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Investigation of Graphene Oxide as a Cooperative Catalytic Support and Coating

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ABSTRACT

Investigation of Graphene Oxide as a Cooperative Catalytic Support and Coating

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Graphene and graphene oxide (GO), a highly oxidized form of graphene, are materials with incredibly interesting chemical and mechanical properties. These materials have high surface areas and electrical properties that can be tuned by reducing the amount of oxygenates on the surface. They have already demonstrated their importance in the future of nanotechnology, while their application as a catalyst is just beginning to emerge both as a catalytic support for metal nanoparticles as well as carbon based metal-free catalysts for a variety of chemical transformations.

As a metal-free catalyst, we explored using a 3D graphene oxide framework to create catalytic “pockets” in which we could engineer a micro- or nano- environment to influence catalytic performance. The design target for these ‘pockets’ was to create a partially nanoconfined or sterically hindered environment in which functional groups are placed near each other to work cooperatively to influence the catalytic active site or the reaction mechanism. We synthesized a 3D GO structure with tunable d-spacing that retained free amine functional groups in the nano-environments.

We were also interested in gaining an understanding of GO’s influence on metal nanoparticle catalysis. Gold nanoparticles (AuNPs) were chosen as the metal catalyst of study because they are active for a wide variety of reactions and the reaction rate and selectivity are often highly dependent on the size of the nanoparticle (NP) and the nature of the support. We hypothesized that the catalytic activity of AuNPs on a metal oxide support could be influenced by a graphene oxide over-coat by: 1) reducing metal leaching during reaction, 2) controlling the

monodispersity of the AuNPs, 3) and by modifying catalytic activity by electron donation/withdrawal to the active site or by altering the nanoparticle environment. In this work small (<5 nanometers) AuNPs were formed on an amine decorated nonporous silica support and submicron GO was electrostatically wrapped around the silica effectively coating the gold and silica. The catalytic activity for these gold nanoparticles versus non coated particles was tested for the catalytic reduction of p-nitrobenzaldehyde, the oxidation of cyclohexene, and oxidation of cyclooctene. After catalytic testing the GO was determined to be unsuccessful in reducing metal leaching, or preventing the agglomeration of AuNPs during synthesis or reaction, and no catalytic difference was observed in these reactions for catalysts with or without a GO coating.

While a GO coating didn't have an impact on catalysis for cyclohexene and cyclooctene oxidation reactions some interesting results by other members of the Kung group led to a more in-depth investigation on the role and nature of Au active site in these reactions. Dissolved gold atoms were found to be the catalytically active species for cyclooctene oxidation. We hypothesized that dissolved gold clusters could be the active species for other cycloalkane oxidation reactions and that the small gold species generated in one reaction system could be used to catalyze other reactions. Dissolved gold clusters from a cyclooctene oxidation reaction were active for cyclohexene oxidation. However dissolved gold clusters recovered from a cyclohexene oxidation reaction could not catalyze cyclooctene oxidation if all of the hydroperoxide species in the product was reduced. It is possible that this is a result of the hydroperoxide reductant also acting as a ligand for the dissolved gold and rendering the dissolved gold as inactive in the reaction network.

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1. Introduction

In the last quarter century the use of nanomaterials as catalysts and catalytic supports has grown enormously. Particularly interesting is the rapid growth in research on the use of structured carbon nanomaterials for catalysis. Graphene is a two-dimensional carbon material that can be considered the building block for other carbon materials such as fullerenes (0D), single- and multi-walled carbon nanotubes (1D), and graphite (3D) [1]. These unique materials can be utilized as a support for metals and other catalytic active phases, or as metal-free catalysts. Each carbon nanomaterial has its intriguing properties due to the unique structure, high specific surface area, chemical and electrochemical inertness, as well as the ability for a high degree of functionalization. For a majority of the past quarter century, single-walled carbon nanotubes and multi-walled carbon nanotubes have been studied extensively for their use in catalysis (as well as in electronic and energy devices, as polymer fillers, for drug delivery and other biological applications) [2]. Since the experimental observation of mechanically exfoliated single layer graphene sheets in 2004 [3], there has been an exponential growth in interest to explore its use, as well as that of its derivative the graphene oxide, in various scientific and engineering fields. Reduced graphene oxide (rGO) and graphene oxide (GO) based materials have many unique properties that make them intriguing candidates for catalyst supports. These materials have high surface areas, high adsorption capacities, can transfer π -electron density to supported catalytic metal particles, can have high electron mobility which can facilitate electron transfer during catalytic reactions, and also can be chemically transformed through the large number of oxygenate groups on the surfaces. Due to the high number of transformations that GO can undergo the potential to utilize its inherent catalytic nature and also as a catalytic support for other active sites is very attractive.

Within the scope of this dissertation, we have sought to understand the impact that GO can have on a catalytic environment. We set out to elucidate the possibility of creating metal-free nano “pockets” of cooperative catalytic activity between GO sheets by controlling the d-spacing between layers to understand if nano-confinement effects could be observed. We employed a vast array of characterization techniques to investigate GO modification and demonstrated the ability to bridge the basal planes of GO together while leaving select molecules available to participate in a cooperative manner. We also showed that we can alter the d-spacing of the GO matrix by using different chemistries to bridge the basal planes. We did not move forward with testing for nano-confinement effects or catalysis but used the knowledge gained by applying it as we studied creating a catalytic bilayer as opposed to a 3D structure. Our second approach to understanding the impact of GO on a catalytic active site is to wrap a single layer of GO around another support to create a catalytically active bilayer between the GO and nonporous support. Gold (Au) nanoparticles will be trapped within this bilayer with the GO serving as an overcoat. We hypothesized that the catalytic activity of Au nanoparticles can be modified by a GO overcoat by reducing metal leaching during reaction, controlling the monodispersity of the nanoparticles, and influencing catalytic properties through electron donation/withdrawal and cooperative effects. We synthesized small, less than 5 nanometers (nm), gold nanoparticles on an amine decorated nonporous silica support and submicron graphene oxide was then wrapped around the silica effectively capping/coating the gold and silica. The catalytic activity for these gold nanoparticles versus non coated particles was tested in the catalytic reduction of p-nitrobenzaldehyde, the oxidation of cyclohexene, and the oxidation of cyclooctene. We employed a vast array of characterization techniques to investigate the role that GO modification had on both the catalyst structure and the subsequent catalytic activity/selectivity.

2. Background

2.1. Graphene Oxide Chemistry & Chemical Transformations

2.1.1. Graphene oxide synthesis and theoretical structure

The most common methods to prepare GO, developed by Brodie [4], Staudenmeier [5], and Hummers [6], involve oxidation of graphite with strong oxidizing acids, and all three methods produce samples with similar degrees of oxidation. In recent years, a modified form of the original Hummers method has become popular, which has a shorter reaction time, does not produce hazardous ClO_2 gas, and the pre-oxidation step results in a more complete oxidation [7]. In a typical modified Hummers method, flake graphite powder is preoxidized by stirring it into a mixture of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and phosphorus pentoxide (P_2O_5) dissolved in concentrated sulfuric acid (H_2SO_4). Afterwards, the graphite is further oxidized with a mixture of H_2SO_4 and potassium permanganate (KMnO_4) while chilled to remove the heat from the exothermic reaction. The oxidized graphite is then exfoliated by sonication or mechanically in the presence of surface stabilizing solvents or polymers [8].

By virtue of its preparation procedure and the harsh oxidizing conditions, the resulting GO has a carbon framework that is highly disrupted by a variety of oxygenate functionalities. It does not have a periodic or uniquely defined structure or well-defined stoichiometry, and the location, distribution, and density of various oxygenate functionalities depend on the details of the preparation procedure and the starting graphite source. The structural model proposed by Lerf and Klinowski, shown in Figure 1, is currently the most widely accepted. It indicates that hydroxyl and epoxy groups decorate the basal plane of a GO sheet, whereas carboxylic acid and carbonyl groups decorate the edge [9]. The presence of these groups disrupts the extensive delocalization of the π electrons and renders GO electrically insulating. Their polarity and ability

to participate in hydrogen bonding make GO hydrophilic and easily dispersible in water or polar solvents. The carboxylic acid groups on the edge of the sheets are ionized in aqueous media that are not strongly acidic, and the electrostatic repulsion between these charged groups separates the GO sheets and stabilizes their suspension in aqueous and other polar solvents.

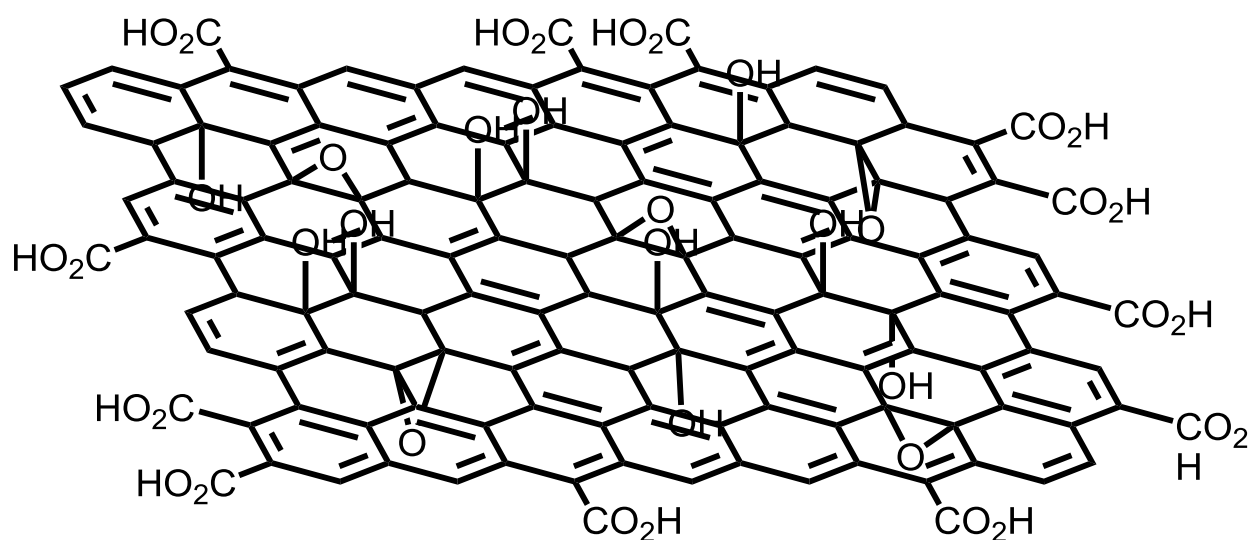


Figure 1. Proposed structure of graphene oxide. GO is thought to be composed of a disrupted honeycomb graphene lattice. The basal plane is decorated with hydroxyl and epoxy groups while the edge and defect sites are populated with carboxylic acid. Adapted from [9].

2.1.2. Reduction

Reduction of GO's oxygen functionalities can restore some of the very unique properties of graphene. After reduction, the material is typically referred to as reduced graphene oxide (rGO), implying that the reduction is not complete. Indeed, complete reduction has not yet been achieved. The common reduction methods to form rGO include chemical, thermal, or electrochemical means, and they all restore the conjugated π - π network to some extent.

GO can be reduced chemically by strong reducing agents, such as lithium aluminum hydride. However, less reactive chemicals, the most common one being hydrazine monohydrate, are preferred because they can avoid dangerous side reactions of lithium aluminum hydride and the reduction can be carried out in aqueous solvents [10]. Other effective chemical reductants include sodium borohydride, hydroquinone, and strong alkaline solutions. The drawback to chemical reduction is that heteroatom impurities can be introduced into the basal plane. It is not fully understood how the nitrogen would incorporate but one of the many possible mechanisms is believed to occur through the reaction of hydrazine with carbonyl groups. These impurities can have a significant effect on the resulting electronic properties. Reduction in a dilute hydrogen atmosphere at elevated temperatures, typically between 500 and 1000°C, is also effective. At the high temperatures, the process is most likely a combination of chemical and thermal reduction.

Thermal reduction of GO to rGO is achieved by heating a sample above 500°C in an inert atmosphere. Higher temperatures, as high as >1000°C, result in a more complete reduction due to thermal cracking of C–O and C–C bonds in processes such as decarboxylation, decarbonylation, dehydration, and dehydrogenation. Evolved gas is a byproduct, which includes carbon dioxide, carbon monoxide, water, and possibly hydrogen, and rapid evolution can generate a high pressure between the graphene oxide layers which results in exfoliation of the sample. Although this exfoliation process tends to yield a higher surface area sample than those obtained by chemical reduction, it also leads to a large (~30%) mass loss and formation of a significant density of defects [11]. These large vacancies can affect the electronic and chemical properties of the rGO. The generation of defects can be moderated by a sequential reduction of chemical followed by thermal reduction.

Electrochemical reduction is the third common method. In this method, a GO sample is placed on a substrate that serves as an electrode, which is submerged in an electrolyte. Reduction is achieved by passing a current between the substrate and a counter electrode [12]. The major disadvantage of this method is that it is difficult to scale up for production of large amounts of rGO samples.

Selective conversion of specific oxygenate functional groups is of interest in material design, and techniques such as using hydrazine vapor as the reductant have been developed that removes different groups in a stepwise manner [13]. Such stepwise reduction, coupled with careful tuning of experimental conditions and combination of methods allows for better control of the composition of the final product and the degree of reduction. However, complete restoration of the extensive π - π network of pristine graphene has not been achieved to date, and the various reduction methods result in rGO samples that are still very heterogeneous in nature with regions of high oxygenate concentrations or high graphitic character [14].

2.1.3. Non-covalently functionalized graphene oxide

Due to the heterogeneous nature of GO's structure there are a wide variety of non-covalent interactions that can be utilized to alter its structure and/or properties. Interactions between the carbon double bond backbone and other moieties that have π electron orbitals can π - π stack onto the graphitic regions of GO. This π - π interaction can also be classified as an interaction in a hydrophobic region. Layer-by-layer assembly of graphene or GO sheets can be accomplished by taking advantage of this type of interaction. In this manner, incorporation of polycyclic aromatic hydrocarbons can easily and robustly attach to the basal plane and can then act as anchors for metal complexes [15].

Taking advantage of the hydrogen bonding between the various oxygenate functionalities of GO, between the GO and other parts of a composite such as a polymer, and between reactants and the surface of the GO catalyst are non-covalent interactions that all can be exploited for catalyst synthesis. See Section 2.1.6 on how this interaction can be used to form 3-D networks of GOs.

Electrostatic forces, another non-covalent interaction, are the driving force behind some of GO's interesting properties. The strong charge-charge repulsion that occurs between the carboxylic acid groups on adjacent sheets keeps the sheets well dispersed in water and other solvents. The negative charge of the sheets can be exploited through interaction with a positively charged surface. Layer-by-layer stacking of graphene oxide and a positively charged material can be achieved through this method.

2.1.4. Covalently functionalized graphene oxide

A wide variety of methods have been developed to modify a GO surface through covalent bond transformations to result in a more versatile material that can then be utilized for various applications. Methods that had been explored to functionalize carbon nanotubes have been found to also be effective on graphene and graphene oxide. For GO, since there is reliable information on the nature of the oxygenate functional groups, well-established chemical reactions that have been developed to transform these oxygenates into other functionalities have been applied. Of particular interest is to selectively transform one type of oxygenate group and not another (e.g. transforming only the epoxy groups on the basal plane). Unfortunately, since techniques are not yet available to definitively demonstrate successful selective transformations, it is not possible to establish successful selective transformation. Nonetheless, these types of transformations are

widely employed, and the most widely utilized reactions, the transformation of carboxylic acid and epoxy group, will be discussed in Chapter 3.

Similar to other organic synthesis methods, transformation of surface carboxylic acid groups typically requires their activation. Once activated, the carbon of the acid becomes more susceptible to nucleophilic attack to form covalent bonds (couple) with nucleophiles. Common activation or coupling reagents include thionyl chloride (SOCl_2) [16–18], 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) or N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI) [19–22], and N,N'-dicyclohexylcarbodiimide (DCC) [19]. Common nucleophiles include those that possess an amine or hydroxyl groups are used to form amide or ester bonds with the GO and tether targeted entities onto the GO surface. Typically, modification of the GO surface by reaction with the epoxy groups is believed to occur through a ring opening mechanism [23–25]. However, these reactions might not be highly selective. For example, aminolysis of epoxide groups may occur simultaneously with the reaction of amine with carboxylic acid.

In addition to using activating or coupling agents, the carboxylic acid and epoxy groups can also be activated using solvothermal methods [26]. In some procedures, a free radical mechanism might be involved [27]. Other methods to functionalize a GO surface include condensation of ethoxy or methoxy groups with surface hydroxyl groups [28], in a manner similar to that used for grafting molecules onto traditional heterogeneous supports such as SiO_2 and Al_2O_3 . Although less common, covalent functionalization of the graphitic region of a rGO with diazonium salts, which proceeds through a radical mechanism, is also utilized in catalyst synthesis [29, 30].

2.1.5. Heteroatom-doped graphene

Heteroatom-doped graphene catalysts are generally synthesized using two methods, in-situ growth or post-treatment of graphene or GO. Thus far, nitrogen-doping (N-doping) is the most studied, and the subject has been reviewed in depth recently [31, 32]. The in-situ growth method involves incorporation of heteroatoms during the growth process by mixing in an N-containing reagent, such as by chemical vapor deposition (CVD). The advantage of the in-situ method is that it not only allows the graphene material to retain many of the intrinsic physical and chemical properties of pristine graphene but also provide new catalytic properties. CVD can be used to prepare N-doped graphene by flowing a gaseous mixture of NH_3 , CH_4 , and H_2 in an Ar carrier over a substrate. The nitrogen can be incorporated into the graphene aromatic structure in a variety of forms such as pyridine and pyrrolic nitrogen. Other in-situ methods include solvothermal synthesis processes. For example, lithium nitride is reacted with tetrachloromethane during its pyrolysis in a stainless steel autoclave.

The post-treatment synthesis method incorporates heteroatoms by treating graphene or GO materials with a variety of compounds through chemical or physical means such as by flowing NH_3 over GO at high temperatures or mixing GO with compounds that serve as nitrogen sources including melamine, dicyanodiamide, and pyrrole, followed by a post treatment method such as chemical or thermal reduction. Nitrogen atoms could be incorporated in various forms depending on the experimental details.

2.1.6. Three dimensional graphene frameworks

One of the challenges encountered when utilizing graphene materials for catalytic applications is regraphitization and reduction in surface area when the catalyst is dried to a powder. The graphene layers restack because of strong π - π interaction, and this stacking leads to

reduction in accessible areas and trapping or enclosure of active sites that makes them inaccessible. A number of methods have been explored to reduce this restacking interaction by creating 3D structures, such as graphene-organic-frameworks (GOFs), graphene aerogels, and graphene hydrogels, and a rather comprehensive look at these methods can be found in recent review articles by Li et al [33] and Bai et al [34]. The most common methods utilized to generate such structures for catalysis involve solvothermal self-assembly. These methods seek to balance the hydrophilic–hydrophobic interactions between the attractive interplanar van der Waals forces and the repulsive electrostatic interaction from charged carboxylic acid groups by tuning them with a change in the pH of the solution, by concentration of the suspension, or by utilizing covalent bond forming cross-linking molecules. These self-assembly methods allow the GO sheets to retain a larger d-spacing than a conventionally filtered and dried sample in which these forces are not optimized. This increased d-spacing also results in a larger surface area for the final material and easier access to catalytically active sites. Other techniques to produce 3-D graphene samples have been explored, including template-guided approaches and self-assembly at an interface.

2.2. Graphene Oxide Catalysis

2.2.1. Catalytically important interactions between GO/rGO and supported NPs

The catalytic activity and selectivity of supported metal nanoparticles is highly dependent on the nature of that support. A good support should have a large surface area, provide nanoparticle stabilization through strong metal-support interactions which also helps to prevent metal agglomeration, and produce a cooperative effect by enhancing chemical pathways of interest. Graphene and graphene oxide based materials have the potential to meet all of these targets and extensive research has already been conducted, and is ongoing, working to

investigate their use as catalytic supports for metal nanoparticles[35]. Nanoparticles on graphene based supports can be utilized as catalysts for oxidation, reduction, coupling reactions, and many more reactions.

Graphene oxide, with its oxygen rich basal plane, provides an ample amount of grafting sites for adsorption of metal ions. The oxygen groups act as an anchoring point to stabilize the metal nanoparticles as they are reduced; this also helps to keep the NP size small. In addition to the absorption of metal NPs GO can also be used to adsorb metal oxide NPs. When metal oxide NPs are adsorbed onto a GO support the oxide can share oxygen groups with the GO support forming a strong attachment between the GO and oxide [36]. The GO support can also be reduced to rGO either simultaneously during the NP reduction step or post NP formation to regain some of the properties of graphene, such as electron mobility and conductivity. If rGO is utilized the extended π orbitals in the graphitic regions can also interact strongly with both NPs and reaction substrates. The interactions discussed here that are of catalytic interest between the GO/rGO support and NPs are depicted in **Error! Not a valid bookmark self-reference..**

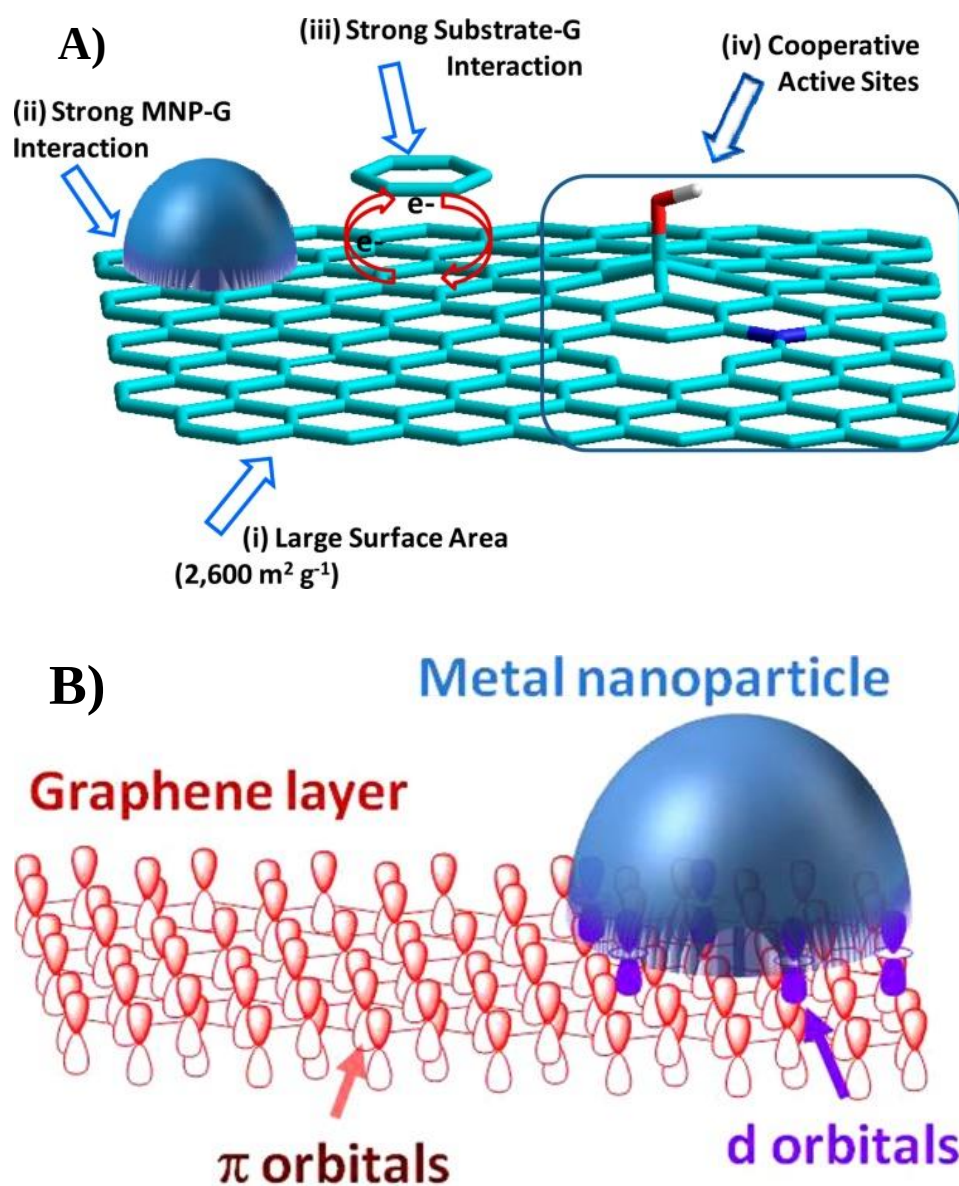


Figure 2. Visual representation of the different interactions that could enhance catalysis for nanoparticles when using a graphene based support. A) A large surface area, a strong nanoparticle/support interaction, strong substrate/support interactions and cooperative interactions with residual oxygen functionalities or defect sites could all enhance the catalysis of metal nanoparticles on graphene based supports. B) Interaction of the extended network of π orbitals with deposited NPs, these π orbitals can facilitate electron donation or withdrawal which can influence catalysis. Reprinted with permission from ref [35].

