Design and synthesis of nanostructured palladium catalysts by atomic layer deposition

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DESIGN AND SYNTHESIS OF NANOSTRACTURED PALLADIUM CATALYSTS BY ATOMIC LAYER DEPOSITION

by

MAR PIERNAVIEJA HERMIDA

A DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
The Department of Mechanical Engineering with a specialization in Chemical Engineering to
The School of Graduate Studies of
The University of Alabama in Huntsville

HUNTSVILLE, ALABAMA

2016
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DISSERTATION APPROVAL FORM

Submitted by Mar Piernavieja Hermida in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering and accepted on behalf of the Faculty of the School of Graduate Studies by the dissertation committee.

We, the undersigned members of the Graduate Faculty of The University of Alabama in Huntsville, certify that we have advised and/or supervised the candidate on the work described in this dissertation. We further certify that we have reviewed the thesis manuscript and approve it in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering.

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ABSTRACT
The School of Graduate Studies
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Degree Doctor of Philosophy
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Name of Candidate Mar Piernavieja Hermida
Title Design and Synthesis of Nanostructured Palladium Catalysts Using Atomic Layer Deposition.

Atomic layer deposition (ALD) has been shown to be effective at controlling metal and metal oxide sites and demonstrated to be a promising tool to apply oxide overcoating layers onto supported metal catalysts with atomically precise thickness control, which allowed optimizing both the stability and activity. The mechanisms for depositing Al₂O₃, TiO₂, palladium and ZnO were investigated with quartz crystal microbalance (QCM) and ellipsometry in order to better understand and improve the process. Presented is a study of ALD from nanometer to single atom size palladium catalysts. There are many uses for of palladium nanoparticles, catalysts, polymer membranes, sensor, plastics and fuel cells as many others.

Currently single atom catalysts have been of much interest due to higher activity performance and much investigation due to poor stability. Displayed is a study of palladium single atom catalysts with protective oxide coatings synthesized by ALD to improve the thermal stability. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), scanning transmission electron microscope (STEM) and X-ray absorption spectroscopy (XAS) revealed the presence of palladium single atoms. The catalytic activity of these Pd₁ catalysts was evaluated using formic acid and methanol...
decomposition as probe reactions. The observation of surface nanoparticles supported the further search of alternative mechanisms to stabilize single atoms by ALD.

In an additional palladium deposition study, the growth of nanometer size palladium on ZnO-passivated carbon was examined by ALD. X-ray diffraction (XRD), scanning electron microscopy (SEM) and XAS were essential to determine the structure of the catalysts which were tested as cathode material in a rechargeable lithium-oxygen battery. These palladium catalysts synthesized by ALD, showed highly active catalytic effect as regards to electrochemical reactions.

The discoveries in this work contribute to a better understanding on various ALD systems in order to stabilize single atoms.
ACKNOWLEDGMENTS

I would like to give my sincere gratitude and appreciation to my advisor, Professor Yu Lei, for his guidance and advice throughout my Ph.D. studies and giving me the opportunity to work on this exciting research.

The author has great appreciation for Professors Michael Banish and Ramon Cerro for their valuable advice and guidance through my undergraduate and graduate studies and Professor George Nelson for his valuable advice and time.

I would like to express my deep appreciation to Dr. Zili Wu for giving me the opportunity to learn and work at Oak Ridge National Laboratory. Thank you for your insight.

I would like to express great appreciation to co-author Xiangyi Luo for her work on the battery project, Jianguo Wen, from Argonne National Laboratory, for his help with TEM imaging for the Li-O$_2$ battery project and Tianpin Wu, from Argonne National Laboratory, for her help with EXAFS data on both the TiO$_2$ coating to stabilized Pd$_1$ single atoms and the battery project.

I would also like to thank my colleague, Zheng Lu, for his help on EXAFS data for both Pd$_1$ single atom projects. And for all his help through my graduate studies. Also, Anderson White, for his help on EXAFS data on the TiO$_2$ coating to stabilized Pd$_1$ single atoms project.

I would like to thank the UAHuntsville Department of Chemical Engineering for providing financial support and Argonne National Laboratory and Oak Ridge National Laboratory for the usage of their facilities.
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CHAPTER ONE

1. Introduction

1.1. Heterogeneous Catalysis

Catalysis is an essential key behind the development of the chemical industry.\(^1\) It is a main element in order to use natural resources efficiently while making the chemical industry processes environmentally friendly. The essential method for industrially converting oil, gas, coal or biomass to products such as fuels and chemicals is through chemical or biological catalysts. It is calculated that the annual catalyst market is approximately $15 billion and approximately one third of the U.S. GDP depends on catalytic technologies.\(^2\) Heterogeneous catalysts, which are an important element in industrial chemical processing, fuels reforming, and renewable energy reactions, are preferred due to a solid catalyst (metal or metal oxides) being easily separated from a final product. Preferred heterogeneous catalysts that have been extensively used in medicine production, new energy and the petrochemical industry are noble metals, such as Pt, Pd, Ru, Rh, and Ir. Some methods which have been used over a century to synthesize heterogeneous catalysts are impregnation, ion exchange, and precipitation.\(^3\)
In the case of supported metal catalysts, the disadvantage of these techniques is the broad distribution of particle sizes and irregular morphology, and each metal particle may possess multiple active sites with different performances instead of the desirable single site.\textsuperscript{4} The mixture of metal sites producing a mixture of reaction products evolve in a non-uniformity of sites creating an imbalance between activity, selectivity and stability. Over the 20\textsuperscript{th} century great progress was made to achieve higher activities for many catalytic processes while the difficulty in the 21\textsuperscript{st} century it is to improve the selectivity of the catalyst.

The metal particle sizes influence the activity and selectivity of heterogeneous catalysts which at the same time influence both the surface coordination number and particle support interaction.\textsuperscript{5,6} The coordination number and concentration of active sites depend on the crystallographic planes exposed, nanometer sized particles exhibit more edges and corners than larger particles.\textsuperscript{7} As the size of supported metal particle is reduced, higher amount of surface atoms appear and locate in a low-coordination position, together with quantum-size effect and the strengthen metal support interaction, these surface atoms become increasingly active to specific reactions.\textsuperscript{8} In order to improve reaction performance and understanding catalytic mechanisms\textsuperscript{9} the development of catalysts with well-defined single active centers is necessary. Subsequently, reducing the catalyst sizes to well define atomically distributed metal active sites, i.e. single-atom catalysts, will be the most efficient way to use each and every metal atom of the supported metal catalyst and therefore accomplishing the final purpose of fine dispersion.\textsuperscript{10-12}
1.2. Single-Atom Catalysts

Single-atom catalysts (SACs) have distinctive and isolated metal atoms that are hold to a particular support and can act as active centers for heterogeneous catalysis. The idea behind SAC is innovative and the catalysts are completely dissimilar from conventional heterogeneous catalysts, which are composed of numerous metal nanostructures and supports with enormous specific areas. Single-atom catalysts have superior activities and enable the maximum usage of supported metals, moreover supplying single active sites, which provides higher selectivity as homogeneous catalysts. Single-atom catalysts may be considered the connection between heterogeneous and homogeneous catalysis. SACs research will assist the progress of understanding the catalytic mechanisms and provide analytical approaches for the design of innovative catalysts.

There have been several research investigations in regards to the synthesis of single-atom catalysts and the comprehension of their catalytic performance. For instance, high surface area supports are required, but more relevant it is the necessity to supply some distinguishing anchoring sites to firmly hold the atoms and prevent sintering.

Moreover, many elements should be considered when designing and studying single-atom catalysis, which involve understanding the different support characteristics, like the species of supported atoms, the surface atomic and electronic structures of the supports and the interaction between single atoms and the support.
Some single-atom investigations using metal oxides\textsuperscript{11,15,16} metal nanoparticles,\textsuperscript{17} and carbon materials\textsuperscript{18,19} as supports have been described. These researches open the path for more accurate design and distinct catalysts in the near future.

Although single-atom catalysts have a big interest and potential in heterogeneous catalysis, the characterization and preparation of SACs is challenging. Even though for a long time the productivity of single-atoms was questionable, and was not clear if catalytically these were active or stable, the latest technologies improvements have made it possible to prepare and characterize SACs.\textsuperscript{11,20,21}

For SACs applications it is necessary to prepare highly dispersed single-atoms on appropriate supports which show a major challenge due to the tendency of single-atom aggregation. Finding methods to prepare SACs have been proven challenging. The mass selected soft landing technique\textsuperscript{22} is powerful but expensive and not suitable for industrial applications of heterogeneous catalysis.\textsuperscript{8} Preparation of site-isolated single-atom supported on high surface area oxides catalysts has recently been realized via wet chemistry.\textsuperscript{11,23} In the past five years Zhang and co-workers have triumphantly synthesized Au, Pt, or Ir single-atom catalysts.\textsuperscript{11,23-25}

Nowadays, the main challenge of single-atom catalyst is to synthesize catalysts with isolated single atoms precisely, closely compacted, and firmly anchored to the support. Aggregation of single-atoms appears to be inevitable due to the high surface free energy of the former. Stabilization of surface single atoms is difficult due to high mobility and facile sintering even when these single atoms are dispersed finely on the support.\textsuperscript{26} Therefore, these single atoms lack capability of facing practical use such as
resisting higher temperatures. Consequently it is essential, in order to resolve these challenges, to obtain sturdy anchor sites through strong support metal interactions (SMSIs).\textsuperscript{27} In the case of some supports, the surface defects or vacancies are considered suitable anchoring sites for single atoms, for instance in the case of Pt atoms using the cation vacancies on FeO\textsubscript{x} or γ-Al2O3.\textsuperscript{11,28} A different route would be to use nonmetallic elements on the support surface, like C, N, O, as anchor to the single metal atoms.\textsuperscript{29} For example, the activation energy for metal-carbon bonds are in the order of $\approx 200–300$ kJ·mol\textsuperscript{-1}, therefore enough to retain stable under many catalytic reaction conditions.\textsuperscript{29,30}

Single-atom catalysts have proven to be powerful catalysts with high activity, selectivity and stability for several reactions such as CO$^{11}$ or HCHO$^{31}$ oxidation, the water-gas shift reaction,$^{32,33}$ styrene and acetylene hydrogenation,\textsuperscript{34} or nitroarenes hydrogenation,\textsuperscript{35} and methane conversion$^{36}$. Single-atom catalysts have been proven as a promising new type of catalyst with strong prospective applications. In order to create more efficient SACs several challenges would need to be overcome. First, SACs synthesis would need to be controllable and facile, with finely dispersed single atoms. Secondly, a sturdy stabilization between the single atoms and the support has to be achieved. Thirdly, the strong metal-support interactions in SACs need adjusting and understanding. Finally, accurate and rational design of active sites in single-atom catalysts at the atomic level needs to be performed.

1.3. Atomic Layer Deposition

Synthesis of single atom catalysts can be synthesized through vacuum deposition techniques, such as atomic layer deposition (ALD).
ALD has been shown to be effective at controlling metal and metal oxide sites and demonstrated to be a promising tool to apply oxide over-coating layers onto supported metal catalyst with atomically precise thickness control, which allowed optimizing both the stability and activity.\textsuperscript{37-39} Atomic layer deposition has been proven efficient to synthesized single-atoms.\textsuperscript{40,41}

Atomic layer deposition (ALD) is based on sequential, self-limiting surface reactions. This unique growth technique can provide atomic layer control and allow conformal films to be deposited on very high aspect ratio structures. Palladium-based catalysts prepared by ALD have effectively been used in several catalytic systems, such as decomposition of methanol.\textsuperscript{42} ALD has the capability of tailoring size from single-atom, sub-nanometer clusters to nanoparticles of metal and metal oxides.\textsuperscript{43}

The idea behind atomic layer deposition was discovered in 1960s by Professors Aleskovskii and Koltsov in the Soviet Union under the name “molecular layering” (ML)\textsuperscript{44} and in the 1970s by Tuomo Suntolo in Finland under the name “atomic layer epitaxy” (ALE).\textsuperscript{45,46} Because these studies focused on the thin film growth of the first 10 cycles and used high surface area substrates as silica gel, they resemble the basis of today’s ALD for catalyst synthesis.\textsuperscript{47} Such high-surface-area substrates have been a topic of interest in ALD studies due to their importance in heterogeneous catalysis, and because they propose lot of materials for detailed chemical characterization.\textsuperscript{48}
A rise in ALD research and development starting in the late 1990s continues to the present day. Subsequently, the amount of available ALD materials has increased including oxides, nitrides, sulfides, and metals.\textsuperscript{49} Moreover, various ALD chemistries for any given material have been developed. Furthermore, molecular layer deposition (MLD) has been developed parallel to ALD using solely organic compounds to deposit thin film polymer layers.\textsuperscript{50,51}

Many examples of successful catalysts synthesized by ALD have been demonstrated in the past few years, such as employing ALD to control metal growth on surfaces,\textsuperscript{52} alloy and core-shell catalysts,\textsuperscript{53-55} and protective over-coatings.\textsuperscript{39,56} These new catalysts show improved selectivity for specific catalytic reactions and are more stable. Additionally, bimetallic catalysts were the location of each metal is precisely controlled could be synthesized by ALD, showing high activity.\textsuperscript{54,55}

1.4. Objective

The objective of this research is to synthesized nanostructured palladium, via atomic layer deposition, as catalyst for various reactions. This work can be divided into two main research projects. The first project is the stability of single atom catalysts using ALD. In order to achieve stability, single-atom palladium catalysts will be coated with different amount of Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} ultrathin metal oxide protective coatings prepared as well by ALD. The over-coatings aim to prevent sintering and therefore possible deactivation of the catalyst. In order to test the stability of SACs, the catalysts are tested under reaction conditions for CO chemisorption, methanol decomposition and formic acid decomposition.
The second project, focus on nanometer size palladium, on ZnO-passivated porous carbon synthesized by ALD. This palladium catalyst will be used as new cathode architecture for lithium-oxygen batteries in order to increase the electrochemical catalytic activity in Li-O₂ cells as well as reduce the charge overpotential.

