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Major Goals: Summary:

1) Tune Growth Mechanism of Pd/Pt:
2) Expand ALED Scope:
2a. ALED on Nanoporous Substrates
2b. ALED of Cu on Pd particles

Detailed Major Goals:

1) Can the degree of adlayer particle nucleation versus adlayer particle growth be tuned by controlling the concentration and rate of addition of adlayer precursor solution?

Background:
For many applications of bimetallic materials an atomically thin adlayer of the alloying metal is desirable. In these cases, a surface adlayer metal tunes the energy of the d-band at the catalyst interface. In other cases, islands of adlayer atoms are desirable, for example to resist catalyst poisoning, or as so-called single atoms catalysts, leaving some fraction of underlying substrate exposed.
A potential feature of Atomic Layer Electroless Deposition (ALED, Figure 1) is the ability to tune growth mechanism, hence growth morphology, by altering conditions. In this funded effort, we set out to probe this possibility by controlling the addition rate of adlayer metal during deposition cycles (galvanic displacement of Pt-H surface hydrides with Pd^{2+} ions) and measuring changes in surface morphology. Based on a LaMer mechanism of particle growth, we hypothesized that high concentrations of Pd^{2+} resulting from fast addition would exceed a critical nucleation concentration, leading to a more uniform adlayer, while slow addition would favor particle growth leading to islands of adlayer metal.
Specific Objectives:

•   Preparation of Pd/Pt (Pd adlayer/Pt substrate) with varying addition rate:
A syringe pump was utilized to vary addition of Pd^{2+} solution to Pt-H surfaces all at once and at rates of 0.12 and 0.6 mL·min-1.

•   Characterization of Pd/Pt (Pd adlayer/Pt substrate):
Bulk atomic composition measurements were made using atomic absorption (AA) spectroscopy and X-ray

photoelectron spectroscopy (XPS) analysis was carried out to measure surface-sensitive atomic composition.

2) Can the scope of ALED be broadened to include nanostructured substrates and substrates and adlayers other than noble metals?
A. Nanoporous Substrates

Background:

Structural features in nanoparticles (NP) and nanoporous materials have been shown to positively influence the performance of noble metals in such applications as fuel cell catalysts, supercapacitors, batteries and hydrogen/hydrogen isotope storage media. In addition to effects arising from nanoscale topology, compositional features in multi-component catalysts ranging from core/shell and superlattice structures to simple substitutional alloying have been shown to have profound effects on catalyst performance. Controlled preparation of nanostructured alloys is particularly challenging given the high aspect ratio and high surface area of such materials. As such, other forms of atomic layer deposition such conventional gas-phase ALD and electrochemical ALD are incompatible with these substrates.
This aspect of the funded effort focused on using ALED for controlled deposition on nanoporous Pt (npPt), which was synthesized using a surfactant-templated/reduction approach.

Specific Objectives:

• Preparation of npPt:
Using a modification of literature procedures,liquid crystalline surfactant was used as a template for reduction of K2PtCl6. The metal salt/surfactant mixture was extruded and then purged with hydrogen in nitrogen gas to reduce Pt2+ to Pt0. npPt metal, thus prepared, containing a hexagonal array of nanopores, was utilized as an ALED substrate after characterization using transmission electron microscopy and nitrogen porosimetry.

• Preparation of Pd/npPt (Pd adlayer/npPt substrate):
ALED was carried out by galvanic displacement of npPt surface hydride by Pd2+ ions, (Figure 1). Samples were prepared by addition of K2PdCl4 to npPt suspended in electrolyte, in single and multiple cycles. In addition, control experiments were performed, in which npPt suspended in electrolyte was subjected to cycling between hydrogen and nitrogen purges. The purpose of these experiments was to decouple the effect of hydriding/dehydriding on nanopore structure from that of galvanic displacement by Pd2+.

• Characterization of Pd/npPt (Pd adlayer/npPt substrate):
The amount of Pd deposited during cycles of ALED was measured using XPS and AA. The surface area and nanopore structure of npPt was measured before and after ALED cycles using nitrogen porosimetry. Our expectation was that pore size would decrease somewhat due to Pd deposition. At this stage we anticipated risks such as nanopore collapse due to atomic rearrangement during galvanic displacement as well as nanopore occlusion by adlayer material.

B. Expand the Scope of ALED to Cu/Pd (Cu adlayer/Pd Substrate)

Background:

Oxides of Cu and Pd metal have both been shown to be effective in oxidative decomposition of simulants of CWA such as sarin and mustard gas. Deep oxidation of molecules containing carbon-sulfur and carbon-phosphorous bonds was demonstrated with high turnover numbers. Furthermore, the combination of Pd and Cu has shown enormous potential in catalyzing very challenging and industrially relevant chemical transformations such as hydroxylation of benzene produce phenol and low molecular weight alkanes such as methanol and butanol to their corresponding alcohols in the presence of oxygen and a reductant such as carbon monoxide or hydrogen. The mechanism that has been suggested to account for this activity involves distinct roles for the two metals. Pd is known to catalyze the two electron reduction of oxygen to hydrogen peroxide at the expense of hydrogen. Subsequently, Cu2+ reacts with hydrogen peroxide produced in-situ to form hydroxyl radicals or other oxidants that decompose the substrate. In one investigation it was demonstrated that a bimetallic catalyst comprising Pd and Cu dispersed on a silica support was capable of hydroxylating benzene to phenol when the reaction mixture was sequentially exposed to oxygen and hydrogen gas. No attempts were made to control the composition of the catalyst and it was not characterized in detail. Nonproductive, Pd-catalyzed decomposition of H2O2 has been recognized as a significant challenge in this system and it has been suggested that amount of free H2O2 in solution

