

**Novel Gold/Metal Oxide Nanocomposite Materials:
Synthesis, Structure, and Catalytic Activity**

Senior Honors Thesis

Department of Chemical Engineering, Tufts University

Forrest Gittleson

May 2009

Table of Contents

1.	Introduction.....	1
2.	Experimental	2
2.1	Gold Nanocrystal Synthesis	2
2.2	Separation	2
2.2.1	Ionic Liquid Phase Transfer	2
2.3	Deposition	3
2.3.1	Coprecipitation.....	3
2.3.2	Deposition-Precipitation	3
2.3.3	Gold Growth on Zinc Oxide	4
2.4	Catalytic Activity	4
3.	Results and Discussion	5
3.1	Gold Nanoparticle Synthesis and Extraction	5
3.2	Gold Deposition on Metal Oxides	6
3.3	Gold/Zinc Oxide	8
4.	Conclusions and Future Work.....	13
5.	Acknowledgements.....	14
6.	References.....	15

1. Introduction

Given the market and political imperatives to develop and disseminate new clean energy technologies, much research has recently focused on the catalysis of chemical reactions to improve the efficiency of energy generation and decrease harmful emissions. Some of this work has concentrated on reactions that reduce emissions by converting unwanted products (i.e. carbon monoxide conversion to carbon dioxide) or on fuel reforming reactions (i.e. generation of hydrogen via the water-gas shift reaction). Significant progress in catalysis research has been made on multiple fronts involving everything from processes to improve selectivity and conversion to synthesis of new materials that hold promise for further advances.

There is great promise for catalysis research in nano-scale materials synthesis and testing. Devising materials at the nano-scale allows researchers to broaden their focus to materials that, though they may not be active in bulk, hold special properties at the nano-scale. Gold is one such material that exhibits remarkably different characteristics in atomic amounts. Published work to date has shown that nano-scale gold is an active catalyst for many reactions of interest including the carbon monoxide (CO) oxidation and water-gas shift (WGS) reactions. Both of these reactions are important for their applications to fuel cell technology. The CO oxidation reaction represents a method by which to remove carbon monoxide from fuel reforming product gases (syngas) that are used to generate energy in a fuel cell. In this circumstance, CO is known to poison platinum electrocatalysts at the anode, decreasing power output; therefore its removal is essential. The WGS reaction, which increases the yield of hydrogen from

steam reforming, also represents a target for improved catalysis by gold.

Synthesis of gold-containing nanomaterials for these purposes can be quite challenging and thus poses an obstacle to their further study. Nevertheless, this work seeks to advance a unique line of research into gold-containing nanomaterial synthesis, characterization, and activity testing for the catalysis of various energy-related reactions. A more refined focus is specific to nanocrystalline gold and its interactions with metal oxide supports to provide potentially better activity for the CO oxidation and WGS reactions.

Preliminary studies involved gold nanoparticle colloid synthesis and separation, the goal of which was to develop unsupported gold nanoparticles with islands of metal oxide deposited on their surface. However, separation of gold nanoparticles from solution proved to be an insurmountable obstacle. To synthesize gold coordinated with metal oxides, several deposition methods were then studied. The structures formed were unique, yet again difficult to extract, making activity testing a challenge. These studies eventually led to a narrowed focus on gold/zinc oxide (Au/ZnO) nanocomposite materials. Adapting several methods seen in the literature concerning the Au/ZnO system, procedures were tuned to obtain Au/ZnO from zinc oxide nanocrystals, rods, and wires. Subsequent activity testing for the CO oxidation reaction showed that these materials are active, though perhaps not ideal at this early stage of study.

The work presented here should serve as a foundation for further research into gold/metal oxide nanocomposite materials for the catalysis of energy-related reactions.

Particular emphasis is placed on the promise of Au/ZnO nanocomposites.

2. Experimental

The focus of this work has evolved significantly since its inception and as such covers several different topics, all of interest to gold nanoparticle synthesis, characterization, and activity evaluation. What follows is a summary of the significant experimental procedures employed during this project.

2.1 Gold Nanocrystal Synthesis

Many procedures for gold nanoparticle colloid synthesis are available in the literature. The procedure used for this project was adapted from Sau and Murphy (2004) and employs cetyltrimethylammonium bromide (CTAB) surfactant to stabilize sub-10nm gold particles in aqueous solution. In a typical procedure, 0.25mmol of chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was dissolved in 25mL of water. Then 7.5mmol of CTAB was added to 75mL of water and heated to approximately 70°C until dissolution. The CTAB solution was added dropwise into the heated gold precursor solution. Next, 0.6mmol of sodium borohydride (NaBH_4) was dissolved in 60mL and chilled in an ice bath. The chilled solution was then added dropwise into the Au/CTAB solution to reduce gold and form Au nanoparticles. The colloid was allowed to mix for approximately 2 hours.

2.2 Separation

Because of the small particle size of the gold suspended in aqueous solution and its stability due to the CTAB surfactant, it was judged that centrifugation would not be a useful method of extracting gold particles

from solution¹. As an alternative, phase transfer using an ionic liquid was evaluated.

2.2.1 Ionic Liquid Phase Transfer

For the extraction of gold nanocrystals from aqueous solution, 1-butyl-3-methylimidazolium hexafluorophosphate (ionic liquid) was employed in a phase transfer procedure adapted from Wei, et al. (2004). Typically, the ionic liquid was added to aqueous gold stock solution in weight ratios ranging from 1:5 to 1:20 ionic liquid to aqueous stock solution. With vigorous mixing of the two phases, the aqueous phase (originally a deep purple hue) became colorless and transparent while the (originally yellow) organic phase became purple, indicating the phase transfer of gold particles. Following the extraction, the aqueous portion was analyzed by UV spectroscopy, showing that no gold was present in the supernatant².

For removal of the gold nanoparticles from the ionic liquid phase, several methods were tested. Because of the ionic liquid's high viscosity at room temperature, it was necessary to heat that phase to reduce viscosity and induce precipitation of the gold particles coordinated in the imidazole ring. Experiments involved heating the ionic liquid with coordinated gold in the presence of residual water. The result was a color change in the ionic liquid from purple to brown, possibly indicating decomposition of ionic liquid or aggregation of gold

¹ Testing of this hypothesis later showed that centrifugation of the gold colloid produced an aggregation of gold particles with particle sizes larger than those in solution. This method was also limited by the low gold concentration of the colloid and the size of the centrifuge tubes available.

