Utilization of Nano-Catalysts for Green Electric Power Generation

by

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Mechanical Engineering and Materials Science in the Graduate School of Duke University

2015
ABSTRACT

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Abstract

Nano-structures were investigated for the advancement of energy conversion technology because of their enhanced catalytic, thermal, and physiochemical interfacial properties and increased solar absorption. Hydrogen is a widely investigated and proven fuel and energy carrier for promising “green” technologies such as fuel cells. Difficulties involving storage, transport, and availability remain challenges that inhibit the widespread use of hydrogen fuel. For these reasons, “on-board” hydrogen production has been at the forefront of research in the renewable and sustainable energy field. This means that the hydrogen is generated via a chemical reaction and immediately used as opposed to having to purchase, transport and store large tanks of hydrogen. A common approach for hydrogen generation is the reforming of alcoholic and hydrocarbon fuels from fossil and renewable sources to a hydrogen-rich gas mixture.

Unfortunately, an intrinsic byproduct of any fuel reforming reaction is toxic and highly reactive CO, which has to be removed before the hydrogen gas can be used in fuel cells or delicate chemical processes. In this work, Au/α-Fe₂O₃ catalyst was synthesized using a modified co-precipitation method to generate an inverse catalyst model. The effects of introducing CO₂ and H₂O during preferential oxidation (PROX) of CO were investigated. For realistic conditions of (bio-)fuel reforming, 24% CO₂ and 10%
water the highest document conversion, 99.85% was achieved. The mechanism for PROX is not known definitively, however, current literature believes the gold particle size is the key. In contrast, we emphasize the tremendous role of the support particle size. A particle size study was performed to have in depth analysis of the catalysts morphology during synthesis. With this study we were also able to modify how the catalyst was made to further reduce the particle size of the support material leading to ~99.9% conversion. We also showed that the resulting PROX output gas could power a proton exchange membrane (PEM) fuel cell with only a 4% drop in power without poisoning the membrane electrode assembly.

The second major aim of this study is to develop an energy-efficient technology that fuses photothermal catalysis and plasmonic phenomena. Current literature has claimed that the coupling of these technologies is not possible because the localized nature of the heat production is not substantial enough to drive a chemical reaction[1]. Here we demonstrate the fabrication of reaction cells for plasmon-induced photocatalytic hydrogen production. The localized nature of the plasmon resonance allows the entire system to remain at ambient temperatures while a high-temperature methanol reforming reaction occurs at the plasmonic sites. Employing a nanostructured plasmonic substrate, we have successfully achieved sufficient thermal excitation (via localized surface plasmon resonance (LSPR)) to facilitate a heterogeneous chemical reaction. The experimental tests demonstrate that hydrogen gas can indeed be generated in a cold
reactor, which has never been reported before. Additionally, the proposed method has the highest solar absorption out of several variations and significantly reduces the cost, while increasing the efficiency of solar fuels.
Dedication

To my niece, Skylar Claire.
Contents

Abstract..................................................................................................................................................iv

List of Tables ...........................................................................................................................................xi

List of Figures ..........................................................................................................................................xii

Acknowledgements ..............................................................................................................................xv

1. Introduction .........................................................................................................................................1
   1.1 Energy ...............................................................................................................................................1
   1.2 Nano-catalysis ..................................................................................................................................3

2. Reformed alcohol fuel cell systems ...............................................................................................7
   2.1 The CO Problem ..............................................................................................................................8
   2.2 Experimental Background ............................................................................................................11
      2.2.1 Preferential Oxidation (PROX) .............................................................................................11
   2.3 Experimental Procedure ...............................................................................................................13
      2.3.1 Catalyst Synthesis ..................................................................................................................14
   2.4 Catalyst Characterization .............................................................................................................16
      2.4.1 Transmission Electron Microscopy (TEM) ............................................................................16
      2.4.2 X-ray Diffraction (XRD) Analysis .........................................................................................17
      2.4.3 Surface Area and Pore Size Distribution Analysis (BET) .....................................................18
      2.4.4 Atomic Absorption Spectrometry (AAS) ............................................................................19
      2.4.5 Reaction Test Apparatus .......................................................................................................19
   2.5 Experimental Conditions ...............................................................................................................22
List of Tables

Table 1: Time and corresponding compounds as they appear in the GC for the most realistic reformate gas. .................................................................................................................. 21

Table 2: Dry Gas Mixtures (Mole fractions in %) [22] .......................................................................................................................... 23
List of Figures

Figure 1: Schematic of breakdown of global energy use in 2004 [2].............................. 2

Figure 2: Average about of renewable energy sources that are readily available and the amount of constant power needed to power the globe [3]. ........................................... 2

Figure 3: Exothermic reaction process with (red) and without (black) the addition of a catalyst .......................................................................................................................... 4

Figure 4: Schematic of the mechanisms that generate electricity from a PEM fuel cell...... 7

Figure 5: Schematic of solar-powered methanol reforming fuel cell miniature power plant................................................................................................................................. 9

Figure 6: TEM image of Au/α-Fe₂O₃ catalyst before (left) and after testing (right)....... 24

Figure 7: XRD spectrum of the inverse Au/α-Fe₂O₃ catalyst with markers indicating the location of α-Fe₂O₃ and Au via the ICDD Powder Diffraction File database....................... 25

Figure 8: Pore size distribution of Au/α-Fe₂O₃ catalyst ................................................. 26

Figure 9: CO conversion under optimized conditions with ideal reformate gas ......... 27

Figure 10: CO conversion in the presence of CO₂.......................................................... 28

Figure 11: CO conversion in the presence of H₂O ......................................................... 29

Figure 12: Conversion in the presence of CO₂ and H₂O .............................................. 29

Figure 13: CO conversion tested over 200 hours, for 24% CO₂ and 3% H₂O at 80°C...... 31

Figure 14: Set up for testing fuel cell parameters for optimization: 1. gas bottles, 2. flow controllers, 3. humidification unit, 4. PEMFC, 5. condenser unit .............................................. 39

Figure 16: TEM image of catalyst before precipitating agent was added.................... 41

Figure 17: TEM image of PROX catalyst during synthesis at pH=1.94 (a)at low magnification and (b) at higher magnification ................................................................. 41

Figure 18: TEM image of PROX catalyst at a pH=4.................................................... 42
Figure 19: TEM image of PROX catalyst at pH=6 during synthesis. ........................................... 42

Figure 20: TEM image of final state of PROX catalyst at pH=8.2 during synthesis (a) before incorporation into a reactor (b) after incorporation into a reactor................................. 43

Figure 21: Plot of the Au and Fe$_2$O$_3$ particle size vs. pH during synthesis......................... 44

Figure 22: Comparison of PROX CO oxidation activity before and after reactor fabrication modification. ........................................................................................................................................... 45

Figure 23: Conversion vs. time of new catalyst at 70 and 80°C for 8 hours.............................. 45

Figure 24: Power vs. time plot depicting the impact of varying air flow rates on the fuel cell performance. ........................................................................................................................................... 47

Figure 25: Power vs. time plot depicting the effect of varying the H$_2$ flow rate on the fuel cell performance. ........................................................................................................................................... 48

Figure 26: Power vs. time plot depicting the effect of varying the fuel cell operating temperature on the fuel cell performance. ........................................................................................................................................... 49

Figure 27: Power vs. time plot depicting the effect of CO$_2$ concentration on the fuel cell performance. ........................................................................................................................................... 50

Figure 28: Power and CO conversion vs. time plot depicting the effect of PROX output gas on the PEMFC ........................................................................................................................................... 51

Figure 29: COMSOL simulation of polystyrene coated in metal and the enhancement of the magnitude of the electronic field at the LSPR sites .............................................................. 56

Figure 30: Proposed set up for plasmon assisted hydrogen production............................... 57

Figure 31: (a) Fabricating monolayer of PS on glass slide based on self-assembly on water-air interface method. (b, c) Monolayer of PS on microscope glass slide at two different viewing angles. (d) SEM image of a 520 nm PS monolayer covered by a 200 nm-thick metal film. Scale bars in (b, c): 10 mm, (d): 2 µm........................................................................ 60

Figure 32: UV-Vis spectroscopy depicting the change in absorbance with the addition of CZA catalyst................................................................................................................................. 64
Figure 33: SEM image at 20 kV, 20k magnification and working distance of 5.1 mm of plasmonic substrate after drop-casting deposition of CZA. .................................................. 65

Figure 34: SEM images of the nanowave substrate (a) before and (b) after deposition of the CZA catalyst. ........................................................................................................ 66

Figure 35: Time lapse of hydrogen production. .............................................................. 67

Figure 36: (a) Hexagonal configuration of plasmonic materials (b) specific LSPR site. ... 68

Figure 37: Apparent localized temperature and plasmonic area fraction depending on the plasmonic propagation length. ........................................................................... 71
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1. Introduction

1.1 Energy

Our world relies heavily on fossil fuels, such as coal, natural gas and petroleum. Figure 1 shows the breakdown of the global energy usage per year. There are multiple issues with our overconsumption of fossil fuels. The resulting air and water pollution from transportation, agriculture, power plants, etc. has led to the deterioration of the ozone layer and, subsequently, global warming. Fossil fuels are also not renewable or sustainable, which means their quantity is limited and eventually will be depleted. Globally we only require an average of 15 TW constant power of the ~86,000 TW of theoretically available renewable power provided by solar, hydro, and wind energy worldwide, Fig. 2. There has been a push in recent years for renewable and sustainable energy sources in an effort not only to improve the environment, but also to provide electricity to parts of the world where it is not readily available.
In the field of sustainable energy research, the identification of alternative energy sources is of greatest interest. A promising new concept is the utilization of liquid
alcoholic fuels in a reformed fuel cell system where a primary fuel, such as methanol, is first reformed by steam reforming to a hydrogen-rich gas mixture, which can be subsequently converted to electricity in a fuel cell [4, 5]. Ideally, the alcoholic fuel is generated from biomass and the evaporation and reforming of the fuel is accomplished by sunlight, achieving a highly efficient and carbon-neutral system [5-7].

Additionally, research of photovoltaic (PV) systems converting abundant solar energy to electricity is extensively pursued today. Photovoltaic systems have progressed over the last few decades to improve the efficiency while lowering the cost of materials. The current “third generation” of PV focuses on utilizing hot carriers, multiple electron-hole pair generation, and multiple energy threshold processes [8].

1.2 Nano-catalysis

Microtechnology has revolutionized our lives. The most prominent area of influence is in computer technology and the miniaturization of our devices. Today, research is focusing on structures that are in the nanometer-size range, hence the term nanotechnology. A nanomaterial is defined as a material between 1-100nm. To give some perspective on the size of 1 nm, a strand of hair is between 10,000-100,000 nm, a tennis ball is 100,000,000 nm and the width of a DNA double helix is 2 nm. The nanomaterials discussed in this work ranges from 5-25 nm.
In solid materials, it is known that the properties of nanomaterials differ from those in bulk. As a result the properties of nanomaterials are closely related to the states of the individual molecules and molecular interfacial interactions.