must be optimized.10a

Cu/Pd materials prepared by ALED should have well-controlled and varied Cu coverage. This approach mirrors the precisely optimized architecture of enzyme active sites, in which all components of a chemical reaction are brought together in a small reaction volume. ALED-prepared Cu/Pd will allow us to gain insight on the optimal stoichiometry for a bimetallic, bifunctional catalyst with substrate turnover that is tightly coupled to H_2O_2 production. Catalysts with a greater number of exposed Pd sites should favor H_2O_2 production but may be more susceptible to decomposition. On the other hand, on surfaces with fewer exposed Pd sites and more catalytic Cu sites, decomposition of H_2O_2 by Pd would be minimized at the expense of less overall production of H_2O_2. While all ALED carried out so far made use of noble metal substrates and adlayer metals, the reduction potential of Cu^{2+} (0.34 V vs. SHE) suggested to us that it should be compatible with this process. In this phase of the funded efforts our goal was to prepare Cu adlayers on Pd particles using $CuCl_2$ as a precursor. Our hypothesis is that this material will be a potent, bifunctional oxidation catalyst.

Specific Objectives:

• Cu/Pd Preparation:
Single and multiple cycles of ALED were carried out by addition of aliquots $CuCl_2$ in 0.1M H_2SO_4 solution to Pd powder substrate suspension after preparation of surface hydride using H_2/N_2 gas (Figure 1).

• Characterization of Cu/Pd using XPS and AA:
Cu/Pd ALED materials were characterized by AA and XPS to obtain bulk and surface composition.

Accomplishments: Summary:

1) Tune Growth Mechanism of Pd/Pt:
• Positive evidence of tunable surface morphology

2) Expand ALED Scope:
a. ALED on Nanoporous Substrate
• Positive evidence of ALED of Pd on npPt while maintaining pore structure

b. ALED of Cu on Pd particles
• Positive evidence of successful Cu ALED on Pd particles

1) Growth Mechanism of Pd/Pt:
Preparation of ALED materials by varying flow rate:
A syringe pump was used to prepare Pd/Pt at three different addition rates. Figure 2 shows the open-circuit voltage (OCV) traces of a Pt wire working electrode that was used to monitor the cell during each deposition process. The increase in cell potential, which occurs upon addition of Pd^{2+} solution, occurs most abruptly after rapid metal salt addition. This rise becomes more gradual with slower addition of the adlayer metal salt, though the resulting cell potential is similar in all cases. These traces indicate that, though the timescale of deposition is varied, the extent of deposition is similar in all three cases.

A comparison of bulk atomic fraction, obtained by AA spectroscopy and surface atomic fraction (Figure 3) provides evidence that the surface morphology is different in the three samples. The bulk Pd fraction for the samples with slow, intermediate and fast addition rate are very similar at 0.46±0.03%, 0.48±0.01%, and 0.51±0.01%, respectively. This is consistent with what is expected for a single cycle of ALED, since the substrate has a surface area of 5 $m^2 \cdot g^{-1}$ (measured by N_2 porosimetry), corresponding to ~2% surface atoms. In contrast, XPS data shows large variability in the surface Pd fractions (Figure 3). These values are much larger than those measured by AA since this technique measures only the surface (1.5 – 2 nm). Taken together these data suggest that the surface morphology of the three samples is much different while the amount of Pd deposited remains the same. As illustrated in the inset of Figure 3, a conformal Pd layer would show the largest % Pd since nearly all atoms would be at the surface and relatively few Pt atoms would be exposed. In contrast, island growth would show less Pd by XPS since some of the Pd atoms would be buried, and relatively more of the Pt atoms would be exposed.

Conclusion and Outlook:
The data summarized in Figure 3 and described above are evidence that the growth morphology of ALED materials can be controlled. The trend above is opposite to what was originally hypothesized. It is possible that the key parameter for galvanic displacement reactions is the difference between the reduction potential of the adlayer metal (E_{ad}) and that of the surface hydride (E_{MH}) rather than critical nucleation concentration. In that case, decreasing the concentration of the adlayer metal would decrease the overpotential $(E_{ad} – E_{MH})$ and slow the reaction and

this slower rate may facilitate more uniform deposition.
2) Expanding ALED scope:

A. Nanoporous Pt as substrate

Nanoporous Pt prepared:

This phase of the funded efforts was successful, with preparation and characterization of samples of npPt having surface areas from 23 – 26 m2·g-1 (Figure 4). This is a notable accomplishment in itself since these values are comparable to the highest reported for unsupported nanoporous metals. Thus-prepared npPt was used as a substrate for single and multiple cycles of ALED.

ALED Preparation of Pd/PtNP (Pd adlayer/nanoporous Pt substrate):

OCV traces of Pd/npPt prepared by ALED are shown in Figure 5. Though qualitatively similar to those obtained during ALED with other substrates, the reduction of surface oxides on these nanoporous substrates requires longer due to the higher surface area compared to nonporous powders, and the overall preparation of a stable surface hydride takes considerably more time. An increase in cell potential occurs upon addition of Pd2+ in a fashion similar to that previously observed.