² No peak was visible at the 520nm wavelength that corresponds to the absorption by gold. UV spectroscopy also showed that surfactant was present in the supernatant following extraction, indicating that a substantial portion of the surfactant did not transfer into the ionic liquid phase.

nanoparticles into larger gold clusters³. To avoid the presence of water, fresh ionic liquid coordinated with gold was redispersed (and dissolved) separately in methanol and in ethanol by heating after the aqueous layer was removed. Reprecipitation of the ionic liquid from ethanol and methanol by cooling in an ice bath produced a white organic phase containing the gold particles⁴. After removal of the alcohol, the ionic liquid was heated again, boiling off any residual alcohol, reducing the viscosity, and inducing precipitation of the gold species. During heating, gold particles precipitated out of solution. Because of the small amount of ionic liquid being used, the total amount of gold precipitated was in the 1mg range, close to the calculated weight of gold present in the original aliquot of stock solution used.

Removal of the precipitated gold from ionic liquid was conducted by adding additional ethanol and heating until ionic liquid dissolution, then decanting off the supernatant. Transmission electron microscopy (TEM) was used to determine the particle size of the extracted gold.

2.3 Deposition

Because of the limitations of the ionic liquid extraction procedure, a new method was sought to enable unsupported nanoparticle gold synthesis. Procedures for gold deposition on metal oxides or vice versa vary widely and include coprecipitation (CP), deposition-precipitation (DP), as well as other more unique methods of nanocomposite synthesis.

³ Swatloski, et al. (2003) suggests that residual water is the culprit, as decomposition of the ionic liquid occurs readily in water.

⁴ For the ethanol sample after reprecipitation, a UV spectrogram showed no gold particles in the ethanol supernatant solution.

2.3.1 Coprecipitation

Preliminary attempts at coprecipitation of gold and metal oxides varied considerably from those found in Fu, et al. (2001). Though ceria and zinc oxide were used, gold stock solution with 5-10nm gold crystals was substituted for gold precursor. In one trial, an aliquot of gold stock solution was mixed with cerium(III) nitrate solution in a molar ratio of 1:9 gold to cerium (III) nitrate. To maintain the pH around 10, 0.25M NaOH was added dropwise, leading to the precipitation of the metal oxide species. The same procedure was also repeated with zinc nitrate in place of cerium(III) nitrate. These trials did not include the final drying and calcination steps found in Fu, et al. (2001).

Another “coprecipitation” procedure was devised involving the ionic liquid extraction mechanism. It was thought that by simultaneously extracting gold nanoparticles and coordinated metal oxide, the size of metal oxide structures would not be significantly larger than those of the gold. This, in fact, proved to be the case. Prior to the ionic liquid extraction, cerium(III) nitrate was mixed with aqueous stock solution in a ratio of 10:1 gold to cerium(III) nitrate by weight. That solution was then contacted with ionic liquid and agitated. Subsequent extraction steps were the same as those above. TEM was used to determine the presence of ceria as well as the approximate sizes of gold and ceria particles.

2.3.2 Deposition-Precipitation

A deposition-precipitation procedure similar to that found in Fu, et al. (2001) was used to produce gold/zinc oxide nanocomposite materials from zinc oxide nanocrystals, rods, and wires. Synthesis of ZnO rods and wires was adapted from Cheng, et al. (2006), which describes several factors that affect zinc oxide crystal growth. For the synthesis

of ZnO wires, 1.15g of zinc acetate dihydrate was mixed with 15mL of methanol in a Teflon coated autoclave-safe container. Next, 22.5mL of Me₄NOH (25w/w in water) and 7.5mL of Me₄NOH (25w/w in methanol) were mixed and added to the zinc acetate solution. The solution was stirred for 30 minutes then transferred to a furnace for heating at 75°C for 24 hours. Afterwards, the white precipitate was centrifuged at 9,000 rpm for 20 minutes and washed four times with water to obtain a neutral pH. The ZnO precipitate was then dried in an oven for 48 hours at 70°C and crushed to a powder. ZnO nanorods were synthesized in much the same way, with the only difference being the water content. Water content for ZnO nanorod synthesis was decreased by using 7.5 of Me₄NOH (25w/w in water) and 22.5mL of Me₄NOH (25w/w in methanol). Zinc oxide nanocrystals were synthesized using only 30mL of Me₄NOH (25w/w in methanol).

After obtaining zinc oxide rods and wires, deposition of gold was conducted by the DP method. First, 0.2g of ZnO was dispersed in 10mL of water to which was added 0.24g of (NH₄)₂CO₃ (acting as a buffer). Next, 0.01g of chloroauric acid was dissolved in 5mL of water. The gold solution was added dropwise to the zinc oxide suspension. After stirring for 10 minutes the precipitate was filtered under vacuum and washed twice with water. The solid was dried on filter paper at 60°C for 24 hours. After crushing the dried powder, it was placed in an autoclave-safe container and calcined in a furnace at 250°C for four hours. Gold crystal growth was obvious from the color change following calcination.

2.3.3 Gold Growth on Zinc Oxide

As an alternative to deposition-precipitation, another gold/zinc oxide structure was synthesized by growing gold nanocrystals in the presence of zinc oxide nanorods. This

procedure was adapted from that in Zhang, et al. (2008), the only difference being that the methanol solution containing zinc oxide was not treated by nitrogen purging before extended heating. ZnO nanorod synthesis involved first preparing a zinc acetate in methanol solution and a KOH in methanol solution. The KOH solution was then added dropwise to the zinc acetate solution and allowed to stir at 60°C for two hours. The mixture was cooled and purged with air to reduce the volume and left to mix at 60°C for 12 hours. Because most of the methanol evaporated over the course of the 12 hours, leaving only a white precipitate paste, the zinc oxide was redispersed in ethanol, washed several times with dilute trisodium citrate solution, and centrifuged.

To promote gold crystal growth on zinc oxide, 0.4mmol ZnO nanorods were dispersed (via sonication) in 3.0mM trisodium citrate solution. To that solution was added 0.008mmol of chloroauric acid dispersed in water. The solution was allowed to stir for 12 hours. The precipitate was collected by centrifugation at 50,000 rpm for 45min and dried at 60°C for 4 hours. In addition to this 50:1 ZnO to Au sample, 100:1 and 25:1 samples were also made. The 25:1 sample was produced in a larger quantity to ensure sufficient yield after collection. TEM images of these samples show nanoparticulate gold and zinc oxide coordinated together.

2.4 Catalytic Activity

Testing catalytic activity for the CO oxidation reaction involved using a packed bed reactor with approximately 0.1g of catalyst per trial. A mixture of 2% carbon monoxide, 1% oxygen and the balance helium was flowed over the bed at a flow rate of 75mL/min. Programs were initiated to evaluate CO conversion to CO₂ at temperatures ranging from 25°C to 250°C.