In nature, nanoscopic objects make up entire functional nanosystems. For example, a molecule is contained inside of a cell compartment, which is contained inside of cells, and the cells are contained inside of tissue that makes up an organ.

Catalysis is the acceleration of a reaction via a material called a “catalyst”. Figure 3 shows the reaction process for an endothermic reaction (the reaction absorbs heat). The activation energy, $E_a$, is the amount of energy has to be input into the system in order for the reaction to occur. This energy can come in many forms, such as, heat, spark, electronic potential, etc. When a catalyst is added, $E_a$ is decreased. Meaning, the reaction can occur with less stimulation or in other words, the reaction is more efficient.

Figure 3: Exothermic reaction process with (red) and without (black) the addition of a catalyst
This idea of integrating small functional objects into a broader system is commonly used in technical applications. This work focuses on combination of nanomaterials and catalysis called “nano-catalysis”. I integrate nano-catalysts into systems to advance the most promising areas of sustainable energy, fuel cell systems and solar cells, for the production of green electric energy. In general, nano-catalysts have a higher surface-to-volume ratio and stronger interfacial interactions. The increase in surface area for surface-based catalytic reactions leads to a decrease in the activation energy. Specifically for solar applications, an increase in surface area leads to an increase in solar absorption.

In Chapter 2, I will be discussing a fuel cell system that reforms a methanol-steam mixture into hydrogen-rich gas. In this chapter I will discuss the problem with the reformate gas of the system, the production of CO, and my solution via an inverse Au/α-Fe₂O₃ nano-catalyst for preferential oxidation (PROX).

In Chapter 3, I modified the synthesis of the nano-catalyst in Chapter 2 to improve its efficiency and conversion. With this enhancement I was also able to fuse the PROX nano-catalyst with the PEMFC, which represents the first documented results of its kind.

Finally, in Chapter 4 I introduce work that is done in collaboration with the Vo-Dinh lab group in the biomedical engineering department at Duke University. The Vo-Dinh group synthesizes plasmonic nanoparticles whose unique characteristics produce
localized heating. Using this technology and the high temperature methanol-steam reforming nano-catalyst used in the t-sel lab, we successfully produce hydrogen in an overall low temperature system.
2. Reformed alcohol fuel cell systems

A fuel cell is a device that converts chemical energy supplied from a fuel to electricity. It consists of an anode and cathode separated by an electrolyte, and a catalyst that is incorporated into the electrode-electrolyte interfaces. Between the anode and the electrolyte the fuel is broken down into electrons and ions. The anode conducts electrons that are freed from the fuel molecules, often hydrogen, so they can be used in an external circuit. Between the cathode and the electrolyte the ions react with oxygen to a “waste” product, which is usually water. The cathode conducts electrons back from the circuit to the catalyst, Fig 4. There are many types of fuel cells, and the type is dependent on the electrolyte material [9].

![Figure 4: Schematic of the mechanisms that generate electricity from a PEM fuel cell](image)

A proton exchange membrane fuel cell (PEMFC) utilizes a solid Nafion © membrane with porous carbon electrodes with platinum catalyst [9]. The membrane is
impermeable for gases, blocks electrons and only conducts protons. The advantages of
the PEMFC are its simple design, high power density per mass and volume, and low
operating temperature.

2.1 The CO Problem

Since hydrogen as fuel is difficult to store and not readily available due to the
lack of infrastructure, a common solution is the on-board production of a hydrogen-rich
gas mixture by reforming a hydrocarbon fuel, for example methanol (equation 1). The
proposed system realizing a solar-powered methanol reforming fuel cell miniature
power plant is shown in Fig. 5. A major issue with any reformed methanol fuel cell
(RMFC) system is the production of ~1% carbon monoxide (CO) of the reformate gas in
the methanol reformer, equation 2 [10]. CO is highly toxic to conventional, low-
temperature PEM fuel cells, since it agglutinates on the surface of the platinum catalyst
leading to its deactivation. Only a small amount (~0.5-1%) is required to decrease the
efficiency of the fuel cell by 100%. It has been observed that the CO saturation level for a
Pt catalyst is reached after only 2 hours of measurements [11].

\[ CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \]  \hspace{1cm} (1)

\[ CH_3OH \rightarrow 2H_2 + CO \]  \hspace{1cm} (2)
Most PEM fuel cells still require a CO mole fraction far below 100 ppm, preferably below 20 ppm (0.002% of the reformate gas mixture), to guarantee efficient long-term operation [12-14]. Since the CO tolerance of PEM catalysts is expected to remain a problem in the near future until cheaper and reliable high-temperature PEM fuel cells are commercially available, successful solutions to reduce the CO content in the reformate gas must be found.

Several different approaches have been investigated in the past to decrease the CO mole fraction, such as preferential CO oxidation, water-gas shift reaction (WGS), methanation, and selective diffusion [15]. Preferential oxidation (PROX) of CO has been seen as one of the most promising approaches in terms of cost and efficiency [14]. Generally, there are two temperature regimes possible for CO-PROX, namely the high temperature regime of 150 – 250°C by making the anode of the fuel cell more tolerant of the CO by introducing Pt/Rh catalysts. The second option is to utilize a preferential oxidation to reduce residual CO in the low temperature regime below 100°C using Cu and Au catalysts. The second option is less expensive and easier than the first one. Also,
working with temperatures below 100°C is ideal because this is identical with the PEM fuel cell temperature [12, 16].

The major goal of this work is the creation of a catalytic nano-material for PROX of CO and the experimental investigation of this new catalyst. The main objective of this study is to bridge the remarkable recent progress in the development of low-temperature PEM fuel cells and in the area of (bio-) fuel reforming. Without an energetically and cost-wise efficient solution to the problem of substantial CO concentrations in the product gas of any alcoholic [4, 17] or hydrocarbon [18-21] fuel reforming process, the direct coupling with a low-temperature fuel cell is impossible.

The successful operation of a catalyst in a system where H₂ is generated by reforming hydrocarbons or alcohol needs to achieve high CO conversion in the presence of excess CO₂ as well as excess H₂ and H₂O. Hence, for successful operation as a selective CO oxidation catalyst in a reformer-PEM system, the catalyst must operate at about 80°C with a complex feed comprising CO, O₂, H₂, CO₂, H₂O, and N₂, and be capable of reducing the CO concentration from about 1% to below 50 ppm - this is equivalent to a CO conversion of at least 99.5%[22, 23]. Furthermore, this conversion must be achieved without the addition of excess O₂ and the competitive oxidation of H₂ must be minimized. Taken together, this represents a demanding target and until now this has not been achieved.
2.2 Experimental Background

2.2.1 Preferential Oxidation (PROX)

Avgouropolous et al. came closest to achieving the target: Their system used an Au/α-Fe₂O₃ catalyst calcined at 400°C, but required excess O₂, low levels of CO₂ (15 vol.%), and a relatively high reaction temperature (100°C to achieve 99.5% CO conversion) [12]. Avgouropoulos et al. studied and compared the catalytic activity of three different types of PROX catalysts, Pt/γ-Al₂O₃, Au/α-Fe₂O₃, and CuO-CeO₂, prepared by three different methods (wet impregnation, co-precipitation, and sol-gel, respectively). They found that, regardless of the amount of CO₂, H₂O, or both in the reactant gas the Au/α-Fe₂O₃ catalyst performed the best at low temperatures (<80-120°C). However at higher temperatures, the CuO-CeO₂ catalyst performed the best. The Pt/γ-Al₂O₃ catalyst was the most resistant to deactivation/degradation [12].

Landon et al. investigated the effects of gold with Fe₂O₃ and alternative supports, TiO₂ and Al₂O₃, to determine whether they were as effective [13]. They found that the TiO₂ and Al₂O₃ were catalytically inactive for oxidation of CO and H₂. They also produced an Au/Fe₂O₃ catalyst that they calcined twice at 440°C and 550°C, but it required low levels of H₂O (4.7%) to have a conversion of 99.8% at 80°C. Daniells et al. investigated Au/Fe₂O₃ catalysts under water gas shift conditions (CO reacts with H₂O to produce CO₂ and H₂) [24]. They show that traces of water enhance the rate of CO oxidation at ambient temperature; however, much higher temperatures are required
when higher concentrations of water are used. At higher temperatures any cationic gold was reduced to metallic gold. Haruta and co-authors demonstrated that supported gold nanoparticles could be active at very low temperatures (down to 0°C), but precious H₂ was oxidized together with CO at temperatures greater than 70°C [25, 26]. Kahlich et al. studied Au/Fe₂O₃ catalysts calcined at 400°C, but found that again significant H₂ oxidation occurred at 80°C [14]. Qiao and Deng showed that non-calcined Au/Fe₂O₃ catalysts, dried only at 120°C, were very selective for CO oxidation in the presence of H₂ at 25°C, but the selectivity was lost at higher temperatures [27]. Some of the best results for this demanding reaction have been reported by Grigorova et al. for an Au/CeO₂ catalyst promoted with SnO₂, but even this catalyst yields to significant H₂ conversion (ca. 5 %) at temperatures greater than 70°C, with CO conversions of about 40–60 % [28]. Schumacher et al. have shown that H₂ competes with CO for adsorption on Au/TiO₂ by raising the reaction order for CO significantly [29]. Calla and Davis have demonstrated that the addition of H₂O decreases the reaction order of CO on Au/Al₂O₃ [30].

Pansare et al. have shown that the particle size of the gold is an important factor, with high dispersion catalysts giving the highest activity, as would have been expected from the extensive studies on CO oxidation carried out with these catalysts [31]. Recently, Corma and co-workers reported a nanocrystalline CeO₂-supported gold catalyst that gave appreciable selectivity at 60°C with a dry CO/H₂ mixture [32]. Jain et al. have also shown the high activity of Au/CeO₂ catalysts [33], and Lomello-Tafin et al.
have demonstrated that Au/ZrO$_2$ also displays high activity for the preferential oxidation of CO [34]. However, a recent study by Rossignol et al. has shown that the support effects observed for the oxidation of CO alone decrease in the presence of added H$_2$, and that Au/Al$_2$O$_3$, Au/TiO$_2$, and Au/ZrO$_2$ all show similar activity [35].

Gold is widely known as an element that is catalytically inert due to its highly stable chemical structure. Haruta et al. have shown that gold becomes extremely active catalytically when its size is reduced to <15 nm and prepared in the presence of 3d transition metal oxides [16]. Lopez et al. demonstrated a $1/d^3$ relationship between Au particle size and CO conversion capability [36]. The catalytic activity of Au is enhanced by metal oxides supports that have high oxygen mobility, such as TiO$_2$, Fe$_2$O$_3$, NiO$_x$, and CoO$_x$. As a result of this increased oxygen transfer, the conversion dependence on the gold nanoparticle size becomes secondary. The catalyst chosen for this work was Au/α-Fe$_2$O$_3$ because of its documented potential [23].