Characterization of Pd/npPt:

The data collected in Table 1 illustrate that ALED is compatible with nanoporous substrates. The first two entries show the surface area of the two prepared npPt substrates that were used for ALED experiments. Samples in the third and fourth row were prepared as controls: by suspending npPt in electrolyte and cycling between N2 and H2/N2 purge, we demonstrate that hydriding and dehydriding the surface alone causes minor loss of surface area. The final four entries demonstrate that one cycle of Pd2+ deposition on npPt results in effective deposition (as evidenced by AA and XPS) while maintaining the integrity of the pore structure. The relatively small loss of surface area is similar to that observed in the control experiments. In contrast, multiple cycles of deposition either destabilize the nanopore structure or block the pores, leading to drastic loss of surface area.
The data in Table 1 also provide evidence that deposition occurs using Pt-H from within the nanopores and not just from the surface of the particles. TEM imagery shows that the npPt particle diameters range from several hundred nm to microns. Since such large particles consist of < 1% surface atoms, and the stoichiometry for Pd2+ deposition is 2:1 with respect to Pt-H, the maximum expected % Pd per cycle is <0.5%. The single-cycle deposition samples in Table 1 show two and four times that amount by AA, consistent with galvanic displacement of Pt-H within the pores.

Conclusion and Outlook:
Single cycle ALED on unsupported nanoporous metal with retention of high surface area is demonstrated by the data above. Additional experiments, some of which are currently underway, will include:
i.   ALED with smaller Pd2+ aliquot size per cycle
ii. ALED at lower Pd2+ concentration
iii. Electron microscopy

These experiments are directed at performing multiple cycles without loss of surface area and directly probing the surface composition at the nanoscale.

B. Expand Scope of ALED to Cu/Pd

Cu/Pd preparation and Characterization:

Accomplishments in this phase of the funded effort include ALED preparation and characterization of single and multiple cycle Cu/Pd. As shown in Figure 6, one and two cycles of ALED result in deposition of Cu0 on Pd. Bulk % Cu after one cycle of deposition, measured by AA is consistent with that expected for roughly ½ ML on powder particles of ~3 m2·g-1 (measured by nitrogen porosimetry.) Measurements suggest a complete ML is formed after two cycles. These data confirm that ALED is compatible with a non-noble metal adlayer. Further, it is very interesting to note that two cycles of ALED seem to "cap" the substrate Pd and surface hydride does not appear to form after re-exposure to H2/N2. In the "three-cycle" experiment shown in Figure 6, ALED was carried out as in the two-cycle experiment but subsequently exposed to H2/N2 for a third cycle. The lack of potential drop suggests that

no surface hydride forms. This result is also consistent with ½ ML deposition per cycle of ALED. It is known that there is a barrier to dissociative chemisorption of hydrogen on Cu surfaces, however the extent to which H2 can adsorb on clusters remains an active research area.

Conclusion and Outlook:
The results discussed in the last section suggest that a bimetallic CuPd catalyst with tailored surface properties can be prepared using ALED. They will facilitate reactivity experiments discussed above, to investigate the hypothesis that ALED Cu/Pd will be a potent oxidation catalyst. Furthermore, these results will facilitate an unforeseen application. Monolayer deposits of Cu deposited electrochemically (so-called underpotential deposition (UPD)) provide a well-studied means of preparing multimetallic materials. In this case, Cu acts as a sacrificial reductant that is galvanically displaced by other adlayer materials. Electrochemically prepared UPD surfaces are difficult to scale – this has been identified as an important obstacle to widespread adoption of this technique for catalyst preparation, a problem that can be mitigated with ALED.

Training Opportunities: Sita Gurung:

Sita was a second year Ph.D. student as the start of this funded effort. As such, this period included a great deal of mentoring on the part of the PI and learning on the part of Sita. Other than a general refinement of analytical technique, presentation preparation and experimental skill, Sita received training in several specific areas:

• Electrochemical techniques and design of electrochemical experimental apparatus
• X-ray photoelectron spectroscopy, experimental acquisition and data reduction
• Atomic Absorption spectroscopy, experimental acquisition and data reduction
• Transmission Electron Microscopy, experimental acquisition and data reduction
• Nitrogen Porosimetry, experimental acquisition and data reduction

• Sita presented her work on this project at the 2017 JCF-Frühjahrssymposium in Mainz, Germany, April, 2017
• Sita also presented her work on this project at the Fall, 2016 Materials Research Society Meeting in Boston, MA.

Sita also gained valuable mentoring experience working with a senior undergraduate students, April Munro and Amber Cyr.