2.2.2. Inherent catalytic activity of GO

It is widely known that carbon and carbon-based material such as activated carbon and graphitic carbon are useful catalytic materials, and that functionalized carbons are often more active and/or selective catalysts than their unfunctionalized counterparts. The properties of these materials and their commercial applications have been reviewed [37–39]. In general, however, the heterogeneity of these functionalized carbons makes it difficult to characterize them at the atomic level, or to determine the detailed reaction mechanism or the nature of the specific active site. Functionalized carbon are active for a variety of reactions including selective oxidative dehydrogenation of hydrocarbons [40, 41], oxidation of aromatic compounds [42], and decarboxylation of fatty acids [43]. Knowing that activated carbons are catalytically interesting researchers began to focus on graphene and GO-based materials for catalysts.

As synthesized graphite oxide and the exfoliated version, graphene oxide, is a highly disrupted graphene network. The ease of preparation, low-cost synthesis, ease of recovery by filtration, and high surface-to-volume ratio make GO a very attractive material for a wide variety of catalytic applications, as covered in a review by Dreyer and Bielawski [37]. As mentioned previously the basal plane and edges of GO are decorated with various oxygen functional groups, including epoxy, carbonyl, hydroxyl, and carboxylic acids. These groups impart GO with inherent acidity, and oxidative, chemical and catalytic activity. Indeed GO has been shown to be catalytically active for a variety of reactions. In 2010, Bielawski and coworkers demonstrated that GO effects the oxidation of a wide variety of alcohols to ketones and aldehydes, alkenes to diketones, and alkynes to the hydrates in air between 75-150 °C [44]. Many of these reactions proceed with high selectivities. For example, the yield in the oxidation of cis-1,2-diphenylethane-1,2-diol to 1,2-diphenylethane-1,2-dione was 96%, and >98% for

diphenylmethanol to benzophenone. Interestingly, whereas GO oxidized 1,2-diphenylethene to 1,2-diphenylethane-1,2-dione with 56% conversion, it was either inactive or could only catalyze isomerization of other alkene systems. Thus, it appears that the activity towards cis-1,2-diphenylethene is due to a combination of aromatic substituents and cis geometry. In order to ascertain that GO functions as a catalyst, the authors performed the experiments in ambient and inert nitrogen environments and observed much less oxidation without the presence of oxygen. In addition, the GO could be separated from the reaction mixture and reused for multiple cycles. However, the activity was low, and carbon to substrate weight ratios as high as 200% were used to obtain reasonable yields in 24 h. Even taking into consideration the high loading and low activity, a GO catalyst has a higher turnover frequency per dollar when compared to other oxidation catalysts thus making it a very attractive alternative.

GO was found to catalyze other reactions, including the oxidation of sulfides to sulfoxides and the coupling of thiols to disulfides [45], dehydrogenation of various hydrocarbons and oxidation of methylbenzenes to their respective aldehydes, diarylmethanes to their respective ketones, and other hydrocarbons with sp³-hybridized C–H bonds [46]. It has also shown high activities for the Claisen–Schmidt coupling reactions [47], Friedel–Crafts reactions [48], Aza-Michael additions [49], and ring opening polymerization [50]. It is a solid acid catalyst for the preparation of dipyrromethane and calix-4-pyrroles [51], an auto-tandem oxidation–hydration–aldol coupling catalyst performing multiple reactions in a single reaction chamber [47], a photocatalyst for H₂ generation from water (but the carbon might be oxidized at the same time) [52], and a catalyst for the aerobic oxidative coupling of amines to imines [53]. All of these reactions were carried out under mild conditions that require a high weight loading of GO relative to the substrate for reasonable yields. Interestingly, in the study of the oxidative coupling

of amines, Loh and coworkers developed a method to reduce the catalyst loading to as low as 5% and still achieved yields up to 98% by subjecting the GO to a sequential base and acid treatment, which created defects on the GO basal planes and enhanced the catalytic activity [30]. Table 1 provides a summary of the types of reactions that can be catalyzed by graphene oxide. The advantage of using GO as a catalyst in most of these reactions is that desirable reaction conversions can be achieved without the use of a metal catalyst. GO can also enhance the selectivity of reaction systems; in the preparation of dipyrromethane and calix-4-pyrroles, a GO catalyst had 97% selectivity to dipyrromethane whereas an Amberlyst-15 catalyst yielded no dipyrromethane and a selectivity of 83% calix-4-pyrrole and 14% other products [51].

In addition to typical organic reactions, GO exhibits other interesting catalytic properties. When mixed with polymer monomers, GO can act as a dehydrating polymerization catalyst [54–56]. In these polymerization reaction systems, the GO was partially reduced, thus serving as part oxidant and part catalyst. Usually, it is not separated from the polymer matrix after the reaction, instead serving to enhance the strength and conductivity of the polymer composite. GO porous foams that were prepared by unidirectional freeze-drying are active for the oxidation of SO_2 gas to SO_3 [57]. In this reaction, the GO also acts as a catalyst and an oxidant, and is partially reduced after coming into contact with the SO_2 gas. The catalyst would have to be reoxidized to regain full activity. The fact that the reaction proceeds at room temperature and that GO is a metal free system makes it a very attractive alternative to other traditional systems for the treatment of SO_2 gas.

The oxygenated groups inherent in GO can act as catalysts also. In fact, there is the potential that the activity can be tuned by changing the density of a specific group. Depending on pH value, temperature, and reagent concentration in the system, GO containing a higher

percentage of carboxylic acid groups was found to have a peroxidase-like activity, capable of catalyzing the reaction of peroxidase substrate 3,3',5,5'-tetramethylbenzidine in the presence of H_2O_2 for glucose detection at a rate comparable or superior to a natural horseradish peroxidase [58].

2.2.3. Metal Free Functionalized GO catalysts

Similar to traditional oxide supports, such as SiO_2 and Al_2O_3 , GO can serve as a platform for catalytically active species. It also has the potential to exert influence on the catalytic activity through effects such as cooperativity between GO and functional group(s), thus offering another system to investigate for tuning the selectivity and activity of reactions [59, 60]. In metal-free catalytic systems, GO acts mainly as a tethering point for catalytically active moieties.

A graphene-based solid acid catalyst can be prepared by anchoring sulfonic acid-containing aryl radicals to a rGO surface [29], which was active for the hydrolysis of ethyl acetate (64.0% conversion). It can also be prepared by hydrothermally treating rGO with fuming sulfuric acid [61]. The catalyst was active for the esterification of acetic acid with cyclohexanol (79.5% conversion), the esterification of acetic acid with 1-butanol (89.1% conversion), the Peckmann reaction of resorcinol with ethyl acetoacetate (82.1% conversion), and the hydration of propylene oxide (66.8% conversion). In both studies, the graphene-based acid catalyst was found to have comparable or superior activity to the unsupported catalyst of concentrated sulfuric acid (~80% conversion for the hydrolysis of ethyl acetate) and other traditional solid acid catalysts, such as Amberlyst 15 (58.9% conversion for the esterification of acetic acid with cyclohexanol). Sulfonic acid tethered to amorphous carbon also exhibits excellent catalytic activity, and based on characterization of the solid and reaction rate analysis, the acid groups are

presumed to be in regions within the carbon structure where functionalized graphene clusters reside [62–64].

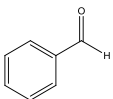
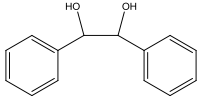
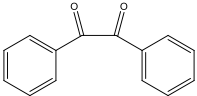
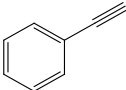
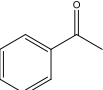
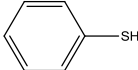
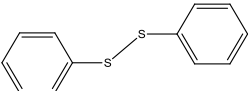
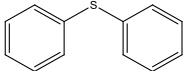
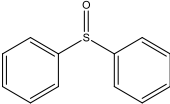
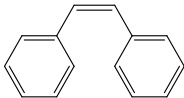
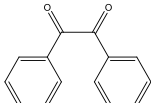
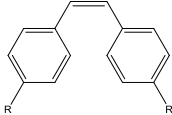
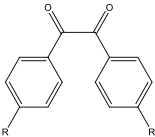
Graphene-based basic catalysts have also been explored as solid base catalysts. Functionalizing the support with basic amino groups has been shown to render activity for the hydrolysis of ethyl acetate with an activity slightly higher than that observed with a sulfonated graphene catalyst [65]. Table 1 summarizes various reactions catalyzed by functionalized GO.

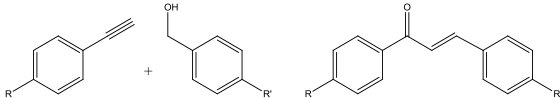
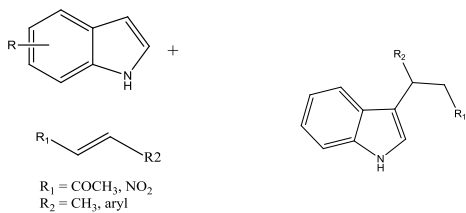
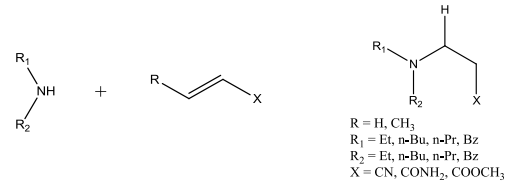
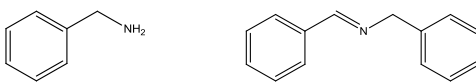
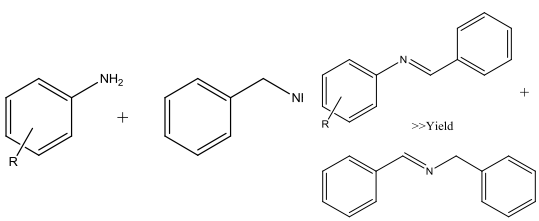
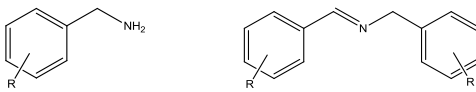
Whereas there hasn't yet been an example showing that GO functions as an active participant in a cooperative effect, there are examples of using GO to support two different catalytic moieties that can then perform as a cooperative catalyst. One example is GO functionalized with a primary (3-aminopropyltriethoxysilane) and tertiary amine (3-(diethylamino)propyltrimethoxysilane) for the synthesis of trans- β -nitrostyrene. It was hypothesized that the tertiary amine activates the nucleophile and the primary amine activates the carbonyl compound by forming an imine intermediate [28]. Although this example demonstrates one potential role for GO, it is possible that GO could have a broader range of effects by tuning its hydrophobicity, acidity, electrical conductivity, and/or 3-D structure.

Nitrogen-doped (and heteroatom-doped) graphene materials are excellent catalysts for the oxygen reduction reaction (ORR) for electrocatalysis in fuel cell and battery applications [31, 66–70]. Nitrogen incorporation into the graphene structure changes the spin density and charge distribution of the surrounding carbon atoms and widens the band gap. There are three forms of N incorporated into the carbon lattice: quaternary (graphitic) N, pyridinic N, and pyrrolic N. In addition, amino nitrogen groups can also decorate the edges and defects. The distribution of the various forms depends on the synthesis method, which could change the catalytic properties of the material. It is still under debate how to correctly characterize the different forms of nitrogen

[32], which makes it difficult to correlate catalytic properties to a specific nitrogen form. Despite this, the impact of the different forms of nitrogen on the ORR has been observed, and it is generally thought that the enhanced activity can be correlated with the amount of pyridinic and/or quaternary nitrogen [67, 71]. Use of N-doped graphene has also been explored for other catalytic reactions such as the oxidation of benzene to phenol [72] and of a range of benzylic alcohols [73]. Synthesized by flowing NH_3 over GO, quaternary nitrogen atoms were attributed to be responsible for the increased catalytic activity in the oxidation of benzylic alcohols to the corresponding aldehydes. Increasing the temperature at which nitrogen was doped into the GO altered the amount and type of nitrogen incorporation, and flowing NH_3 at 900°C over GO resulted in a catalyst with the highest amount of quaternary nitrogen incorporation.

Table 1. Reactions catalyzed by graphene oxide

Starting Material	Product	Catalyst (wt. % GO) ^a	Conditions	Yield (%)	Ref.
		200	100°C 24 h	92	[74]
		200	100°C 24 h	96	[74]
		200	100°C 24 h	>98	[74]
		60	100°C 10 min	100	[45]
		300	100°C 24 h	86	[45]
		400	100°C 24 h	68	[46]
		400	100°C 24 h	R electron withdrawing <25 R electron donating ≥48	[46]

	na	80°C-100°C 14-24 h	R or R': electron withdrawing <30 R or R':electron donating >50	[47]
	20			[48]
	na	Room Temp <30 min	>85	[49]
	50	5 atm O ₂ 100°C	98	[53]
	50	5 atm O ₂ 100°C	>97 conv.	[53]
	5 ^b	90°C 12 h	>93	[30]

2.3. Gold Nanoparticle Catalysis

Gold was first uncovered as a remarkable catalyst when Haruta [75] and Hutchings [76] synthesized small gold particles for the low temperature oxidation of CO and the hydrochlorination of ethylene respectively. Since those remarkable discoveries research has uncovered that gold nanoparticles are active for a wide variety of reactions, including C-C bond formation, selective hydrogenation, selective oxidation, the water gas shift reaction, and carbonylation. There are a number of great review papers that cover the wide ranging application of gold nanoparticles as catalysts as well as the synthesis methods [77–81].

One of the critical parameters that can impact catalytic activity and selectivity is the size of the gold nanoparticles. Depending on the reaction and desired selectivity catalysts are synthesized with a narrow and particular NP diameter to optimize conversion and/or selectivity. In some reactions decreasing the AuNP size will drastically improve reaction outcome [82] but in other reactions such as the oxidation of styrene [83] the smaller diameter (<4nm) gold nanoparticles are inactive for the reaction and instead there is a range of larger sizes that will do the catalysis. Because of these variations it is typically best to compare catalytic activity of different sized NPs within the same reaction system to truly understand the catalytic impact of varying the size.

Choosing a support for the AuNPs is also a very critical parameter that can have a drastic impact on catalytic activity and selectivity. Changing the support can affect catalysis in two main ways: 1) holding the synthesis method the same but changing the support can affect the final particle size of the Au so it's important if possible to explore different particle sizes on the same support to try to deconstruct those two variables 2) there can be support/gold interaction depending on the surface chemistry of your support that could increase or decrease the binding

energy or provide a more favorable cooperative environment for the catalytic reaction of interest.

Figure 3 shows the impact that changing the support can have on the amount of carbon monoxide taken up by the catalyst [84]. The use of different metal oxide supports can drastically alter the reactivity of a gold catalyst; ceria can have very strong metal support interactions due to active lattice oxygen atoms, alumina is pretty inert but has surface hydroxyl groups that can act as an acid or a base, and silica is also pretty inert but its surface hydroxyl groups are acidic.

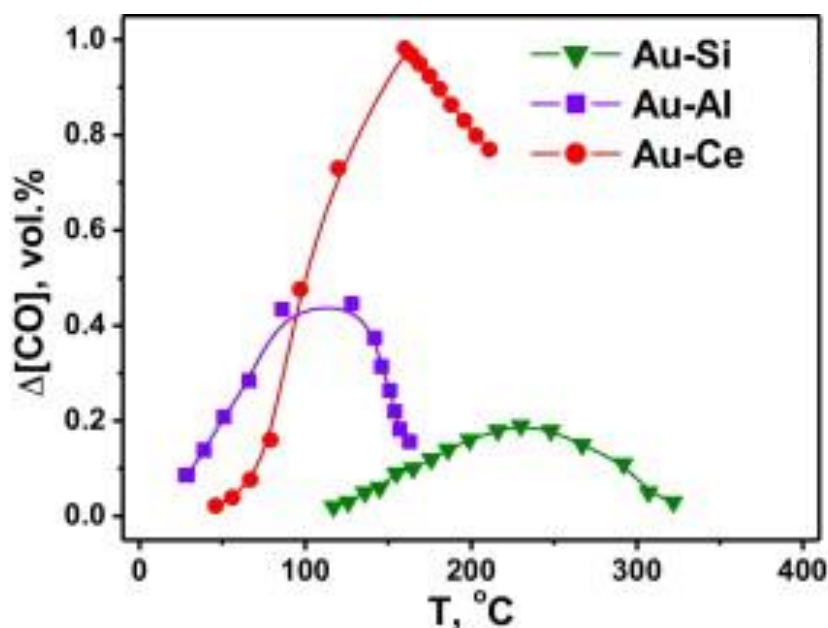


Figure 3. Comparing the impact of the support on the uptake of carbon monoxide on various supported gold catalysts. This variation in uptake can greatly impact catalytic reactivity. Reprinted with permission from ref [84].

2.3.1. Catalytic activity of gold on GO and other graphene supports

Traditionally most catalytic studies exploring Au catalysis use Au NPs that are supported on inorganic metal oxides. However in the last decade there has been increasing interest in exploring carbon materials as supports because of their high chemical stability and the interesting properties of graphene and carbon nanotube based materials. The interesting

properties that graphene based materials have for metal nanoparticle supports are discussed in section 2.2.1. Often when pristine graphene is used as a support for metal nanoparticles a composite material is formulated with other materials (polymers, oxides, other carbon materials) because graphene lacks anchoring/stabilization points that can help keep nanoparticles small and disperse. Computational/theoretical investigation into how Au NPs would form or interact on a graphene support indicated that Au has a much weaker interaction with graphene than other transition metals traditionally used as supports. This weak interaction was predicted because Au has full d orbitals and therefore can only interact with graphene supports by a weak physisorption[85]. Using graphene materials that are functionalized such as GO, hetero-doped GO, or chemically modified GO can provide these stabilization/adsorption sites that are lacking in pristine graphene. Avoiding the steric blocking of the gold NP surface that are a result of the addition of the composite material in these graphene gold composites is an additional advantage to using functionalized GO as a support. [86]

Gold nanoparticles supported on graphene and graphene oxide supports shown activity for a wide variety of reactions including: the oxidation of benzyl alcohol and its derivatives[87–89], the hydrogenation of phenylacetylene to styrene[90], the reduction of 4-nitrophenol[91], the oxidation of ethyl benzene[92], the oxidative esterification of aldehydes[92], and the hydroamination of phenylacetylene with aniline [93].

2.3.2. Reduction of 4-Nitrophenol

The reduction of 4-nitrophenol (4-NP) using sodium borohydride (NaBH_4) is a model catalytic reaction for studying variations in catalyst structure. This reduction yields a single product, 4-aminophenol (4-AP), at mild temperatures, in water, and does not proceed in the absence of a catalyst. Additionally the reduction of nitroaromatic compounds is of significant

interest because these compounds are toxic in nature whereas the reduced products are less environmentally concerning compounds that usually find applications in other industrial processes. [94]

The reduction of 4-NP is catalyzed by introducing an excess of the reductant NaBH_4 along with a metal catalyst that can extract the hydrogen from the reductant (forming a Metal-H species). Several metal nanoparticles are active for this reaction including gold, silver, palladium, platinum, and nickel nanoparticles. Gold nanoparticles have been extensively investigated for this reaction because they are active under very mild conditions, and the catalytic activity can be directly related to the particle shape and/or size. Additionally this reaction can be easily monitored in situ with UV-vis spectroscopy by monitoring the decrease in the 4-NP absorption peak at 400 nm. However, hydrogen gas evolution during the reaction can impeded some UV-vis absorbance measurements which can cause variations in the baseline/background wavelengths under some reaction conditions.

The active site for 4-NP reduction with a gold catalyst is generally understood to be at the surface of the gold nanoparticle. Kinetic modeling of this reaction is described with a Langmuir-Hinshelwood model, which reveals that the rate limiting step is the reaction on the surface of the nanoparticle. The diffusion and adsorption of the reactants to and from the surface of the nanoparticle is very fast and can be modeled as an equilibrium process described by a Langmuir isotherm.[95] The reaction rate constant, as described by the Langmuir-Hinshelwood model, is proportionate to the Au NP surface and a thus Au catalysts in the nanosize range are more reactive because the surface to volume ratio increases.

Gold nanoparticles can be supported on a wide range of oxides, carbon, and polymer supports for this reduction reaction. Gold NPs have been synthesized on a wide variety of metal

oxide supports including SiO_2 , Al_2O_3 , CeO_2 , TiO_2 , $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ and mixtures of these oxides. On these oxide supports the Au nanoparticles are generally easily deposited and dispersed which helps prevent agglomeration, therefore the catalytic activity remains high and the catalyst is easily recovered for reuse. An additional advantage of metal oxide supports, especially SiO_2 , is the ability to finely tune the pore size distribution of the support which can influence the resulting size distribution of the Au catalyst. Carbon supports for Au NPs are also interesting because carbon can be stable in both acidic and basic environments and is generally very chemically and thermally stable but can also be burned away to recover the gold. In many other Au catalyzed reactions the support can play a large cooperative role to influence catalysis (see Section 2.3). However, for the reduction of 4-NP it seems that the main role of the support is to enable the synthesis of small nanosize particles that are stable throughout the reaction and for reuse.

2.3.3. Cycloalkene Oxidation Reactions with Gold Catalysts

The oxidation of alkenes is an important industrial process for a variety of fine chemicals, intermediate chemicals, and end products. Typically, these oxidation reactions required stoichiometric amounts of a reactive oxygen species, such as the permanganate or dichromate ions, and these oxygen species can produce environmentally hazardous wastes. This can drastically increase the processing cost because of the high cost of oxidant and the increased safe handling measures that are required. As a result there has been a lot of interest in discovering a more environmentally “green” and cost effective synthesis: using molecular oxygen in solvent free conditions. Industrially only ethylene and higher olefins that do not contain allylic hydrogen atoms are oxidized using molecular oxygen, the ideal “green” oxidant. Other high carbon alkenes generally are oxidized on the industrial scale using hydrogen peroxide or alkylperoxides. The

selective addition of oxygen to an unactivated alkene without the use of these harsh oxidizers is a major challenge in oxidation chemistry.