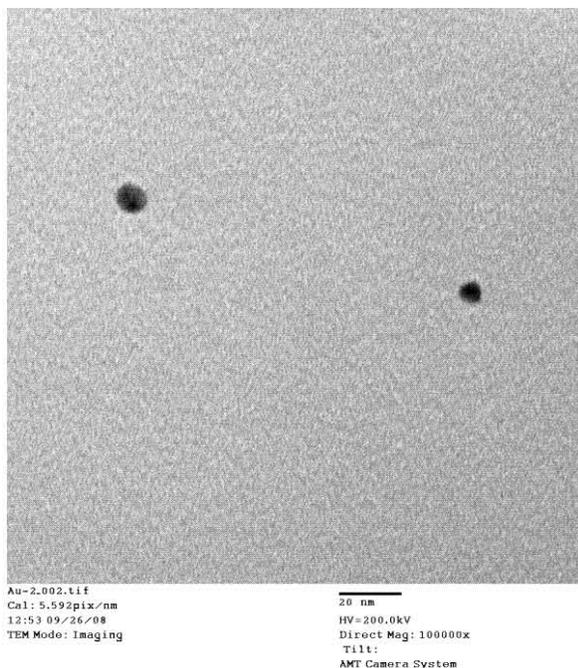


Figure 1: Gold nanocrystal colloid

Light-off curves showing conversion as a function of temperature were constructed using peak area data from a gas chromatograph connected to the output stream of the packed bed. Only steady-state data were collected. Accordingly, at each temperature, data were collected for one hour and averaged.

3. Results and Discussion

The results of the experiments are presented and discussed in the following sections.

3.1 Gold Nanoparticle Synthesis and Extraction

Though the original focus of this work was to prepare nanostructures of gold with metal oxide islands as a way of inverting the structure of active water-gas shift catalysts (including gold on ceria, lanthana, and zinc oxide), this proved to be more difficult than originally expected. In fact, the biggest obstacle to the pursuit of these structures was the extraction of intact gold nanoparticles from aqueous solution.

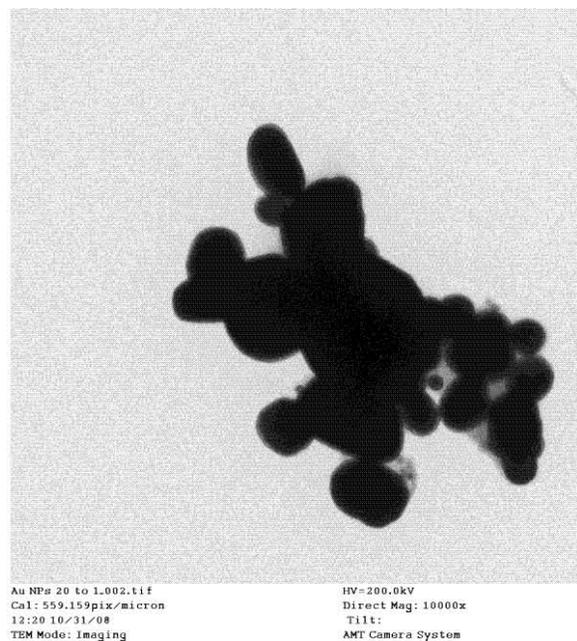


Figure 2: Gold nanoparticle cluster after ionic liquid extraction

Nevertheless, gold colloidal suspensions were synthesized and characterized by TEM.

Of the gold colloid syntheses conducted, several trials did not succeed in producing homogeneous suspensions, perhaps due to insufficient dissolution of CTAB before addition to the gold precursor solution. Varying the procedure to allow for CTAB dissolution prior to mixing with gold precursor solved these problems. The homogeneous gold colloid sample that constituted the aqueous stock solution used in subsequent procedures had a concentration of 1.42mM Au. This sample was subjected to a UV spectrograph, which showed peaks at 520nm, consistent with absorption by gold nanoparticles. TEM images, such as that seen in Figure 1, indicate the presence of single-crystal gold of approximately 5-10nm. Though this size is not ideal for water-gas shift catalysis, it would likely be active for the CO oxidation reaction once extracted from solution.

Because centrifugation of the aqueous gold stock solution at 40,000 rpm was not sufficient to collect gold, other extraction methods were attempted. Simply boiling off the solvent was, as expected, unsatisfactory due to the precipitation of CTAB along with gold. With the ionic liquid extraction procedure adapted from Wei, et al. (2004), gold nanocrystals were removed from the aqueous solution. However, this procedure, involving multiple dissolution and precipitation steps, was labor intensive, costly (primarily due to the cost of the ionic liquid), and had low yield⁵. Furthermore, TEM images of the gold collected via this procedure (as seen in Figure 2), show that aggregation occurs and particle size is not preserved⁶. This suggests that even if a large amount of gold could be extracted using this method, it would not be ideal for either WGS or CO oxidation reactions. Nevertheless, these larger gold nanoparticles may still be used to attempt a deposition of metal oxide islands, per the initial goal of this project. A material produced using vapor deposition of ceria or zinc oxide on gold may be quite active for CO oxidation or WGS.

3.2 Gold Deposition on Metal Oxides

With the obvious limitations of the gold nanoparticle extraction procedures and the desire to investigate the interaction between gold nanoparticles and metal oxides, the logical next step was to evaluate coprecipitation methods. Because there is

⁵ Several weight ratios of gold stock solution to ionic liquid were tested to determine the minimum amount of ionic liquid that could be used to extract a given amount of gold. That maximum ratio was found to be approximately 20:1 gold solution to ionic liquid, which still would only lead to the collection of gold in milligram amounts per trial.

⁶ Gold particle size in these trials has noticeably grown from 5-10nm to 50-200nm due to this procedure, perhaps due to multiple heating steps and the removal of surfactant during phase transfer.

much published literature on the topic of gold on metal oxides (especially ceria, lanthana, and zinc oxide), the target for further research was defined as nanocomposite materials in which metal oxide particles would be roughly the same size as the gold coordinated with them. This concept suggested that an increase in surface area interaction between gold and metal oxide could be attainable, perhaps increasing catalytic activity⁷.

For this study, gold/metal oxide composites were synthesized with ceria and zinc oxide starting from single-crystal gold of size 5-10nm (from the aqueous gold stock solution). It was thought that a coprecipitation procedure might be able to either encapsulate these gold particles in a core-shell structure or alternatively form nanoparticles that would coordinate with the gold in a “dumbbell” type structure⁸. For the gold/ceria nanocomposites, the results were somewhat unanticipated. As seen in Figure 3, the structure of gold/ceria particles produced from a ratio of 1:9 gold to cerium(III) nitrate are non-spherical and of roughly 100nm. Though it is difficult to distinguish the gold from the ceria in these images, we believe that this structure is similar to the core-shell model in which the gold particle is coated completely with ceria. If this theory is true then the non-spherical shape is likely caused by gradual formation of ceria at different seed points on the surface of the gold particle. Because CTAB surfactant was present in solution during the formation of these structures, it is foreseeable that ceria selectively grew on the gold particles in areas where the surfactant

⁷ It has been suggested in several papers including Fu, et al. (2001) that coordination of gold with oxygen containing materials improves catalytic activity for the water-gas shift reaction.