April Munro:

April was a senior undergraduate student at the start of the funded efforts. While, as an undergraduate researcher, her role was far less than Sita's, she participated in many of the efforts above, helping Sita accomplish her goals. In addition, she received specific training in:

• Infrared Spectroscopy, experimental acquisition and data reduction
• Transmission Electron Microscopy, experimental acquisition and data reduction

Amber Cyr:

Amber participated in the final month of the funded effort by collecting porosimetry data. As such she received the following specific training:

• Nitrogen Porosimetry, experimental acquisition and data reduction

Results Dissemination: Nothing to Report

Honors and Awards: Ph.D. student Sita Gurung was awarded a place in the 2016/17 Northeastern ACS section German Exchange program. This was a highly competitive process and Sita was selected for the delegation alongside graduate students from Harvard, Boston University and Northeastern University. She presented her work on this project at the 2017 JCF-Frühjahrssymposium in Mainz, Germany, April, 2017

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Faculty
Participant: Patrick Cappillino
Person Months Worked: 9.00   **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Sita Gurung
Person Months Worked: 9.00   **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: April Munro
Person Months Worked: 7.00   **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Amber Cyr
Person Months Worked: 1.00   **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Short-Term Innovative Research Program:
Research Area 7.4 Reactive Chemical Systems: Multifunctional, Bimetallic Nanomaterials Prepared by Atomic Layer Electroless Deposition (ALED)

Patrick Cappillino
University of Massachusetts Dartmouth

Major Goals:

Summary:

1) **Tune Growth Mechanism of Pd/Pt:**

2) **Expand ALED Scope:**
   a. ALED on Nanoporous Substrates
    b. ALED of Cu on Pd particles

Detailed Major Goals:

The Goals of these funded efforts were to address two fundamental questions about Atomic Layer Electroless Deposition (ALED):

1) **Can the degree of adlayer particle nucleation versus adlayer particle growth be tuned by controlling the concentration and rate of addition of adlayer precursor solution?** If so this will decouple adlayer thickness from fractional coverage and allow these parameters to be separately optimized for different applications. This would accomplish an important goal in heteroepitaxial film growth.

Background and Significance:

For many applications of bimetallic materials an atomically thin, conformal adlayer of the alloying metal is desirable. In these cases, a surface or subsurface adlayer metal effectively tunes the energy of the d-band at the catalyst interface.[1] In other cases, small islands, or clusters of adlayer atoms are desirable, for example to resist catalyst poisoning,[2] or as so-called single atoms catalysts[3] while leaving some fraction of underlying substrate exposed.
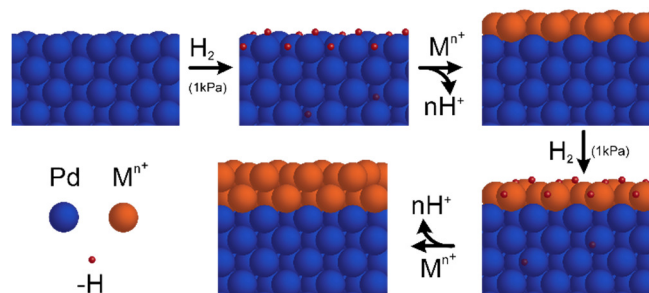
Figure 1. Schematic of ALED process. Dilute H_2 in N_2 gas is added to substrate suspended in electrolyte forming a surface hydride. Metal salt is added, galvanically displacing the surface hydride and forming an adlayer. The process can be cycled to form thicker adlayers.

A potential feature of Atomic Layer Electroless Deposition (ALED, Figure 1)[4] is the ability to tune growth mechanism, hence growth *morphology*, by altering deposition conditions. In this funded effort, we set out to probe this possibility by carefully controlling the addition rate of adlayer metal during deposition cycles (galvanic displacement of Pt-H surface hydrides with Pd^{2+} ions) and subsequently measuring changes in surface morphology. Based on a LaMer

mechanism[5] of particle growth, we hypothesized that high concentrations of Pd^{2+} resulting from fast addition would greatly exceed a critical nucleation concentration, leading to a more uniform adlayer, while slow addition would favor particle growth leading to islands of adlayer metal.

Specific Objectives and Approach:

- Preparation of Pd/Pt (Pd adlayer/Pt substrate) with varying addition rate:
  A syringe pump was utilized to vary addition of Pd^{2+} solution to Pt-H surfaces all at once and at rates of 0.12 and 0.6 mL·min^{-1}.

- Characterization of Pd/Pt (Pd adlayer/Pt substrate):
  Bulk atomic composition measurements were made using atomic absorption (AA) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis was carried out to measure **surface-sensitive** atomic composition. The short inelastic mean free path of Pd and Pt photoelectrons generated during XPS measurements (1.5 – 2 nm)[6] has two consequences; (i) the Pd atomic fraction should be greatly enriched compared to bulk, AA measurement, and (ii) the measurements should be sensitive to surface morphology. Larger Pd atomic fraction for a given bulk concentration would suggest a greater fraction of Pd atoms near the surface (i.e., conformal adlayer) whereas smaller Pd atomic fraction would suggest more Pd atoms are buried at a depth of > 2nm and there are more exposed Pt atoms (i.e., island growth).

2) **Can the scope of ALED be broadened to include nanostructured substrates and substrates and adlayers other than noble metals?** If so this will expand the significance of ALED to a diverse array of potential applications.

   A. Nanoporous Substrates

   Background and Significance:

   Structural features in nanoparticles (NP) and nanoporous materials have been shown to positively influence the performance of noble metals in such applications as fuel cell catalysts, supercapacitors, batteries and hydrogen/hydrogen isotope storage media.[7] In addition to effects arising from nanoscale topology, compositional features in multi-component catalysts ranging from core/shell and superlattice structures to simple substitutional alloying have been shown to have profound effects on catalyst performance.[8] Controlled preparation of nanostructured alloys is particularly challenging given the high aspect ratio and high surface area of such materials. As such, other forms of atomic layer deposition such conventional gas-phase ALD and electrochemical ALD are incompatible with these substrates.