**2.3 Experimental Procedure**

The catalyst was prepared by a modified co-precipitation method and a gas chromatograph was used to characterize the output gas, testing for CO conversion. TEM images were obtained of the catalyst. The particle size was determined using surface area analyzer that generates a Brunauer-Emmett-Teller (BET) measurement. Finally, the specific weight percentage of gold in the catalyst was quantified using an atomic absorption spectrometer (AAS).
Realistic methanol steam reformate gas consists of up to 25% CO₂ and ~10 % H₂O at 80°C. Therefore, the effects of the addition of these species were investigated. The goal was ≥99.8% CO conversion at 80°C, which is a significantly higher conversion than results reported in literature for separate and combined addition of CO₂ and H₂O, representing the demanding target that until now has not been achieved [12, 13].

2.3.1 Catalyst Synthesis

The Au/α-Fe₂O₃ catalyst was prepared using a modified co-precipitation method. To prepare the samples, respective amounts of gold(III) chloride trihydrate solution, 0.882 g HAuCl₄·3H₂O (Sigma-Aldrich, ≥99.9% trace metals basis) dissolved in 36 ml deionized water, were mixed with iron nitrate nonahydrate, 4.79 g Fe(NO₃)·9H₂O (Sigma-Aldrich, 99.99% trace metals basis) dissolved in 200 ml deionized water. To prepare 0.75 g of 3 wt.% of Au, 4.08 ml of HAuCl₄·3H₂O solution was mixed with 200 ml of Fe(NO₃)·9H₂O solution. The deionized water was “molecular grade” by VWR. Initially the mixture has a pH value of 1.3. The mixture was heated to 80°C, displayed a very low pH value of 0.3, and was vigorously stirred with a magnetic stirrer. This drop in pH is attributed to the increased amount of H⁺ ions as a result of the increased temperature. 0.25 M solution of sodium carbonate, 17.89 g Na₂CO₃·10H₂O (Sigma-Aldrich, 99.999% trace metals basis) dissolved in 250 ml deionized water, was added dropwise with a syringe until the pH value rose to 8.2. This step took about 25 minutes. The pH measurement device was a PHH-37 pH/mV and Temperature Meter by
OMEGA Engineering. Polymer body sealed combination pH/reference electrodes were used with the pH meter.

Initially, the solution is an orange color when the synthesis starts at low pH value. As the pH increases, the Fe(NO$_3$) starts to react with Na$_2$CO$_3$, according to the equations 3 & 4

$$3Fe(NO_3)_3 + 4.5Na_2CO_3 + 1.5H_2O \leftrightarrow Fe(OH)_3 \cdot Fe_2(CO_3)_3 + 9NaNO_3 + 1.5CO_2 \quad (3)$$

and

$$2Fe(NO_3)_3 + 3Na_2CO_3 + 3H_2O \leftrightarrow 2Fe(OH)_3 + 3CO_2 + 6NaNO_3 \quad (4)$$

where the former reaction is dominant close to a pH value of 7 and the latter becomes dominant for higher pH values[22]. In the earlier phase, the solution turns black, due to the Fe$_3$(CO$_3$)$_5$, and finally reaches a brown color when the synthesis of Fe(OH)$_3$ is emphasized. Simultaneously, pH values above 7 allow the synthesis of Au particles due to the reaction in equation 5.

$$4HAuCl_4 + 8Na_2CO_3 \leftrightarrow 4Au + 2H_2O + 3O_2 + 8CO_2 + 16NaCl \quad (5)$$

The reducer of the Au salt is OH$^-$ that is created from the hydrolysis of Na$_2$CO$_3$.

Reaching the final pH value, the solution was aged for 1 hour under moderate stirring conditions at 80°C. The pH value further increased from 8.2 to 8.6 during that process. The mixture was then vacuum filtered through two Whatman 50 filter rounds and washed with 1 L of 80°C warm deionized water. The captured water was then recycled and used to wash the catalyst 2 more times. The precipitate was then removed.
from the filter paper and put into open glass vials to be covered with layers of parafilm with holes. It was subsequently dried in a tube furnace for 19 hours in flowing air at 120°C. Afterwards, the coal-like residuals were ground to powder with pestle and mortar yielding ca. 750 mg of catalyst that was stored in the dark in sealed glass vials. A similar fabrication method was also used by Landon et al, however, the pH was changed to achieve an inverse catalyst with largely reduced particle size of the Fe₂O₃ support[13]. The catalyst was synthesized a number of times, the synthesis method appeared very reproducible, and each batch of catalyst generated the same results.

2.4 Catalyst Characterization

2.4.1 Transmission Electron Microscopy (TEM)

A transmission electron microscope (TEM) uses a high voltage (100-400 kV) electron gun and a source to generate electrons. The beam of electrons is focused by the electromagnetic condenser lens system and accelerated by an anode held at earth potential beneath the Wehnelt cylinder (a cylindrical polished cap). The beam that enters the microscope column is characterized by the effective source size, the divergence angle of the beam, the energy of the electrons, and the energy spread of the electron beam. The standard specimen in a TEM is only 3 mm in diameter and 0.1 µm in thickness to allow most of the high-energy electrons to pass through without significant loss of energy. An image is formed from the interaction of the electrons transmitted through the specimen [37]. The TEM used was a computer controlled FEI Tecnai G² Twin and is a
high magnification imaging tool. Its resolution is on the order of 0.3 nm and reproducibility of 0.3 μm. The TEM has a magnification 25x to 700,000x, a kV range from 2 to 200, and a drift of ≤ 1 nm/minute. The sample was dispersed in molecular grade deionized water. A drop of this solution was deposited onto a 200 mesh copper TEM grid and dried in static air. TEM images were useful to see the general behavior of the catalyst as well as determine the relative size of artifacts in the images.

2.4.2 X-ray Diffraction (XRD) Analysis

When radiation strikes an object it will either be scattered or absorbed. When the scattered radiation is “elastic” no energy is lost and the wavelength of the scattered radiation remains unchanged. The regular arrays of atoms in a crystal lattice interact with radiation of a short wavelength elastically and yield a diffraction spectrum that depicts the intensity of the scattered beam as a function of scattering angle. For the analysis in this work the crystalline material was identified from its diffraction spectrum by comparing the diffraction angles that correspond to peaks in the spectrum and their relative intensities with a diffraction standard [37].

The Au/α-Fe₂O₃ sample was pressed onto double-sided tape and adhered to a glass slide. The XRD device used was a Panalytical X’Pert PRO MRD HR X-Ray Diffraction System and compared with the ICDD Powder Diffraction File (PDF) database. The x-ray source was a Cu Kα (1.5405 Å) and the goniometer had a high resolution of 0.0001 minimum step size [37].
2.4.3 Surface Area and Pore Size Distribution Analysis (BET)

In physical gas adsorption, an inert gas, mostly nitrogen, is adsorbed on the surface of a solid material. This occurs on the outer surface and, in case of porous materials, also on the surface of pores. Most widely known is the determination of the BET surface area by gas adsorption. Adsorption of nitrogen at a temperature of 77 K leads to a so-called adsorption isotherm, sometimes referred to as BET isotherm, which is mostly measured over porous materials [38]. The device was a Beckman Coulter SA 3100 Surface Area Analyzer that utilizes nitrogen adsorption and uses the static dosing method. This reference method uses nitrogen to measure the sample tube free-space for highly accurate data (<2% accuracy). From this the surface area was determined using the Brunauer–Emmett–Teller (BET) theory. This theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. BET uses equation 6

\[
\frac{1}{v[(p_0/p)^{-1}]} = \frac{c-1}{vmc} \left( \frac{p}{p_0} \right) + \frac{1}{vmc} \quad (6)
\]

where p and p₀ are the equilibrium and saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity, vₘ is the monolayer adsorbed gas quantity, and c is the BET constant [39].
2.4.4 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry (AAS) is a device that quantitatively determines the presence of chemical elements using the absorption light by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples [40].

2.4.5 Reaction Test Apparatus

The flow rates of the input gases were regulated and the inlet gas pressure measured by Cole Palmer flow controllers. The gas line was then connected to the reactor, which was placed into a Thermo Scientific Lindberg Blue M tube furnace. The reactors were all made inside of a 4 mm inner diameter and 6 mm outer diameter glass tube and put inside the tube furnace whose temperature was controlled manually. The catalyst was held in place by fixing Restek deactivated wool fiberglass plugs on either side of it and the gas line was connected to the reactor using stainless steel tubing. The metal was bonded to the glass using Small Parts 3/16” PEEK shrink tubing at 345°C creating a gas tight seal. The thermal treatment of the bond took approximately 10 minutes. The 50 mg catalyst reactors were diluted with a 1:3 mass ratio with Sigma-Aldrich white quartz sand (50+70 mesh). A 7890A Agilent gas chromatograph (GC) was used to determine the amount of CO conversion for a reactor. The GC has a gas-sampling loop and uses helium as the carrier gas. The columns used were a HP-PLOT/Q
and HP-MOLESIEVE, both 30 m in length and 0.53 mm in diameter. The HP-PLOT/Q had a 40 μm film and the HP-MOLESIEVE column 50 μm. When the reactor was being tested with water vapor, the product gas was fed through a “bubbler”. The bubbler consists of a 50 mL flask filled with 25 mL of deionized water. This small vial was then placed into a water bath and the entire bath was placed onto a VWR 7” x 7” (VWR) hotplate/stirrer to control the water saturation through the temperature of the water bath. When the reactor was being tested with water vapor the tubing connecting the bubbler to the reactor inside of the tube furnace was wrapped with a Omegalux FGR heating rope whose temperature was kept 15°C above the temperature of the water bath to prevent the water vapor from condensing in the gas line. When the reactor was being tested with water vapor, the gas line connecting the gas line to the GC was then connected to a liquid trap to remove the majority of the water vapor from the output gas to avoid flooding the GC with water. The liquid trap was constructed the exact same way as the bubbler, but instead of the water being heated the water was chilled with ice. The time-on-stream of the catalyst for each experimental condition was approximately 30 min before taking a GC measurement and an entire set of temperature-dependent experiments from 25 to 100°C took 4.5 hours. A new reactor was used for each set of experiments. Experiments were performed at least three times and the catalyst achieved reproducible results every time. Several different batches of catalyst were produced and no significant difference from batch to batch could be found.
To determine the amount of CO converted, first, a baseline was established with a “calibration gas” mixture. “Calibration gas” is the synthetic methanol-steam reformate mixture and it was run directly into the GC without the PROX reactor. The results from the GC show peaks with area of arbitrary units as a function of time. Each time point corresponds to a specific compound shown in Table 1.