⁸ This “dumbbell” structure is seen in the results of Wang, et al. (2007) and Lee, et al. (2008) involving gold/zinc oxide structures.

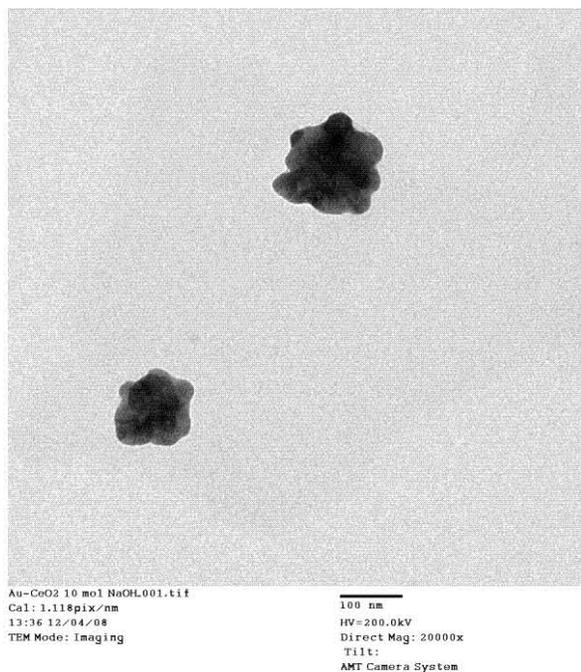


Figure 3: Coprecipitation of Au/CeO₂ in 1:9 ratio

molecules were in low concentration – thus, even growth over the entire surface did not occur. This theory is contingent upon the determination that both gold and ceria are present in the structure viewed here. It is generally recognized that in TEM images, ceria is less dark than gold because it is less dense. The fact that the outer lobes of the particle are less dark than the interior is thus the basis of this determination. Without x-ray diffraction (XRD) analysis it is impossible to know for sure the nature of this particle. It may be the case that the entire particle consists of smaller aggregated gold particles stabilized by the surfactant in this odd shape. If particles are determined to contain gold and ceria, the use of scanning transmission electron microscopy (STEM) with mapping by energy dispersive x-ray spectroscopy (EDS) would reveal whether gold encapsulation has occurred. Further study of this sample would be interesting but may be stymied by difficulties in extraction due to the presence of surfactant.

A second coprecipitation sample of gold and ceria was made with higher gold content to

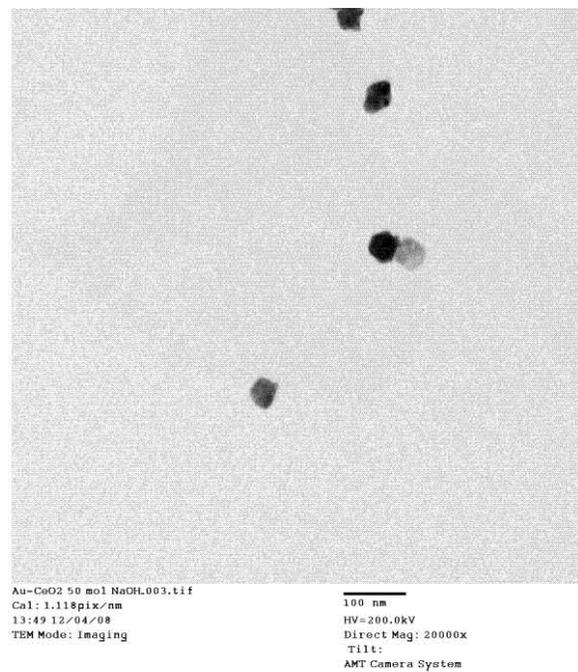


Figure 4: Coprecipitation of Au/CeO₂ in 1:1 ratio

determine if the structure would change based on concentration. A sample synthesized from a 1:1 gold to cerium(III) nitrate ratio indeed produced a noticeably different structure. The particles seen in Figure 4, from this sample, clearly adhere more to the “dumbbell” model than to the core-shell model suggested previously. It is worth noting that several of the particles in Figure 4 are individual – they are either gold or ceria separately, as distinguished by their shade – which is likely the result of significant dilution and low ceria concentration. The middle particle representing the tangentially conjoined “dumbbell” of gold and ceria is interesting to consider because of its similarity to the structures composed of gold and zinc oxide from Wang, et al. (2007) and Lee, et al. (2008). Of course the synthesis method used was different from that in either paper because of the use of ceria. Yet it was more similar to that in Lee, et al. (2008), in which gold nanoparticles were synthesized first, then added to a solution from which zinc oxide was precipitated. It was thought that these “dumbbell” structures might have

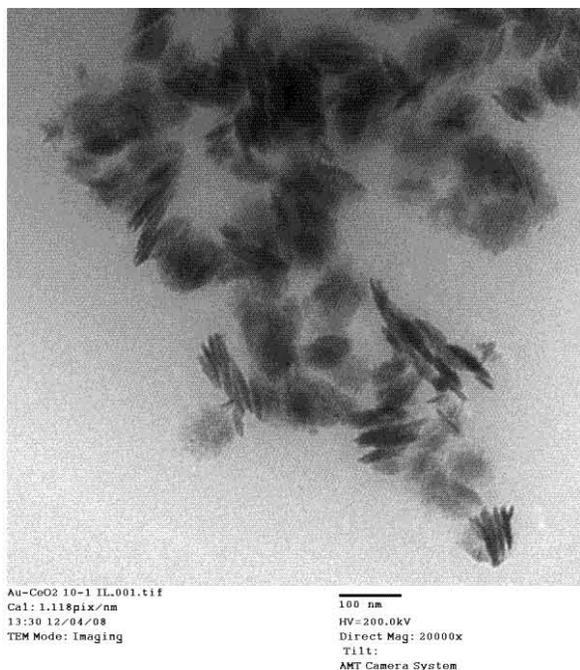


Figure 5: Au/CeO₂ after ionic liquid extraction

some unique catalytic activity because of the intimacy of the two particles in the conjoining region. Nevertheless, extraction again proved to be an obstacle in the further study of this structure.

An entirely separate coprecipitation procedure, not similar to the others (and likely unfit to be called coprecipitation), involved the same ionic liquid extraction method used earlier on gold colloidal solutions. After using this method to extract a solution of gold colloid containing cerium(III) nitrate in 10:1 gold to cerium(III) nitrate ratio, the product was analyzed by TEM. The image seen in Figure 5 shows a unique nanocomposite structure of gold and ceria. The needle-like shapes are consistent with a known structure of ceria, as are the amorphous lightly colored regions. It is difficult to distinguish gold particles in this picture because of the darkness of the ceria needles; however, it is known that they are present because of the dark purple hue of the precipitate. In fact, we would suspect gold to be present in this structure simply by merit of the ionic liquid

extraction procedure⁹. The size of the gold particles in this composite structure have likely been preserved because there are no signs of aggregation (no larger dark particles). Thus, it is possible that with these ceria needles and small-sized gold, this structure could be active for either WGS or CO oxidation reactions. Unfortunately, due to the labor involved in this extraction procedure and the cost of the ionic liquid, this avenue was not pursued.