Moreover, combining state-of-the-art in situ spectroscopic techniques (DRIFTS, EXAFS, XANES) with the atomically precise synthesis of ALD, provided structural and electronic characterization of the catalysts.

1.5. Organization of Dissertation

This dissertation is composed of six chapters. The introduction to this research, background on heterogeneous catalysis, single-atom catalysts and atomic layer deposition are described in Chapter One.

Several experimental techniques applied in this research are described in detail in Chapter Two. Palladium single-atom catalysts synthesized by ALD on TiO₂ and Al₂O₃ substrates are presented in Chapters Three and Four respectively. These catalysts have been employed for methanol decomposition or formic acid reactions in order to observe the amount of hydrogen selectivity obtained and the stability of single-atoms.

Moreover, Chapter Five describes the synthesis of uniformly dispersed palladium nanoparticles on ZnO-passivated porous carbon synthesized by atomic layer deposition. The palladium nanostructured architecture was used as cathode material catalyst in a rechargeable Li-O₂ battery. Finally, the conclusions obtained from each work performed in this research and future work recommendations are explained in Chapter Six.
CHAPTER TWO

2. EXPERIMENTAL METHODS

In this research, the preparation of nanostructured palladium catalysts was characterized by a variety of techniques including, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), extended x-ray absorption fine structure (EXAFS), quadrupole mass spectrometry (QMS), and quartz crystal microbalance (QCM), which will be explained in detail in this chapter.

2.1. Atomic Layer Deposition (ALD)

A general ALD process consists of sequential alternating gaseous chemical precursors pulsed into the reactor, separated by purging periods, and subsequent surface reaction of the precursors. Each precursor is pulsed into a chamber under vacuum conditions for a specified amount of time, which saturates the surface with a monolayer of that precursor. This results in a self-limiting process facilitating the growth of conformal thin films, and even if excess precursor is added no additional precursor will be deposited on the already grown film. The purging between precursor doses is performed with nitrogen in order to remove unreacted precursor or reaction byproducts. The ALD process is illustrated in Figure 2.1.
Figure 2.1. Schematic representation of an ALD process. (a) Substrate surface. (b) Precursor A is pulsed reacting with the surface. (c) Purged with nitrogen removed reaction by-products and excess precursor. (d) Precursor B is pulsed reacting with the surface. (e) Purged with nitrogen removed reaction by-products and excess precursor. (f) Steps (b-e) are repeated until desired material thickness is achieved.

As the surface area of the substrates increase, the pulsing and purging times also need to be increased to allow the dispersion of the precursor gas into all substrate features. Therefore, when using substrate powders with higher surface areas, the reaction time inside the chamber is increased by closing the valve that isolates the chamber from the vacuum pump. The valve is closed before precursor dosing, isolating the chamber. Once the precursor is pulsed, it is allowed to remain for a specific amount of time (several seconds) to ensure saturation of the entire surface before opening the valve and purging the chamber.
In some cases, due to the limited number of reactive sites\textsuperscript{48} and the steric hindrances between bulky ligands\textsuperscript{59} only a fraction of monolayer may be deposited in each cycle.

### 2.2. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Diffuse reflectance is described as the energy that penetrates one or more particles and is reflected in all directions. The DRIFT cell reflects radiation to the powder and collects the energy reflected back over a large angle. Diffusely scattered light can be collected directly from material in a sampling cup or, alternatively, from material collected by using an abrasive sampling pad.\textsuperscript{60} DRIFT is particularly useful for sampling powders or fibers. Figure 2.1 illustrates diffuse reflectance from the surface of a sample.

![Diagram of Diffuse Reflectance](image)

**Figure 2.1.** Illustration of Diffuse Reflectance.

Kubelka and Munk developed a theory describing the diffuse reflectance process for powdered samples which relates the sample concentration to the scattered radiation intensity. The Kubelka–Munk equation is described below\textsuperscript{60}:\n
\[
\frac{1 - R^2}{2R} = \frac{c}{k} \quad (Eq. 2.1)
\]
where R is the absolute reflectance of the layer, c is the concentration and k is the molar absorption coefficient. In near-infrared diffuse reflectance spectroscopy an alternative relationship between the concentration and the reflected intensity is used as follows:\textsuperscript{60}:

$$\log \left( \frac{1}{R} \right) = k'c \quad (Eq. 2.2)$$

where k’ is a constant.

IR spectra were collected continuously through CO adsorption using a Thermo Nicolet Nexus 670 spectrometer, with a MCT/A detector with a spectral resolution of 4 cm\(^{-1}\), in diffuse reflectance mode. The exiting stream from the DRIFTS reactor, a Pike Technologies HC-900 with nominal cell volume of 6 cm\(^3\) (see Figure 2.2 and Figure 2.3), was analyzed using a quadrupole mass spectrometer (Omnistar GSD-301 O2, Pfeiffer Vacuum).
Figure 2.2. DRIFTS reactor (Pike Technologies HC-900)

Figure 2.3. DRIFTS reactor cell.
2.3. Extended X-ray absorption fine structure.

The spectrum obtained from (X-ray Absorption Spectroscopy) is composed of two regions, EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-Ray Absorption Near Edge Structure). EXAFS corresponds to the oscillating part of the spectrum to the right of the absorption edge starting at ~50 eV and extending to about 1000 eV above the edge (shown in Figure 2.4).

![Figure 2.4. Regions of the X-Ray absorption spectrum.](image)

The Lambert-Beer law relates intensities $I_0$ and $I$ to the absorption coefficient:

$$\ln \frac{I_0}{I} = \mu x \quad Eq. 2.3$$

where $I_0$ and $I$ are the photon intensities before and after the absorber of thickness $x$. 
By analyzing X-ray absorption spectrum, EXAFS spectroscopy provides structural information about a sample. The chemical environment of an element can be determined regarding inter-atomic distances, the number and type of its neighbors, and structural disorders. This information is determined from a distance given by the mean free path of the photoelectron in the condensed matter, which is between 5 and 10 Å radius from the element.\(^6\)

The EXAFS signal \((k)\) is defined as a function of the wave vector \(k\). It is defined as:

\[
\chi(k) = \frac{\mu_x - \mu_1x}{\mu_1x} = \frac{\mu_x}{\mu_1x} - 1 \quad \text{Eq. 2.4}
\]

where \(\mu_x\) is the experimental absorption coefficient and \(\mu_1x\) is the intrinsic atomic absorption coefficient. Dividing by \(\mu_1x\) normalizes the signal. Therefore, this definition means that \((k)\) contains only the oscillatory part of the absorption coefficient.

The analysis of the EXAFS data was performed using WinXAS software. A simultaneously pre- and post-edge background removal step was carried out and the resulting spectra were normalized by dividing by the height of the absorption edge. Once normalized, spectra were converted to \(k\)-space using a \(k\)-weighting of two. A cubic weighted spline was used to remove the background of the \(\chi(k)\) function. Finally the \(k^2\)-weighted results were Fourier transformed to \(R\)-space. Phase and amplitude parameters from reference samples were used to in the curve fitting of the WinXAS. Coordination number, interionic distance and Debye-Waller factor were obtained by the least-square fittings in \(k\)-space.
2.4. Quadrupole Mass Spectrometry

The identity of gas phase chemical species can be inferred from the data collected by a mass spectrometer. Once molecules are ionized (bombardment by electrons from a hot filament) and sometimes fragmented, they are separated in the quadrupole region according to their mass to charge ratios. When the fragments of molecules of interest overlapped, the ratios of characteristic fragments assisted in distinguishing each species. The mass filter consists of four parallel metal rods and the arrangement is shown in Figure 2.5.

Figure 2.5. Diagram of a quadrupole mass filter.
Rods with positive sign have an applied potential of \((U+V\cos(\omega t))\) while the other two rods with negative signs have a potential of \(-(U+V\cos(\omega t))\), where \(U\) is a dc voltage and \(V\cos(\omega t)\) is an ac voltage. The applied voltages affect the trajectory of ions traveling down the ion path centered between the four rods. For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path. By monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied, a mass spectrum is achieved.

### 2.5. Quartz Crystal Microbalance

In 1959 Sauerbrey,\(^{62}\) first investigated the feasibility of using quartz crystal resonators as measuring mass quantitatively. The added mass of the deposited film appeared to be proportional to the decrease of the resonant frequency of a thickness shear vibrating quartz crystal resonator (with AT or BT cut)\(^{63}\).

\[
\Delta f = -\frac{f_q^2 M_f}{N \rho_q S} = -\frac{f_q^2 m_f}{N \rho_q} \quad \text{Eq. 2.5}
\]

where \(f_q\) is the fundamental resonant frequency of the quartz, \(N\) is the frequency constant of the specific crystal cut (\(N_{\text{AT}} = 1.67 \times 10^5\) Hz cm; \(N_{\text{BT}} = 2.5 \times 10^5\) Hz cm), \(\rho_q = 2.65\) kg/dm\(^3\) the quartz density and \(S\) is the surface area of the deposited film (its mass is \(M_f\)).

When the deposited film covers the quartz resonator in order to calculate the film thickness, \(l_f = m_f/\rho_f\), where \(\rho_f\) is the density of the deposited film, it is simpler to use the areal density \(m_f = M_f/S\).\(^{63}\) A typical gold quartz crystal resonator is shown in Figure 2.6.
Figure 2.6. A typical gold quartz crystal resonator.

The electrodes on the quartz resonator are vacuum deposited gold or silver films. The electrodes are connected to an oscillator, AC voltage is applied over the electrodes and the quartz crystal starts to oscillate at its resonance frequency. The bakeable sensor (figure 2.7), where the quartz crystal is placed, is connected to an external monitor which measures rate and thickness in the thin film deposition process.

Figure 2.7. Bakeable sensor.
CHAPTER THREE

3. Towards the ALD Thin Film Stabilized Single-Atom Pd$_1$ Catalysts

3.1. Introduction

Nanomaterials are known to possess dramatically different electronic, chemical, and physical properties compared to their bulk counterparts. For instance, when the dimensions of supported precious metals approach the nanometer and subnanometer scale, unique catalytic properties emerge related to under-coordinated surface atoms, electronic structure, and diffusion barriers of surface species. In ultra-high vacuum (UHV) experiments using well-defined single crystals, Heiz and Schneider were the first to observe size-dependent catalytic activity in an atom-by-atom fashion for CO oxidation by gold clusters and the cyclotrimerization of acetylene by palladium clusters. Since then, significant research has been performed to explore size-dependent catalysis with atomic precision using the so-called size-selected cluster deposition technique. More recently, in a combined scanning tunneling microscopy (STM), DFT and temperature-programmed desorption (TPD) study, Flytzani-Stephanopoulos and Sykes found that isolated Pd$_1$ atoms alloyed with the Cu(111) surface showed highly selective hydrogenation of styrene and acetylene.
The improved selectivity was attributed to low-barrier hydrogen dissociation at Pd atom sites and weak binding of the products to Cu.

Preparation of site-isolated single atom supported on high surface area oxides catalysts has recently been realized via wet chemistry. The single atom catalysts have shown unexpectedly high activity and selectivity to valuable products under realistic catalytic reaction conditions. Single-atom Pt\(_1\) supported by FeO\(_x\) nanocrystallite substrates showed extremely high atom efficiency for preferential oxidation of CO in H\(_2\).\(^{77}\) DFT calculations showed that the high activity and selectivity is correlated with the partially vacant 5\(d\) orbitals of positively charged, high-valent Pt atoms. Other successful examples at the lab scale include well-defined Pt\(_1,\)\(^78\) Pd\(_1,\)\(^79\) Rh\(_1,\)\(^15\) Au\(_1,\)\(^32,80,81\) and Ir\(_1\)\(^82\). In industrial scale production, titanium silicalite (TS-1) is a commercial catalyst for propylene epoxidation with hydrogen peroxide.\(^83\) The isolated Ti active sites of TS-1 provide a high selectivity towards propylene oxide, since propylene oxide molecules that adsorb on adjacent Ti sites lead to catalyst deactivation and the formation of unwanted byproducts.\(^84-87\)

Despite these successes, the thermal stability of precious metal single site catalysts under reaction conditions remains a significant challenge. The synthesis of highly active single-atom catalyst with improved thermal stability attracts both fundamental and industrial interest.\(^88\) In addition, obtaining uniform, thermally stable single atom catalysts under reaction conditions is a critical step towards precisely identifying catalyst active sites.
Here we demonstrate an approach to improve the thermal stability of uniformly dispersed Pd₁ single atom catalysts using ultrathin metal oxide protective coatings prepared by atomic layer deposition (ALD).

3.2. Experimental Details

3.2.1. Catalyst Synthesis

The Pd catalyst materials were synthesized using a commercial benchtop ALD reactor (Arradiance, Gemstar-6) equipped with an *in situ* quartz-crystal microbalance (QCM, Inficon). Ultra-High purity nitrogen carrier gas (Airgas, 99.999%) was further purified using a Supelco gas purifier (Sigma-Aldrich) to trap hydrocarbon, moisture and oxygen-containing impurities before entering the reactor.

