig. 4.19 for a better view of the LSPR shift.

The path of the LSPR wavelength in response to humidity is similar in shape to those from mercury exposures, but in the opposite direction (Fig. 4.20). Initially the red-shifting $v_{\text{LSPR}}$ was $1 \times 10^{-3}$ nm/sec (Fig. 21), making the humidity effect for 70% RH at 17.8 °C on the same order as $\mu g/m^3$ concentrations of mercury. The saturation occurred after 4 nm of shift. The response is repeatable; four runs at 5 LPM 70% RH shifted an average of $9.3 \times 10^{-4}$ nm/sec.

Figure 4.20 Displacement of the LSPR wavelength showing the red shift and saturation during 2 hours of exposure to 70% RH air.
Saturating the nanoparticles with water before introducing the sample may remove the interference of the sample air humidity. It is possible that water-saturated nanoparticles respond to mercury vapor while no longer adsorbing water. We have not completed those experiments. The saturation in Fig. 4.20 suggests that there is a point where the red shifting response stops and the $v_{\text{LSPR}}$ is no longer affected by humidity.

4.3 Conclusions

Before this study the LSPR of gold nanoparticles, in both solutions and films, had been observed shifting after exposure to mercury vapor. These experiments are unique in that they demonstrate the quantitative strength of this LSPR sensitivity. Previous mercury vapor studies have used saturated mercury vapor ($15 \text{ mg/m}^3$). We have calibrated nanoparticle films, spherical and baculiform, to trace mercury samples down to $1 \mu\text{g/m}^3$. While not the limit of detection for the nanoparticle platform, their performance competes with state-of-the-art commercial mercury monitoring equipment.

Sensitivity, regenerability, and time resolution were best for films composed of 5 nm nanoparticles exposed to impinging samples. The small spherical particles are stable through the regeneration while also providing a larger surface-area-to-volume ratio. Impinging flow maximizes the adsorptive flux to the nanoparticle surfaces. To further develop this technique we will need a complete study of the vapor phase interferents. Humidity will obscure the presence of mercury vapor due the inverse response of the film to water adsorption. Sample purification, protective monolayer films, or presaturation with water may be solutions to the humidity interference.

5. Influence of mass transfer on gold nanoparticle based mercury sensing
5.1 Introduction

A chemical sensor has two roles: receptor and transducer; before generating a meaningful signal some minimum analyte mass must enter the system. A low analyte concentration can extend the collection time and increase the required sample volume. The minimum sample volume, with 100% collection efficiency, is the product of the inverse of the concentration and the mass limit of detection (LOD_mass) of the sensor. Lower collection efficiencies necessitate larger volumes; for a fixed flow rate this means longer collection times as well. The time resolution of the sensor is the minimum collection time needed for a measurement. Optimizing for sample volume and time resolution means designing a sensor with high collection efficiency while minimizing the LOD. Using the models and experimental results discussed herein helped us collect mercury a thousand times faster than our original setup.

Understanding the influence of mass transfer on chemical sensors is key to their design. In studying the hydrogen sensitivity of palladium metal-oxide-semiconductors (MOS), Ackelid and Petersson found that the performance of Pd-MOS capacitors varied with type of carrier gas, flow rate, and total pressure. They suggested the variances were a function of mass transfer limitations and provided a model of stagnant radial diffusion to a point sink for comparison. Later, Johansson et al. provided a model of the mass transfer and concentration profiles for catalytic-metal-gate gas sensors with internal laminar flow. While they did not attempt to model a case of turbulent flow, they predicted that turbulence would reduce the mass transfer limitation of the sensors. Lezzi et al. applied a numerical solution to the transient concentration distribution of CO in a gas sensor. Their model dealt with laminar impinging flow onto the solid-state gas sensor chip housed in a cylindrical enclosure. Unlike the previous two models, the sensor surface removed no analyte from the system. Each of these studies details the influence of mass transfer on gas sensing, and addresses, to varying degrees, issues analogical to our mercury sensor. The sensor response is not a function of mercury concentration alone, but also depends on the conditions of the mass transfer.