3.3 Gold/Zinc Oxide

Further research concentrated on the synthesis and activity testing of gold/zinc oxide nanocomposites. Specific targets of investigation included gold on zinc oxide nanorods and wires. While there are some unique findings from this work, further research is necessary to confirm findings and gain a better understanding of the structure-activity relationship.

The first zinc oxide composite material was synthesized with gold via the same coprecipitation procedure used to generate the Au/CeO₂ composites from aqueous gold stock solution. This produced large particles of zinc oxide with 5-20nm gold on the surface and in the interior (as seen in Figure 6). Though this sample is not unique in its structure¹⁰, it does show that coprecipitation by this method can form Au/ZnO structures with acceptable gold dispersion. It might even exhibit catalytic activity for the CO oxidation reaction, though it was not tested.

⁹ The imidazole ring in this particular ionic liquid coordinates with metals like gold to enable nanoparticle extraction. We have no mechanism to suggest that ceria could be extracted via phase transfer with the ionic liquid other than if it were directly coordinated with the gold.

¹⁰ Coprecipitation of zinc oxide with gold nanoparticles is common in papers such as Wang, et al. (2002).

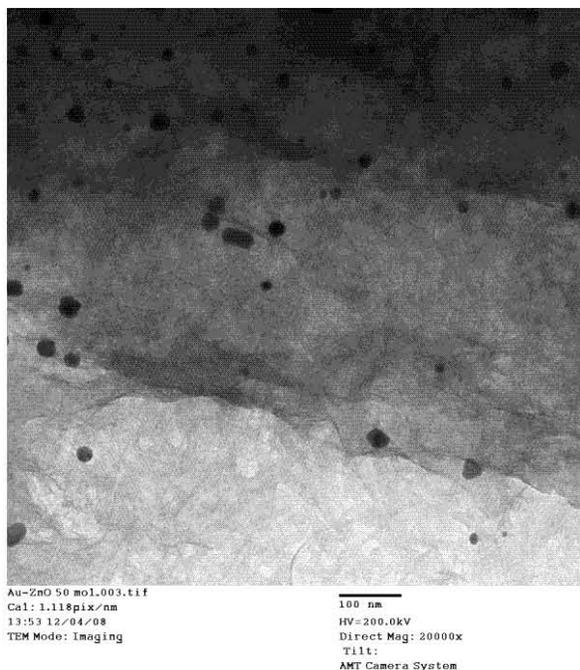


Figure 6: Au/ZnO by coprecipitation

The size of gold particles and structure of zinc oxide in this homegrown sample can be contrasted with those in a commercial sample of Au/ZnO from AuTEK, seen in Figure 7. The overall particle size of the zinc oxide in the commercial sample is much less than in the prepared sample and appears to take on several different structures (recognized as three distinct regions). Not knowing the method in which the commercial sample was prepared, little can be gleaned from these differences other than to say that the size distribution of the gold particles in the commercial sample appears to be bimodal¹¹. Of the gold particles in this sample, those in the lower size range appear adequate for catalysis of the WGS reaction¹². The commercial sample may also permit greater access of reactant gases to the gold particles during catalytic reactions due to the smaller zinc oxide particle size, leading to a higher activity. Without

¹¹ Gold particle sizes in this commercial sample are within the ranges of 1-2nm or 10-20nm.

¹² This hypothesis was proven when the AuTEK sample showed some activity for WGS.

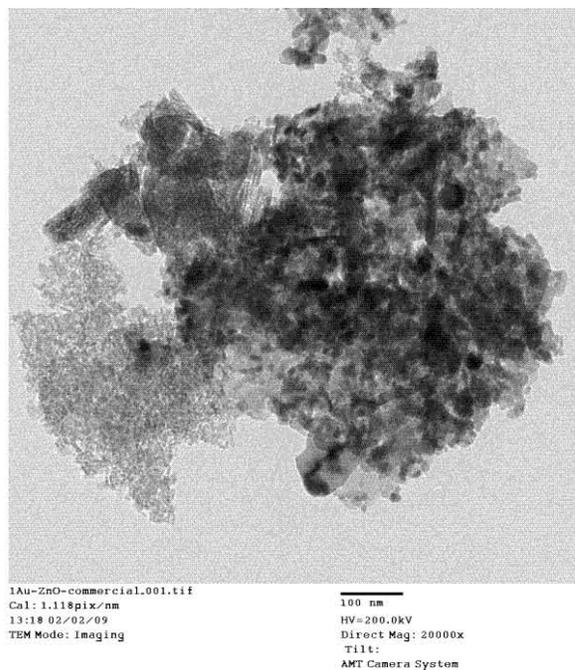


Figure 7: AuTEK commercial sample: Au/ZnO with 1% Au

porosity measurements of either sample further comparisons are nothing more than speculation.

A second procedure to specifically target nanocomposites of Au/ZnO focused on the synthesis of ZnO nanorods followed by gold crystal growth. This procedure, adapted from Zhang, et al. (2008), was performed to explore the selectivity of gold growth on ZnO nanorods. As stated in Zhang, et al. (2008), gold can grow at the tip of the ZnO rod or on the side, though a lattice mismatch of Au on the ZnO tip might make that location more favorable. As part of this exploration, ZnO rods were grown in methanol with KOH at 60°C for several hours. Once collected, ZnO nanorods were redispersed in a trisodium citrate solution to which was added chloroauric acid. Over 12 hours the gold precursor was reduced by the citrate to form nanocrystals on the zinc oxide, the result of which is pictured in Figure 8. It is clear from these images that gold did not selectively deposit on the tips of the rods. The results of Zhang, et al. (2008),

