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Synthesis, characterization and photocatalytic activity of Au-ZnO heterostructures

Oshadha Kanchana Ranasingha

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Synthesis, characterization and photocatalytic activity of

Au-ZnO heterostructures

Oshadha Kanchana Ranasingha

Dissertation submitted to the

**Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Physics**

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**Morgantown, West Virginia
2015**

**Keywords: Au-ZnO heterostructures, plasmonic heating,
photocatalysts, Au nanoparticles, CO₂ conversion**

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Abstract

Synthesis, characterization, and photocatalytic activity of Au-ZnO heterostructures

Oshadha Kanchana Ranasingha

Heterostructures of semiconductor metal oxides and metals have been studied extensively due to the synergistic photocatalytic activity they display. Gold-Zinc oxide (Au-ZnO) heterostructured photocatalysts are one of the most widely studied photocatalysts due to the high photocatalytic activity of ZnO and the ability of Au to transfer photoexcited electrons away from ZnO, which leads to enhanced carrier separation and improved catalytic activity. Au heterostructuring is also known to alter the electronic structure of ZnO leading to better photochemical band alignment and a decreased work function which both contribute to enhanced catalytic activity. The use of Au to form heterostructures with ZnO also opens the possibility of using its plasmonic activity for engineering the photophysics of this system through plasmonic heating or optical field enhancement. As such, it is interesting to synthesize a variety Au-ZnO heterostructures and correlate the catalytic activity of these materials with structural details such as nanoparticle morphology, lattice dynamics at the interface, and the general crystallinity of the two materials forming the heterostructure.

In this work, I have synthesized, characterized, and investigated two types of Au-ZnO heterostructured catalysts and evaluated their activity for carbon dioxide (CO₂) conversion and waste-water remediation applications. The Au-ZnO catalysts were characterized using Transmission Electron Microscopy, Scanning Electron Microscopy, X-Ray Diffractometry, Raman spectroscopy, UV-Vis absorption spectroscopy and Fourier Transform Infrared spectroscopy. Initial efforts focused on simple heterostructures made by soaking nanocrystalline

ZnO in a Au salt with a subsequent heat treatment to reduce the Au to its metallic state. This resulted in ~20 nm Au particles dispersed on ZnO at ~5 wt % loading. Plasmonic excitation of the Au nanoparticles also heats the ZnO substrate it is grown on up to ~600 °C and drives the catalytic conversion of CO₂ and hydrogen (H₂) to methane (CH₄), carbon monoxide (CO), and water (H₂O) on the ZnO portion of the heterostructure. In addition, I have also investigated methods to increase the Au-ZnO ratio and to improve the degree of contact between these two materials. For these efforts, ZnO nanopyrramids were grown on Au seeds using a wet-chemical method. Electron microscopy was used to characterize an unusual and large lattice expansion for ZnO at the Au interface in these samples. Optical measurements of these samples point to subtle electronic structure changes caused by the Au that improve band alignment for the production of radicals from photoexcited carriers in the ZnO. The improved production of radicals in turn leads to an enhanced photodegradation of organic contaminants in water. In addition to experimental work, computational calculations were performed in order to calculate vibrational modes, phonon spectral density and plasmon relaxation time constants. Two Au clusters (Au₂₀ and Au₅₅) which contain 20 and 55 of Au atoms respectively were used for the calculations.

Dedicated to my father Mr. Danasiri Ranasinghe and my mother Mrs. Chandralatha Ranasinghe.

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Chapter 1

Introduction

1.1 Heterogeneous photocatalysts

Heterostructures of semiconductor metal oxides and metals have been studied extensively over the past few decades for photocatalysis due to their enhanced catalytic activity over just the semiconductor metal oxide alone.¹⁻⁸ Size and shape tunable properties of metal nanoparticles will open a wide range of applications for metal-oxide heterostructures such as photovoltaics, optoelectronics, plasmonics, CO₂ conversion, photodegradation of organic pollutants, photochemical water splitting, solar energy conversion, bio-medical applications, solar vapor generation and sterilization of surgical equipment.^{6, 9-15} The heterogeneous photocatalysis is still continuously investigated in the fields of Physical Chemistry, Applied Physics, Chemical Engineering and Materials Science due to their higher demand.^{22, 23}

The heterogeneous photocatalysis can be identified as a material which increases the rate of the photo reaction in the presence of the heterostructured catalyst.²² The discovery of photo-electrochemical water splitting in to hydrogen and oxygen in 1972 by Fujishima and Honda²⁴ using a n-type TiO₂ as a photoanode irradiated with UV inspired many researches to focus on heterogeneous photocatalysis. Wide band gap semiconductor metal oxides such as TiO₂ and ZnO are among the two materials most widely investigated semiconductor metal oxide based photocatalysts due to their low cost, long term photo stability and nontoxicity.²⁵ However, poor optical activity, rapid electron-hole recombination after the photoexcitation, low efficiency of

carrier separation and unfavorable band alignment for photo-reactions can be identified as major problems with these wide band gap semiconductor metal oxide photocatalysts.²⁶⁻²⁸ One of the main goals of this dissertation work is, addressing the above mentioned major problems in metal-semiconductor metal oxide photocatalysts. Heterostructures of semiconductor metal oxides and metals such as Au-ZnO, Ag-ZnO, Au-TiO₂ and Ag-TiO₂ can be identified as one of the solutions for above mentioned problems.^{1, 4, 8, 29-32} These heterostructured photocatalysts usually show higher photocatalytic activity over the oxide itself due to improved charge separation mechanism, plasmonic heating and field enhancement created by surface plasmon resonance of metal.^{12, 15, 22, 33} Since noble metal particle plays a main role in the catalysis process, it can be identified as a metal co-catalyst.²²

1.2 Au-ZnO heterostructures

ZnO is a wide band gap (3.3 eV) semiconductor metal oxide with high exciton binding energy (60 meV) and high electron mobility at room temperature ($157 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).^{13, 34-36} Many researchers attempted to overcome the major problems of the catalytic efficiency of ZnO which were mentioned earlier (mainly poor optical activity and electron-hole recombination).³⁷⁻⁴² In fact, heterostructures of Au and ZnO are one of the most widely studied photoactive materials due to the higher charge separation efficiency and enhanced photocatalytic activity imparted to the ZnO by the addition of Au.^{2-4, 6} As such, Au-ZnO heterostructures can be used for CO₂ conversion, solar energy conversion to electricity, photodegradation of organic pollutants, and photochemical water splitting.^{6, 12-15} Due to the large band gap of 3.3 eV ($\lambda \sim 375 \text{ nm}$), ZnO can only absorb UV radiation which is 4-5 % of the solar spectrum (Figure 1.1).³⁶ Therefore, it is still challenging to utilize the solar spectrum effectively with ZnO based catalysts. The surface plasmon resonance of Au

nanoparticles in Au-ZnO heterostructures enable it to access the visible range of solar spectrum. Figure 1.2 shows the diffuse reflectance spectra for pure ZnO and Au-ZnO heterostructures.¹² The broad absorption peak between 500 - 600 nm is due to the surface plasmon resonance of Au nanoparticles.

Figure 1.1 Comparison of solar intensity as function of wavelength¹⁶

Figure 1.2 Comparison of diffuse reflectance spectra of pure ZnO and Au-ZnO¹²

1.2.1 Surface plasmons

Optical properties of metallic nanoparticles have a very long history and beautifully colored stain glass windows in historic chapels is an evidence for this. However, the first scientific observation of surface plasmons was done by Robert W. Wood in 1902.⁴³ In 1904 James Clerk Maxwell Garnett explained the bright colors observed in metal doped glasses using the Drude theory of metals with the help of electromagnetic properties of small spheres derived by Lord Rayleigh.⁴⁴⁻⁴⁶ Then in 1908, Gustav Mie introduced the famous theory of light scattering by small spherical particles.⁴⁷ In 1956, David Pines theoretically explained the characteristic energy losses experienced by fast electrons travelling through metals and he called these oscillations as “plasmons”.⁴⁸ In the same year, Robert Fano introduced the term “polaritons” for the coupled oscillations of bound electrons and light inside transparent media.^{45, 49, 50} In 1957, Rufus Ritchie studied electron energy losses in thin films and published the first theoretical description of surface plasmons.⁵¹ Then in 1968, Ritchie explained the anomalous behavior of metal gratings in terms of surface plasmon resonance excited on the gratings.⁵² In the same year, Otto and Kretschmann proposed methods for the optical excitation of surface plasmons on metallic films.^{53, 54} In 1970, for the first time Kreibig and Zacharias explained the optical properties of metal nanoparticles in terms of surface plasmons and they compared the responses of optical and electronic properties of gold and silver nanoparticles.⁵⁵ After that, research based on plasmon resonance was rapidly expanded due to the wide range of practical applications like surface enhanced Raman scattering (SERS), data storage, solar cells and sensors etc.^{45, 50, 56}

Surface plasmons can be identified as collective oscillations of free electrons in the interface between metals and dielectrics.^{45, 57} Generally, surface plasmons are divided in to propagating

surface plasmons and localized surface plasmons.^{56, 58} Propagating surface plasmons can be excited in metallic films and localized surface plasmons can be excited in metallic nanoparticles.⁵⁶ Surface plasmons are responsible for strong enhancement of local electromagnetic field due to the strong interaction with light.⁵⁷ Oscillations of the free electrons on metals that are responsible for localized surface plasmons are confined to the surface of the metallic nanoparticles and strongly interact with light. When irradiated with light at the plasmon resonance frequency of metallic nanoparticles, they generate an intense local electromagnetic field at the surface of those metallic nanoparticles.⁵⁷ The plasmon resonance frequency depends on the material of the nanoparticles, surrounding medium, size of the nanoparticles and shape of the nanoparticles.⁵⁷ Figure 1.3 shows the field distribution at metal-dielectric interface and the decay of electric field strength in the direction of Z axis.⁵⁹

Figure 1.3 (a) The field distributions of electron charge density fluctuations in metal-dielectric interface (b) The exponential decay of the electric field in the direction Z at the metal-dielectric interface with the characteristic lengths¹⁹

Figure 1.4 shows the absorption, scattering and extinction spectra of different shapes and sizes of Ag nanoparticles. A similar trend can be observed for Au nanoparticles.¹⁹ This allows to tune the surface plasmon resonance frequency of noble metal particles in a wide range.

Figure 1.4 Calculated extinction (black), absorption (red), and scattering (blue) spectra for Ag nanoparticles of different shapes: (a) sphere (b) cube (c) tetrahedron (d) octahedron and (e) triangular plate.¹⁸ (f) Calculated extinction spectra of rectangular Ag nano bars with different aspect ratios of 2 (black), 3 (red), and 4 (blue).²¹

1.2.2 Surface plasmons induced hot electron assisted photocatalytic activity of Au-ZnO

The hot electron injection from plasmonic Au nanoparticles to ZnO (semiconductor metal oxide) was reported by several previous work.^{2, 5, 20, 60} However, hot electron injection from metal to semiconductor is still inefficient due to the energy loss by ultrafast relaxation of hot electrons to lower energy level via electron-electron and electron-phonon scattering.⁶¹⁻⁶³ In these metal – semiconductor heterostructured catalysts, there is a Schottky barrier which is formed at the metal – semiconductor interface.^{42, 64, 65} In general, Schottky barrier forms when two materials with different work functions are in contact. The work function of ZnO and that of Au are 5.3 eV and 5.1 eV respectively.^{66, 67} Since Au has a lower work function compared to the ZnO, during the formation of the Schottky barrier electrons flow from Au to ZnO in order to equilibrate the Fermi level.⁶⁰

This Schottky barrier inhibits the rapid recombination of electron-hole pairs.³⁰ Since new Fermi energy level is below the conduction band of the semiconductor, photo excited electrons can transfer from semiconductor to the metal which avoids the recombination of photoexcited electrons and holes.³⁰ However, hot electrons should have an energy higher than the Schottky barrier in order to overcome the barrier.⁶⁸ Figure 1.5 shows a schematic diagram for the organic dye degradation using the Au-ZnO heterostructures illuminated by visible light.⁶⁰ Plasmon induced hot electrons are injected in to the conduction band of the ZnO from Au. Here, the role of Au is visible light harvesting and facilitating the charge transfer process.²⁰ Injected electrons in conduction band react with adsorbed O₂ to generate superoxide radicals (O₂^{•-}). Then, superoxide radicals generate hydroxyl radicals (OH[•]) with water. Also, *Yu et al*²⁰ reported that holes in Au

also generate the $\text{OH}^\bullet$ radicals. Both radicals are responsible for degradation of organic dye molecules.⁶⁰

Figure 1.5 Proposed mechanism for the photodegradation of organic dyes with Au-ZnO heterostructures under visible light illumination.²⁰

1.2.3 Photocatalytic activity of Au-ZnO under UV illumination

The photocatalytic activity of Au-ZnO heterostructures is more efficient under the UV illumination compared to the visible light illumination.²⁰ Under UV illumination, hot electron generation is very efficient due to the band gap excitation of ZnO. Photodegradation of organic dyes using the Au-ZnO under UV illumination was reported in several previous work.^{1, 4, 6, 8, 20, 69-71} The photodegradation mechanism under UV illumination is slightly different compared to visible light illumination. Under UV illumination, it is possible to excite the band gap of ZnO as well as surface plasmons of Au in Au-ZnO heterostructures. Therefore, both mechanisms might be responsible for generation of reactive oxygen species under broadband illumination. Since both mechanisms generate the same reactive oxygen species, it is difficult to evaluate the efficiency of each

mechanism using broadband or white light illumination. However, it is possible to evaluate the efficiency of each mechanism separately when using the long pass filters (more details discussed in Chapter 6). *He et al*⁷¹ identified the reactive oxygen species generated from Au-ZnO under simulated sunlight illumination. Figure 1.6 shows the proposed mechanism by *Fageria et al*⁶⁰ for photodegradation mechanism of organic dyes using Au-ZnO heterostructures under UV illumination.

Figure 1.6 Proposed mechanism for the photodegradation of organic dyes with Au-ZnO heterostructures under UV light illumination.²⁰

Under UV (energy greater than the band gap = 3.3 eV) illumination, photoexcited electrons in the conduction band of ZnO will be injected in to the Au while holes are created at the valence band of the ZnO.²⁰ In this mechanism, the role of Au is very important since Au acts as an electron

reservoir to avoid the quick electron-hole recombination in ZnO. Hydroxyl radicals are generated at the valence band of the ZnO in addition to the conduction band of ZnO and surface of the Au.²⁰

1.3 Plasmonic heat generation

Noble metal nanoparticles have an extremely large absorption cross section at their plasmon wavelength.⁷² In other words, metal nanoparticles can absorb a large amount of light and almost completely convert it to heat at the surface plasmon resonance frequency.⁷² Plasmonic heat generation from the metal nanoparticles have been already reported by several previous work.⁷²⁻⁷⁸ Due to the possibility of synthetically tuning the surface plasmon resonance frequency in visible and near infrared range, these metal nanoparticles are suitable candidates for laser induced drug release, bio imaging, thermally driven photocatalysis, steam generation, sterilization, water-ethanol distillation and developing sensors.^{10, 12, 77, 79} When the nanoparticles are illuminated by an electromagnetic field, a portion of the electromagnetic field is scattered and the rest is absorbed by the nanoparticles.⁸⁰

The scattered light does not contribute to the plasmonic heating and only the absorbed light generates heat. After the light absorption by nanoparticles, the electromagnetic field at the interface of the metal-dielectric drastically increases. This very high electromagnetic field is highly localized and the generated heat is transferred in to the vicinity of few nanometers. In other words, it is possible to heat up the highly localized area surrounded by the Au nanoparticles in Au-ZnO heterostructures without increasing the temperature of the bulk sample. The amount of heat generation depends on various factors such as material of the nanoparticles, size of the nanoparticles, geometrical shape of the nanoparticles, surrounding medium and the intensity of the

illuminating electromagnetic radiation.¹⁷ Figure 1.7 shows calculated heat generation for different shapes of Au nanoparticles.¹⁷ When the aspect ratio were changed from spheres to tubes, the maximum heat generation peak was red shifted and it can be attributed to the red shifting of the wavelength of plasmon resonance. *Govorov et al*⁸¹ used simplified Mie theory in order to calculate the temperature at the surface of spherical shaped Au nanoparticles. Chapter 5 discusses the plasmonic heat assisted photocatalytic activity of Au-ZnO heterostructures in detail.

Figure 1.7 Calculated heat generation spectra for different sizes of Au nanoparticles. Aspect ratios starting from sphere 1:1, 1.4:1, 2:1, and 3:1.¹⁷

1.3.1 Importance of ZnO for plasmonic heating assisted photocatalysis

ZnO based catalysts such as Cu-ZnO are a good candidate for methanol synthesis from CO₂ using water-gas shift reactions. However, the reactions should be carried out at higher temperatures in order to achieve maximum efficiency.^{82, 83} Since increasing the temperature of ZnO using an energy source which generates CO₂ is not worthwhile, plasmonic heating was used to increase the temperature of ZnO in this work (see Chapter 5 for more details). Since plasmonic heat generation is a highly localized process in nanoscale, still there is no method to directly measure the local temperature. The temperature dependent behavior of some Raman modes of ZnO such as $E_2(\text{high})$ can be used to investigate the local temperature of ZnO.⁸⁴⁻⁸⁷ Since ZnO has good catalytic activity for CO₂ conversion and possibility to investigate the local temperature using temperature dependent Raman spectra, ZnO was identified as a good candidate for making heterostructures with Au for plasmonic heating-assisted CO₂ conversion.