The receptor of a chemical sensor often employs a selectively adsorptive surface. In those cases, the collection efficiency is determined by a combination of convective and diffusive mass transfer. Diffusive mass transfer is well modeled by Fick’s Law. It states that the mass flux (J – kg/m²s) is inversely proportional to the product of the coefficient of diffusion (D – m²/s) and the gradient (spatial derivative) of the concentration (c – kg/m³). In one spatial dimension it takes its simplest form:

\[
J_1 = -D_1 \frac{\partial c_1}{\partial x}
\]

(5.1)

In his 1855 paper Fick recognized the analogy of his model for diffusion with heat and electricity: “it was quite natural to suppose, that this law for the diffusion of a salt in its solvent must be identical with that, according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same which Ohm applied with such extraordinary success, to the diffusion of electricity in a conductor.”

The time rate of change for the concentration of a diffusing species is found by inserting Fick’s Law into the conservation equation:

\[
\frac{\partial c_1}{\partial t} = J_1 \frac{\partial}{\partial x} = D_1 \frac{\partial^2 c_1}{\partial x^2}
\]

(5.2)
Bulk fluid motion enhances diffusion at the surface and increases adsorption. Flow will mix virgin sample with the lower concentration fluid near the adsorbing surface. This process increases the concentration gradient, driving faster sample collection. The analogy between diffusion and conduction allows the adaptation of convective heat transfer models to predict convective mass transfer, the mass diffusivity (D) being analogous to the thermal diffusivity (α).

Elution of trace mercury vapor from air using gold traps has widespread use in all categories of mercury analysis. Mercury vapor has a sticking coefficient of one at a gold surface, but the sticking coefficient decays as the surface collects mercury and eventually saturates at a surface coverage of about 40%. Adsorption drives a mercury concentration gradient in the fluid where mercury far from surface, at the bulk concentration, diffuses along the concentration gradient towards the lower concentration near the surface.

A model of the collection process illuminates our experimental results and directs the time resolution optimization. The LOD mass is a function of both the sensitivity of a nanoparticle film’s LSPR to adsorbed mercury and our ability to measure the changes spectrometrically. For a film of 5 nm nanoparticles with 15% surface coverage the LOD mass is 40 pg/mm², a mass of mercury that produces a 1 nm shift in the film’s LSPR. Modeling gold with a unity mercury vapor sticking coefficient simplifies the modeling and allows the assumption of zero mercury vapor concentration at the vapor/gold interface.

5.2 Diffusion in a semi-infinite medium

In the simplest case where 1-D adsorption occurs from a semi-infinite stagnant medium initially at uniform concentration, the mass flux can be calculated directly from Fick’s Law. At times greater than zero the concentration at the surface (x=0) is zero. The solution to equation 5.2 for the given boundary conditions is found through separation of variables and follows the form:

\[ c(x, t) = c_0 \text{erf} \left( \frac{x}{\sqrt{4Dt}} \right) \]  

\[ (5.3) \]
Figure 5.1 Hg concentration profiles for adsorption from semi-infinite stagnant air for times of 1 minute (--), 30 minutes (••), 1 hour (•••), 2 hours (-).

Figure 5.1 shows how the concentration profile develops with time for dilute mercury vapor in air at 295 K. The model uses a diffusion coefficient of mercury in air ($D_{Hg-Air}$) of 0.13 cm$^2$/sec at 295 K. The concentration gradient at the wall decays and the region of depleted concentration propagates into the volume. The distance from the wall that describes the volume of the depleted region at a given time is called the diffusion length ($L_D = 2\sqrt{Dt}$). The concentration at $L_D$ from the wall is 84.27% of the initial bulk concentration.