**Table 1: Time and corresponding compounds as they appear in the GC for the most realistic reformate gas.**

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Compound</th>
<th>Average Calibration Area (a.u.)</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3</td>
<td>CO₂</td>
<td>14,041</td>
<td>0.218</td>
</tr>
<tr>
<td>~8</td>
<td>H₂</td>
<td>502</td>
<td>0.681</td>
</tr>
<tr>
<td>~10</td>
<td>O₂</td>
<td>1,812</td>
<td>0.018</td>
</tr>
<tr>
<td>~12</td>
<td>N₂</td>
<td>7140</td>
<td>0.727</td>
</tr>
<tr>
<td>~17</td>
<td>CO</td>
<td>567</td>
<td>0.009</td>
</tr>
</tbody>
</table>

From this data the calibration areas are equated to a mole fraction, \( \epsilon_x \), for each compound using the flow rate and composition, equation 7.

\[
\epsilon_x = \frac{n_x (FR_1) + n_x (FR_2)}{FR_{tot}} \quad (7)
\]

Where FR is the flowrate and \( n_x \) is the moles of compound “x”. Next the PROX reactor was added to the set up and the gas was analyzed in the GC. The PROX output
gas has less CO (because it is converted to CO₂) and O₂ (because it is being used to oxidize the CO). To calculate the conversion of CO equation 8 was used which:

\[
\tau = \left(1 - \frac{\epsilon_{\text{out}}}{\epsilon_{\text{in}}} \right) \times 100 \quad (8)
\]

where \(\tau\) is the % of CO conversion and \(\epsilon\) is the mole fraction of CO. \(\epsilon_{\text{in}}\) is the CO mole fraction before the gas mixture comes in contact with the PROX reactor, therefore this value is calculated with the calibration data. \(\epsilon_{\text{out}}\) is the CO mole fraction after the gas mixture is sent through the PROX reactor, so this value is determined with the GC data with converted CO. It is assumed that the total molar flow rate is only insignificantly changed due to the chemical reactions. This assumption has been validated by the experimental results.

With Au/\(\alpha\)-Fe₂O₃ as a catalyst the activation energy of CO oxidation is lower than the activation energy of H₂ oxidation, 31 kJ/mol and 50 kJ/mol, respectively [14]. As a result, at high temperature (> 50°C) the impact of hydrogen oxidation is more of an issue. The carbon monoxide-to-oxygen ratio, \(\lambda\), is defined as the number of CO molecules present relative to the number oxygen atoms, is kept constant at \(\lambda = 3\) for all experiments to optimize the compromise between conversion and selectivity. The selectivity of CO refers to the catalyst’s level of preference to oxidize CO over H₂.

**2.5 Experimental Conditions**

The reformate mix consists of the CO containing gas and any additional CO₂ or water added to the system. The dry gas mixtures used for experimentation are shown in
Table 1. The water is eventually added to the dry gas mixture (already containing fuel gas and air) before entering the reactor (labeled as 3-15% H₂O). The used flow rates are 10 ml/min of CO containing reformate gas and 0.7 ml/min of synthetic air producing 10.7 ml/min of dry gas mixture with compositions shown in Table 2.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>N₂</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal reformate</td>
<td>1.03</td>
<td>-</td>
<td>65.4</td>
<td>32.3</td>
<td>1.37</td>
</tr>
<tr>
<td>15% CO₂</td>
<td>1.03</td>
<td>14.0</td>
<td>41.1</td>
<td>42.5</td>
<td>1.37</td>
</tr>
<tr>
<td>17.5% CO₂</td>
<td>1.00</td>
<td>16.4</td>
<td>40.0</td>
<td>41.4</td>
<td>1.34</td>
</tr>
<tr>
<td>20% CO₂</td>
<td>0.97</td>
<td>18.7</td>
<td>38.9</td>
<td>40.2</td>
<td>1.30</td>
</tr>
<tr>
<td>22.5% CO₂</td>
<td>0.94</td>
<td>21.1</td>
<td>37.7</td>
<td>39.0</td>
<td>1.26</td>
</tr>
<tr>
<td>25% CO₂</td>
<td>0.91</td>
<td>23.5</td>
<td>36.6</td>
<td>37.8</td>
<td>1.22</td>
</tr>
<tr>
<td>24% CO₂</td>
<td>1.03</td>
<td>22.4</td>
<td>70.1</td>
<td>5.2</td>
<td>1.37</td>
</tr>
</tbody>
</table>

**Table 2: Dry Gas Mixtures (Mole fractions in %) [22]**

2.6 Results

In Fig. 6, the lighter structures are the Fe₃O₅ support particles and the darker portions are the Au particles. The Au particles are well dispersed throughout the Fe₃O₅ particles. From these images it was determined that the Fe₃O₅ particles are ~5-7 nm before testing and they grow slightly to 7-10 nm during preparation of the reactor (curing of PEEK tubing) and the initial testing. The Au particle sizes range from ~15-25 nm and stay the same before and after testing. This proves successful synthesis of an inverse catalyst. Figure 7 shows the results from the XRD. The catalyst was hit with a Cu Kα beam and depending the intensity of the scattered beam was plotted with respect to the scattering angle. Once this data is collected I performed a search in the ICDD
Powder Diffraction File database for all forms of Fe₂O₃ and Au. Then I overlayed the plots from the database with the plot generated by the XRD of my sample. As it can be seen in Fig. 7, the XRD data of as-prepared catalyst clearly shows the diffraction peaks of α-Fe₂O₃ and Au. I indicated the database peaks locations above the major peaks.

Figure 6: TEM image of Au/α-Fe₂O₃ catalyst before (left) and after testing (right)
Figure 7: XRD spectrum of the inverse Au/α-Fe$_2$O$_3$ catalyst with markers indicating the location of α-Fe$_2$O$_3$ and Au via the ICDD Powder Diffraction File database.

The monolayer formation of gas molecules on the surface is used to determine the specific surface area, while the principle of capillary condensation can be utilized for assessing the presence of pores, pore volume and pore size distribution. Just prior to the measurement, the sample is pre-treated at elevated temperature in flowing gas in order to remove any contaminants. The surface area analyzer determined by BET measurements (discussed in section 2.4.3) the specific surface area of the catalyst to be 223 and 120 m$^2$/g for as-prepared and used catalyst, respectively. This is consistent with the TEM images obtained and this surface area is higher than reported data with the most competitive results [11, 12]. Figure 8 shows the pore size distribution of the catalytic nanoparticles, confirming the dominant particle size of 7-10 nm. A secondary peak is visible at 28 nm.
For AAS analysis first a calibration curve was formulated using standard Au solutions with concentrations that varied from 10 to 40 ppm. The curve plots concentration as a function of absorbance and the absorbance of each solution was determined by the AAS. Next the Au/α-Fe₂O₃ catalyst was dissolved in 1:3 HCl/HNO₃ acid solution. The solution was then diluted 20-fold with deionized water to make it suitable for analysis. From the calibration plot the weight percent of Au in the catalyst was determined to be 3.3 wt%.

The first tested input gas had a composition of 1% CO, 29% N₂, and 70% H₂ plus synthetic air. This mixture is known as the “ideal” reformate gas because it does not contain any CO₂ or water [41]. Figure 9 shows the results: At room temperature there was ~92% CO conversion and 100% conversion at 40-70°C. There is a decrease in
conversion at higher temperatures because of competitive H₂ oxidation, however, there is still 99.83% conversion at 80°C. At room temperature the selectivity towards CO oxidation is 100%, as the temperature is increased the selectivity decreases until it reaches a minimum of ~34% at 70°C (not shown in the figure). These first tests establish a baseline for the catalyst to compare the effect of the addition of CO₂ and H₂O to the results without their presence.

Figure 9: CO conversion under optimized conditions with ideal reformate gas

The effect of CO₂ on the catalyst was tested by varying the amount of CO₂ in the inlet gas, with CO₂ mole fractions of 15-25%. This variation was achieved by modifying flow rates of the pure CO₂ tank, while keeping the amount of CO at ~1%. The reactor was tested up to the maximum amount of CO₂ observed in a methanol steam former to determine its behavior under the most extreme, but realistic, conditions. The result of introducing CO₂ was an increase in CO conversion at all temperatures, showing 100% conversion at 80°C for all amounts of CO₂, as seen in Fig. 10.
Figure 10: CO conversion in the presence of CO₂

The effect of water vapor was also tested by passing the gas feed through a “water bubbler” in front of the reactor. The amount of water vapor was varied by changing the temperature of the water in the bubbler. The result of this test was decreased conversion at very low temperatures but as the temperature was increased, the conversion increased to 100% conversion at 80°C for 0-10% water vapor, as shown in Fig. 11. 12.5% and 15% water vapor was tested because we wanted to see the behavior of the reactor under very high humidity condition. At very high concentrations of water vapor the conversion decreases significantly, at the temperature of focus (80°C) the conversion with 12.5% and 15% H₂O was 99.1% and 97.97%, respectively.
Finally, the catalyst was tested under the most realistic conditions simultaneously. With 24% CO₂ and 10% H₂O, the catalyst still performed exceptionally. At 80°C, conversion of 99.85% was achieved, as seen in Fig. 12.

Using the experimentally determined CO reaction rates, the turn-over frequency (TOF) can be calculated (all TOF values presented here are determined at 80°C). For the dry gas mixture without any CO₂ and H₂O, the TOF is 0.150 s⁻¹. By adding 15% CO₂, the resulting TOF is not affected (still 0.150 s⁻¹) and it decreases slightly to 0.132 s⁻¹ for 25%
CO₂. The addition of 10% H₂O has again no significant effect, and 15% H₂O lead to a minimal decrease to 0.147 s⁻¹. Finally, the simultaneous introduction of 10% H₂O and 24% CO₂ leads to an unaffected TOF of 0.150 s⁻¹, and to 0.141 s⁻¹ for 15% H₂O and 24% CO₂. These values for TOF are among the highest values reported in the literature in the absence of H₂O and CO₂ [6, 29]. This result highlights the impact of the presented catalyst, achieving very high CO conversion and TOF even in the presence of CO₂ and H₂O, which otherwise suppress the catalytic activity.

To demonstrate the long-term activity of the catalyst, one reactor was tested with the gas mixture containing of 24% CO₂ and 3% H₂O for a total of 200 hours at a constant temperature of 80°C. In Fig. 13, the CO conversion during the test is shown. For the very first measurement, 100% conversion was detected. After 30 min, any measurement achieved 99.85% CO conversion, indicating a CO level below the GC resolution of 10 ppm. No change in catalytic performance could be found for the entire duration of the test.
Figure 13: CO conversion tested over 200 hours, for 24% CO\textsubscript{2} and 3% H\textsubscript{2}O at 80°C.

Finally, to determine the effect of Au, a series of CO conversion tests via the GC with Fe\textsubscript{2}O\textsubscript{3} without Au (synthesized in the same manner as the Au/Fe\textsubscript{2}O\textsubscript{3} catalyst) has been performed. Without Au, the Fe\textsubscript{2}O\textsubscript{3} nanoparticles achieve less than 5% CO conversion for temperatures below 100°C, with and without CO\textsubscript{2}. For temperatures up to 180°C, the CO conversion reaches only 15%. It is obvious that Fe\textsubscript{2}O\textsubscript{3}, while being a highly effective support material, is not the primary contributor to the catalytic activity of the tested catalyst.

2.7 Discussion

The dominant mechanisms for the PROX reaction proposed by the literature rely on the Au particle size. It has been continuously suggested that the decrease of Au particle size below 10 nm should lead to a drastic increase in conversion[36]. For the
catalyst synthesized in this work, however, the gold particle size ranges from \( \approx 15-25 \) nm higher conversion was observed, especially under harsh conditions in the presence of high amounts of H\(_2\)O and CO\(_2\). The support particle size is believed to play a significant role in the PROX capabilities and that this significance has been neglected in previous literature\([13, 16, 36]\).