1.4 Importance of CO₂ conversion

The energy demand of the United States as well as in the world increases every year with increasing population and the growth of the economy.¹² According to statistics, fossil fuels will supply 80 % of the world energy demand for at least next few decays.⁸⁸ Burning of fossil fuels release tons of CO₂ in to the environment. CO₂ is a greenhouse gas and excess CO₂ mainly results in increasing the earth's temperature. As a result of increased earth's temperature, a variety of critical problems can be expected such as melting polar ice and rising sea level, undesirable effects on agriculture, extreme weather conditions and spread of diseases. The main natural CO₂ removal method is the photosynthesis by plants. However, increasing deforestation results in inefficient

photosynthesis. The natural option is unable to handle huge amounts of CO₂ outputs from the world fossil fuel consumption. Therefore, atmospheric CO₂ concentration increases each year. The atmospheric CO₂ concentration was ~ 280 ppm before the industrial revolution and it is expected to reach ~ 570 ppm at end of this century.⁸⁹

1.5 Computational calculations

It is very important to understand the properties of the materials using computational calculations. Even though it is difficult to model the actual experimental work, it will help to explore more insight of the materials. In this work, computational calculations were performed in order to calculate vibrational modes, phonon spectral density and plasmon relaxation time constants. Two Au clusters (Au₂₀ and Au₅₅) which contain 20 and 55 of Au atoms respectively were used for the calculations. The diameter of Au₅₅ is around ~ 1.4 nm and it is not possible to use larger Au nanoparticles due to long simulation times and necessity of the high computational power.

The eigen vectors of vibrational modes of the Au₂₀ cluster were used to calculate the phonon spectral density. Au₅₅ has a moderate size and the Density Functional Theory (DFT) calculations on it gives more reliable data which can be compared with experimental data. It was used to investigate the plasmon relaxation dynamics. For all the DFT calculations, BLYP (Becke's 1988 exchange functional with the correlation functional by Lee, Yang, and Parr) method and SNP (Single Numerical basis set including d-polarization function) basis were used to describe the electronic wave function.

1.6 Structure of the dissertation

Chapter 2 explains the brief theory behind each of the various type of experimental technique which were utilized for material characterization. Chapter 3 explains the computational work for vibrational modes and phonon spectral density calculations for the Au_{20} cluster. Plasmon relaxation dynamics of Au_{55} is explained in Chapter 4. Chapter 5 consists of all the details of synthesis and characterization of Au-ZnO heterostructures, plasmonic heating assisted CO_2 conversion and local temperature estimation using the temperature dependent phonon model. Chapter 6 discusses the study of Au-ZnO heterostructures as a photocatalyst for waste water remediation.

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Chapter 2

Experimental Techniques

2.1 Introduction

In order to characterize the Au-ZnO heterostructures, various experimental techniques were used. Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffractometry (XRD), Fourier Transform Infra-Red spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), diffuse reflectance spectroscopy and UV-VIS absorption spectroscopy were mainly used for characterization. Gas Chromatography was used to identify the products of CO₂ reduction reactions. In addition to characterization and product identification, Raman spectroscopy was used to develop an indirect method to estimate the local temperature of ZnO nanoparticles. Also, O₂ plasma etching was used to remove the excess organic molecules after the synthesis of Au-ZnO nanopyrramids.

2.2 Transmission Electron Microscopy (TEM)

JEOL JEM-2100 Transmission Electron Microscope (TEM) equipped with a Lanthanum hexaboride (LaB₆) thermal filament was used to obtain both conventional and high resolution TEM images. Since the work function of LaB₆ is lower than the work function of tungsten, LaB₆ filament is more efficient than the tungsten filament.¹ There are two digital Gatan cameras available in this TEM including ES500W which is capable of high speed and high quality imaging with a field of view larger than a traditional TEM film. ES500W is used to obtain conventional TEM images. SC1000 Orius is the latest generation retractable and fiber optical coupled 11

Megapixel CCD camera which provides high quality and > 14 frames per second fast images for high resolution images.

TEM follows the same basic principle as light microscope.² However, TEM uses a high energy electron beam as the source instead of light in the light microscope. Also, TEM uses electromagnetic lenses instead of usual glass lenses to focus the electron beam.^{3, 4} The circular electro magnets generates a precise circular magnetic field which acts like an optical lens to focus the electron beam.⁵ The high energy electron beam generated from cathode goes through the specimen and some of the electrons are scattered from the atoms of the material. The electron beam is accelerated by the positive anode.⁵ The aperture is a thin disk with a small circular hole (2-100 μm) which is used to restrict the electron beam and filter out the unwanted electrons.⁵ The unscattered electrons are focused in to the fluorescent screen to make a shadow image.² The darkness of the image depends on the density of the material in that area.² Three types of lenses can be seen in TEM. The purposes of the condenser lens and objective lens are to control the illumination of the sample and magnify the sample respectively.⁴ At the end of the electron beam path, the projection lens generates an amplified image.⁴ The most important component of the TEM is the electron gun. Also, it is necessary to maintain an Ultra-High Vacuum (UHV) to create insulation between the anode and the cathode.⁴ Figure 2.1 shows the schematic diagram of the TEM.⁶ According to Abbe's equation, the theoretical resolution of a microscope can be calculated as follows:⁴

$$R = \frac{0.61\lambda}{\eta(\sin \theta)} \quad (\text{Equation 2.1})$$

where R is the resolution of the microscope, λ is the wavelength of the light, η is the index of refraction of the environment surrounding the lens and ϑ is the angle of illumination. The denominator of the above equation represents the numerical aperture of the objective lens.⁴ According to the wave-particle duality of light, it is possible to calculate the wavelength of the electrons using the DeBroglie wave equation:^{4, 7}

$$\lambda = \frac{h}{mv} \quad (\text{Equation 2.2})$$

where λ is the wavelength of the accelerated electrons, h is the plank's constant, m is the mass of the electron and v is the velocity of the electrons.

Figure 2.1 The schematic diagram of the Transmission Electron Microscope⁶

If the electron is accelerated with the potential drop V , the wavelength of the electron can be written as,

$$\lambda = \frac{h}{\sqrt{2m_0V(1+\frac{V}{2m_0c^2})}} \quad (\text{Equation 2.3})$$

where m_0 is the rest mass of the electron. The usual operating voltage of TEM is around 100-300 kV. Therefore, it is possible to observe the samples in atomic scale (10^{-10} m). Also, when it is operated in high resolution mode (HRTEM), it is possible to observe the atomic planes which help to measure the lattice spacing of the crystal planes.

2.3 Scanning Electron Microscopy (SEM)

JOEL JSM-7600F Scanning Electron Microscope (SEM) is equipped with a thermal field emission gun as an electron source and was used to investigate the surface morphology of the Au-ZnO heterostructures. Electron beam is focused using the electromagnetic lenses as same as in TEM (Figure 2.2).⁸ In general, the electron beam is accelerated by 200 V – 40 kV voltage and a nanometer level resolution can be achieved.⁴ The electron beam bombards the surface of the sample and the secondary electrons are collected while the electron beam striking position is moving smoothly.⁹ Two pairs of scanning coils are used to deflect the electron beam in x and y directions in order to perform the line by line scan (raster scan). The electron beam penetrate (depth of the interaction volume) around 2 μm (Figure 2.3) and several types of signals can be detected after bombarding the primary electron beam in to the sample.^{4,5} Different types of detectors collect the output signals from the sample to generate the image.

Figure 2.2 The schematic diagram of the Scanning Electron Microscope⁸

Figure 2.3 Illustration of the sample interaction volume and corresponding particles emitted from sample depth⁵

The Secondary Electron (SE) and Backscattered Electron (BSE) detectors are the mostly used detectors. The inelastic scattering of electrons by atoms generate low energy secondary electrons with energy less than the 50 eV.⁴ Due to their low energy, these secondary electrons needed to be accelerated to the photomultiplier via a scintillator. Also, they originate close to the sample surface. The elastic scattering of electrons by atomic nuclei of the sample generate the backscattered electrons with energy greater than the 50 eV up to the energy of the incident beam. Since they have higher energy, they can get scattered out of the interaction volume. The brightness of the backscattered electrons depends on the atomic number of the specimen. Elements with higher atomic numbers are brighter than the elements with lower atomic numbers.⁸ Secondary electrons provide a high resolution image and back scattered electrons provide a relatively low resolution image compared to the secondary electrons. The inelastic scattering near to the surface (Figure 2.3) generate Auger electrons which is useful for surface chemical analysis.⁴ The characteristic X-rays are generated at the lower sample depths (Figure 2.3) due to the inelastic scattering of the electrons.⁴

2.4 Diffuse reflectance spectroscopy

Perkin Elmer LAMBDA 1050 UV/Vis/NIR Spectrophotometer was used to characterize the powder samples of Au-ZnO heterostructures that is mentioned in Chapter 5. There are several reflection types that can be used for material characterization such as specular reflection, diffuse reflection, internal reflection and attenuated total reflection.⁸ The specular reflection usually occurs on smooth polished surfaces.⁸ In fine powder samples, there are a large number of particles with smooth surfaces. Therefore, when the incoming radiation strikes the fine powder sample, specular reflection occurs on all smooth surfaces (Figure 2.4).¹⁰ However, since these smooth

surfaces of the particles are randomly oriented, the incoming radiation reflects in all the directions. Typically, the intensity of the reflected radiation is independent of the viewing angle.⁸

Figure 2.4 The schematic diagram showing the difference between specular reflection and diffuse reflection¹⁰

The most common model for the intensity of reflected radiation that was originally developed by Kubelka-Munk and Fullar-Griffith showed that the relative intensity of the reflected radiation of the powder sample can be given by the following equation.¹¹⁻¹³

$$f(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{k}{S} \quad \text{(Equation 2.4)}$$

where R_{∞} is the ratio of reflected intensity of the sample to a non-absorbing standard like finely ground KCl, k is the molar absorption coefficient of the analyte and S is the scattering coefficient. Usually, the percentage of R_{∞} is plotted with the wavelength.⁸

2.5 UV-VIS absorption spectroscopy

Agilent 8453 UV/Vis/NIR Spectrophotometer was used with a quartz cuvette to obtain the absorption spectra of Au-ZnO nanopyramids dissolved in hexane. Also, it was used to obtain absorption spectra of methylene blue dye during the dye degradation experiments discussed in Chapter 6. Ultra Violet (190 nm to 400 nm) – Visible (400 nm to 800 nm) absorption spectroscopy is commonly used for the quantitative analysis of a variety of inorganic, organic and biological species.^{8, 14} Incoming radiation is absorbed by the atoms, ions or molecules in an analyte solution due to the electron transition from lower energy states to the higher energy states. According to the Beer-Lambert law, absorption is linearly proportional to the concentration and path length of the sample as follows:^{13, 14}

$$A = -\log T = \log \frac{P_0}{P} = \epsilon bc \quad (\text{Equation 2.5})$$

where A is the absorbance, T is the transmittance, P_0 is incident the radiation power, P is the transmitted radiation power, ϵ is the molar absorptivity, b is the path length of the sample and c is the concentration of the absorber.⁸

As shown in Figure 2.5, two air-wall interfaces and two solution-wall interfaces are in the beam path and those interfaces are responsible for beam attenuation.^{8, 15} Also, the scattering from larger atoms, ions or molecules and absorption from the walls of the glass cell affects the transmitted radiation power.⁸ A glass cell with only the solvent is usually used as a reference to remove these affects.

Figure 2.5 The schematic diagram of the UV-Vis spectrophotometer¹⁵

2.6 X-ray diffractometry

PANalytical X'pert Pro powder X-Ray diffractometer was used to take the X-ray diffraction data in order to identify the crystal structures of Au-ZnO heterostructures as well as for Rietveld refinement analysis. X-ray diffraction is a very common experimental technique that is used to investigate the structure of crystalline materials. X-ray beams are generated in four different ways such as by bombarding a metal target with a beam of high energy electrons (Figure 2.6), by exposing a substance to a primary beam of X-rays to generate a secondary beam of X-ray fluorescence, by a radioactive decay process and from synchrotron radiation sources.^{8, 16} When the X-ray beam reaches the atomic planes of the material; transmittance, absorption, refraction, scattering and diffraction can be occurred. By collecting the diffracted X-ray photons, it is possible to plot a graph of intensity versus scattering angle. Each crystalline element has a unique X-ray

diffraction pattern which is characteristic of the crystalline structure of that element. There are two main requirements for X-ray diffraction.

1. The spacing between the layers of atoms is roughly equal to the wavelength of the X-ray radiation.
2. The scattering centers must be spatially distributed in a highly regular way

Using the Bragg's law (41), it is possible to calculate the distance between two atomic planes (d – spacing) in a crystalline structure. Bragg's law:

$$n\lambda = 2d \sin\theta \quad (\text{Equation 2.6})$$

where n is the order of the diffracted beam, λ is the wavelength of the X-ray radiation, θ is the incidence angle of the X-ray beam and d is the distance between the adjacent atomic planes.

Figure 2.6 The schematic diagram of the X-ray generation from high energy electrons¹⁶

2.7 Fourier Transform Infra-Red spectroscopy (FTIR)

Perkin Elmer – Spectrum 100 Optica FTIR spectrometer was used to obtain FTIR spectra of Au-ZnO nanopyramids before and after O₂ plasma etching in order to confirm the removal of organic ligands. Since molecules are made with a unique combination of atoms, their vibrational spectra are also unique.¹⁷ Also, these vibrations are in IR region which means IR spectra can be used to identify the materials. Since the size of the IR peak is proportional to the amount of the material present in the sample; this technique was used to confirm the removal of the organic molecules. In FTIR spectrometers, an interferometer is used to measure all the frequencies simultaneously and it generates a unique signal (interferogram) which contains the information about all the IR frequencies generated from the source.¹⁷ This signal is converted to a frequency spectrum by a computer algorithm and this method is extremely fast compared to the old dispersive type instruments. Figure 2.7 shows the schematic diagram of the generation of an FTIR spectrum.¹⁸

Figure 2.7 The schematic diagram of the generation of FTIR spectrum¹⁸

2.8 Gas Chromatography (GC)

Perkin Elmer Clarus 600 Gas Chromatograph equipped with Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID) was used to identify the CO₂ reduction products that are discussed in Chapter 5. The basic principle of GC is volatilization of the sample in a heated inlet followed by the separation of components in the special columns and detect at the detector according to the retention time of each component.¹⁹ Therefore, materials which vaporize without decomposition can be analyzed using the GC. In general, a carrier gas or mobile phase (usually H₂ or He) transfers the sample from the inlet to the detector. The stationary phase is coated in the inner wall of the column. The separation of the components depend on the distribution of each component between the mobile phase and the stationary phase.¹⁹ For an example, a component which stays a little longer in the stationary phase will leave the column later. In other words, the peak corresponding to the component that stays a longer time in the stationary phase can be seen at end of the “intensity versus retention time” graph. There are several detectors specifically designed for the GC such as TCD (Thermal Conductivity Detector) and FID (Flame Ionization Detector).

2.8.1 Thermal Conductivity Detector (TCD)

Thermal Conductivity Detector (TCD) is a non-destructive detector and it consists of two channels (Figure 2.8): one for the mobile phase with the eluate and the other for the pure mobile phase.²⁰ Since TCD is non-destructive, it is possible to transfer the eluate to a different detector after the TCD. The TCD acts as a Wheatstone bridge circuit with four filaments (resistors).¹⁹ The components with different thermal conductivities change the temperature and resistance of the

filament compared to the reference channel. Since helium has a higher thermal conductivity than the most analytes, usually helium is used as the mobile phase.

Figure 2.8 The schematic diagram of the thermal conductivity detector²⁰

2.8.2 Flame Ionization Detector (FID)

FID is mostly used to detect the components which have C-H bonds.¹⁹ FID needs hydrogen gas and air to make a flame at the tip of the flame jet (Figure 2.9).²¹ Analyte eluate burns at the flame and produces ions and the amount of the ions is proportional to the concentration of the component. The positive ions are collected by the negatively biased collector and are amplified electronically.²¹

Figure 2.9 The schematic diagram of the flame ionization detector²¹

2.9 Oxygen (O_2) plasma etching

March PX-250 O_2 Plasma Asher was used to remove the excess organic ligands in Au-ZnO nanopyrramids after the wet chemical synthesis. Plasma etching is a chemical etching method which means the unnecessary molecules can be removed from the sample after a chemical reaction between the plasma and the atoms in the sample. In general, O_2 plasma is generated in a vacuum chamber which has a constant O_2 gas flow and a radio frequency potential generator.²² O_2 gas is partially ionized when it is exposed to the radio frequency potential at the reduced pressure (~ 300 mTorr in this work). As a result of this ionization, it creates atomic oxygen which are more active than the oxygen molecules.⁶ Atomic oxygen reacts with organic molecules and converts them in to water and carbon dioxide that will be removed from the chamber via a vacuum pump (Figure 2.10).²³

Figure 2.10 The schematic diagram of the O_2 plasma etching²³

2.10 Raman spectroscopy

Renishaw InVia Raman Spectrometer with a Crystal 532-100 green laser was used to investigate the plasmonic heating effects of Au-ZnO heterostructures. In general, Raman spectroscopy is used to identify the vibrational states of the materials based on the inelastic scattering of monochromatic radiation.^{10, 24} The changing polarizability of the molecule is responsible for the Raman scattering.²⁵ The scattered light can be divided into two components as Rayleigh scattering which has the same frequency (ν_{ex}) as incident light (elastic scattering) and Raman scattering which has a slightly higher or lower frequency ($\nu_{\text{ex}} \pm \nu_{\text{v}}$) compared to the incident light. ν_{v} is the vibrational frequency of the molecule.²² Also, Raman scattering is very weak and usually the signal intensity is 10^5 times lower than the incident light intensity.²² The higher frequencies ($\nu_{\text{ex}} + \nu_{\text{v}}$) and lower frequencies ($\nu_{\text{ex}} - \nu_{\text{v}}$) are called as anti-stokes peaks and stokes peaks respectively (Figure 2.11).⁸

²² Under the laser illumination, molecules get excited into a virtual energy state from a low energy vibrational state and then relax back. Since the population is higher in ground vibrational state compared to first excited vibrational state, stokes peaks (Figure 2.11) are relatively more intense than the anti-stokes peaks.