Equation 5.1 states that the mass transfer to the surface is inversely proportional to the derivative of the concentration profile at the surface ($x=0$). Combing equations (3) and (2) one finds the time dependent adsorptive flux to follow the form:

$$J_{ads} = c_0 \frac{D}{\pi t}$$  \hspace{1cm} (5.4)

The unsteady adsorption decays rapidly ($\alpha \ t^{1/2}$), limiting the functionality of a chemical sensor relying on collection from a stagnant medium. To find the concentration dependence of the time resolution we first integrate equation 5.4 with respect to time:

$$\int_0^t J_{ads} \, dt = 2c_0 \frac{D_{Hg-Air}t}{\pi} = \bar{m}_{ads}$$  \hspace{1cm} (5.5)
Here $\bar{m}_{ads}$ is the total mass adsorbed per unit area at time $t$. The time resolution ($t_{res}$) is the time when $\bar{m}_{ads}$ reaches the LOD$_{mass}$. Substituting LOD$_{mass}$ for $\bar{m}_{ads}$ and solving for $t$ we get:

$$t_{res} = \frac{\pi (\text{LOD}_{mass})^2}{4D_H \mu_{\text{g}} - A_{\text{eff}} c_g^2}$$  \hspace{1cm} (5.6)

Typical concentrations of interest are between 1-1000 µg/m$^3$; over this range the time resolution varies from 3 years to 16 minutes. A plot of $t_{res}$ over a range of µg/m$^3$ concentrations in Fig. 2 shows a log-log slope of -2 in accordance with the proportionality with concentration in equation 5.6. The nonlinear concentration dependence of the time resolution makes the low concentration measurements impractically slow without convective mass transfer. In somewhat elevated concentrations, for instance the concentrations of concern for occupational safety 25-100 µg/m$^3$ (OHSA), measurements can be taken within a reasonable time scale. The disregard for convection in this model limits its use because most all gaseous volumes have some mixing. Even though it is unlikely to encounter a truly stagnant medium in a monitoring application, this model provides a boundary on the pace of mercury collection by gold surfaces.

![Time resolution dependence on mercury concentration for adsorption from a stagnant semi-infinite medium initially at uniform concentration.](image)

**Figure 5.2.** Time resolution dependence on mercury concentration for adsorption from a stagnant semi-infinite medium initially at uniform concentration.

### 5.3 Convective mass transfer

Modeling convective mass transfer requires accounting for both the velocity and species profiles. The fluid properties at the surface differ from the upstream fluid, in our case all upstream fluid is considered uniform in speciation. The no-slip condition requires
that no relative fluid velocity occur at the surface. Similarly, a sticking coefficient of one between gold and mercury vapor forces the mercury concentration at the surface to zero. A continuum of velocities and concentrations bridge the distance between the properties at the surface and that in the free stream. This distance is called the boundary layer thickness and corresponds to the distance from the surface where a property is 99% of its free stream condition. The boundary layer for momentum is not necessarily of the same dimensions as the concentration boundary layer.

5.3.1 Diffusion in cross flow

Our first experimental method for exposing gold nanoparticle films to mercury was in cross flow at a low flow rate (15 cc/min). Sample air flowed across a nanoparticle-decorated quartz chip in a flow cell while we collected UV-Vis absorption spectra. Figure 5.3 shows the arrangement of the chip in the flow and the characteristic shape of the boundary layers.

\[ U_0, \ C_{Hg} = C_0 \]

\[ \text{boundary layer} \]

\[ \text{gold nanoparticle film on quartz chip} \]

\[ C_{Hg} = 0 \]

Figure 5.3 Diagram of laminar cross-flow

The stagnant model loses relevance upon the introduction of any bulk fluid motion near the surface. Experiments with a flowing sample demonstrate steady state adsorption of mercury and time resolutions proportional to concentration. This result is in direct disagreement with the stagnant semi-infinite model, which shows unsteady adsorption and a non-linear relationship between time resolution and concentration. A more appropriate model is necessary to consider the effects of the flow. We found the Blasius solution, otherwise termed the similarity solution, to explain the steady state adsorption and concentration proportional to the time mentioned above. It is important to note that the Blausius solution is a simplified model of our experiment. The discussion here will focus on the analytical model and later we will address fitting the model to our results and the issues that arise.