The oxidation of cycloalkenes proves to be more difficult than linear alkenes primarily due to steric hindrance and the oxidation of these compounds can vary drastically depending on the size of the ring, the reaction temperature, and nature of the catalyst [96]. As the number of carbon atoms in the ring increases the reactivity was found to decrease however selectivity for these larger compounds to the epoxide was increased due to lessened ring strain. The mechanism for oxidation of cycloalkenes is generally thought to be a radical substitution mechanism. Gold NPs have superior activity as catalysts for these reactions. Initiation of the radical mechanism was generally thought to need a catalytic amount of a radical initiator such as tert-butyl hydroperoxide (TBHP) in addition to the gold catalyst in order for a surface bound Au-OH* radical to be formed and for the reaction to proceed. Nano-gold catalysts have been shown to be effective catalysts for the aerobic oxidation of cycloalkenes using molecular oxygen in solvent free conditions. The choice of support for the gold catalyst can impact both selectivity and activity, for example in the oxidation of cyclooctene a graphite support shows the highest activity and selectivity to epoxide and a silica support has about equal reactivity to alumina but the selectivity to epoxide is higher with silica. [96] In the oxidation of cyclohexene, using a tungsten trioxide support gave a higher selectivity to cyclohexene oxide whereas a metal-organic-framework (MIL-101) resulted in a higher selectivity to the ketone product.[97]

Recently, the role of the radical initiator in cycloalkene oxidation reactions was investigated more thoroughly and it was determined that the radical initiator main use was to overcome the effects of the stabilizer that is added to cycloalkenes to prevent peroxide formation from autoxidation. Often the cycloalkene as purchased contains a small amount of stabilizer that

might not even be listed on the label. After sourcing cycloalkene specifically without the stabilizer or by removing the stabilizer from the sourced material, it was determined that without the stabilizer the oxidation preceded identically whether or not the initiator, TBHP, was added for C5 through C8 cycloalkene oxidations. In reactions with stabilizer and without TBHP there was no conversion. These investigations were performed using an Au/graphite catalyst. [98]. There was no further investigation into the active site or reaction mechanism and as was generally agreed upon in literature the active site for initiating these radical autoxidation reactions is thought to be on the surface of the AuNP. The impact of NP size was also investigated and researchers found that for cyclohexene oxidation AuNPs less than 2nm in size were not active but that over the course of the reaction the nanoparticles could agglomerate into larger particles and once the size was greater than 2 nm the reaction proceeded. When catalysts with less than 2 nm Au NPs were used an induction period was observed and this time period was attributed to the time it took for particles to grow in diameter. [99]

However recently published results within the Kung group [100] have revealed that very small dissolved gold clusters are actually the active catalytic species that generates radicals for cis-cyclooctene oxidation. At the beginning of a solvent-, initiator-, and stabilizer- free cyclooctene oxidation reaction a very small amount of cyclooctene is oxidized and these oxygenated products, the diol product was found to be most effective in this role, serve as ligands to pull, solubilized, and stabilize Au atom clusters into solution from the solid Au or Au ion catalyst. These Au atom clusters then can activate molecular O₂ and initiate autoxidation. An induction period was observed during these reactions and could be attributed to the time it takes for Au to be solubilized from the surface of the solid catalyst. Additionally the induction period was eliminated when instead of using a supported gold catalyst the filtrate from a completed

reaction cycle with no solid catalyst was utilized as the catalyst. This indicates that the active species for reaction was not at the surface of the nanoparticle but was instead solubilized Au clusters. It is likely that other cycloalkane and alkene reactions can also be catalyzed in a similar manner; this research showed that dissolved platinum clusters could also perform cyclooctene oxidation.

3. Controlling the Distance between Acid/Base pairs with a GO 3D Structure

3.1. Introduction and synthesis approach

The goal of creating a metal free cooperative catalyst using GO as a support began with the investigation into synthesis methods that could generate a 3D GO based framework in which catalytic ‘pockets’ could be engineered between the stacked basal plane sheets. These ‘pockets’ would be designed to create a partially nanoconfined or sterically hindered environment in which functional groups (acid/base pairs) are placed near each other to work cooperatively and influence the reaction mechanism pathways (see Figure 4 for illustration of target structure). The functional groups chosen to test the cooperative catalytic nature of the GO structure were carboxylic acid and amine functional groups. In order to overcome the problems of regraphitization and reduced surface area an additional goal was to chemically modify the basal planes of GO with more rigid molecules (i.e. phenyl groups) to bridge two GO sheets together and thus providing a more rigid three dimensional structure.

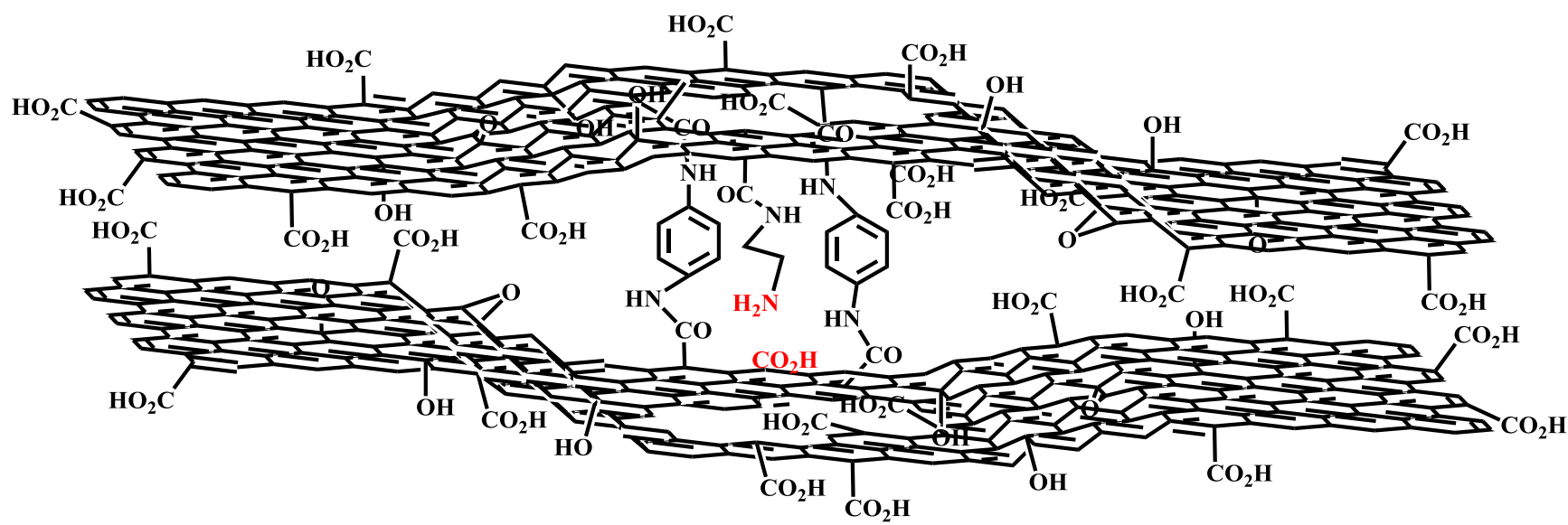


Figure 4. Theoretical structure of 3D cooperative catalytic "pocket" between two bridged GO basal planes.

The overall synthetic approach involved 3 steps: 1) synthesize GO structures with a high density of planar carboxylic acid groups; 2) utilize traditional small molecule chemical transformations to link the basal planes of two GO sheets together and 3) ensure that catalytically relevant functional groups are found near each other within the nano-”pocket”. The purpose of having GO sheets with a high density of -COOH groups is two-fold: to increase the number of bridging groups between the GO sheets and also leaving residual acid groups in the catalytic pocket to investigate cooperative interactions. 4-aminobenzylamine (4-ABA) was chosen as the molecule of study for bridging the GO sheets together. 4-ABA is a diamine compound that also had a benzyl ring, which could provide some rigidity to the final 3D GO structure. Catalytically relevant amine groups were introduced by incorporating N-Boc-p-phenylenediamine. One amine of this group is free to attach to the GO sheet while the other is protected with a tert-butyloxycarbonyl protecting (Boc) group. After the 3D structure is formed the Boc group can then be removed either by chemical or thermal methods leaving behind the now unprotected amine which can then participate in cooperative catalysis.

3.2. Carboxylic acid functionalized graphene oxide

There are a number of ways documented in literature to increase the carboxylic acid content of GO, including: transformation of the alcohol groups[20] and introducing more defect sites via physical ball milling [101] or chemical methods[102]. A synthesis route in which surface alcohols are converted into carboxylic acid groups [103] and a second method in which more defect sites are introduced that was developed for battery research within the Kung research group[102] were explored for increasing the density of carboxylic acid groups on GO.

Converting alcohol moieties into carboxylic acid groups was performed by adding a 12 g of sodium hydroxide (NaOH) and 10 g of chloroacetic acid (ClCH_2COOH) to 50 milliliter (mL)

of a 2 milligram/mL GO in water solution. The mixture was stirred for 30 min to ensure the hydroxide and acid were dissolved and then bath sonicated for 2 h. The energy from the sonication transforms some of the alcohol groups to carboxylic acid groups via conjugation of acetic acid moieties. The resulting GO suspension was centrifuged and washed a minimum of 6 times to remove unreacted chloroacetic acid and NaOH. The -COOH decorated GO sample produced in this manner will be referred to as GO-COOH.

The second method that was explored for the synthesis of -COOH decorated GO was initially developed in the Kung lab to increase the number of surface defects in the GO sheet to allow for quicker transport of lithium ions in batteries. Introducing basal plane defects also resulted in additional carboxylic acid groups because they decorate the edges of the defects. Graphene oxide that was synthesized with the modified Hummers method was diluted with distilled, de-ionized (DDI) water in 20 mL vials to ~0.075% w/w solution and then concentrated nitric acid was added to give a final GO concentration of ~0.03% w/w solution. The mixture was sonicated in a bath sonicator (100 W, 50/60 Hz) at room temperature for 1 h. After sonication, the mixture was allowed to settle at room temperature for an hour before being centrifuged at 20,000 rpm, and washed with water until the pH of the supernatant was neutral. The GO prepared by this method will be referred to as HGO.

Both synthesis methods were successful in increasing the GO carboxylic acid content. Analysis of GO-COOH and HGO indicates that there was an approximately 3 fold increase in the number of carboxylic acid groups over the as synthesized GO starting material. See Table 2 for full XPS results. Since the final carboxylic acid content was similar for both samples the HGO synthesis was settled on because in addition to having a high -COOH content we

hypothesized that the defect holes could also alleviate diffusion challenges of getting the reactants to the active cooperative catalytic sight.

Table 2. Comparison of carboxylic acid content, determined by XPS, of carboxylic acid decorated GO samples.

Sample	C1s XPS (percentage)			XPS (percentage)		C:O ratio
	C-C and C=C	C-O	C=O	O1s	C1s	
Graphene Oxide	47.9	46.4	5.8	29.5	68.8	2.33
HGO	40.8	41.8	17.4	33.6	64.9	1.93
GO-COOH	35.4	47.5	17.1	32.5	63.3	1.95

3.3. Amide bond formation for bridging GO basal planes

In order to couple the amine groups of the bridging diamine (4-ABA) to the carboxylic acid groups on the HGO sample, activation the carboxy groups to more reactive intermediate was necessary[104]. Three different synthesis methods were explored to activate the carboxyl groups: conversion of carboxy groups into acyl chlorides, thermally induced coupling to form amide groups, and amide formation with a coupling reagent. In each synthesis method during or after the carboxy groups activation, the bridging and protected amine molecules (4-aminobenzylamine and N-Boc-p-phenylenediamine respectively) were added in a ratio of 25 milligrams (mg) HGO:4 millimoles (mmol) bridging: 2 mmol protected. A 2:1 bridging to protected ratio was chosen so that the higher density of bridging groups could provide more rigidity between the HGO layers and allow better access of the reactants to the theoretical nano-”pocket” active sites.

3.3.1. Conversion of Carboxy Groups into Acyl Chlorides

Thionyl chloride has been used to convert GO carboxy groups into acyl chlorides for the chemical modification of graphene oxide. The acyl chloride group is generally more reactive than a carboxylic acid group and should react readily with amine moieties[17]. The conversion of carboxy groups to acyl chloride groups was accomplished by first freeze drying a sample of HGO to remove water, because the thionyl chloride will react with any residual water and may produce hydrochloric gas. After freeze drying 25 mg of the HGO was refluxed for 24 h at 70°C with 15 mL thionyl chloride and 0.38 mL N,N-dimethyl formamide (DMF). At the end of the reaction the mixture was distilled to remove the excess SOCl_2 and DMF. The bridging and protected amine groups in a 15 mL solution of tetrahydrofuran (THF) were then added to the acyl chloride decorated GO and refluxed at 66°C for 24 h. The sample was then centrifuged and washed with DDI water twice to remove the THF and unreacted amines, then twice with a 0.5M hydrochloric acid solution to remove the Boc protecting group, followed by additional washes with DDI water (a minimum of 3 times) to neutralize and remove residual salt. This sample will be referred to as HGO-Cl Activated. One of the drawbacks of using an acyl chloride, aside from a safety and health hazard of hydrochloric gas, is that hydrochloric species can also initiate deprotection of the N-Boc protecting group. If the Boc groups are removed before bridging occurs the now unprotected amines can also act as bridging groups, thus reducing the total number of potential catalytically active sites. Figure 5 shows a simplified synthesis scheme for this method.

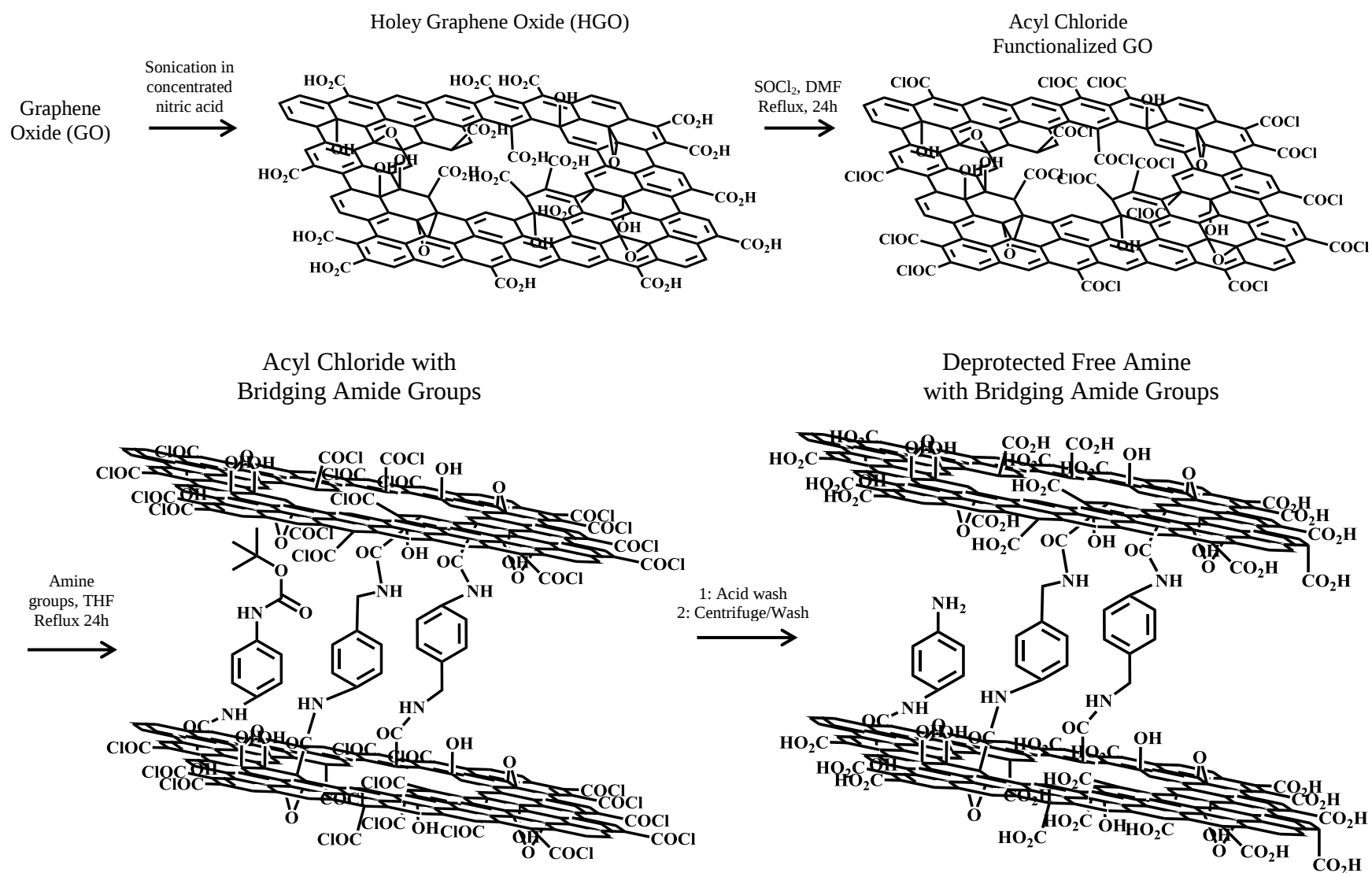


Figure 5. Simplified synthesis scheme for generating a 3D GO structure with nano-‘pockets’ by first converting the carboxy groups into acyl chlorides.

3.3.2. Thermally Induced Coupling to Form Amide Groups

A nucleophilic substitution reaction between the amine groups on the bridging and protected compounds and the GO carboxylic acid groups can be achieved at temperatures of 80°C without chemical activation. A paper by Zhi et al showed that stirring a diamine compound with GO for 24 h at 80°C resulted in the diamine acting as a bridging compound between GO sheets but that stirring for 24 h at 30°C resulted in only one end of the diamine compound being bound to the GO sheet. An increase in the x-ray diffraction (XRD) d-spacing between the sheets of GO and observing the changes in the N1s XPS peak confirmed the bridging nature of the diamine.[26]

The synthesis of a catalytic nano-“pocket” with this method was carried out by first bath sonicating 25mg of HGO (~0.03% w/w solution in water) in a glass media bottle for 30 min. The bridging and protecting amine groups were then added and this mixture was stirred at 80°C for 24 h. The sample was then centrifuged and washed with a 0.5M hydrochloric acid solution twice to remove the Boc protecting group and then with DDI water (a minimum of 3 times) to remove residual salt, unreacted amines, and to neutralize. This sample will be referred to as HGO-Thermal Bridging.

3.3.3. Amide Formation with a Coupling Reagent

A reaction between the diamine and GO carboxylic acid groups with an activating agent was also explored. In protein/peptide synthesis a common coupling agent for the synthesis of amide bonds from amine and carboxylic acid groups is dicyclohexylcarbodiimide (DCC) together with a catalytic amount of 4-dimethylaminopyridine (DMAP)[104]. There are a number of different possible coupling agents/catalyst choices however there is precedence that shows that the DCC/DMAP combination can perform the amidation reaction with GO sheets[105]. The

DCC/DMAP mixture helps facilitate this coupling reaction when the negatively charged oxygen in the carboxy group acts as a nucleophile, attacking the central carbon in DCC. DCC with the former carboxy group forms a highly electrophilic intermediate, making nucleophilic attack by the amino group of the bridging diamine compound more efficient. Synthesis began by freeze drying 25 mg of HGO and then suspending the dried HGO in DMF (~0.03% w/w solution in DMF) by bath sonicating for 30 min. The bridging and protected amine groups were then added and this mixture was stirred at 50°C for 24 h. The sample was then centrifuged and washed with DDI water twice to remove the DMF and unreacted amines, twice with a 0.5M hydrochloric acid solution to remove the Boc protecting group, and finally with DDI water (a minimum of 3 times) to neutralize and remove residual salt. This sample will be referred to as HGO-DCC Bridging.

3.3.4. Materials Characterization and Discussion

XRD spectroscopy was used to monitor the basal plane bridging between GO sheets. The initial d-spacing for the HGO starting material was calculated to be 1 nm. An increase in d-spacing for the HGO-Thermal Bridging and HGO-DCC Bridging samples to 1.05 nm and 1.12 nm respectively was observed. However the intensity of the HGO-DCC Bridging signal was very low and there was also a broad peak in the 20°-25° range which could indicate significant reduction of the basal plane and re-graphitization. No XRD d-spacing 001 peak could be observed for the HGO-Cl Activated sample. Figure 6 shows the XRD diffraction patterns for these samples.

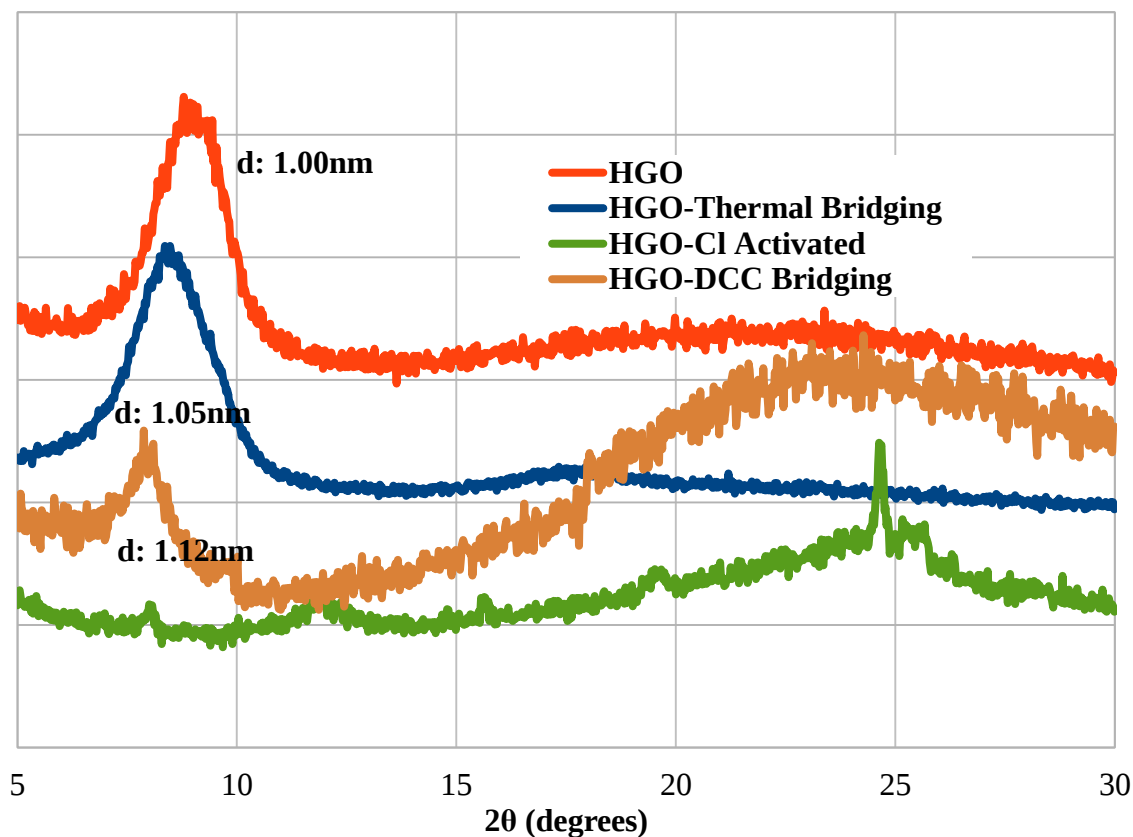


Figure 6. XRD patterns for the 3D GO structures that were synthesized utilizing amide bond formation routes

XPS was used to analyze which oxygen functionalities were reacting during the bridging synthesis steps, gain insight into the nature of the remaining amine groups, and look for residual carboxylic acid groups that would be important for probing the cooperative catalytic nature of the 3D structure. Table 3 shows the atomic percentages, a closer look at the deconvolution of the C1s peak, and the carbon:oxygen (C:O) ratio for each of the amide bond formation synthesis techniques. An example C1s deconvolution, for HGO-Thermal Bridging, can be found in Figure 7. Five different components can be revealed with XPS analysis of the C1s peaks: C–C (~284.9 eV) of the sp² carbons in the basal plane of the graphene sheets, C–O (~286.3 eV), C=O (~288.1 eV), O–C(O) (~289.2 eV), and C–N (~286.7) [106]. Comparison of the XPS data shows that all

three synthesis methods saw a drastic reduction in the C:O ratio and a large increase in the percentage of the C1s peak that can be attributed to the C-C sp² carbons indicating an overall reduction of the GO and most likely an increase in graphitic regions that give graphene its interesting properties. The HGO-Cl Activated sample retains the largest degree of carboxylic acid groups and has the lowest C:O ratio of the three synthesized samples. The HGO-Thermal Bridging and HGO-DCC Bridging samples were very similar when analyzed except that more nitrogen seemed to be incorporated in the DCC sample. This aligns with the XRD where the HGO-DCC Bridging sample had the largest d-spacing; more bridging (i.e. more nitrogen content) could mean there are more bridging molecules to keep the basal planes separated and thus an overall increase in d-spacing is observed.

Table 3. XPS peak table comparing the impact the amide bond formation synthesis route had on the final 3D GO structure.