   This aspect of the funded effort focused on using ALED for controlled deposition on nanoporous Pt ($_{np}$Pt), which was synthesized using a surfactant-templated/reduction approach.[7b, 9]

   Specific Objectives and Approach:

   - Preparation of $_{np}$Pt:
     Using a modification of literature procedures,[7b, 9b] liquid crystalline surfactant was used as a template for reduction of K_2PtCl_6. The metal salt/surfactant mixture was extruded

and then purged with hydrogen in nitrogen gas to reduce Pt^{2+} to Pt^0. $_{np}Pt$ metal, thus prepared, containing a hexagonal array of nanopores, was utilized as an ALED substrate after characterization using transmission electron microscopy and nitrogen porosimetry.

- Preparation of Pd/$_{np}$Pt (Pd adlayer/$_{np}$Pt substrate):
  ALED was carried out by galvanic displacement of $_{np}Pt$ surface hydride by Pd^{2+} ions, (Figure 1).[4] Samples were prepared by addition of K_2PdCl_4 to $_{np}Pt$ suspended in electrolyte, in single and multiple cycles. In addition, control experiments were performed, in which $_{np}Pt$ suspended in electrolyte was subjected to cycling between hydrogen and nitrogen purges. The purpose of these experiments was to decouple the effect of hydriding/dehydriding on nanopore structure from that of galvanic displacement by Pd^{2+}.

- Characterization of Pd/$_{np}$Pt (Pd adlayer/$_{np}$Pt substrate):
  The amount of Pd deposited during cycles of ALED was measured using XPS and AA. The surface area and nanopore structure of $_{np}Pt$ was measured before and after ALED cycles using nitrogen porosimetry. Our expectation was that pore size would decrease somewhat due to Pd deposition. At this stage we anticipated risks such as nanopore collapse due to atomic rearrangement during galvanic displacement as well as nanopore occlusion by adlayer material.

B. Expand the Scope of ALED to Cu/Pd (Cu adlayer/Pd Substrate)

Background and Significance:

Oxides of Cu and Pd metal have both been shown to be effective in oxidative decomposition of simulants of CWA such as sarin and mustard gas.[10] Deep oxidation of molecules containing carbon-sulfur and carbon-phosphorous bonds was demonstrated with high turnover numbers. Furthermore, the combination of Pd and Cu has shown enormous potential in catalyzing very challenging and industrially relevant chemical transformations such as hydroxylation of benzene produce phenol and low molecular weight alkanes such as methanol and butanol to their corresponding alcohols in the presence of oxygen and a reductant such as carbon monoxide or hydrogen.[11] The mechanism that has been suggested to account for this activity involves distinct roles for the two metals. Pd is known to catalyze the two electron reduction of oxygen to hydrogen peroxide at the expense of hydrogen.[11a] Subsequently, Cu^{2+} reacts with hydrogen peroxide produced *in-situ* to form hydroxyl radicals or other oxidants that decompose the substrate.[11a] In one investigation it was demonstrated that a bimetallic catalyst comprising Pd and Cu dispersed on a silica support was capable of hydroxylating benzene to phenol when the reaction mixture was sequentially exposed to oxygen and hydrogen gas.[11a] No attempts were made to control the composition of the catalyst and it was not characterized in detail. Nonproductive, Pd-catalyzed decomposition of H_2O_2 has been recognized as a significant challenge in this system and it has been suggested that amount of free H_2O_2 in solution must be optimized.[11a]

Cu/Pd materials prepared by ALED should have well-controlled and varied Cu coverage. This approach mirrors the precisely optimized architecture of enzyme active sites, in which all components of a chemical reaction are brought together in a small reaction volume. ALED-prepared Cu/Pd will allow us to gain insight on the optimal stoichiometry for a bimetallic, bifunctional catalyst with substrate turnover that is tightly coupled to H_2O_2 production. Catalysts with a greater number of exposed Pd sites should favor H_2O_2 production but may be more susceptible to decomposition. On the other hand, on surfaces with fewer exposed Pd sites and

more catalytic Cu sites, decomposition of H_2O_2 by Pd would be minimized at the expense of less overall production of H_2O_2. While all ALED carried out so far made use of noble metal substrates and adlayer metals, the reduction potential of Cu^{2+} (0.34 V *vs.* SHE) suggested to us that it should be compatible with this process.[12] In this phase of the funded efforts our goal was to prepare Cu adlayers on Pd particles using $CuCl_2$ as a precursor. Our hypothesis is that this material will be a potent, bifunctional oxidation catalyst.[11b, 11c, 11e, 13]

Specific Objectives and Approach:

- Cu/Pd Preparation:
  Single and multiple cycles of ALED were carried out by addition of aliquots $CuCl_2$ in 0.1M H_2SO_4 solution to Pd powder substrate suspension after preparation of surface hydride using H_2/N_2 gas (Figure 1).

- Characterization of Cu/Pd using XPS and AA:
  Cu/Pd ALED materials were characterized by AA and XPS to obtain bulk and surface composition.