Figure 2.11 The schematic diagram of the stoke and anti-stokes lines⁸

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Chapter 3

Vibrational modes and phonon spectral density of Au₂₀ clusters

3.1 Introduction

Vibrational spectroscopy can be used as an efficient tool to identify the different isomers of small gold clusters.¹ Using vibrational spectroscopy, *Gruene et al* confirmed the pyramidal structure (tetrahedral) for neutral Au₂₀.² The tetrahedral Au₂₀ cluster was widely studied due its high symmetry. The group theory predicted 23 non-degenerate vibrational modes (Equation 3.1) with irreducible representation of tetrahedral Au₂₀.³

$$\Gamma_{\text{vib}} = 4A_1 + A_2 + 5E + 5T_1 + 8T_2 \quad (\text{Equation 3.1})$$

According to the group theory, 9 vibrational modes with symmetry of A₁ and E are Raman active and 8 modes with T₂ symmetry are both Raman and IR active. The modes with A₂ and T₁ are silent for both Raman and IR.³ In previous work, vibrational modes of Au₂₀ that were calculated using different approximations, methods and basis can be found.¹⁻⁷

Geometrical structure optimization, molecular dynamic (MD) simulations and vibrational modes calculations were performed using the FIREBALL⁸⁻¹⁰; a local-orbital density functional theory (DFT) package. For all the calculations BLYP method and SNP basis were used. The phonon density of states of tetrahedral Au₂₀ were calculated by taking the Fourier transform of the velocities from MD simulations.

3.2 Geometrical structure optimization of Au₂₀

The geometrical structure optimization was run until it reached a very stable structure. The time step size was 1 fs and RMS cutoff was set as 0.05. The structure reached RMS value after 823 time steps and the calculated band gap was 2.18 eV. Figure 3.1 shows the optimized structure of Au₂₀ and Figure 3.2 shows the variation of the total energy during the geometrical structure optimization. Tetrahedral Au₂₀ cluster consists of 3 types of atoms such as 4 apex atoms with coordination number = 3, 4 center atoms with coordination number = 9 and 12 edge atoms with coordination number = 6.³⁻⁶ Also, it contains 54 Au-Au bonds including 6 bonds between middle edge atoms, 24 bonds between center atoms and edge atoms, 12 bonds between middle edge atoms in opposite edges and 12 bonds between apex atoms and edge atoms.⁷

The bond distances and bond angles of optimized Au₂₀ structure were measured using the Jmol; an open-source Java viewer for chemical structures in 3D.¹¹ Table 3.1 shows the detail comparison of the main parameters of the Au₂₀ cluster with previous work. Differences between calculated values from previous literature can be seen in Table 3.1 since the calculated values largely depend on the calculation method and basis set. In this work, the band gap for the tetrahedral Au₂₀ cluster was found to be 2.18 eV and this value is fairly large when compared to the experimental value of 1.77 eV measured by *Li et al*⁶ using X-ray photoelectron spectroscopy. Also, *Flores*⁷ calculated the band gap as 1.90 eV using PBE method and DNP basis. *Molina et al*³ calculated the band gap of Au₂₀ cluster as 1.92 eV and 2.96 eV using BP86 and B3LYP methods respectively. However *Molina et al*³ used the same LANL2DZ basis for both calculations, which means almost ~ 1 eV difference of the band gap can be observed just for the difference in the calculation method.

Our calculated a-e bond distances (see the Figure 3.1) well matched the values calculated by *Kryachko et al*⁵ and *Flores*.⁷ Also, the longest e-e bond distance in this work was compatible with the values of *Kryachko et al*⁵ while the c-e bond distances agreed with the values published by *Kryachko et al*⁵ and *Flores*.⁷ The c-c bond distance was within the error less than 10 % of the value calculated by the *Molina et al*.³ The Au-Au-Au bond angles which were calculated in this work well matched the values reported by *De et al*⁴ within the error less than 5 %. Also, to the date there is no theoretical calculations of Au₂₀ cluster available with BLYP method and SNP basis.

Figure 3.1 Optimized tetrahedral structure of Au₂₀, 'a','c' and 'e' represent apex, center and edge atoms

Figure 3.2 Variation of the total energy during the geometrical structure optimization

3.3 Vibrational modes of Au₂₀

The vibrational modes of Au₂₀ cluster were calculated using the eigen values of dynamical matrix which was calculated using the FIREBALL package. The dynamical matrix consists of second derivatives of the energy with respect to the geometry of elements.¹² Forces are the first derivatives with respect to the geometry. The second derivatives were calculated using the two forces in to opposite directions and the displacement. As the first step, one atom of the optimized structure was moved in to one direction and self-consistent field¹³ (SCF) calculations were performed to obtain the force. Then, the same atom was moved in to the opposite direction and performed SCF calculations and obtained the force. After that, the difference of these two forces was divided by the displacement of the atom in order to get the second derivatives of the energy with respect to the geometry. This procedure was performed for all Au atoms in x,y and z directions.

Table 3.1 Comparison of main parameters of the tetrahedral Au₂₀ neutral cluster after the geometrical structure optimization.

Reference	Method	Basis	ΔE_{HL} (eV)	HOMO (eV)	Highest vibrational frequency (cm ⁻¹)	Lowest vibrational frequency (cm ⁻¹)	Au-Au distances (Å)	Au-Au-Au bond angles (Å)
This work	BLYP	SNP	2.18	-4.64	195.80	25.32	a-e (longest) = 2.76 a-e (shortest) = 2.75 e-e (longest) = 3.09 e-e (shortest) = 2.68 c-e (longest) = 2.89 c-e (shortest) = 2.81 c-c (longest) = 3.44 c-c (shortest) = 3.06	e-a-e (largest) = 68.3 e-a-e (smallest) = 63.8 e-c-e (largest) = 177.2 e-c-e (smallest) = 163.4 a-e-e (largest) = 178.2 a-e-e (smallest) = 175.5 e-e-e (largest) = 63.1 e-e-e (smallest) = 57.2
Sekhar De et al ⁴	B88	RECP					a-e = 2.80 e-e = 2.74 c-e = 2.93 c-c = 3.34	e-a-e = 67.0 e-c-e = 170.4 a-e-e = 175.6 e-e-e = 60.0
Kryachko et al ⁵	BP86	LANL2DZ		-6.02	172	28	a-e = 2.76 e-e (longest) = 3.01 e-e (shortest) = 2.71 c-e = 2.86	
Kryachko et al ⁵	B3LYP	LANL2DZ		-6.40	161	26	a-e = 2.80 e-e (longest) = 3.08 e-e (shortest) = 2.73 c-e = 2.91	
Flores ⁷	PBE	DNP	1.9		181.4	16.2	a-e = 2.75 e-e (longest) = 3.00 e-e (shortest) = 2.71 c-e = 2.86	
Molina et al ³	BP86	LANL2DZ	1.92	-6.03	172.35	29.13	2.71, 2.76, 2.87, 3.01, 3.13	
Molina et al ³	B3LYP	LANL2DZ	2.96	-6.41	162.22	26.42	2.73, 2.79, 2.91, 3.08, 3.21	
Li et al ⁶	X-Ray Photoele ctron Spectros copy (experi mental)		1.77				2.68, 2.71, 2.83, 2.97 3.12 (calculated)	

60 frequencies were obtained since there are $3n$ (n = number of atoms) degrees of freedom in Au_{20} cluster in x, y and z directions. However, $3n$ degrees of freedom include translational and rotational motion of the Au_{20} cluster as well. The first six frequencies of the FIREBALL output correspond to the 3 rotational frequencies and 3 translational frequencies. The remaining 54 frequencies are actual vibrations. The highest vibrational frequency found to be as 195.80 cm^{-1} in this calculations which is 8 % higher than the calculated value by *Flores*.⁷ The lowest vibrational frequency found to be as 25.32 cm^{-1} , which well agrees with the calculations done by the *Kryachko et al.*⁵ All 54 vibrational modes can be seen in Figure 3.3. Due to the tetrahedral structure of Au_{20} , there is a large number of degenerate modes. The 23 distinct vibrational modes (Equation 3.1) were identified by *Molina et al.*³

Figure 3.3 Vibrational modes of Au_{20} cluster

The schematic diagrams of eigen vectors from *Molina et al*³ were used to identify the symmetry of vibrational modes of this work. Figure 3.4 shows the eigen vectors for highest vibrational mode (195.80 cm^{-1}) which is the 4th mode of A_1 symmetry. Only the tangential atoms were involved in this A_1 vibrational mode and there is no considerable displacement in four center atoms. The Raman breathing mode (3rd mode of A_1 symmetry) with the frequency of 105.32 cm^{-1} can be seen in Figure 3.5. This breathing mode shows identical radial displacement in all 20 atoms. Also, degeneracy of some symmetries were identified. For an example, the 6th mode of T_2 symmetry has a degeneracy of 3 around 129.05 cm^{-1} (Figure 3.6)

Figure 3.4 Schematic diagram of a highest vibrational mode (4th mode of A_1 symmetry)

Figure 3.5 Schematic diagram of a Raman breathing mode (3rd mode of A_1 symmetry)

Figure 3.6 Schematic diagram of a degenerate 6th mode of T_2 symmetry (mode 49, 50 and 51)

3.4 Phonon spectral density of Au₂₀

Phonon spectral density is another way to investigate the vibrational spectrum of Au₂₀. The phonon spectral density gives the number of vibrational states that can occupy the phonons per unit volume of crystal per unit energy.¹⁴ The Fourier transform of the velocity auto-correlation (VAC) function was taken to calculate the phonon spectral density.^{8, 14-16} The Molecular Dynamics (MD) simulations were performed at 300 K in order to obtain the atomic velocities. The time step was 1 fs and the total duration of the MD simulation was 50 ps. The velocity auto-correlation function can be expressed as follows¹⁴:

$$VAC(t) = \frac{1}{N} \sum_{n=1}^N \frac{\langle v_n(t).v_n(0) \rangle}{\langle v_n(0).v_n(0) \rangle} \quad (\text{Equation 3.2})$$

where,

$$\langle v_n(t).v_n(0) \rangle = \frac{1}{M} \sum_{m=1}^M v_n(t_m).v_n(t_m + t) \quad (\text{Equation 3.3})$$

$$\langle v_n(0).v_n(0) \rangle = \frac{1}{M} \sum_{m=1}^M v_n(t_m).v_n(t_m) \quad (\text{Equation 3.4})$$

t is the time, N is the number of atoms and M is the number of time origins (time steps). $v(t_m)$ and $v(t_m + t)$ are the atomic velocities at the reference time and delay time in the simulation respectively. $v_n(0)$ is the velocity at the zero correlation time. The phonon spectral density (PDS) given by¹⁴,

$$PDS(\omega) = \int_{-\infty}^{\infty} VAC(t) \cos(\omega t) dt \quad (\text{Equation 3.5})$$

The VAC function was calculated over all 20 atoms in Au₂₀ cluster for all x, y and z directions. Four MD simulations were run in order to reduce the signal to noise ratio that might affect the PDS

spectrum. Figure 3.7 shows VAC functions for four different MD simulations and Figure 3.8 shows the average VAC function which was used to calculate the PDS spectrum. During the MD simulations, there are strong interatomic repulsive and attractive forces acting on the atoms, but the atomic positions will remain nearly constant. Therefore, the motion of the atoms can be seen as oscillations. The atoms vibrate forward and backward while reversing the velocity at the end of each oscillation.¹⁷ As a result of this, VAC function shows a strong oscillatory behavior at the beginning and decays eventually.

Figure 3.7 VAC function for 4 different MD simulations

Figure 3.8 Average VAC function which used to calculate the phonon spectral density

The calculated phonon spectral density spectrum can be seen in Figure 3.9 and it closely agrees with the vibrational modes which were calculated in section 3.3. The most dominant peak can be seen around 46.7 cm^{-1} and based on the eigen vectors of the vibrational modes it can be identified as the 1st mode of A_1 symmetry where only the center atoms are displaced perpendicular to the plane.

Figure 3.9 Phonon spectral density spectrum of Au₂₀ cluster. Red lines show the distinct peaks

3.5 Conclusion

Most stable tetrahedral structure⁶ for Au₂₀ (among the other possible structures such as icosahedral and octahedral) was used for calculations. The vibrational spectrum of the Au₂₀ cluster was investigated in two different methods (vibrational modes calculations using dynamical matrix and phonon spectral density calculation). The Au-Au bond distances and Au-Au-Au bond angles of optimized structure well agreed with the values reported in literature. The symmetry of some vibrational modes were identified using the eigen vectors. Some discrepancies can be found in this work and previous work probably due to the differences of computational methods. However, there is no experimental work to compare these results yet.

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Chapter 4

Phonon-induced relaxation of plasmon excitation in Au₅₅ clusters

4.1 Introduction

Noble metal nanoparticles have been extensively studied in different areas such as bio-sensing, photocatalysis, nanophotonics, plasmonics, solar cells and data storage for years due to their remarkable optical activity. Surface plasmons are mainly responsible for this remarkable optical response and this is potentially useful for many applications. Therefore it is very important to understand the surface plasmon relaxation dynamics of metal nanoparticles in order to develop novel systems with surface plasmons. Usually relaxation of plasmons via electron-phonon interactions takes from 1 to 10 ps.¹

The electron density localization of each energy state allows to identify them as bulk, surface or plasmon states.² *Guo et al*² showed the difference between the electron density localization in the Ag₁₀₄ for bulk, surface and plasmon states. The electron densities of the plasmon states are highly delocalized compared to the bulk and surface states. The delocalization of electron density increases with the energy of the plasmon states.¹ A nano cluster consists of 55 Au atoms was used in this work in order to investigate the plasmon relaxation dynamics in Au nanoparticles. The Au₅₅ was extensively investigated in both computational and experimental works.³⁻⁸ Also, the size of Au₅₅ (d ~ 1.4 nm) is a moderate size for the Density Functional Theory (DFT) calculations and gives more reliable data which can be compared with experimental data.⁴ However, electron relaxation dynamics for the Au₅₅ is not well understood. There are two previously proposed

electron relaxation pathways; molecular like relaxation⁸ and bulk like relaxation⁷ based on the electron relaxation of ligand attached Au₅₅ clusters. Therefore, it is worthwhile to perform a computational investigation for plasmon relaxation dynamics in Au₅₅.

4.2 Geometrical optimization

The icosahedral structure⁴ of Au₅₅ (Figure 4.1) which is the most stable structure⁹ among the other high symmetry structures such as cuboctahedral and decahedral was used for this work. First, geometrical structure optimization of Au₅₅ was performed at 300 K using FIREBALL¹⁰⁻¹²; a local-orbital DFT package to identify the lowest energy structure. Time step size was 1 fs and RMS cutoff was set as 0.05. The variation of total energy of the Au₅₅ cluster can be seen in Figure 4.2.

Figure 4.1 Icosahedral structure of Au₅₅

Figure 4.2 The variation of total energy of the Au₅₅ cluster during the geometrical structure optimization

4.3 Identify the plasmon states

Electron densities of all the energy states which are above the LUMO (lowest unoccupied molecular orbital) state were investigated in order to identify the highly delocalized plasmon states. The arbitrary state number came from the computational output but they represent consecutive energy states. The difference of the electron density localization between surface states and plasmon states can be clearly seen. Figures 4.3 to 4.5 show the electron densities of HOMO (highest occupied molecular orbital) state, LUMO state and the first state above the LUMO state respectively. Figures 4.6 to 4.10 show five plasmon states which were chosen based on the localized electron densities for this work. According to Figures 4.6 to 4.10, electron densities extended far away with respect to the Au atoms for plasmon states.

Figure 4.3 HOMO state (S_{303})

Figure 4.4 LUMO state (S_{304})

Figure 4.5 State 305 (S_{305})

Figure 4.6 Plasmon state (S_{338})

Figure 4.7 Plasmon state (S_{339})

Figure 4.8 Plasmon state (S_{341})

Figure 4.9 Plasmon state (S_{342})

Figure 4.10 Plasmon state (S_{343})

The energies of the HOMO state (S_{303}) and LUMO state (S_{304}) were found to be -3.85 eV and -3.25 eV respectively. Table 4.1 shows the energies of the 5 plasmon states which were investigated in this work. The position of the energy eigen value was used as the state number. Figure 4.11 show the locations of each HOMO, LUMO and 5 plasmon states along with the density of states of Au_{55} .