Spherical alumina powder (NanoDur, 99.5%, Alfa Aesar) was used as the substrate without further treatment. Substrate was uniformly spread onto a stainless steel sample tray with a stainless steel mesh top to contain the powder while still supplying access to the ALD precursor vapors. The loaded sample tray was placed into the center of the reactor and kept for at least 30 min at 200 °C in a 50 sccm flow at 0.5 Torr pressure to allow temperature stabilization.

The ALD timing sequences can be expressed as \( t_1-t_2-t_3-t_4 \), where \( t_1 \) and \( t_3 \) correspond to the exposures times of the two precursors, \( t_2 \) and \( t_4 \) are the nitrogen purge times between precursor exposures and all units are given in seconds. 500 mg of Al₂O₃ NanoDur was modified using 3 ALD cycles of TiO₂. The TiO₂ coating used alternating exposures to TiCl₄ (Sigma-Aldrich, 99.9%) and deionized water with time sequence (80 s− 160 s−80 s−160 s) at 150 °C.
For the TiO$_2$ overcoat, 1, 7, and 14 cycles were used. The Pd ALD used exposures to Pd (II) hexafluoroacetylacetonate (Pd(hfac)$_2$, Sigma-Aldrich, 98%) at 100 °C with time sequence (300 s–300 s) at 100 °C. The samples were denoted as 1cTiPd$_1$, 7cTiPd$_1$, 14cTiPd$_1$, respectively. For each sample, the mass was measured with an analytical balance before and after ALD to determine the Pd loading. Weight percent of palladium in Pd$_1$ catalysts was estimated to be 0.5 wt%.

### 3.2.2. In situ Quartz Crystal Microbalance Analysis

Quartz Crystal Microbalance (QCM) studies were performed for Pd ALD using a Maxtek BSH-150 bakeable sensor, AT-cut quartz sensor crystals (Colorado Crystal Corporation), and a Maxtek TM400 film thickness monitor. To monitor the Pd growth on Al$_2$O$_3$ and TiO$_2$ supports with QCM, a thick layer (3 nm) of Al$_2$O$_3$ or TiO$_2$ was first deposited on the QCM at the same temperature as used for Pd ALD. The Al$_2$O$_3$ layer was grown by sequential exposures of TMA and water for about 60 cycles; TiO$_2$ was grown by sequential exposure of TTIP and water for 100 cycles; and Pd was grown by sequential exposures of Pd(hfac)$_2$ and formalin. The QCM mass measurements were converted to Pd film thicknesses assuming a density for Pd of 12.0 g/cm$^3$.

### 3.2.3. BET Surface Area Measurements

Brunauer–Emmett–Teller (BET) surface area of all palladium catalysts were measured via nitrogen adsorption at 77 K by using a Micromeritic Gemini 275 system.
3.2.4. Aberration-Corrected Scanning Transmission Microscopy (STEM)

The TEM characterization was performed on an aberration-corrected scanning transmission electron microscope (STEM) equipped with a 200 keV Schottky cold-field emission gun, a high-angle annular dark field (HAADF) detector, and an annular bright field (ABF) detector.

3.2.5. In situ X-ray Absorption Spectroscopy (XAS)

Pd K-edge (23.564 keV) XAS was performed at the 10-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. The amount of the sample in use was optimized to achieve a XAS step height of about 1. The XAS spectra were recorded in transmission mode. Standard procedures based on WINXAS 3.1 software were used to fit the data in the extended X-ray absorption fine structure (EXAFS) regime.

Pd L₃-edge (3.173 keV) XAS was carried out at the 9-BM beamline at the APS. The sample was measured in the fluorescence mode. The Pd catalysts were pressed as a pellet and installed in a stainless steel sample holder housed in an aluminum environmental chamber. The temperature of the sample holder was controlled using K-type thermocouples and a ceramic heating plate. The catalyst of interest was first reduced in 3.5% hydrogen/helium at 250 °C for 30 minutes. Then the ultrahigh purity helium was used to purge the chamber at 250 °C to remove the hydrogen. The resultant catalyst was fully reduced Pd without adsorbate. XANES spectra were taken for the clean Pd surface.
The system was then purge with 10 sccm flow 1% CO to generate CO adsorbed Pd. XANES were then taken under the steady state flow of CO. Multiple XANES spectra were taken and averaged to enhance signal to noise.

3.2.6. Catalytic Performance

For each test, 30 mg of Pd catalysts were used on a plug-flow, temperature-controlled microreactor system (Altamira AMI 300). The sample, loaded into a U-shaped quartz tube (4 mm i.d.) and supported by quartz wool, was pretreated in flowing 4% H₂/He (25 mL/min) at 250 °C for 30 minutes and cooled down to room temperature (RT) in He atmosphere. In the case of methanol decomposition, He was bubbled through methanol at 25 cm³/min. All gases were provided by Air Liquide with the ultrahigh purity (UHP, 99.999%) helium as balance gas.

A downstream quadrupole mass spectrometer (QMS) was utilized in order to obtain the catalytic activity of the Pd catalysts by using the methanol decomposition reaction. A calibration experiment was performed were methanol was kept at temperatures 5 °C, 10 °C, 15°C and 20 °C (using a water bath) until the QMS was stabilized at each temperature, and the respective intensities of methanol (monitored at m/z 31) were recorded. A linear fit of the respective intensities versus the methanol concentration at the indicated temperatures, obtained from the vapor pressures, was plotted. The intensity and slope was then utilized to calculate the respective methanol concentrations for the different catalyst reactions. During the decomposition reaction, methanol was kept at 20 °C, therefore the methanol conversion was calculated using the different concentrations of methanol during the reaction and the concentration at 20 °C.
3.2.7. CO Chemisorption

In order to quantify the amount of CO adsorbed on Pd surface, CO pulse chemisorption was carried out on a plug-flow microreactor system (Altamira AMI 300) and a downstream quadrupole mass spectrometer (QMS) (OmniStar GSD-301 O₂, Pfeiffer Vacuum). Approximately 35 mg of sample was loaded in a U-shaped microreactor and reduced in 4% H₂/He (25 mL/min) at 250 °C for 30 minutes. The sample was cooled down to room temperature in He (25 mL/min). After being stabilized at room temperature, 2%CO/2%Ar/He was pulsed multiple times onto the sample in He flow (25 mL/min), and a mass spectrum was collected until there was no change in the CO peak intensity monitored by QMS. One pulse of CO was brought to the sample via a 6-way valve, with a volume of 0.5 cm³. The CO peak intensity was calibrated by pulsing 2%CO/2%Ar/He through the reactor bypass.

3.2.8. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS measurements on CO adsorption were performed using a Thermo Nicolet Nexus 670 spectrometer, with a MCT/A detector with a spectral resolution of 4 cm⁻¹, in diffuse reflectance mode while the exiting stream was analyzed by QMS. A Pike Technologies HC-900 DRIFTS cell with nominal cell volume of 6 cm³ was used. Before each of the following IR experiments, the palladium sample was pretreated in the DRIFTS cell in flowing 4% H₂/He (25 mL/min) at 250 °C for 30 minutes and then cooled to room temperature.
In CO adsorption experiments, the pretreated sample was purged with helium at room temperature before switching to 2%CO/2%Ar/He (25 mL/min) flow for 30 min. The sample was then purged with helium at rt for another 30 min. IR spectra and QMS profiles were recorded continuously during these processes. All reported IR spectra are difference spectra referenced to a background spectrum collected after pretreatment but prior to CO adsorption.

3.2.9. **In situ Fourier Transform Infrared Spectroscopy (FT-IR)**

The *in situ* FT-IR measurements under the practical ALD conditions for TiO$_2$ overcoating was conducted in a specially design ALD reactor described previously.\(^{89}\) The FT-IR data were collected using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. ZrO$_2$ powders was used as substrates and pressed into a metal grid. Pd and TiO$_2$ ALD was subsequently performed. The ALD recipes are identical as those described in session 3.2.1. FT-IR spectra were recorded after each chemical exposure.

3.3. **Results and Discussion**

Palladium hexafluoroacetylacetonate (Pd(hfac)$_2$) is used as the ALD metal precursor for preparing Pd catalyst, in order to confirm surface chemistry and film growth rates during Pd ALD quartz crystal microbalance study was performed (Figure 3.1).

![Scheme 3.1](image)

**Scheme 3.1.** Schematics of thermally stable Pd1 catalysts synthesized using ALD. (1) Depositing Pd(hfac) on spherical Al$_2$O$_3$ substrate, (2) creating nanocavity structure using TiO$_2$ ALD, and (3) removing –hfac ligands using HCHO.
The strategy used to synthesize stable Pd\(_1\) single atom catalysts is described in Scheme 3.1. After chemisorbing Pd(hfac)\(_2\) onto the substrate surface (1), the remaining hfac ligands prevent growth on the Pd during the subsequent metal oxide ALD. ALD TiO\(_2\) is deposited using alternating exposures to titanium tetrachloride (TiCl\(_4\)) and deionized water, but the TiO\(_2\) grows selectively on the substrate and not on the chemisorbed Pd(hfac)\(_2\) (2). As a consequence, the bulky structure of the –hfac ligands of diameter of ca. 5.2 Å templates the formation of a nanocavity of similar dimension around the Pd. Finally, the –hfac ligands are removed using formalin (HCHO) to generate TiO\(_2\) nanocavity protected Pd\(_1\) sites (3). 1-cycle, 7-cycle and 14-cycle TiO\(_2\) thin film stabilized Pd\(_1\) were prepared using this strategy, denoted as 1TiPd, 7TiPd and 14TiPd, respectively. The equivalent thicknesses of these thin films are 0.7 Å, 4.7 Å, and 9.4 Å, for 1c, 7c and 14c TiO\(_2\), respectively, determined using \textit{in situ} quartz crystal microbalance (QCM) (Figure 3.2). In particular, the nanocavity generated using 7c TiO\(_2\) has a similar height of the surface Pd(hfac) species, while the depth of 14c TiO\(_2\) is about twice the height of Pd(hfac). An unprotected Pd sample (0TiPd) was also synthesized and used as reference.
Figure 3.1. *In situ* QCM studies of Pd ALD using Pd(hfac)$_2$ and formalin as precursors at 200 °C. (a) 0-100 cycles, (b) first two cycles of Pd ALD on TiO$_2$, (c) first two cycles of Pd ALD on Al$_2$O$_3$.
Figure 3.2. In situ QCM studies of TiO$_2$ ALD using TiCl$_4$ and H$_2$O as precursors at 100 °C. $\Delta m_1$ and $\Delta m_2$ represent the mass gain during TiCl$_4$ and H$_2$O exposure, respectively. The total mass gain $\Delta m$ of a complete TiO$_2$ ALD cycle is ca. 0.3 µg/cm$^2$. As the TiO$_2$ density of 4.5 g/cm$^3$, the growth rate of TiO$_2$ is ca. 0.67 Å per ALD cycle.
All of the ALD TiO$_2$ stabilized Pd$_1$ catalysts were prepared on commercial spherical aluminum oxide nanoparticles (Al$_2$O$_3$, Alfa Aesar, NanoDur$^\text{TM}$, 99.5%). Brunauer-Emmett-Teller (BET) surface area measurements showed that the ALD TiO$_2$ stabilized Pd$_1$ treatment did not change the surface area of the substrate. The bare Al$_2$O$_3$ substrate and all the ALD catalysts have a surface area of $\sim$33 m$^2$/g (see Figure 3.3 and Table 3.1).

![Figure 3.3](image)

**Figure 3.3.** BET surface area of (a) 0TiPd, (b) 1TiPd, (c) 7TiPd, and (d) 14TiPd.
Table 3.1. BET surface areas of Pd catalysts for methanol decomposition.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m²/g)</th>
<th>CO Chemisorption (µmol/ g catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Al₂O₃</td>
<td>33.8 ± 0.5</td>
<td>-</td>
</tr>
<tr>
<td>0TiPd</td>
<td>31.7 ± 0.2</td>
<td>32.0</td>
</tr>
<tr>
<td>1TiPd</td>
<td>32.9 ± 0.2</td>
<td>60.7</td>
</tr>
<tr>
<td>7TiPd</td>
<td>31.4 ± 0.2</td>
<td>64.9</td>
</tr>
<tr>
<td>14TiPd</td>
<td>31.9 ± 0.2</td>
<td>67.2</td>
</tr>
<tr>
<td>Commercial Pd/Al₂O₃</td>
<td>89.7 ± 0.3</td>
<td>790.1</td>
</tr>
</tbody>
</table>

*BET measurement has ~ 1% systematic error

X-ray diffraction showed that the Al₂O₃ support has a mixed structure of delta and gamma Al₂O₃ (Figure 3.4). The XRD patterns of ALD TiO₂ overcoated Pd/Al₂O₃ catalysts (no shown) are identical to that of bare Al₂O₃ substrate, suggesting that the ALD Pd and TiO₂ deposits are either amorphous, or too small for detection by conventional XRD.

Figure 3.4. XRD of Spherical Al₂O₃ (black) compared with gamma-Al₂O₃ (red) and delta-Al₂O₃ (blue).
Representative scanning transmission electron microscope (STEM) images of the bare Al₂O₃ support and the as-prepared TiO₂ protected Pdₐ single atom catalysts are illustrated in Figure 3.5.