	Atomic %			Percentage of C1s peak					C:O ratio
	C1s	O1s	N1s	C-C	C-O	C=O	C(O)-O	C-N	
HGO	64.9	33.6	1.5	40.8	41.8	13.4	4		1.9
HGO-Thermal Bridging	72.5	22.2	5.3	52.6	26.2	7.6	8.3	5.3	3.3
HGO-Cl Activated	69.6	23.4	5.7	44.1	22.9	13.8	13.5	5.6	3.0
HGO-DCC Bridging	72.4	19.9	7.8	51.8	27.9	7.7	4.7	7.8	3.6

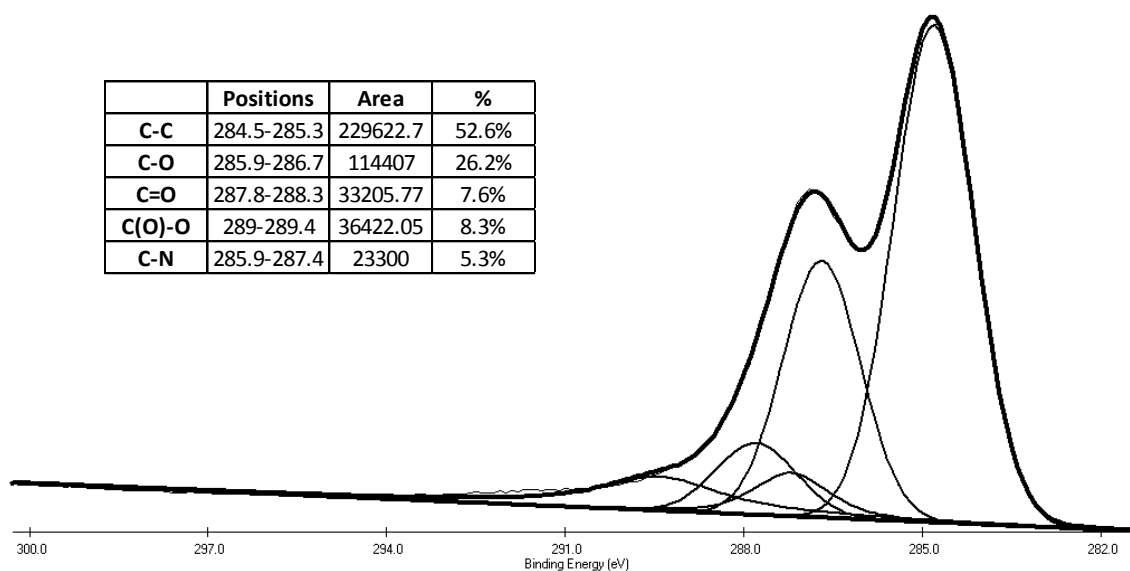


Figure 7. Deconvolution of the C1s XPS peak for the HGO-Thermal Bridging sample. Five different C1s components were revealed: C–C (~284.9 eV) of the sp² carbons in the basal plane of the graphene sheets, C–O (~286.3 eV), C=O (~288.1 eV), O–C(O) (~289.2 eV), and C-N (~286.7) [106].

The drawback to all three of these amide bond formation synthesis methods is that it is extremely challenging to distinguish between the amide bonds formed from between the HGO sample and the bridging amines and the amide bonds on the protected amine molecule. It's additionally difficult to try to quantify what percentage of the bridging amine groups are bound to the HGO sheet with both amine groups. This is a huge issue when within the structure the goal is to try to control the spacing between the catalytic amine and carboxylic acid groups for cooperative catalysis reactions. Due to these challenges a click chemistry synthesis method was introduced.

3.4. Click Chemistry for bridging GO basal planes

In order to better identify which groups were for bridging and which were for catalysis, a click chemistry synthesis approach was developed. Azide and alkyne functionalized GO samples were prepared and were “clicked” together forming a 5-membered heteroatom ring (see synthesis methods below) using a copper bromide catalyst or via a thermal reaction. Using FTIR the disappearance of the azide peak could easily be tracked and the near completion of the basal plane bridging as well as the remaining potential catalytic amine groups. Figure 8 shows a simplified synthesis scheme of this click chemistry approach.

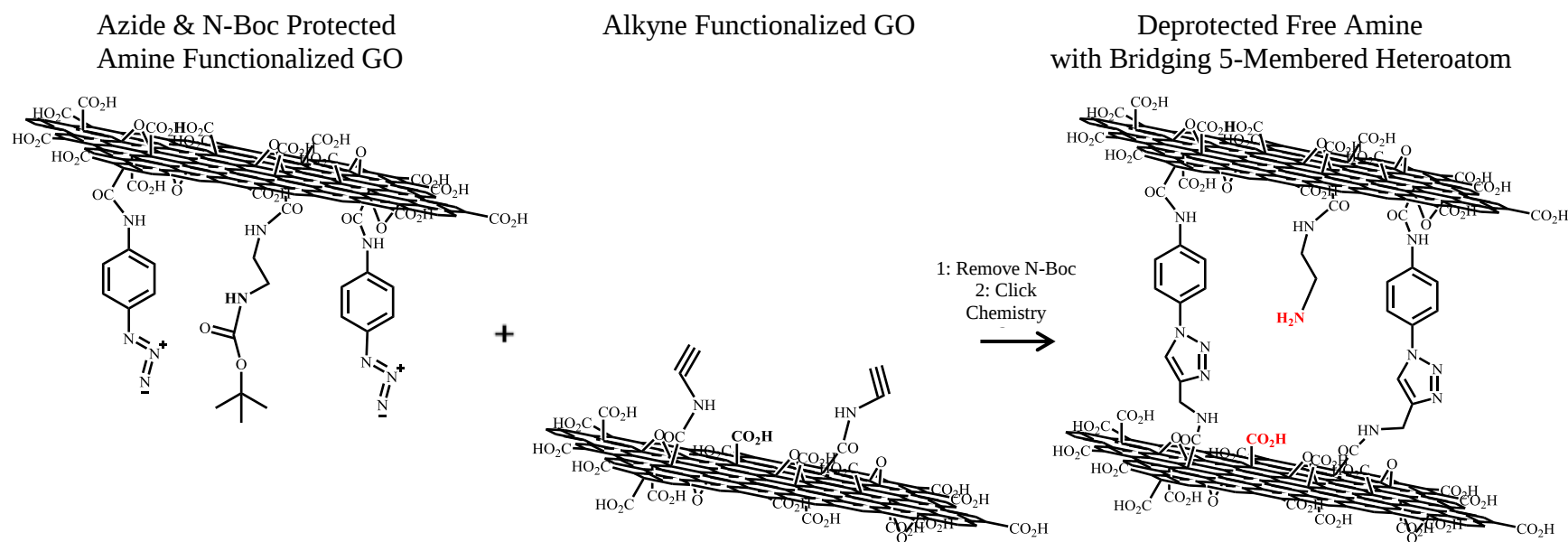


Figure 8. Simplified synthesis scheme for generating a 3D GO structure with nano-‘pockets’ using a click-chemistry synthesis technique.

3.4.1. Azide functionalized GO

Freeze dried HGO, 10mg, was suspended in 50 mL of DMF by bath sonicating for 30 min. The DCC/DMAP coupling agent was then used to attach the amine group of propargylamine to HGO. Four mmol of propargylamine, 4.8 mmol of DCC, and 1 mmol of DMAP were then added to the suspended HGO and stirred at 50°C for 24 h. The sample was then centrifuged and washed with DDI water three times to remove the DMF and unreacted amines. This sample will be referred to as HGO-Azide.

3.4.2. Alkyne functionalized GO

Freeze dried HGO, 10mg, was suspended in 50 mL of DMF by bath sonicating for 30 min. The DCC/DMAP coupling agent was then added to aid in the attachment of the amine group of propargylamine to the carboxylic acid groups on HGO. Four millimoles of 4-azidoaniline hydrochloride, 2 mmol of N-Boc-ethylenediamine, 7.2 mmol of DCC, and 1.5 mmol of DMAP were added to the suspended HGO and stirred at 50°C for 24 h. The sample was then centrifuged and washed with DDI water twice to remove the DMF and unreacted amines, then twice with a 0.5M hydrochloric acid solution to remove the Boc protecting group, and finally with DDI water (a minimum of 3 times) to neutralize and remove residual salt. This sample will be referred to as HGO-Alkyne.

3.4.3. Click chemistry of azide and alkyne functionalized GO

The catalytic method for clicking the azide and alkyne functionalized GO samples together uses a copper (I) bromide catalyst. The catalytic click chemistry synthesis method began with freeze drying the alkyne and azide functionalized GO samples. Ten milligrams of each sample were then added to a 100 mL round bottom flask with 75 mL of DMF. Copper (I) bromide (0.4 g) was added to the round bottom flask and the mixture was stirred for 24 h at room

temperature. The sample was then centrifuged and washed with DDI water three times to remove the DMF and some catalyst. This sample will be referred to as HGO-Cu-Clicked. One drawback to this catalytic approach is that Cu (I) can be oxidized to Cu (II) during this reaction and divalent ions are known to induce the formation of three dimensional structures with GO[107]. The copper ions can be washed out of the 3D structure using an acidic solution. Removal of the copper ions was accomplished by centrifugation and washing of the sample twice with a 0.5M hydrochloric acid solution, followed by washes with DDI water (a minimum of 3 times) to neutralize. This washed sample will be referred to as HGO-Cu-Clicked-Wash. Additionally a non-catalytic click reaction was also investigated to avoid the possibility of residual metal catalyst in the final 3D GO structure.

The non-catalytic click chemistry approach began with freeze drying the alkyne and azide functionalized GO samples. Ten milligrams of each sample was then added to 75 mL of DMF. The sample was stirred for 5 days at 120°C, then centrifuged and washed with DDI water three times to remove the DMF. This sample will be referred to as HGO-Therm-Clicked.

3.4.4. Materials Characterization and Discussion

The main objective of the click chemistry approach was to be able to follow the bridging reaction more closely. FTIR was utilized to monitor the disappearance of the azide group, which gives an indication that the alkyne and azide groups are reacting to form a 5-membered heteroatom ring that will hold the HGO basal planes together. Figure 9 shows the FTIR spectrums in the 1700-4000 cm^{-1} range for the azide, alkyne, and clicked materials. The azide peak at 2098 cm^{-1} is clearly visible for the HGO-Azide material but doesn't show up in any of the other scans for final clicked materials. This indicates that the click reaction went to completion and there are no azide functional groups remaining in the final bridged products. The

peaks at $\sim 2925\text{ cm}^{-1}$ and 2855 cm^{-1} are attributed to the symmetric and asymmetric stretching of aliphatic CH_2 and CH_3 bonds. The peaks at $\sim 2400\text{ cm}^{-1}$ are from asymmetric carbon dioxide (CO_2) (in the gas phase). There is a very large, broad peak around $\sim 3400\text{ cm}^{-1}$ from to the vibration and deformation bands of the O-H bond. This broad peak is due to absorbed water in the samples. However in the HGO-Azide and HGO-Cu-Clicked samples additional sharper peaks were observed in this water region. Although further characterization of this peak was not undertaken it is interesting to note that the double peak in this region for the HGO-Cu-Clicked sample reproducibly was eliminated with washing to remove the copper bromide catalyst. One hypothesis is that the copper ion is interacting with the absorbed water causing a change to the vibration of these molecules. The peak in the HGO-Azide peak could be an amide peak (C-H stretching bands) observed at $\sim 3300\text{ cm}^{-1}$ although this same peak should also then be present in the rest of the samples.

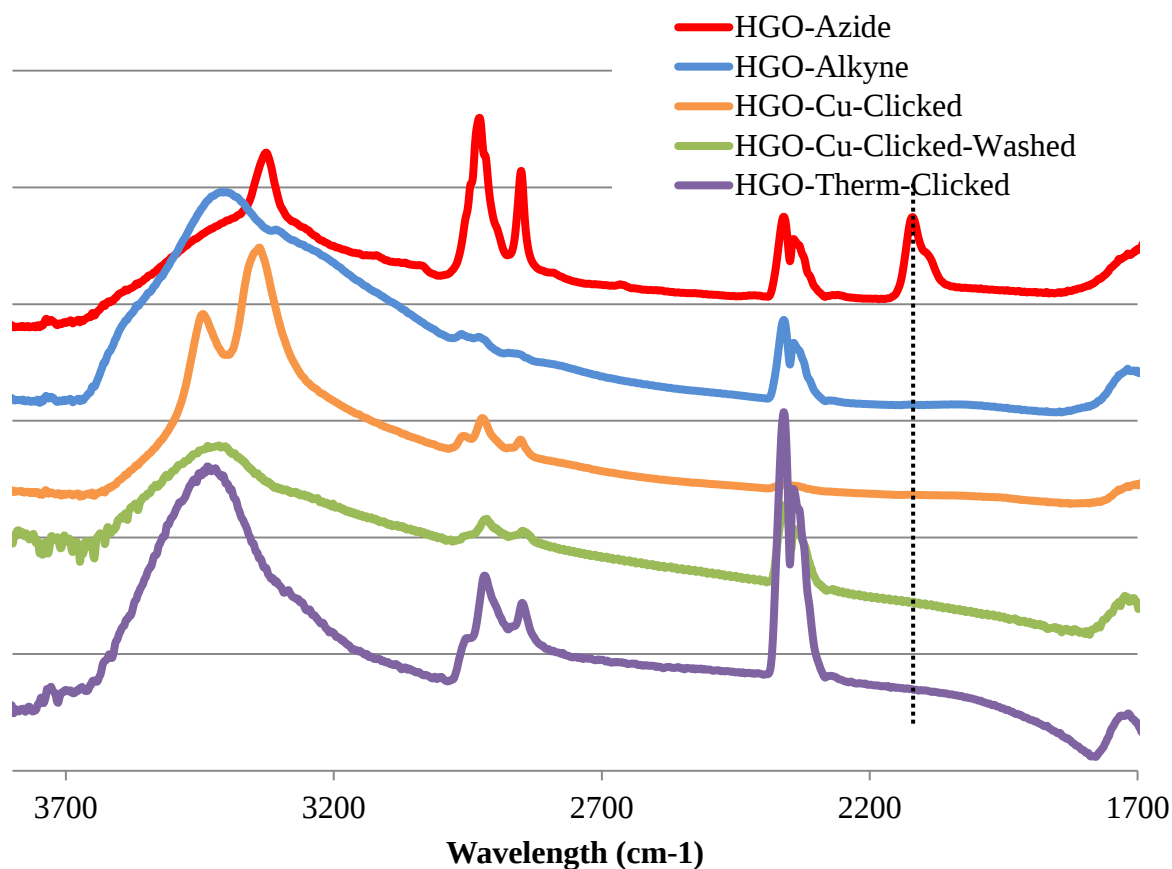


Figure 9. Comparison of FTIR spectrum, in the 1700-4000 cm^{-1} wavelength range, for azide, alkyne, and clicked HGO materials. The azide peak at 2098 cm^{-1} is clearly visible for the HGO-Azide material and doesn't show up in any of the other scans for final clicked materials.

XPS was used to observe changes in the types of oxygen functionalities remaining after the bridging reaction occurred.

Table 4 shows the atomic percentages, a closer look at the deconvolution of the C1s peak, and the carbon:oxygen (C:O) ratio for each of the click chemistry synthesis techniques. Four different components of the C1s peak were considered: C–C (~ 284.9 eV) of the sp^2 carbons in the basal plane of the graphene sheets, C–O (~ 286.3 eV), C=O (~ 288.1 eV), and O–C(O) (~ 289.2 eV) [106]. Comparison of the XPS data shows that all three synthesis methods saw a drastic reduction in the C:O ratio compared to the starting HGO sample. The C1s XPS data for

the HGO-Therm-Clicked sample was drastically different than what was observed for the other clicked samples; the main peak was C-O in this case instead of the C-C peak which is the predominate peak for all of the other samples. However, no further investigation was done to try to reconcile the data from this sample. XPS analysis was crucial to determining if there was residual copper bromide catalyst remaining after washing with hydrochloric acid when work was done to optimize the washing step.

One of the drawbacks with the click chemistry approach to synthesizing a 3D GO structure was the use of the copper catalyst. Ensuring that the final product is truly free of residual metal catalyst is crucial because even a small amount of residual catalyst could impact the cooperative reaction network. The thermal click method seemed to work reasonably well but had a very long synthesis time and there were some anomalies observed during the characterization of this material.

Table 4. XPS peak table comparing the atomic composition of the starting, intermediate, and final click chemistry materials for generating a 3D GO structure.

**7.1 atomic % Cu2p3 all other samples no detectible levels of Cu2p3 peak.

Sample	Atomic %			Percentage of C1s peak				C:O Ratio
	C1s	O1s	N1s	C-C	C-O	C=O	C(O)-O	
HGO	64.9	33.6	1.5	40.8	41.8	13.4	4.0	1.9
HGO-Azide	70.9	21.1	8.0	48.3	32.1	10.8	8.9	3.4
HGO-Alkyne	69.3	27.8	2.9	54.3	28.5	8.1	9.2	2.5
HGO-Cu-Clicked**	61.8	26.8	4.4	56.1	23.9	8.7	11.3	2.3
HGO-Cu-Clicked-Washed	69.8	27.2	3.1	58.6	29.4	8.7	3.3	2.6
HGO-Therm-Clicked	71.7	25.1	3.2	15.3	50.1	22.5	12.0	2.9

3.5. Conclusion

A vast array of characterization techniques was utilized to investigate GO modifications and demonstrate the ability to of these methods to bridge the basal planes of GO together while leaving select molecules available to participate in a cooperative manner. Changes to the d-spacing of the GO matrix were observed by using different chemistries to bridge the basal planes. Ultimately these materials were not utilized to test cooperative catalysis reactions but the knowledge gained was instrumental to guiding the research in Chapter 4.

4. Investigation of Graphene Oxide Coatings on Nano-Gold Catalysis

4.1. Introduction

Our second approach to understanding the impact of GO on a catalytic active site is to wrap a single layer of GO around another support to create a catalytically active bilayer between the GO and nonporous support (see Figure 10 for theoretical target synthesis and structure). Gold NPs will be trapped within this bilayer with the GO serving as an overcoat. We hypothesize that the catalytic activity of Au nanoparticles can be modified by a GO overcoat by reducing metal leaching during reaction, controlling the monodispersity of the nanoparticles, and influencing catalytic properties through electron donation/withdrawal and cooperative effects.

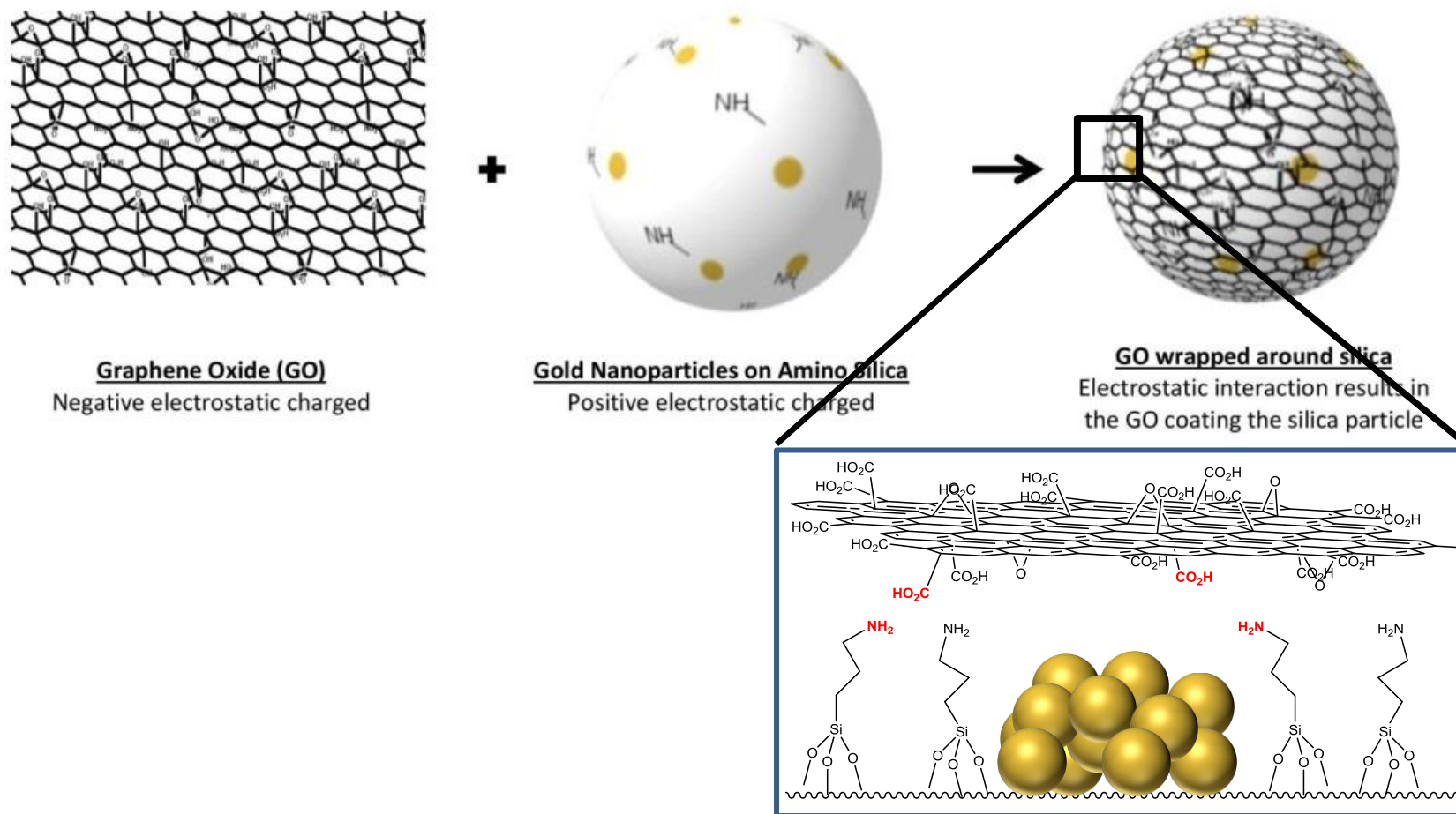


Figure 10. Simplified synthesis target showing the goal of trapping AuNPs in a catalytic bilayer by wrapping GO around a Stober silica support to study the impact that a GO coating has on the Au catalyst.

This synthesis challenge was broken into two pieces 1) wrapping a single layer of GO around a silica support and 2) depositing small uniformly dispersed gold nanoparticles on a low-surface area support directly beneath the GO coating. In order to ensure that any interesting material properties or catalytic effects could be attributed to the GO coating it was imperative that the GO sheets be near, or ideally directly on top of, the gold nanoparticles. The silica support was chosen to be non-porous and 1.5 micron in diameter and the non-porous nature of the silica guarantees that the NPs are on the surface and not sitting in a pore where access to the NP surface could possibly be blocked. The next material consideration was that as synthesized GO has an average lateral dimension of 3 micron and when this GO was used to create the GO coating a large number of silica particles ended up wrapped within a single sheet of GO. If the GO sheets are allowed to wrap many silica particles the gold deposited onto the silica could be sitting on the surface of the silica but between silica particles and not next to the GO. One final consideration/challenge was to deposit small (<10nm) gold NPs onto the silica without a stabilizing agent. Very few examples exist in the literature demonstrating the ability to deposit <10 nm Au NPs without the use of a stabilizing ligand or a support with a medium-high surface area.

Catalysts with and without a GO coating were tested and compared for the above hypotheses. A number of different synthesis methods were explored to optimize the non-porous silica supported AuNP coated with GO and both oxidation and reduction reactions were investigated to see if the GO coating influenced catalytic activity or selectivity.

4.2. Wrapping a single layer of GO around a silica support

Synthesis of the GO coated catalyst began by exploring how a spherical silica particle could be electrostatically coated with a single or few layers of GO. Both a positively charged

silica support coated with a negatively charged GO sample and a negatively charged silica support wrapped with a positively charge GO sample were explored.

The surface charge and surface charge density of silica has been extensively studied and is known to be impacted by the size of the particle and the properties of the solution the silica is suspended in such as, ionic concentration and pH [108–110]. The surface density of silanol groups can be influenced by the synthesis method and post treatment protocols. The density of silanol groups can impact the surface charge. When Stöber silica is dispersed in pH 7 DDI water the surface charge is negative and had a measured zeta potential of -35 mV.

The surface charge and charge density of GO has been studied in great detail [111, 112] and it is known that GO has a negative surface charge in neutral pH water. The negative charge can mainly be attributed to the carboxylic acid groups at the edges and defect sites. The negative charge of these groups produces the charge-charge repulsion that helps keep the GO sheets well dispersed in water. When they are in close proximity the hydroxyl groups on the basal plane can also stabilize the carboxylate anions; this added stabilization also contributes to GO's excellent water dispersibility. As synthesized the GO has a zeta potential of -37 mV.

In neutral aqueous media both silica and GO are negatively charged. Thus an electrostatic wrapping is not possible with the as is materials. With the knowledge and experience gained while working on the 3D GO structure the first approach taken to solve this problem was to chemically modify the GO to be positively charged. Amine functionalized silica was synthesized by refluxing 3-aminopropyltriethoxysilane (3-APTES) with freeze dried GO in a non-aqueous solvent such as toluene, ethanol, or THF for 6 hours. The GO was then washed via centrifugation 3 times with fresh solvent, to remove any unreacted silane, and centrifuged an additional 3-6 times to solvent switch into water. The choice of solvent was influential for decoration of the GO

sheet with an amine. The target system was one in which the solvent would aid the incorporation of a high number of nitrogen/amine groups, increasing the potential number of positive charges, onto GO and would reduce the carboxyl peaks, negative charge bearing group. All three solvents systems allowed for the condensation of the amine onto the surface and the reduction of the carboxylic acid content, see Table 5 for a comparison of the XPS characterization.