Table 4.1. Energy of each initial plasmon state

Plasmon state	Energy (eV)
S_{338}	-0.2116
S_{339}	-0.1820
S_{341}	+0.3973
S_{342}	+0.6832
S_{343}	+0.8090

Figure 4.11 Density of states of Au₅₅ and energy of plasmon states

4.4 Non-adiabatic molecular dynamics (NAMD) simulations

4.4.1 Computational method

For non-adiabatic molecular dynamics (NAMD) simulations, it is necessary to keep the inter relation between nuclear motion and electronic quantum state while atoms follow the classical trajectories.¹³ The time dependent Schrodinger equation was used to explain the time evolution of

the electronic wave function.¹³ Usually single particle Hartree Fock (HF) or Kohn-Sham (KS) orbitals are used to solve the time dependent Schrodinger equation.¹³ The different potential energy surfaces (PES) can be calculated using these single particle orbitals.¹³

The time evolution of single particle KS orbital¹³ can be written as:

$$\hat{H}_{KS}\varphi_P = i\hbar \frac{\partial \varphi_P}{\partial t} \quad (\text{Equation 4.1})$$

$$\hat{H}_{KS}(R)\psi_i = \varepsilon_i(R) \psi_i \quad (\text{Equation 4.2})$$

is the single particle KS Hamiltonian and

$$\varphi_P(r, t) = \sum_i a_i(t) \psi_i(r, R) \quad (\text{Equation 4.3})$$

is the time evolving KS orbitals. The $a_i(t)$ in the Equation 4.3, can calculate using the equation:

$$\frac{\partial a_i(t)}{\partial t} = a_i(t) \varepsilon_i(R) - i\hbar \sum_j a_j(t) d_{ij} \cdot V \quad (\text{Equation 4.4})$$

where $d_{ij} \cdot V$ represent the coupling between classical motion of the nuclei and the electronic quantum state.¹³

$$d_{ij} \cdot V = \sum_{\alpha} d_{ij}^{\alpha} V_{\alpha} \quad (\text{Equation 4.5})$$

where $d_{ij}^{\alpha} \equiv \left\langle \psi_i \left| \frac{\partial \psi_j}{\partial R_{\alpha}} \right. \right\rangle$ are the non-adiabatic coupling vectors (NACV) between the single particle

KS states¹³ and $V_{\alpha} = \frac{\partial R_{\alpha}}{\partial t}$ is the atomic velocity.¹⁴

Usually, Ehrenfest dynamics^{15, 16} and surface hopping^{17, 18} are used for NAMD simulations. The surface hopping method is better than the Ehrenfest method where changes in electronic populations affects the nuclear motion. The fewest switches surface-hopping (FSSH) algorithm¹⁷ was used for NAMD methodology. The hopping probability depends on both non-adiabatic coupling vector and the atomic velocity.¹⁴ NACV's are calculated during the simulation using the previously implemented efficient algorithm.¹³ During the electronic transitions, nuclear velocities were rescaled to conserve the energy.¹⁴ If the kinetic energy present is sufficient, hopping in to the higher energy state is possible. As a result of this, it is possible to see up and down electron transition among the energy states during the NAMD simulations.

4.4.2 NAMD simulations

An electron was removed from the HOMO state and placed it in one of the 5 plasmon states in order to simulate the plasmon excitation. The excited electron relaxes during the NAMD simulation which was performed for 10,000 time steps at 300 K. The total simulation time was 30 ps (time step size is 3 fs). Fifty NAMD trajectories were performed in order to reduce the error for each plasmon excitation. Random initial coordinates and initial velocities were generated using an automated python script.

The electron population of each energy state between the specific plasmon state and HOMO state were extracted for all the 50 NAMD trajectories and the average was used to generate the population plots (Figures 4.12 to 4.16). For an example, there were 36 energy states involved in electron relaxation from the S₃₃₈ (plasmon state) to S₃₀₃ (HOMO state). Similarly 37, 39, 40 and 41 energy states were involved for electron relaxation from the states of S₃₃₉, S₃₄₁, S₃₄₂ and S₃₄₃ in

to the state S_{303} . Figures 4.12 to 4.16 show the variations of average population of all the energy states which were involved for the electron relaxation from each plasmon state. It was found that state S_{331} highly populated during the electronic relaxation process regardless of the energy of the initial plasmon state. The HOMO state in black color, initial plasmon state in blue color and state S_{331} in red color can be seen. The populations of the other states were faded for clarity of the major states.

Figure 4.12 The populations of all the states between HOMO state and initial plasmon state S_{338}

Figure 4.13 The populations of all the states between HOMO state and initial plasmon state S_{339}

Figure 4.14 The populations of all the states between HOMO state and initial plasmon state S_{341}

Figure 4.15 The populations of all the states between HOMO state and initial plasmon state S_{342}

Figure 4.16 The populations of all the states between HOMO state and initial plasmon state S_{343}

The maximum average population (from 50 trajectories) of each energy state (except HOMO state and plasmon state) were plotted as a function of state number (Figure 4.17).

Figure 4.17 Average maximum populations at each state for five different initial plasmon states

According to the Figure 4.17, state S_{331} at -0.8148 eV shows the dominant maximum average population compared to the other states regardless of the energy of the initial plasmon state. Then, the populations of the state S_{331} were investigated and it was found that the population remain above 0.4 for more than 1 ps during the relaxation from all 5 initial plasmon states (Figures 4.18 to 4.22). Also, it is very clear to identify the average population variation of highly populated long living state S_{331} in Figures 4.12 to 4.16 (in red color). The average population variation of initial plasmon state, S_{303} (HOMO state) and state S_{331} showed a similar pattern among all the 5 initial plasmon states. No other energy state showed a higher average population or a long living during the relaxation (Figures 4.12 to 4.17).

Figure 4.18 The populations of state S_{343} for initial plasmon state S_{338}

Figure 4.19 The populations of state S_{343} for initial plasmon state S_{339}

Figure 4.20 The populations of state S_{343} for initial plasmon state S_{341}

Figure 4.21 The populations of state S_{343} for initial plasmon state S_{342}

Figure 4.22 The populations of state S_{343} for initial plasmon state S_{343}

The overall electronic relaxation can be identified as a 3 step process. First, the excited electron was relaxed in to the state S_{331} from initial plasmon state through the other states in ~ 1 ps regardless of the energy of the initial plasmon state. Then, it stayed in state S_{331} for ~ 3 ps and after that it gradually relaxed to the HOMO state through the other states. The lack of a conical

intersection¹⁴ between state S_{331} and state S_{330} in first ~ 4 ps might be the possible reason for the long living of the electron at state S_{331} during the relaxation process. Even if there is a conical intersection between state S_{331} and state S_{330} , the probability of electron hopping depends on the both non-adiabatic coupling vector and the atomic velocity (Equation 4.5).¹⁴ The relaxation was almost completed in ~ 11 ps for all the 5 initial plasmon states.

4.4.3 Conical intersections and electron hopping

The evolution of energies in states S_{332} , S_{331} and S_{330} along a single trajectory were investigated in order to understand the electronic transition (hopping) to states S_{331} and from S_{331} . For an example, Figure 4.23 shows evolution of energies in states S_{332} , S_{331} and S_{330} for one of the trajectories of initial plasmon state S_{338} . The electron hop in to the state S_{331} at the 1434 fs and stays there for around 1600 fs. There is a short term (66 fs) transition to state S_{332} that can be seen at 3075 fs. At 4041 fs, electron hop in to the state S_{330} . There is no conical intersection between state S_{331} and state S_{330} for the NAMD simulation time range from 1434 fs to 4041 fs. In Figure 4.23, the electron stay 3 – 3.5 ps in state S_{331} which is a good representation for all 50 trajectories. The electronic transitions happen almost at the conical intersections. However, it is not necessary to have an electronic transition at the conical intersection because hopping probability is not always 100 %.

Over 90 % of trajectories relaxed through the state S_{331} and more than 75 % of them hop in to state S_{330} from state S_{331} . This is valid for all five initial plasmon states.

Figure 4.23 The evolution of energies of state S_{332} , S_{331} and S_{330} along one trajectory of initial plasmon state S_{338}

4.5 Plasmon relaxation time

Since there are 3 main steps (initial state to state S_{331} , stay at state S_{331} and state S_{331} to HOMO state) in the overall relaxation process, the best way is to investigate the [1-population of HOMO state] in order to calculate the total relaxation time constant. The relaxation time constant of [1- S_{HOMO}] (τ_0) and duration of staying at 1 of [1- S_{HOMO}] curve (t_0) were used to calculate the total relaxation time constant. The relaxation time constants of [1- S_{HOMO}] (τ_0) were obtained by fitting the population data in to the following Gaussian function¹.

$$f(t) = A \exp[-(t/\tau)^2] \quad (\text{Equation 4.6})$$

The normalization constant A was fixed to the first population value after plateau at 1 for $[1-S_{\text{HOMO}}]$ curve. An example Gaussian fit can be seen in Figure 4.24. The $[1-S_{\text{HOMO}}]$ data can be seen in black dots and Gaussian fit can be seen in red line.

Figure 4.24 The Gaussian fit for the $[1-S_{\text{HOMO}}]$ data

Figures 4.25 to 4.29 show the relaxation time constants of $[1-S_{\text{HOMO}}]$ (τ_0) and the durations of staying at 1 of $[1-S_{\text{HOMO}}]$ curve (t_0) for all the initial plasmon states. The durations of staying at 1 of $[1-S_{\text{HOMO}}]$ curve (t_0) is always greater than 3.6 ps. In other words, any of the trajectories did not relax in to the HOMO state during the first 3.6 ps of NAMD simulations due to the long living state S_{331} .

Figure 4.25 Relaxation time constants for initial plasmon state S_{338}

Figure 4.26 Relaxation time constants for initial plasmon state S_{339}

Figure 4.27 Relaxation time constants for initial plasmon state S_{341}

Figure 4.28 Relaxation time constants for initial plasmon state S_{342}

Figure 4.29 Relaxation time constants for initial plasmon state S_{343}

The calculated relaxation time constants for all the initial plasmon states can be found in Table 4.2.

Table 4.2 Summary of the relaxation time constants

Initial plasmon state	Relaxation time constants (ps)		
	t_0	τ_0	τ_{TOT}
338	3.92	3.06	6.98
339	3.67	3.14	6.81
341	3.71	3.05	6.76
342	3.94	2.95	6.89
343	3.61	2.93	6.54

According to the Table 4.2, the overall relaxation time constant was found to be ~ 6.8 ps and it is independent of the energy of the initial plasmon state. This Au₅₅ electron relaxation dynamics are very different compared to the previously reported electron relaxation dynamics of Ag₆₈ clusters.¹ According to *Neukirch et al*¹ the relaxation time constant depends on the energy of the initial plasmon state for Ag₆₈. For high energy plasmon excitation in Ag₆₈, the electron stays a longer time in low energy plasmon states before relaxes in to the bulk states. But for low energy plasmon excitation, the electron quickly relaxes in to the bulk states. There is a clear difference between the relaxation time constants of high energy ($\tau = 1.21$ ps) and low energy ($\tau = 0.68$ ps) plasmon excitations in Ag₆₈.¹ In Ag₆₈, the energy difference between the investigated lowest energy plasmon state and highest energy plasmon state was ~ 0.3 eV. However in this work for Au₅₅, the energy difference between the state S₃₃₈ (lowest energy plasmon state) and S₃₄₃ (highest energy plasmon state) found to be ~ 1 eV and the difference between the relaxation time constants for these 2 states was ~ 0.44 ps ($\sim 6\%$).

4.6 Conclusion

*Smith et al*⁷ experimentally found a ~ 1 ps relaxation time constant for the Au₅₅ clusters and a ~ 7 ps relaxation time constant for the 15 nm Au nanoparticles. The relaxation time constant for Au₅₅ from this work is considerably larger than the experimental values reported by *Smith et al*.⁷ The attached ligands in experimental work would be one reason for this difference. Also *Smith et al*⁷ probed hot electrons using only one energy. So there is a possibility to miss some long living states below or above the probe energy. The following equation which includes both electron-phonon coupling and surface collision rate was used by *smith et al*⁷ to explain the changes of the relaxation time constant of different sizes of nanoparticles.

$$\frac{1}{\tau_{obs}} = \frac{aR^\alpha}{\tau_{bulk}} + \frac{bv_f}{R}, \quad (\text{Equation 4.7})$$

where τ_{obs} and τ_{bulk} are observed and bulk relaxation time constants, v_f is Fermi velocity of the electrons, R is radius of the nanoparticle, α is a positive integer, a and b are constants specific for the given material. Since the 2nd term of the above equation was derived from the surface collision, if the surface collision is dominant in the relaxation process, when decreasing the size of the nanoparticle the relaxation time constant should be decreased. But longer relaxation time constant for Au₅₅ ($2R \sim 1.4$ nm) helps to easily rule out the surface collision dominant relaxation process for Au₅₅. Since 1st term of the above equation was derived from the electron-phonon coupling, if the electron-phonon coupling is dominant in the relaxation process, when decreasing the size of the nanoparticle the relaxation time constant should be increased. Probably due to the weakening of the electron-phonon coupling⁷ in smaller size nanoparticles. Therefore, the longer relaxation time constant of Au₅₅ in this work can be attributed to the long living state S₃₃₁ or weak electron-phonon coupling or both. Also previously reported molecular like relaxation dynamics⁸ for Au₅₅ can be rule out base on this results.

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Chapter 5

Plasmonic heating assisted CO₂ reduction using **Au-ZnO heterostructures**

5.1 Introduction

More than 80 % of the world's energy demand will be full filled by burning of fossil fuels at least for next few decades. However, in addition to energy, burning of fossil fuels releases a massive amount of CO₂ to the environment. Even though energy efficient equipment and alternative energy methods help to reduce the CO₂ emission, world population growth compete with it. The net result is the increasing atmospheric CO₂ concentration annually and still there is no promising method to reduce the excess CO₂ in the environment. Most of the artificial photocatalytic reduction of CO₂ approaches is not efficient in large scale applications. The poor optical activity is one of the main problems of mostly used wide band gap metal oxide photocatalysts. The wide band gap metal oxides such as TiO₂ and ZnO can only utilize the ultra violet region of the solar spectrum which is less than 5 % of the total light coming to the earth's surface. Also, most of these photocatalysts depend on the electron-hole pair generation to drive the CO₂ reduction reactions. However, the efficiency of electron-hole pair generation and their transfer in to reactants in large scale applications is very low. The oxidative corrosion^{1,2} is a another problem of photocatalysts which needs to be addressed with sacrificial hole scavengers.³

Remarkable optical properties of metal nanoparticles⁴ can be used to improve the efficiency of photocatalysis⁵⁻⁸. The surface plasmon resonance of metal nanoparticles^{9, 10} can be tuned to cover

the entire range of visible light and extend in to near infrared range of the solar spectrum. Various plasmonic nanoparticles enhance the performance of photocatalysts under visible light excitation due to their efficient charge transfer¹¹⁻¹³ and electric field enhancement effects.^{14, 15} In addition to that, metal nanoparticles can generate heat under surface plasmon resonance conditions.^{4, 16-18} In general, thermally driven catalytic processes have higher yields and are easy to implement into larger scale reactors. Therefore, it is feasible to start this in industrial settings and it is important to implement this approach to wide range of reactions utilizing this technique with high surface area heterogeneous catalysts.

It is found that there are extensive industrial applications of ZnO based catalysts at higher temperatures such as methanol synthesis from CO₂ and water-gas shift reactions.^{19, 20} Therefore, a low cost and efficient heating method for ZnO based catalysts will open the paths for a large number of industrial applications. In this work, the temperature of ZnO was elevated using the heat generated by Au nanoparticles under the surface plasmon resonance conditions. The heated ZnO catalytically convert the CO₂ and H₂ gas mixture in to CH₄ and CO.

5.2 Light absorption and heat generation from the Au nanoparticles

Simple model calculations were performed in order to understand the light absorption and heat generation of Au nanoparticles under different conditions. Only the absorbed light is responsible for plasmonic heating of metal nanoparticles and heating effect is very efficient and strong when the frequency of incoming electromagnetic radiation matches the surface plasmon resonance frequency of the metal nanoparticles.²¹ Since the dielectric constant of metals depends on the

frequency of the applied electric field, the amount of heat generation from Au nanoparticles also depends on the frequency of the applied electric field.

The absorption cross section was calculated according the example shown in *Ohodnicki et al.*²² The wavelength dependent dielectric constant of the Au which contains both standard contribution of a Drude model and the contribution from interband transitions was calculated according to *Etchegoin et al.*²³ The optical parameters (Table 5.1) were obtained from previous reports.²³⁻²⁵ The following equations give absorption cross section (Q_{abs}) and wavelength dependent dielectric constant($\epsilon_{Au}(\lambda)$):

$$Q_{abs} = \frac{4\pi^2 a^3 \sqrt{\epsilon_m}}{2\lambda} \text{Im} \left[\frac{\epsilon_{Au} - \epsilon_m}{\epsilon_{Au} + 2\epsilon_m} \right] \quad (\text{Equation 5.1})$$

$$\epsilon_{Au}(\lambda) = \epsilon_\infty - \frac{1}{\lambda_p^2 \left(\frac{1}{\lambda^2} + \frac{i}{\gamma_p \lambda} \right)} + \sum_{j=1,2} \frac{A_j}{\lambda_j} \left[\frac{e^{i\phi_j}}{\left(\frac{1}{\lambda_j} - \frac{1}{\lambda} - \frac{i}{\gamma_j} \right)} + \frac{e^{-i\phi_j}}{\left(\frac{1}{\lambda_j} + \frac{1}{\lambda} + \frac{i}{\gamma_j} \right)} \right] \quad (\text{Equation 5.2})$$

Where a is the radius of the nanoparticle, ϵ_m is the dielectric constant of the matrix phase, λ is optical wavelength, ϵ_∞ is the high frequency limit dielectric constant, λ_p is the plasma wavelength, γ_p is the damping (expressed as a wavelength), λ_j is the interband transition wavelength, γ_j is the transition broadening (expressed as a wavelength), A_j is the dimensionless critical point amplitudes and ϕ_j is the phase which was fixed in to $-\pi/4$ according to *Etchegoin et al.*²³

Table 5.1 Optical parameters

Parameter	Value	Source
a	2.5 nm	Average radius from the TEM images
$\epsilon_m(\text{Hexane})$	1.88	<i>Mopsik</i> ²⁵
$\epsilon_m(\text{ZnO})$	3.70	<i>Azad et al.</i> ²⁴
ϵ_∞	1.53	<i>Etchegoin et al.</i> ²³
λ_p	145 nm	<i>Etchegoin et al.</i> ²³
γ_p	17000 nm	<i>Etchegoin et al.</i> ²³
λ_1	468 nm	<i>Etchegoin et al.</i> ²³
λ_2	331 nm	<i>Etchegoin et al.</i> ²³
γ_1	2300 nm	<i>Etchegoin et al.</i> ²³
γ_2	940 nm	<i>Etchegoin et al.</i> ²³
A_1	0.94	<i>Etchegoin et al.</i> ²³
A_2	1.36	<i>Etchegoin et al.</i> ²³
ϕ_1	$-\pi/4$ rad	<i>Etchegoin et al.</i> ²³
ϕ_2	$-\pi/4$ rad	<i>Etchegoin et al.</i> ²³

The Real and imaginary parts of the wavelength dependent dielectric constant of the Au are shown in Figures 5.1 and 5.2.