**Figure 3.5.** HAADF-STEM images of (a) clean spherical aluminum oxide surface, and (b) thin film stabilized 7TiPd₁ catalysts on aluminum oxide.

The ALD TiO₂ treatment markedly improved the dispersion of the Pd on the Al₂O₃ substrate. Compared with the clean Al₂O₃ surface shown in Figure 3.5 (a), white dots representing isolated Pd₁ atoms are clearly shown in STEM images in Figure 3.5 (b) after carrying out the synthesis strategy discussed in Scheme 3.1. Unfortunately, Pd nanoparticles (NPs) also co-exist with Pd₁ on the substrate (Figure 3.6) with an average diameter of 3.4 ± 0.9 nm. Although the ratio of Pd₁ vs. Pd NPs is larger than 1000 : 1, only ca. 52% of the palladium was present as single atoms. TiO₂ cannot be clearly seen in the STEM images due to its small quantity and low contrast with the support Al₂O₃.
The surface composition of the Pd₁ catalysts were quantitatively analyzed using X-ray photoelectron spectroscopy (XPS). For the 1c, 7c and 14c TiO₂ thin film stabilized catalysts, the surface Ti/Al ratio increases with increasing TiO₂ ALD cycles from 0.65 to 1.04, while the Pd/(Ti+Al) ratio decreases from 0.16 to 0.05 (see Figure 3.7).
The Pd 3d XPS spectra for the as-prepared Pd catalysts show that the as-prepared Pd nanoparticles apparently have two peaks at 337.9 eV and 336.3 eV which are assigned to Pd$^{2+}$ and Pd$^{0}$, respectively.$^{90,91}$

*In situ* FTIR was performed in an ALD chamber under practical ALD conditions to understand the reason for the formation of Pd nanoparticles (see Figure 3.8).
Figure 3.8. Infrared absorbance spectra of Pd(hfac)$_2$ exposure and subsequent TiO$_2$ ALD cycle using TiCl$_4$ and H$_2$O as precursors.

The infrared peaks have been assigned in previous work.$^{89,90,92}$ The features at 1652 and 1605 cm$^{-1}$ are assigned to the stretching vibration modes of C=O in the -hfac ligands. In particular, the peak at 1605 cm$^{-1}$ is assigned to the C=O stretching vibration mode in the surface Pd(hfac) species, while 1652 cm$^{-1}$ is related to the C=O stretching vibration mode in the surface –hfac species chemisorbed on Al$_2$O$_3$ surface (i.e. Al(hfac)), where the hfac ligands have spilled over from the Pd(hfac)$_2$ during adsorption.$^{90}$ This feature at 1605 cm$^{-1}$ almost completely disappeared after only 2 cycles of TiO$_2$ ALD, suggesting a reaction between the TiO$_2$ ALD precursors and the surface –Pd(hfac) species. As the –hfac ligands are thought to play an important role in stabilizing PdI on the Al$_2$O$_3$ surface, the loss of –hfac may increase the Pd mobility leading to agglomeration, and Pd NP formation on the surface during TiO$_2$ ALD.
The thermal stability of the as-prepared Pd$_1$ catalysts under oxidation condition was tested by calcination at 300 °C in air. Aberration corrected STEM images (see Figure 3.9) revealed that the 14TiPd$_1$ sample was relatively unchanged by calcination, and remains essentially as Pd$_1$ (Figure 3.9e, f).

**Figure 3.9.** Aberration corrected STEM images of (a) as-prepared 0TiPd, (b) 0TiPd after calcination, (c) as-prepared 7TiPd$_1$, (d) 7TiPd$_1$ after calcination, (e) as-prepared 14TiPd$_1$, (f) 14TiPd$_1$ after calcination. Calcination was performed at 300 °C in air.
In contrast, both the 0TiPd and 7TiPd showed extensive aggregation to 4.6 ± 1.0 nm and 2.9 ± 0.7 nm, respectively, after 300 °C calcination. These results demonstrate that the nanocavity TiO$_2$ layer with the proper thickness can prevent the migration of Pd atoms and subsequent agglomeration at high temperature.

The thermal stability of the thin film stabilized Pd$_1$ catalysts under hydrogen reduction conditions were studied using the X-ray absorption spectroscopy (XAS) at the Pd K edge. As shown in Figure 3.10, both the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra of the as-prepared 14TiPd$_1$ catalyst resemble those of the Na$_2$PdCl$_4$ reference.

**Figure 3.10.** Pd K-edge (a) XANES and (b) EXAFS Fourier transform of the Pd$_1$ catalysts and reference samples.
After reduction in hydrogen at 250 °C, the XANES and EXAFS spectra of the reduced 14TiPd\textsubscript{1} catalyst (14TiPd\textsubscript{1}\_r) are similar to those of Pd NPs prepared using incipient wetness impregnation (IWI). The parameters extracted from fitting the extended X-ray absorption fine structure (EXAFS) spectra in K- and R- space are listed in Table 3.2 and the fitting quality is show in Figure 3.11 and 3.12, respectively.

**Table 3.2.** Pd K edge EXAFS fits of the as-prepared Pd\textsubscript{1} catalysts before and after hydrogen reduction at 250 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>scatter</th>
<th>CN</th>
<th>R, Å</th>
<th>DWF (×10\textsuperscript{3})</th>
<th>E\textsubscript{0}, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1TiPd\textsubscript{1}</td>
<td>Pd-Cl</td>
<td>3.5</td>
<td>2.30</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Pd-O</td>
<td>0.5</td>
<td>2.02</td>
<td>0.7</td>
<td>4.6</td>
</tr>
<tr>
<td>1TiPd\textsubscript{1}_r</td>
<td>Pd-Pd</td>
<td>3.6</td>
<td>2.77</td>
<td>2.0</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>Pd-Cl</td>
<td>0.6</td>
<td>2.29</td>
<td>0.3</td>
<td>-3.1</td>
</tr>
<tr>
<td>7TiPd\textsubscript{1}</td>
<td>Pd-Cl</td>
<td>3.9</td>
<td>2.30</td>
<td>0.3</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>Pd-O</td>
<td>0.1</td>
<td>2.00</td>
<td>0.7</td>
<td>3.2</td>
</tr>
<tr>
<td>7TiPd\textsubscript{1}_r</td>
<td>Pd-Pd</td>
<td>5.6</td>
<td>2.77</td>
<td>2.0</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>Pd-Cl</td>
<td>0.5</td>
<td>2.31</td>
<td>0.3</td>
<td>-1.4</td>
</tr>
<tr>
<td>14TiPd\textsubscript{1}</td>
<td>Pd-Cl</td>
<td>3.9</td>
<td>2.30</td>
<td>0.3</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>Pd-O</td>
<td>0.1</td>
<td>1.99</td>
<td>0.7</td>
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<tr>
<td>14TiPd\textsubscript{1}_r</td>
<td>Pd-Pd</td>
<td>5.6</td>
<td>2.77</td>
<td>2.0</td>
<td>-0.5</td>
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<tr>
<td></td>
<td>Pd-Cl</td>
<td>0.6</td>
<td>2.31</td>
<td>0.3</td>
<td>-0.8</td>
</tr>
</tbody>
</table>
Figure 3.11. Pd K edge XAFS fittings of the as-prepared catalysts in (a) k-space, and (b) Fourier transform.
Figure 3.12. Pd K edge XAFS fittings of Pd catalysts after hydrogen reduction at 250 °C in (a) k-space, and (b) Fourier transform.
The as-prepared Pd\textsubscript{1} atoms are coordinated with c.a. 4 chlorine atoms. The presence of chlorine is due to the TiO\textsubscript{2} ALD process using TiCl\textsubscript{4} as precursor. This residual Cl is consistent with TiCl\textsubscript{4} attacking the surface –Pd(hfac) species during TiO\textsubscript{2} ALD as postulated from the \textit{in situ} FTIR measurements. The reduced Pd catalysts have coordination numbers from 3.6 to 5.6. As the coordination number of Pd nanoparticle of 3-4 nm in diameter can be estimated to be about 9 to 10,\textsuperscript{93} the ALD thin film stabilized Pd catalysts are likely to contain both single atoms and nanoparticles, consistent with the observation from the STEM imaging. Pd K edge XANES linear combination fittings (LCFs) were used to calculate the coordination of Pd. The results of XANES LCFs are similar to the results obtained from EXAFS fittings (see Table 3.3 and Fig. 3.13).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
 & Pd-O & Pd-Cl & Pd-Pd \\
\hline
1TiPd1 in air & 13.6\% & 86.4\% & - \\
1TiPd1 reduced & - & 36.9\% & 63.1\% \\
\hline
7TiPd1 in air & 8.8\% & 91.2\% & - \\
7TiPd1 reduced & - & 25.6\% & 74.4\% \\
\hline
14TiPd1 in air & 9.1\% & 90.9\% & - \\
14TiPd1 reduced & - & 29.4\% & 70.6\% \\
\hline
\end{tabular}
\caption{Pd K edge XANES Linear Combination Fit.}
\end{table}

The XANES LCF generally has 10\% systematic error.
Figure 3.13. Composition of Pd obtained from Pd K edge XANES and EXAFS spectra for the (a) as-prepared Pd$_1$ catalysts, and (b) Pd$_1$ catalysts after hydrogen reduction.
In situ DRIFTS CO chemisorption has been an effective tool to assess the existence of site-isolated species such as Rh\textsubscript{1},\textsuperscript{94} and Pt\textsubscript{1}\textsuperscript{95}. The CO molecules can only adsorb linearly on single atoms. The feature representing atop CO adsorbed on single atoms is normally distinguishable from that on nanoparticles. Although the infrared spectral assignment of CO adsorbed on Pd has been studied intensively,\textsuperscript{96,97} the determination of CO chemisorption feature on single site Pd\textsubscript{1} is not straightforward as CO can cause single atom sintering observed by Diebold and coworkers using scanning tunneling microscopy over Pd\textsubscript{1}/Fe\textsubscript{3}O\textsubscript{4} model catalysts.\textsuperscript{98} Figure 3.14 and Figure 3.15 show CO adsorption on thin film stabilized Pd\textsubscript{1} at room temperature resulting in adsorption features as atop CO species (2160 cm\textsuperscript{-1}, 2116 cm\textsuperscript{-1} and 2094 cm\textsuperscript{-1}), bridge-bonded CO (1975 cm\textsuperscript{-1} and 1944 cm\textsuperscript{-1}) and 3-fold hollow sites (1882 cm\textsuperscript{-1}).

![Figure 3.14. DRIFTS spectra of CO adsorption. The spectra were obtained after room temperature purging of gas phase CO with He and reference to the background spectra recorded before exposure to CO.](image-url)
Figure 3.15. DRIFTS spectra of CO adsorption on 14TiPd. The spectra were obtained after room temperature flow of CO over time. After 0.5 minutes (cyan), 1 minute (green), 2 minutes (red), 4 minutes (blue), 6 minutes (magenta), 8 minutes (olive), 10 minutes (orange) and 30 minutes (gray).

The features at 2160 cm$^{-1}$, 2116 cm$^{-1}$ and 2094 cm$^{-1}$ can be assigned to CO chemisorption on Pd$^{2+}$, Pd$^+$ and Pd$^0$, respectively. The small feature at 2160 cm$^{-1}$ is most likely associated with the CO adsorption on single atom Pd$_1$, while the other two peaks represent CO adsorption on Pd nanoparticles.

With the small intensity of 2160 cm$^{-1}$ and the dominant features of CO chemisorption on bridge- and 3-fold hollow sites, we believe that agglomeration of adatom Pd occur during the CO chemisorption, similar to what observed in the Pd$_1$/Fe$_3$O$_4$
model catalyst system. The intensities of these bands decreased and some of the bands shifted slightly with increasing TiO$_2$ ALD cycles, indicating that Pd is progressively covered by the ALD TiO$_2$. Similar results have been observed for Al$_2$O$_3$ ALD overcoats on Pd surface and TiO$_2$ ALD on Au.$^{38,100}$

The catalytic activity of the TiO$_2$ thin film stabilized Pd$_1$ catalysts was evaluated using methanol decomposition as a probe reaction. Figure 3.16 shows the reactivity for methanol decomposition at 240 °C and 300 °C as a function of TiO$_2$ ALD cycles.

![Graph showing methanol conversion as a function of ALD TiO$_2$ cycles.](image)

**Figure 3.16.** Methanol conversion as a function of ALD TiO$_2$ cycles in the methanol decomposition reaction.

The lightoff curves during heating and cooling mostly overlapped with each other (see Figure 3.17), suggesting no significant changes such as sintering or coke deposition. The catalysts were also tested under methanol decomposition conditions at 300 °C for 24 hours without significant deactivation.
Figure 3.17. Methanol decomposition light-off curves using the catalyst (a) 0TiPd, (b) 1TiPd, (c) 7TiPd, and (d) 14TiPd. Black, Heating; Red, cooling.