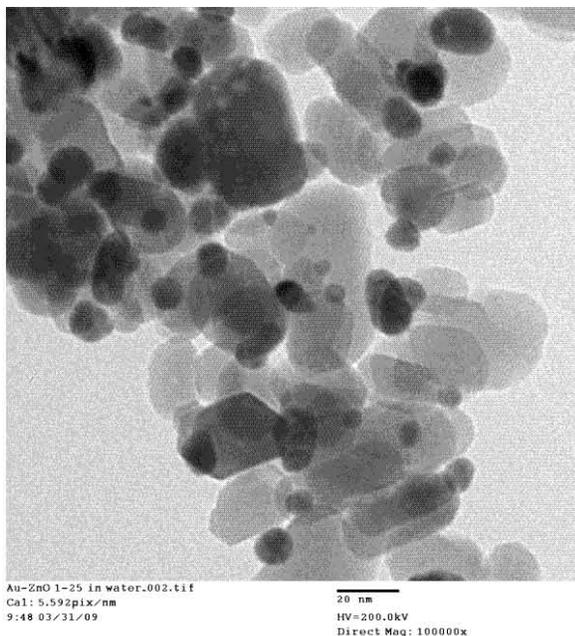


Figure 8: Au/ZnO from Au growth on ZnO rods (25:1 ZnO to Au ratio)

which employ slightly higher aspect ratio ZnO rods, show gold deposited on the tips of ZnO rods under low concentration conditions. Thus it may be that in our sample, the low 3:1 ZnO aspect ratio has caused this selectivity to be overridden by a much larger surface area of ZnO and proportionally more tips. It is worth noting that Figure 8 represents the condensed form of the Au/ZnO solution following centrifugation. By condensing the suspended solid crystals into a pellet, gold and zinc oxide are forced together, increasing contact. This should make for a relatively good active CO oxidation or WGS catalyst. Unfortunately, due to time constraints, this testing was not conducted.

Further studies of the gold/zinc oxide system employed the deposition-precipitation method which involved contacting previously synthesized zinc oxide with gold precursor followed by calcination to promote gold growth. This was the main method used to investigate the theory that Au/ZnO synthesized from different ZnO morphologies would exhibit a difference in

activity. The morphologies of zinc oxide evaluated in these trials were nanorods and nanowires. Adapting the procedure for ZnO rod and wire growth from Cheng, et al. (2006), the ZnO aspect ratio was controlled by varying the water content during synthesis. Since water factors into the mechanism of zinc oxide crystal growth, it is thought to promote the formation of larger aspect ratio ZnO (wires as opposed to rods)¹³. The synthesis procedure for ZnO was conducted according to this theory holding all other variables constant¹⁴.

The resulting ZnO structures before gold deposition are seen in Figures 9 and 10. By comparing these images, it appears that there is little difference in the morphologies other than that the “nanowire” sample has a slightly higher concentration of larger particles. Both samples show ZnO of approximately 10-30nm in length by approximately 10nm in diameter (a maximum aspect ratio of 3:1). The hexagonal shape of the rods is consistent with similar structures seen in the literature. Because of the similarity between the two samples, we would consider this synthesis to be a failure if it were not for the results following gold deposition.

¹³ Cheng, et al. (2006) explains that for ZnO growth at high temperature, syntheses with high water content are dominated by the nuclei that formed at room temperature. This contrasts with the low water content scenario where increasing temperature causes an increase in OH⁻ concentration, favoring the formation of more nuclei over crystal growth.

¹⁴ Other variables affecting ZnO growth from Cheng, et al. (2006) include temperature, time, and base concentration.

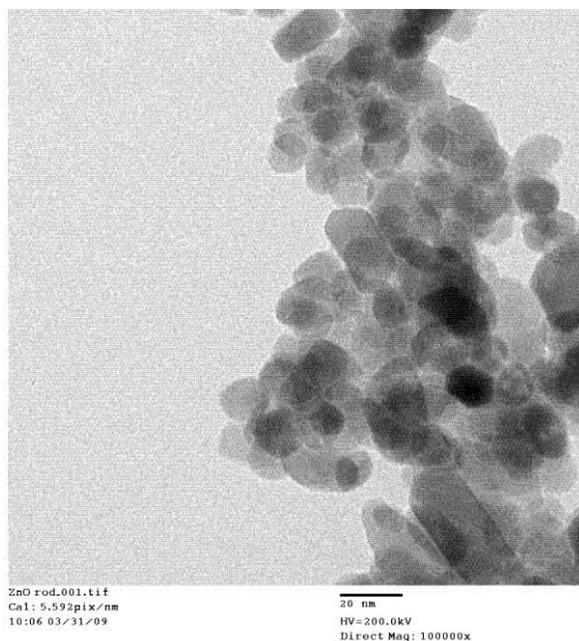


Figure 9: ZnO nanorods

Gold deposition was conducted by dispersing the dried ZnO rods and wires in water and mixing them with chloroauric acid. After filtering and drying the precipitate, calcination at 250°C led to gold nanoparticle growth. Because zinc oxide is known to be unstable at high temperatures, morphological changes occur readily during calcination. Rearrangement and aggregation of ZnO in these two samples is obvious from the resulting TEM images (Figures 11 and 12). In both images, one can see gold nanocrystals of approximately 2-5nm throughout the zinc oxide. It appears from these images that many of the gold particles lie beneath the ZnO surface but still should be accessible to reactant gases through pores (since the ZnO surface is not smooth). This indicates that both materials would be active for the CO oxidation reaction and perhaps for the WGS reaction¹⁵.

¹⁵ In fact, it was shown using a similar sample of Au/ZnO synthesized from ZnO wires and exhibiting gold particle sizes of 1-2nm that WGS activity was nearly nonexistent.

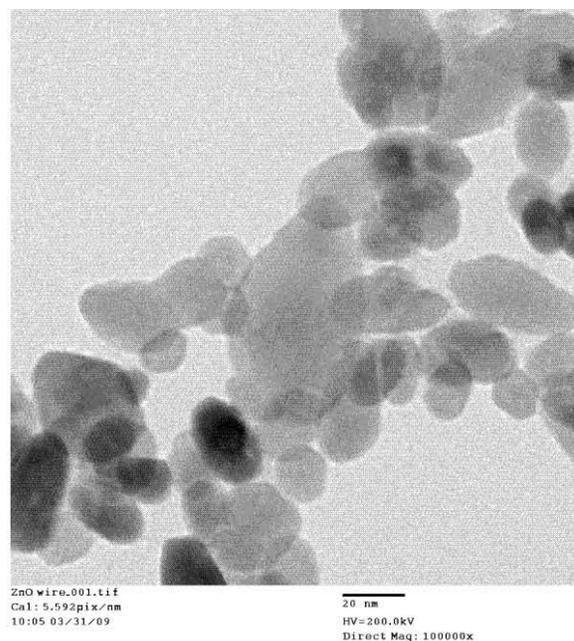


Figure 10: ZnO nanowires

Activity testing of both samples for the CO oxidation reaction was conducted using 75mL/min of 1%CO and 2%O₂ and 0.1g of catalyst (with space velocity approximately 15000h⁻¹). During these trials, temperature was controlled on an increasing ramp with plateaus of one hour to collect steady-state data. The activity of the Au/ZnO sample from ZnO wires was tested in the temperature range 25-250°C while the sample synthesized from ZnO rods was tested in the temperature range 25-100°C¹⁶. From the gas chromatograph peak area measurements, light-off curves were constructed to show conversion of CO as a function of temperature. These results are seen in Figure 13.