Laminar flow over a flat plate is one of a few systems with an analytical solution to the transport equations, but a number of simplifying assumptions are necessary. The flow is assumed to be laminar, steady, and incompressible with negligible viscous dissipation. The velocity boundary layer behaves independently of the concentration distribution and is solved first in accordance with Blasius’ method. The hydrodynamic solution is then coupled with the species continuity equation (shown in equation 5.7).
\[ u \frac{\partial c_{Hg}}{\partial x} + v \frac{\partial c_{Hg}}{\partial y} = D_{Hg - Air} \frac{\partial^2 c_{Hg}}{\partial y^2} \]  \hspace{1cm} (5.7)

where \( u \) and \( v \) are velocities in the x and y-direction respectively.

We then determine the mass flux to the surface,

\[ J_{ads} = 0.664 \frac{c_0 D_{Hg - Air} L}{L} Re^{1/2} Sc^{1/3} \]  \hspace{1cm} (5.8)

where \( Sc \) is the Schmidt number, and \( Re \) is the Reynolds number. Schmidt number is the mass transfer equivalent to the Prandtl number, and is calculated by the ratio of the momentum diffusivity (viscosity) to the mass diffusivity (equation 5.9). Reynolds number is a non-dimensional number used to describe the relative importance of viscous and inertial forces at a point in the flow (equation 5.10). For Reynolds numbers below 5 x 10^5 the flow over a flat plate is expected to be laminar.

\[ Sc = \frac{\mu}{\rho D_{Hg - Air}} \]  \hspace{1cm} (5.9)

\[ Re = \frac{\rho L u_0}{\mu} \]  \hspace{1cm} (5.10)

From equation 5.7 we see that the mass flux is steady, linearly related to concentration, and proportional to the square of the free stream velocity. To generate a prediction of the time resolution we integrate equation 5.8 with respect to time, set the result equal to the LOD_{mass}, and solve for the time:

\[ t_{res} = \frac{L + LOD_{mass}}{0.664 c_0 D_{Hg - Air} L} Re^{-1/2} Sc^{-1/3} \]  \hspace{1cm} (5.11)

At 1 μg/L/m^3 laminar flow outpaces stagnant exposure by a large margin. Even a rather slow velocity of 1 cm/sec outpaces the stagnant condition by more than three orders of magnitude, and increasing the flow to 10 m/sec decreases the \( t_{res} \) by another order of magnitude. At that moderate fluid velocity (Mach number of 0.029, \( Re = 11900 \)) a 1 μg/L/m^3 measurement is predicted to take 22 minutes. A plot of the fluid velocity dependence on the \( t_{res} \) for a sample of 1 μg/L/m^3 is shown in Fig. 5.4.
Figure 5.4 Time resolution dependence on fluid velocity found for laminar cross-flow using the similarity solution.

5.3.2 Comparison of laminar cross-flow experimental results with model

A comparison between the observed response of the sensor and the predictions of the model demonstrates the strengths and limits of the analytical solutions. While both the experiments and model are in cross-flow geometry, adapting the model to the experiments requires some assumptions. In the experiments the nanoparticle film is on a 1 cm square quartz chip mounted in a flow cell. This structure differs from the model, which addresses a flat plate introduced to an external and uniform flow field. To adapt the model we approximate the free stream velocity as the velocity of the fluid in the flow cell. The chip is mounted in a 1.2 cm pyrex tube, and we take the fluid velocity to be the average velocity in the tube. If the boundary layer on the chip is on the order of the tube radius, a model for internal flow may be required. To check this assumption we use equations 5.12 and 5.13 to find the boundary layer thicknesses. As the boundary layer thicknesses approach the tube radius (6 mm), the experiment performs less like the external flow described in the model.

\[
\delta = \frac{5L}{\sqrt{\text{Re}}} \tag{5.12}
\]

\[
\frac{\delta}{\delta_c} \approx Sc^{1/3} \tag{5.13}
\]

Another assumption is that the gold nanoparticle film acts similarly to the continuous bare gold film. The particles are neither continuous (they are near close packed) nor bare (they are stabilized by a polymer layer). Mirsky et al. coated gold films
with alkyl-thiol monolayers to stop them from adsorbing water. The coating suppressed the adsorption of mercury vapor as well, reducing the sticking coefficient by 50%.

The use of nanoparticles as opposed to continuous films may appear to reduce the adsorptivity because the non-adsorbing substrate is exposed. A film of 5 nm nanoparticles covering 15% of the chip’s surface provides gold of a surface area (calculated as the spherical surface area of all the particles combined) that is 60% the surface area of the chip.