The catalysts performance clearly depends on the cycles of overcoat. At 240 °C, all three thin film stabilized Pd₁ catalysts showed enhanced performance than the Pd nanocatalysts. The 7c TiO₂ thin film stabilized Pd catalysts (7TiPd₁) showed the best performance with ~ 24% methanol conversion while Pd nanoparticles had close to ~15% methanol conversion. The enhanced performance can be explained by the enhanced thermal stability of the Pd₁ catalysts which possessed more surface active sites than the Pd nanoparticles, i.e., all the Pd atoms in Pd₁ catalysts can potentially act as active site
while only the surface atoms on Pd nanoparticles can catalyze chemical reaction. The 14c TiO$_2$ thin film stabilized Pd$_1$ catalysts showed slightly lower conversion at ~ 20% than 7TiPd$_1$ even it has showed the best thermal stability observed by STEM. This seems to suggest that 14c TiO$_2$ not only deposits around Pd$_1$ to enhance it thermal stability but it also starts to cover the Pd surface. This has been evidenced by the DRITFS CO chemisorption studies where the intensity of the CO bands decreased with increasing TiO$_2$ ALD cycles. The blue shift, 29 cm$^{-1}$, observed on 3-fold hollow sites CO on 14TiPd$_1$ from the DRIFTS data suggests that at 14 cycles, the deposited TiO$_2$ mostly deposit on the Pd (111) sites on Pd nanoparticles.

At 300 °C, 7TiPd$_1$ still showed the best performance with respect to methanol conversion. To our surprise, 14TiPd$_1$ was the less active catalysts at 300 °C, even worse than the Pd nanoparticles. A simplified mechanism for the methanol decomposition reaction is summarized in the following two surface reactions (1) and (2).

\[
\text{CH}_3\text{OH}_{(\text{ad})} \rightarrow \text{CO}_{(\text{ad})} + 4\text{H}_{(\text{ad})} \quad (1)
\]

\[
2\text{H}_{(\text{ad})} \rightarrow \text{H}_2(\text{g}) \quad (2)
\]

Upon adsorption to the Pd surface, methanol can decompose into chemisorbed carbon monoxide CO$_{(\text{ad})}$ and hydrogen H$_{\text{ad}}$ well below room temperature. Surface science studies performed by Goodman and Bowker showed that H$_2$ and CO desorbed from Pd surface at 27 °C and 207 °C, respectively, indicating that methanol decomposition is desorption limited.$^{101}$ This is also known as the carbon monoxide self-poisoning effect: the CO product molecules strongly adsorb on the catalyst surface, preventing the methanol reactant from accessing the catalyst and the reaction terminates.
As CO is one of the products for methanol decomposition, a hypothesis is that CO binds much more strongly on Pd$_1$ than on Pd nanoparticles, which suppress the activity of Pd$_1$ catalysts. To test this hypothesis, EXAFS measurements at the Pd L$_3$ (3173 eV) edge was carried out to probe the adsorption of CO at room temperature and 250 °C. The palladium L$_3$ edge represents dipole-allowed $2p \rightarrow 4d$ transition, and the L$_3$ absorption probes the density of states (DOS) of palladium $d$ character. The L$_3$ edge is characterized by the presence of intense resonances, “white line”. Changes in the L$_3$ XANES whiteline after chemisorption of an adsorbate on the Pd surface reflects electronic structural changes caused by orbital hybridization. The $\Delta$XANES (XANES spectrum of the precious metal with the adsorbate minus that of the clean surface) has a unique shape with respect to the type of adsorbate and the intensity increases with adsorbate concentration, and therefore it can be used to both identify and quantify the adsorbates.$^{102,103}$ Figure 3.18 shows Pd L$_3$ XANES and $\Delta$XANES spectra for Pd NPs (0TiPd) and Pd$_1$ (14TiPd$_1$) catalysts in a steady state flow of helium and CO at 25 °C and 250 °C, respectively. For Pd NPs, there is significant CO uptake at 25 °C because of the strong CO adsorption. But at 250 °C, there is almost no CO coverage on the Pd surface, indicating a fast desorption of CO on the surface.
In sharp contrast, even at 250 °C, there is still significant CO adsorbed on the Pd₁ atoms. Assuming the CO adsorption sites at 25 °C are potential active sites for catalyzing methanol decomposition, and normalizing the CO coverage to these sites, ca. 70% of the surface adsorption sites were still covered by CO at 250 °C for 14TiPd₁. Therefore, the surface is still largely “poisoned” by the chemisorbed CO molecules. This result suggests that CO adsorbs much more strongly on supported Pd₁ single atoms than Pd nanoparticles. This is also consistent with the surface science studies on a series of size-selected Pdₙ (n = 1 – 25) clusters, which reported that TiO₂ supported single atom Pd₁ showed the highest Pd 3d binding energy and lowest CO oxidation activity. The authors ascribed this phenomenon to the stable valence structure of Pd₁/TiO₂.
3.4. Conclusion

In summary, we developed a novel strategy to synthesize thermally stable single atom Pd\textsubscript{1} catalysts by combining Pd ALD and templated-TiO\textsubscript{2} ALD. Although there were Pd nanoparticles formed on the surface, \textit{in-situ} FT-IR under reaction conditions reveal that it can be avoided in the future by choosing mild precursors that would not attack the surface -Pdhfac species during the metal oxide ALD. Overall, the ALD TiO\textsubscript{2} overcoat dramatically enhanced the stability of single atom Pd\textsubscript{1} catalysts under both oxidation and reduction conditions. These thin film stabilized Pd\textsubscript{1} catalysts are promising catalysts for methanol decomposition reaction. The reactivity seems strongly depending on the cycles of overcoats, representing a combining effect of thermal stability and amount of exposure sites of surface Pd. The single-atom Pd\textsubscript{1} catalysts protected by 14 cycles ALD TiO\textsubscript{2} showed greatly enhanced thermal stability with no obvious agglomeration after 300 °C calcination. Interestingly, it was also the least active catalysts for methanol decomposition at 300 °C. The 14TiPd\textsubscript{1} catalysts have dramatically different chemical behavior as compared to Pd NPs as evidenced by the much stronger adsorption of CO on Pd\textsubscript{1} seen by \textit{in situ} Pd L\textsubscript{3} edge XANES and ΔXANES.
CHAPTER FOUR

4. *In situ* Observation of ALD Single-Atom Palladium CO Reduction at Low Temperature

4.1. Introduction

Hydrogen is considered as one of the most important energy carriers of the future.\(^{104}\) The increasing demand in alternative energy, due to reduction of fossil fuel reserves and environmental issues, has attracted extensive efforts in studying on hydrogen production, storage and utilization. As the most abundant element in the universe and the seventh most abundant element on earth, hydrogen represents a promising, environmental friendly and inexpensive renewable energy.

Hydrogen can be produced from a variety of feedstocks. Some of these include fossil resources such as natural gas by means of different chemical processes. In chemical industry, 95% of the hydrogen in the US is produced via steam reforming coupling water-gas shift reaction in the industrial scale.\(^{105}\) Hydrogen can also be produced from renewable sources such as biomass, electrolysis, solar and wind.\(^{106}\)

One important application of hydrogen is the hydrogen fuel cell, as a replacement for combustion based energy sources, which efficiently generates electricity without pollution.\(^{107,108}\) Hydrogen fuel cell provides an alternative system to power vehicles.
The tank-to-wheel efficiency of a fuel-cell vehicle can reach 22% if the hydrogen is stored on board as high-pressure gas, and 17% as liquid hydrogen. Both hydrogen storage methods pose significant safety risk in practice; suffer from high costs, low energy densities and loss of hydrogen.\textsuperscript{109,110} Formic acid, a strong, corrosive and stable acid, has been studied in order to obtain hydrogen with its decomposition.\textsuperscript{111-113} Formic acid decomposition can be transformed into hydrogen at low temperatures (100 °C). The low temperature decomposition of formic acid to form carbon dioxide and hydrogen may provide a valuable source of hydrogen for fuel cells.

\[ \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \]

Catalysts based on precious metals such as iridium, palladium, platinum, ruthenium and rhodium, have shown high activity for formic acid decomposition at 150 °C by Solymosi and co-workers.\textsuperscript{114} Although activity was high, hydrogen was produced with much higher than 100 ppm of CO on all catalysts. Therefore, further research has applied the usage of a secondary metal such as Pd-Au and Pd-Ag which have decreased the CO coproduction to lower values than CO ppm.\textsuperscript{115-117} Ojeda and Iglesia\textsuperscript{118} showed that highly dispersed gold nanoparticles present higher formic acid decomposition activity than platinum nanoparticles when the former were decreased in particle size, producing CO free H\textsubscript{2}. This was also confirmed after the observation of active metal sites situated on isolated gold atoms.

The size of metal particles is one of the major factors that dictate the performance of a catalyst.\textsuperscript{64,119} Recent studies demonstrate that sub-nanometer clusters or single atoms can achieve higher activity and selectivity than nanometer sized particles.\textsuperscript{81}
By reducing the diameter of the metal particles to atomic size, the active surface area of the catalyst increases and therefore increasing the catalytic activity in a wide range of reactions. Single atom catalysts have been reported showing superior activity for the oxidation of CO, methane conversion, water–gas shift reaction, oxygen reduction reaction and Ullmann reaction. The synthesis of single atom catalysts is challenging due to the high mobility and easiness of the atoms to sinter under reaction conditions. This leads to a reduction of the surface area of the metal and therefore causing deactivation of the catalyst. An advanced technique that can achieve atomic level control on the catalyst synthesis is desired.

ALD is based on sequential, self-limiting surface reactions. It has the capability of tailoring size from single atom, sub-nanometer clusters to nanoparticles of metal and metal oxides. ALD has been demonstrated to be a promising tool to apply oxide over-coating layers onto supported metal catalyst with atomically precise thickness control, which allows optimizing both the stability and activity.

The objective of the present work is to investigate the stability of Pd single atoms synthesized by ALD using an Al₂O₃ protective coating as an alternative to TiO₂, investigated on our previous work. In this study we are interested in understanding the capability of CO as reducing agent to Pd single atom catalysts at room temperature in order to evaluate the stability of Pd. Changes in metallic palladium state can be observed through in situ XAS of Pd.
4.2. Experimental Details

4.2.1. Synthesis

The Pd catalysts were synthesized using a commercial benchtop ALD reactor (Arradiance, Gemstar-6) equipped with an in situ quartz-crystal microbalance (QCM, Inficon). Ultra-High purity nitrogen carrier gas (Airgas, 99.999%) was further purified using a Supelco gas purifier (Sigma-Aldrich) to trap hydrocarbon, moisture and oxygen-containing impurities before entering the reactor.

Spherical alumina powder (NanoDur, 99.5%, Alfa Aesar) was used as the substrate without further treatment. Substrate was uniformly spread onto a stainless steel sample tray with a stainless steel mesh top to contain the powder while still supplying access to the ALD precursor vapors. The loaded sample tray was placed into the center of the reactor and kept for 30 min at 150 °C in a 50 sccm flow at 0.5 Torr pressure to allow temperature stabilization.

The ALD timing sequences can be expressed as $t_1$-$t_2$-$t_3$-$t_4$, where $t_1$ and $t_3$ correspond to the exposures times of the two precursors, $t_2$ and $t_4$ are the nitrogen purge times between precursor exposures and all units are given in seconds. 500 mg of Al$_2$O$_3$ NanoDur was used as a substrate. The Al$_2$O$_3$ coating used alternating exposures to dimethylaluminum isopropoxide (DMAI, Sigma-Aldrich, 99.9%) and deionized water with time sequence (2.5 s−75 s−3.75 s−150 s) at 150 °C. For the Al$_2$O$_3$ overcoat, 1, 3, and 10 cycles were used. The Pd ALD used exposures to Pd (II) hexafluoroacetylacetone (Pd(hfac)$_2$, Sigma-Aldrich, 98%) at 150 °C with time sequence (500 s−1500 s). The samples were denoted as 1cAlPd$_1$, 3cAlPd$_1$, and 10cAlPd$_1$.  

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For each sample, the mass was measured with an analytical balance before and after ALD to determine the Pd loading. Weight percent of palladium in Pd$_1$ catalysts was estimated to be 0.2 wt%.

4.2.1. In situ Quartz Crystal Microbalance Analysis and Ellipsometry

Quartz Crystal Microbalance (QCM) studies were performed for Al$_2$O$_3$ ALD, using an Inficon BK-A0F bakeable sensor, HT-cut quartz gold sensor crystals (Colnatec), and an Inficon SQM-160 film thickness monitor. To monitor the Al$_2$O$_3$ synthesized by DMAI-H$_2$O, a thick layer (7 nm) of Al$_2$O$_3$ (TMA-H$_2$O) was first deposited on the QCM at a temperature of 150 °C. The Al$_2$O$_3$ layer was grown by sequential exposures of DMAI and water for about 80 cycles. The QCM mass measurements were converted to Al$_2$O$_3$ film thicknesses assuming a density for Al$_2$O$_3$ of 2.6 g/cm$^3$.

Al$_2$O$_3$ films were analyzed using ex situ ellipsometry. Thickness measurements of the Al$_2$O$_3$ films were performed using a J.A. Woollam Co. alpha-SE Spectroscopic ellipsometer. Ellipsometric data were collected with a 70 incidence angle and was fit to a Cauchy model.

4.2.2. BET Surface Area Measurements

Brunauer–Emmett–Teller (BET) surface area of all palladium catalysts were measured via nitrogen adsorption at 77 K by using a Micromeritic Gemini 275 system.
4.2.3. **Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)**

DRIFTS measurements on CO adsorption were performed using a Thermo Nicolet Nexus 670 spectrometer, with a MCT/A detector with a spectral resolution of 4 cm$^{-1}$, in diffuse reflectance mode while the exiting stream was analyzed by QMS. A Pike Technologies HC-900 DRIFTS cell with nominal cell volume of 6 cm$^3$ was used.