Tetrahydrofuran was ultimately chosen moving forward because, although the nitrogen incorporation and C:O ratios were about the same for each solvent, the ratio of silicon to nitrogen was closest to the theoretical 1:1, and THF was easy to remove by centrifugation and washing with water. Grafting the amine onto the GO resulted in only a modest change in the zeta potential of the sample; it increased to -29.9 mV.

Silica particles remain negatively charged until they cross their isoelectric point (between pH 2-3) so the next step was to determine the isoelectric point of amine-GO and if at any pH above the isoelectric point of silica the amine-GO has a positive zeta potential, then we could potentially electrostatically wrap the positively charged amine-GO around a negatively charged silica support. Adjusting the pH of a 1 mg/mL amine-GO aqueous suspension with a 0.5M hydrochloric acid (HCl) solution, the zeta potential of the amine-GO was measured at a variety of pH points. Unfortunately with the continual addition of acid the amine-GO agglomerated and fell out of suspension at pHs below ~4. Different acids, nitric and glacial acetic acid, were also tested to see if a different acid would induce a more stable suspension but all amine-GO samples began to fall out of suspension around a pH of 4. The zeta potential of the amine-GO at this pH is possibly slightly positive; this is a difficult measurement to obtain since the sheets are agglomerating and falling out of suspension at this pH which interferes with the zeta potential measurement. Ionic salt concentrations are known to impact the zeta potential of silica, thus

sodium chloride (NaCl) was added prior to wrapping to compare wrapping in systems with 0 weight percent (wt%) NaCl versus a system with 10 wt% salt. The procedure used to wrapped positively charged amine-GO around negatively charged silica is detailed here. A stock solution with the desired pH (2 or 4) and desired salt concentration (0wt% or 10wt%) was prepared. Next half a gram of silica was suspended by sonication into 50 mL pH adjusted water and 5 mg amino-GO was suspended into a separate 50 mL of water. The suspended silica was slowly added to the amine-GO solution while stirring and was then stirred for 24 hours. The sample was then centrifuge to remove any unwrapped amino-GO followed by vacuum drying. Scanning electron microscopy (SEM) images of the wrapped samples can be found in **Error! Reference source not found.** No change in experimental zeta potential were observed for variations in both pH and ionic concentration. Additionally, by SEM, no visually observable differences between samples were noticed. In all cases wrapping of the amino-GO around the silica looked similar to a sample in which GO was negatively charged and the silica was positively charged (see below for the details of synthesis) as observed by SEM. The SEM images in Figure 11 also showed us that the lateral dimension of the amino-GO sheets were much too big to wrap a single silica particle.

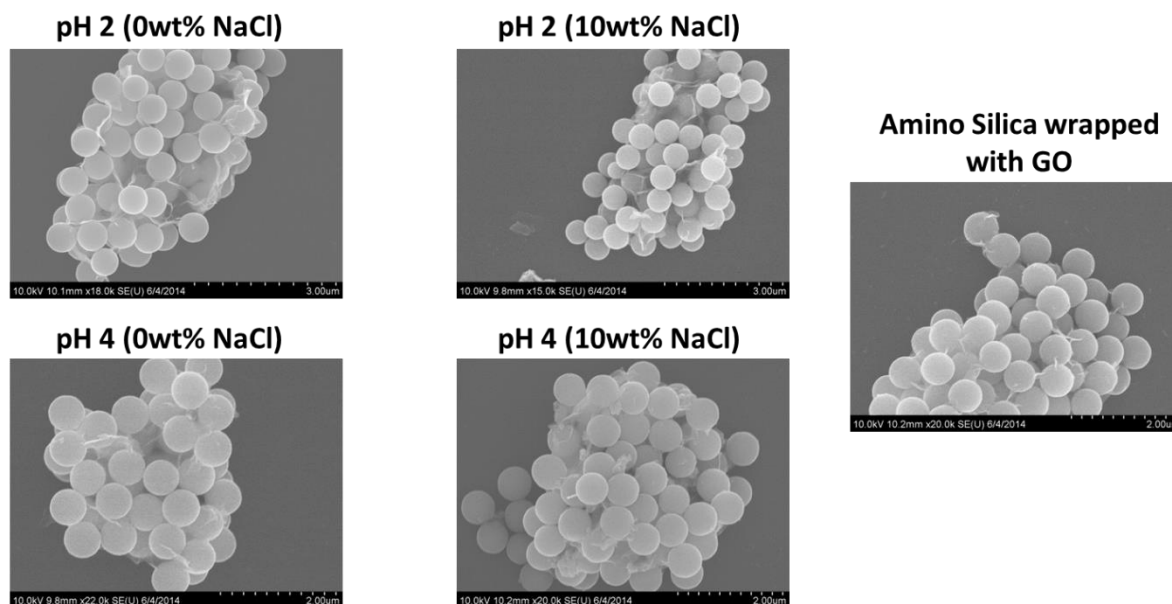


Figure 11. Wrapping Amino-GO around Silica at various pH and ionic concentrations.

Table 5. XPS results comparing how different solvents effect incorporation of amine groups and changes to the C:O ratio.

Solvent	C1s XPS (percentage)			XPS (percentage)				C:O ratio
	C-C and C=C	C-O	C=O	O1s	C1s	Si2p	N1s	
Ethanol	68.3	22.2	9.5	25.3	59.3	9.9	5.5	2.34
THF	58.2	26.3	14.1	27.6	56.3	6.9	5.9	2.04
Toluene	73.4	16.4	10.2	23.2	60.7	10.6	5.4	2.61

Due to the challenges encountered with keeping positively charged GO suspended in water, investigation of the opposite scenario, positive silica/negative GO. Amine-SiO₂, was pursued. This sample was synthesized by suspending 3 g of 1.5 micron Stöber silica in 75 mL of a 10 % (v/v) 3-APTES in toluene. The mixture was refluxed at 111°C in an oil bath with stirring

for 6 h. The amino decorated silica particles (now defined as $\text{NH}_2\text{-SiO}_2$) were collected by centrifugation, re-suspended in toluene and washed, via vacuum filtration, with *N,N*-dimethylformamide (DMF; 2×100 ml) and ethanol (2×100 ml). Thermal gravimetric analysis (TGA) was used to determine that the loading of the amine group on the silica support was 0.09 mmol/m^2 and the zeta potential was $+12.3 \text{ mV}$. With a positive surface charge, $\text{NH}_2\text{-SiO}_2$, is now able to electrostatically interact with the negatively charged GO sample (-37 mV), see **Error! eference source not found.**, and both samples are easily suspended and stay dispersed in water. The challenge with this wrapping procedure is that a single sheet of GO was being wrapped around multiple silica particles.

The target structure has a single sheet of GO wrapped around a single silica sphere. In order to obtain this structure, the lateral dimension of GO needed to be decreased significantly. As synthesized GO has an average lateral dimension of ~ 3 micron as determined by dynamic light scattering (DLS). Each 1.5 micron silica particle has a surface area of $7.1 \times 10^6 \text{ nm}^2$. Therefore the GO needs to theoretically have a lateral dimension of less than 2 micron. We chose a goal of between $500\text{-}700 \text{ nm}$ for the lateral dimension to give a better chance of a single sheet wrapping only one silica particle.

One method for sorting the sheets of GO by size and surface chemistry is sucrose gradient centrifugation[113]. Sucrose solutions of high to low concentrations are layered in a centrifuge tube and a layer of GO is deposited on top, see Figure 12. Sucrose gradient centrifugation takes advantage of the differences in sedimentation rate between various sized GO sheets. According to Stokes' law larger sheets will have a high sedimentation rate and the increase of both density and viscosity at the gradient layer boundary will slow down the smaller GO sheets. After some trial and error the sucrose step gradient that gave the resulting $500\text{-}700$

nm GO sheet size was a 25% (w/w) sucrose solution layered on top of a 30% sucrose solution; 15 mL of each sucrose solution was placed in a centrifuge tube and then 5 mL of a 5 mg/mL GO solution was added to the top. The sample was centrifuged for 10 min at 50,000 G. The top layer (25% sucrose) was collected and then centrifuged/washed 6 times with water to remove the sucrose. This GO sample with a smaller average lateral size will subsequently be referred to as grad-nano-GO.

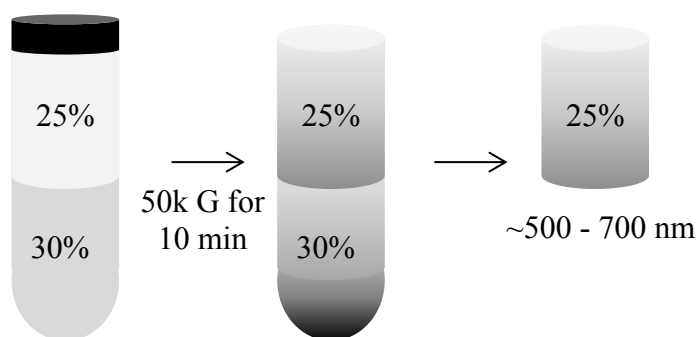


Figure 12. Sucrose gradient centrifugation to separate GO sheets by size

Another method to synthesize smaller GO sheets is to use the energy from a high power probe sonicator to break the sheets apart[114]. Using a Q700 Qsonica sonicator, a 2 mg/mL GO solution was sonicated for 1 hour with a total energy delivered of 125,000 J. The GO solution was kept in an ice bath to prevent overheating of the sample. After sonication the sample was centrifuged for 90 min at 48,000 G and the supernatant was discarded. The remaining GO, subsequently called probe-GO, was re-suspended in water and had average lateral dimensions of 395 nm as measured by DLS. Both grad-nano-GO and probe-GO samples have zeta potentials between -55 mV and -60 mV in water which indicates that they also have a higher density of carboxylic acid groups; this was also confirmed with XPS. Probe sonication ended up being preferable to the sucrose gradient centrifugation method because sucrose gradient centrifugation is very time consuming and a larger portion of the original GO ends up being discarded if you

don't first reduce the lateral size of the parent GO solution prior to sucrose centrifugation. Table 6 summarizes the differences in surface charge and lateral dimension for these different GO samples.

Table 6. Comparing surface charge and lateral dimensions for different synthesis methods to product small negatively charged GO sheets.

Sample	Zeta Potential (mV)	Average Hydrodynamic Diameter (nm)
HGO	-37.1	927
Grad-Nano GO	-60.1	514
Probe GO	-56.5	395

Probe-GO sheets were wrapped around $\text{NH}_2\text{-SiO}_2$ by bath sonicating a gram of $\text{NH}_2\text{-SiO}_2$ into 100 mL DDI water and slowly adding 1 mL of the GO solution (which typically had a concentration of 1.5-2 mg/mL). The mixture was allowed to stir overnight, then centrifuged to remove any GO sheets not wrapped around a silica particle and vacuum dried. Centrifugation will not separate silica particles that are wrapped and unwrapped; an excess of GO was added to minimize the number of unwrapped silica particles.

4.3. Synthesis of small Au NPs on a low-surface area support

The next challenge to creating a GO coating over a gold catalyst was depositing small uniformly dispersed gold nanoparticles on a low-surface area support. Typically, to deposit small uniformly sized AuNPs, the NPs are stabilized using strong ligands or placing them on very high surface area supports to keep the particles from agglomerating. The $\text{NH}_2\text{-SiO}_2$ particles in this study have a low surface area, $8.8 \text{ m}^2/\text{g}$, and thus methods such as incipient wetness with a gold ionic salt solution results in large and non-uniform AuNPs on the surface.

4.3.1. Polymer wrapped AuNPs

A method was developed in the Kung lab to deposit sub-nanometer gold particles on a silica support [115] in which chloro(tetrahydrothiophene) gold(I) is added to an amine functionalized polymethylhydrosiloxane polymer and reduced with triethylsilane. This polymer wrapped gold colloid is then deposited on amine-functionalized silica with a 0.1wt% Au loading. The low loading is necessary to keep the size of the nanoparticles small and mono-disperse, 3.1 ± 0.6 nm. The typical synthesis scheme is shown in Figure 13.

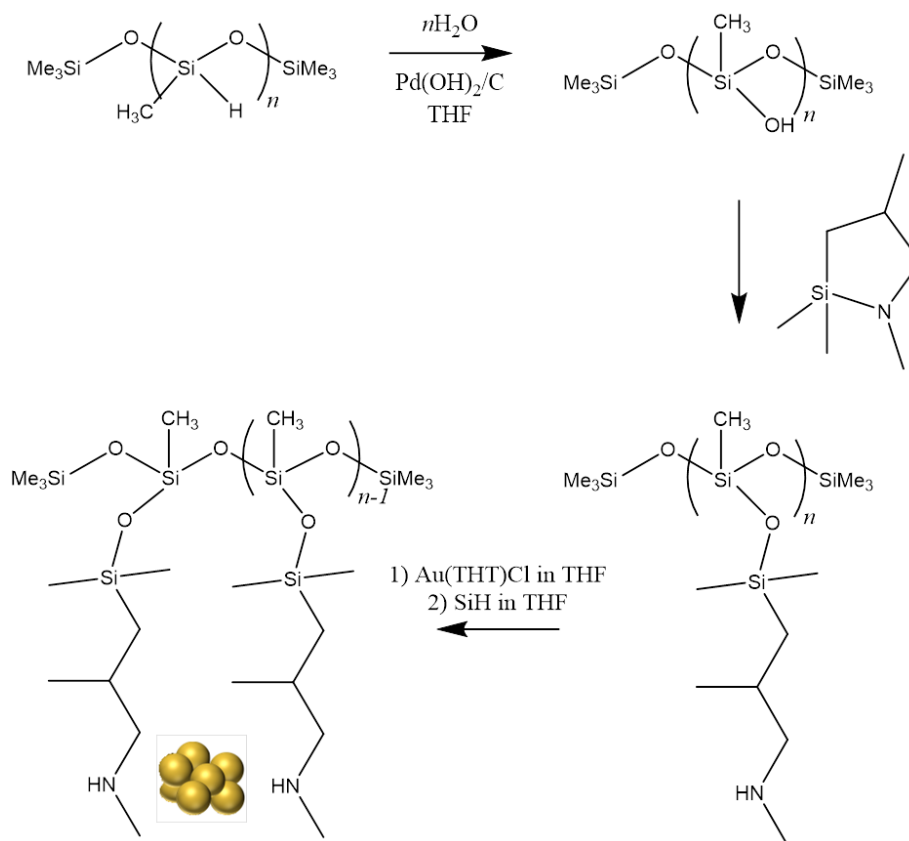


Figure 13. Synthesis overview for wrapping AuNPs in a PMHS polymer.

Chloro(tetrahydrothiophene) gold(I)

Chloro(tetrahydrothiophene) gold(I) ($\text{Au}(\text{THT})\text{Cl}$) was synthesized according to previous literature procedure [115, 116]. Synthesis of this gold complex began with 1.875mmol gold (III)

chloride trihydrate being added to 1.25 mL DDI water and 6.25 mL ethanol. While stirring at room temperature, 3.97 mmol tetrahydrothiophene was added dropwise and then stirred for 15 min. The mixture was filtered and washed with 20 mL ethanol and then vacuum dried.

Amine functionalized polymethylhydrosiloxane polymer

Synthesis conditions of the amine-PMHS polymer were chosen based on previous results by Wang et al [115]. 0.64 mL PMHS was added to 10 mL THF in a Schlenk flask. 35 mg of Pearlman's catalyst (20 wt% Pd(OH)₂/C) and 0.3 mL (an excess) of DDI water were added. The conversion of the silane to silanol was monitored by tracking the amount of hydrogen gas evolution. Following this reaction, the Pd catalyst and excess water were removed using column chromatography. Under nitrogen flow, the product was flowed over a column containing of a layer of CaSO₄ sandwiched between layers of Celite using diethyl ether as the eluent. This dried silanol-PMHS polymer was then reacted quantitatively with N-methyl-aza-2,2,4-trimethylsilacyclopentane to become the amine-PMHS polymer. Finally the solvent was removed from the amine-PMHS under low pressure.

Gold wrapped with amine-PMHS polymer

A 6 mM Au(THT)Cl in THF solution was prepared. The amine-PMHS polymer was dissolved in THF and a small amount of Au(THT)Cl was added to be in a 1:10 amine to Au molar ratio. This mixture was allowed to stir for an hour in an ice bath. Triethylsilane was then added in a 10:1 SiH: Au ratio and the total volume of the solution was brought up to 10 mL with the addition of THF. The mixture was again stirred for an hour in an ice bath. The concentration of gold in this final solution is 3 mM.

Depositing Au-Amine-PMHS onto NH₂-SiO₂

The surface area of the 1.5 micron $\text{NH}_2\text{-SiO}_2$ was measured to be $8.8 \text{ m}^2/\text{g}$. An amount of $\text{NH}_2\text{-SiO}_2$, 0.75 g, was bath sonicated for 30 min in 4.5 mL THF. The target gold loading of this catalyst was 0.1 wt%, so 1.3 mL of the Au-Amine-PMHS solution (3 mM Au) was added to the $\text{NH}_2\text{-SiO}_2$ and allowed to stir for 1 h before the THF was evacuated. The catalyst was then heated to 150°C with a $0.12^\circ\text{C}/\text{min}$ ramp and held at 150°C for 1 h in a 10% ozone flow to remove the organic groups from the polymer. These AuNPs had an average diameter of $3.1 \pm 0.6 \text{ nm}$.

Investigation into the impact of coating with GO

As a first attempt to investigate if a GO coating could help keep the AuNP size small, Au-Amine-PMHS was deposited onto $\text{NH}_2\text{-SiO}_2$ by changing the order of the steps in the synthesis procedure detailed above. Instead of reduction with triethylsilane in solution before deposition onto the support, the polymer/Au ion matrix was first deposited onto $\text{NH}_2\text{-SiO}_2$. The sample was then either reduced using triethylsilane or wrapped with GO, according to the procedure described in Section 4.2, followed by reduction with triethylsilane. Both samples were then heat treated in ozone to remove organic groups from the polymer backbone.

When the catalyst was reduced prior to deposition onto the silica support the AuNPs had an average diameter of $3.1 \pm 0.6 \text{ nm}$ however when the reductant was added after deposition onto the silica the average particle size was $7.9 \text{ nm} \pm 1.4 \text{ nm}$, as measured by TEM. Additionally when the GO coating was added prior to the addition of the reductant and thus coated prior to AuNP formation the average particle diameter was $6.1 \text{ nm} \pm 0.9 \text{ nm}$. And while the standard deviation of these two approaches is different a very small number of particles could be counted from the TEM images (<30), and therefore it's unclear if this difference was statistically significant.

Although the AuNPs diameter is pretty small with the original synthesis method (see Figure 13) the NPs were also probably coated with a layer of residual silica from the polymer backbone and as a result elucidating an Au/GO interaction might not be straightforward. Because of this challenge, new synthesis methods were sought to make small AuNPs without the help of a stabilizing polymer/agent.

4.3.2. Ethylene diamine gold

In gold catalysis work being carried out by another member of the Kung research group, a gold cation was deposited onto a negatively charged silica surface. In a first attempt to deposit small unstabilized gold, a gold ethylene diamine chloride ($\text{Au(en)}_2\text{Cl}_3$) complex was added with a theoretical Au weight loading of 1% to suspended non-porous Stöber silica, which was then functionalized with 3-APTES added after gold loading for GO wrapping.

Synthesis of gold ethylene diamine chloride ($\text{Au(en)}_2\text{Cl}_3 \text{HCl}$)

Half of a gram of gold (III) chloride hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was added to 2 mL water and 10 mL ethanol. The mixture was stirred for 10 min at 200 rpm. Then 0.23 mL ethylene diamine was added and the mixture was stirred for an additional 10 min at 200 rpm. The precipitate was filtered and washed with 3x100 mL ethanol and then vacuum dried.

Depositing $\text{Au(en)}_2\text{Cl}_3 \text{HCl}$ onto Stöber silica

In a first attempt to deposit small unstabilized gold, 22 mg of $\text{Au(en)}_2\text{Cl}_3 \text{HCl}$ was added to 100 mL of water along with 1 g of 1.5 micron diameter Stöber silica and stirred for 10 min in a 40°C oil bath. This gives a theoretical Au weight loading of 1 wt%. The pH of the solution was adjusted to 9 by dropwise addition of a 0.5M ethylene diamine solution. The solution was removed from the oil bath and allowed to stir vigorously for 2 h at room temperature. The sample was then filtered and washed with 4x300 mL heated (40°C) water and vacuum dried. The

catalyst was then heated to 150°C with a 0.12 °C/min ramp in a 10% ozone flow to ensure the removal of residual ethylene diamine groups and to reduce the gold.

Grafting 3-aminopropyltriethoxysilane onto gold loaded silica and coating with GO

A gram of the above gold loaded silica was added to 150 mL ethanol and stirred at 400 rpm for 1 h before 10 mL of 3-aminopropyltriethoxysilane (~40 mmol) was introduced. This mixture was allowed to stir for 24 h at room temperature before being centrifuged and washed 3 times with ethanol. Finally this catalyst was filtered and vacuum dried. Nano-GO was wrapped onto the surface according to the procedure described in Section 4.2.

Results and Characterization

Many challenges were encountered with this synthesis method. The huge differences between the silica substrates were not thought through in enough detail before this direct translation of a small gold deposition from another group member. The 10x difference in surface area between the silica supports had a huge impact on the adsorption of gold onto the surface. Additionally having the extra synthesis steps to add amine and the GO to the surface each introduced an additional opportunity for gold to be lost from the silica surface.

The small surface area was a factor in the large particle size of the deposited gold. The nanoparticles had an average size that was measured to be 9.4 ± 3.9 nm. Initially the theoretical gold loading calculated by the total amount of gold added in the first adsorption step was 1 wt% however the samples prepared as detailed in this section had a final gold loading of less than 0.05 wt% as determined by ICP. Large particle size and low weight loading make this a very unattractive synthesis avenue going forward.

4.3.3. Gold chloride

More digging into the literature[117] revealed that indeed small (6-8 nm) gold can be deposited onto Stöber or other large non-porous silica spheres. Research conducted by Phonthammachai and White[117] showed that residual ammonium from the Stöber silica synthesis method was a key component in keeping the gold particle size small and the loading high. The two major deviations from this literature synthesis procedure were the surface area of the silica spheres (0.2 μm vs 1.5 μm diameters) and free ammonium vs amine charged species. Experiments were planned to investigate if an amine could act similarly to the residual ammonium and help to keep gold nanoparticles small (less than 5 nm).

Depositing HAuCl_4 onto 3-APTES decorated Stöber silica

3-APTES was reacted with 1.5 micron Stöber silica as described in Section 4.2 as the synthesis for $\text{NH}_2\text{-SiO}_2$. Three g of $\text{NH}_2\text{-SiO}_2$ and 15 mL ethanol was added to a 20 mL vial and bath sonicated for 30 min. In a 500 mL flask gold (III) chloride hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was added to 300 mL of DDI water and the pH of this solution was adjusted to pH=7 by dropwise addition of a 0.1M ammonium hydroxide (NH_4OH) solution. The amount of HAuCl_4 added was calculated based on a theoretical loading (if all of the gold deposited onto the silica) of 0.5 wt%, 1 wt%, or 3 wt%. The 500 mL flask was then placed into a 65°C oil bath stirring at 600 rpm and the temperature allowed to equilibrate for 10 min. The $\text{NH}_2\text{-SiO}_2$ suspended in ethanol was then quickly added to the 500 mL flask and this mixture was allowed to stir in the oil bath for 15 min. The flask was then removed from the oil bath and the mixture was centrifuged and re-suspended in water 3 times to remove any un-deposited gold and also to remove residual NH_4OH . The sample was then vacuum dried overnight. For coated samples, GO was added according to the

procedure described in Section 4.2 and the gold was reduced by heating to 150°C with a 0.12°C/min ramp in an O₂ flow.