Figure 5.1 Real part of the wavelength dependent dielectric constant of Au

Figure 5.2 Imaginary part of the wavelength dependent dielectric constant of Au

A simple calculation which was based on simplified Mie theory was performed according to the *Govorov et al*²¹ in order to calculate the temperature at surface of the spherical shape Au nanoparticle. The usual heat transfer equation can be used to explain the heat transfer of metal nanoparticles when there is no phase transformation.²¹

$$\rho(r)c(r)\frac{\partial T(r,t)}{\partial t} = \nabla k(r)\nabla T(r,t) + Q(r,t) \quad (\text{Equation 5.3})$$

where $T(r,t)$ is the temperature as a function of position r and time t , $\rho(r)$ is the mass density of the nanoparticle, $c(r)$ is the specific heat of nanoparticles, $k(r)$ is the thermal conductivity of nanoparticles and $Q(r,t)$ is the local heat intensity.

The local heat intensity can be described as follows²¹,

$$Q(r,t) = \langle j(r,t) \cdot E(r,t) \rangle_t = -\frac{1}{2} \text{Re} \left[i\omega \frac{\epsilon(r)-1}{4\pi} \tilde{E}(r) \tilde{E}^*(r) \right] \quad (\text{Equation 5.4})$$

where $j(r, t)$ is the current density, $E(r, t) = \text{Re}[\tilde{E}(r)e^{-i\omega t}]$ is the induced electric field, $\epsilon(r)$ is the relative permittivity of the nanoparticles.

The external electric field which uses to excite the surface plasmon of metal nanoparticles is, $E_0(t) = \text{Re}[\tilde{E}_0(t)e^{-i\omega t}]$ and the light intensity is $I(t) = I_0 = cE_0^2 \sqrt{\epsilon_s}/8\pi$ where c is the velocity of light and ϵ_s is the relative permittivity of the surrounding medium.

Then temperature distribution outside the spherical nanoparticle²¹,

$$\Delta T(r) = \frac{V_{NP}Q}{4\pi k_s r} (r > R_{NP}) \quad (\text{Equation 5.5})$$

where V_{NP} is the volume of the nanoparticles, R_{NP} is the radius of the nanoparticles and k_s is the thermal conductivity of the surrounding medium. Then, the local heat intensity can be re-written as²¹,

$$Q = -\text{Re}\left[i\omega \frac{\epsilon_{NP}-1}{8\pi} E_0^2 \left| \frac{3\epsilon_s}{2\epsilon_s + \epsilon_{NP}} \right|^2\right] \quad (\text{Equation 5.6})$$

where ϵ_{NP} is the relative permittivity of the metal nanoparticles. The maximum temperature at the surface of the nanoparticle²¹,

$$\Delta T_{max}(I_0) = \frac{R_{NP}^2}{3k_0} \text{Re}\left[i\omega \frac{1-\epsilon_{NP}}{8\pi} \left| \frac{3\epsilon_s}{2\epsilon_s + \epsilon_{NP}} \right|^2\right] \frac{8\pi I_0}{c\sqrt{\epsilon_s}} \quad (\text{Equation 5.7})$$

Figure 5.3 shows the absorption cross section of the 20 nm single spherical Au nanoparticle in air and in ZnO media as a function of illumination wavelength. The absorption maxima can be seen around 481 nm and 552 nm for Au nanoparticle in air and in ZnO respectively. The illumination

intensity was $2.5 \times 10^5 \text{ W/m}^2$. Since the absorption cross section directly affects the heat generation one can expect the maximum heating effects to be around the maximum absorption cross section.

Figure 5.3 Absorption cross section of 20 nm spherical shaped Au nanoparticle in air and in ZnO media

Figure 5.4 shows the maximum temperature increase at the surface of the 20 nm spherical shaped Au nanoparticle embedded in ZnO under $2.5 \times 10^5 \text{ W/m}^2$ light illumination. The maximum temperature difference can be observed at 552 nm which also confirms that the maximum heat generation occurs at the maximum absorption. Figure 5.5 shows the temperature increase at the surface of different sizes of Au nanoparticles as function of the illumination light intensity. For a given size of Au nanoparticle, the heat generation linearly increases with the illumination light intensity. Also, according to the Figure 5.5, the heat generation increases with the size of the Au nanoparticle for a given illumination light intensity. However, *Govorov et al*²¹ recommended not to use this method to calculate the heat generation of Au nanoparticles which are larger than the 50 nm since they used a simplified Mie theory to derive the above equations. The heat generation

can be strongly enhanced in the presence of more than one Au nanoparticle due to the cumulative effect and Coulomb interactions.²⁶

Figure 5.4 Temperature increase of 20 nm spherical shaped Au nanoparticle embedded in ZnO

Figure 5.5 Temperature increase of different sizes of spherical shaped Au nanoparticles embedded in ZnO

Based on the above model calculations; the surrounding medium, size of the Au nanoparticles and the illumination light intensity play critical roles in plasmonic heat generation. In order to achieve the maximum light-to-heat conversion efficiency, it is necessary to have a narrow plasmon resonance peak which closely matches the illumination light frequency or a broadband light source that matches the bandwidth of the resonance. A single Au nanoparticle which is fully embedded in ZnO was considered for the above model calculations. Also, it was assumed that there are no other Au nanoparticles in the vicinity (assumed that there is no accumulative effects and coulomb interactions). However, if the Au nanoparticles are agglomerated (clustering) heat generation might be increased by several orders of magnitude. *Govorov et al*²¹ showed the 5 fold increase of heat generation in a 4*4 array (total of 16 nanoparticles) of Au nanoparticles compared to the single Au nanoparticle. This allows us to hypothesize that the local temperature of ZnO can be increased by a couple of hundreds of degrees, via the simultaneously illumination of clusters which contain a large number of Au nanoparticles.

Therefore, the first objective in this work was to synthesize Au-ZnO heterostructures with moderate size Au nanoparticles which show a strong and narrow absorption peak close to 532 nm (illumination wavelength). The simple wet chemical method was implemented in order to achieve this objective is discussed in detail in Section 5.3.

5.3 Materials preparation

Hydrogen tetrachloroaurate(III) hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$), 99.9%, was purchased from Alfa Aesar. ZnO nanoparticles and SiO_2 (99.995+%) were obtained from Meliorum Technologies and Sigma-Aldrich, respectively.

5.3.1 Synthesis of Au-ZnO heterostructured catalysts

ZnO nanoparticles (0.3 g) were dispersed in a small amount of methanol to form a paste. Then, $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (according to Table 5.1) was dissolved in a small amount of methanol and was slowly added to the ZnO paste under vigorous stirring to form a uniform mixture. The uniform mixture was dried under a small N_2 flow until methanol was evaporated. The dried sample was heat treated at the annealing temperature ($100\text{ }^\circ\text{C} - 800\text{ }^\circ\text{C}$) for 1 hour in air. The temperature was increased from room temperature to annealing temperature with the rate of $10\text{ }^\circ\text{C min}^{-1}$. After cooling the sample to the room temperature, a pink-red colored powder was observed. These Au-ZnO powder samples were used for characterizations, Raman spectral analysis and CO_2 reduction reactions, without further processing. Ten different samples (Table 5.2) were synthesized according to the above procedure at different annealing temperatures and Au concentrations. Au- SiO_2 was synthesized using the same method as Au-ZnO.

Table 5.2 Au-ZnO samples synthesized at different annealing temperatures and different Au concentrations

Sample #	Annealing temperature ($^\circ\text{C}$)	Au concentration by weight %
1	100	5
2	200	5
3	200	10
4	200	15
5	300	5
6	300	10
7	300	15
8	400	5
9	600	5
10	800	5

5.4 Characterization of the Au-ZnO heterostructures

5.4.1 Diffuse reflectance spectroscopy characterization

The optical properties of the Au-ZnO and ZnO were characterized using the Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer equipped with an integrating sphere. Right after the synthesis diffuse reflectance spectra were taken for all the samples. Au-ZnO samples which were annealed at 200 °C and 300 °C showed very narrow absorption peaks compared to the other samples close to the 532 nm wavelength (Figure 5.6). The broadening of the absorption peak was observed when increasing the annealing temperature due to the large size distribution. All the samples showed an absorption peak around 532 nm due to the surface plasmon resonance of Au nanoparticles. However, the above mentioned two samples can be identified as the best Au-ZnO candidates to excite the surface plasmon resonance of Au nanoparticles using the 532 nm green laser. Among the three different Au concentrations (5%, 10% and 15%) which were annealed at 200 °C and 300 °C, 5% Au-ZnO samples (for both annealing temperatures) showed a very strong absorption peak close to 532 nm wavelength (Figure 5.7) most probably due to the narrow size distribution. The higher concentration of Au may increase the size distribution of the Au nanoparticles.

According to the model heat generation calculations the maximum heat generation can be achieved at the maximum light absorption. Since 5% Au-ZnO heterostructure sample which annealed at the 300 °C shows the strong and narrow light absorption around ~ 538 nm due to the surface plasmon resonance of Au nanoparticles, it was the best Au-ZnO candidate for the maximum heat generation under the 532 nm light illumination.

Figure 5.6 Diffuse Reflectance spectra for 5% Au-ZnO heterostructure samples at different annealing temperatures

Figure 5.7 Diffuse Reflectance spectra for Au-ZnO heterostructure samples with different Au concentration annealed at 200 °C

Figure 5.7 Diffuse Reflectance spectra for Au-ZnO heterostructure samples with different Au concentration annealed at 300 °C

It was expected the convenient resonance of the surface plasmon of Au nanoparticles with 532 nm green lasers which were utilized for the experiments in this work. This can be confirmed by the comparison of Diffuse Reflectance spectra of pure ZnO and 5% Au-ZnO (Figure 5.8). According to the Figure 5.8, it can be clearly seen that the 532 nm green light absorption only happens on Au-ZnO heterostructures. Also the surface plasmon resonance peak around ~ 538 nm is consistent with the calculated absorption spectra of 20 nm Au nanoparticle embedded in ZnO which shows the absorption maximum at 552 nm. The Au nanoparticles in 5% Au-ZnO sample were around ~ 20 nm (see the section 5.3.4) but they were not fully embedded in ZnO. Since the surrounding dielectric medium directly affects the absorption cross section, it is acceptable to see a small difference between the calculated and experimental values. The strong absorption around ~ 380 nm can be attributed to the band edge absorption of the ZnO.

Figure 5.8 Comparison of Diffuse Reflectance spectra for pure ZnO and 5% Au-ZnO

The reproducibility of the catalyst is very important in large scale industrial applications. Therefore, three batches of 5% Au-ZnO heterostructure samples were synthesized in order to confirm the reproducibility. The Diffuse Reflectance spectra were well consistent with each other with the same absorption maximum around ~ 538 nm (Figure 5.9).

Figure 5.9 Comparison of Diffuse Reflectance spectra for 3 different batches of 5% Au-ZnO

5.4.2 Scanning Electron Microscopy characterization

JEOL JSM-7600F Scanning Electron Microscope was used to investigate the surface morphology of the Au-ZnO samples. Back scattered detector (COMPO2) at 15 kV was used to enhance the contrast of the Au nanoparticles, relative to the contrast of ZnO nanoparticles. Secondary electron detector (SEI) gives better images than back scattered detector but due to the similarity of shape and order of the particle size it is hard to see the difference between Au and ZnO (Figure 5.10). The bright white dots represent the Au nanoparticles in SEM images which were obtained with back scattered detector.

Figure 5.10 Comparison of SEM images at the same position of Au-ZnO sample using two different detectors (a) SEI and (b) COMPO2

According to the Figures 5.11 to 5.16, an uneven distribution of Au nanoparticles in all Au-ZnO samples can be clearly observed. Au nanoparticles are decorating the ZnO surface at random positions. Figure 5.17 shows SEM images of four different positions of the 5% Au-ZnO which was annealed at the 300 °C. This is an evidence to confirm the arbitrary locations of the Au nanoparticles in Au-ZnO samples. However, at least a few Au nanoparticles can be found when consider the 13 μm experimental laser spot size which has used for the Raman spectral analysis and catalytic reactions. Also, the larger Au clusters were observed for all the Au-ZnO samples. It is difficult to make any accurate measurement of the size of the Au nanoparticles because of the clustering of the particles. But Au-ZnO samples which were annealed at 400 °C, 600 °C and 800 °C show a larger particle size distribution compared to the Au-ZnO sample which was annealed at 300 °C. This larger size distribution is consistent with the broadening of the Diffuse Reflectance spectra for the Au-ZnO samples which were annealed at higher temperatures. Only 5% Au-ZnO which was annealed at 300 °C used for the rest of the experiments.

5.4.3 BET surface area measurements

Surface areas of the catalysts were determined from N₂ adsorption isotherms at 77 K using a Quantachrome Autosorb 1-C. Multipoint BET measurements were performed at relative pressures (P/P_0) in the range of 0.1 – 0.3. Prior to the measurements, samples were degassed under vacuum at 110 °C for 4 h. The BET surface areas of ZnO (Meliorum) (after calcination at 300 °C for 1 h in air) and 5% Au-ZnO catalyst are 10 and 12 m² g⁻¹ respectively.

Figure 5.11 5% Au-ZnO annealed at 100 °C

Figure 5.12 5% Au-ZnO annealed at 200 °C

Figure 5.13 5% Au-ZnO annealed at 300 °C

Figure 5.14 5% Au-ZnO annealed at 400 °C

Figure 5.15 5% Au-ZnO annealed at 600 °C

Figure 5.16 5% Au-ZnO annealed at 800 °C

Figure 5.17 Different positions of 5% Au-ZnO sample

5.4.4 Transmission Electron Microscopy characterization

JEOL JEM-2100 Transmission Electron Microscope was used to take both conventional and High Resolution Transmission Electron Microscope images. Instrument was operated at 200 kV. Conventional images were obtained using the Gatan ES500W digital camera which is capable of high speed and high quality imaging with a field of view larger than the traditional TEM film. High resolution images were obtained using the Orius SC1000, which is the latest generation of large format (11 Megapixel) retractable and fiber-optical coupled CCD cameras. Figure 5.18 shows the TEM image of 5% Au-ZnO and Figure 5.19 shows the HRTEM image of the 5% Au-ZnO. The average size of the Au nanoparticle was found to be ~ 20 nm.

Figure 5.18 TEM image of 5% Au-ZnO sample

Figure 5.19 HRTEM image of 5% Au-ZnO sample

5.4.5 X-Ray Diffraction patterns characterization

PANalytical X'pert Pro powder X-Ray diffractometer was used to investigate the crystal structure information of Au-ZnO heterostructures and instrument was operated at 40 kV and 40 mA. According to the X-Ray diffraction patterns, Au nanoparticles showed cubic structure and ZnO nanoparticles showed hexagonal wurtzite structure with high crystallinity (Figure 5.20).

Figure 5.20 X-Ray Diffraction patterns of 5% Au-ZnO

5.5 Local temperature estimation studies of the Au-ZnO heterostructures

ZnO is a well-known catalyst for CO₂ reduction at higher temperatures. Therefore ZnO is a good candidate for plasmonic heating assisted catalysis. It is very challenging to measure the temperature increases on ZnO due to the heat generation by the Au nanoparticles under surface plasmon resonance. Since heat generation of Au nanoparticles is a highly localized process in nanoscale. Bulk instruments cannot directly measure the local temperature of ZnO. However, it is very important to know the local temperature of ZnO for the industrial catalysis applications. In this work, temperature dependent phonon spectrum of ZnO was used to estimate the local temperature of ZnO.

5.5.1 Optical phonon modes of ZnO

The hexagonal wurtzite and zincblende are the two main structures of ZnO. However, hexagonal wurtzite structure (Figure 5.21) is the most stable and the common one. The melting point is $\sim 1975^\circ\text{C}$ for bulk ZnO.

Figure 5.21 Crystal structure of wurtzite ZnO. Grey color represents Zn atoms and red color represents O atoms. Highlighted atoms are inside the unit cell

ZnO which has the hexagonal wurtzite type lattice structure belongs to the C_{6v}^4 symmetry group.^{27,}

²⁸ There are four atoms in the primitive unit cell and group theory predicted the following irreducible representation for the optical phonons at Γ point of the Brillion zone.²⁷⁻²⁹

$$\Gamma_{\text{opt}} = A_1 + E_1 + 2E_2 + 2B_1$$

Both A_1 and E_1 modes are polar modes and exhibit the different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) phonons.³⁰ Also they are active in Raman and infrared spectroscopy. B_1 mode is a silent mode, it cannot be detected in either Raman or infrared spectroscopy.^{27, 29} Since E_2 modes are non polar modes, they are not infrared active but they give two distinct frequencies due to the motion of O atoms and Zn sub lattice (Figure 5.22) in Raman spectra which are called as $E_2(\text{high})$ and $E_2(\text{low})$ modes respectively.^{27, 29}

Figure 5.22 Eigen vectors of the ZnO optical phonon modes. The bold arrows represent the dominating displacement vectors, while grey circles represent Zn atoms and white circles represent O atoms. Superscripts 1 and 2 showed the low and high frequencies.