In CO adsorption experiments, the pretreated sample was purged with helium at room temperature (rt) before switching to 2%CO/2%Ar/He (25 mL/min) flow for 30 min. The sample was then purged with helium at rt for another 30 min. IR spectra and QMS profiles were recorded continuously during these processes. All reported IR spectra are difference spectra referenced to a background spectrum collected after pretreatment but prior to CO adsorption.

4.2.4. **In situ X-ray Absorption Spectroscopy (XAS)**

Pd K-edge (23.564 keV) XAS was performed at the 10-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. The amount of the sample in use was optimized to achieve a XAS step height of about 1. The XAS spectra were recorded in transmission mode. Standard procedures based on WINXAS 3.1 software were used to fit the data in the extended X-ray absorption fine structure (EXAFS). The two-shell model fit of the $k^2$ – weighted EXAFS data was obtained between $k = 2.9 – 11.7$ Å and $r = 1.3 – 2.9$ Å, respectively.
4.2.5. Catalytic Performance

For each test, 10 mg of Pd catalysts diluted with SiO$_2$ gel (Silicycle, S10040M) were used on a plug-flow, temperature-controlled microreactor system (Altamira AMI 300). The sample, loaded into a U-shaped quartz tube (4 mm i.d.) and supported by quartz wool. For formic acid decomposition, He was bubbled through formic acid at 30 cm$^3$min$^{-1}$. All gases were provided by Air Liquide with the ultrahigh purity (UHP, 99.999%) helium as balance gas.

A downstream quadrupole mass spectrometer (QMS) was utilized in order to obtain the catalytic activity of the Pd catalysts by using the formic acid decomposition reaction. A calibration experiment was performed were formic acid was kept at temperatures 5 °C, 10 °C, 15°C and 20 °C (using a water bath) until the QMS was stabilized at each temperature, and the respective intensities of formic acid (monitored at m/z 29) were recorded. A linear fit of the respective intensities versus the formic acid concentration at the indicated temperatures, obtained from the vapor pressures, was plotted. The intensity and slope was then utilized to calculate the respective formic acid concentrations for the different catalyst reactions. During the decomposition reaction, formic acid was kept at 20 °C.

4.3. Results and Discussion

The strategy used to synthesize stable Pd$_1$ single atom by ultrathin TiO$_2$ coating by ALD, described in our previous work,$^{122}$ showed after in situ FTIR palladium nanoparticles in the surface.
In order to prevent this situation, it was concluded that an alternative mild precursor should be chosen in order not to attack the surface –Pdhfac species during the metal oxide ALD deposition. Therefore dimethylaluminum isopropoxide (DMAI, Al(CH$_3$)$_2$OC$_3$H$_7$) was selected as a milder alternative precursor in order to deposit a protective coating on Pd single atoms.

As a novel precursor, DMAI was studied in our ALD reactor in order to determine the ideal conditions to control single atoms. This investigation was performed through in situ Quartz Crystal Microbalance (QCM).

Mass changes were monitored with QCM (Figure 4.1). The growth rate of Al$_2$O$_3$ from alternative exposures to Al(CH$_3$)$_2$OC$_3$H$_7$ (DMAI) and H$_2$O was determined to be 0.96 Å/cycle. The Al$_2$O$_3$ ALD growth rate is constant at 0.96 Å/cycle, however, the ellipsometry data suggests a slightly lower Al$_2$O$_3$ ALD growth rate of 0.76 Å/cycle at 80 AB cycles. The mass increase during Al(CH$_3$)$_2$OC$_3$H$_7$ (DMAI) adsorption is labeled in Figure 4.1 as $\Delta m_1$. 

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Figure 4.1. In situ QCM studies of Al₂O₃ ALD using DMAI and H₂O as precursors at 150 °C. ∆m₁ and ∆m₂ represent the mass gain during DMAI and H₂O exposure, respectively. The total mass gain ∆m of a complete Al₂O₃ (DMAI-H₂O) ALD cycle is ca. 0.05 μg/cm². As the Al₂O₃ density of 2.6 g/cm³, the growth rate of Al₂O₃ is ca. 0.96 Å per ALD cycle.
During H\textsubscript{2}O pulse the mass decrease could be due to desorption of isopropoxide from the Al\textsubscript{2}O\textsubscript{3} surface. A bump during H\textsubscript{2}O pulse can be observed due to the effect of H\textsubscript{2}O adsorption and desorption. The mass increment during a complete ALD cycle is identified as \(\Delta m_2\), which is linearly related to the growth rate. Figure 4.2 presents four possible reaction mechanisms and their corresponding \(\Delta m_2/\Delta m_1\) ratios.

In order for mechanisms 1b and 2b (Figure 4.2) to occur, there should be a mass gain after H\textsubscript{2}O deposition, due to CH\textsubscript{3} surface groups replaced by the slightly heavier -OH groups, but as observed from QCM data (Figure 4.1) there is a mass loss after H\textsubscript{2}O. The \(\Delta m_2/\Delta m_1\) ratio obtained from the QCM data is 0.7 which is close enough to the result obtained from mechanism 1a (Figure 4.2) which is 0.6. Therefore Al\textsubscript{2}O\textsubscript{3} ALD film growth proceeded according to the following two self-limiting surface reactions. Reactions 2a and 2b happening simultaneously. The DMAI and H\textsubscript{2}O yield Al\textsubscript{2}O\textsubscript{3} ALD according to the following two reactions:

\[
(1) \quad Al - OH^* + Al(CH_3)_2OC_3H_7 \rightarrow Al - O - Al(CH_3)OC_3H_7^* + CH_4
\]

\[
(2a) \quad Al - CH_3^* + H_2O \rightarrow Al - OH^* + CH_4
\]

\[
(2b) \quad Al - OOC_3H_7^* + H_2O \rightarrow Al - OH^* + HOOC_3H_7
\]

where the asterisks denote the surface species.
Figure 4.2. Possible reaction mechanisms for (DMAI) – H₂O process and the corresponding m₀/m₁ ratios.
In this work dimethylaluminum isopropoxide (DMAI, Al(CH₃)₂OC₃H₇) precursor was selected as an alternative, in order to deposit Al₂O₃ oxide coatings on Pd single atoms for stabilization, using the same strategy to synthesize Pd₁ as previous work. Three catalysts were prepared using 1-cycle, 3-cycle and 10-cycle Al₂O₃ thin film Pd₁ overcoating, denoted as 1AlPd₁, 3AlPd₁ and 10AlPd₁, respectively. The equivalent thickness of these Al₂O₃ thin films are 1 Å, 2.9 Å and 9.6 Å, for 1c, 3c and 10c Al₂O₃, respectively determined using in situ quart crystal microbalance (QCM).

All of the ALD Al₂O₃ stabilized Pd₁ catalysts were prepared on commercial spherical aluminum oxide nanoparticles (Al₂O₃, Alfa Aesar, NanoDur™, 99.5%). Brunauer-Emmett-Teller (BET) surface area measurement was performed on the catalyst with higher amount of over-coating cycles, 10AlPd₁, to show that Al₂O₃ treatment did not vary the surface area of the substrate. The bare Al₂O₃ substrate and 10AlPd₁ catalysts have a surface area of ~35 m²/g (see Figure 4.3).

![Figure 4.3. BET surface area of (a) Bare Al₂O₃, and (b) 10AlPd₁.](image-url)
In order to evaluate the stability of the new Al₂O₃ protective coating, CO adsorption was performed on the catalyst 3AlPd₁ and investigated through X-ray absorption spectroscopy (XAS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to observe Pd–CO surface intermediates (DRIFTS) and Pd oxidation state and geometry (XAS).

During X-ray absorption Spectroscopy, catalyst 3AlPd₁ was exposed to the set of treatment temperatures and gas environments described in Figure 4.4. The sample was exposed to four sequential test conditions, which are labeled 1 through 4. All conditions were conducted at 25 °C, beginning with as prepared sample in air (1), applying 5% CO/He for 1 hour (2), then sample was oxidized in 20%O₂/He at 250 °C for 30 minutes and brought back to room temperature. Steps 3 and 4, conducted at 25 °C after oxidation, 20%O₂/He at 25 °C (3) and a final measurement at room temperature in 5% CO/He (4).

**Figure 4.4.** EXAFS experimental conditions. (1) XAS was measured at room temperature in air. (2) XAS–DRIFTS measured as 5% CO was flown for 1 hour. The sample was then heated to 250 °C in 20% O₂ and held for 30 min. (3) XAS was measured under 20%O₂ at room temperature for 30 minutes, (4) and a final measurement was taken in 5%CO after 30 minutes of flow.
X-ray absorption near edge spectroscopy (XANES) of 3AlPd is shown in Figure 4.5.

![Figure 4.5. X-ray absorption near edge spectra (XANES) of sample 3AlPd](image)

The peak at 24.375 keV represents PdO, and peaks at 24.370 keV and at 24.390 keV are characteristic of Pd metal. The XANES spectrum of 3AlPd catalyst shows resemblance to PdO spectrum which implies +2 valence state. The transition of PdO to Pd can be most easily followed by observing the simultaneous decrease of the 24.375 keV PdO peak and increase of the 24.390 keV Pd metal peak. Catalyst contained PdO after all treatments (1-4), there was significantly reduction of the corresponding PdO peak after CO flow at 25 °C (2). After heating to 250 °C and introduction of O₂, the Pd on the alumina support was mostly oxidized. Second flow of CO (4) indicated further reduction, which may indicate the sample wasn’t fully oxidized during the XAFS measurement at (3).
Extended X-ray absorption fine structure (EXAFS) of the 3AlPd₁ catalyst (Figure 4.6) showed the initial presence of only Pd–O and the absence of Pd second-shell paths, consistent with bulk PdO, could indicate the presence of palladium single atoms.

Figure 4.6. EXAFS of 3AlPd₁ catalyst.

After CO exposure at room temperature a portion of the PdO in the 3AlPd₁ sample became metallic, as seen by the reduction in the Pd–O feature and increase in the Pd–Pd feature. After O₂ exposure, the catalyst was not fully oxidized as can be observed from figure 4.6 where Pd-Pd bond features don’t disappeared. In the same manner, O₂ wasn’t fully removed (2, 4) when CO was introduced to the system, where PdO was reduced and Pd–Pd feature became very intense. The parameters extracted from fitting the extended X-ray absorption fine structure (EXAFS) spectra in K- and R- space are listed in Table 4.1 and the fitting quality is show in Figure 4.7.
Table 4.1. Pd K edge EXAFS fits of the as-prepared Pd\(_1\) catalysts before and after co-chemisorption and oxidation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>scatter</th>
<th>CN</th>
<th>R, Å</th>
<th>DWF ((\times10^3))</th>
<th>E(_0), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>3AlPd(_1)</td>
<td>Pd-O</td>
<td>2.6</td>
<td>2.02</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>3AlPd(_1)_CO</td>
<td>Pd-Pd</td>
<td>5.4</td>
<td>2.76</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Pd-O</td>
<td>1.8</td>
<td>2.05</td>
<td>0.7</td>
<td>5.0</td>
</tr>
<tr>
<td>3AlPd(_1)_O(_2)</td>
<td>Pd-Pd</td>
<td>2.5</td>
<td>2.72</td>
<td>2.0</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Pd-O</td>
<td>2.4</td>
<td>2.05</td>
<td>0.7</td>
<td>3.44</td>
</tr>
<tr>
<td>3AlPd(_1)_COx2</td>
<td>Pd-Pd</td>
<td>5.8</td>
<td>2.75</td>
<td>2.0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Pd-O</td>
<td>1.4</td>
<td>2.08</td>
<td>0.7</td>
<td>7.08</td>
</tr>
</tbody>
</table>

The Pd-O bond distance of 2.02 Å is consistent with that of the bulk material and indicative of Pd\(^{2+}\)-O bonding. PdO bulk catalysts consist of a 4 fold Pd-O, while 3AlPd\(_1\) catalyst was initially 3-fold Pd–O (R = 2.02 Å) consistent with PdO in the surface. After application of CO the appearance of metallic Pd-Pd bond at 2.76 Å and a coordination number of 5.4, lower than bulk palladium metal (N = 12), is explained by the coexistence of oxide and metallic Pd species, where the Pd-O coordination number decreases to 1.8. Application of CO slightly increased the Pd–O bond distance to 2.05 Å, although this change may be within experimental uncertainty.

When O\(_2\) was introduced, Pd-Pd coordination decreased to 2.5 (R = 2.72 Å) and a Pd-O coordination of 2.4 (R = 2.05 Å) appeared. CO was reintroduced, but the catalyst wasn’t fully reduced, the catalysts showed Pd–Pd coordination at around 5.8 (R = 2.75 Å) and a Pd-O coordination of 1.4 (R = 2.08 Å).
The 3AlPd\textsubscript{1} catalyst under O\textsubscript{2} at 25 °C (condition 3) had short Pd–Pd bond distances (R = 2.72 Å), which is what would be expected for a Pd metal with substantial subsurface oxygen content.
Figure 4.7. Pd K edge XAFS fittings of the as-prepared catalysts in (a) k-space, and (b) Fourier transform.
Further information on the 3AlPd$_1$ catalyst was determined using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) as observed from Figure 4.8.

![DRIFTS spectra of CO adsorption on 3AlPd$_1$](image)

**Figure 4.8.** DRIFTS spectra of CO adsorption at room temperature on 3AlPd$_1$ (a) during 30 minutes of CO flow and (b) after purging of gas phase CO with He. Reference to the background spectra recorded before exposure to CO. After 0.5 minutes (green), 1 minute (cyan), 2 minutes (red), 4 minutes (blue), 6 minutes (magenta), 8 minutes (olive), 10 minutes (orange), 15 minutes (gray), 20 minutes (dark cyan), 25 minutes (dark yellow) and 30 minutes (violet).