In most works the final step of catalyst synthesis is calcination to allow the Fe\(_2\)O\(_3\) to grow to \( >15 \) nm. In this work, the catalyst is not calcined after the co-precipitation synthesis and the Fe\(_2\)O\(_3\) particles are grown in a highly acidic solution to further decrease the size of the Fe\(_2\)O\(_3\) to \( \approx 5 \) nm, to create an inverse catalyst. Suttiponparnit et al. showed that metal oxides grown in an acidic solution reduce their particle size \([42]\). Fe\(_2\)O\(_3\) is an “active” support material: Schubert et al. showed a mechanism for PROX that involves the oxygen in the inlet gas adsorbing to the Fe\(_2\)O\(_3\) support, then disassociating, and surface oxygen being transported to the Au, where it reacts with CO \([23]\). This is the beginning of the proposed PROX mechanism taking place on our catalyst. Meanwhile, the CO is being adsorbed to the Au particles, acting as a holding cell for the molecule. The Au\(^0\)-CO bond generates thermal energy, which leads to an increase in temperature at the Au-Fe\(_2\)O\(_3\) interface. The CO covers the Au particle generating a cloud of thermal energy (110-120 kJ mol\(^{-1}\) of CO) that covers large portions of the Fe\(_2\)O\(_3\) \([43]\). The adsorbed surface oxygen is now able to thoroughly oxidize the CO. As the size of the Fe\(_2\)O\(_3\) decreases, creating one of the largest documented surface areas for this specific catalyst,
the amount of surface oxygen present on the support increases. This decreases the PROX
dependence on Au particle size, leading to the increased conversion compared to
conventional catalysts. This mechanism was confirmed when the catalyst of this work
was calcined at 400°C for 2 hours, the Fe₅O₃ particles grew to >10 nm, and there was a
decrease in conversion by 10-20% requiring higher temperature and less water vapor to
achieve high conversion.

When CO₂ is introduced, there is an increase in conversion for all temperatures
and levels of CO₂. In traditional catalysts, the deactivation with introduction of CO₂ into
the gas mixture is attributed to competitive adsorption of CO₂ and CO on the catalyst
[44]. With our inverse catalyst, there is an increase in the support surface area. As a
result, there is an increase in the amount of active sites for the CO₂ to adsorb onto. The
oxygen adsorbs to the support and dissociates. The CO bonds to the Au and then reacts
with a hydroxide ion on the support forming a carboxyl group [45-48]. The CO₂ bonded
to the support reacts with a hydroxide ion forming bicarbonate on the support. The
carboxyl group reacts with oxygen adsorbed on the support forming another
bicarbonate [47, 48]. The bicarbonate on the support reacts with a water molecule on the
support and forms CO₂, and the bicarbonate on the Au actively disassociates into CO₂
[48].

Based on the durability test, the catalyst is capable of maintaining >99.9% CO
conversion over more than 200 hours in the presence of CO₂ and H₂O. The finding is
significant because other catalysts of the same composition showed significant
deactivation within the first 75 hours in the presence of 15% CO₂ and without water [11].
When water was added to the previously reported catalysts, the conversion increased to
∼99%, but this was achieved only after the temperature was increased to 100°C to
maintain the ∼99% [11].

2.8 Conclusion

The Au/α-Fe₂O₃ catalyst was chosen for its documented PROX superiority and
was prepared using a modified co-precipitation method where the particles were grown
in an acidic solution. Its catalytic behavior was tested in the presence of varying
amounts of CO₂ and H₂O. The results of this synthesis method were exceptional, 100%
conversion at 80°C for all tested amounts of CO₂ and for up to 10% of H₂O. Under the
most realistic and harsh conditions (24% CO₂ and 10% H₂O) the catalyst still performed
well reaching our goal of ≥99.8% conversion. This exceeds the results of current
literature for CO preferential oxidation in presence of large amounts of CO₂ and H₂O.
The results were achieved under feasible operating conditions of an entire reformed
alcohol fuel cell system. A long-term test of 200 hours showed no significant
deactivation of the catalyst at a temperature of 80°C in presence of 24% CO₂ and 3%
water. Finally, kinetic models supported by these findings were proposed to explain the
increased catalytic activity of the presented catalyst, even in the presence of large
quantities of H₂O and CO₂.
The focus of this study was high conversion with 24% CO₂ and 10% H₂O to demonstrate the robustness of the synthesized inverse catalyst. In a typical fuel cell system there would be a condenser unit after the steam reformer because the output gas would be ~200°C. This temperature is too high for effective PROX and fuel cell operation. Therefore, for all of the following PROX experiments the focus will be on high CO conversion with high levels of CO₂ and room temperature water vapor, 3%. 
3. Optimization of CO PROX Catalyst for Realistic Use in a PEMFC System

The direct and successful combination of alcohol-steam reforming and PEMFCs has never been shown experimentally, only numerically, due to the missing link of efficient CO removal between H₂ generation and fuel cells [4]. In this study, we investigate the ability of the catalyst to effectively oxidize CO in a H₂, H₂O, and CO₂-rich environment by integrating the novel PROX catalyst into a low-temperature PEMFC [49]. First, we optimize the operating conditions for CO PROX via particle size investigation. We demonstrate how the toxic and non-toxic products of methanol-steam reforming affect the performance and robustness of the PEMFC over time using synthetic gas mixtures. Finally, we show the first fully integrated steam reformer-PROX-fuel cell system and demonstrate that the Au/α-Fe₂O₃ material has sufficient catalytic activity to operate the PEMFC under high performance without significant long-term deactivation.

3.1 Particle Size Study

With the synthesis of an inverse catalyst, we proved the importance of reducing support material particle size. Under the most realistic methanol-steam reformate conditions we were able to achieve the highest documented CO conversion with Au/α-Fe₂O₃ [22]. So, it was hypothesized that additional reduction of support material would further improve the CO oxidation activity of the catalyst.
In order to determine the factors that may affect the particle size of the catalyst during synthesis, it was imperative to implement an in-depth study of the synthesis method. This study would provide insight into the growth mechanism of the particles during synthesis of the inverse catalyst. With this data, we made deliberate efforts to reduce the size of the support material.

### 3.2 PEMFC with Realistic Reformate Conditions

A proton exchange membrane (PEM) fuel cell uses input gases, hydrogen and oxygen, to generate electricity with heat and water as the resulting exhaust[9]. The proton exchange membrane performs the chemical reactions. The most important component is the platinum catalyst found in the membrane’s carbon matrix. The reactions that occur are hydrogen splitting and protonization of oxygen into water, equation 9 & 10, on either side of the membrane due to the diffusion of protons through the membrane. While the protons are able to diffuse through the membrane, the electrons travel from the anode through an external circuit to reach the cathode, generating current [50]. Equation 9 represents the so-called global reaction, combining the half reactions 7 and 8 of both electrodes.

\[
H_2 \rightarrow 2H^+ + 2e^- \quad (9)
\]

\[
0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (10)
\]

\[
H_2 + 0.5O_2 \rightarrow H_2O + heat \quad (11)
\]
Most commonly, fuel cells are run with pure hydrogen and air, to supply the oxygen, flowing through the inlets. Over 95% of all hydrogen production is via hydrocarbon-steam reforming. In order to determine accurate power outputs with real-world conditions, we used a synthetic methanol-steam reformate gas mixture and ran it through the PEMFC. The optimal FC temperature, humidification percentage, H₂ and air flow rates needed to be determined for maximum power output over time. For this study we used a hydrogen-rich mixture that also contains CO₂, N₂, and O₂ in one inlet and air through the other. The flow rates were regulated using flow controllers and humidity was added into the mixture using bubblers. A condenser unit was also used to prevent flooding of the system.

**3.3 Experimental Procedure**

**3.3.1 Particle Size Study**

The catalyst was synthesized as stated in Section 2.3.1. A 0.5 mL sample was taken using a single channel pipet when: 1) when the HAuCl₄·3H₂O and Fe(NO₃)·9H₂O were mixed initially, 2) at a pH = 1.4 after the precipitation agent is added, 3) at pH = 4, 4) at pH = 6, and 5) at the final pH = 8.2. The samples were put into an ice bath immediately after extraction to stop the reaction. Then the samples were diluted with 2 mL of deionized water in preparation for TEM imaging on Cu copper grid samples. From the TEM images we were able to determine average particles sizes at different stages.
3.3.2 Determining the Optimal Operating Conditions for the PEMFC

The voltage and resulting current output of the PEM fuel cell are measured using a 2244 Keithley Voltage Sources & Volt Meter. The gas mixture was simulated using gas bottles and the composition was regulated using flow controllers. PEM fuel cells also require humidification of the input gases. Humidification enhances the proton conductivity of the exchange membrane and thus the fuel cell performance. The exhaust gas was run through a chilled flask to condense out the water and prevent water blockages in the system. The fuel cell set up is shown in the schematic below, Fig 14.

Figure 14: Set up for testing fuel cell parameters for optimization: 1. gas bottles, 2. flow controllers, 3. humidification unit, 4. PEMFC, 5. condenser unit

The parameter set to generate I-V curves and determine the maximum power output of the fuel cell were input into computer software, LabTracer. Each measurement is conducted with a start voltage of 0.93 V and stop voltage of 0.1 V.
3.3.3 Fusing the PROX Catalyst with the PEMFC

Operating a PEMFC with the direct output gas from PROX reactor has never been tested before. In most cases, fuel cells, are run with pure hydrogen, which is unrealistic for on-board hydrogen production applications. To demonstrate the behavior of the PEMFC with output gas from a PROX reactor, the PROX and PEMFC experimental set-ups were combined, Fig. 15. A switching system was incorporated after the tube furnace to direct the PROX output gas mixture to either the GC for analysis or to the PEMFC for power generation.

![Diagram](image)

Figure 15: Set up for testing the fusion of the PROX catalyst with the PEMFC: 1. gas bottles, 2. flow controllers, 3. humidification unit, 4. PEMFC, 5. PROX reactor, 6. PROX catalyst, 7. condenser unit

3.4 Results

3.4.1 Particle Size Study Results

Sample 1, seen in Fig. 16, was taken when the HAuCl₄ was mixed with the Fe₃(NO₃) Initially and before heating. The TEM image shows ~15nm gold particles present in the solution and an absence of Fe₃O₅ particles at this stage.
Figure 16: TEM image of catalyst before precipitating agent was added

At pH = 1.94 only 10-15 drops of the precipitating agent (Na₂CO₃) had been added. In the TEM image, Fig. 17a, when zoomed out we saw a lot of large darker grey structures that are ~50nm in diameter. Upon further examination, we saw that these large structures were actually clusters of small particles, Fig. 17b. These clusters are nucleation sites for Fe₂O₃ and the individual particles are ~1nm in size.

Figure 17: TEM image of PROX catalyst during synthesis at pH=1.94 (a) at low magnification and (b) at higher magnification
Sample 3 was taken at a pH of 4, Fig. 18, here we see that the Fe₂O₃ clusters have grown to 2-5nm as well as the gold particles to 16-19nm.