The Raman active $E_2(\text{high})$ mode of ZnO is temperature dependent and the temperature dependent linewidth broadening and frequency shifting for $E_2(\text{high})$ are already reported.^{28, 31-33} The linewidth broadening can be attributed to the temperature dependent phonon damping which is mainly due to the decay in to the lower energy phonons.³² In this work, linewidth broadening of $E_2(\text{high})$ mode was used to estimate the local temperature of ZnO.

Several phonon decay processes can be found in literature for $E_2(\text{high})$ mode. *Samanta et al*³² reported a decay of $E_2(\text{high})$ phonon mode (441 cm^{-1}) in to three symmetric phonons (quadratic anharmonicity) with the frequency (147 cm^{-1}). *Cusco et al*²⁸ and *Serrano et al*³⁴ used sum of two phonons (250 cm^{-1} and 190 cm^{-1}) (cubic anharmonicity) and difference of two phonons (cubic

anharmonicity) to explain the decay channel of $E_2(\text{high})$ phonon mode. Also *Cusco et al*²⁸ reported that the rate of sum of two phonons decay is dominant over the difference of two phonons.

5.5.2 Temperature dependent intensity dependent Raman spectra of ZnO

A Renishaw InVia Raman Microscope with 1.0 cm^{-1} resolution was used to collect the Raman spectra of ZnO. The samples were excited with a 532 nm green laser (CL-532-100). A 5X magnification microscope objective was used in the experiments. Numerical aperture size was 0.12. The experimental laser spot size was measured using a calibration slide and was determined to be $\sim 13 \text{ }\mu\text{m}$. A Linkam high temperature stage (THMS 600) and temperature controller (TMS 94) were used to obtain temperature dependent Raman spectra of the samples in the temperature range of $25 \text{ }^\circ\text{C}$ to $450 \text{ }^\circ\text{C}$ with $25 \text{ }^\circ\text{C}$ steps under $2.6 * 10^5 \text{ W/m}^2$ continuous wave (cw) 532 nm laser excitation (Figure 5.23). A series of Raman spectra were also collected for ZnO at different laser excitation intensities to measure the temperature change under laser illumination (Figure 5.24).

The $E_2(\text{high})$ mode of each Raman spectra was fitted in to Lorentzian line shape to determine the position and the full width half maximum (FWHM) or linewidth after the background subtraction. Both the linewidth and the position of the $E_2(\text{high})$ mode for temperature dependent Raman spectra were drastically changed with increasing temperature (Figure 5.25). The decreasing peak position and increasing linewidth for $E_2(\text{high})$ mode has been already reported.^{28, 31}

Figure 5.23 Raman spectra of ZnO at different temperatures

Figure 5.24 Raman spectra of ZnO at different laser intensities

But for the laser intensity dependent Raman spectra at room temperature, both linewidth and position of the $E_2(high)$ mode didn't show any considerable variation while increasing the laser intensity (Figure 5.26). *Alim et al*³⁰ also previously reported the negligible laser heating effects for $E_2(high)$ mode of ZnO using the stokes and anti-stokes peak intensities. These results confirmed the negligible contribution of the laser intensity to the linewidth broadening of temperature dependent Raman spectra of ZnO. In other words, there is no contribution of the laser intensity to the increasing temperature of ZnO. The thermal expansion of the material affects the position of the Raman peaks but there is no effect on linewidth.^{31, 32}

Figure 5.25 Raman shift and linewidth variation of $E_2(high)$ mode of ZnO at different temperatures

Figure 5.26 Raman shift and linewidth variation of $E_2(\text{high})$ mode of ZnO at laser intensities

5.5.3 Theoretical model for the linewidth broadening of the $E_2(\text{high})$ mode

The temperature dependent linewidth of the optical phonons in ZnO is described in several previous reports^{27, 28, 31, 32, 34, 35} using the model derived by *Menendez et al.*³⁶ The temperature dependence of linewidth of the $E_2(\text{high})$ mode of ZnO can be explained using the following equation:

$$T(T) = T_0 + A(1 + \sum_{j=1}^2 n_j(\omega_j, T)) + B(1 + \sum_{j=1}^3 n_j(\omega_j, T) + n_j^2(\omega_j, T)) \quad (\text{Equation 5.8})$$

where $T(T)$ is the temperature dependent linewidth, T_0 is the background contribution to the linewidth due to impurity and/or defects scattering, $n_j(\omega_j, T) = \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) \right]^{-1}$ is the Bose-

Einstein distribution function and A and B are cubic and quadratic anharmonic coupling constants respectively. As mentioned in section 5.4.1, several proposed decay mechanisms for $E_2(\text{high})$ mode can be found in the literature. *Yadav et al*³¹ noted that cubic anharmonicity is dominating during the decay process but quadratic anharmonicity also is necessarily required. Therefore, in this work the both the sum of two phonons (250 cm^{-1} and 190 cm^{-1}) (cubic anharmonicity) and sum of three symmetric phonons (quadratic anharmonicity) with the frequency (147 cm^{-1}) were considered. The background contribution and anharmonic coupling constants were optimized using the experimental linewidth data and above theoretical equation. The optimized values for T_0 , A and B found to be 2.56 cm^{-1} , 4.58 and -0.08 respectively. This calibration curve (Figure 5.27) was used to estimate the local temperature of Au-ZnO samples at different laser intensities.

Figure 5.27 Linewidth of $E_2(\text{high})$ mode of ZnO as a function of temperature (black dots) under $2.6 \times 10^5\text{ W/m}^2$ cw 532 nm laser excitation. The red line is the fit based on the theoretical equation

5.5.4 Raman spectra of ZnO and Au-ZnO at room temperature under different laser excitation intensities

Raman spectra were collected for Au-ZnO sample at room temperature under different laser intensities. The linewidth of the $E_2(\text{high})$ mode was determined using the Lorentzian shape peak fitting. Neutral density filters were used to adjust the laser power beyond the limits of Raman spectrometer software. The linewidth of the ZnO shows a negligible variation under all the laser excitations (Figure 5.26). But the linewidth of the Au-ZnO showed a significant broadening when the laser intensity increased compared to the linewidth of the ZnO (Figure 5.28). Also, linewidth broadening is linearly dependent on the laser intensity. These results confirmed the heat generation (plasmonic heating) of Au-ZnO sample under different laser intensities.

Figure 5.28 Linewidth of $E_2(\text{high})$ mode of ZnO (black squares) and Au-ZnO (red dots) as a function of different intensities of cw 532 nm laser excitation. The red line is a linear fit of the linewidth variation of the Au-ZnO

The steady state local temperature of the Au-ZnO at given laser intensity was determined using the calibration curve (Figure 5.27). The calibration curve was slightly extrapolated to estimate the local temperature at laser intensity $8.0 \times 10^5 \text{ W/m}^2$. Table 5.3 and Figure 5.29 show the estimated local temperature of Au-ZnO at different laser intensities. The local temperature linearly increases as laser intensity increases which is well agreed with the Equation 5.7. But due to the clustering of Au nanoparticles this estimated local temperature can't be compared with the calculated temperature increases in Figures 5.4 and 5.5. Since plasmonic heating is highly localized, this estimated local temperature reflects an average steady state temperature of the ZnO surface. The local temperature in close proximity to the Au-ZnO interface could be significantly higher than the estimated local temperature.

Figure 5.29 Estimated local temperature of Au-ZnO under different laser intensities

5.6 CO₂ reduction reactions

A gas-tight photocatalysis cell was constructed using a stainless steel spacer (MDC Vacuum Products) with conflat flange components and fitted with two inlet/outlet valves, one gas chromatography (GC) sampling port (HP 5890) connected *via* Swagelok fittings, and two UV quartz viewports. The two UV quartz viewports along the laser irradiation direction ensured that no metal part of the photocatalysis cell would be illuminated by the 532 nm laser. The volume of the photocatalysis cell was 40 mL. A watch glass was placed at the bottom of the UV quartz viewport of the photocatalysis cell, on which 10 to 15 mg of the catalyst samples were loaded for photocatalysis reactions. After a new septum was placed in the sampling port and a catalyst sample was loaded, the photocatalysis cell was purged with 25% CO₂ + 75% H₂ of gas mixture for 20 minutes. The photocatalysis cell was subsequently irradiated through the top quartz viewport using a *cw* 532 nm laser (Figure 5.30). The laser spot size was ~150 μm and illumination time was 5 hr. Gas chromatography (GC) analysis of photoreduction products was performed using a Perkin Elmer Clarus 600 Gas Chromatograph with a heated sample inlet. Sample detection was achieved using both a thermal conductivity detector and a flame ionization detector with methanizer, joined in sequence. Gas samples were injected manually using a 5 mL gas-tight syringe.

Figure 5.30 The schematic diagram of laser illumination and homemade photocatalysis cell

The 532 nm *cw* laser was used for plasmonic heating assisted CO₂ reduction which allowed to directly match the intensities used in Raman experiments to estimate the local temperatures of Au-ZnO. After the laser illumination, two reaction products (CH₄ and CO) were detected using the GC. Then CO₂ conversion rate (Figure 5.31) and product generation rates (Figures 5.32 and 5.33) were calculated based on moles of products, amount of catalyst and illumination time. The reaction rate 4.22 μmol/g/h of the Au-ZnO catalyst under $\sim 8 * 10^5$ W/m² *cw* 532 nm laser illumination is nearly 4 times higher than the previously observed using PbS/Cu/TiO₂ catalysts under visible light excitation in a similar reaction cell using the same gas product detection method.³⁷ The control experiments with ZnO and SiO₂ didn't show any considerable activity even at the highest laser intensity (Figure 5.31).

Figure 5.31 CO₂ conversion rate at different laser intensities with Au-ZnO, with the corresponding local temperature due to the plasmonic heating as the top x -axis

Figure 5.32 CO production rate at different laser intensities with Au-ZnO, with the corresponding local temperature due to the plasmonic heating as the top x -axis

Figure 5.33 CH_4 production rate at different laser intensities with Au-ZnO, with the corresponding local temperature due to the plasmonic heating as the top x -axis

Wang *et al*³⁸ suggested following four possible reaction schemes for CO_2 conversion reactions using the thermodynamic calculations.

Reaction scheme 1: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ (Reversed Water Gas Shift (RWGS))

Reaction scheme 2: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ (RWGS); $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ (Methanol synthesis)

Reaction scheme 3: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ (RWGS); $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ (CO-methanation)

Reaction scheme 4: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ (RWGS); $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ (Methanol synthesis); $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ (CO-methanation)

The 3rd reaction scheme is consistent with the detected products for CO₂ reductions reactions using the Au-ZnO in this work. First CO₂ react with H₂ in the presence of plasmonically heated ZnO (photocatalyst) and generate CO and H₂O (Reversed water gas shift). Then CO further react with H₂ to generate the CH₄ (CO methanation). Both reactions (Reversed water gas shift and CO methanation) are thermally driven and production rates depend on the reaction temperature (Figures 5.32 and 5.33). The temperature programmed reaction studies were performed in order to further confirm the thermal driven catalytic activity of ZnO.

5.6.1 Temperature programmed reactions

Temperature programmed reaction was performed using a Micromeritics Autochem 2950 HP equipped with a Thermostar mass spectrometer (MS) to verify that CO and CH₄ were thermochemically produced using the ZnO and Au-ZnO catalysts. ZnO was dispersed in a pH ~ 2 HCl solution, dried, and calcined at 300 °C in air for 1 h before cooling to room temperature, to follow the similar steps which were used for synthesis of Au-ZnO heterostructures. Au-SiO₂ and SiO₂ were also studied as control experiments. The 25% CO₂ + 75% H₂ of gas mixture (100 cm³ min⁻¹) was introduced to 300 mg of the samples while the reactor pressure was kept at atmospheric pressure. The catalyst temperature was subsequently raised linearly at the rate of 10 °C min⁻¹ from room temperature to 650 °C. Fragments of the gas components in the outlet stream of the reactor (H₂, CH₄, H₂O, CO, CH₃OH and CO₂) were monitored using a ThermoStar mass spectrometer.

These control experiments were done in the dark and both ZnO and Au-ZnO show similar catalytic activity as laser illumination CO₂ reduction experiments by producing the CO and CH₄ from CO₂ reduction. The production rates for both CO and CH₄ are qualitatively identical to the laser

illumination CO₂ reduction experiments (Figures 5.34 and 5.35). The generation of CO starts just below 150 °C in laser illumination experiments while generation of CO in temperature programmed dark experiments start around 425 °C. Also CH₄ production starts below 100 °C for laser illumination experiments while CH₄ production in temperature programmed dark experiments start around 275 °C. The increasing CO production rate with the increasing temperature also well agrees with laser illumination experiments. The increasing and decreasing behavior of the CH₄ production rate is also observed in both laser illumination experiments and temperature programmed dark experiments. The maximum CH₄ production rate was achieved around 250 °C and 425 °C for laser illumination experiments and temperature programmed dark experiments respectively. Also Au-SiO₂ didn't show considerable activity compared to the ZnO and Au-ZnO for temperature programmed dark experiments respectively (Figures 5.34 and 5.35). These results can be identified as a strong evidence to confirm the thermally driven catalytic activity of ZnO for CO₂ reduction which follows the 3rd reaction scheme. Also, this indicates that plasmonic heating is occurring and it can drive purely thermal catalytic reactions. By comparing the results of the laser illumination experiments and temperature programmed dark experiments; one can point out that only difference is the shift in the temperature axis. The Raman spectra based local temperature estimation most probably underestimates the local temperature.

Figure 5.34 CO production detected by a mass spectrometer as function of temperature for ZnO, Au-ZnO and Au-SiO₂

Figure 5.35 CH₄ production detected by a mass spectrometer as function of temperature for ZnO, Au-ZnO and Au-SiO₂

5.6.2 Plasmonic heating assisted catalytic activity of Au-ZnO

Based on Raman spectral analysis, laser illumination experiments and temperature programmed dark experiments confirm the plasmonic heating assisted purely thermal driven CO₂ reduction. The nanoparticle size distribution, nanoparticle densities, available reaction channels, illumination light intensity and its resonance with surface plasmons can be identified as the main parameters which directly affect the production efficiency. Also, it is very important to have a strong resonance of surface plasmon with illumination light to generate the maximum heat. The surface plasmon resonance of Au nanoparticles in this work (~ 538 nm) were well resonated with 532 nm laser illumination and it could be one reason to have a higher CO₂ conversion rate. Since illumination light intensity is directly proportional to the local temperature increase (Equation 5.7, Figures 5.4 and 5.29) the local temperature of the catalyst can be easily changed by just changing the illumination light intensity. The temperature dependent product selectivity was confirmed by both laser illumination experiments and temperature programmed dark experiments (Figures 5.32, 5.33, 5.34, 5.35). This is very important for large scale industrial applications and it allows controlling the amount of products as it needed. For an example; at the lower intensities it can generate more CH₄ than the CO but at higher intensities it can generate more CO than the CH₄. Also it is possible to get 1:1 ratio of CO and CH₄ at middle intensities (Figure 5.36).

Figure 5.36 The experimental CO (blue squares) and CH_4 (red circles) selectivity as a function of laser intensity and corresponding catalyst temperature in top x -axis

Since long term catalytic stability is an important factor for large scale, this Au-ZnO catalyst was used to run five consecutive CO_2 reduction cycles. The catalyst was illuminated for 5 hours using a 532 nm *cw* laser with the intensity of $8.0 \times 10^5 \text{ W/m}^2$ (maximum laser intensity used for CO_2 reduction reactions). At the end of each illumination cycle photocatalysis cell was purged with new 25% CO_2 + 75% H_2 gas mixture for next illumination. The variation of CO_2 conversion rate was < 15 % in non-systematic fashion (Figure 5.37). This high stability of the Au-ZnO can be attributed to the thermally driven CO_2 conversion. In most photo-redox systems, oxidative corrosion of the catalyst and depletion of hole scavengers directly impact the long-term stability of the catalyst. Also, this confirms that the laser induced damage does not occur under the 532 nm *cw* laser illumination.

Figure 5.37 The CO₂ conversion rate for Au-ZnO catalyst after 5 hour laser illumination cycle

5.7 Conclusion

In this work, plasmonic heating assisted efficient CO₂ conversion was proved and this method has a higher potential to develop in large scale applications. In addition to that this plasmonic heating effect of Au-ZnO can be used for several other applications such as steam generation and drug delivery. The Au-ZnO sample reached close to ~ 600 °C under 532 nm (visible light) laser illumination. The plasmonic heating drive the thermally driven CO₂ reduction reactions under laser illumination. The minimum light intensity that needs to start the CO₂ conversion can be achieve using the currently available solar concentrators. The higher robustness of the Au-ZnO is very important factor for industrial applications.

The plasmonic heating effect was investigated in detail using the temperature dependent Raman spectroscopy. Temperature programmed reaction experiments, excitation intensity dependent

catalysis reactions and thermodynamics simulations verified the plasmonic heating assisted CO₂ reduction. This method will enable a more efficient method to convert CO₂ in to viable chemicals using heterogeneous catalysts with metal nanoparticles and metal oxide under concentrated sun light.