The time resolution appears to follow the predicted square root flow rate dependence but the model under-predicts the time resolution by a factor of ~6 (Fig. 5.5). Both the model and experiments show a linear relationship between $t_{res}$ and concentration. The low $t_{res}$ predicted by the cross flow model could be in part be explained by the existence of the coating on the nanoparticles and the reduced gold surface area in the somewhat disperse film. We can assume that the adsorptive flux rate is halved due to the surface coating and that the mass collection efficiency is proportional to the total gold surface area. Then the disparity between model and experiment is then less than a factor of 2.

The collection efficiency compares the actual collection rate to the ideal case, perfect collection. Beyond offering another method of comparing two exposure methods, the collection efficiency gives an engineer a sense of how much room for improvement remains for a design. In the best performing cross-flow experiment, lowest $t_{res}$, the adsorptive flux during a 1 µg/m$^3$ exposure at 57 LPM was 0.28% of the total mercury mass flow rate. For a steady flowing system the collection efficiency is independent of mercury concentration.

We can check the appropriateness of the external flow model by comparing the boundary layer thicknesses (momentum and concentration) at the end of the chip. In the case of a 20 LPM flow the momentum and concentration boundary layer thicknesses are 1 and 3 mm respectively by the end of the chip. These boundary layers, while smaller than the radius of the tube (6 mm), are large enough to make the experimental flow noticeably different than the external flow of the model. The momentum profile in particular will be affected by the momentum gradient caused by the flow retarding tube walls.
Figure 5.5 Comparison of calculated and observed $t_{res}$ for cross flow as a function of flow rate for a mercury concentration of 1 µg/m$^3$.

An obvious feature of the experimental $t_{res}$-data is the divergence from the square root dependence for the tests at 57 LPM (two points in the lower right corner of Fig. 5.5). At these flow rates the sensor responds much faster than predicted by the lower flow rate experimental trend of square root dependence on flow rate. This result can be explained by a transition to turbulence in the flow cell. The tube diameter is 1.2 cm and should transition to turbulent flow at around 45 LPM. Turbulent mass transfer to a flat plate, in the external flow condition has a stronger dependence on flow rate and the $t_{res}$ is predicted to follow,

$$t_{res} = \frac{L^* \cdot LOD_{mass}}{0.0370 c_0 D_{Hg-Air}} \cdot Re^{-4/5} \cdot Sc^{-1/3}$$  \hspace{1cm} (5.14)

Equation 5.14 is not predictive for our experiments because the Reynolds number of the tube-flow is high enough to cause turbulence while the chip’s Reynolds number is still below the transition point. The Reynolds number dependence, which is equivalent to velocity dependence, suggests that turbulent flows have a sharper decrease in time resolution with increases in velocity. The experimental results at 57 LPM show a drastic decrease in $t_{res}$ but no higher flow rates were tested due to the limits of our compressed air source and the pressure head in our manifold. Higher Reynolds number flows in a small diameter flow cell would require less volumetric flow rate but we were limited in this respect by the dimensions of our nanoparticle film chip. Rather than changing a
successful protocol for making the sensor chips to fit a smaller flow cell we decided to explore other flow geometries.

5.3.3 Impinging flow

Impinging flow from a jet of fluid onto a surface is used in industrial processes for enhanced drying, cooling, and heating. Flow over the surface under highly turbulent jets will have narrow boundary layers with sharp gradients that expedite heat and mass transfer. Another advantage is the spatial control and flexibility of an impinging jet system; the size, number, and arrangement of the jets are all variable.

The simplest case, a single jet perpendicular to the surface from a round nozzle, will be discussed here. A diagram of the jet showing the geometry and qualitative flow character appears in Fig. 5.6. The flat velocity profile at the nozzle exit is characteristic of turbulent flow, but after leaving the nozzle the jet diameter grows, decreases in fluid momentum, and the velocity profile changes shape. The flow is symmetric about the jet centerline and therefore the mass transfer solution at the surface has only a radial spatial variation. There are no transverse (radial) velocity components at the centerline but near the surface in the impingement zone the normal velocity is diverted into transverse causing radial acceleration in the flow. Moving further away from the stagnation point (r and y=0) there is transverse deceleration as the wall jet boundary layer grows in its cylindrical cross section.