![Figure 18: TEM image of PROX catalyst at a pH=4](image)

Sample 4, the pH of the mixture is 6 and the catalyst is beginning to resemble its final state. The dark clusters are starting to dissipate which corresponds to continued growth of the Fe₂O₃ particles, Fig. 19.

![Figure 19: TEM image of PROX catalyst at pH=6 during synthesis.](image)
Based on the results from this study, we observed that the final particle at pH=8.2 had a smaller particle size, ~5nm, than our “as-used”, ~7-10nm, Fig. 20a and 20b. This growth was determined to occur during the reactor fabrication process because the catalyst is exposed to 345°C temperatures to create the gas tight seal. So effort was focused on improving our reactor fabrication method to further improve the catalytic ability of the PROX catalyst. Figure 21 shows the particle size vs. pH plot for the catalyst and the change in particle size after reactor fabrication.

![TEM image of final state of PROX catalyst at pH=8.2 during synthesis (a) before incorporation into a reactor (b) after incorporation into a reactor.](image)

Figure 20: TEM image of final state of PROX catalyst at pH=8.2 during synthesis (a) before incorporation into a reactor (b) after incorporation into a reactor.
3.4.2 Modification of Reactor Fabrication

The fabrication method for PROX reactors used in chapter 2 requires the entire reactor, including the catalyst, to be heated to 345°C to melt the shrink tubing and create a gas tight seal that is imperative to our set-up. The catalyst was added prior to heating the reactor to bond the shrink tubing, subsequently heating the catalyst. This results in the Fe₂O₃ particles growing from ~5nm to 7-10 nm. By eliminating this step, we would be able to retain the ~5nm particle size. The reactor fabrication method was deconstructed to find a way to incorporate the nano-catalyst after the shrink tubing step. By removing the Swagelok fittings that act as an adapter for the gas lines to connect to the input and output into the reactor we could access the glass tubing after heating. As a result, the reactor was heated without the catalyst, allowed to cool to room temperature, and then the catalyst was added and fixed into place with fiberglass wool. The catalyst was tested using 3% H₂O, and compared to the data in chapter 2 to determine if the
change in particle size improved the CO conversion, Fig. 22. We saw an improvement with the CO oxidation for all temperatures and we were able to achieve 100% conversion at lower temperatures.

![Graph showing CO conversion vs. temperature](image)

**Figure 22:** Comparison of PROX CO oxidation activity before and after reactor fabrication modification.

Finally, since we observed an improvement over the entire temperature profile, we tested the catalyst with 24% CO₂ and 3% H₂O for 8 hours at 70 and 80°C. This would demonstrate how robust the new catalyst is over time at a lower temperatures, Fig. 23.

![Conversion vs. time graph](image)

**Figure 23:** Conversion vs. time of new catalyst at 70 and 80°C for 8 hours.
3.4.3 Optimal Operating Conditions for PEMFC

3.4.3.1 Impact of Air Flow Rate

The first condition tested was the impact of the air flow rate on the PEMFC performance. To combat blockages in the fuel cell that result from built up of water droplets in the serpentine channels an excess amount of air is flowed through the fuel cell. It is an “excess” amount because it exceeds the amount of oxygen needed stoichiometrically to perform the reactions necessary to run the fuel cell efficiently. There is a delicate balance between have too little air (leading to blockages) and too much air (leading to dehydration of the membrane). As a result it is important to determine the optimal flow rate for air into the system. The air flow rate was varied from 20-50 ml/min and the results are shown in Fig. 24. The air flow rate of 20 ml/min leads to the lowest power level of 0.24 W. This result can be attributed to being below the threshold of sufficient air flow to prevent blockage. Flow rates of 30, 40, and 50 ml/min produced the same amount of power ~0.25 W. 30ml/min was chosen as the optimal flow rate for air because it exhibited the most stable power output over time. Additionally, the latter flow rate also exhibits a lower reaction stoichiometry, hence less air is discarded without being applied for electricity production.
3.4.3.2 Impact of H₂ Flow Rate

The second condition tested was the hydrogen flow rate. The flow rate was varied from 0.7-5 ml/min and the air flow rate was kept constant at 30 ml/min. The results are shown in Fig. 25. When the H₂ flow rate was set to 5, 4 and 3 ml/min over 120 minutes, the maximum power output remained stable at ~0.25 W. When the flow rate was decreased below 2 ml/min, the maximum power output also decreased to a minimum of 0.17 W for a flow rate of 0.7 ml/min.
Figure 25: Power vs. time plot depicting the effect of varying the H₂ flow rate on the fuel cell performance.

3.4.3.3 Impact of Fuel Cell Operating Temperature

In general, as the temperature of a PEM fuel cell is increased the maximum power output also increases [51]. However, just as with the air flow rate, there is a balance between having the fuel cell be too hot (leading to dehydration of the membrane causing the power to plummet) and the fuel cell being too cool (exacerbating the amount of water present in the fuel cell causing blockages in the serpentine channels). As a result, it is necessary to find the optimal operating temperature for the fuel cell for testing. The fuel cell temperature was tested at 65, 70, and 75°C while keeping the air and H₂ flow rates constant at 30 and 3 ml/min, respectively. The results are shown in Fig. 26. The maximum power out for 65 and 70°C are approximately the same, ~0.25 W. When the fuel cell was heated to 75°C there was a slight but obvious decrease in the power output to 0.24W.
3.4.3.4 Impact of CO$_2$

CO$_2$ can have significantly negative impact on the performance of a PEM fuel cell, especially when a platinum based Nafion membrane is applied [52]. Since hydrogen is produced by methanol steam reforming, the influence of reforming byproducts needs to be evaluated. Other gas components are nitrogen, water, carbon monoxide and also carbon dioxide [53]. The impact of the latter component is investigated. Figure 27 exemplifies the impact of CO$_2$ on the power output of the PEM fuel cell. Experiments with 0, 10, 20 and up to 30% CO$_2$ are conducted consecutively. When increasing the fraction of CO$_2$, the power output decreases by trend, as expected. Regarding the 10% CO$_2$ run, a drop of the power output can be registered after 90 min. This power level is stable even after increasing the CO$_2$ content up to 20% over the whole experimental time. Thus, history effects can be assumed. Conducting the experiment with 30% CO$_2$
the next day shows a higher power output compared to 10 and 20% CO$_2$. The impact of CO$_2$ on the fuel cell performance depends on the daily condition of the fuel cell. This is consistent with de Brujin et al., reporting small up to significant losses in performance, depending on the composition and microstructure of the fuel cell anode [53]. De Brujin et al. explain the negative effect by reverse water gas-shift reaction on platinum sites, causing formation of CO, bonding with platinum and thus inactivating the proton exchange membrane [53].

![Image](image.png)

**Figure 27**: Power vs. time plot depicting the effect of CO$_2$ concentration on the fuel cell performance.

### 3.4.4 Fusing the PROX catalyst with the PEMFC

The results from the PROX-PEMFC fusion are shown in Figure 28. It shows that prior to connecting the two systems the PROX catalyst was converting ~99.9% (<10 ppm) of CO and the fuel cell achieved an average power output of 0.25 W while running on
pure H₂ and air. After the PROX output gas was switched to flow through the fuel cell, average power slowly dropped to 240 mW and stayed stable, a variation of only ±1 mW, at this level for 145 minutes. After 5 hours the gas was switched so that the output gas from the PROX would flow to the GC. The fuel cell was run with pure H₂ and air again and the power recovered to its original 250 mW.

![Figure 28: Power and CO conversion vs. time plot depicting the effect of PROX output gas on the PEMFC](image)

### 3.5 Discussion

#### 3.5.1 Particle Size Study

This study provided us with in-depth knowledge of the nucleation and growth of the PROX nano-catalyst. With the addition of the precipitating agent the Fe₂O₃ particles begin nucleating. The nucleation stage is initiated by a reaction called hypereutectic cooling. The eutectic temperature is the temperature which a solution is cooled below its melting point and forms a solid [54]. In the case with the PROX catalyst the iron nitrate solution is rapidly cooled by the sodium carbonate, forming the Fe₂O₃
particles. Also, as more and more of the sodium carbonate solution is added we saw a change in the pH as well as the particle size of both species precipitated out of the solution. The cooling is classified as hypereutectic because the formation of Fe₂O₃ is dominant over the formation of any other solid [54].

3.5.2 Reactor Fabrication Modification

By changing the reactor fabrication technique there was an important decrease in CO from 15 ppm to 10 ppm at 70°C for the realistic reformate gas mixture. Recall that the threshold for the CO level necessary for long term PEMFC use is < 20 ppm. Prior to the modifications, although low enough to function well, the CO level was close to the threshold. With this further improvement of the conversion we are now at a very secure level of CO. Also, carrying out this reaction at a lower temperature indicates a reduction in the activation energy required for preferential oxidation of CO. This means that not only have we achieved the highest documented conversion but we have also made our system more efficient by requiring less energy input.

3.5.3 Fusion of PROX and PEMFC

The average power output when the PEMFC was run with pure hydrogen was 247.5 mW with the air flow rate = 30 ml/min, the hydrogen flow rate = 3 ml/min, and the fuel cell at an operating temperature of 70°C. This established a baseline for the fuel cell power during operation with the PROX catalyst output gas. We observed after running the fuel cell with the PROX output gas that the drop in power was only by 4%. This drop
can be attributed to the dilution of the H₂ with 25% CO₂. After 145 minutes of testing the fuel cell was run with pure hydrogen again and the average power recovered to its original levels. This indicates no MEA poisoning from the PROX output gas.

### 3.6 Conclusion

In conclusion, we successfully synthesized an inverse Au/α-Fe₂O₃ catalyst using a modified co-precipitation method and produced Fe₂O₃ particles that were 7-10 nm and 25 nm Au particles. We tested the catalyst under the harshest conditions and achieved high CO conversion, 99.85%, under all conditions. We were able to further improve the CO conversion, to 99.9%, by reducing the Fe₂O₃ particle size to 5 nm. This work represents the current state-of-the-art PROX CO conversion.

We were able to successfully fuse the PROX and PEMFC set-ups, representing the first documented successive combination of these technologies. We saw that PEMFC was not poisoned during this test and that it was still able to produce high power even with the addition of CO₂.
4. Plasmon Induced Hydrogen Production

4.1 Solar Energy Capture and Methanol-Steam Reforming Techniques

Solar fuels are an approach to capturing solar energy and storing it in form useful fuels. Solar-heated reforming of bio-fuel is a promising way to generate “on-board” hydrogen, because it utilizes the sun’s energy to drive the chemical reaction and does not require the storage of hydrogen [55, 56]. The three ways of using solar energy as an energy source are: photovoltaics (PV), solar thermal, and direct photocatalyst/artificial photosynthesis. Photovoltaics has been in the forefront of solar electricity production, however, there are limits to its efficiency and the cost of PV materials is too high for large-scale introduction into the electric grid. Solar thermal applications utilize solar collectors and absorbers. They require high temperatures and also very expensive materials to engineer these collectors[57]. Artificial photosynthesis uses sunlight to directly split water into hydrogen fuel. The disadvantage to this method is the limitation in the efficiency.