The most obvious finding from this graph is that conversion is relatively low for both samples when compared with Au/ZnO composite materials seen in Al-Sayari, et al. (2007) and Wang, et al. (2002). In these

¹⁶ This lower range for the sample synthesized from ZnO rods was suggested based upon the hypothesis that conversion would be high even at lower temperatures.

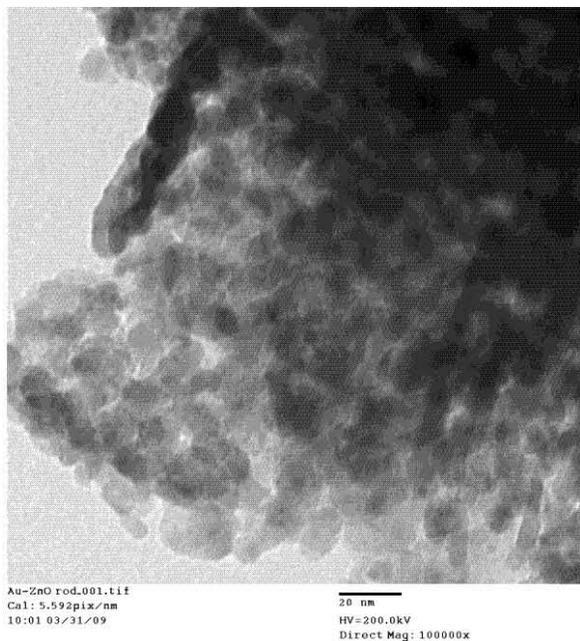


Figure 11: Au/ZnO from ZnO rods (2.7% Au) after calcination

papers, 100 percent conversion was achieved at temperatures below 100°C¹⁷. In contrast, the better of the two prepared samples only achieved 70 percent conversion at close to 200°C. Thus, the activity of these materials seems less than ideal for the CO oxidation reaction. On a positive note, however, neither material is prone to deactivation at raised temperatures – a difficulty noted in the literature. Conversion data collected on the cooling ramp corresponds exactly to those on the heating ramp for the Au/ZnO sample from ZnO wires. For the Au/ZnO sample from ZnO rods, there is a slight increase in conversion apparent on the cooling ramp (data not included in Figure 13). This might indicate an increase in gold dispersion at higher temperatures which is preserved after cooling, or other morphological changes which occur in zinc oxide that serve to increase activity after a period of heating.

¹⁷ The flow rate in Al-Sayari, et al. (2007) was only 20mL/min with 0.5% CO (space velocity is not given). Thus, comparison to these samples is not direct or ideal.

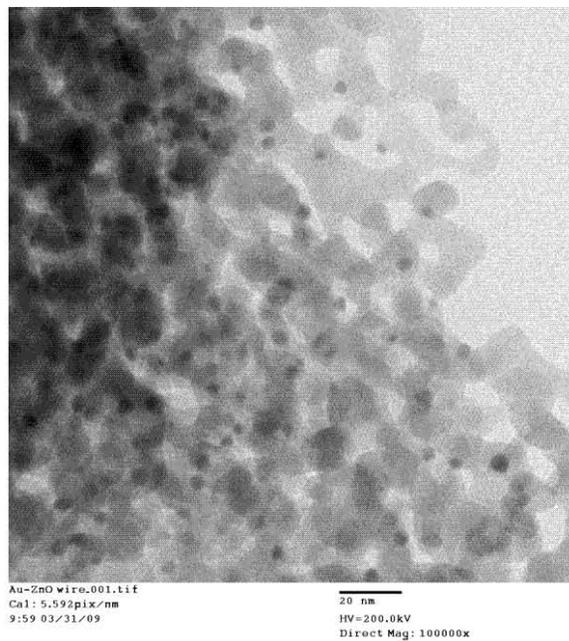


Figure 12: Au/ZnO from ZnO wires (2.7% Au) after calcination

The most interesting finding from this data is the fact that, despite the noted similarities in structure after calcination and initial ZnO morphology, there is a distinct difference in activity between the sample synthesized from ZnO wires and that from rods. The sample from ZnO wires is significantly more active for CO oxidation than that from rods at low temperatures. Because the trial for the ZnO rods sample was limited to lower temperature ranges, it is impossible to say if activity remains lower than for the ZnO wires sample at higher temperatures¹⁸. Explanation of these findings is difficult having noted the structural similarities between the two samples. Since gold content was kept the same for both samples (2.7% Au), it should not be a factor in the activity difference. Access to subsurface gold, may serve as an explanation since Figure 11 appears to show a more densely packed ZnO structure than in Figure 12. Decreased porosity in the ZnO support would certainly affect the activity, although, with our current

¹⁸ This is likely the case from simple extrapolation or intuition.

data, porosity cannot be determined¹⁹. Explanation beyond this would require additional syntheses and testing of these materials. Nevertheless, these results do show that the difference in initial ZnO morphology has an effect on activity after gold deposition.

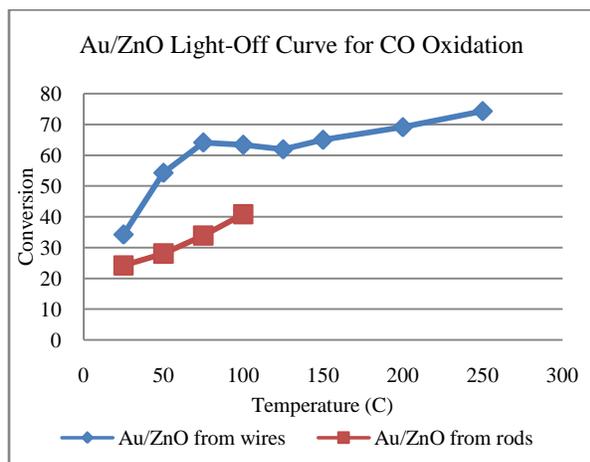


Figure 13: Au/ZnO light-off curve for CO oxidation, 1% CO, 2% O₂ in He (SV=15000h⁻¹)

4. Conclusions and Future Work

Throughout the course of this research many unique materials have been synthesized and tested. New methods have been developed for extraction and crystal growth of nano-scale materials and gold-containing nanocomposites have been explored in greater depth as potential catalysts for CO oxidation and WGS reactions. This work should by no means be considered complete at this early stage. There is significant promise in developing catalysts from gold and metal oxides. While some previous literature has suggested that gold/zinc oxide materials are not optimal catalysts for the WGS and other reactions, the results presented here indicate the potential for improvements in structure that may make Au/ZnO competitive with other widely used materials.

¹⁹ The BET adsorption technique using the Micromeritics apparatus would aid in surface area determination for future work.

The finding that initial ZnO morphology has a significant effect on catalytic activity for the CO oxidation reaction suggests the possibility of future improvements. Continuing work should focus on the relationship between ZnO aspect ratio before calcination and gold particle size afterwards. Surface area following calcination should also be analyzed by BET adsorption techniques. Correlating CO oxidation activity to initial ZnO aspect ratio in a more complete way should follow. Because this DP method has been shown to produce 2-5nm gold particles, it should also be more thoroughly examined for WGS activity.