Figure 5.6. Impinging flow diagram.

Heat and mass transfer with impinging jets at solid surfaces have been widely studied. Martin compiled five sets of data for single round nozzles and averaged the results to generate an empirical correlation for the transfer coefficients. The result was
the following empirical equation for the Sherwood number (Sh), the mass transfer equivalent of the Nusselt number:

\[
\frac{Sh}{Sc^{0.42}} = \frac{D}{r} \left( 1 - \frac{1.1D}{r} \right) F(Re) \]

(5.15)

This representation is found to be applicable for radial distances more than 2.5 nozzle diameters. The function of Reynolds number, F(Re), can be approximated by a range appropriate power function:

\[
F(Re) = \begin{cases} 
1.36Re^{0.574}, & (2000 < Re < 30,000) \\
0.54Re^{0.667}, & (30,000 < Re < 120,000) \\
1.51Re^{0.775}, & (120,000 < Re < 400,000)
\end{cases}
\]

Martin also presented continuous function for F(Re):

\[
F(Re) = 2Re^{1/2} \left( 1 + \frac{Re^{0.55}}{200} \right)^{0.5}
\]

(5.16)

having a suggested range of validity:

\[
2000 \leq Re \leq 400,000 \\
2.5 \leq r/D \leq 7.5 \\
2 \leq h/D \leq 12
\]

The Reynolds number for the single round nozzle is based on the nozzle diameter and flow rate:

\[
Re = \frac{\rho VeD}{\mu} \quad (5.17)
\]

\[
Ve = Q \frac{4}{\pi D^2} \quad (5.18)
\]

where Q is the volumetric flow rate (m³/sec). For a given flow rate the Reynolds number is therefore inversely related to the nozzle diameter.

This model is steady state; therefore the time resolution is the ratio of the LOD mass and the mass flux to the surface. Adapting equation 5.15 to calculate the \(t_{res}\):

\[
J_{ads} = c_0 D_H g - A_{ir} Sh/r \\
\frac{t_{res}}{J_{ads}} = \frac{LOD}{J_{ads}} \quad (5.19)
\]

(5.20)

Similar to the cross-flow system, the mass flux is proportional with concentration but the much greater turbulence is possible at the same flow rates. The curve in Fig. 5.7 follows the sensitivity of the time resolution to changes in the nozzle diameter for a fixed volumetric flow rate (20 LPM) and mercury concentration (3 µg/m³). The time resolution is on the order of a few minutes for nozzles between 1.1-6 mm. The reduction in \(t_{res}\) projected by switching from a cross-flow to an impinging sample exposure is more than a factor of 10.
Figure 5.7. Model prediction of \( t_{\text{res}} \) for impinging flow for different nozzle diameters.

In response to the projected accelerated response, we built an apparatus for impinging exposures. Using the same nanoparticles the response to the impinging flow was 10 times faster than the cross flow for the same flow rate and concentration. While the response is relatively quick, the collection efficiency is still small. For the 1 mm diameter nozzle the square centimeter chip only adsorbs 1.6% of the total mercury in the sample.

Our impinging flow exposure apparatus consisted of a steady flow of sample gas from a nozzle closely spaced and perpendicular to the sensor chip. We ran two runs with the following conditions for comparison with the model:

\[
D = 1.9 \text{ mm} \\
Q = 20 \text{ LPM} \\
h = 10 \text{ mm} \\
c_0 = 3 \mu g/m^3
\]

where \( Q \) is the volumetric sample flow rate. \( D \) and \( h \) are the nozzle diameter and separation distance from the surface (as shown in Fig. 5.6).

The measured time resolution averaged 320 seconds. The model predicts a \( t_{\text{res}} \) of 162.3 seconds. The error is about one third that between the cross-flow model and experiments. The slower response of the experiment may be due to the surface coating on the particles, under-coverage of the surface by the particles, and/or dilution by the
ambient air (the set up was uncontained and vulnerable to mixing). Correcting for these potential sources of error would require experimental investigation of their individual effects.