The method proposed in this work for fuel production is an innovative approach, which lowers the activation energy required to convert methanol-water into hydrogen, equation 10. Contrary to conventional solar thermal methods, the need to heat the entire system is circumvented by utilizing localized surface plasmon resonance (LSPR). LSPR occurs on the plasmonic nanoparticles when exposed to sunlight resulting in localized heating that will thermally drive our desired chemical reaction. Methanol is most
commonly used because its easily stored as a liquid, has a high conversion efficiency and relatively low conversion temperature of 200°C compared to the 500°C needed for ethanol. When accompanied with steam the catalytic conversion of this hydrocarbon to hydrogen only yields a small amount of by-product of CO (equation 13) as opposed to ethanol, methane, and gasoline [9].

\[
CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \tag{12}
\]

\[
CH_3OH \rightarrow 2H_2 + CO \tag{13}
\]

The Vo-Dinh Lab group, from the Biomedical Engineering Department at Duke University, has developed plasmonic technology that utilize localized surface plasmon resonance or LSPR with photons from the sun to generate heat [58]. LSPR occurs when photons interact with nanomaterials with a high number of free electrons and match the resonance energy of the oscillation of the surface valence electrons against the restoring of the positively charged surface nuclei [59, 60]. For Ag, Au, and Cu, this resonance occurs in the visible regime. The interaction of resonant photons and surface electrons initially leads to the coherent oscillation of electrons in space and energy leading to the confinement of photon energy to the surface of nanostructured materials for much longer time scales than photons traveling at the speed of light [1]. As a result of the very high absorption coefficient of photons in resonance with plasmon excitation and the capacitive coupling between clusters of plasmonic particles, LSPR excitation produces a large buildup of photon intensity (strong electric fields) and a high concentration of
energetic electrons at nanostructured surfaces. For example, resonant photon excitation of isolated cubic shaped Ag nanoparticles have been shown to locally enhance incoming light intensity up to $10^3$ fold and junctions between Ag particles can enhance the light intensity by up to $10^6$ times [61]. Low energy electrons couple up to phonon modes and at 1 ps and heat up the metal lattice. Then there is thermal dissipation into the surrounding lattice from 10-100 ps [62, 63]. This heating results in a transfer to absorbates; the fact drives chemical reactions through an Arrhenius dependence of rate surface temperature and does not obey classical heat conduction due to the unique composition of nanoparticles [64]. The combination of these two events generate strong photothermal heating of nanoparticles that requires only a small amount of optical energy and does not significantly heat the entire supporting structure, Fig. 29 [65, 66].

Figure 29: COMSOL simulation of polystyrene coated in metal and the enhancement of the magnitude of the electronic field at the LSPR sites
This work focuses on fusing two technologies, nanocatalytic reforming for hydrogen production and plasmonic technology, to achieve photothermal catalysis via plasmonic heating for hydrogen production. Due to the localized nature of the heat generation, we will reduce the amount of heat loss and also have a bio-fuel reforming system without the need to heat the entire set-up.

The proposed set up for the proof-of-concept is a continuous flow chamber filled with the methanol-water fuel. The plasmonic particles are deposited onto a glass substrate and the catalyst is deposited in the LSPR sites. The entire substrate will be submerged in the fuel and irradiated with a solar simulator. Upon illumination the LSPR sites will be activated and begin to heat the catalyst and the fuel to the desired temperature for reformation and produce hydrogen gas, Fig. 30.

![Diagram of proposed set up for plasmon assisted hydrogen production.](image)

**Figure 30: Proposed set up for plasmon assisted hydrogen production.**

### 4.2 Experimental Conditions

The solar simulator used was an Oriel Sol1A simulator by Newport (AM1.5 global and class ABB) with a 450 W xenon arc lamp. The beam size was 4” x 4” with an
intensity of 1000 W/m² and it had a class A spectral match. The uniformity was class B and temporal instability was also class B. To focus the sunlight on the plasmonic substrate a Nikon L Plan SLWD 20x/0.35 objective lens was fixed under the lamp. The objective lens focused a portion of the original beam to a new diameter of ~2.3 mm, which had an intensity of 12.23 kW/m² (solar concentration of 12.23).

4.3 CuO/ZnO/Al₂O₃ (CZA) synthesis with Flame Spray Pyrolysis.

The catalyst used for bio-fuel reforming in this study was CuO/ZnO/Al₂O₃ (CZA) because it achieves 100% methanol conversion for reasonable flow rates at temperatures as low as 220°C [55]. This catalyst was made using a synthesis technique called “Flame Spray Pyrolysis” (FSP). FSP is a technique that produces metal-oxide nanoparticles by burning/oxidizing alcoholic metal precursors in a flame. This process produced a 65:25:10 weight percentage of CuO/ZnO/Al₂O₃, respectively, and the diameter of the particles is ~20 nm [55].

The methanol-water fuel had a 1:1.2 molar ratio and was allowed to rest for an hour to degas. The fuel was pipetted into the reactor using a single channel micropipette.

4.4 Experimental Procedure

4.4.1 Plasmonic Substrate

Fabrication of the plasmonics-active nanowave substrate is relatively simple with high reproducibility and low-cost using self-assembly on water-air interface method.
Microscope glass slides were cleaned by immersion in a freshly prepared piranha solution (3:1 96% H$_2$SO$_4$: 30% H$_2$O$_2$) for 1 hour at 90 °C. The glass slides were then washed with copious amounts of DI water before being sonicated in a 5:1:1 DI/NH$_4$OH/H$_2$O$_2$ solution for 1 hour. The glass slides are then stored in DI until use. The polystyrene beads (PS) were mixed with ethanol and a trace amount of polyethylene oxide (PEO, 2 mg PEO for 1 mL mixture of PS and ethanol). The PEO’s function is to bind PS together as PS assembly. Self-assembly at the water-air interface produced monolayers of PS on glass slides, Fig. 31a. A thin layer of water was created on a cleaned, hydrophilic glass slide by pipetting 1.5 mL DI water on the glass slide. A small amount of SDS surfactant (5 µL of 2 mM SDS) was added on the water layer and serve as a soft barrier. The PS solution was injected on the edge of the water layer using a KD Scientific KDS200 syringe pump. With the assistance of ethanol, PS quickly spread on the water film and self-assemble into a monolayer at the water–air interface. PS was continuously injected until the whole water surface is covered with a monolayer of PS. The water film was carefully removed, leaving a monolayer of PS on the glass slide. The glass slide with a monolayer of PS was kept in a Petri dish at room temperature with the lid slightly open so that the rest of the water could evaporate. Upon water evaporation, a large-area monolayer of PS on glass slide will be obtained, Fig. 31b and 31c. The prepared monolayer of PS on glass slide will be annealed in an oven at 80°C for 1 h to induce area contact between PS and the glass surface. This annealing process enhanced
the PS and glass slide bonding. The annealed substrate was sequentially coated with 5 nm Ti (2 Å/s) and 195 nm in total of Ag (5 Å/s) and/or Au (10 Å/s). All metals will be deposited under $5 \times 10^{-6}$ mTorr using Kurt Lesker PVD 75 electron beam evaporator. The obtained substrates, Fig. 31d, will be stored in desiccator at room temperature [58, 65-67].

Figure 31: (a) Fabricating monolayer of PS on glass slide based on self-assembly on water-air interface method. (b, c) Monolayer of PS on microscope glass slide at two different viewing angles. (d) SEM image of a 520 nm PS monolayer covered by a 200 nm-thick metal film. Scale bars in (b, c): 10 mm, (d): 2 µm.

4.4.2 Building the Reactor

0.2 mg of CZA catalyst was weighed and sonicated in 1 mL of ethanol for 30 minutes to adequately disperse the nanoparticles in the solution. The plasmonic substrate was heated to 45°C on a 4”x 4” VWR hotplate. Once the solution was ready, the catalyst was drop-cast onto the warm substrate using a single channel micropipette. The method used for catalyst deposition, drop-casting, produces a “coffee-ring stain” effect that is brought upon by reversed Marangoni flow. This mechanism is
characteristic of particles dispersed in a solution just as our catalyst. The substrate was fixed to a stand and submerged into a vial that was filled with the methanol-water fuel, to make the reactor.

4.4.3 Testing the Reactor

The samples analyzed were: 1) a plasmonic substrate with catalyst, 2) a plasmonic substrate without catalyst, and 3) a glass substrate with catalyst. The purpose of these tests was not only to prove the production of hydrogen in the cold reactor, but to also show the lack of hydrogen production without the novelty of coupling the catalyst with the plasmonic substrate.

Two system configurations were used to analyze the system, open and closed. The closed system is required for GC analysis to ensure the capture of the produced gas. However, in the closed system the plasmon-induced evaporation, which converts fuel into vapor, has to overcome the higher liquid pressure inside of the reactor. As a result, the closed system produces a reduced amount of gas until it reaches a maximum pressure where the plasmonic evaporation is completely suppressed. In order to more accurately visualize the gas production, an open system operating at essentially ambient pressure, was fabricated. All of the images in the results section show the results for an open system.

The plasmonic substrate was tested without the addition of catalyst. This test produced little to no activity. The plasmon resonance was occurring and increasing the
temperature of the irradiated area, but without the catalyst the produced water-methanol vapor was unable to be converted into a hydrogen-rich gas. As a result, the bubbles that were produced consisted of vapor and condensed back into the liquid after a short period of time.

Finally, the catalyst was deposited on a glass substrate without the nanowave substrate and tested. No gas or vapor bubbles were formed during this test. Without the plasmonic technology the temperature required for the evaporation reforming to occur would require larger magnitudes of energy put into the reactor.

The produced gas in the closed system was extracted with a gas tight syringe and manually injected into the GC for analysis. The resulting data showed the presence hydrogen and carbon dioxide with the expected 75%:25% molar proportions expected for methanol steam reforming. This was achieved while keeping the reactor chamber cold below 35°C, without any external heating as required in conventional systems.

4.5 Characterization

4.5.1 UV-Vis Spectroscopy

Optical spectrum measurements were performed using a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer. This device excites a sample at a specific wavelength between 185 nm-3300 nm and determines how much of the light is absorbed, reflected, or transmitted. For this study, we only tested wavelengths in the visible spectrum (400-800 nm) because we irradiated samples with only visible light.
4.5.2 Scanning Electron Microscope (SEM)

An SEM is an electron microscope that produces a high-resolution image by scanning a sample with a focused beam of electrons. These electrons interact with the sample and produce a signal that is detected and provides information about the topography of a sample [37]. The SEM was an FEI XL30 SEM-FEG with a high magnification imaging tool. The resolution of the device is on the order of 2 nm.

4.6 Results

4.6.1 Characterization

4.6.1.1 UV-Vis Spectroscopy

The resulting absorbance, reflectance, and transmittance data shown in Fig. 32 depicts the optical response of the plasmonic substrate to incoming light as well as the manner in which the addition of a layer of catalyst particles affects this response. The plasmonic substrate without catalyst particles produced the spectral response consistent for Au, with two resonance peaks around 450 nm and 630 nm. With the addition of a catalyst layer, there was a slight red shift of the resonance peaks as well an increase in absorbance and a decrease in reflectance and transmittance over the visible wavelength range. In addition to the beneficial catalytic properties of this added layer, it is likely that the increased absorbance (and decreased reflectance and transmittance) of visible light improves reactor performance by absorbing more photons and therefore increasing the plasmonic activity of the underlying substrate.
Figure 32: UV-Vis spectroscopy depicting the change in absorbance with the addition of CZA catalyst.