Accomplishments:

Summary:

1) **Tune Growth Mechanism of Pd/Pt:**
   - Positive evidence of tunable surface morphology

2) **Expand ALED Scope:**
   a. ALED on Nanoporous Substrate
   - Positive evidence of ALED of Pd on npPt while maintaining pore structure

   b. ALED of Cu on Pd particles
   - Positive evidence of successful Cu ALED on Pd particles

Detailed Accomplishments:

1) **Growth Mechanism of Pd/Pt:**

Preparation of ALED materials by varying flow rate:

A syringe pump was used to prepare Pd/Pt at three different addition rates. Figure 2 shows the open-circuit voltage (OCV) traces of a Pt wire working electrode that was used to monitor the cell during each deposition process. The ~40-60 min. plateau near 0.5V vs Ag/AgCl corresponds to reduction of surface
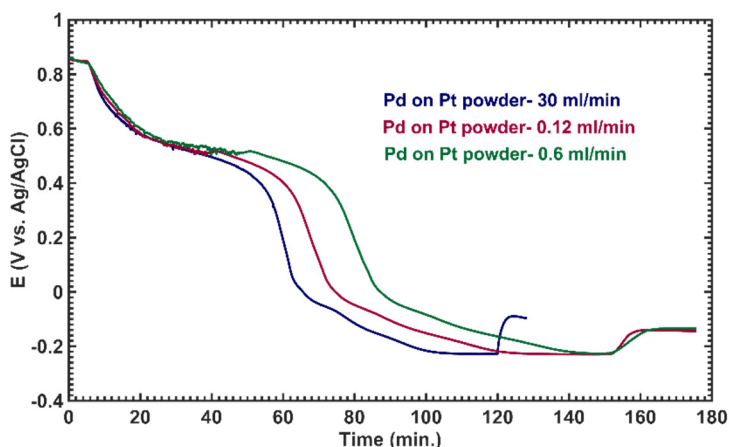
Figure 2. OCV traces during Pd deposition on Pt substrate, collected using a Pt wire working electrode, Pt wire counter electrode and a Ag/AgCl reference electrode.
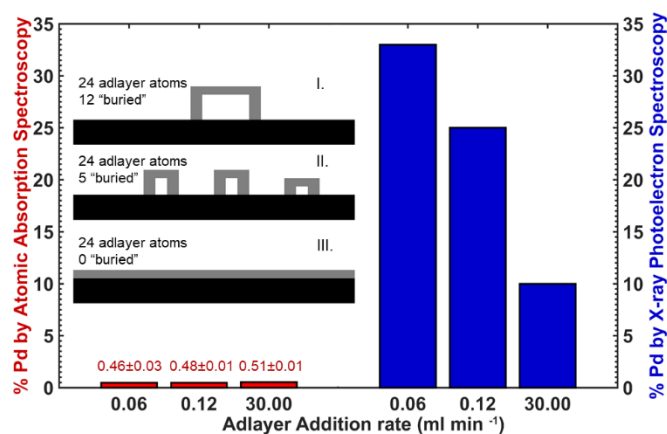
oxides on the Pt powder substrate.[4] The following drop and plateau near -0.2 V vs Ag/AgCl correspond to preparation of Pt-H surface hydrides. The increase in cell potential, which occurs upon addition of Pd^{2+} solution, occurs most abruptly after rapid metal salt addition. This rise becomes more gradual with slower addition of the adlayer metal salt, though the resulting cell potential is similar in all cases. These traces indicate that, though the ***timescale of deposition is varied,*** the ***extent of deposition is similar*** in all three cases.

A comparison of bulk atomic fraction, obtained by AA spectroscopy and surface atomic fraction (Figure 3) provides strong evidence that the surface morphology is different in the three samples. The bulk Pd fraction for the samples with slow, intermediate and fast addition rate are very similar at 0.46±0.03%, 0.48±0.01%, and 0.51±0.01%, respectively. This is consistent with what is expected for a single cycle of ALED, since the substrate has a surface area of 5 $m^2 \cdot g^{-1}$ (measured by N_2 porosimetry), corresponding to ~2% surface atoms. In contrast, XPS data shows large variability in the surface Pd fractions at 33%, 25%, and 10%. These values are much larger than those measured by AA since this technique measures only the surface (1.5 – 2 nm). Taken together these data suggest that the ***surface morphology*** of the three samples is much different while the amount of Pd deposited remains the same. As illustrated in the inset of Figure 3, a conformal Pd layer would show the largest % Pd since nearly all atoms would be at the surface and relatively few Pt atoms would be exposed. In contrast, island growth would show less Pd by XPS since some of the Pd atoms would be buried, and relatively more of the Pt atoms would be exposed.

Conclusion and Outlook:

The data summarized in Figure 3 and described above constitute strong evidence that the growth morphology of ALED materials can be controlled in this way. We note, however, that the morphology change is opposite to what we outlined in the original hypothesis included in our STIR proposal, based on a LaMer mechanism of particle growth.[5] In that case, initial burst nucleation is considered instantaneous and proceeds until the concentration drops to some critical value, at which point growth occurs. We reasoned that by slow addition, at low concentration, nucleation would be suppressed and 3-dimensional growth would be favored.