5.4 Conclusions

The three models presented describe the adsorption of mercury vapor from air that can be used in the design of mercury collecting and measuring devices. The simplest case, adsorption from a semi-infinite stagnant medium is unsteady (at \( t^{1/2} \)) and quickly decays to an adsorption rate insufficient for useful mercury measurements or removal. By adding convective transport the rates are greatly increased, up to seven orders of magnitude, by collecting the samples from an impinging jet.

Experimental results for the two convective cases were used to evaluate the utility of the simplified models. The result of the cross-flow model accurately predicts the observed \( t_{res} \) dependence on the flow rate. The impinging model was in closer agreement with the experimental results but still generated time resolutions 27% the experimental results. The models tend to over estimate the adsorptive flux. Treating the nanoparticle film as a continuous bare gold film may to blame for this error. The actual gold surface area in the nanoparticle film is 60% that of a continuous film and the surface is coated with a polymer to stabilize the particles through the assembly process. Future experiments with bare nanoparticle films and varying surface packing of the particles are necessary to assess these factors.

The models also suggest improvements to \( t_{res} \) without changing the characteristics of the film (coating, packing, LOD). By shrinking the nozzle diameter in the impinging jet the time resolution will go down, but the pressure difference across the nozzle will increase. Increasing turbulence through the use of obstructions in the flow will also increase the collection efficiency without the need for higher flow rates. Single digit collection efficiencies are unlikely to be the limit of a feasible collector, so by implementing one or more of these tactics, nanoparticle based mercury sensing should advance its position to the most sensitive method for mercury sensing.

References


59. Witucki, L. A silane primer : chemistry and applications of alkoxy silanes. 65, (Federation of Societies for Coatings Technology: Blue Bell, PA, ETATS-UNIS, 1993).
70. James, J. Z., D. Lucas & C. Koshland Mercury vapor interaction with individual gold nanorods.
Appendix I

This appendix includes a discussion of an alternative model to that provided in section 3. The models both attempt to relate the effects composition changes on the optical response of individual gold nanorods to saturation with mercury vapor and the role of the initial particle geometry on the magnitude of the shift in LSPR peak. The intent of the model is to explain the experimentally observed phenomena and to inform the optimization of the mercury sensor.

Individual nanorods exposed to elemental mercury vapor have a limited capacity for mercury adsorption. After exposure to μg/m³ mercury vapor sample for 1 hour the LSPR wavelength of particles tested in section 3 (~20x60 nm) blue-shifted an average of 3
nanometers. These shifts did not depend on the concentration of mercury vapor during exposure, suggesting that the particles were saturated. The observed saturation agrees with previous work with gold nanoparticles exposed to mercury vapor.\textsuperscript{51,52,54} EDX analysis of the saturated particles found them to be 1.5±1.1% mercury; this percentage is equivalent to 45% monolayer coverage of mercury. A similar capacity (~40% monolayer) for mercury adsorption was found for single crystal gold films.\textsuperscript{67} Mercury vapor adsorbed onto gold surfaces does not immediately diffuse into the gold to create a homogenous alloy, but remains near the surface.\textsuperscript{54,67} Therefore, the gold/mercury nanoparticles are likely composed of a gold core and a mercury enriched surface.

We simulate the scattering of these bimetallic baculiform nanoparticles by approximating them as confocal core/shell ellipsoids. Liu et al. proposed a core/shell model to reproduce the experimentally observed spectra of gold/silver core shell nanorods.\textsuperscript{91} Our model is analogous to that of Liu et al., with mercury instead of silver as the shell material. Our prediction required an additional consideration for calculating the dimensions of the shell for a given core geometry. The Liu et al. model describes a prolate spheroidal dielectric ($\epsilon_1$) core, with semiaxes $a_1 = b_1 < c_1$, is coated with a confocal spheroidal dielectric ($\epsilon_2$) shell with semiaxes $a_2 = b_2 < c_2$. In the confocal condition the shell and core geometries follow the relation:

$$c_2^2 - a_2^2 = c_1^2 - a_1^2$$  \hspace{1cm} (1)