Results and Characterization

Particle Size Dependence

Three different theoretical gold loadings, 0.5 wt%, 1 wt%, and 3 wt%, were investigated for their impact on final gold loading and particle size. After the samples were calcined in O₂ they were analyzed with TEM and ICP. The synthesis for each of these samples was identical except for the amount of gold and ammonium hydroxide as detailed above. The lower theoretical weight loadings resulted in smaller gold particles sizes that were below the less than 5 nm diameter target. A 0.5 wt% theoretical loading was chosen because the increase from 0.5 to 1 wt% resulted in only a small incremental increase in actual gold loading. Table 7 details these results.

The hypothesis that a GO coating could be used to keep the AuNP size smaller and/or more monodisperse was also tested by comparing Au particle size in samples where HAuCl₄ was deposited onto 3-APTES decorated Stöber silica and performing thermal treatment prior to or after GO wrapping. The gold particle size was not impacted by the addition of a GO coating prior to this thermal reduction. Section 4.5.2 also details the investigation to see if the coating could help reduce the growth of the particle size after a reaction cycle. The gold loading possibly was reduced because of the additional processing step. However the statistical significance of that difference has not been evaluated. These results are summarized in Table 7.

Table 7. Comparison of different theoretical gold loading amounts impact on AuNP size and actual weight loading

Sample	TEM (nm)	ICP
	Particle Diameter	Au (wt%)
0.5 wt% Au-NH ₂ -SiO ₂	4.1 ± 1.3	0.09
0.5 wt% Au-NH ₂ -SiO ₂ -GO	4.5 ± 1.1	0.07
0.5 wt% Au-SiO ₂	3.7 ± 1.7	NM
1 wt% Au-NH ₂ -SiO ₂	5.8 ± 0.9	0.10
3 wt% Au-NH ₂ -SiO ₂	10.77 ± 5.2	0.95

4.3.4. Characterization of Materials

Gold Particle Size

The three synthesis methods that were investigated, 1) polymer wrapped AuNPs, 2) ethylene diamine gold, and 3) gold chloride, resulted in differing gold particle sizes. The polymer wrapped AuNPs consistently had the smallest particle size at 3.1 ± 0.6 nm. However because these nanoparticles were coated in polymer/silica this synthesis method was abandoned. The ethylene diamine method resulted in the largest particles of the three methods with an average size of 9.4 ± 3.9 nm. This method did remove the polymer/silica coating obstacle but the size and large standard deviation were sub-optimal. The third and final method, gold chloride, gave a particle size with an average diameter of 4.1 ± 1.3 nm and did not need a polymer/silica coating to keep the particle size small. Figure 14 shows TEM imaging results from each preparation method.

One hypothesis on the GO coating's impact was that the wrapping could help to keep the AuNP size small and monodispersed. TEM analysis showed that GO did not impact the size of the resulting NP. The NP diameter for samples that were wrapped with GO before (4.5 ± 1.2 nm)

or after (4.1 ± 1.3 nm) the thermal treatment to reduce the gold were statically the same, see Table 8.

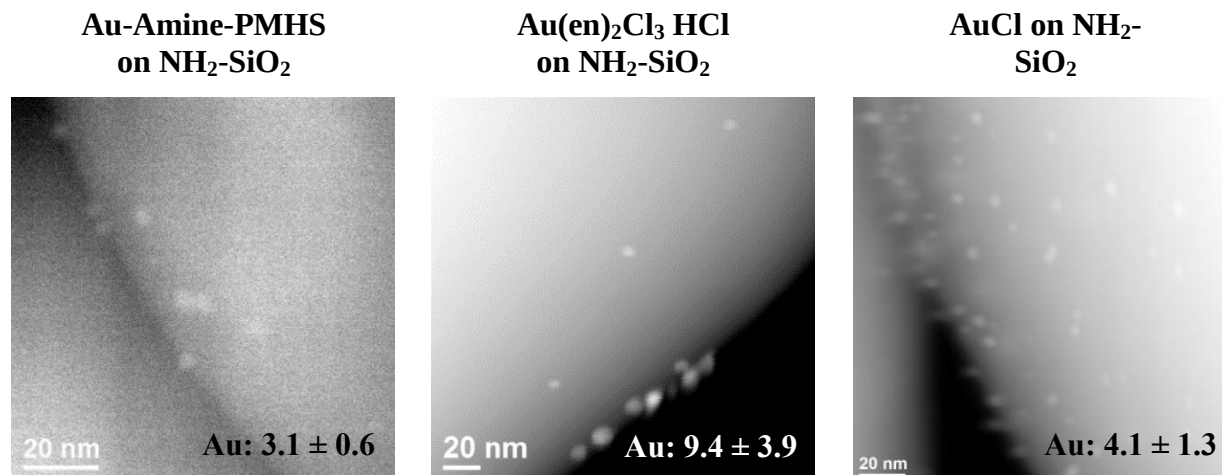


Figure 14. Comparison of TEM images showing the three explored synthesis methods for producing small AuNPs on a Stöber silica surface.

GO Sheet Thickness and Shape

The GO coating on the silica substrate was very difficult to characterize. Single layer GO is very nearly transparent and difficult to image with traditional spectroscopy instruments, SEM and TEM. In order to determine the nature of and how many layers of GO were wrapped and how the sheets were arranged around the silica sphere a multi-characterization approach using TGA and AFM was applied.

First, it was necessary to determine that the nano-GO and/or probe-GO was single layer in suspension by exposing the suspensions to amine decorated mica to mimic the amine decorated silica. AFM analysis determined that the thickness of the GO samples was ~ 1 nm, see Figure 15. AFM samples were prepared by dip coating a diluted GO sample onto aminosilane functionalized mica. This characterization method cannot be used to directly correlate the AFM

preparation to the catalytic sample, however knowing that the starting GO sample was single layer is an essential first step. The average number of GO layers on the sample surface was determined by measuring the sample weight loss with TGA when GO was combusted off of the sample. The theoretical weight loss for a sample where the 1.5 micron silica particles are wrapped with a single layer of GO was calculated to be between 0.16%-0.22%, depending on the carbon/oxygen ratio. The $\text{NH}_2\text{-SiO}_2\text{-GO}$ sample was analyzed using TGA and after adjusting for the weight loss contribution from burning off the amine groups, condensation of silanols, and water in the silica the weight loss was measured to be 1.2%, about 6x the theoretical amount. The source of discrepancy between the measured and theoretical amounts could be because there was more than a single layer of GO coating the surface. Another possible contributing source was the unknown amount of water adsorbed on the hydrophilic GO layer.

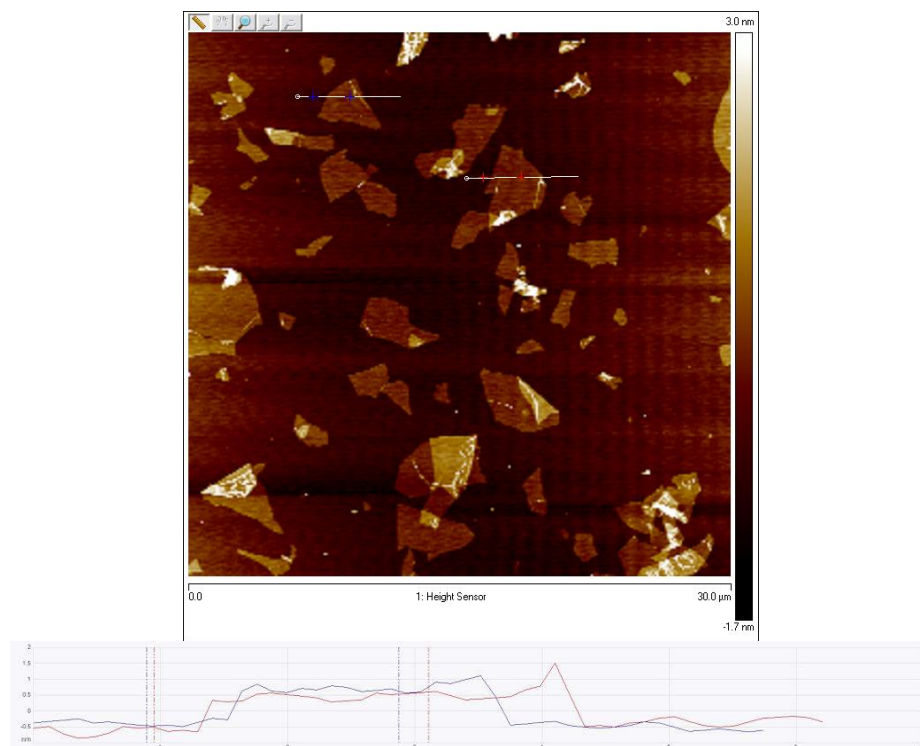


Figure 15. Atomic Force Microscopy image showing single layer GO

Since the quantitative amount of GO on the surface could not be determined, SEM and TEM were used to get a qualitative look at how the GO sheets were laying on the surface. Resolution of the surface of the coated particle with SEM was performed by first coating the sample with osmium. Single layer graphene is optically transparent so adding a 5 nm osmium coating helped reduce surface charging and provided details of the surface morphology. SEM could not be used to determine the thickness of the coating but could provide information on the folding and overlapping of the sheets on the surface.

The possibility of the GO overcoat concurrently being reduced during the thermal reduction of gold was investigated with XPS analysis. If the GO was being reduced during this step the oxyginate functionalities on the overlapping sheets could be condensing and forming covalent bonds. This bond formation could increase the stability of the coating linking nearby sheets together, forming a more complete coating. XPS analysis of samples that were wrapped

with GO after the thermal treatment to reduce the gold retained a higher percentage of C-O and C=O bonds compared to samples that were first wrapped with GO then thermally treated, see Table 8 and Figure 16. Determination of whether or not this reduced GO wrapping imparted more strength/stability to the coating was challenging since it's difficult to use spectroscopic characterization techniques to show increased stability of the GO coating. An experiment to visually image the change was explored.. If during the reduction a more complete spherical coating was produced then if the silica support was etched out what's left should be a hollow sphere of GO. A small amount of Au-NH₂-SiO₂-GO was added to a 10 wt% hydrofluoric acid (HF) solution and was left at room temperature overnight. The material was then filtered through a 0.2 μ polyethersulfone (PES) membrane and washed with water until the filtrate was free of fluoride ions (tested with fluoride test strips). The remaining GO material was collected from the filter with water and visualized with SEM and TEM (see Figure 17). The images revealed that the GO did not form a complete shell wrapped around the silica sphere. The GO was crumpled and decorated with larger gold nanoparticles (average diameter: 8.5 nm) although in some parts of the sample the GO had retained the partial shape of the silica sphere (see Figure 17b).

Table 8. XPS analysis showing impact of wrapping Au catalyst with GO before or after thermal treatment to reduce the gold.

Solvent	C1s XPS (percentage)			AuNP diameter (nm)
	C-C and C=C	C-O	C=O	
Au reduced-GO	47.4	40.3	12.4	4.1 $\pm$ 1.3
GO-Au reduced	54.3	35.3	10.4	4.5 $\pm$ 1.2

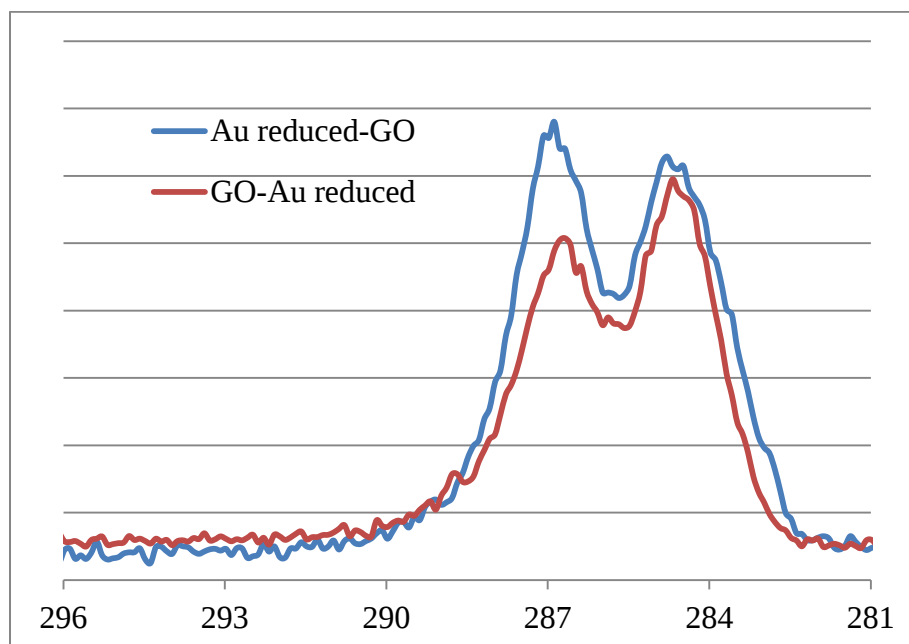


Figure 16. XPS C1s peak comparison of Au catalysts thermally treated before or after being wrapped with GO.

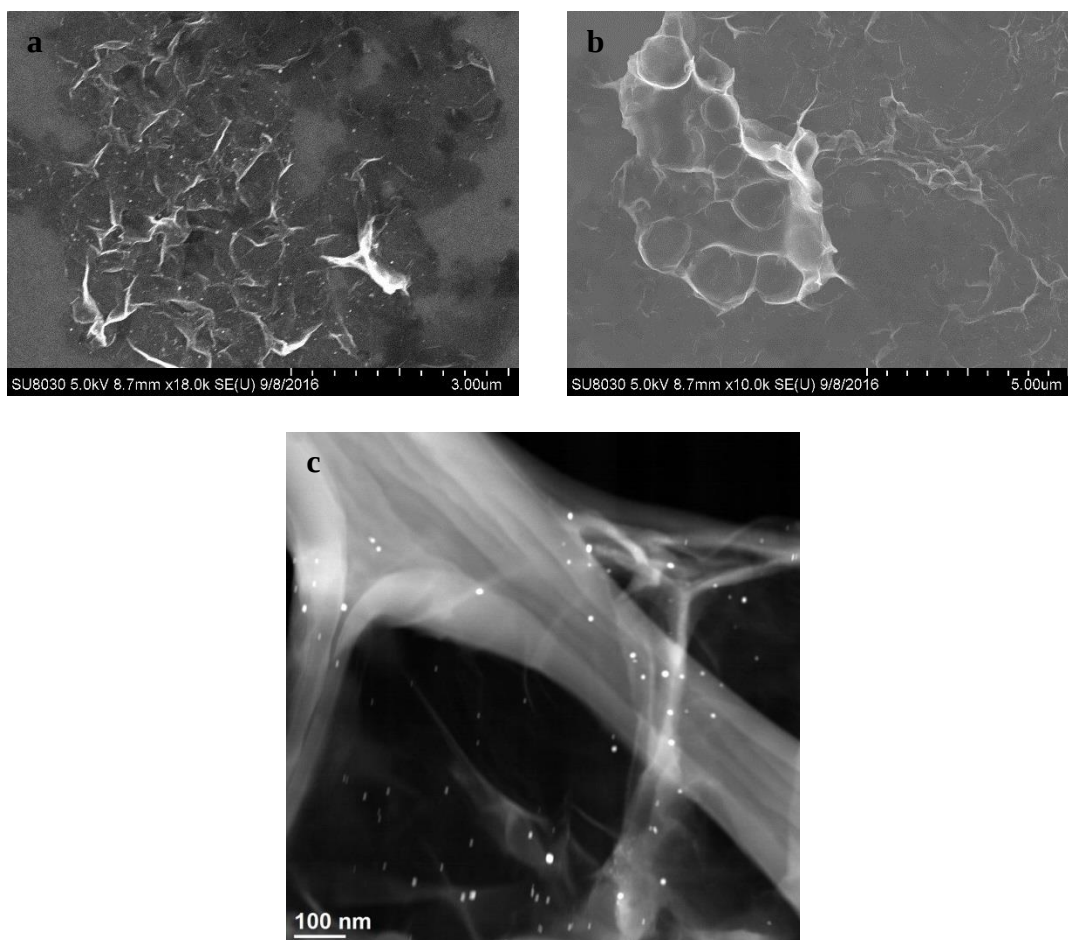


Figure 17. Spectroscopic images of an Au-NH₂-SiO₂-GO sample in which the silica is etched out with hydrofluoric acid. **a-b)** SEM **c)** TEM

GO Coating's Impact on Au Oxidation

The graphitic regions on GO are known to be highly electron conductive and have the ability to participate in electron donation or withdrawal. The reduction of gold ions can be influenced by its environment. XPS was used to make comparisons of the Au4f signal in samples that were made with and without GO to determine if the GO coating could influence the degree of gold reduction. The sample in which the GO coating was added after calcination in oxygen is labeled *Au-NH₂-SiO₂-GO Au reduced after GO*. The XPS results, which are shown in Figure 18, show that in this system the GO did not have a drastic impact on the gold oxidation state. All

samples showed a dominate Au(0) peak at ~84 eV whereas if there was residual gold ions a positive shift would be expected.

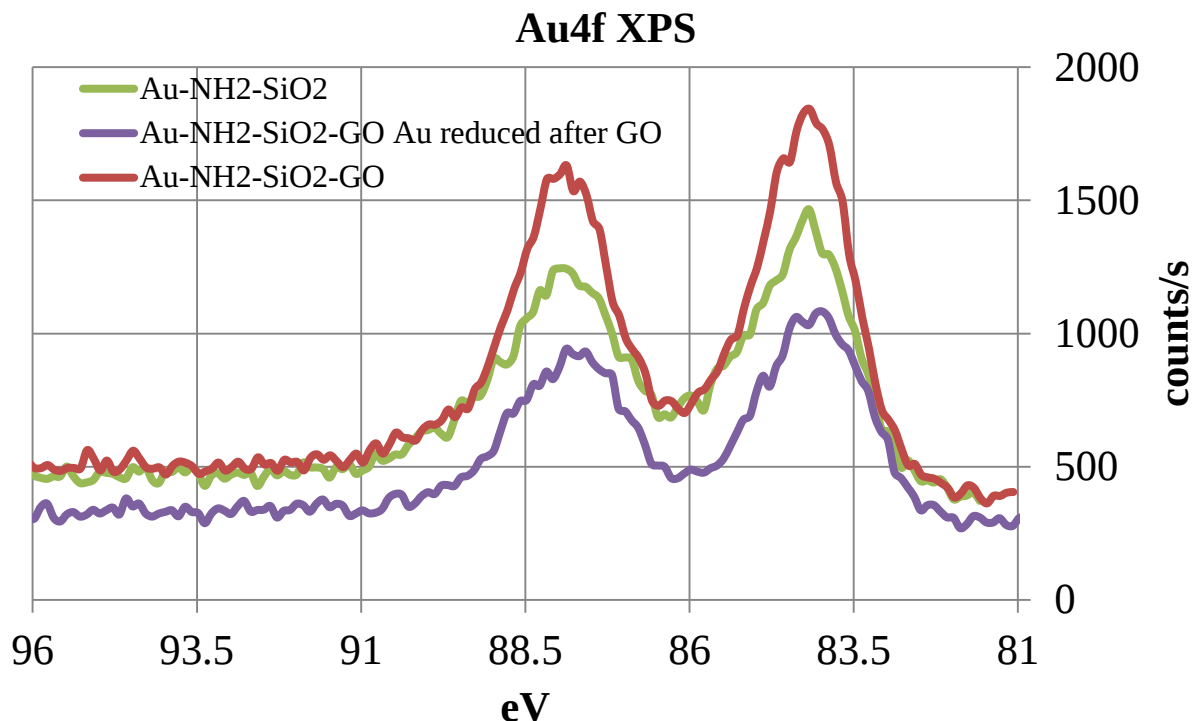


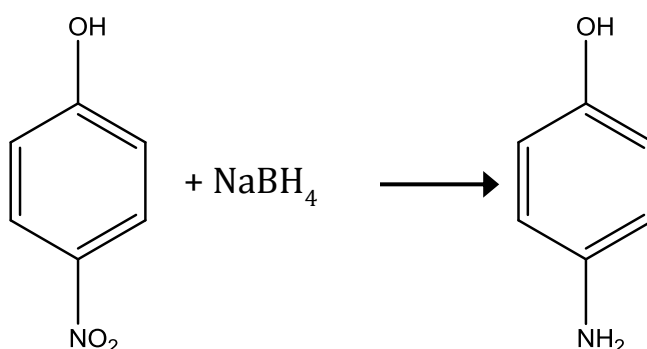
Figure 18. Au4f XPS signal comparing the gold oxidation state of catalysts and the influence of a GO coating.

4.4. Catalytic Testing & Results

4.4.1. Reduction of p-Nitrophenol

The reduction of p-nitrophenol (4-NP) (see Reaction Scheme 1) was chosen as a probe reaction to compare GO coated and uncoated catalysts because it has been extensively studied in academic literature and because it's a relatively fast reaction. The catalytic active site for this reduction reaction with a gold catalyst is generally agreed upon in literature to be at the surface of a small gold nanoparticle. However poisoning experiments conducted by Nigra et al [118] pointed to very small amount of dissolved gold species as the active site and that the ligand on the dissolved gold can influence the kinetics and induction time, thus the hypothesis that GO can

prevent NP leaching could also be tested. When the reaction rate is modeled as a Langmuir-Hinshelwood mechanism the active site is the surface of the nanoparticle and the rate limiting step is the reaction between hydrogen on the AuNP surface and adsorbed 4-NP. Diffusion of the reactants to and from the AuNP surface is fast in comparison to the reaction step. Therefore, this reaction could be used to investigate if a GO coating could prevent or slow down the adsorption of the reactants to the surface of the NPs.



Reaction Scheme 1. Reduction of 4-nitrophenol with sodium borohydride to form 4-aminophenol.

The reduction of 4-NP was carried out by mixing a sodium borohydride solution (final concentration of $6.67 \times 10^{-3} \text{M}$) with a 4-nitrophenol solution (final concentration of $1 \times 10^{-4} \text{M}$) and then either Au-NH₂-SiO₂ or Au-NH₂-SiO₂-GO was added (holding the gold concentration at $6.25 \times 10^{-7} \text{M}$). The reaction mixture was stirred at 1000 rpm and small liquid aliquots were taken at predetermined time points for UV-vis analysis by extracting 0.5 mL of reaction mixture, filtering the solid particles off and rinsing the filter with 2.5 mL water. In-situ UV-vis measurement could not be completed because the silica particles cause a significant amount of scattering. The reaction was monitored by following the disappearance of the 4-NP UV-vis peak at 400 nm and the appearance of a 4-aminophenol peak at $\sim 300 \text{ nm}$.

The reduction happened quickly for both the GO coated catalysts as well as the uncoated sample and typically went to near completion within 60 min. In all trials with gold the concentration of 4-NP dropped significantly within the first minute. Initially the explanation for this drop was thought to be due to 4-NP adsorbing onto the surface of the silica catalyst or via π - π stack onto the GO coating, thus being pulled out of the reaction mixture. However samples without gold (both $\text{NH}_2\text{-SiO}_2$ and $\text{NH}_2\text{-SiO}_2\text{-GO}$) were tested and this drop in concentration was not observed and no reaction took place even after 2 hours of stirring. So the initial reaction rate of these catalysts was concluded to be true to the measured concentration of 4-NP.

Figure 19 shows UV-vis data for an $\text{Au-NH}_2\text{-SiO}_2\text{-GO}$ catalyst. The UV-vis peak at 400 nm was ascribed to the formation of the 4-nitrophenolate ion, which formed after adding NaBH_4 to the 4-NP solution. The peaks that were formed as time proceeded at 298 nm and 231 nm were attributed to the formation of 4-aminophenol. Comparing data from reactions with coated or non-coated catalysts did not show a significant difference between catalysts.