Figure 3. % Pd vs. addition rate by AA and XPS. AA data (standard deviation) given in red. Inset shows three model surface morphologies from a single, "24 atom" particle (I) to a uniform "24 atom" conformal layer (III).

We consider two alternative hypotheses to explain the observed behavior. First, LaMer assumes that nucleation occurs much faster than particle growth.[5] If, in contrast, growth occurs more rapidly or on a similar time-scale, and with a different rate law, slow addition of the adlayer metal (i.e., low concentration) may decrease the rate of growth to a greater extent than the rate of nucleation. Second, rather than 'critical nucleation concentration', the key parameter for galvanic displacement reactions may be the difference between the reduction potential of the adlayer metal (E_{ad}) and that of the surface hydride (E_{MH}).[14] In that case, decreasing the concentration of the

adlayer metal would decrease the overpotential ($E_{ad} - E_{MH}$) and slow the reaction. Since galvanic displacement takes place between a solid surface hydride and a solution-phase metal salt, this slower rate may facilitate more uniform deposition, as has been observed in other systems.[15] We propose to investigate the effect of chloride ions on ALED, which would alter the overpotential for the galvanic replacement reactions without changing Pd_{2+} concentration, probing the latter hypothesis. With this final series of experiments we plan to submit this work for publication.

2) Expanding ALED scope:

A. Nanoporous Pt as substrate

Nanoporous Pt prepared:

This phase of the funded efforts was successful, with preparation and characterization of samples of $_{np}$Pt having surface areas from $23 - 26$ $m^2 \cdot g^{-1}$ (Figure 4). This is a notable accomplishment in itself since these values are comparable to the highest reported for unsupported nanoporous metals.[7b, 9b, 16] Thus-prepared $_{np}$Pt was used as a substrate for single and multiple cycles of ALED.

ALED Preparation of Pd/Pt$_{NP}$ (Pd adlayer/nanoporous Pt substrate):

OCV traces of Pd/$_{np}$Pt prepared by ALED are shown in Figure 5. Though qualitatively similar to those obtained during ALED with other substrates, it is notable that the reduction of surface oxides on these nanoporous substrates requires several hours due to the higher surface area compared to nonporous powders, and the overall prepa ration of a stable surface hydride, as judged by a stable potential ~-0.2V vs. Ag/AgCl, takes considerably more time. An increase in cell potential occurs upon addition of Pd^{2+} in a fashion similar to that previously observed.
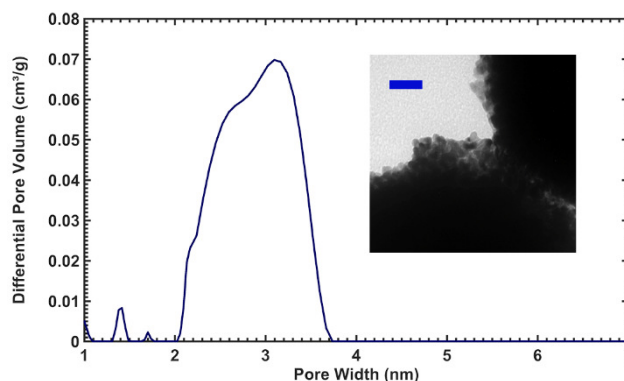
Figure 4. Pore size distribution measured using N$_2$ porosimetry and TEM image of $_{np}$Pt. Scalebar = 20 nm.

Characterization of Pd/$_{np}$Pt:

The data collected in Table 1 illustrate several important results and indicate that ALED is compatible with nanoporous substrates. The first two entries show the surface area of the two prepared $_{np}$Pt substrates that were used for ALED experiments. Samples in the third and fourth row were prepared as controls: by suspending $_{np}$Pt in electrolyte and cycling between N$_2$ and H$_2$/N$_2$ purge, we demonstrate that hydriding and dehydriding the surface alone causes minor loss of surface area. The final four entries demonstrate that one cycle of Pd^{2+} deposition on npPt results in effective deposition (as evidenced by AA and XPS) while maintaining the integrity of the pore structure. The relatively small loss of surface area is similar to that observed in the control experiments. In contrast, multiple cycles of deposition either destabilize the nanopore structure or block the pores, leading to drastic loss of surface area.

The data in Table 1 also provide preliminary evidence that deposition occurs using Pt-H from within the nanopores and not just from the surface of the particles. TEM imagery shows that the $_{np}$Pt particle diameters range from several hundred nm to microns. Since such large particles consist of < 1% surface atoms, and the stoichiometry for Pd^{2+} deposition is 2:1 with respect to Pt-H, the maximum expected % Pd per cycle is <0.5%. The single-cycle deposition samples in Table 1 show two and four times that amount by AA, consistent with galvanic displacement of Pt-H within the pores.

Figure 5. OCV recorded during Pd/npPt preparation. Pt wire working electrode, Pt wire counter electrode, Ag/AgCl

Conclusion and Outlook:

Single cycle ALED on unsupported nanoporous metal with retention of high surface area is clearly demonstrated by the data above. Additional experiments, some of which are currently underway, will include:

i. ALED with smaller Pd^{2+} aliquot size per cycle
ii. ALED at lower Pd^{2+} concentration
iii. Electron microscopy

Table 1. OCV recorded during Pd/npPt preparation. Surface area and composition data for Pd/$_{np}$Pt samples. A. Based on surface area of substrate, B. total for all cycles, C. BET analysis by N_2 porosimetry, D. Value (standard deviation).