Since it is not worth to reach the melting point of Au by increasing the heat generation it is worth to investigate the efficient heat generation of Au-ZnO using the lower light intensity probably natural sunlight. It may possible to achieve this by changing the size, shape and density of the Au nanoparticle. An attempt to increase the heating efficiency of ZnO by increasing the Au particle density was discussed in next chapter (chapter 6)

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Chapter 6

Synthesis, characterization, and photocatalytic activity of Au-ZnO nanopyramids

6.1 Introduction

The previous chapter shows that the plasmonic heating occurs in 5% Au-ZnO heterostructure under the 532 nm *cw* laser illumination. Also, it was found that the density of Au nanoparticles affect the final temperature increase at the ZnO nanoparticles. Therefore, the main objective of this work was increasing the plasmonic heating efficiency by increasing the Au to ZnO ratio. However, the synthesis procedure which was used for synthesis of 5% Au-ZnO was not suitable for this. Au-ZnO nanopyramids were the first choice because every ZnO nanoparticle has a Au nanoparticle attached in to the basal surface. Since plasmonic heating is a highly localized process, it was expected to transfer the plasmonically generated heat from Au nanoparticle to ZnO nanoparticle. In 5% Au-ZnO sample in previous chapter, all the ZnO particles do not have attached Au nanoparticle. Au nanoparticle distribution was uneven throughout the ZnO. Therefore plasmonic heating was occurring at certain few hot spots in 5% Au-ZnO sample (Figure 6.1). But when consider the large area in micrometer size for laser illumination, it is difficult to identify these hot spots separately. Since Au-ZnO nanopyramids has at least one Au nanoparticle attached in to the ZnO, every ZnO nanoparticle can be considered as a hot spot for plasmonic heating (Figure 6.2). The examples for hot spots can be found inside the red circles in Figures 6.1 and 6.2.

However, due to several possible reasons Au-ZnO nanopyramids didn't show any plasmonic heating activity under the same laser intensities as 5% Au-ZnO heterostructures. But Au-ZnO showed excellent photocatalytic activity for organic dye degradation reactions with the band gap excitation of ZnO.

Figure 6.1 Schematic diagram of 5% Au-ZnO

Figure 6.2 Schematic diagram of Au-ZnO nanopyramids

Several papers in the literature describe how the size and shape of Au-ZnO heterostructures can be controlled by using different synthetic approaches.¹⁻³ Yao *et al.*³ were able to selectively photo-deposit Au particles at the tips of ZnO nanoparticles with a pyramid shape. Li *et al.*² and Flomin *et al.*¹ used wet chemical methods to grow well-formed ZnO nanopyramids from the surfaces of Au seeds and evaluated the photocatalytic activity of these heterostructures. He *et al.*⁴ have reported on heterogeneous powders of Au-ZnO heterostructures which have been evaluated for the photodegradation of bacteria.

All of these works find that very subtle changes in the synthetic approaches yield dramatic changes in the general morphology of Au-ZnO particles. In particular, the synthetic steps

can be used to control where the Au is deposited as well as the structural details of the Au-ZnO interface. Currently, there is little understanding in the literature of how these subtle structural details impact localized changes in electronic structure near the interface, defects arising from the heterostructuring step, and the final photocatalytic activity of the heterostructure. As such, more investigations are needed to develop insight into the final chemical properties of these materials.

In this work, Au-ZnO heterostructures were synthesized using a wet chemical method that attempts to minimize the use of organic surfactants that can block catalytically active surface sites. In this system, Au nanoparticle seeds are used to nucleate the growth of ZnO structures with a pyramidal-type structure. A previously unreported lattice expansion of ~3.5% is found for ZnO in the first ~1.5 nm of the Au-ZnO interface. Photocatalytic dye degradation studies of Au-ZnO find that direct gap excitation is required to initiate photodecomposition and that the heterostructure has significantly higher catalytic activity than pure ZnO. This work provides experimental evidence that the Au nanoparticles contribute to the higher catalytic activity of Au-ZnO by widening the band gap of ZnO, improving band alignment for the injection of charge carriers into solution species, and by increasing spatial separation of photogenerated charge carriers.

6.2 Materials preparation

Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), 99.9 %, Zinc acetate dihydrate, methanol, 99.9 %, hexane, 99.9 % and acetone, 99.9 % were purchased from Alfa Aesar. Tert-butylamine borane complex, oleylamine, C18 content 80-90 % and dodecanol, 98 % were purchased from Acros Organics.

6.2.1 Synthesis of Au nanoparticles

Au nanoparticles were synthesized using the procedure of *Peng et al.*⁵ $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.5 mmol) was added to a three-neck flask with the mixture of oleylamine (2 ml) and hexane (20 ml) at room temperature. This precursor mixture was purged under flowing N_2 for ~ 10 minutes. Tert-butylamine borane complex (1 mmol) was dissolved in oleylamine (2 ml) and hexane (2 ml) in a glove box. Then, this reducing solution was quickly injected to the precursor solution in the three-neck flask. The reduction reaction started instantaneously and the color of the precursor solution changed to a deep purple within a few seconds. This solution was stirred for 1 hour at room temperature. Ethanol was then added to the colloidal solution in order to precipitate the Au nanoparticles followed by centrifugation for 20 minutes at 3000 rpm to collect the Au nanoparticles. 60 mg of precipitate (Au nanoparticles) were re-dispersed in 5 ml of hexane. The primary modification of Peng's recipe involves replacing tetralin with hexane, since tetralin was difficult to fully rinse from the sample and seemed to block surface access during photocatalytic studies.

6.2.2 Synthesis of Au-ZnO nanopyramids

Synthesis of Au-ZnO heterostructures was completed using a previously reported recipe which had been modified to reduce the use of heavier organic solvents that tend to leave surface residue on the samples.² Almost all the parameters in the synthesis procedure is critical to get a high quality ZnO nanoparticle. First, it is important to find the correct amount of gold and zinc precursors. If there is excess amount of zinc precursor, it is possible to have free ZnO nanoparticles without Au seeds which is against the main objective. If there is excess amount of gold precursors, it is possible to have free Au nanoparticles in the Au-ZnO sample which might be a problem at least by adding some volume and weight to the catalyst. The organic solvents act a critical role for maintaining the correct shape and size of the ZnO nanoparticles. *Li et al*⁶ reported that synthesis of different shapes (nanopyramids, bullet like nanocrystals, pencil like nanorods) can be achieved by changing the amount of organic solvents. Also, synthesis temperature and reaction time affects the number of incomplete ZnO nanoparticles and quality of the facets.⁶ The shape, size and quality affect the photocatalytic performance. Also, remaining organic solvents in the sample after the synthesis may reduce the photocatalytic performance by blocking the active sites. In other words, the amount of these parameters in the synthesis procedure are competing each other with respect to catalytic performance. Therefore it is important to optimize each parameter one by one to achieve the best Au-ZnO nanopyramids. Several attempts were made in order to optimize the recipe to get high quality Au-ZnO nanopyramids with lower levels organic molecules in the synthesis steps (Table 6.1). In most of these samples, Au-ZnO heterostructures were not observed. For the first time, sample 26 (Table 6.1) resulted high quality Au-ZnO heterostructured nanopyramids. Sample 26 shows pyramid shape ZnO

nanoparticles with attached Au nanoparticles at the basal surface. Also free ZnO nanoparticles were not observed that much. Again, a few attempts were made to further reduce the organic molecules while maintaining the quality of Au-ZnO heterostructures in order to minimize the active site blocking by heavy organic molecules. Since sample 31 has similar quality of Au-ZnO nanopyramids with less amount of organic solvents compared to sample 26, it was chosen as the optimized recipe. Figures 6.3- 6.10 show the Transmission Electron Microscope images of sample 21- 31 respectively.

Zinc acetate dihydrate (275 mg) was added to a mixture of oleylamine (1.5 ml) and dodecanol (6 ml) in a three-neck flask which was then purged for 10 minutes under N₂ flow. After that, pre-prepared Au seeds (60 mg dispersed in 5 ml hexane) were quickly injected into the flask and the temperature was slowly increased to and held at 140 °C for 90 minutes. The sample was then allowed to cool to room temperature. The cooled solution was rinsed with an excess of methanol several times, centrifuged, and then rinsed with acetone, centrifuged, and dispersed in hexane. After removing the liquid phase, acetone was added to the test tubes and centrifuged for 10 minutes. The precipitate was dissolved in a small amount of hexane and combined to one test tube. Then, methanol was added to the solution and centrifuged for 10 minutes. This last step was repeated one more time. The precipitate was dried under N₂ flow for few minutes. At this stage, precipitate was no longer soluble in hexane due to the lack of organic capping molecules for solubility. Then, the sample was further cleaned with oxygen plasma for 60 minutes to remove any excess organic molecules.

Table 6.1 Au-ZnO nanopyramids synthesis parameters

Sample #	Au precursor (mg)	Zinc precursor (mg)	Oleylamine (ml)	Dodecanol (ml)	Reaction temperature (°C)	Reaction time (minutes)
1	60	92	3	6	180	5
2	6	92	3	6	180	5
3	12	92	3	6	180	5
4	24	92	3	6	180	5
5	36	92	3	6	180	5
6	48	92	3	6	180	5
7	60	92	3	6	140	5
8	60	92	3	6	220	5
9	60	92	3	6	180	60
10	60	92	3	6	180	30
11	60	920	3	6	180	30
12	60	184	3	6	120	60
13	60	368	3	6	120	60
14	60	92	3	6	160	30
15	60	184	3	6	160	30
16	60	184	3	6	100	60
17	60	368	3	6	100	60
18	60	92	3	6	140	30
19	60	184	3	6	140	30
20	60	184	3	6	140	90
21	60	184	3	6	140	30
22	60	275	3	6	140	30
23	60	275	3	6	140	180
24	60	368	3	6	140	180
25	60	275	3	6	140	120

26	60	275	3	6	140	90
27	3	275	1.5	6	140	90
28	6	275	0.5	3	140	90
29	12	275	0.5	3	140	90
30	60	275	0.5	3	140	90
31	60	275	1.5	6	140	90

Figure 6.3 TEM image of Au-ZnO (sample 21)

Figure 6.4 TEM image of Au-ZnO (sample 22)

Figure 6.5 TEM image of Au-ZnO (sample 23)

Figure 6.6 TEM image of Au-ZnO (sample 26)

Figure 6.7 TEM image of Au-ZnO (sample 27)

Figure 6.8 TEM image of Au-ZnO (sample 29)

Figure 6.9 TEM image of Au-ZnO (sample 30)

Figure 6.10 TEM image of Au-ZnO (sample 31)

6.2.3 Synthesis of pure ZnO and Au-SiO₂

The pure ZnO nanoparticles were synthesized using the exact same procedure described above for the Au-ZnO heterostructures, except the Au seeds were omitted. Au-SiO₂ was prepared as a control catalyst by mixing 60 mg of Au seeds with 275 mg of commercial SiO₂.

6.3 Methylene blue degradation reactions

Prior to dye degradation runs the catalysts were treated with an O₂ plasma for ~ 60 minutes to remove surface-bound organics from the synthesis steps that could interfere with surface adsorption and photocatalytic activity. The FTIR spectra before and after the plasma etching for pure ZnO and Au-ZnO, respectively, illustrate the complete removal of organics (Figure 6.11 and 6.12).

Figure 6.11 FTIR spectra of pure ZnO before (black) and after (red) the plasma etching

Figure 6.12 FTIR spectra of Au-ZnO before (black) and after (red) the plasma etching

Methylene blue (MB) dye photodegradation was used as a model reaction in order to investigate the catalytic performance of Au-ZnO. The catalyst (27 mg) was placed into 10 ml of 20 μmol/L MB and soaked overnight (~15 hours) in the dark to stabilize the surface adsorption and desorption equilibrium of the dye. A Newport 300 W Xe arc lamp with a manual shutter was used to illuminate the sample. Agilent 8453 UV/Vis/NIR spectrophotometer was used to collect the absorption spectra during the MB degradation

reactions. Edmunds TECHSPEC longpass filters were used for wavelength dependent experiments. In photocatalysis studies, the sample mixture above was exposed to light for a predetermined period of time. Then 6 ml of the reaction solution was centrifuged to separate the solid catalyst from solution. The optical spectrum of the centrifuged solution was then taken. Absorption spectra were recorded every 10 minutes for a total of ~80 minutes. The spectral area under the absorption peak around 664 nm which is the characteristic peak for MB was calculated after the correction of baseline shift and background subtraction to get an accurate estimation for MB concentration.

6.4 Results and Discussion

6.4.1 Characterization of nanoparticle samples using UV-Vis absorption spectra

Figure 6.13 shows the UV-Vis absorption spectra for the Au seeds, pure ZnO, and Au-ZnO heterostructures used in this study. The broad absorption peak around 510 nm for the Au seeds is due to the plasmon resonance of these nanoparticles. After growth of the ZnO on the seeds, this plasmon resonance red-shifts and narrows due to Ostwald ripening of the Au nanoparticles which occurs at the temperatures used for the growth of ZnO.² The peak maximum for the Au plasmon resonance in Au-ZnO was observed around 522 nm. The changing dielectric environment caused by the newly formed Au-ZnO interface is an additional physical mechanism that likely contributes to the red-shifting of the plasmon feature.^{7, 8} To confirm this mechanism we have conducted a simple model calculation (Figure 6.14) using the quasi-static approximation⁹ to estimate the plasmon peak positions and expected shift due to differences in the dielectric environment. The calculations was

done according following an example shown in *Ohodnicki et al.*⁹ (see the section 5.2 for detail calculation procedure)

Figure 6.13 UV-Vis absorption spectra for Au seeds (black), pure ZnO (blue) and Au-ZnO heterostructures (red).

Our model calculation predicts that 5 nm Au seeds in hexane have a plasmon resonance at ~504 nm that shifts by ~48 nm when fully encapsulated in ZnO. Considering that our Au particles are slightly larger than 5 nm, have a distribution in sizes, and are not fully encapsulated by ZnO, the resonance features and red-shift noted in Figure 6.13 are reasonable and qualitatively consistent with a shift due to dielectric changes. Additionally, *Khan et al*¹⁰ have attributed the red-shift noted above, in part, to electron density changes which occur when charge flows from Ag to ZnO as Fermi levels equilibrate. A similar electron density change in Au-ZnO would also cause red-shifting of the plasmon resonance,

although quantifying this effect relative to the spectral changes mentioned above is difficult.

Figure 6.14 Comparison of Au nanoparticle suspended in hexane and full embedded in ZnO

Figure 6.15 shows the Tauc plots of the absorbance spectra to estimate the direct and indirect band gaps of Au-ZnO and ZnO. Tauc plots estimate the direct band gap of ZnO at ~ 405 nm (3.06 eV) in the pure ZnO sample and ~ 383 nm (3.23 eV) in the Au-ZnO sample. There is a strong scattering contribution to the pure ZnO spectra that can complicate band gap estimates; however, the peak spectral features associated with the band edge for the Au-ZnO and ZnO samples are also shifted from each other. While the mechanism responsible for this bandgap shift is not fully understood,

*He et al.*⁴ have also reported a Au-loading dependent bandgap in Au-ZnO heterostructures formed by the reduction of H_{AuCl}₄ on pre-formed ZnO nanoparticles.

Figure 6.15 Tauc plots for the direct (black) and indirect (blue) band gap estimations of pure ZnO and Au-ZnO

6.4.2 Characterization of TEM and HRTEM images

Pure ZnO was synthesized without the use of Au seeds. In these samples the ZnO has particle sizes of ~20-30 nm (Figure 6.16). The average size of the Au seeds used to nucleate the growth of ZnO is between 4-6 nm (Figure 6.17). Representative TEM images of the Au-ZnO heterostructures find Au sizes between 5-7 nm (Figure 6.18). The increase in Au particle size in the heterostructure is consistent with the red-shifted plasmon feature noted in Figure 6.13. Au nanoparticles that are unattached to ZnO can also be seen in Figure 6.18 with diameters of ~ 8-9 nm. These large Au nanoparticles also likely contribute to the red-shifting of the Au plasmon resonance peak. As a result of the free Au seeds, the photocatalysis experiments described below also evaluated similar Au nanoparticles deposited on an inert SiO₂ in order to assess their contribution (or lack of) to the photodegradation of methylene blue (see photocatalysis discussion in section 6.4.4).

The TEM images in Figure 6.18 show that the ZnO particle sizes in the heterostructures are around 18-22 nm. Additional TEM and HRTEM images (Figures 6.19 and 6.20) illustrate the ZnO is single-crystalline and possesses a pyramidal-type morphology with a hexagonally shaped base. A similar nanopyramid shape has been reported previously for the ZnO component of Au-ZnO heterostructures, which are grown using a similar synthetic procedure as we report here.² Likewise, similar nanopyramids resulted from a one-pot strategy capable of depositing the Au either at the base or tips of the pyramids.¹ This type of nanopyramidal ZnO was also reported in a study that synthesized the ZnO structures first and later photodeposited Au particles at the tips.³ The more heterogeneous nature of the nanopyramids in this study can be attributed to the lower levels of surfactants employed for both the Au seed and ZnO synthesis. Since organic contamination can interfere with subsequent catalysis studies by blocking the access to surface sites, their usage was minimized as much as possible.