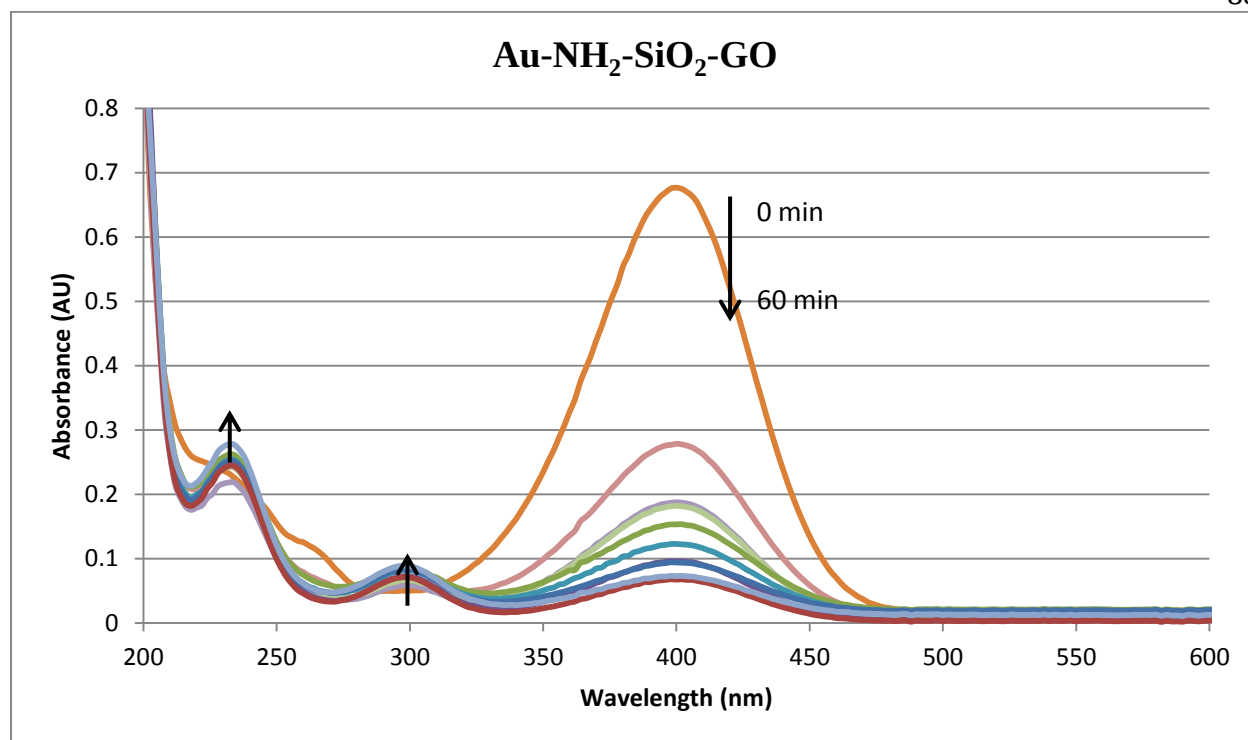


Figure 19. UV-vis reaction data for the catalytic reduction of 4-nitrophenol to 4-aminophenol using an Au-NH₂-SiO₂-GO catalyst. 4-nitrophenol: 400 nm; 4-aminophenol: 298 nm and 231 nm.

Unfortunately due to the experimental challenges of not being able to conduct the reaction with in-situ UV-vis it could not be definitively concluded whether or not there was a catalytic difference between the two Au catalysts. One of the things that contributed to not being able to perform in-situ analysis during the reaction was that the large silica particles were difficult to keep suspended and homogeneously dispersed. Various reactor sizes and stirring speeds were investigated but settling of the catalyst to the bottom of the reactor was always a challenge. Another challenge was that the GO wrapped samples have a different surface tension with water and getting the Au-NH₂-SiO₂-GO sample to suspend into the aqueous reaction mixture took longer than the samples without GO and thus the true reaction kinetics are hard to

measure because the GO coated catalyst sat on top of the reaction liquid for longer and thus wasn't added at exactly at time equal to zero. During one trial the gold catalyst was added to the 4-nitrophenol solution prior to the addition of sodium borohydride in an attempt to incorporate the catalyst into the reaction liquid prior to time equal to zero and no difference in catalytic rate was observed. During these trials the reaction was determined to be first order with a rate constant of 0.06 min^{-1} for both catalysts (see Figure 20).

In order to determine if gold was leaching from the silica supports, the reaction was allowed to proceed with a solid catalyst present for 40 min and then the reaction liquid was filtered through a 0.22micron filter to remove the solid catalyst and added to a fresh reaction mixture of 4-NP and NaBH_4 . Reactions using filtrate (from reactions using both coating and uncoated Au) as the catalyst did not proceed even after extended reaction time up to 2 hours. So if gold was leached from the support, the leached species were not acting as the active site for this reaction. Solid catalysts were not tested for recyclability.

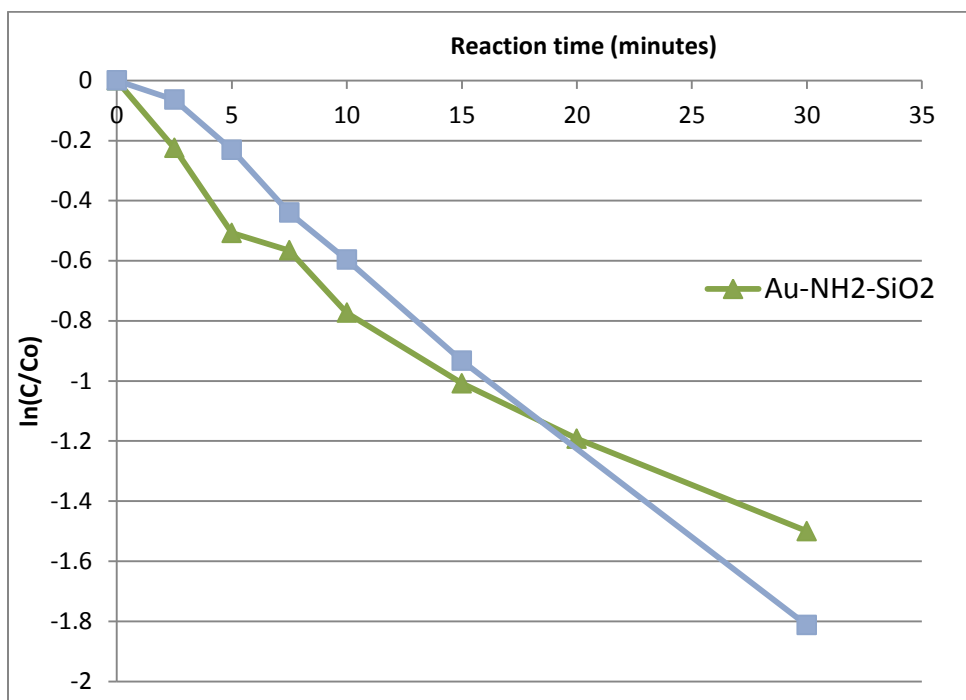


Figure 20. Plot of the natural logarithm of the concentration of 4-NP divided by the initial concentration versus time. The slope of the line is the negative rate constant for a first order reaction.

4.4.2. Cyclohexene oxidation

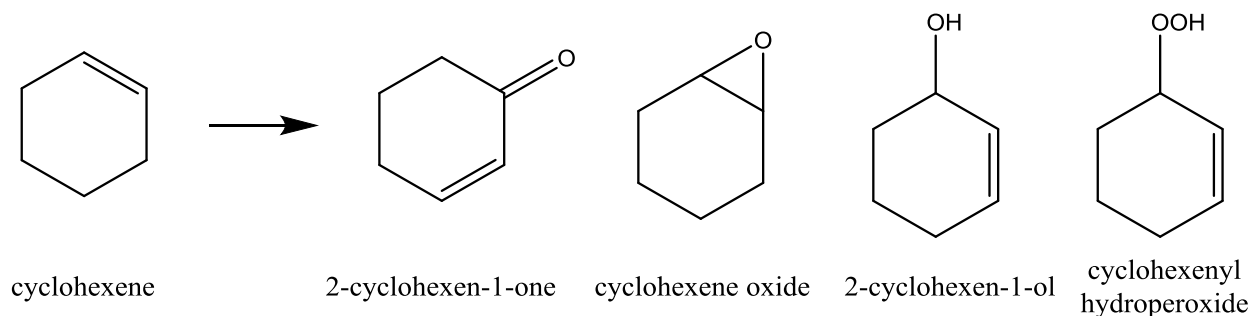
The surface of an AuNP was thought to be the active site for cyclohexene (C₆) oxidation. The reaction activity and selectivity were also thought to be dependent on the AuNP size. Golovko *et al* reported that for cyclohexene oxidation in solvent free conditions supported gold nanoparticles that were less than 2 nm were inactive. However when a sufficient number of larger than 2 nm particles were formed the reaction proceeded. The activity of the catalyst would decrease again when the particles grew to large due to a decrease in the surface area to volume ratio [99]. In the process of assigning the active site to the gold particle surface, researchers usually ignored or don't consider the dissolved/leached gold catalytic contribution. Cyclohexene oxidation reactions using reaction filtrate as the catalyst as opposed to recycled solid catalysts are usually not conducted. Additionally researchers do not address if there was any residual organic

peroxide contamination in the stabilizer free solvent and if this had an impact on the oxidation.

The gold nanoparticles synthesized in this work both with and without a GO coating were larger than 2 nm in diameter. Thus according to precedence from literature should be active for the oxidation of cyclohexene and since as the gold particles grow in size they become less active the GO coating could serve to keep the particle size small and uniform during reaction. In addition to the reactions with the solid catalysts, filtering studies were carried out in order to better identify the contribution from small dissolved gold species.

The catalytic activity of the Au-NH₂-SiO₂-GO versus Au-NH₂-SiO₂ catalysts was tested in solvent free conditions for cyclohexene oxidation without the addition of a radical initiator. Reaction Scheme 2 shows the major products for the cyclohexene oxidation reaction. The reaction was performed in a three-neck glass reactor equipped with a reflux condenser and a fritted gas bubbler. Ten milliliters of stabilizer free cyclohexene, 1 mL decane (as an internal standard), 200 mg of catalyst, and a Teflon-coated magnetic stir bar were added to the reactor. The mixture was stirred at 650 rpm in an oil bath at 60°C. Oxygen was introduced to the system through the fritted gas disperser at a rate of 10 ml/min and the reflux condenser was set to -10°C. The flow rate and condenser temperature were chosen to minimize the evaporative losses of cyclohexene (boiling point 83°C). The evaporative losses, of 0.72 mmol/h, were determined by running the reaction in the absence of catalyst. It is important to note that after extended reaction without a gold catalyst, a small amount of conversion due to radical autoxidation did occur (~2% after 20 h of reaction) and was expected [119]. Additional control experiments were performed using NH₂-SiO₂-GO and NH₂-SiO₂ samples, because GO can act as a catalyst in many oxidation reactions (see section 2.2.2), and no reaction was observed above the baseline autoxidation that were observed when there was no solid catalyst of any kind. Samples of the reaction mixture

were taken through the third-neck of the glass reactor with a syringe equipped with a long needle. The reaction mixture was immediately filtered through a 0.45 μm syringe filter. At the conclusion of the reaction time the reaction was stopped by turning of the O_2 flow to the bubbler and cooling the reactor to room temperature by removing the reactor from the oil bath. The remaining reaction liquid and solid catalyst was syringed out of the reactor and the solid catalyst was removed from the liquid with a syringe filter. When the goal was recovery of the solid catalyst, as opposed to the reaction liquid, the reaction mixture was vacuum filtered, rinsed with 10 mL of acetone, and vacuum dried at room temperature.



Reaction Scheme 2. Cyclohexene oxidation major products

The liquid samples were analyzed by either nuclear magnetic resonance (NMR) spectroscopy or gas chromatography (GC-FID). The reaction solution concentrations were quantified using solutions of reference compounds with known concentrations. The addition of PPh_3 did not change the concentration of 2-cyclohexen-1-one, which implied that the peroxide was not being decomposed during the GC-FID analysis. In studies that were analyzed by NMR the liquid reaction mixture was diluted in deuterated chloroform (CDCl_3) for analysis. The solution concentrations were quantified using the known amount of internal standard (decane). The concentration of cyclohexenyl hydroperoxide was determined by creating a calibration curve by carefully reducing the peroxide with known amounts of triphenylphosphine (PPh_3), see Figure

21. The calibration curve revealed that the amount of mmol of PPh_3 required to reduce the amount of peroxide was not stoichiometric. Titration of the peroxide with PPh_3 revealed that for every mmol of peroxide roughly twice as much PPh_3 is required to reduce the peroxide.

Both $\text{Au-NH}_2\text{-SiO}_2\text{-GO}$ and $\text{Au-NH}_2\text{-SiO}_2$ catalysts were active for cyclohexene oxidation. After reaction for ~ 12 h the selectivity and conversion for coated and uncoated Au catalysts were similar (67% and 65% respectively). The reaction proceeded with both catalysts with no notable induction period (see Figure 22). Additionally, as shown in Table 9, the resulting reaction selectivity was similar for both solid catalysts and when the filtrates of these initial oxidation cycles were utilized as the catalyst for another cyclohexene oxidation cycle again the selectivities were very similar with cyclohexenyl-hydroperoxide as the major product.

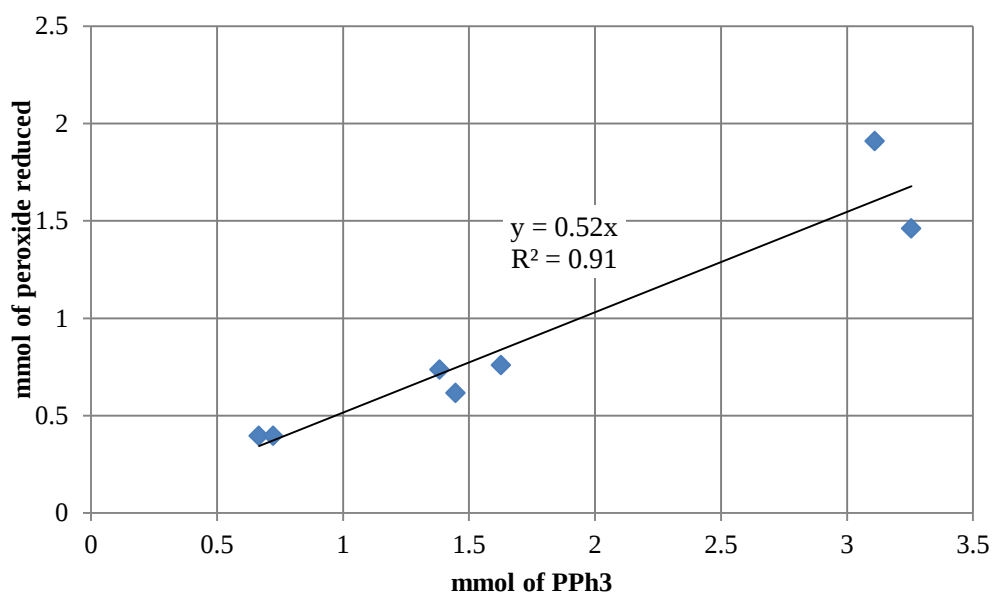


Figure 21. Calibration curve to determine amount of PPh_3 required to reduce the cyclohexenyl-hydroperoxide.

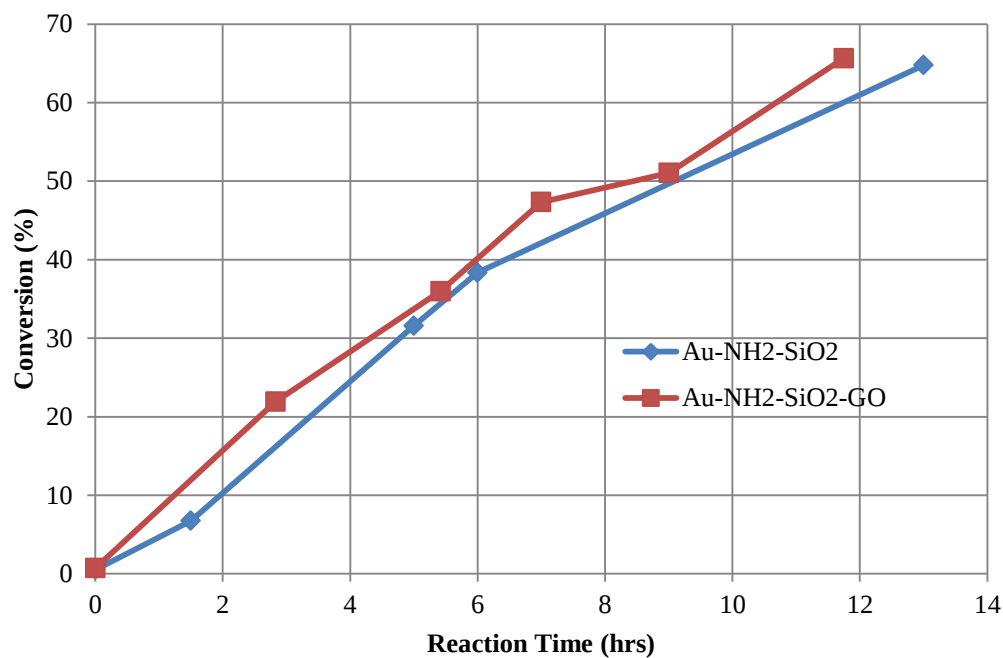


Figure 22. Cyclohexene oxidation conversion data with GO coated and uncoated catalysts.

Table 9. Cyclohexene reaction activity and selectivity data for the GO coated, the uncoated Au catalyst, and the filtrates from each of the solid catalyst. Reaction time for all runs: 12 h.

Catalyst	Conversion (%)	Selectivity (%)			
		Oxide	Ketone	Alcohol	Peroxide
Au-NH ₂ -SiO ₂	65	4	24	19	44
Au-NH ₂ -SiO ₂ -GO	67	5	22	16	53
Filtrate from Au-NH ₂ -SiO ₂	31	6	25	18	38
Filtrate from Au-NH ₂ -SiO ₂ -GO	42	8	25	17	38

In order to separate the oxidation effect of the peroxide from the possible contribution of the dissolved gold, it was necessary to remove the cyclohexenyl hydroperoxide from the reaction filtrate before using the filtrate for subsequent cyclohexene oxidation cycles. ICP of the filtrate

prior to reduction with triphenylphosphine revealed that the concentration of gold in the filtrate was ~14 ppb. The hydroperoxide from 2 mL of reaction filtrate was removed by quantifying the number of millimoles of hydroperoxide in the sample and adding a 1:1 molar ratio of triphenylphosphine. The removal of hydroperoxide was confirmed with a peroxide test strip and by disappearance of the peroxide peak in NMR. Often a slight molar excess of triphenylphosphine was needed to completely reduce the peroxide. The consumption of the triphenylphosphine by reaction with the peroxide was tracked with ^{31}P NMR. As the peroxide was reduced the triphenylphosphine was oxidized to triphenylphosphine oxide. Triphenylphosphine oxide was not as soluble in cyclohexene as PPh_3 and precipitated out of solution at room temperature; however warming the sample to reaction temperature (60°C) did allow the triphenylphosphine oxide to redissolve. After full removal of the hydroperoxide from the 2mL filtered reaction media, 8 mL of fresh cyclohexene and 1 mL of decane were added for a new reaction cycle. After reaction for 16 hours the reactor was cooled to room temperature and the mixture was analyzed for reaction products. When the hydroperoxide in the filtered reaction mixture was completely reduced with PPh_3 and used as a catalyst for further cyclohexene oxidation cycles it did not make a difference if the filtrate was from GO wrapped or unwrapped catalysts as both filtrates showed no further reaction activity. The complete elimination of catalytic activity of the dissolved gold for the cyclohexene oxidation reaction could be for two reasons: 1) the active site is, in fact, at the surface of the gold nanoparticle or 2) the phosphine ligands strongly complex with the dissolved gold thus making them inactive as catalysts.

In order to understand the role the triphenylphosphine plays in reducing catalytic activity, the hydroperoxide was only partly reduced and the amount of catalyst from filtrate was varied (see Table 10). When the total amount of gold was held constant (Rxn A and Rxn C) but the total

amount of hydroperoxide remaining was varied, the cyclohexene oxidation conversions were very similar after 16 h. However if the amount of gold was doubled and the remaining number of millimoles of hydroperoxide in the reaction mixture was held constant, the conversion for the reaction with doubled gold content was approximately half of the conversion when there was less gold. This is thought to be a result of the increased amount of PPh_3 needed to achieve similar levels of remaining hydroperoxide. There was much less PPh_3 per gold in Rxn C and the increased PPh_3 needed in Rxn B might ligate to more of the active gold. Still even with these comparison reactions, the contribution from the autoxidation versus the contribution from dissolved gold was difficult to parse.

Table 10. Cyclohexene oxidation reactions varying the gold and hydroperoxide content.

	Rxn A	Rxn B	Rxn C	Rxn D
ng/mL Gold	2.8	5.5	2.8	5.5
mmol PPh_3	1.3	3.3	0.7	4.8
mmol of peroxide remaining	1.0	1.5	1.5	0
Conversion (16 h)	9.0%	5.5%	10.8%	0%
Selectivity to oxide	1.3%	-	1.4%	-
Selectivity to alcohol	29.6%	15.7%	31.6%	-
Selectivity to ketone	37.2%	38.6%	36.2%	-
Selectivity to peroxide	31.9%	45.7%	30.8%	-

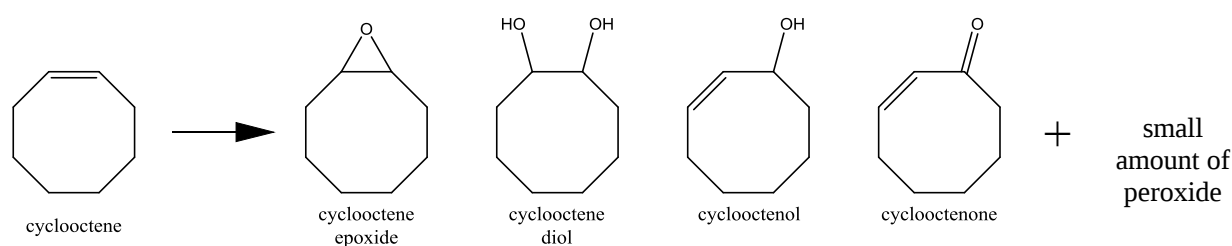
In conclusion, we were not able to contradict the established notion that the catalytic active site for the oxidation of cyclohexene is the surface of the gold nanoparticle. However there is convincing evidence that the PPh_3 acts to remove some of the dissolved Au from the reaction system, thus altering the activity and selectivity. More analysis is needed to understand this

balance between PPh_3 as a reductant and as potential ligand to dissolved Au. If the hydroperoxide species was reduced by some other species that doesn't interact with the dissolved gold that would be an interesting comparison.

4.4.3. Cyclooctene oxidation

Gold nanoparticles can also be used for the oxidation of cyclooctene (C8) using molecular oxygen under solvent-free conditions without the addition of a radical initiator [98]. The active site for a long time was thought to be on the surface of the gold nanoparticle. It was also thought that radical initiator (usually TBHP) was necessary, possibly with a multifaceted role that included cleaning the active sites and establishing the intermediates (peroxides) that propagate the reaction. Recent studies have shown another possible key role, which was to offset the role of the peroxide stabilizer that is usually added to stock cyclooctene solutions; i.e. if this stabilizer is no longer present the initiator is not necessary for the induction of the reaction[98]. Additionally new results from the Kung research group have shown that the active site for this oxidation reaction is small dissolved gold clusters and not on the surface of the nanoparticle[100]. In cyclooctene oxidation reactions run by the Kung group with gold nanoparticles supported on silica as the catalyst under solvent and initiator free conditions with molecular oxygen, an induction period was observed which was attributed to the time it took to dissolve gold from the surface of the nanoparticle. In these reactions, selectivity was greater than 80% for cyclooctene epoxide when conversion reached ~50%.. At the completion of this reaction, the solid catalyst was removed by filtration from the reaction mixture. Triphenylphosphine was used to reduce any trace cyclooctene hydroperoxide and then this filtered reaction product was used as a catalyst in subsequent reaction trials. In reactions using filtrate as the catalyst the induction period was eliminated and again selectivity for the epoxide

was greater than 80% with a conversion greater than 50% after 10 h. It was determined via ICP-MS and fluorescence spectroscopy that the amount of gold that was being leached off of the solid nanoparticles into the reaction mixture was around 30 ppb and that the gold clusters were typically in the range of 6-8 atoms large. The GO coated catalysts synthesized in this work along with their respective reaction filtrates were also tested for cyclooctene oxidation and the results are described below.



Reaction Scheme 3. Cyclooctene oxidation major products

Au-NH₂-SiO₂-GO and Au-NH₂-SiO₂ solid catalysts were both explored for cyclooctene oxidation. The catalytic oxidation of cyclooctene was performed under solvent free conditions without the addition of a radical initiator. Stabilizer free cyclooctene was prepared in small batches (50 mL) from a commercially available cyclooctene with stabilizer solution. Fifty milliliters of cyclooctene with stabilizer was washed twice with 50 mL of a 3M potassium hydroxide solution, and twice with 50 mL DDI water and each time the aqueous layer was removed with a separation funnel. The cyclooctene was then dried overnight with sodium sulfate and finally distilled with the first and last 5 mL fractions discarded.