Pt surface (mol x 10^5)^A	Pd^{2+} added (mol x 10^5)^B	Cycles	surface area ($m^2 \cdot g^{-1}$)^C	% Pd AA	% Pd XPS
6.5	0	0	26	-	-
5.7	0	0	23	-	-
5.7	0	1	20	-	-
5.7	0	3	16	-	-
5.7	1.2	1	16	0.97(0.04)	17
5.7	2.5	2	3	3.05 (0.03)	27
6.6	2.5	1	21	2.16 (0.03)	53
5.8	6.5	3	1	9.19 (0.1)	77

These experiments are directed at performing multiple cycles without loss of surface area and directly probing the surface composition at the nanoscale.

B. Expand the Scope of ALED to Cu/Pd

Cu/Pd preparation and Characterization:

Accomplishments in this phase of the funded effort include ALED preparation and characterization of single and multiple cycle Cu/Pd. As shown in Figure 6, one and two cycles of ALED result in deposition of Cu^0 on Pd. Bulk % Cu after one cycle of deposition, measured by AA is consistent with that expected for roughly ½ ML on powder particles of ~3 $m^2 \cdot g^{-1}$ (measured by nitrogen porosimetry.) Measurements suggest a complete ML is formed after two cycles. These data confirm that ALED is compatible with a non-noble metal adlayer. Further, it is very interesting to note that two cycles of ALED seem to "cap" the substrate Pd and surface hydride does not appear to form after re-exposure to H_2/N_2. In the "three-cycle" experiment shown in Figure 6, ALED was carried out as in the two-cycle experiment but subsequently exposed to H_2/N_2 for a third cycle. The lack of potential drop suggests that no surface hydride forms. This result is also consistent

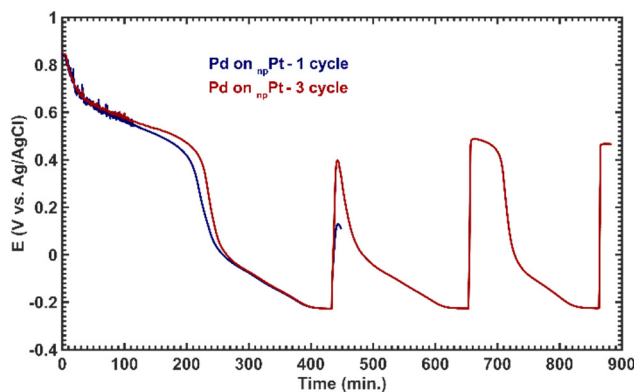with ½ ML deposition per cycle of ALED. It is known that there is a barrier to dissociative chemisorption of hydrogen on Cu surfaces, however the extent to which H_2 can adsorb on clusters remains an active research area.[17]
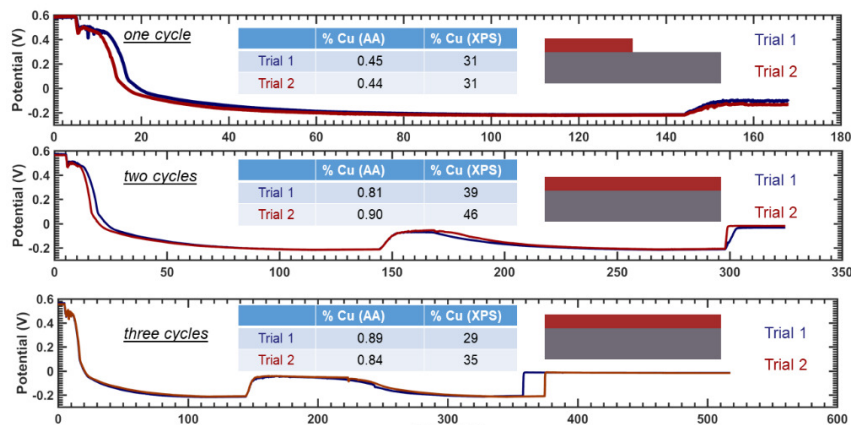
Conclusion and Outlook:

The results discussed in the last section suggest that a bimetallic CuPd catalyst with tailored surface properties can be prepared using ALED. They will facilitate reactivity experiments discussed

Figure 6. OCV traces for one, two and "three" cycles of Cu/Pd ALED. Pt wire working electrode, Pt wire counter electrode, Ag/AgCl reference electrode. Inset table show AA and XPS quantification of atomic fraction Cu. Right inset shows a schematic of ostensible surface composition based on the surface area of the substrate, the quantification of Cu and the lack of surface hydride formation after two cycles of ALED.

above, to investigate the hypothesis that ALED Cu/Pd will be a potent oxidation catalyst. Furthermore, these results will facilitate an unforeseen application. Monolayer deposits of Cu deposited electrochemically (so-called underpotential deposition (UPD)) provide a very well-studied means of preparing multimetallic materials.[18] In this case, Cu acts as a sacrificial reductant that is galvanically displaced by o ther adlayer materials. Electrochemically prepared UPD surfaces are difficult to scale – this has been identified as an important obstacle to widespread adoption of this technique for catalyst preparation.[14] We hope to publish the data discussed above along with addition experiments directed at galvanic displacement of the Cu ML with other adlayer elements.

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