Further understanding of activity can be gained by leaching gold-containing samples (usually with cyanide) to remove excess gold. We might expect from this procedure that atomic gold would remain on the ZnO surface. In this way, the activity of leached samples could be compared to those prior to leaching to determine if activity stems from atomic gold coordinated with ZnO or from the larger gold particles. If leaching is a success, we could reasonably expect some catalytic activity for the WGS reaction.

Future work on the Au/ZnO system should also involve the procedure of growing gold crystals on ZnO nanorods and wires. Though the sample synthesized from this procedure was not tested for CO oxidation, it is likely active – a claim that should be verified. An expanded focus on this material should also include studies that seek to more conclusively determine if gold preferentially grows on the tips of ZnO rods. Experiments to evaluate the effect of ZnO polarity at the rod tips as well as the lattice mismatch theory should also be conducted.

Additional examination of the Au/CeO₂ samples synthesized by coprecipitation and

ionic liquid extraction would also be informative. For those samples synthesized by coprecipitation, future investigations should involve advanced characterization techniques such as STEM/EDX for the proposed CeO₂ encapsulated gold sample. With this technique, one can determine if a core-shell structure is truly present. Further synthesis and testing of these samples should also examine the effect of the gold to ceria ratio since different structures appear to form with different ratios. Because of the uniqueness of the Au/CeO₂ sample generated by ionic liquid extraction, this structure should not be abandoned either. Scale-up of the ionic liquid extraction should enable the production of enough sample to allow for characterization by the aforementioned methods and perhaps even activity testing.

Because this project's initial goal was to generate gold nanoparticles with deposited metal oxide islands, we cannot ignore the possibility that these structures may still be synthesized. Opportunities for future work in this area involve the generation of larger gold particles (i.e. by the ionic liquid extraction of a gold colloid). The synthesis of larger gold crystals or rods, as seen in the literature, may also make centrifugation a viable option for extraction. Once these larger particles are obtained, vapor deposition can be used to introduce metal oxides and form unique new nanocomposites.

The least onerous opportunities lie, however, in attempting reproducibility of the results shown here. Generating similar structures from the procedures explained above will serve to verify these findings. The samples can then be used to more exhaustively evaluate activity for CO oxidation or WGS. Completing the light-off curves (such as that shown in Figure 13) at

higher and lower temperatures will give a better understanding of the structure-activity relationship.

The work presented here touches on many aspects of gold-containing nanocomposite synthesis, characterization, and testing. Without focusing too narrowly on any one aspect, the goal was to pursue a unique line of inquiry for the purpose of augmenting scientific knowledge, improving understanding, and overcoming the obstacles to further study. Despite the large amount of work conducted, these results should be treated as but a few steps on the path toward further developments in nanocomposite synthesis for catalytic uses. In that sense, this project has been a success.

5. Acknowledgements

The author would like to acknowledge: Dr. Rui Si for all of his assistance with TEM imaging and equipment training as well as his invaluable insight into synthesis methods; Matthew Boucher for helping to narrow the focus of this project on Au/ZnO composite materials and providing interesting hypotheses to test; Yanping Zhang for training and calibration associated with the packed bed reactor system; and the entirety of the Tufts Nano Catalysis and Energy Laboratory. Many thanks go to Professor Maria Flytzani-Stephanopoulos whose guidance and expertise in nanoparticle catalysis was essential to this project's success, and without whom this work would not have been possible.

6. References

- Al-Sayari, Saleh, Albert F Carley, Stuart H Taylor, and Graham J Hutchings. "Au/ZnO and Au/Fe₂O₃ catalysts for CO oxidation at ambient temperature: comments on the effect of synthesis conditions on the preparation of high activity catalysts prepared by coprecipitation." *Topics in Catalysis*, 2007: 123-128.
- Cheng, Bin, Wensheng Shi, Joette M Russel-Tanner, Lei Zhang, and Edward T Samulski. "Synthesis of Variable-Aspect Ratio, Single Crystalline ZnO Nanostructures." *Inorganic Chemistry*, 2006: 1208-1214.
- Fu, Qi, Adam Weber, and Maria Flytzani-Stephanopoulos. "Nanostructured Au-CeO₂ catalysts for low-temperature water-gas shift." *Catalysis Letters*, 2001: 87-95.
- Imai, Hiroyuki, Masakazu Date, and Susumu Tsubota. "Preferential Oxidation of CO in H₂-Rich Gas at Low Temperatures over Au Nanoparticles Supported on Metal Oxides." *Catalysis Letters*, 2008: 68-73.
- Lee, Myung-Ki, Tae Geun Kim, Woong Kim, and Yun-Mo Sung. "Surface Plasmon Resonance (SPR) Electron and Energy Transfer in Noble Metal-Zinc Oxide Comoposite Nanocrystals." *The Journal of Physical Chemistry*, 2008: 10079-10082.
- Qian, Kun, et al. "Low-temperature CO oxidation over Au/ZnO/SiO₂ catalysts: Some mechanism insights." *Journal of Catalysis*, 2008: 269-278.
- Sau, Tapan, and Catherine Murphy. "Seeded High Yield Synthesis of Short Au Nanorods in Aqueous Solution." *Langmuir*, 2004: 6414-6420.
- Swatloski, Richard, John Holbrey, and Robin Rogers. "Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate." *Green Chemistry*, 2003: 361-363.
- Wang, Guiying, Wenxiang Zhang, Honglei Lian, Qingsheng Liu, Dazhen Jiang, and Tonghao Wu. "Effect of Au Loading, H₂O and CO Concentration on the Stability of Au/ZnO Catalysts for Room-Temperature CO Oxidation." *Reaction Kinetics Catalysis Letters*, 2002: 343-351.
- Wang, Xin, Xianggui Kong, Yi Yu, and Hong Zhang. "Synthesis and Characterization of Water-Soluble and Bifunctional ZnO-Au Nanocomposites." *The Journal of Physical Chemistry*, 2007: 3836-3841.
- Wei, Guor-Tzo, Zusing Yang, Chia-Ying Lee, Hsiao-Yen Yang, and C.R. Chris Wang. "Aqueous-Organic Phase Transfer of Gold Nanoparticles and Gold Nanorods Using an Ionic Liquid." *Journal of the American Chemical Society*, 2004: 5036-5037.
- Zhang, Wei-Qing, Yang Lu, Tie-Kai Zhang, Weiping Xu, Meng Zhang, and Shu-Hong Yu. "Controlled Synthesis and Biocompatibility of Water-Soluble ZnO Nanorods/Au Nanocomposites with Tunable UV and Visible Emission Intensity." *The Journal of Physical Chemistry*, 2008: 19872-19877.