4.6.1.2 SEM

The method used for catalyst deposition, drop-casting, produces a “coffee-ring stain” effect that is brought upon by reversed Marangoni flow. This mechanism is characteristic of particles dispersed in a solution just as our catalyst. The result is an uneven deposition of catalyst over the entire substrate, Fig. 33.
Figure 33: SEM image at 20 kV, 20k magnification and working distance of 5.1 mm of plasmonic substrate after drop-casting deposition of CZA.

The plasmonic nanoparticles were deposited on silicon (as stated in section 4.4.1) substrates for the purpose of imaging in the SEM. Figure 34a shows the nanowaves before deposition of the catalyst. The darker portion the spheres are the polystyrene and the lighter cap is the gold coating. The polystyrene spheres are ~520 nm in diameter and the gold coating is ~200 nm thick. Figure 34b shows the substrate after catalyst deposition. The catalyst forms a relatively even layer over the nanowaves and successfully deposit between the spheres (the areas with high LSPR).
Figure 34: SEM images of the nanowave substrate (a) before and (b) after deposition of the CZA catalyst.

4.6.2 Quantification of hydrogen production and percentage of cell used

The plasmonic activity drove the hydrogen production on the section of the substrate under mildly focused illumination. After initial irradiation, bubbles ~0.224 mm immediately appeared, detached from the surface and rose to the top of the reactor, Fig. 35. These small bubbles were consistently produced during operation. In a closed system, used so that gas could be collected for analysis in the GC, the rate of hydrogen production and size of produced bubbles decreased and eventually completely stopped. The reduction in hydrogen production is due to the build-up of pressure inside the closed reactor system as an increasing amount of gas was produced.
Figure 35: Time lapse of hydrogen production.

Figure 36a shows an illustration of the top-down configuration of the plasmonic substrate. Note the hexagonal structure and the 12 LSPR sites. Figure 36b shows a specific LSPR site. The size of the site is dependent on the size of the plasmonic particles and the active site has a rectangular shape. The plasmon propagation length, $L_p$, is the length that the two plasmonic hemispheres have to be within to experience a plasmonic effect. The points farthest from each other with just $L_p$ between them will be the rectangular shape seen in Fig. 36b. Based on the size of the plasmonic spheres there is a minimum distance that is required in order to have the LSPR effect. We estimated that $L_p$ is 5-10 nm because of the size of the particles and using equations 13 & 14 [58].
Figure 36: (a) Hexagonal configuration of plasmonic materials (b) specific LSPR site.

The percentage of the area where LSPR can occur ($\Phi$) is defined by the following equations:

\[ y = \sqrt{2Rx - x^2} \quad (13) \]

and

\[ A_{\text{actual}} = 4xy \quad (14) \]

where $R$ is the radius of the plasmonic hemisphere and $x$ and $y$ are opposing halves of the plasmon propagation length in the rectangular area of LSPR activity. $A_{\text{actual}}$ is the area of activity where LSPR should occur, which is the area of the rectangle. The area of the focused beam of light, $A_{\text{beam}}$, is

\[ A_{\text{beam}} = \frac{d_{\text{beam}}^2}{4} \pi \quad (15) \]

where $d_{\text{beam}}$ is the beam’s diameter. For our set-up the diameter of the beam is 2.288 mm, which results in an $A_{\text{beam}}$ value of $4.11 \times 10^{-6}$ m$^2$. 
The hexagonal packing of the plasmonic hemispheres leads to a packing efficiency, $PE$, of 0.9069 [68]. From this value we calculated the area of illuminated hemispheres $A_{\text{pack}}$ with the following equation

$$A_{\text{pack}} = PE \times A_{\text{beam}} \quad (16)$$

The total number of illuminated LSPR active areas was calculated with the following equations:

$$A_{\text{sphere}} = R^2 \pi \quad (17)$$

$$N_{\text{sphere}} = \frac{A_{\text{pack}}}{A_{\text{sphere}}} \quad (18)$$

$$N_{\text{actual}} = 3N_{\text{sphere}} \quad (19)$$

and

$$A_{\text{actual tot}} = N_{\text{actual}} A_{\text{actual}} \quad (20)$$

where $A_{\text{sphere}}$ is the area of an individual hemisphere that is illuminated by the concentrated beam, $N_{\text{sphere}}$ is the number of hemispheres, and $N_{\text{actual}}$ is the actual number of LSPR active sites. From this we calculated $A_{\text{actual tot}}$, which is the total area of the active illuminated areas. Finally, $\Phi$ is calculated with the following equation

$$\phi = \frac{A_{\text{actual tot}}}{A_{\text{beam}}} \times 100 \quad (21)$$

From this it was determined that the percentage of the illuminated substrate where LSPR can occur is 0.5-1.2%.

To calculate the percentage of gas produced, we first had to determine the approximate bubble diameter. We observed multiple bubbles and averaged their
diameters, ~0.224 mm. It was also observed that the rate of bubble production was ~4 bubbles every 9 seconds. From this information the volume of gas produced, $V_{\text{gas}}$, was calculated using the following equation

$$V_{\text{gas}} = V_{\text{bub}}N_{\text{bub}}$$ (22)

where $V_{\text{bub}}$ is the volume of a bubble and $N_{\text{bub}}$ is the number of bubbles produced per second. By manipulating the ideal gas law, $PV = nRT$, the number of moles of gas, $n_{\text{gas}}$ was calculated. The ratio of moles of $\text{H}_2$ to total moles of gas is 3:4, so to find the amount of moles of $\text{H}_2$ generated we multiplied the total moles of gas by 0.75. The flux of moles of $\text{H}_2$, $n_{\text{flux}_{\text{H}_2}}$, is found using the following equation

$$n_{\text{flux}_{\text{H}_2}} = \frac{n_{\text{H}_2}}{A_{\text{beam}}} = 2.4 \text{ l/}(\text{hr} \cdot \text{m}^2)$$ (23)

Using an Arrhenius type equation, we calculated the apparent localized temperature and the molar rate production of hydrogen gas, $n_{\text{H}_2}$, assuming ideal gas conditions around the activity site and that there is a thin layer of gas directly above the active site and below the fuel. The apparent localized temperature was 210-225°C for an $L_p$ between 5-10 nm. The plasmonic area fraction was determined to be between 0.5 and 1.4%. Figure 37 shows that the apparent local temperature, plasmonic area fraction, and plasmonic propagation length are all dependent on one another.

$$n_{\text{H}_2} = \frac{\Phi m_{\text{cat}}^p}{2.2RT} \times A_R \exp \left(-\frac{E_R}{RT}\right)$$ (24)
Where \( m_{\text{cat}} \) is the total mass of catalyst, \( A_R \) is the Arrhenius pre-coefficient, and \( E_R \) is the Arrhenius activation energy. The molar rate of hydrogen production was \( 1.12 \times 10^{-10} \) mol/s.

![Graph showing apparent localized temperature and plasmonic area fraction depending on the plasmonic propagation length.](image)

**Figure 37**: Apparent localized temperature and plasmonic area fraction depending on the plasmonic propagation length.

### 4.7 Discussion

This work has proven that hydrogen production via high temperature methanol-stem reforming while keeping the system cool. Using this method is more fuel efficient and has a lower activation energy to carry out the chemical reaction. Although the process is still endothermic, since the reaction is localized to the LSPR sites they overall system does not require heating. For an \( L_p = 5-10 \) nm it was determined that the apparent local temperature is 210-225°C. This confirms our original hypothesis that the LSPR sites reach a temperature capable of reforming the methanol-water fuel. It was also concluded that the plasmonic area fraction was between 0.5 and 1.4%. This means that the illuminated area of plamonics is inactive over more than 98%. Knowing this justifies
the low hydrogen production rate of our system. A conventional solar-thermal collector, using the same CZA catalyst, is capable reforming 6.5 l/min m² [57]. Compared to the 2.4 l/hr m² generated by the plasmonics system, it seems that the plasmonics system produces significantly less hydrogen. However, if we consider the fact that only 1.4% of the illuminated area of the plasmonics is active we find that the results of this work comparable to the hydrogen production of a conventional set-up.
5. Future Work

There are definite areas for optimization with the plasmonics topic. The catalyst deposition technique needs to be optimized. Currently, with the drop-cast method, the deposition over the entire substrate is extremely uneven. Having uneven deposition can effect the overall hydrogen production and limit the amount of active LSPR sites that are available. Spray coating the catalyst onto the substrate will enable even dispersion of the CZA catalyst. Since it is unknown whether a light, moderate, or heavy deposition of catalyst is needed, with spray coating we can deposit a specific amount of layers. With the variability of the layers we can directly compare the number of layers to the bubble formation activity.

The current reactor set up only allows for GC analysis with a closed system which limits the amount of bubbles seen macroscopically and in the GC. Ideally, we would engineer a continuous flow system that would have a flowing carrier gas that pushes the generated hydrogen out of the system and directly into the GC.

Finally we would like to scale up the set-up to produce more hydrogen. We were limited by the size of the vial holding the substrate and the focused beam spot size. With a larger set-up we could test a larger substrate. Also, finding a lens that has a larger focused spot size will allow activation of a larger area of the plamonics.

Finally, in the Vo-Dinh lab group they have not only synthesized nanospheres on a substrate for plasmonic applications, but also nanostars and nanospheres in solution.
We want to compare the plasmonic activity of the nanostars to our current set-up. We also want to make solutions with nanospheres and catalyst and deposit them simultaneously. We believe that with the plasmonic solutions we may be able to have more LSPR sites because of increased contact.
References


Biography

Titilayo Shodiya was born on July 25, 1987 in Washington DC and was raised in Upper Marlboro, Maryland. She attended The Pennsylvania State University where she obtained a Bachelor of Science degree in Materials Science and Engineering with a minor in Mathematics in May 2010. She obtained a Master of Science degree in Electrical and Computer Engineering in August of 2012 from Duke University. In 2013 Titilayo published a paper titled “Novel Nanoscale Au/α-Fe:O₃ Catalyst for the Preferential Oxidation of CO in Biofuel Reformate Gas” in the Journal of Catalysis. She also has a manuscript submitted to The Journal of Power Sources titled “Integration of Novel Au/α-Fe:O₃ Catalyst into a Proton Exchange Membrane (PEM) Fuel Cell”. Finally, Titilayo has a paper in preparation for submission to Nature Photonics titled “Utilization of Plasmonic technology for Localized High Temperature Hydrogen Production”. She received a Sigma Xi Grants-In-Aid award and was also awarded the Dean’s Award for Excellence in Mentoring in 2014. She is a member of Sigma Xi Scientific Research Honor Society, American Society of Mechanical Engineers (ASME), The Materials Research Society (MRS), and the American Association for the Advancement of Science (AAAS).