The cyclooctene oxidation reaction was performed in a three-neck glass reactor equipped with a reflux condenser and a fritted gas bubbler. Ten milliliters of stabilizer free cyclooctene, 1 mL decane (as an internal standard), 200 mg of catalyst, and a Teflon-coated magnetic stir bar were added to the reactor. The mixture was stirred at 650 rpm in an oil bath at 100°C. Oxygen

was introduced to the system through the frit at a rate of 30 ml/min and the reflux condenser was set to -10°C . The flow rate and condenser temperature were chosen to minimize the evaporative losses of cyclooctene (boiling point 145°C - 146°C). The evaporative losses, of 0.08 mmol/h, were determined by running the reaction in the absence of catalyst. Samples of the reaction mixture were taken through the third-neck of the glass reactor with a long needle and syringe. The reaction mixture was immediately filtered through a $0.45\ \mu\text{m}$ syringe filter. At the conclusion of the reaction time the reaction was stopped by turning off the flow of oxygen and cooling the reactor to room temperature by removing the reactor from the oil bath. The remaining reaction liquid and solid catalyst was collected and the solid catalyst was removed from the liquid with a syringe filter. Induction times for both catalysts was monitored closely to observe if the GO coating would cause an increase in induction time, which would be indication that the coating was able to reduce or at least slow down metal leaching into the reaction mixture. However, no difference in induction time was observed (see Figure 23) and both coated and uncoated catalysts were active for the reaction with a selectivity that was greater than 90% for cyclooctene epoxide and a conversion of 77% and 85% respectively after 24 hours (see Table 11). Additionally control experiments were performed using Au free- $\text{NH}_2\text{-SiO}_2\text{-GO}$ and $\text{NH}_2\text{-SiO}_2$ samples, because GO can act as a catalyst in many oxidation reactions (see section 2.2.2) and there was no reaction above the baseline autoxidation that was observed when there was no solid catalyst of any kind.

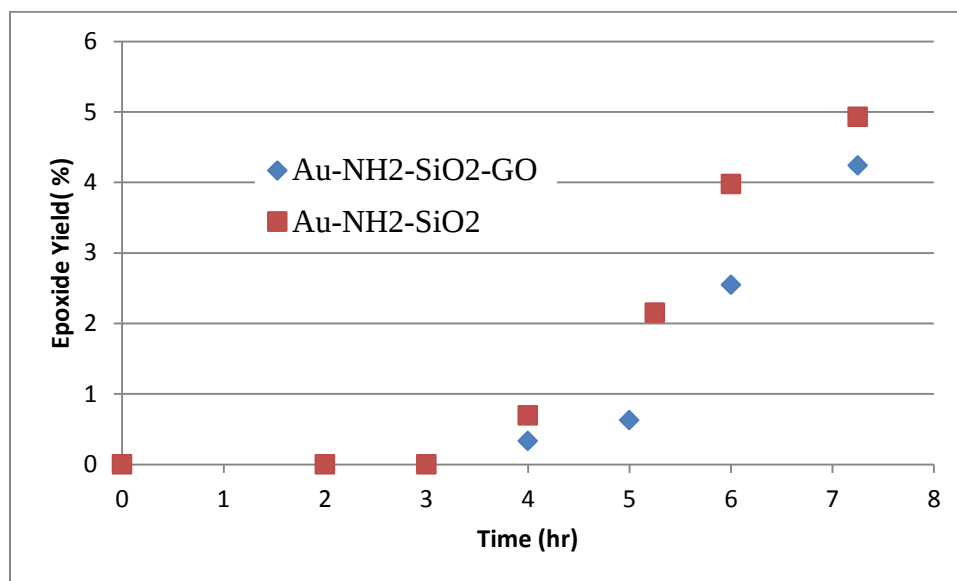


Figure 23. Investigation of differences in induction time by looking at cyclooctene epoxide yield for GO coated and uncoated catalysts.

As described above, at the conclusion of the reaction the solid catalyst was removed by filtration and the filtrate was explored as a catalyst. A small amount (50 mg, ~ 0.2 mmol) of PPh_3 was added to ensure complete reduction of any residual cyclooctenyl hydroperoxide in the system. A careful study to compare the induction time for the reactions using filtrate as the catalysts was not performed. Both coated and uncoated catalytic reaction medias (GO-C8F-R and C8F-R respectively), when the solids were removed the filtrate could be reused as a catalyst (conversion after 24 hours for both systems was around 90%, see Table 11) without the solid. These filtrate catalyst were more active than the solid catalyst for cyclooctene oxidation, presumably because an induction period is not required as the active species had already built up in the system and reaction began immediately. These results corroborated the previous findings of the Kung group that the active site for this reaction system is dissolved gold and the induction period observed while using solid catalysts is necessary for the dissolved gold to build up in the reaction media.

Table 11. Comparison of cyclooctene oxidation results using solid and filtrate catalysts after 24 hours of reaction.

Catalyst	Conversion	Cyclooctene Epoxide Selectivity
Au-NH ₂ -SiO ₂	85.2%	90.4%
Au-NH ₂ -SiO ₂ .GO	76.8%	92.3%
C8F-R	91.8%	85.6%
GO-C8F-R	91.3%	79.8%

4.4.4. Filtrate cross reactions

The new assignment of the active site in the oxidation of cyclooctene prompted a study to try to verify that the active site for the oxidation of cyclohexene was truly the nanoparticle surface. Identification of the active site for cyclohexene oxidation has been investigated in literature [97, 99] and researchers have tried to work to rule out the contribution from intermediates and cyclohexenyl hydroperoxide and concluded that the surface of the nanoparticle must be the active site. In this work, solvent and initiator free cyclohexene oxidation was performed with both GO coated and uncoated Au catalysts (see section 4.4.2). Results showed that the GO coating did not impact reaction selectivity or activity and did not aid in more definitively elucidating the role of dissolved gold as a catalyst for cyclohexene oxidation. ICP-MS results did show that gold was removed from the solid catalyst in both the cyclooctene and cyclohexene reaction systems. The challenges for uncovering the role of dissolved gold for cyclohexene oxidation included the high yield of cyclohexenyl -hydroperoxide and the difficulty of reducing the hydroperoxide without also possibly ligating the dissolved gold with the reductant (PPh₃). In the cyclooctene system the hydroperoxide species yield was very low so very little (or none at all) reductant was needed to remove the autoxidation peroxide species. Knowing that dissolved gold is active for cyclooctene oxidation and the autoxidation species are

minimal in the final reaction mixture the dissolved gold in the filtrate from the cyclooctene reaction was investigated as a possible catalyst for cyclohexene oxidation. Additionally the filtrate from cyclohexene oxidation was probed as a catalyst for cyclooctene oxidation.

Cyclohexene oxidation experiments using cyclooctene filtrate (2 mL) were performed using the procedure described in Section 4.4.2. The cyclooctene filtrate was analyzed with NMR and hydroperoxide test strips to determine if residual autoxidation species were present prior to being utilized as a catalyst. When cyclooctenyl hydroperoxide was present a small amount (50 mg, ~ 0.2 mmol) of PPh_3 was added to reduce these species until the hydroperoxide test strips showed no detectible levels of hydroperoxide. Table 12 shows that selectivity for cyclohexene oxidation was similar for both solid ($\text{Au-NH}_2\text{-SiO}_2$) and C8 filtrate (C8F-R) catalysts. Conversion was higher with the solid catalyst, presumably because there was more catalyst in the system. No C6 oxidation occurred when the filtrate from a C6 reaction (C6F-R) was used as a catalyst after all of the hydroperoxide species had been reduced with PPh_3 . These results show that a solid catalyst is not necessary and that the dissolved gold can be the active site for this C6 oxidation system.

It is still unclear what form the dissolved gold must be in for it to be catalytically active for C6 oxidation. Experiments conducted on C8 oxidation with dissolved gold catalysts by other Kung group members indicated that 1,2-cyclooctanediol could be an important player in stabilizing the dissolved gold clusters since its addition resulted in a more catalytically active catalyst. Even when a hydroperoxide reducing agent was present the gold in C8 oxidation systems remained active. Is the gold in C6 oxidation systems not stabilized enough to keep PPh_3 from replacing its solvent stabilizing environment and becoming a ligand? Experiments to investigate whether 1,2-cyclooctanediol could stabilize the gold in a C6 oxidation environment

were conducted by adding 1,2-cyclooctanediol in a ratio of ~1000:1 (1,2-cyclooctanediol:gold) to 0.5 mL of filtrate from a cyclohexene oxidation reaction that was collected from a reaction in which an Au-NH₂-SiO₂ solid catalyst was used. The filtrate with the 1,2-cyclooctandiol addition was allowed to stir at room temperature for 1 hour before PPh₃ was added to reduce the hydroperoxide species. After complete reduction of the peroxide 1 mL of decane and either 9.5 mL of fresh cyclohexene or cyclooctene was added and the reaction performed as described in sections 4.4.2 or 4.4.3, respectively. This diol stabilized and reduced filtrate catalyst (C6F-diol-R) was inactive as a catalyst for cyclooctene oxidation; no reaction took place after 16 hours. A small amount of conversion for cyclohexene oxidation using this diol stabilized (C6F-diol-R) catalyst was observed and Table 12 shows that the selectivity was different compared to reaction results using a solid or cyclooctene filtrate as a catalyst. This small amount of conversion could also be the result of autoxidation after extended reaction time; a conversion of around 2.2% was observed for cyclohexene oxidation without a catalyst after 20 hours. Additionally when this ‘stabilized’ catalyst was used for stabilizer free cyclooctene oxidation no reaction was observed even after an extended reaction time of 24 hours (see Table 13 for comparison to other catalysts used for cyclooctene oxidation).

The reverse cross filtrate reaction, cyclooctene oxidation using filtrate from cyclohexene reactions as the catalyst was also investigated. The catalyst was produced by reducing the hydroperoxide species in 2 mL of filtrate from a cyclohexene reaction with PPh₃ until NMR and peroxide test strips showed no peroxide was present. This catalyst (C6F-R) was added to decane (1 mL), as an internal standard, and stabilizer free cyclooctene (8 mL). The reaction was performed following the protocol for a cyclooctene oxidation reaction using a solid catalyst (see Section 4.4.3). As the cyclohexenyl hydroperoxide was reduced in the cyclohexene filtrate the

triphenylphosphine oxide produced during the reduction began precipitating out of the liquid. Heating the catalyst up to reaction temperature (100°C) redissolved this precipitate. However, even after an extended reaction time of 24 hours no oxidation was observed (see Table 13 for comparison to other catalysts used for cyclooctene oxidation).

Table 12. Comparison of conversion and selectivity for the oxidation of cyclohexene with different catalysts.

Catalyst	Conversion	Selectivity after 16 hours of reaction			
		cyclohexene oxide	2-cyclohexen-1-ol	cyclohexenyl hydroperoxide	2-cyclohexen-1-one
C8F-R	31.8%	1.6%	32.7%	31.5%	34.2%
C6F-R	0%	NA	NA	NA	NA
Au-NH ₂ -SiO ₂	45.8%	2.1%	31.5%	28.1%	38.2%
C6F-diol-R	2.1%	0.9%	21.1%	36.4%	41.6%

Table 13. Comparison of conversion and selectivity for the oxidation of stabilizer free cyclooctene, after 24 h of reaction, with cyclohexene filtrate catalysts versus solid and cyclooctene filtrate catalysts.

Catalyst	Conversion	Cyclooctene Epoxide Selectivity
C6F-R	0%	NA
C6F-diol-R	0%	NA
Au-NH ₂ -SiO ₂	85.2%	90.4%
C8F-R	91.8%	85.6%

4.5. Results and Discussion

4.5.1. Prevention of nanoparticle leaching

Extensive investigation into the use of reaction filtrate as a catalyst for subsequent reaction cycles for cyclohexene and cyclooctene oxidation revealed that the GO coating over the

supported AuNPs was unable to prevent or even slow down metal leaching. The C6 and C8 reactions using filtrate from reactions run using an Au-NH₂-SiO₂ or Au-NH₂-SiO₂-GO solid catalyst had similar conversions and selectivity.

4.5.2. Ability to keep nanoparticles monodispersed

The hypothesis for comparing the catalytic activity and selectivity of the wrapped and unwrapped solid catalysts for cycloalkane oxidation was 1) that the wrapped catalyst could do a better job of keeping the gold particle size from growing after reaction and 2) possibly the GO coating would slow diffusion to the active site on the surface of the catalyst. In order to test hypothesis two, kinetic studies with time points taken every hour for the first 4 hours were taken. After 12 hours of reaction the conversion was 81% for Au-NH₂-SiO₂ and 71% for Au-NH₂-SiO₂-GO. The selectivity for each of the products was similar with the major product in both reactions being cyclohexenyl hydroperoxide. Unfortunately the total amount of gold on the Au-NH₂-SiO₂-GO solid catalyst was not able to be quantified by inductively coupled plasma mass spectrometry (ICP-MS) so the discrepancy in activity could be due to gold losses from the additional synthesis steps needed to synthesize the Au-NH₂-SiO₂-GO catalyst. Solid catalysts were recovered and the gold particle size was analyzed with TEM to test hypothesis one. After 12 h of exposure to reaction conditions the solid catalyst was filtered, rinsed with 10 mL of fresh cyclohexene and then 10 mL of acetone before being vacuum dried at room temperature. Spent Au-NH₂-SiO₂ catalysts had a particle size of 6.7 nm ± 2.7 nm (was 4.1 nm ± 1.3 nm prior to reaction) and spent Au-NH₂-SiO₂-GO catalysts had a gold particle size of 7.6 nm ± 2.9 nm (was 4.5 nm ± 1.1 nm prior to reaction). The particle size when comparing the spent catalysts is not statistically different. Evaluation of the Au particle size after cyclooctene oxidation also saw a drastic increase in AuNP size to 19.1 nm ± 9.5 nm and 17.6 nm ± 11.5 nm for uncoated and GO coated

samples respectively (see Table 14 for summary of particle sizes). After just one cyclooctene reaction cycle the particle size grew to drastically size and thus the catalytic activity of subsequent reaction cycles would likely be decreased due to a decrease in the surface area to volume ratio of the gold.

Table 14. Summary of the AuNP sizes before and after cycloalkene oxidation reactions. The GO coating did not have the ability to stop AuNP aggregation during reaction.

Sample	TEM	ICP
	Particle Size (nm)	Auf (Wt%)
Au-NH ₂ -SiO ₂	4.1 ± 1.3	0.12
Au-NH ₂ -SiO ₂ -GO	4.5 ± 1.1	0.07
Au-NH ₂ -SiO ₂ Spent C6 Rxn	6.7 ± 2.7	ND
Au-NH ₂ -SiO ₂ -GO Spent C6 Rxn	7.6 ± 2.9	ND
Au-NH ₂ -SiO ₂ Spent C8 Rxn	19.1 ± 9.5	ND
Au-NH ₂ -SiO ₂ -GO Spent C8 Rxn	17.6 ± 11.5	ND

4.5.3. Impact on catalytic activity and selectivity

The final hypothesis under investigation for the use of a GO coating was that the coating could influence catalytic activity or selectivity. For the reaction systems investigated in this work there was no discernable difference in selectivity or activity when compared to a catalyst without a GO coating. However this hypothesis warrants further investigation to determine if by reducing the GO basal planes and restoring some of the interesting electron properties to the GO sheet the catalysis could be impacted.

5. Closing Remarks

5.1. Conclusions and Reflections

Through the experiments carried out in this body of work, a number of different transformations to GO materials were performed to try to better understand the impact the local catalytic environment had on catalysis. I demonstrated the ability to bridge the basal planes of GO together while leaving residual amine molecules free to possibly participate in a cooperative catalytic active site. The d-spacing of the GO matrix was observed to be impacted by using different synthesis approaches to bridge the basal planes in a 3D network and although these materials were not tested for cooperative effect I gained significant experience and insight that was helpful for the direction of the subsequent projects. I also developed a synthesis method to coat a gold on silica catalyst with GO and verified its structure with a vast array of characterization techniques. We hypothesized that the GO overcoat could reduce metal leaching, control the monodispersity of nanoparticles during synthesis and after reaction, and influence the catalytic nature of the AuNP. After testing the coating for the reduction of 4-NP and cyclohexene and cyclooctene oxidation we conclude that the GO coating was not able to impact these three parameters for these particular reaction systems. Finally we were able to demonstrate that dissolved Au clusters are a likely active site for cyclohexene oxidation, although challenges in removing the hydroperoxide clouds this data, and that the dissolved Au in the filtrate from cyclooctene oxidation can subsequently catalyze the oxidation of cyclohexene.

5.2. Recommendations for Future Work

Even though for the reactions explored the GO coating did not significantly alter catalysis, I believe further investigation is warranted to determine if by reducing the GO basal planes and restoring some of the interesting electron properties of rGO to the GO sheet the

catalysis could be impacted. Additionally, it would be interesting to alter the GO coating synthesis method to covalently link the GO sheet to the surface of the silica support, as opposed to electrostatic wrapping, to determine if this stronger bond between the GO and the support can slow down metal leaching or cause catalytic confinement effects that were not observed in the current work.

6. General Experimental Procedures

6.1. Nuclear Magnetic Resonance (NMR)

NMR spectra were acquired either with a Varian Inova 500 MHz instrument (^1H NMR, ^{13}C NMR) or with a 400 MHz Agilent DD MR-400 system (^1H NMR, ^{13}C NMR, ^{31}P NMR). NMR samples were prepared by diluting in a deuterated solvent, usually d-chloroform. The deuterated solvent was the internal reference for ^1H and ^{13}C , and triphenylphosphine oxide was used as the external reference for ^{31}P .

6.2. X-ray Diffraction (XRD)

A Rigaku Smartlab diffractometer was used for XRD analysis. The instrument was equipped with an incident beam multilayer optic with a parabolic profile. The alignment slits were set to 0.5 mm for data collection, which results in resolution at the detector of $\sim 0.1^\circ$. Freeze dried GO samples were mixed with a small amount of acetone and pressed into a thin layer/film on a quartz sample holder and allowed to air dry.

The interlayer spacing (d-spacing) can be calculated using Bragg's law

$$\lambda = 2d \sin(\Theta)$$

where λ is the wavelength of the X-ray beam (0.154 nm), d is the distance (nm) between the adjacent GO sheets or layers, and Θ is the diffraction angle.

6.3. Transmission Electron Microscopy (TEM)

TEM images were obtained using a JEOL JEM-2100 FasTEM transmission electron microscope with a field emission gun at 200 kV. High angle annular dark field (HAADF) STEM images had a spatial resolution of 0.2 nm. Samples were prepared by bath sonicating a small amount of sample ($\sim 1 - 5\text{mg}$) in $\sim 3\text{ mL}$ isopropanol for 10 min. After sonication, a drop was placed onto a 400 mesh copper grid with holey carbon or ultrathin carbon film (Ted Pella). The

grid was then evacuated for a minimum of one hour at room temperature. ImageJ was used for particle size analysis.

6.4. Scanning Electron Microscopy (SEM)

SEM images were obtained using a Hitachi SU8030 scanning electron microscope operating with a cold source field emission gun between 5-10kV, depending on the sample. Samples were prepared by bath sonicating a small amount of sample (~1 - 5mg) in ~3 mL isopropanol for 10 min. After sonication, the sample was drop cast onto a silicon wafer strip attached to the SEM stub using double-sided conductive tape. The sample/stub was then evacuated for a minimum of one hour at room temperature. An SPI osmium coater was used to coat the samples with 5 nm of osmium to reduce surface charging before analysis.

6.5. Surface Area - Brunauer-Emmet-Teller (BET)

The Brunauer-Emmet-Teller (BET) surface area was measured by a Micromeritics ASAP 2010 instrument. Nitrogen was used as the analysis and free space gas. Samples were degassed under vacuum overnight at 200 °C before analysis.

6.6. Inductively Coupled Plasma (ICP)

Thermo iCap7600 ICP-OES was used for inductive coupling plasma (ICP) to determine metal loading. Samples without GO were dissolved in a mixture of concentrated hydrofluoric acid, nitric acid, and hydrochloric acid. Samples with GO were first heated to ~850°C in flowing air to combust away the GO coating. The residual silica/gold was then dissolved in a mixture of concentrated hydrofluoric acid, nitric acid, and hydrochloric acid. Reaction liquid filtrate samples were placed in a ceramic crucible and heated to ~850°C to boil off the cycloalkenes and cycloalkene oxidation products. The crucible was then rinsed with a mixture of nitric acid and

hydrochloric acid to solubilize the gold now coating the crucible. Au standards were prepared from 1000 mg/L ICP standard solutions from Sigma-Aldrich Co, LLC.

6.7. Thermogravimetric Analysis (TGA)

A Mettler Toledo SDTA 851 thermogravimetric analysis system was used for TGA. Prior to analysis samples were dried overnight under low vacuum at room temperature. Analysis was carried out in the temperature range of 50°C to 800°C at a heating rate of 10°C per minute in air and unmodified Stöber silica was used as the baseline. The weight added due to the group of interest (surface amine or GO coating) was calculated by subtracting the unmodified baseline weight loss observed from the measured weight loss of the sample and calculating the loading by knowing the molecular weight of the compound of interest. The molecular weight of GO was calculated assuming a carbon to oxygen ratio of 2. The theoretical weight loss expected to be observed if the silica was coated with exactly a single layer of GO with minimal defect sites was calculated to be 0.18% (assuming no additional water was introduced because of the GO coating).

6.8. Fourier-transform Infrared (FTIR)

A Nicolet Nexus 670 Fourier-transform infrared (FTIR) spectrometer equipped with a mercury-cadmium-telluride (MCT) detector was used for diffuse reflectance FTIR. Samples were prepared by diluting a 10 mg sample into 100 mg of potassium bromide (KBr) powder. Nitrogen was flowed to the sample cell to reduce environmental signal and scattering. Data was collected with 4 cm⁻¹ resolution and 1000 scans were averaged. A background of KBr was collected and subtracted from each sample run using a Kubelka-Munk transformation.

6.9. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi equipped with an electron flood gun and Al K α radiation (1486.6 eV) was used as an excitation source. Samples were evacuated overnight at room temperature in the instrument's preparation chamber prior to analysis. A linear background was removed from each data curve and the binding energy scale was calibrated with respect to either carbon (1s) or silica (2p) before deconvolution.

6.10. Gas chromatography (GC)

Liquid reaction samples were analyzed by gas chromatography (GC-FID) using a Agilent 6890 GC instrument equipped with an Agilent DB-624 capillary column (30 m $\times$ 0.32 mm $\times$ 1.80 μ m).

The products of cyclohexene oxidation were identified by GC–mass spectrometry and quantified using solutions of reference compounds at known concentrations. The addition of PPh₃ to the reaction mixture prior to GC analysis did not change the concentration of 2-cyclohexen-1-one, this indicates that there was no decomposition of cyclohexenyl hydroperoxide during GC analysis. The concentration of cyclohexenyl hydroperoxide was calibrated by incrementally reducing the hydroperoxide with PPh₃ and correlating the increase in 2-cyclohexen-1-ol with the changing peak areas.

The products of cyclooctene oxidation were identified by GC–mass spectrometry and NMR and quantified using solutions of similar reference compounds at known concentrations.

6.11. Dynamic Light Scattering (DLS) and Zeta Potential Measurements

Hydrodynamic diameter and zeta potential were measured using a Zetasizer Nano instrument equipped with a He–Ne laser (633 nm). The hydrodynamic diameters and zeta potentials of the GO sheets were calculated by the supplied instrument software (Zetasizer DTS).

6.12. Ultraviolet-visible (UV-Vis) Spectroscopy

Ultraviolet– visible (UV–vis) spectra were measured using a HP (Agilent) 8452 diode array spectrophotometer and either disposable or quartz cells with 1 cm path length and a spectral window of 200–800 nm. All samples were analyzed at room temperature.

6.13. Atomic Force Microscopy (AFM)

Tapping-mode AFM experiments were performed with a Dimension FastScan Atomic Force Microscope. Aqueous graphene oxide dispersions were drop-cast onto a mica plate that had been cleaned and aminated with 3-aminopropyltriethoxysilane. Samples were vacuum dried for multiple hours before analysis.

7. References

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