The spectral ranges in which IR bands have been attributed to surface carbynlys of Pd$^{n+}$ are: linear Pd$^{2+}$-CO features observed at 2215-2145 cm$^{-1}$; Pd$^+$-CO complexes observe between 2140-2110 cm$^{-1}$. 

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Bridging carbonyls Pd\(^+\)-CO-Pd\(^+\) have been assigned by different studies to bands at at 1995-1975 cm\(^{-1}\),\(^{126}\) or at 1930 cm\(^{-1}\).\(^{125}\) Bands at wavenumbers below 2100 cm\(^{-1}\) are generally characterized of metallic palladium.\(^{126,129-132}\)

Adsorption of CO on oxidized Pd samples in a CO flow is characterized by reduction of Pd\(^{n+}\) to Pd\(^0\) which suggests spectra at wavenumbers below 2100 cm\(^{-1}\) in the IR spectra.\(^{133}\) Three main peaks identify adsorption of CO on oxidized Pd/Al\(_2\)O\(_3\); at 2170-2145 cm\(^{-1}\) (Pd\(^{2+}\)-CO), 2135-2110 cm\(^{-1}\) (Pd\(^{+}\)-CO), and 2100-2050 cm\(^{-1}\) (Pd\(^0\)-CO).\(^{126,128,129,133}\) Figure 4.8a show CO adsorption on thin film palladium at room temperature, resulting in adsorption features at atop CO species (2162 cm\(^{-1}\), 2127 cm\(^{-1}\), 2098 cm\(^{-1}\) and 2062 cm\(^{-1}\)), bridge-bonded CO (1975-1971 cm\(^{-1}\) and 1937 cm\(^{-1}\)) and 3-fold hollow sites (1898-1868 cm\(^{-1}\)). Band at 2162 cm\(^{-1}\) can be identified as Pd\(^{2+}\), 2127 cm\(^{-1}\) assigned as Pd\(^+\), 2098 cm\(^{-1}\) as Pd\(^0\) and 1975 and 1937 as Pd\(^+\)-CO-Pd\(^+\).\(^{125}\) During purging of gas phase CO with helium (figure 4.8b), all the band intensities decrease, being high frequency bands less stable. The feature at 2155 cm\(^{-1}\) is most likely associated with the CO adsorption on single atom Pd\(_1\), while 2133 cm\(^{-1}\), 2097 cm\(^{-1}\) and 2063 cm\(^{-1}\) represent CO adsorption on Pd nanoparticles. With the dominant intensities of CO chemisorption on bridge and 3-fold hollow sites, we believe that the agglomeration of adatom Pd occur during the CO chemisorption similar to previous studies.\(^{122}\)

After CO exposure at 25 °C, 3AlPd\(_1\) produced a more intense peak at 2098 cm\(^{-1}\) ascribed to atop sites on an oxidized Pd (Pd\(_1\) \(^{5+}\) –CO) as well as features at 1725, 1587, and 1480 cm\(^{-1}\) associated with adsorption of CO\(_2\) by the alumina support as carbonates and bicarbonates.\(^{129,134,135}\)
After CO was purged for 30 minutes the atop site shifted to 2090 cm\(^{-1}\) indicating the formation of linear CO on metallic Pd. When exposed to CO, the catalyst formed carbonyls within 1 minute.

As the PdO surface becomes reduced from CO exposure, CO adsorbs on bridge and 3-fold hollow sites as soon as different Pd crystallites facets appear, and this change in oxidation state is also observed by XANES. The bridge and 3-fold hollow sites corresponding IR bands increased in intensity, as observed from figures 4.8 and 4.9, under CO flow. DRIFTS spectra verified the reduction of PdO to Pd at room temperature, as observed in the Pd XANES spectra, with the loss of the band observed at 2155 and reduction of 2137 cm\(^{-1}\)\(^{136}\) (Figure 4.8b).

An unprotected Pd sample (0AlPd\(_{1}\)) was also synthesized and used as reference to be compared with the 3AlPd\(_{1}\) catalyst. Catalyst 0AlPd\(_{1}\) DRIFTS data is observed in Figure 4.9. The IR bands at 2137/2132 cm\(^{-1}\) and 2098 cm\(^{-1}\) show the same intensity after 30 minutes (figure 4.9) while on 3AlPd\(_{1}\), the peak at 2098 cm\(^{-1}\) (figure 4.8) corresponding to metallic Pd double sizes in regards to 2132 cm\(^{-1}\) feature and compared to the same peak on 0AlPd\(_{1}\). This finding suggests that the Al\(_2\)O\(_3\) protective coating might be reacting with the precursor Pd(hfac)\(_2\) and therefore attacking the surface –Pdhfac species during the metal oxide ALD deposition. With increasing amount of CO flow introduced into the 0AlPd\(_{1}\) catalyst, the feature at 1988 cm\(^{-1}\) (figure 4.9b) increases much faster than the feature at 1937 cm\(^{-1}\), due most likely to the formation of reduced Pd surface sites.\(^{129}\)
Figure 4.9. DRIFTS spectra of CO adsorption at room temperature on 0AlPd$_1$ (a) during 30 minutes of CO flow and (b) after purging of gas phase CO with He. Reference to the background spectra recorded before exposure to CO. After 0.5 minutes (green), 1 minute (cyan), 2 minutes (red), 4 minutes (blue), 6 minutes (magenta), 8 minutes (olive), 10 minutes (orange), 15 minutes (gray), 20 minutes (dark cyan), 25 minutes (dark yellow) and 30 minutes (violet).

From our previous work, methanol decomposition was proven to be size dependent and in favor of large nanoparticles. Therefore, an alternative reaction was implemented. The catalytic performance of Pd$_{1}$/Al$_2$O$_3$ catalyst was evaluated in formic acid decomposition. The three catalysts were tested for formic acid decomposition at 120 °C for 8 hours. Figure 4.10 shows the reactivity for formic acid at 120 °C after 5, 6 and 7 hours as a function of Al$_2$O$_3$ ALD cycles. Formic acid conversion obtained was much lower than what observed in literature for palladium at similar temperatures.$^{137}$ No carbon
monoxide was observed from the QMS data, but because QMS has been proven unreliable in this work and only CO\(_2\) and H\(_2\) products were observed with sum up selectivity’s at 50 \%, the data could not be fully trusted. In order to check for CO products, DRIFTS was performed at 120 °C during 30 minutes of formic acid flow (see figure 4.10). As can be observed from the DRIFTS data there is CO production, supporting the idea of the unreliable QMS data.

![DRIFTS spectra of CO adsorption at 120 °C after 30 minutes of formic acid flow.](image)

**Figure 4.10.** DRIFTS spectra of CO adsorption at 120 °C after 30 minutes of formic acid flow.
The 3cAlPd\textsubscript{1} catalysts showed slightly better performance than 10cAlPd\textsubscript{1} with ~40\% formic acid conversion while 1AlPd\textsubscript{1} had ~27\% formic acid conversion (figure 4.11).

![Graph showing formic acid conversion over time for different catalysts.](image)

**Figure 4.11.** Formic acid decomposition at 120 °C for 8 hours.

### 4.4. Conclusion

The reduction of Pd\textsubscript{1} catalysts during CO adsorption, in an attempt to find a suitable precursor to synthesize thermally stable Pd\textsubscript{1} single-atom catalysts, that prevented the attack of surface –Pdhfac atoms, was observed. Using *in situ* EXAFS spectroscopy and DRIFTS technique have revealed change in oxidation state to metallic Pd at room temperature. Unfortunately, DRIFTS data on 3AlPd\textsubscript{1} suggested that the Al\textsubscript{2}O\textsubscript{3} oxide coating synthesized with DMAI, reacted with –Pdhfac as observed from the Pd\textsuperscript{0} IR band.
CHAPTER FIVE

5. Palladium Nanoparticles on ZnO-Passivated Carbon for Enhanced Performance in LiO$_2$ Batteries

5.1. Introduction

The lithium-oxygen battery has received significant interest because of its extremely high theoretical energy density which exceeds that of any other existing energy storage systems.$^{138-159}$ The cathode in the Li-O$_2$ battery consists of a porous matrix in which the discharge solid products, generated from the reaction of Li cations with O$_2$ form. The cathode of a Li-O$_2$ cell requires a catalyst to promote the discharge reaction. It has been found that a diversity of factors dictate the nature of electrochemical reactions in Li-O$_2$ cells such as the nature, morphology and surface area of the catalysts as well as the type of organic electrolyte being used.$^{143,153,154,160-162,163}$

One of the main challenges faced by the development of Li-O$_2$ batteries is the high overpotentials on charge and discharge. These high potentials are a consequent of the necessity of a rechargeable Li-O$_2$ battery. A large overpotential during charge, even at very low current densities, result in very low round-trip efficiencies (<60%), low power capability and poor cycle life. In order to lower the charge overpotential in the Li-O$_2$ cells, different electrocatalysts have been examined, such as carbons, metals and metal oxides.$^{138,139,151-154,156,164-168}$
However, some of the early work was based on carbonate electrolytes, including catalysts such as MnO₂ or PtAu, which were found unstable in the cells as the electrolytes decompose in Li-O₂ batteries.

The design of next generation of cathode materials for Li-O₂ batteries are complicated in that the batteries’ capacity, discharge/charge potential and their life length can be affected by many factors which range from the interactions at the atomic level to heat and mass transport in the battery cell which may be operated under a wide range of conditions.¹⁶⁹ To understand the intrinsic properties of the cathode materials, it is necessary to reduce the number of these variables to a tractable level. Therefore, well-defined cathode architectures were designed and synthesized in this work using atomic layer deposition (ALD).

ALD enables conformal coatings of thin films and nanoparticles on both planar and porous substrates.¹⁷⁰-¹⁷² It employs the surface self-limiting reactions between organometallic precursors and the targeted substrate allowing atomic precision control over the composition and thickness of the thin film, as well as the diameter of the nanoparticles. The composition and thickness of the coating materials can be precisely tuned by mixing the proper order, number and ratio of the ALD processes. In addition, by taking advantage of the difference in surface reaction rate, i.e., the surface reaction on one type of surface is significant faster than the other, and therefore the ALD process on a second surface is negligible, one can selectively deposit the coating materials onto the targeted surface.¹⁷³-¹⁷⁵ This characteristic is attractive for the synthesis of nanostructured architecture, e.g., core-shell nanoparticles and tandem bilayer nanostructure.
This work describes an approach based on a cathode architecture that has a protective ZnO coating passivation layer on a porous carbon substrate. ALD was applied to prepare these cathode architectures, which addresses the electrolyte decomposition problem by passivating the surface defect sites on the porous carbon. As a consequence, the air cathode based on this modified architecture shows promising results for solving the charge overpotential problem.

Bulk zinc oxide (ZnO) has a direct band gap of 3.3 eV, much smaller than the 8.8 eV wide bandgap of bulk Al₂O₃. ZnO ALD using alternating exposures to diethylzinc and water is well understood and provides conformal coatings. In addition, the growth rate of Pd is faster on ZnO surface than Al₂O₃ surface. All the above advantages make ZnO a promising material as the passivating layer on carbon.

In this study, we described a new cathode architecture for the LiO₂ cells that demonstrates that uniformly dispersed palladium nanoparticles onto a porous carbon substrate prepared by ALD show high electrochemical catalytic activity. ALD was used to deposit, on a porous carbon, ZnO and nanostructured palladium as cathode material for Li-O₂ cells. The cathode architecture reduced the charge overpotential to almost 0 V. A charge overpotential as small as 0.2V, has only been previously reported by Jun Lu et al., for a non-aqueous Li-O₂ cell.

5.2. Experimental Details

The Pd/ZnO/carbon cathode materials were synthesized using ALD. Pd and ZnO ALD were carried out in a commercial benchtop ALD reactor (Arradiance, Gemstar-6) equipped with an in situ quartz-crystal microbalance (QCM, Inficon).
Ultra high purity nitrogen carrier gas (Airgas, 99.999\%) was further purified using a Supelco gas purifier (Sigma-Aldrich) to trap hydrocarbon, moisture, and oxygen-containing impurities before entering the reactor.

Graphitized carbon black (Sigma-Aldrich) with an average particle size of 330 nm and a surface area of 70 m$^2$/g was used as the substrate without further treatment. Graphitized carbon black was uniformly spread onto a stainless steel sample tray with a stainless steel mesh top to contain the powder while still supplying access to the ALD precursor vapors. The loaded sample tray were placed into the center of the reactor and kept for at least 30 min at 200 °C in a 100 sccm flow of at 0.5 Torr pressure to allow temperature stabilization and to outgas the carbon. After loading, the graphitized carbon was allowed to outgas in the ALD reactor for 30 min at 200 °C in 480 mTorr of flowing ultrahigh purity nitrogen.