The particle is immersed in a medium ($\epsilon_m$). With the dipole approximation, the polarizabilities along the principal axes are

$$\alpha_1 = \alpha_2 = \frac{v[(\epsilon_2 - \epsilon_m)(\epsilon_2 + (\epsilon_1 - \epsilon_2)(L_1^{(1)} - fL_1^{(2)})] + f(\epsilon_1 - \epsilon_2))}{[(\epsilon_2 + (\epsilon_1 - \epsilon_2)(L_1^{(1)} - fL_1^{(2)})][\epsilon_m + (\epsilon_2 - \epsilon_m)L_1^{(2)}] + fL_1^{(2)}\epsilon_2(\epsilon_1 - \epsilon_2))}$$  \hspace{1cm} (2)

$$\alpha_3 = \frac{v[(\epsilon_2 - \epsilon_m)(\epsilon_2 + (\epsilon_1 - \epsilon_2)(L_3^{(1)} - fL_3^{(2)})] + f(\epsilon_1 - \epsilon_2))}{[(\epsilon_2 + (\epsilon_1 - \epsilon_2)(L_3^{(1)} - fL_3^{(2)})][\epsilon_m + (\epsilon_2 - \epsilon_m)L_3^{(2)}] + fL_3^{(2)}\epsilon_2(\epsilon_1 - \epsilon_2))}$$  \hspace{1cm} (3)

where $v = 4\pi a_2^2 c_2 / 3$ is the volume of the particle, $f = a_1^2 c_1 / a_2^2 c_2$ is the volume fraction occupied by the core, and $L_1^{(k)}$ and $L_3^{(k)}$ ($k = 1, 2$) are the geometrical factors defined as\textsuperscript{91}

$$L_3^{(k)} = \frac{1}{e_k^2} \left( \frac{1}{2e_k} \ln \frac{1+e_k}{1-e_k} - 1 \right)$$  \hspace{1cm} (4)

$$e_k^2 = 1 - \frac{a_k^2}{c_k^2}$$  \hspace{1cm} (5)

$$L_1^{(3)} = \frac{1}{2} (1 - L_3^{(k)})$$  \hspace{1cm} (6)

The scattering cross section is evaluated by the optical theorem,

$$C_{sca} = \frac{\omega^4 \varepsilon_m^2}{6\pi \varepsilon^4} \left[ \left( \frac{2}{3} \right) |\alpha_1|^2 + \left( \frac{1}{3} \right) |\alpha_3|^2 \right]$$  \hspace{1cm} (7)

We assume that the mass of mercury adsorbed at saturation is proportional to the surface area of the particle. We set the factor between surface area and mercury mass using the EDX composition measurement (1.5% Hg) and the average particle dimensions (20x62 nm). The resulting simulated spectra reproduce the results very well (Fig. 1). We also tested the predictive power of the model by feeding it with all the measured particle dimensions. The results are shown in Fig. 2. The average percent difference is 6.75%. 

94
Figure 1 Modeled scattered spectra from 20 x 62 nm particle for before (green) and after (blue, dashed) saturation with mercury ($\epsilon_m = 2.5$).
Figure 2 Model predicted shifts (squares) at saturation compared to the experimental results (circles).

The core/shell model also agrees with the observed trends in particle shape. Both aspect ratio and surface area to volume ratio show positive correlation with blue shift in LSPR wavelength at saturation (Fig. 3 and 4). The two models, core/shell and homogenous alloy (described in section 3), provide equivalent reproduction of the experimental results. One advantage of the core shell model is that it predicts the entire scattered spectrum and not simply the location of the bimetallic particle LSPR peak wavelength. Both models achieve their purpose; they provide an analytical framework to predict the response of gold nanoparticles to mercury vapor, which can direct the optimization of a practical sensor.
Figure 3 Core/shell model approximation of shifts at saturation for a range of aspect ratios with a constant surface area to volume ratio.
Figure 4 Core/shell model approximation of shifts at saturation for a range of surface area to volume ratios and a constant aspect ratio (3).