Figure 6.16 TEM images of pure ZnO nanopyramids

Figure 6.17 TEM images of Au seeds

Figure 6.18 TEM images of Au-ZnO nanopylramids

The HRTEM images in Figure 6.19 provide additional insight on the microstructure of the Au-ZnO samples. The ZnO component of the heterostructure is single-crystalline with ZnO (002) lattice fringes observed. The Au can be identified as polycrystalline particles with multiple Au (111) facets observed having domain sizes of ~ 2.6 nm. This value agrees with the Au (111) domain size of 2.7 nm from the Rietveld analysis (see the section 6.4.3). The large number of Au (111) facets minimize the surface energy and strain due to the formation of twinned defects.¹¹ The ZnO (002) plane appears to be parallel to the Au (111) plane at the interface. The basal surface of the ZnO structure is perpendicular to the ZnO (002) direction and the HRTEM images suggest the ZnO crystal starts growing in the [0001] direction, along the *c*-axis, on top of the Au seed. This growth mechanism was proposed by *Flomin et al.*¹ using TEM images of aliquots obtained during different stages of the synthesis.

Figure 6.19 HRTEM image of the Au-ZnO interface

TEM images of the Au-ZnO heterostructures also suggest there is variation in the general position of the Au on the basal surface of the ZnO nanopyramid, which is shown in both the images and schematic of Figure 6.20. This variation has not been noted in previous structural characterizations of this interface¹⁻³ and may result from the changes in surfactants used in the synthesis reported here. In general, it appears that the Au particle does not strictly occupy a position at the center of the ZnO basal plane and can instead occupy a variety of positions. Currently, the role of this structural detail on the photophysics of these samples is not understood.

The HRTEM images of 9 Au-ZnO interfaces were analyzed using ImageJ software. A rectangular area in the middle of the ZnO nanoparticle consisting of 2.5 nm width and 4 lattice planes of length was chosen for the analysis (Figure 6.21). The average *d*-spacing of these 4 lattice planes was used as an estimate of the *d*-spacing of the corresponding rectangular area. Up to 20 lattice planes from the Au-ZnO interface were analyzed. The final results and standard deviations can be found in Table 6.2 and which are the average values of all 9 Au-ZnO interfaces. Figures 6.22, 6.23, 6.24 and 6.25 show the HRTEM images of additional Au-ZnO interfaces.

Figure 6.20 (a) Schematic diagram for possible orientations of Au nanoparticles on the basal surface of the ZnO nanopyramids (b) TEM images of different basal surfaces of the ZnO nanopyramids.

Figure 6.21 *d*-spacing analyzing method of ZnO(002) lattice plane

Table 6.2 d-spacing values of Au-ZnO interfaces

Lattice planes	d-spacing (Å)										Standard deviation
	I-1	I-2	I-3	I-4	I-5	I-6	I-7	I-8	I-9	Average	
0-4	2.65	2.75	-	2.72	2.70	2.65	-	2.65	2.70	2.69	0.04
4-8	2.62	2.55	2.67	2.60	2.55	2.70	2.60	2.77	2.70	2.64	0.07
8-12	2.72	2.67	2.55	2.55	2.57	2.55	2.70	2.70	2.62	2.63	0.07
12-16	2.57	2.60	2.60	2.57	2.60	2.62	2.72	2.72	2.62	2.62	0.06
16-20	2.62	2.55	2.60	2.67	2.57	2.55	2.60	2.50	2.65	2.59	0.05

Figure 6.22 Au-ZnO interface 1

Figure 6.23 Au-ZnO interface 2

Figure 6.24 Au-ZnO interface 3

Figure 6.25 Au-ZnO interface 4

Interestingly, the d -spacing corresponding to the ZnO (002) plane experiences a $\sim 3.5\%$ expansion relative to the bulk value of $2.60 \text{ \AA}$ (Figure 6.26). This expansion has not been well documented in previous studies of Au-ZnO made by similar synthetic approaches.^{1, 2} This expansion only occurs within $\sim 1.5 \text{ nm}$ of the ZnO interface with Au (Figure 6.27). This lattice expansion gradually decreases and completely disappears $\sim 4.5 \text{ nm}$ away from the interface where the spacing approaches a constant bulk value of $2.60 \text{ \AA}$. The plain ZnO nanoparticles do not experience any measurable lattice expansion relative to bulk values (not shown). For comparison, *Shim et. al.*¹² have previously reported $\sim 1\%$ lattice contraction in CdTe near the CdSe interface of linear barbell heterostructures. The lattice spacing of the CdTe tips on these barbells then approaches bulk values further away from the interface.

Figure 6.26 Line scan along the Au-ZnO interface with average lattice spacings for the ZnO (002) plane in the regions shown.

Figure 6.27 Average d -spacing of ZnO (002) at different distances from the interface. Error bars were determined by analyzing 9 different structures.

6.4.3 Characterization of X-Ray Diffraction patterns and Rietveld analysis

Powder XRD patterns confirm the cubic structure of Au nanoparticles and hexagonal wurtzite structure of ZnO (Figure 6.28). Rietveld analysis is performed to evaluate crystal size and microstrain in both pure ZnO and Au-ZnO (Figures 6.29 and 6.30). While particle size determinations from a Rietveld analysis of XRD lineshapes are simple to interpret, the precise origin of microstrain contributions to linewidths is more challenging to attribute to a single structural feature.¹³⁻¹⁵ The microstrain value determined in a Rietveld analysis is interpreted as a generic deviation from the ideal lattice which can be caused by a variety of crystal-level defects, such as dislocations, domain boundaries, and the expansion/contraction of a lattice. As such, microstrain analysis can provide verification of and insight into some of the microstructure and defects noted in the TEM images above.

The calculated Au particle size in the heterostructure is 2.7 nm, which is consistent with the polycrystalline nature of the Au particles and the (111) domain sizes noted in Figure 6.19. The calculated particle size for the pure ZnO sample is 25.9 nm, which is consistent with the TEM images of Figure 6.16. The calculated ZnO particle size in Au-ZnO is 20.5 nm which also agrees well with the size determined from TEM images (Figure 6.18). The Rietveld analysis estimates a 0.324 % microstrain for the Au in Au-ZnO which provides evidence for the distribution of Au(111) domains noted in Figure 6.19. Microstrain estimates for pure ZnO were 0.047 %. The calculated microstrain for the ZnO in the Au-ZnO sample is 0.146 %, which is 3 times larger than that for pure ZnO. In comparison, *Khusaimi et al.*¹⁶ previously reported a 0.257 % microstrain of ZnO in Au/ZnO heterostructures on a Si substrate.

Microstrain for ZnO in the heterostructures can be attributed the increased to the lattice expansion noted in Figures 6.26 and 6.27. The XRD measurement is a bulk probe and averages this defect over the entire sample, including regions where ZnO retains its normal lattice, which likely reduces the magnitude of the microstrain estimate. In fact, the average lattice expansion in Figure 6.26 using the entire ZnO portion of the image (interface and non-interface regions) is only ~0.38 %, compared to ~3.5% at the interface, which illustrates how easily the structural characteristics of the interface can be averaged out.

Figure 6.28 Comparison of X-ray diffraction patterns of pure ZnO and Au-ZnO nanopyrramids

Figure 6.29 High resolution XRD patterns with calculated Rietveld pattern for pure ZnO

Figure 6.30 High resolution XRD patterns with calculated Rietveld pattern for Au-ZnO

6.4.4 Photocatalytic performance

Figure 6.31 shows representative UV-Vis absorption spectra used to determine the kinetics of MB photodegradation under $\lambda > 295$ nm irradiation. Figure 6.32 shows photodegradation kinetics for pure ZnO, Au-ZnO, Au-SiO₂ and a stock solution of 20 $\mu\text{mol/L}$ MB (no catalyst) also at $\lambda > 295$ nm. After 60 minutes of illumination, Au-ZnO photodegrades ~98 % of the MB. In comparison, pure ZnO only degrades ~17 %, the Au/SiO₂ control ~ 4 %, and the stock solution of MB (without catalyst) ~10 %. Plots of $\ln(C/C_0)$ versus time are linear (Figure 6.33) which confirm the pseudo first order reaction kinetics and associated degradation mechanisms noted in many MB photodecomposition studies.⁸ The exceptional activity for Au-ZnO combined with the low or lack of activity for ZnO, Au-SiO₂ and MB alone, point to the synergistic role of the Au and ZnO in the heterostructured materials.

Figure 6.31 UV-Vis absorption spectra for MB degradation using Au-ZnO with $\lambda > 295$ nm

Figure 6.32 MB degradation results for Au-ZnO (black), ZnO (red), MB solution (no catalyst) (blue) and Au-SiO₂ (magenta) with $\lambda > 295$ nm illumination

Figure 6.33 Linear fit for $\ln(C/C_0)$ of MB versus time for Au-ZnO (a) under $\lambda > 295$ nm illumination (b) under $\lambda > 400$ nm illumination

Wavelength dependent photodecomposition studies were employed to help answer mechanistic questions about the photophysics of these samples. Figure 6.34 shows photodegradation kinetics of MB using $\lambda > 295$ nm, $\lambda > 320$ nm and $\lambda > 400$ nm longpass filters. Figure 6.35, illustrates that the catalytic activity of Au-ZnO remains almost constant between $295 \text{ nm} < \lambda < 320 \text{ nm}$. But for $\lambda > 400$ nm, Au-ZnO has no appreciable activity. The calculated pseudo first order rate constants of Au-ZnO were 0.058 min^{-1} , 0.059 min^{-1} and 0.003 min^{-1} for $\lambda > 295$ nm, $\lambda > 320$ nm and $\lambda > 400$ nm illumination, respectively. This confirms the necessity of direct bandgap excitation of ZnO in the Au-ZnO heterostructure (bandgap ~ 383 nm, Figure 6.15) in order to initiate the photodecomposition of MB. P25 TiO_2 has comparable kinetics for MB degradation (Figure 6.35) for $\lambda > 295$ nm, but this activity approaches zero for $\lambda > 320$ nm. P25 TiO_2 has a comparable bandgap to ZnO and we suspect that the large difference in activity towards MB results, in part, from

the lack of metal co-catalysts on the TiO₂ sample for shuttling electrons into solution. In addition, the Au-ZnO heterostructures have subtle changes in electronic structure and band alignments (discussed below) that also likely contribute to their improved activity over P25 TiO₂.

Several previous works have reported higher catalytic activity of Au-ZnO heterostructures over pure ZnO using dye degradation reactions.^{1-4, 8, 17-24} Direct comparisons of these efforts and our own are difficult due to different reaction conditions and dyes used. One reasonable method for comparing these works involves evaluating the differences in % decomposition between the ZnO and Au-ZnO catalysts. *Yao et al.*³ showed that methyl orange decomposition was ~2 times faster with Au-ZnO over ZnO. *Li et al.*² and *Wang et al.*²² showed that rhodamine B decomposition was ~1.5 and ~3 times faster with Au-ZnO versus ZnO respectively. *Lee et al.*¹⁹ showed that the degradation of rhodamine 6G was ~2 times faster with Au-ZnO over ZnO. In our current work, the degradation of methylene blue was ~6 times faster with Au-ZnO than pure ZnO.

Figure 6.34 Wavelength dependent MB degradation with Au-ZnO

Figure 6.35 First order rate constants for MB degradation with Au-ZnO and TiO_2 using different longpass filters

It is interesting to analyse reasons for the enhanced photocatalytic activity of Au-ZnO over ZnO. Plasmonic heating,²⁵ direct electron injection²⁶ from Au, and field-enhancement created by Au plasmon resonance²⁷, can all be easily ruled out from the wavelength dependent studies of Figure 6.34. If the Au plasmon was playing a critical role in the photophysics of this sample, one would expect to see photocatalytic activity at wavelengths longer than 400 nm. The loss of activity towards MB as the irradiation wavelength becomes sub-bandgap clearly points to a mechanism where direct gap excitation generates charge carriers that eventually create the radical species in solution that degrade MB. The lack of catalytic activity seen for Au nanoparticles on SiO₂ (Figure 6.32) helps to rule out any potential mechanisms involving interband transitions from occupied *d*-bands below the Fermi level (E_f) to unoccupied *s-p* bands above the E_f of Au, as was observed experimentally by *Hou et al.*²⁷ for the photocatalytic reduction of CO₂ with Au/TiO₂.

The characterization and photocatalytic activity data presented above allow us to propose how Au enhances the photoactivity of the heterostructures towards MB degradation (Figure 6.36). Direct gap excitation creates electrons and holes, which thermalize to the bottom and top of the conduction and valence bands, respectively, of ZnO. The energy of the conduction band minimum and that of the valence band maximum of ZnO are -0.2 V and +3.0 V respectively, with respect to the Normal Hydrogen Electrode (NHE).²⁸ The Fermi level of Au is +0.45 V with respect to NHE.⁴ Since the Fermi level of Au is below the conduction band of ZnO, the photoexcited electrons are easily transferred to the Au nanoparticles from the conduction band of ZnO.²² The close contact of the ZnO and Au nanoparticles increases this charge separation efficiency helping to reduce carrier

recombination.⁴ The build-up of electrons in Au will shift E_f in a more negative direction but the electron transfer from ZnO to Au would not be altered until E_f approaches the conduction band minimum of ZnO. The electrons at the E_f of Au can be injected into H_2O species to form $OH^\bullet$ radicals. The charge separation described above also facilitates injection of the hole left behind in the valence band into water to generate $OH^\bullet$ radicals, which attack MB directly and contribute to the photodegradation. The products observed from this photodegradation mechanism of MB have been identified in previous works as CO_2 gas, nitrate, sulfate and ammonium.²⁹

Figure 6.36 Approximate band alignment of Au-ZnO. Potentials are with respect to NHE

The photocatalytic degradation of methylene blue in water can be explained according to the mechanism proposed by *Houas et al*²⁹ as follows:

For $\lambda < 359$ nm (band gap of ZnO) illumination,

At valence band of ZnO,

At conduction band of ZnO,

At Au NP surface,

At MB molecules,

In addition to charge separation, the Au in heterostructures is known to decrease the work function of a metal oxide, which can impact carrier generation and injection.³⁰ Sykes *et al.*³⁰ have demonstrated that the work function of TiO₂ can decrease from 5.3 eV to 4.8 eV with increasing Au loading due to an interfacial dipole created as charge flows from Au to TiO₂ in order to equilibrate Fermi levels. The work function of ZnO and that of Au are 5.3 eV and 5.1 eV, respectively, which indicates a similar mechanism could occur with these heterostructures.^{31, 32} The lowered ZnO work function caused by equilibration with the Au Fermi level would increase the transfer rate of conduction band electrons from the ZnO surface to adsorbed O₂ (rate limiting step of the photocatalytic MB degradation) and H₂O to form O₂[•] and HO₂[•] radicals, respectively.^{22, 23, 33, 34}

Finally, the Au is also likely playing a very subtle role in adjusting the band alignment of the Au-ZnO system. The measured bandgap for Au-ZnO was 383 nm (3.23 eV) in comparison to 405 nm (3.06 eV) for ZnO (Figure 6.13). This bandgap increase could result from a shift of conduction band edge in a more negative direction or shift of valence band

edge in a more positive direction.⁴ It is also plausible that both the conduction and valence bands could shift simultaneously in these respective directions to account for the increased bandgap noted. Any shift of the conduction band into more negative direction or any shift of the valence band into more positive direction will improve the energetic band alignment needed for the generation of the $O_2^{\bullet}$, $HO_2^{\bullet}$, and $OH^{\bullet}$ radicals discussed above (see also Figure 6.34). While it can be somewhat counterintuitive, this is an example where a bandgap increase, regardless of whether it occurs through conduction or valence band manipulation, can improve photoactivity.

6.5 Conclusions

Au-ZnO heterostructures were synthesized using a literature recipe that has been modified to reduce the amount of organic surfactants. The resulting Au-ZnO heterostructures have a nanopyramid geometry composed of ZnO with Au nanoparticles attached to the basal surface. The Au-ZnO nanopyramids didn't show plasmonic heating effect as expected. There are several possible reasons for that but still the exact reason is unclear. According to the TEM images, Au nanoparticles are not embedded in the ZnO basal surface and they are just sitting at the surface. Since this reduces the surface contact plasmonic heat transfer to the ZnO nanoparticle via conduction might be not efficient. A large portion of generated heat at the surface of the Au nanoparticle may be lost in to the air. Also even heat efficiently transfer from Au to ZnO, there might be a thermodynamic barrier for the catalytic activity of the ZnO surface which is not possible to overcome in this situation. Finally, the remaining organic molecules even after plasma etching that might affect to the heat transfer

or catalytic activity. Also, $E_2(\text{high})$ mode of ZnO was clearly observed for pure ZnO but it wasn't visible for Au-ZnO in Raman spectra. But reason for this is unclear.

The (002) planes of ZnO expand by $\sim 3.5\%$ in the first ~ 1.5 nm of the interface and approach bulk values of $2.60 \text{ \AA}$ towards the apex of the nanopyramid. The band gap of ZnO increases from 405 nm (3.06 eV) to 388 nm (3.23 eV) due to heterostructuring with Au. Wavelength dependent photodecomposition studies with methylene blue indicate that direct gap excitation of the ZnO component of the heterostructure is required to decompose the dye. Au-ZnO heterostructures decompose the dye 6 times faster than simple ZnO. The improved photocatalytic activity of Au-ZnO is largely attributed to the physical separation of photoexcited electrons and holes caused as electrons are injected from the conduction band minimum of ZnO to the Fermi level of Au which leads to facile generation of radicals in solution which decompose the dye. It was also hypothesized that the slight increase in ZnO bandgap in the heterostructure also contributes to the faster degradation kinetics by improving conduction and valence band energetics for injecting electrons and/or holes, respectively, into solution/reactants. Likewise, it was also hypothesized that heterostructuring ZnO with Au can cause a decrease of the work function of ZnO which would also improve lead to improved electron injection from the conduction band to electron acceptors.

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**Synthesis, characterization and photocatalytic activity of
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