The ZnO ALD used alternating exposures to diethylzinc (DEZ, Sigma-Aldrich, Zn 52.0 wt\%) and deionized water at 200°C. The Pd ALD used alternating exposures to Pd(II) hexafluoroacetylacetonate (Pd(hfac)$_2$, Sigma-Aldrich, 98\%) and formalin (Sigma-Aldrich, 37 wt\% in H$_2$O with methanol added for stability). All the precursor bubblers were kept at room temperature expect DEZ bubbler was kept at 70 °C during the ZnO ALD. ALD timing sequences can be expressed as $t_1$-$t_2$-$t_3$-$t_4$, where $t_1$ and $t_3$ corresponds to the exposures times of the two precursors and $t_2$ and $t_4$ are the nitrogen purge times between precursor exposures and all units are given in seconds. The timing sequence used for the seed layer was: ZnO 0.5-60-0.75-60. Samples were prepared using 2 and 5 cycles of ZnO. For Pd ALD the time sequence utilized was 300-900-200-600.
Graphitized carbon black was first passivated using 2 and 5 ALD cycles of ZnO, followed by 1, 3, and 10 ALD cycles of Pd. The samples were denoted as 1c-Pd/2c-ZnO/C, 3c-Pd/2c-ZnO/C, 10c-Pd/2c-ZnO/C, 3c-Pd/5c-ZnO/C, respectively. An extra sample was performed with alternative exposures to Pd and ZnO on carbon and denoted as Pd/ZnO/Pd/ZnO/Pd/C.

ZnO films were analyzed using ex situ ellipsometry. Thickness measurements of the ZnO films were performed using a J.A. Woollam Co. alpha-SE Spectroscopic ellipsometer. Ellipsometric data were collected with a 70 incidence angle and was fit to a Cauchy model.

The Electrochemical characterization was carried out using a Swagelok-type cell composed of a lithium metal anode, a glass fiber separator impregnated with ether electrolyte (TEGDME 1M LiCF$_3$SO$_3$) and a porous cathode (7/16 inch diameter). The cathode was formed by mixing the as-prepared cathode material and binder in a molar ratio of 80:20. The cells were sealed in 1 bar pure O$_2$ atmosphere, to avoid any negative effects of humidity and CO$_2$. The electrochemical measurements were carried out using a MACCOR cycler, under a constant current density of 100 mA g$^{-1}$. The observed capacity was normalized by the weight of the cathode active material, for comparison in this study. This part of the work was carried out by Xiangyi Luo.

TEM images were taken by a field-emission transmission electron microscope (FEI Titan 80-300ST) with a spherical and chromatic aberration imaging corrector working at 80 kV.
Spherical and chromatic aberration correction enables the microscope to attain resolution better than 0.1 nm (measured by Young’s fringes) at 80 kV. This part of the work was carried out by Jianguo Wen.

Pd K-edge (23.564 keV) X-ray absorption spectroscopy (XAS) was performed at the 9-BM beamline at the APS. The amount of sample used was optimized to achieve an XAS step height of about 1. The XAS spectra were recorded in transmission mode. Standard procedures based on WINXAS 3.1 software were used to fit the data in the extended X-ray absorption fine structure (EXAFS) regime. The EXAFS coordination parameters were obtained by a least-square fit in q- and r-space of the isolated nearest neighbor, $k^2$- weighted Fourier transform data.

Pd L$_3$-edge (3.173 keV) X-ray absorption spectroscopy (XAS) was performed at the 9-BM beamline at the APS. The amount of sample used was optimized to achieve an XAS step height of about 1. The XAS spectra were recorded in transmission mode. Standard procedures based on WINXAS 3.1 software were used to fit the data in the extended X-ray absorption fine structure (EXAFS) regime.

5.3. Results and Discussion

The method used to synthesize palladium nanoparticles through ALD, was to passivate a carbon substrate with alternative exposures to diethylzinc and H$_2$O, in order to deposit a ZnO film, and deposit palladium using different amount of cycles.

In order to study diethylzinc and H$_2$O ALD deposition, silica wafers were used to deposit different amount of ZnO cycles, which then were measured with ellipsometry to observe the growth rate and compared with literature.
Table 5.1 presents the thicknesses measured for ZnO ALD films. The ZnO ALD growth rate decreases from 4.0 Å/cycle at 10 cycles and saturates at 2.0 Å/cycle after 100 cycles. Table 5.1 shows that the ellipsometry measurements at 50-100 cycles at 150 °C are consistent with average growth rates of 2.0 Å/cycle for ZnO ALD which agrees well with the values of 1.75 - 2.1 Å/cycle at temperatures between 130 – 180 °C measured in literature.\textsuperscript{178,179}

**Table 5.1.** Thickness values for ZnO deposition at 150 °C.

<table>
<thead>
<tr>
<th>ZnO cycles</th>
<th>Thickness (Å)</th>
<th>Growth rate (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>40 ± 0.017</td>
<td>4.0</td>
</tr>
<tr>
<td>20</td>
<td>56 ± 0.017</td>
<td>2.8</td>
</tr>
<tr>
<td>50</td>
<td>98 ± 0.017</td>
<td>2.0</td>
</tr>
<tr>
<td>100</td>
<td>196 ± 0.055</td>
<td>2.0</td>
</tr>
<tr>
<td>200</td>
<td>348 ± 0.054</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Dispersed Pd nanoparticles were successfully synthesized by ALD on ZnO-passivated porous carbon. These catalysts were tested as a cathode material in a rechargeable Li-O\textsubscript{2} battery, presenting highly active catalytic effect in relation to electrochemical reactions, especially the oxygen evolution reaction.

The Pd oxidation state and geometry was studied using X-ray absorption spectroscopy (XAS) at the Pd K edge. Figure 5.1 shows XANES spectra for 1c-Pd/2c-ZnO/C, 3c-Pd/2c-ZnO/C and 10c-Pd/2c-ZnO/C. The results revealed that the synthesized Pd occurred in a mixed phase of metallic palladium and palladium oxide.
Figure 5.1. (a) Pd-K edge XANES spectra for the reference samples Pd foil and PdO and for as-prepared Pd/ZnO/C, (b) Zn K-edge XANES spectra 1c-Pd/2c-ZnO/C sample. (from Luo, 2015).
Figure 5.2 shows Pd $L_3$ edge XANES spectra of 3c-Pd/2c-ZnO/C and Pd/ZnO/Pd/ZnO/Pd/C catalysts with different adsorbates; in a steady state flow of helium (25 °C), hydrogen (250 °C) and CO (25 °C).

The $L_3$ edge spectra of 3c-Pd/2c-ZnO/C (Figure 5.2a) showed the whitelines were increased in intensity for possibly increasing particle size. The $L_3$ edge XANES whiteline intensity indicates the number of holes in the 4d band and therefore the local d density of states. The spectrum after hydrogen and carbon monoxide adsorption showed very similar whiteline intensity to that of as prepared sample. There was a positive shift of 0.2 eV in the edge position, suggesting that the Fermi level was pushed up by 0.2 eV. The intensity was enhanced between 3.176 keV and 3.180 keV originating from the interaction of palladium with hydrogen atoms. Both samples showed a broadening of the whiteline.

**Figure 5.2.** Pd $L_3$ XANES spectra for (a) 3cPd2cZnOC, (b) PdZnOPdZnOPdC. Blue, He at 25 °C; Red, CO at 25 °C; Green, H$_2$ at 250 °C
Transmission electron microscopy (TEM) was performed on the 1c-Pd/2c-ZnO/C and 3c-Pd/2c-ZnO/C (figure 5.3) showing Pd nanoparticles with average sizes of 3 nm and 6 nm respectively.

![Figure 5.3](image)

**Figure 5.3.** TEM images for the (a), (b) 1c-Pd/2c-ZnO/C and (c), (d) 3c-Pd/2c-ZnO/C. (from Luo, 2015, courtesy of Jianguo Wen)

In order to reveal the catalytic activity on the oxygen evolution reaction (charging) of the Pd/ZnO/C-based cathodes, a capacity-controlled mode to investigate the discharge/charge behavior of the Li-O_2 is applied. Figure 5.4 shows voltage profiles recorded from the discharge/charge cycles obtained from the cells with Pd/ZnO/C and
ZnO/C cathodes. The cells were operated under a 1000 mAh g$^{-1}$ capacity controlled mode. The voltage profiles display that all the discharge potentials are about 2.7 V; the charge potential is ~4.0 V for the ZnO/C cathode architecture, which is significantly reduced to 3.0 V for all the Pd/ZnO/C cathodes. The low charge potential was able to be maintained over 10 cycles at 1000 mAh g$^{-1}$ capacity and over 20 cycles for the 3c-Pd/ZnO/C cathode. Even though the loading of Pd affects the performance of the Li-O$_2$, it is not the case for ZnO loading on carbon as can be observed from figures 4(c) and (e). These results suggest the effectiveness of the cathode architecture ALD Pd/ZnO on carbon to increase the discharge capacity and reduction of the charge overpotential of Li-O$_2$ batteries. It is believed that the ALD ZnO and Pd play a critical role on enhancing the performance of the cell. ZnO, which is a more conductive material than Al$_2$O$_3$, would be beneficial to the overall conductivity of the carbon cathode when used to passivate the carbon sites. At the same time, highly dispersed Pd ALD acted as electrocatalyst for promoting the discharge and charge reactions and therefore improving the performance of Li-O$_2$ cells.
Figure 5.4. Voltage profiles recorded from the discharge/charge cycles obtained from the cells (a) 2c-ZnO/C, (b) 1c-Pd/2c-ZnO/C and (c) 3c-Pd/2c-ZnO/C, (d) 10c-Pd/2c-ZnO/C and (e) 3c-Pd/5c-ZnO/C. (from Luo, 2015).
The cells started to fade with relatively short discharge/charge cycles. The failure of the battery could be attributed to the degradation of the Li anode as shown by the corrosion of the anode at termination, while the cathode still maintained its porous structure (Figure 5.5). Such corroded anodes are formed due to the oxygen-crossover effect, and made of LiOH and Li$_2$CO$_3$, which have been determined by XRD and FT-IR patterns in previous work.$^{155}$

![Figure 5.5. SEM images for cathodes and images of the degraded Li anode after discharge/charge cycles (stop at charge) (a) 1c-Pd/2c-ZnO/C, (b) 3c-Pd/2c-ZnO/C and (c) 10c-Pd/2c-ZnO/C. (from Luo, 2015, $^{180}$ courtesy of Jianguo Wen)](image)

5.4. Conclusion

Atomic layer deposition was successfully employed to synthesized nanostructured palladium as cathode materials for Li-O$_2$ batteries. The results exhibited an alteration of the oxygen reduction reaction during discharge in the Li-O$_2$ cell when a Pd nanoparticle on ZnO-passivated carbon is used as electrocatalyst. The results suggested that ALD is a promising technique for tailoring the surface composition and structure of nanoporous supports for Li-O$_2$ batteries.
CHAPTER SIX

6. Conclusions and Future Work

The dissertation concentrated on the design and synthesis of nanostructured palladium using ALD for heterogeneous catalysis and electrocatalysis applications. Three different cases of ALD Pd catalysts were studied and discussed in detail. However, there are still several open questions to be addressed.

Chapter three described a novel strategy to synthesize thermally stable single atom catalysts by combining Pd ALD and TiO$_2$ coating ALD. The single-atom Pd$_1$ catalysts protected by 14 cycles ALD TiO$_2$ showed greatly enhanced thermal stability with no obvious agglomeration after 300 °C calcination. Interestingly, it was also the least active catalysts for methanol decomposition at 300 °C. The reactivity seems strongly depending on the cycles of overcoats, representing a combining effect of thermal stability and amount of exposure sites of surface Pd. Overall, the ALD TiO$_2$ overcoat dramatically enhanced the stability of single atom Pd$_1$ catalysts under both oxidation and reduction conditions. Although there were Pd nanoparticles formed on the surface, in-situ FT-IR under reaction conditions reveal that it can be avoided in the future by choosing mild precursors that would not attack the surface -Pdhfac species during the metal oxide ALD.
Therefore an alternative oxide precursor, chlorine free, should be investigated in order to encapsulate the single atoms synthesized by ALD, which will stabilize and protect from any reaction conditions.

In an attempt to find a suitable precursor to stabilize single atom catalysts, dimethylaluminum isopropoxide (DMAI) was studied through quartz crystal microbalance on Chapter four, by combining Pd ALD and Al₂O₃ coating. In the process of investigating the catalysts characteristics, in situ EXAFS spectroscopy and DRIFTS technique revealed the change in oxidation state to metallic Pd at room temperature when carbon monoxide was introduced into the system. DRIFTS data suggested that Pd²⁺ on 3AlPd₁ catalyst reacted with the Al₂O₃ protective coating as observed from the comparison with 0AlPd₁. On the 0AlPd₁ catalyst Pd²⁺ and Pd⁰ show the same intensity after 30 minutes of CO adsorption, while on 3AlPd₁ there is mostly Pd⁰. Therefore, DMAI could not be considered as a successful precursor in order to stabilize single atoms because of its reaction to Pdhfac ligand. Consequently, an alternative precursor to be used as a coating for single atoms, it is still to be found. Titanium isopropoxide (TTIP) used as an alternative precursor to TiO₂, could be proposed as a possible option. TTIP is a less aggressive precursor than TiCl₄ which could successfully protect single atoms synthesized by ALD.

Chapter five proposed an alternative usage of ALD synthesized films. Atomic layer deposition was employed to synthesized nanostructured palladium as cathode materials for Li-O₂ batteries.
The results suggested that ALD is a promising technique for tailoring the surface composition and structure of nanoporous supports for Li-O\textsubscript{2} batteries. It has been shown that ALD ZnO passivated carbon further reduced the charge overpotential compared to Al\textsubscript{2}O\textsubscript{3} passivated carbon. As a further research, different carbon passivated oxides should be investigated, to observe the cathode material improvements, such as TiO\textsubscript{2}, SiO\textsubscript{2} or Fe\textsubscript{2}O\textsubscript{3} among others.
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